Vidya Bharati Shaikshanik Mandal, Amravati's

VIDYA BHARATI MAHAVIDYALAYA, AMRAVATI

Affiliated to Sant Gadge Baba Amravati University, Amravati

Re-accredited 'A' Grade by NAAC (CGPA : 3.26 Second Cycle)

CPE Status by UGC-Thrice

Lead College identified by SGBAU, Amravati,

Mentor College under Paramarsha Scheme of UGC

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	3.3.2 Number of research papers per teachers in the Journals notified on UGC website during the Academc Year 2018-19						
SN	**Title of paper**	**Name of the author/s**	**Department of the teacher**	**Name of journal**	**Year of publication**	**ISSN number**	**Link to the recognition in UGC enlistment of the Journal**
214	Contribution of Artificial Intelligence to the E-learning	S.B.Bele	Computer Application	IRJIET, Volume 2, Issue 5, PP 24-27, 1.98	2018-19	25813048	Not listed in present UGC approved list as well as in deleted approved UGC List
215	Contribution of Artificial Intelligence to the E Learning	S.B.Bele, Ms. S.K. Totade	Computer Application	IJRECE Volume 6, Issue 3	2018-19	23482281	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
216	INNOVATIVE TECHNIQUES IN HIGHER EDUCATION THROUGH E-LEARNING	S.B.Bele, Ms. S.K. Totade, Ms. A.R.Raut	Computer Application	IJRECE Volume 6, Issue 3	2018-19	23482281	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
217	Big Data Storage Technologies and Challenges of Big Data Storage and Management	Ms. S.K. Totade & S.B.Bele and Ms. A.R.Raut	Computer Application	IJRECE Volume 6, Issue 3	2018-19	23482281	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
218	Leap Protocol in Wireless Sensor Network	Ms. A.R.Raut & S.B.Bele & Ms. S.K. Totade	Computer Application	IJRECE ,Volume 6, Issue 3	2018-19	23482281	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
219	A Comparative Study of Grid and Cloud computing	S.B.Bele	Computer Application	IJOCR,Volume 10,Issue 07, page no.71098-71102,	2018-19	0975833X	Not listed in present UGC approved list as well as in deleted approved UGC List
220	Review on social security attacks on online social networking for Rumors Blocking	Ms.S.M.Mohod	Computer Science	International Journal Of Electronics,Communication And Soft Computing Science &Engineering	2018-19	23487143	Not listed in present UGC approved list as well as in deleted approved UGC List
221	Study of Security Challenges in Multilayered Structure and Various Attacks on IoT.	S.B.Sarvaiya	Computer Science	International Journal Of Electronics,Communication And Soft Computing Science &Engineering	2018-19	23487143	Not listed in present UGC approved list as well as in deleted approved UGC List
222	Internet of Things Security Architecture: Challenges and Issues	Ms.S.B.Sarvaiya	Computer Science	An International Multidisciplinary Quarterly Research Journal	2018-19	22775730	Not listed in present UGC approved list as well as in deleted approved UGC List
223	Factors Affecting Segmentation of Web Pages using Web Content Mining	Mr.D.M.Kene	Computer Science	Research Journey,International E-Research Journal	2018-19	22779477	Not listed in present UGC approved list as well as in deleted approved UGC List
224	Discrimination at work Place	R.J.Gajbe	Electronics	New Man International Journal of Mulltidciplinary studies	2018-19	23481390	Not listed in present UGC approved list as well as in deleted approved UGC List

225	Socialite Evenings: A Chronicle of Karuna's journey towards emancipation as a new woman	Dr.R.M.Patil	English	Vidya Warta International Multilingual Refereed Research Journal	2018-19	23199318	Not listed in present UGC approved list as well as in deleted approved UGC List
226	Intertextuality in Ruskin Bond: Bridging The Gap Between Fact and Fiction	Dr.R.M.Patil	English	LangLit An International Peer-Reviewed Open Access Journal	2018-19	23495189	Not listed in present UGC approved list as well as in deleted approved UGC List
227	Baby Haldar's"Life Less Ordinary: An Extraordinary Autobiography	Dr. P.S. Yenkar	English	Ayushi International Interdisciplinary Research Journal (AIIRJ), Special No.26,pp 2652-2654,March 2018,ISSN 2349-678x, www.aiirjournal.comUGC Approved Journal (Journal No. 64259)	2018-19	2349678X	Not listed in present UGC approved list as well as in deleted approved UGC List
228	A Married Woman: an analysis in Feminist Perspective	Prof. V. P.Shekokar	English	Vidya Warta International Multilingual Refereed Research Journal	2018-19	23199318	Not listed in present UGC approved list as well as in deleted approved UGC List
229	Kantowski–Sachs Bulk Viscous String Cosmological Model in $f(R,T)$ Gravity with Time Varying Deceleration Parameter	P. P. Khade, A. P. Wasnik, S. P. Kandalkar	Mathematics	Global Journal of Science Frontier Research	2018-19	22494626	Not listed in present UGC approved list as well as in deleted approved UGC List
230	Yoga and Modern Life	Dr. D. S. Wankhade	Physical Education and Sports	Research Journey Multidisciplinary International	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
231	Aarthatadnya Lokmanya Tilak	Dr. D. S. Rangacharya	Economics	Research Journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
232	Indian Art and Architecture	Dr. A. D. Chauhan	Sociology	Research Journey	2018-19	23487143	GC-Cancelled-List.pdf
233	Haematological responces to endosulfan toxicity in the Indian garden lizard, *Calotes versicolar*	Dr. N. R. Thorat	Zoology	Review of Research	2018-19	2249894X	Not listed in present UGC approved list as well as in deleted approved UGC List
234	Endosulfan and parathion induced effect on liver and kidney of garden lizard Calotes versicolar in respect of metabolites: Glucose and Protein	Dr. N. R. Thorat and S. V. Gudadhe	Zoology	Review of Research	2018-19	2249894X	Not listed in present UGC approved list as well as in deleted approved UGC List
235	Adhunik kalatil : bhartiy stri	Nitin Khobragade	Zoology	Aarahat multidiciplicinary International education Research Journal	2018-19	22785655	Not listed in present UGC approved list as well as in deleted approved UGC List

236	Root Causes of Pesticide poisoning among farmers in different villages of Yeotmal region	N.R. Thorat, Amjad Hussain and Abhishek Kadam	Zoology	Review of Research	2018-19	2249894X	Not listed in present UGC approved list as well as in deleted approved UGC List
237	Design of novel amyloid β aggregation inhibitors using QSAR, pharmacophore modeling, molecular docking and ADME prediction	Lilly Aswathy, Radhakrishnan S. Jisha, Vijay H. Masand, Jayant M. Gajbhiye, Indira G. Shibi	Chemistry	In Silico Pharmacology, 2018, 6:12	2018-19	21939616	Not listed in present UGC approved list as well as in deleted approved UGC List
238	Growing Cybercrimes Threats with Ransomware	R B Patil	Management Studies	SMART INDIA	2018-19	23194979	http://www.viirj.org/declaration.html
239	Exploration, Assesment and ethnobotanical studies of tribe korku inhabited in melghat forest area of Amravati, Maharashtra, India.	N. A. Wagay, Shah Rafiq, M. A. Gazi, A. A. Maheshwari, Nawaid Ahmad,	Botany	Research journal of Life sciences, bioinformatics, Pharmaceutical and Chemical Sciences.	2018-19	24546348	Not listed in present UGC approved list as well as in deleted approved UGC List
240	Cytotoxic Properties of Curcuma inodora Leaf Against (Miapaca-2) Human Pancreatic Carcinoma Cell Line	M.U.Ghurde & S.N.Malode	Botany	Research Journey' International E- Research Journal	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
241	METAPHORICAL EFFECTS OF ORGANOPESTICIDES CARBENDEZIM AND MALATHION ON THE GROWTH AND PHYSIOLOGICAL ACTIVITIES OF CYANOBACTERIA NOSTOC COMMUNE, VAUCHER INHABITING THE RICE FIELD OF BHANDARA DISTRICT	P. G. Bansod and H. A. Khobragade	Botany	International Journal of Current Advanced Research	2018-19	23196475	Not listed in present UGC approved list as well as in deleted approved UGC List
242	Arbuscular mycorrhizal biodiversity associated with *Citrus aurentifolia* from amravati region	L.P.Khalid,Pulate P.V	Botany	International Journal of Life Science	2018-19	23207817	Not listed in present UGC approved list as well as in deleted approved UGC List
243	Embedded System Security	Ms. A.R.Raut & Ms. S.K. Totade	Computer Application	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
244	Study of Advances in Artificial Intelligence and Deep Learning	V.R. Dhawale	Computer Application	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
245	An Overview of "Cloud Computing"	S. B. Bele	Computer Application	Research journey	2018-19	23487143	GC-Cancelled-List.pdf
246	Universal Knowledge Discovery from Big Data	V.N. Mohod	Computer Application	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
247	The Role of Cloud Computing in Education	M. S. Sharma	Computer Application	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf

248	A Survey on one Time Password: That Provides Protection Against Various Password - Based Attacks.	Bhushan R. Padar	Computer Application	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
249	The Risk And Limitations of Security Mechanisms on IoT Environments	S.B.Sarvaiya	Computer Science	International Engineering Journal for Research & Development	2018-19	23490721	Not listed in present UGC approved list as well as in deleted approved UGC List
250	Study of Various Implemented Approaches for Rumour Detection over Social Media Platform.	S.M.Mohod	Computer Science	International Engineering Journal for Research & Development	2018-19	23490721	Not listed in present UGC approved list as well as in deleted approved UGC List
251	Formulation and Evaluation of moisturizing skin serum with hyaluronic acid by using nano technology.	MS. Y.V. DHOTE & DR. S.D. PANDE.	Cosmetic Technology	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
252	Encapsulation of moisturizer in bath preparation to improve skin conditioning	DR. LALIT K. VYAS & MR. BHUSHAN LADDHA	Cosmetic Technology	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
253	The Dead Sea Mud & Salt: Its characterization, Contaminants & Benefical Effects	PROF. P.A. KOLHE & A.V. Gulalkari	Cosmetic Technology	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
254	Activated charcoal used in cosmetics	PROF. RASHMI TALE	Cosmetic Technology	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
255	Formulation and development of clerodendrum sulphate free face wash	KHUSHBU JAIN, & MRUNAL WARANAKAR &	Cosmetic Technology	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
256	Metallic nanotechnology as a novel drug carrier in cosmetics	MS. UNNATI KALMEGH	Cosmetic Technology	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
257	Formulation and development of hydrating gel by using liposome technology	Ms. Ashwini Sangle & Ms.yogita Dhote	Cosmetic Technology	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
258	Formulation and Evaluation Multiple use hair lotion with Herbal actives	Mrs. B.R.Dahikar	Cosmetic Technology	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
259	Formulation and development of antibacterial and antifungal sanitizer	Mrs. R.A. Vishwakarma	Cosmetic Technology	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
260	Characteristiccs of Electronics Transducer in Biomedical Instruments	N.B.Raut	Electronics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
261	Use of AINN Filters for Reduction of Noise From ECG Signals	R.J.Gajbe	Electronics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
262	Necessity of Internatinalization of the Curriculum for Indian Universities	Dr.R.M.Patil	English	RESEARCH REVIEW International Journal of Multidisciplinary	2018-19	24553085	Not listed in present UGC approved list as well as in deleted approved UGC List

263	Dr. BabasahebAmbedkar's Contribution to the Emancipation of Women	Dr. P.S. Yenkar	English	'Ajanta' An International Multidisciplinary Quarterly Research Journal Vol. IX, Issue 2,pp 23-26 April-June 2019, ISSN No. 2277-5730	2018-19	22775730	Not listed in present UGC approved list as well as in deleted approved UGC List
264	Resource Sharing and Knowledge Management System in Acadamic Libraries	Dr.Vishal R.Shekhawat	Library and Information Sciences	International E-Research Journal	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
265	Bianchi Type VI Model With Anisotropic Dark Energy In A Scalar Tensor Theory of Gravitation	A. P. Wasnik, P.P. Khade	Mathematics	Research Journey International E Research Journal	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
266	Sports Nutrition	Dr. D. S. Wankhade	Physical Education and Sports	An international Multidisciplinary Quarterly research Journal	2018-19	22775730	Not listed in present UGC approved list as well as in deleted approved UGC List
267	Synthesis and Humidity Sensing Investigations of Nanostructured ZnO Doped SnO_2 Thick Films	R. M. Agrawal, G. T. Lamdhade	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
268	Effect of UV Radiation on the Dielectric Properties of Salicylic Acid Doped Polymer Thin Film of PMMA	Vidhale S.G. Belsare N. G., Wadatkar A. S., Wasnik T. S.	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
269	Surface Activated Cr_2O_3 Based Thick Film for Ammonia Gas Sensing	P.M. Chandak , F.C. Raghuwanshi , S. V. Agarkar & V.D. Kapse	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
270	Study of Variation of AC Electrical Conductivity of 4:1 PMMA+PS Polyblends With Constant Temperature and Varying Frequency,	H. G. Pande, G. T. Lamdhade, R. V. Joat, T. S. Wasnik	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
271	AC Conductivity and Dielectric Study of Pva Based Solid Polymer Electrolyte	S.R.Jadhao, R.V.Joat, S. P. Bakde	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
272	The DC Electrical Properties of Composites Polymer Electrolytes	S. P. Bakde, R. V. Joat & S. R. Jadhao	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
273	Study of Effect of ZnO on Changing Electrical Properties of Polyprrole Composites	Raulkar K. B. , R. V. Joat & Lamdhade G. T.	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
274	Effect of Oxalic Acid on DC Electrical Conductivity of Doped Polyvinylchloride and Poly(Methyl Methacrylate) Polyblends	A. B. Dakare, G. T. Lamdhade, V. Ganesan	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf

275	Synthesis of Nanocrystalline Tin Oxide Doped With Copper Oxide And Study of Their Electrical Conductivity Under The Influence of CO_2 Gas	V.M.Balkhande, G. T. Lamdhade, F. C.Raghuwanshi, V. Ganesan	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
276	Physical Properties of Nanostructured WO_3 Thin Films Grown by SILAR Method	Ishaque Ahmed Khan & R. V. Joat	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
277	Study of AC Electrical Conductivity of Polypyrrole Based Composites	Nisha S.Bais, T.S. Wasnik , R.V. Joat,	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
278	Synthesis and Characterization of Magnesium Oxide Nanoparticles By Co-Precipitation Method	A.B.Daware, G.T. Lamdhade, T.S. Wasnik, V. Ganesan, M. N. Pawar	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
279	Detection of Carbon Dioxide Using Conducting Polymer Polypyrrole and Polyaniline	Mude B.M., Mude K.M., ZadeR.N., Yenorkar S.M & Yawale S. P., Yawale S.S. , Raulkar K.B.	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
280	Synthesis and Characterization of Proton Conducting Composite Solid Polymer Electrolyte System	R.Risodkar, R. Joat	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
281	Investigations of Polymer Blends: Variation of Conductivity and Dielectric Constant Versus Frequency	P.P.Raut, G. T. Lamdhade, F. C.Raghuwanshi, K. B. Raulkar, T. Shripathi, V. Ganesan	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
282	Water Vapour Sensing Mechanism of PANI Doped With Zno Nanocomposites	T R Ingale, R M Agrawal, G T Lamdhade, F C Raghuwanshi, K. B.	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
283	Study of AC Electrical Conductivity and Dielectric Properties of Polypyrrole Based ZnO Nanocomposites	T S Wasnik, R M Agrawal, K B Raulkar, G T Lamdhade, R V Joat	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
284	Effect of Deposition Rate on The Structural and optical Properties of Copper Sulphide Thin Films	S. S. Kawar ,S.V. Potdar, V.S. Kalyamwar, A. P. Pachkawade, G.T.	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
285	Gas Sensing Study of SnO_2-ZnO (90-10) Nanocomposite Towards H_2S	S.G.Onkar, F.C.Raghuwanshi, G.T.Lamdhade	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
286	CuO Modified ZnO Thick Film Resistors As H2S Gas Sensors	V. S. Kalyamwar, S. S. Kawar, S. V. Potdar, F. C. Raghuwanshi	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf

287	Fabrication and Application of Polyprrole (PPy)-ZnO composites to sense NH3 gas at room temperature	K B Raulkar	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
288	Goldstone Mode fluctuations of ZnO Nanoparticles	G.T. Lamdhade	Physics	Research journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
289	DC HUMIDITY SENSING PROPERTIES OF NANOSTRUCTURE SnO2 SYNTHESIS WITH CO-PRECIPITATION METHOD	R. M. Agrawal, G.T. Lamdhade	Physics	Review Of Research	2018-19	2249894X	Not listed in present UGC approved list as well as in deleted approved UGC List
290	Study on DC Conductivity of PPy-ZnO Nanocomposites	KB Raulkar, TS Wasnik, RV Joat, AS Wadatkar, RM Agrawal, GT Lamdhade	Physics	Materials Today: Proceedings	2018-19	22147853	Not listed in present UGC approved list as well as in deleted approved UGC List
291	Krishitadnya Dr. Bhausaheb Deshmukh	Dr. D. S. Rangacharya	Economics	An International Multidisciplinary Quarterly Research Journal AJANTA	2018-19	22775730	Not listed in present UGC approved list as well as in deleted approved UGC List
292	A Study of Adolescence Mental Health among Joint Family and Nuclear Family	Vidhya T. Ambhore & Dr. Shankar D. Wakode	Psychology	An International Multidisciplinary Quarterly Research Journal AJANTA	2018-19	22775730	Not listed in present UGC approved list as well as in deleted approved UGC List
293	Saurian Fauna inventory of Ladakh region, Jammu and Kashmir, India.	Abid Hussain Amjad Hussain V. T. Tantarpale	Zoology	Research Journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
294	Checklist of Ophidian fauna in Amravati city, Maharashtra, India.	Amjad Hussain Abid Hussain V.T. Tantarpale	Zoology	Research Journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
295	Water analysis of Wadali Lake in Amravati, Maharashtra	Rakshan Rehman Ankit Goud V.T. Tantarpale	Zoology	Research Journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
296	Effect of *Allium sativam* on RNA,DNA and RNA:DNA ratio of Freshwater fish *Ophiocephalus stritants* (Bloch, 1793)	S. H. Rathod N. R. Thorat V.T. Tantarpale	Zoology	Research Journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
297	Nutritional value of Fresh water prowns of Amravati fish market	Padmini Doifode Amjad Hussain V.T. Tantarpale	Zoology	Research Journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf

298	Impact of Biopesticide- Azadirachtin Indica on Testis of Fresh Water Catfish *Heteropneustes fossilis*	Vaishali Panchwate V.T. Tantarpale	Zoology	Research Journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
299	Histological modulation observed in intestine of Freshwater fish Channa Stritus Exposed to Deltrametnrin.	V. R. Gulhane V.T. Tantarpale	Zoology	Research Journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
300	Effect of Norfloxacin on Hatching rate of *Channa punctatus*	S.S. Gijare P. S. Joshi S. B. Borkar V.T. Tantarpale	Zoology	Research Journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
301	Effect *Aloe vera* leaf extract on the developmental stages of *Drosophila melanogaster*	A. D. Patshe Y. D. Akhare	Zoology	Research Journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
302	Limnological Studies of Nalganga Resivoir, Nalgangapur, Dist. Buldhana, M.S. India	Chitra D. Morey V.R. Wankhade	Zoology	Research Journey	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
303	Multiple Quantitative Structure-Activity Relationships (QSARs) analysis for Orally Active Trypanocidal N-Myristoyltransferase Inhibitors	Vijay H. Masand, Nahed N. E. El-Sayed, Mukesh U. Bambole, Vaijant R. Patil, Sumer D. Thakur	Chemistry	Journal of Molecular Structure 1175 (2019) 481-487	2018-19	222860	Not listed in present UGC approved list as well as in deleted approved UGC List
304	QSAR study of anti-Human African Trypanosomiasis activity for 2-phenylimidazopyridines derivatives using DFT and Lipinski's descriptors	S. Chtita, M. Ghamali, A. Ousaa, A. Aouidate, A. Belhassan, A. I. Taourati, Vijay H. Masand, M. Bouachrine, T. Lakhlifi	Chemistry	Heliyon, (2019) 5(3).	2018-19	24058440	Not listed in present UGC approved list as well as in deleted approved UGC List
305	Quinoxalinones Based Aldose Reductase Inhibitors: 2D and 3D-QSAR Analysis	Vijay H. Masand, Nahed N. Elsayed, Sumersingh D. Thakur, Nandkishor Gawhale, Mithilesh M.	Chemistry	Molecular Informatics (2019), DOI: 10.1002/minf.201800149	2018-19	18681751	Not listed in present UGC approved list as well as in deleted approved UGC List
306	Antiinflammatory Activity of Triazine Thiazolidinone Derivatives: Molecular Docking and Pharmacophore Modelling	R. S. SHINDE, V. H. MASAND AND M. K. PATIL	Chemistry	Indian J Pharm Sci 2019;81(5):851-859	2018-19		Not listed in present UGC approved list as well as in deleted approved UGC List
307	SYNTHESIS, SPECTRAL CHARACTERIZATION AND INVESTIGATION OF ANTIMICROBIAL ACTIVITY OF SOME NOVEL SUBSTITUTED PROPANE-1, 3-DIONES DERIVED FROM P-CHLORO-M-CRESOL	Dr Pravin S. Bodkhe and Sushil Pagariya	Chemistry	INTERNATIONAL JOURNAL OF CURRENT ENGINEERING AND SCIENTIFIC RESEARCH (IJCESR)	2018-19	23940697	Not listed in present UGC approved list as well as in deleted approved UGC List

308	To study intermolecular interaction of substituted thiocarbamidophenol and Cu(II) and Cd(II) ion in 70%mixed solvent media	Dr Pravin S. Bodkhe,A.B.Wadekar,R. D.Isankar and D.T.Tayade	Chemistry	International Jouranal of Researchand Analytical Reviews (IJRAR) www.ijrar.org 2018 IJRAR January 2019 , Volume 06, issue 1	2018-19	23481269	Not listed in present UGC approved list as well as in deleted approved UGC List
309	Synthesis, spectroscopic characterisation and antimicrobial screening of some newly synthesized propane-1,3-dione (b-Diketones) Derivatives	Dr Pravin S. Bodkhe	Chemistry	INTERNATIONAL JOURNAL OF CURRENT ENGINEERING AND SCIENTIFIC RESEARCH (IJCESR)	2018-19	23938374	Not listed in present UGC approved list as well as in deleted approved UGC List
310	Synthesis And Characterisation of newly Synthesized Isoxazoline	S.M.Rathore ,V.V.Parhate ,	Chemistry	JETIR March 2019, Volume 6, Issue 3	2018-19	23495162	Not listed in present UGC approved list as well as in deleted approved UGC List
311	Metal-Ligand Stability Constants of Ni(II) and Co(II) ,Cu(II) Metal Ions Complexes With Some Substituted Isoxazoline Ph –Metrically	Shreya Rathore , Dr V.V.Parhate, Dr M.M.Rathore	Chemistry	'RESEARCH JOURNEY' International E- Research Journal Impact Factor - (SJIF)	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
312	Common Pharmacophore Pattern for Anthelmintic Activity of A Pesticide Tolfenpyrad (TFP)	Vijay H. Masand , V.V. Parhatea , M. M. Rathore	Chemistry	'RESEARCH JOURNEY' International E- Research Journal Impact Factor - (SJIF)	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
313	Microwave Synthesis and Wound Healing Effect of Δ2 – Pyrazoles ointment In Albino Rats	P.S.Nandurkar,M. M. Rathore, P. R. Rajput	Chemistry	'RESEARCH JOURNEY' International E- Research Journal Impact Factor - (SJIF) – 6.261, (CIF) - 3.452(2015), (GIF)–0.676 (2013) Special Issue 110 (B) : Chemistry UGC Approved Journal	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
314	Synthesis and growth promoting effects of some newly synthesized bromo and nitro substituted isoxazolines on some edible mushroom.	S. M. Rathore, M. M. Rathore, V. V. Parhate	Chemistry	Current Pharma Research CODEN-CPRUE6	2018-19	22307842	Not listed in present UGC approved list as well as in deleted approved UGC List

315	Assessment of Molecular Interactions of 4-Ethyl Thiocarbamidophenol on Acoustic Parameters Base	Dr Pravin S. Bodkhe,A.B.Wadekar,R. D.Isankar and D.T.Tayade	Chemistry	Journal of Chemistry and Chemical Sciences, Vol.9(2), 45-48, February 2019 (An International Research Journal), www.chemistry-journal.org	2018-19	2229760X	Not listed in present UGC approved list as well as in deleted approved UGC List
316	Viscometric Measurement of (2e)-1-(4-Thiocarbamido phenyl) -3-(3,4-Dimethyl) pro-2-en-1-one in 60% ethanol water mixture at various temperatures and constant concentration	Dr Pravin S. Bodkhe,S.Waghamare,M. Gadpayale and D.T.Tayade	Chemistry	Research Journey international e-research journal Special issue 110 B	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
317	Synthesis and Antimicrobial Screening of some 6-substitutedDerivatives of 2-Phenyl -4H-Cromen -4-one	Sushil Pagariya,A.R.Yadav ,S.K.Rithe and P.S.Bodkhe	Chemistry	Research Journey international e-research journal Special issue 110 B	2018-19	23487143	https://www.ugc.ac.in/pdfnews/5283580_UGC-Cancelled-List.pdf
318	Impact of Information Technology for Business Success	S A Kazi	Management Studies	IJAMCE	2018-19	23479558	Not listed in present UGC approved list as well as in deleted approved UGC List

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Contribution of Artificial Intelligence to the E-learning

Mr. Sanghesh B. Bele

Department of MCA, Vidya Bharati Mahividyalaya, Amravati.

Abstract **- Artificial intelligence (AI) is a property of machines which gives the ability to copy the human thought process. It is concerned with the design of intelligence in an artificial device. This term was defined by McCarthy in 1956.**

There are two ideas in the definition.

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2. Artificial device

This paper highlight to potential contribution of Artificial Intelligence (AI) to the e-learning environment. Artificial Intelligence enhances computer assist instruction systems by providing human like intelligence to the system. Here, we are focusing some AI techniques, which could be the main technology for e-learning. Also we discuss how Intelligent Tutoring System (ITS) is proved as promising field to the training programs and how AI could contribute to issues like Naural intelligence, learning from experience & intelligent interaction between human being & machine.

Keywords: Artificial Intelligence, ITS, CAI, ML, NLP, e-learning, CA, ILE.

I. INTRODUCTION

If you ask to our respected senior citizen those who have retired from service or business, they all have very common thing that, the respect & memories of the educational institutions where they studied and old days traditional teaching. They shared their warm memories which are associated with institutes. In today modern time as the field of computer science and information technology has reformed day-to-day activities of entire human life. The computing field has provided us all that even we could not have dreamt. The remarkable growth of this field has impacted educating in many ways.

Artificial Intelligence (AI) is the science & engineering of making intelligent machine, especially intelligent computer programs. It is related to the similar task of using computer to understand human intelligence. In fact, intelligence involves mechanism & AI research has discussed how to make computers to carry out some of them. AI makes traditional teaching more effective.

II. WHAT IS E- LEARNING

E- Learning refers to learn that is to be delivered or enable via electronic technology. It encompasses learning delivered via a range of technologies such as the internet, television, videotape, intelligent tutoring systems, and computer-based training.

E-learning is subset of two large words, specifically, “information technology” and “education and training”. It can be valuable when used as a part of well-planned and properly supported education and training environment. However, e-learning does not replace or render existing educational theories and approaches.

III. INTELLIGENT TUTORIAL SYSTEM (ITS)

An intelligent tutoring system (ITS) is a computer system that aims to provide immediate and customized instruction to learners, usually without requiring intervention from a human teacher like online teaching. It is difficult to provide a personal training assistant for each learner, however, a virtual training assistant that captures the subject matters and teaching expertise of experienced trainers provides a captivating new option. The concept, known as Intelligent Tutoring System (ITS) has been pursued by researchers in education, psychology and artificial intelligent. ITS can also be classified by model tracing tutor algorithm One of the objectives of Intelligent Tutorial System is to adopt hypermedia courses to each individual user by means of control of learning level, control of the course navigation, revision to available information, revision of the training methodology, explanation of errors, answers to the student’s questions, advice, etc. In other words, intelligent tutoring system is a model which enables student to be evaluated and taught a subject and also for the education to be adapted to the students performance.

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- Curriculum Module / Tutoring model
- Interface Module
- Expert Module contains information about the subject knowledge domain. Its contain the concepts, rules, and problem-solving strategies of the domain which is to be learned.
- Student Module can be thought of as an overlay on the domain model. It contains information about the student's understanding of the knowledge domain. It is considered as the core component of an ITS.
- Curriculum Module contains rules that allow it to judge how well the student's understanding of the subject domain matches actual knowledge structure.
- It also accepts information from the domain and student models and makes choices about tutoring strategies and actions.
- Interface Module presents the user with a uniform environment within which instruction, analysis, remediation, and user driven learning may take place. The user interface component integrates three types of information
- Knowledge about patterns of interpretation and action
- domain knowledge needed for communicating content; and
- knowledge needed for communicating intent

The Aim of ITS is to create a learning environment where the role of human teachers is replaced by the tutor module and domain knowledge module. A system plans and teaches individuals by maintaining its belief about each in the student module and acts according to the best teaching strategy ITS can also be classified by model tracing tutor algorithm.

IV. WHAT AI PRESENT

Teaching and learning is not a simple process. Only train humans can teach effectively. Computer Assisted Instructions (CAI) could be useful in learning at an elementary level and even then cannot compete with train humans in term of teaching quality. The creation of the ALGOL programming language in 1958 which was enabled in many schools and universities for beginning to develop Computer Assisted Instruction (CAI) programs and Computer Aided Learning (CAL) which are lacking "the flexibility and learner- centered orientation of ITS" The complexity of the teaching task is the result of following main factors:

- Adaptive teaching strategies - Depending on the stage in the learning process, different subjects requires different instructional strategies at different levels.
- Continuous assessment of students - Human teachers do not rely on the test result for student's assessments, but they constantly assess the class and individual through various inputs like attention level, understanding level etc.
- Personalized teaching - Human teachers are flexible. To make their teaching effective, they deliver the content ranges from class level down to the individual student's level.

Artificial Intelligence enhances CAI systems by providing human like intelligence to the system. To enhance the efficiency of computer programs in handling the above mentioned factors, computer must be equipped with necessary sensors. They must be able to make sense out of their senses, and then they can act logically. They should be able to learn and be adaptable to new environment. We highlight the current developments in these issues and their applications in intelligent tutoring systems.

i) Aural Capability

Domains such as language and music require hearing ability in computers. The ability to here also implies to an understanding of what is being heard. Advances in speech recognition, speech processing and natural languages processing provides useful applications in many areas including ITS. At the current state-of-the-art, we have enquiry counters where clients can make the enquiries using interactive telephone dialogue. Clients talk to a computer as if they are talking to another human being.

ii) Visual Perception

Many recent works in education address the issues of affects and emotions. Information regarding students' affects could be useful in the adaptation of teaching strategies. This area is however still not mature.

The ability to visualize can be useful in teaching music performance as well. In many performing skills, the techniques are closely related to the poster (e.g. hand-shape, sequence of movements, etc.)

iii) Inference mechanisms

The talking which so far about perceives and acting (via speaking). Perhaps, the most important aspects of intelligent behaviors is about inference power. This is the area where most AI researchers have been investigating.

Logical inference is suitable for domains at a course grain abstraction. For example, the encoding of domain knowledge in a rule-based expert module. Probabilistic and statistical inferences are suitable in handing uncertainties in the domain.

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Bayesian networks, artificial neural networks are the most popular inference techniques.

iv) Machines that learn (ML)

One of the main secret ingredients for the success of any ITS system is the accuracy of its student model. Real students are dynamic. As such, ITS systems must possess the learning capability so that changes in students could be tracked. Learning is along standing research in AI and this is one of the areas where AI could make a useful contribution to ITS in e-learning environments.

v) Interactive learning environment (ILE)

Finally, we would like to comment on the interaction between human and machine. The interaction between learner and computer in the main ingredient in the success of an ITS. Information from the interactions serves three purposes:

- To perceive useful information from the environment,
- To model an accurate student model, and
- To actuate the environment (e.g., feedback) with useful information.

V. APPLICATION IN E-LEARNING

Here we highlight AI application in ITS which a part of the e-learning environment. Let us look one application of language teaching.

Language Teaching

Teaching language involves the teaching of reading and writing skills. The whole scene involves content development, the delivering of content and an assessment of the delivering process. Here, we highlight the assessment dimension in language teaching.

Speech recognition is a hard problem. Same words or phrase contribute two different meaning in two different contexts. However, with a supplied context, this is not too hard problem. Given a word, a phrase, or a sentence, assessment of pronunciations could be automated using speech technology. This opens up a whole new approach for language teaching and learning. An ITS could be very useful in enhancing essay writing. Students have a constant need for tutors to give feedbacks on errors or mistake as well as meritorious use of language. Highlighting errors and mistakes could be easily automated using the spelling check and grammar check utilities. One of the major restrictions in most spelling check and grammar check utilities is the lack of context analysis (CA). To handle context dependency, sophisticated Natural Language Processing (NLP) techniques could be employed then the promise of an ITS which could benefits writing skills is not far away.

VI. CONCLUSION

Many traditional instructional methods presents learners with facts and concepts followed by test questions, but artificial intelligence involves in capturing domain knowledge, providing intelligent assessment power and providing intelligent feedback etc. Thus as compare to old days of our citizens, use of information technology in general and Artificial Intelligence in particular area makes the education highly interactive, highly accessible, and highly individualized.

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INNOVATIVE TECHNIQUES IN HIGHER EDUCATION THROUGH E-LEARNING

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Abstract- The term E-learning refers to a novel teaching and learning in education. This educational high technology is an important part of today's world, which delivers supports and enhances the quality of learning. E-learning involves the participation of educator, and students who are use this technology to update their work. E-learning is the technique for how to understand and how to memorize the topic for long time. The E-learning is the use of technologies to improve knowledge and performance, and gives the advantage of 24x7 and 365 days a year. E-learning technologies offer learners control over content, learning sequence, pace of learning, time and often media, allowing them to adapt their experiences with to collect their personal learning objectives. Innovation in e-learning technologies point toward a revolution in education, especially higher education allowing learning to be individualized, enhancing learner's interaction with others and transforming the role of educator / teacher in higher education.

Keyword: *ALT, ITS, ICT, VLE, MIS, VRT*

1. Introduction

The brisk growth of the information age has made a big impact on the educational process in the last few years. The growth of information together with recent technological achievements has led to Computer Assisted Learning (e-learning) is enabling wider access to education to an increasing variety of people, independent of time or location.

E–learning is defined as acquisition of knowledge and skill using electronic technologies such as computer and Internet-based courseware at local and wide area networks. Electronic learning or e-learning is general term used for to refer to computer enhanced learning. It is commonly associated with the field of advanced learning technology (ALT), which deals with learning using network and/or multimedia technologies, it uses various technological tools that may be web based, web distributed or web capable for solving the purpose of education. E-learning facilities, such as 3D models and animations which are elements of Virtual Reality Technology, used for acquiring new knowledge.

The main objective of e-learning is to improve the quality of the learning experience for students who are in higher education.

2. What is E- learning

Learning system based on formalized teaching but with the help of electronic resources is known as E-learning. While teaching can be based in or out of the classrooms, the use of computers and the Internet forms the major component of E-learning. E-learning can also be termed as a network enabled transfer of skills and knowledge, and the delivery of education is made to a large number of recipients at the same or different times.

E- Learning refers to learn that is to be delivered or enable via electronic technology. It encompasses learning delivered via a range of technologies such as the internet, television, videotape, intelligent tutoring systems, and computer-based training.

E-learning is subset of two large words, specifically, "information technology" and "education and training". It can be valuable when used as a part of well-planned and properly supported education and training environment. However, e-learning does not replace or render existing educational theories and approaches.

3. Importance of E-learning in Higher Education

A student who is learning in higher education is a way that uses information and communication technologies (ICTs) by using e-learning. Following are different types of capability:

- Internet access to digital versions of materials unavailable locally.
- Internet access to search, and transactional services.
- Interactive diagnostic or adaptive tutorials.
- Interactive educational games
- Remote control access to local physical devices.
- Personalized information and guidance for learning support.
- Simulations or models of scientific systems.
- Communications tools for collaboration with other students and teachers.
- Tools for creativity and design.

- Virtual reality environments for development and manipulation.
- Data analysis, modeling or organization tools and applications.
- Tele-Medicine

For each of these, there is a learning application that could be exploited within higher education. Each one encompasses a wide range of different types of interaction – internet access to services, for example, includes news services, blogs, online auctions, self-testing sites, etc. Imagine, for example, a remotely controlled observatory web cam embedded in an on line conference environment for astronomy students, or computer aided design (CAD) device embedded in role play environment for students of urban planning.

The range and scale of possible applications of new technologies in Higher Education is almost beyond imagination because, while we are trying to cope with what is possible now, another technological application is becoming available that will extend those possibilities even further. Everything will need updating again when 3G/4G or even advance generations in mobile phones begin to have an impact on our behavior.

4. Intelligent Tutorial System (ITS)

An **intelligent tutoring system** (**ITS**) is a computer system that aims to provide immediate and customized instruction to learners, usually without requiring intervention from a human teacher like online teaching. It is difficult to provide a personal training assistant for each learner, however, a virtual training assistant that captures the subject matters and teaching expertise of experienced trainers provides a captivating new option. The concept, known as Intelligent Tutoring System (ITS) has been pursued by researchers in education, psychology and artificial intelligent. ITS can also be classified by model tracing tutor algorithm One of the objectives of Intelligent Tutorial System is to adopt hypermedia courses to each individual user by means of control of learning level, control of the course navigation, revision to available information, revision of the training methodology, explanation of errors, answers to the student's questions, advice, etc. In other words, intelligent tutoring system is a model which enables student to be evaluated and taught a subject and also for the education to be adapted to the students performance.

The traditional ITS model contains four components:

- Expert Module / Domain model / cognitive model / expert knowledge model
- Student Module / model tracing
- Curriculum Module / Tutoring model
- Interface Module.

5. Advantages of ITS:-

Intelligent Tutoring systems (ITS) are effectively used for teaching the course of the specified domain with following features and benefits:

- Increases student / instructor ratio from around 1:1 so that it reduce training costs extremely, and still deliver close to a one on - one learning experience.
- Shortens training time and / or improve skill level.
- Automatically optimizes individual learning.
- Builds "student module" for each student that includes: Performance on training exercises.
- Details of information / remediation received
- Details of knowledge mastered / failed / unknown / misunderstood.
- Performance on remediation activities.
- Student preferred learning style.

It is important because e-learning can make a significant difference: to how learners learn, how quickly they master a skill, how easy it is to study, and equally important, how much they enjoy learning. Such a complex set of technologies will make different kinds of impact on the experience of learning:

- Cultural: - Students are comfortable with e-learning methods, as they are similar to the forms of information search and communications methods they use in other parts of their lives.
- Intellectual: - Interactive technology offers a new mode of engagement with ideas via both material and social interactivity online.
- Social: - The reduction in social difference affordable by online networking fits with the idea that students should take greater responsibility for their own learning.
- Practical :- e-learning offers the ability to manage quality at scale, and share resources across networks; its greater flexibility of provision in time and place makes it good for widening participation.
- Financial :- Networks and access to online materials offer an alternative to place-based education which reduces the requirement for expensive buildings, and the cost of delivery of distance learning materials

6. Technology used in E-learning

Many technologies can be, and are used in E-learning, including:

- Blogs
- Classroom Response System.
- Collaborative Software.

- Computer Aided Assessment.
- Discussion Boards.
- E-mail.
- Educational animation.
- Electronic Performance Support System.
- ePortfolios
- Games.
- Hypermedia in general.
- Learning Management Systems(LMS)
- PDA's
- MP3 players with multimedia capabilities.
- Interactive Board
- Virtual Classrooms
- Web-based teaching materials

In higher education especially, the increasing tendency is to create Virtual learning Environment (VLE) which is sometimes combined with a Management Information System (MIS) to create a Managed Learning Environment. in which all aspects of a course handled through a consistent user interface standard throughout the institution. While some programs require students to attend some campus classes or orientations, many are delivered completely online. In addition, several universities offer online student support services, such as online advising and registration, e-counseling, online textbook purchase, student governments and student newspapers. E-learning can also refer to education web site such as those offering learning scenarios, worksheets and interactive exercise for children. The term also used extensively in the business sector where it generally refers to cost effective on line training.

7. Advantages of E-Learning

- More active learning class
- Diversified teaching method
- Better student attention and realization
- Effective time management for lecturers
- Visual stimulation
- Convenient for students
- Lower cost
- Up-to-date learning materials
- Flexible way of learning
- World-wide learning society
- Scalable e-learning systems
- Higher degree of freedom for students
- Better maintenance

8. Objectives:

E-learning represents an innovative shift in the field of learning, providing a rapid access to specific knowledge and information. It offers online instruction that can be delivered anytime and anywhere through a wide range of electronic learning solution such as web based courseware, online discussion groups, live virtual classes, video and audio streaming, web chat, online simulations, and virtual mentoring.

E-learning enables organizations to transcend distance and other organizational gaps by providing a cohesive virtual learning environment. Companies must educate and train their employees, partners, and clients to stay competitive, and elearning can provide such just in time training in a cost-effective way.

Following are main objectives of E-Learning:-

- Computer based learning.
- Computer based training.
- To reduce learning costs.
- To motivate employees.
- To improve flexibility of course delivery.
- To expand the capabilities of the business.

9. Methodology

The implementation of e-learning into contact teaching allows elimination of number of hours of contact teaching and giving space to individual work with student. The implementation of e-learning into distance learning allows simulating classical forms and methods of education by creating a virtual environment, which imitates classical classroom with whiteboard and the possibility of visual communication.

The following methods are used for the implementation of e-learning.

- Survey of existing tools for creation of information infrastructure.
- Comparison of individual programs for creation of electronic teaching materials and selection of the most appropriate ones.
- Distance learning project team training.
- CASE tool method for the creation of databases.

10. Conclusion

E-learning refers to the use of Internet technologies (IT) to deliver overseas array of learning modes that enhance learner's knowledge and performance. E-learning for higher education is designed, implemented and delivered. For students, e-learning can provide an educationally- superior alternative to traditional lectures, in which learning can take place outside the lecture hall/Class room. E-learning is also providing a model for students on how to become self directed independent learners, which may support them to lifelong learners. They also used for easily and useful understanding of subject by using Graphical / Pictorial form and can be remembered for long times.

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Big Data Storage Technologies and Challenges of Big Data Storage and Management

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Abstract - Big data is a term to refer to huge data sets, have high Velocity, high Volume and high Variety and complex structure with difficulties of management, analyzing storing and processing. Due to characteristics of big data it becomes very difficult to management, analysis, storage, Transport and processing the data using the existing traditional techniques. This paper introduces Big Data Analysis and Storage Technologies, Challenges of Big Data Storage and Management and Suggestions for Big Data Storage and Management. Storage and Management are major concern in this era of big data. The ability for storage devices to scale to meet the rate of data growth, enhance access time and data transfer rate is equally challenging. These factors, to a considerable extent, determine the overall performance of data storage and management.

Keywords: *Big Data Definition, Characteristics, Data Storage Technologies, Challenges Of Big Data Storage And Management, Suggestion For A Big Data Storage And Management.*

Big Data Definition

"Big Data is at the foundation of all the megatrends that are happing."

Chris Lynch, Vertica Systems

Data is everywhere, in fact the amount of digital data that is growing at a rapid rate, and changing the way. This is the field that didn't even exist 20years back. Now data is growing faster than ever faster before and by the year 2020; about 1.7megabytes of new information will be created every second for every human being on the planet.

Data is essentially just raw bits of information science.

Big data is basically a term that describes large amount of data. Big data sets those are so big and complex that traditional data-processing application software is in adequate to deal with them. Big data challenges include capturing data, data storage, data analysis, search, sharing, transfer, visualization, querying, updating, information privacy and data source. There are number of concepts associated with big data: originally there were 3 concepts volume, variety, and velocity. Other concepts later attributed with big data are veracity (i.e., how much noise is in the data) and value.

The position of big data storage within the overall big data value chain can be seen in **figure 1.** Big data storage systems typically address the volume challenges by making use of distributed shared nothing architectures. This allows addressing increased storage requirements by scaling out new nodes providing computational power and storage. New machines can seamlessly be added to a storage cluster and storage system takes care of distributing the data between individual nodes transparently. Storage solutions also need to cope with the velocity and variety of data.

Velocity is important in the sense of query latencies, i.e. how long does it take to get a reply for a query? This is particularly important in the face of high rate of incoming data. For instance, random write access to a database can slow down query performance considerably if it needs to provide transactional guarantees. In contrast, variety relates to the level of effort that is required to integrate the work with the data that originates from a large number of different sources. For instance graph databases are suitable storage systems to address these challenges.

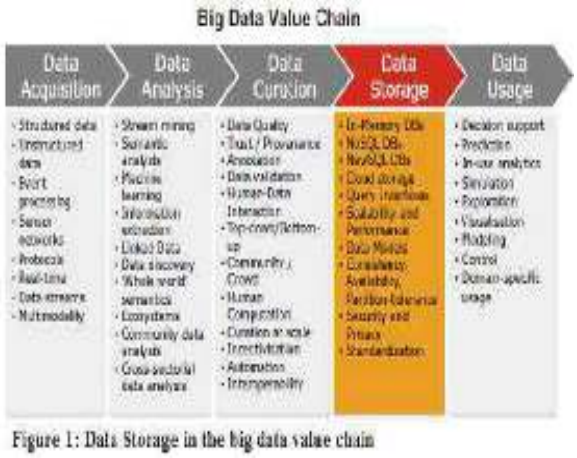

Figure 1: Data Storage in the big data value chain

Big Data Characteristics

The three Vs (volume, velocity and variety) are known as the main characteristics of big data. The characteristics are described in **figure 2** below.

Volume: refers to amount of data and there are many factors that can contribute to the volume increase in data it could amount to hundreds of terabytes or even pet bytes of information generated for everywhere. The number of sources of data for an organization is growing.

Figure 2: 3 Vs of big data

Figure 2 shows that the data volume is growing from megabytes (106) to petabytes(1015) and beyond.

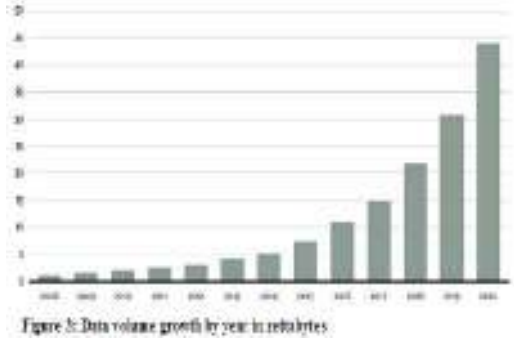

Figure 3: Data volume growth by year in zettabytes

Figure 3 indicates that the volume of data stored in the world would be more than 40 zettabytes(1021) by 2020 .

Velocity: refers to data speed measures the velocity of information creation, gushing and collection, velocity is the most misunderstood big data characteristic. The data velocity is also about the rate changes, and about combining datasets that are coming with different speeds. The velocity of data also describes bursts of activities, rather than the usual steady tempo where velocity frequency equated to only real-time analytics.

Figure 4: Examples of big data velocity

Figure 4 shows few examples of the pace of data. Data speed administration is significantly more than a bandwidth issue; Figure 2 also reflect velocity as characteristics of big data, showing how it requires near real-time and/or real-time analytics.

Variety: Other than typical structured data, big data contains text, audio, images, videos, and many more unstructured and semi-structured data, which are available in many analog and digital formats. From an analytic perspective, variety of data is the biggest challenge to effectively use it. Some researchers believe that, taming the data variety and volatility is the key of big data analytics.

Figure 5 shows the comparison between increment of unstructured, semi-structured data and structured data by years.

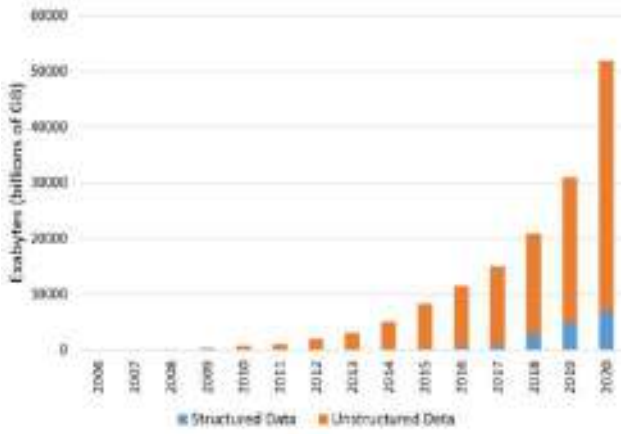

Figure 5: Growth of data variety by years

This paper investigates and analyzes big data storage technology from the following four aspects: distributed file system, NoSQL database, new-type data storage technology of MPP architecture and database all-in-one machine.

- **Distributed File Systems:** File system such as Hadoop file system(HDFS)

HDFS is an integral part of the Hadoop framework and has already reached the level of de-facto standard. It has been designed for large data files and is well suited for quickly ingesting data and bulk processing Data Storage Technologies

- **Big Data Querying Platforms:** Technologies that provide query facades in front of big data stores such as distributed file systems or NoSQL databases. The main concern is providing a high-level interface, e.g. via SQL like query languages and achieving low query latencies.

- **NoSQL Databases:** Probably the most important family of big data storage technologies are NoSQL database management systems. NoSQL databases use data models from outside the relational world that do not necessarily adhere to transactional properties of atomicity, consistency, isolation, and durability (ACID).

- **NewSQL Databases:** A modern form of relational databases that aim for comparable scalability as NoSQL

databases while maintaining the transactional guarantees made by transactional database systems.

- **Big Data Querying Platforms:** Technologies that provide query facades in front of big data stores such as distributed file systems or NoSQL databases. The main concern is providing a high level interface, e.g. via SQL like query languages and achieving low query latencies.

1. NoSQL Databases :

NoSQL databases are design for scalability, often by sacrificing consistency. Compared to relational databases they often use low-level, non-standardized query interfaces, which make them more difficult to integrate in existing applications that expect an SQL interfaces. The lack of standard interfaces makes it harder to switch vendors. NoSQL databases can be distinguished by the data models they use.

- Key-Value Stores: Key-value stores allow storage of data a schema-less way. Data objects can be completely unstructured or structured and are accessed by a single key. As no schema is used, it is not even necessary that data objects share the same structure.
- **Columnar Stores:** "A column-oriented DBMS is a database management system(DBMS) that stores data table as sections of columns of data rather than as rows of data, like most relational DBMSs". Such databases are typically sparse, distributed, and persistent multi-dimentional sorted maps in which data is indexed by a triple of a row key, column key, and a timestamp.
- **Document Databases:** In contrast to the values in a key- value store, documents are structured. However, there is no requirement of common schema that all document are must adhere to as in the case for records in a relational databases. Thus document databases are referred as a storing semi-structured data similar to key-value stores, documents can be querying their internal structure, such as requesting all documents that contain a field with a specified value.
- Graph Databases: Graph databases store in graph structured making them suitable for storing highly associative data such as social networking graphs.

2. NewSQL Databases :

NewSQL databases are modern form of relational databases that aim for comparable scalability with NoSQL databases while maintaining the transactional guarantees made by transactional database systems. The expectation is that NewSQL systems are about 50 times faster than traditional OLTP RDBMS.

3. Big Data Query Platforms :

Big data query platform provide query facades on top of underlying data stores. They typically offer an SQL like query interface for accessing the data, but differ in their approach and performance.

4. Cloud Storage :

As cloud computing grows in popularity, its influence on big data grows as well. While Amazon, Microsoft, and Google build on their own cloud platforms, other companies including IBM, HP, Dell, Cisco etc., build their proposal around Open Stack, an open source platform for building cloud systems, Cloud in general, and particularly cloud storage, can be used by both enterprises and end users. For end users, storing their data in the cloud enable access from everywhere and from every device in a reliable way. As cloud storage is a service, applications using this storage have less control and may experience decreased performance as a result of networking. These performance differences need to be taken into account during design and implementation stages.

Challenges of big data storage and management

With the rate of data explosion, storage system of organizations and enterprises are facing major challenges from huge quantities of data, and ever increasing of generated data. Data irrespective of its size play a vital role in the industry. Value can be created from large data set. For example, Facebook increases its ad revenue by mining its user personal preferences and creating profiles, showcasing advertisers which products they are most interested in. Google also uses data from Google search, Google hangouts, YouTube, and Gmail accounts to profile user's behavior.

In spite of numerous benefits that can be gained in large data set, big data demand for storage and processing poses a major challenge. The total size of data that will be generated by the end of 2015 is estimated at 7.9 zettabytes(ZB), and by 2020, is expected to reach 35 ZB. It is clear that big data has outgrown its current infrastructure, and pushes the limit on storage capacity and storage network. Existing traditional techniques cannot support and perform effective analysis, due to large scale of data.

Big Data Storage Management

Due to massive increase, and the heterogeneous nature of application data, one main challenge of big data is effectively, manage the petabyte (PB) of data being generated daily. Storage management encompasses technologies and process organization to improve data storage performance. Big data require more efficient technologies in processing large quantities of data within an acceptable time frame. A wide range of techniques and technologies have been developed and adopted to manipulate, analyze and visualize big data. Technologies such as massive parallel processing (MPP) database, data mining grids, distributed file system, cloud computing platforms, and scalable storage systems are highly desirable. The development of Map-Reduce, with Yahoo's Pig, alongside Facebook's Cassandra applications, has gotten the attention of the industry. Google file system, GFS, is designed to meet the increasing demands of big data, such as scalability, reliability and availability. GFS is composed of clusters, which is made up of hundreds of storage servers that support several terabytes of disk space. This meets the scalability issue of big data. Hadoop is free version of Map-reduce implementation by Apache Foundation. Hadoop distributed file system(HDFS), is a distributed file system designed to run on commodity hardware. HDFS can store data across thousands of servers. All data in HDFS is reduced into block size chunk, and distributed across different nodes and are managed by the Hadoop cluster

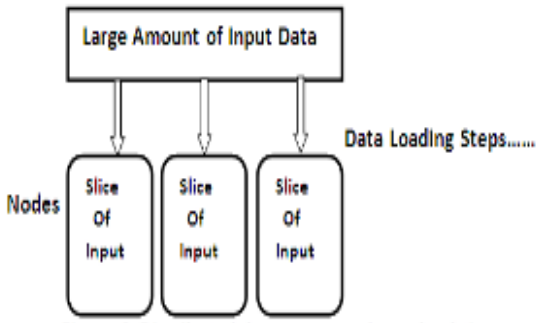

Figure 6: Distributed data across nodes at load time

Figure 6 shows the distribution of data across different data nodes to enhance performance of the entire Hadoop system. Storage vendors such as NetApp, EMC, Hitachi Data Systems, and many more are offering storage management solutions to big data inclined companies. EMC VPLEX enables manageability of storage area network, through a vital storage infrastructure that consolidates heterogeneous storage devices.

Suggestion for a Big Data Storage and Management

System Big data storage and management has been challenge in the face of the increasing volume of organizational data. This paper suggests approaches that we think in our opinion efficiently mitigate challenges of big data storage and management.

1. **Big Data Storage Mediums**: All storage management solutions have at their end, storage devices. The qualities of these storage devices can have significant impact on the entire storage effectiveness; can be critical in the big data environment. We suggest the use of a hybrid storage device, which is an aggregate of hard disk drive (HDDs), and solid state drives (SSDs). HDDs provide huge storage capacity, at a relatively cheap price. This characteristic of the HDDs allows storage system to scale to meet the rate of growth of data. The disadvantage here is that, HDDs has a slow data transfer rate becoming a bottleneck for performance. On the other hand, SSDs provides avenue for high performance and reliability. They have low latency, thus providing a much faster, random access. SSDs are very expensive for the storage capacity they provide. The combination of these storage devices into a logical unit in an array should solve the storage demands posed by large datasets.

2. **Backup Strategies:** Recovery is the main objective for backup. The ability of production system to recover, and in a timely manner is very crucial in the era of big data. From this prospective, this paper recommend full back as a favorable choice over the others. Full backup ensures speedy recovery, through it takes a considerable amount of time to back up a large dataset. Applying full backup to large datasets may increase the data block repetition. Data reduplication technology, significantly reduce the volume of stored data block for every single full backup, and allow users to backup, and recover data within relatively short period of time. Rather than directly from the production system. Replication keeps copy of production data in real time.

3. **Business Continuity and Disaster Recovery:** An optimal business continuity solution, takes into account, two parameters, to a negligible level – Recovery Point Objective (RPO), which is the point in time that a production system, and data must be recovered after a disaster. Recovery Time Objective (RTO) is the time frame within which production system, and data must be recovered after a disaster. In a large dataset, the complexity of business continuity increases, with the influx of a variety of data, which must be maintained in their formats. Business continuity planning requires, saving a copy, or multiple copies of production data, through backups, local or remote replication. The use of enterprise software such as EMC Power path can be beneficial. EMC Power path provides features such as cluster support, dynamic load balancing, configuration and management, automatic path failover.

Conclusion

In the recent years, a academia pays more attention to cloud computing. Big data focuses on “data”, like data service, data acquisition, analysis and data mining which pays more attention on ability on data storage. Cloud computing focuses on computing architecture and practices. Big data and cloud computing are two sides of same issue.

Big data era has brought about an explosive growth of data. The increase of mobile applications, social media, and big data analytic initiatives has cause big data storage challenges to become even greater. Choosing the right storage devices, management tool, and efficient techniques is relevant and determines the rate of growth.

The approaches to big data storage and management can significantly, affect the entire organization. This paper examines and summarizes existing current storage technologies for big data applications. Variables such as capacity, scalability, data transfer rate, access time, and cost of storage devices, are also highlighted. Finally some suggestions are made to curb the problems posed by big data storage.

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Leap Protocol in Wireless Sensor Network

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ABSTRACT- Wireless sensor network are becoming significantly vital to many applications, and they were initially used by the military for surveillance purpose. One of the biggest concerns of WNS is that they are very defenseless to security threats. Due to the fact that these networks are susceptible to hackers, it is possible for one to enter and

render a network. For Example, such network may be hacked into the military, using the system to attack friendly forces, for this a key management protocol for sensor network i.e. LEAP (Localized Encryption and Authentication Protocol) is designed to support in-network processing. The design of protocol is motivated by the observation of different types of messages exchanged between sensor nodes have different security requirements and that single keying mechanism is not suitable for meeting these different security requirements , and LEAP uses four types of key for each sensor node. The prototype implementation of LEAP in sensor network is also reported.

Keywords*: Key Management (four key used by LEAP) , Sensor Network , Designing Goal of LEAP, Working of LEAP, TDMA-slot, TDMA-cycle, NS2Platform.*

INTRODUCTON

Wireless Sensor Network spatially consist of distributed autonomous sensors to monitor physical and environmental conditions such as temperature, sound, vibration, pressure motion and pollutants and to cooperatively pass their data through network to main location with the help of protocol.

Protocol: It specifies the standard for communication and provides detail information on processes involve in data transmission. A single process can handle by more than one protocol simultaneously.

LEAP (Localized Encryption and Authentication Protocol) is a proprietary wireless LAN (Local Area Network) authentication method developed by Cisco System. Important feature of LEAP is dynamic WEP (Wired Equivalent Privacy) Keys and mutual authentication between a wireless client and RADIUS (Remote Authentication Dial In User Service) Server.

LEAP (Localized Encryption and Authentication Protocol) , sometimes called EAP(Extensible Authentication Protocol)-Cisco Wireless, is interesting in that it was really the first commercial use of IEEE 802.1X and EAP(Extensible Authentication Protocol) for wireless LAN(Local Area Network)

LEAP (Localized Encryption and Authentication Protocol) PROTOCOL:

LEAP (Localized Encryption and Authentication Protocol) is the authentication protocol used in wireless network and point-to-point connection. LEAP is designed to provide more secured authentication for 802.11 WLANs (wireless local area networks) that support 802.1X port access control. It is a key management protocol for sensor network that is designed to support in-network processing, while providing security properties similar to those provided by pair wise key sharing schemes. LEAP includes support for multiple keying mechanisms. The design of this mechanism is motivated by the observation that different types of messages exchange between sensor nodes have different security requirements.

DESIGN GOAL

LEAP is designed to support secure communication in sensor network, therefore it provide the basic security services such as confidentiality and authentication. In addition LEAP is to meet several security and performance requirement that are considering more challenging to sensor network.

- Supporting Various Communication Patterns :

There are typically three types of communication pattern in sensor network : unicast (addressing a message to single node) , local broadcast (addressing a message to all the nodes in the neighborhood) , and global broadcast (addressing a message to all the nodes in the network).

- Supporting In-network Processing: Security mechanism should permit in network processing operation such as data aggregation and passive participation. In network processing could significantly reduce energy consumption in sensor network.

- Survivability: Due to the unattended nature of sensor network an attacker could launch various security attacks and even compromise sensor node without being detected. Therefore , a sensor network should be robust against security attacks, and if an attack succeed , its impact should be minimized .

- Energy Efficiency: Due to the limited battery life time, security mechanism for sensor network must be energy efficient. Especially, the no of message transmission and the number of expensive computation should be as few as possible. Moreover size of sensor should not be limited by the pre-node storage and energy resources.

- Avoiding Message Fragmentation: A unique challenge in sensor network is due to small packet size. The default supported packet size is only 36 bytes for increasing the reliability of packet delivery. Thus the message in security

protocol has to be small enough to fit in one packet to avoid message fragmentation.

Key Management Scheme:

LEAP supports the establishment of four types of keys for each sensor node :

An individual key shared with the base station. Every key has unique key that it shares with the base station. This Key is used with secure communication between nodes and the base station. Individual key is used to compute message authentication code for its sensed reading by node, if it is verified by base station.

A pair wise key shared with another sensor nod:

Every node shares pair-wise key with each of its neighboring node. In LEAP pair wise key is used for securing communication that requires privacy and source authentication. Each node can used its pair-wise key to secure the distribution of cluster key to its neighbor or to secure the transmission of its sensor reading to an aggregation node.

A cluster key shared with multiple neighboring nodes:

A cluster key is key shared by node and its neighbors and it is mainly used for securing locally broadcast message i. e. routing control information or securing sensor messages which can benefit from passive participation.

A group key shared by all nodes in the network:

This is globally shared key used that is used by base station for encrypting message that are broadcast to the whole group. For Ex: The base station issues missions , send queries and interests.

Security Requirements for Key Management

To provide secured communication in WSN, sensor node first need to setup pair-wise with each other. There are some majors:

Data Confidentiality: In sensor network data flows from many intermediate nodes and chances of data leak is more hence only encrypted data is used so that only recipient decrypts the data to its original form.

Data Integrity: Data receive by receiver should not be altered or modified is data integrity.

Data Authentication: It is the procedure for confirmation that the communicating nodes is the one that it claims to be. It is important for receiver to do verification that the data is receive from authenticate node.

Data Availability: This means the services are available all the time even in case of some attacks such as Denial of service.

Source Localization: For Data transmission some application use location information of the sink node. It is important to give security to the location information. Non-secured data can be controlled by the malicious node by sending false signal strength or replaying signals.

Self-Organization: In WNS no fixed infrastructure exists , hence every node is independent having properties of adaption to the different situation and maintain self organizing and self healing properties. This is the great challenge for security in WNS.

Working of LEAP

The process is summarized as:

1. The authentication server challenges the device by sending a random string. The device must prove it knows the key by sending response derived from challenge.
2. The device sends a challenge to the authentication server, which must also respond correctly.
3. The authentication server generates and sends a session key to access point with the EAP (Extensible Authentication Protocol) success notification in RADIUS (Remote Authentication Dial In User Service) message.
4. The access point notifies the device of authentication using the EAPOL (Extensible Authentication Protocol Over LAN)-Success message. At this point the client computes the matching session key.
5. The access point sends an EAPOL(Extensible Authentication Protocol Over LAN) key to activate encryption.
6. The device and access point communicate using WEP encryption.

Figure 1: EAP-LEAP

Hardware Technologies

A sensor network is an embedded system, or rather a digital system committed to specific duties. Each node consist of sensor board and a programming board. The sensor board could be differentiating by specific kind of sensor. Light, temperature, humidity but also distance tracking or GPS receiver. The programming board supplies wireless between a

node and a base station. A node is equipped with a microcontroller and low storage memories.

NS2 Platform : It is an open source simulation tool that runs on LINUX . It is a node platform for low power and high data rate sensor network applications designed with dual goal of fault tolerance and development ease. The low power operation of the module is due to the low power T1 MSP430 microcontroller. This 16-bit RISC processor features low active and sleep current consumption. In order to minimize power consumption, the processor in sleep during majority of the time , wakes up s fast as possible to process , then return to sleep mode again.

Software Technologies

It follows the demand of specific ad hoc software technologies. Hence, operating system for WSN nodes are typically less complex than general-purpose operating system. In general operating system in WSN should fulfill requirements like:

1. Robustness: once deployed, a sensor network must work unattended for months and years.
2. Low resource usage: sensor network node includes very small RAM, and run off batteries.
3. Multiple service implementations: application should be able to choose between various implementations.
4. Adaptability to evaluations: mote hardware is in constant evaluation, application and most system service must be portable across hardware generation.
5. Adaptability to application requirements: applications have very different requirements in terms of life time, communication, sensing etc.

Leap implement token passing procedure that:

- Ensures synchronization between nodes and clusters.
- Allows initializing and self configuring to the optimal working point
- Allows for the addition of new nodes

A token is a particular message that carries the information on the duration of TDMA-slot and a TDMA-cycle, the transmitting and receiving schedule of TDMA-cycle, a synchronization message carrying the current execution state of the TDMA-cycle. The controller has all the information to calculate the optimal set of parameters, consequently, it is able to generate a token before the network starts operating. The network initialization algorithm works as :

1. When the network starts all nodes are awake and listening.
2. The controller multi cast the token to all nodes of one of the connected cluster.
3. Nodes of the selected cluster read the information on scheduling and duration of TDMA-slot and TDMA-cycle. Moreover each node acquires the information about the global time and launches periodic timer for CSMA and TDMA slot. In the midtime, a random back-off timer starts for each node before sending an acknowledgement.
4. The first node that expires the back-off time sends the acknowledgement to the controller and become the token forwarder. Then all nodes in the cluster go to sleep.
5. At the beginning of the second TDMA-slot the token forwarder wake up and immediately multi-casts the token to all nodes in the next cluster.
6. With the same random acknowledgement-based scheme, a node is elected token forwarder for nodes in following cluster.
7. Information about routing and TDMA-slot duration needs also to be updated during network operation. Hence, the Controller periodically performs a token refreshing procedure.

Conclusion

The LEAP protocol was implemented and simulated using one base station and fifty sensor nodes situated randomly. Initially, an individual key was generated for each node from a randomly generated master key. Then a cluster key was generated by each node and published to their neighboring nodes using the pair –wise keys. Finally the global key was generated in order to enable public broadcasts.

The whole idea behind LEAP was to implement a system whereby multiple base station have been employed for the soul purpose of improving tha data transmission amongst node and to come up with a solution for base station , should it be compromised.

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RESEARCH ARTICLE

A COMPARATIVE STUDY OF GRID AND CLOUD COMPUTING

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ABSTRACT

The Cloud computing is the development of parallel Computing, Distributed Computing and Grid Computing. The Cloud Computing is not a very new concept because it is connected to Grid Computing Paradigm, whose concept came into thirteen years ago. Cloud computing is not only related to grid computing but also related to utility and cluster computing. Cloud computing is computing platform for sharing resources which include software's, business process, infrastructure and applications. It is also relies on technology of virtualization. In this paper, we will discuss about grid and cloud computing and how cloud computing is different from other. In this paper, we will also highlight the future of computing as cloud computing. Also to find the actuality of the fifth generation computing in the form of Cloud Computing.

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INTRODUCTION

In olden days, there was time shared computing system (Robert, 2009). Grid computing is a processor architecture that associates computer resources from various areas to reach an objective. In grid computing, an individual, computer can connect with network of computer that can perform the task together, thus working as a Super Processor (Devika Rani Dhivya, 2015). The idea of cloud computing is to come to existence to reduce the cost of computing, to increase reliability and increase flexibility by transforming computers (Ian Foster, 2018). Technically speaking, grid computing enables the virtualization of the distributed computing and data resources i.e. processing, network bandwidth and storage capacity to create a single system image, granting users and applications access to vast information technology(IT) capabilities (Rahul Kumar, 2013).

Grid Computing: It is a combination of computer resources which is from multiple administrative domains applied to common task. It is a type of parallel and distributed systems that enable the sharing, selection, aggregation of geographically distributed autonomous resources at runtime which is depending on their availability, capability, performance, cost and user-quality-of-service requirements (Future generation Computer Systems, 2009).

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It is shared collection of reliable and unreliable resources. It is a collection of servers that are clustered together. Grid computing is all about sharing, aggregating, hosting and offering service across the world (Indu Gandotra, 2011). The concept of Grid Computing will get cleared from Fig. 1.

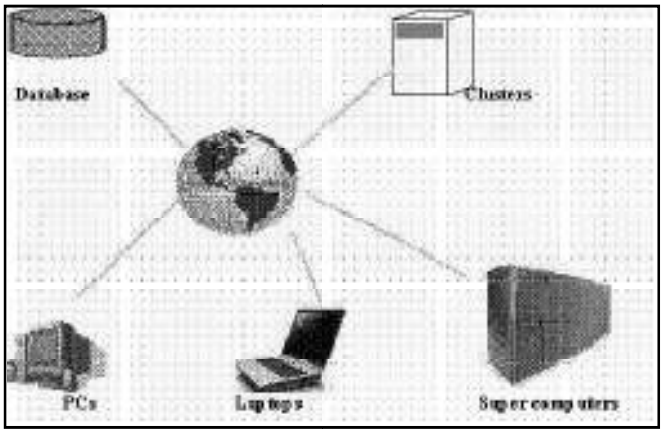

Fig. 1. Grid Computing

Grid Computing Architecture: Grid targeted on integrating existing resources with their hardware, operating system, local resource management and security infrastructure. Grids define and provide a set of std. protocols, middleware toolkits and services built on top of these protocols. Grid provides protocols and services at five different layers as identified in Grid protocols architecture (Devika Rani Dhivya, 2015).

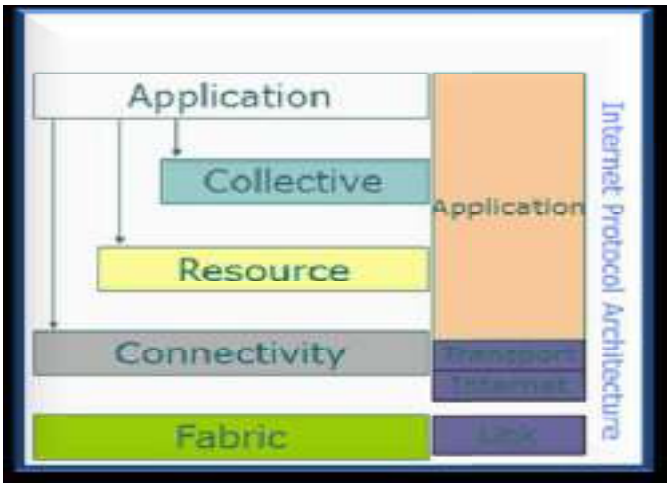

Fig. 2. Architecture of Grid Computing

Fig. 3. Grid computing concept

The above fig. shows the general concept of grid computing which shows that various resources are segregated from across the globe or geographically dispersed locations towards a central location i.e. Grid system.

Types of Grid Computing

Different types of Grids in Grid Computing

- Data Grid
- Computational Grid

Data grid is a grid computing system that deals with the controlled sharing and management of distributed data

- Storage Resource Broker (SRB)
- Computational Grid is a Grid computing system that is concerned with the computation

Applications

A. Advantages of Grid Computing (Grid Computing)

- **Access to Additional Resources:** In addition to CPU and other storage resources, a grid can also provide other resources as well.
- **Resource Balancing:** A grid incorporates large number of systems into a single system image. For applications that are grid enabled, grid performs the resource balancing by scheduling grid jobs on machines that are showing low utilization.
- **Reliability:** The systems in grid are cheap and geographically dispersed. If, for example, there is power or cooling failure at one site, then that will not affect the other site, thus high reliability will be there specially in case of real time systems.

B. Disadvantages of Grid Computing (Grid Computing)

- **Not Stable:** Grid software and standards are not stable in comparison to other computing. Its standards are still evolving.
- **High Internet Connection Required:** Gathering and assembling various resources from geographically dispersed sites require high internet connection which results in high monetary cost.
- **Different Administrator Domains:** Sometimes political issues arise when sharing resources among different domains. Some additional tools are required for having proper syncing and managing among different environment.

Cloud Computing

The main idea behind cloud computing is to make applications available on flexible execution environments located in Internet (Indu Gandotra, 2011). It is a complete new technology. It is the development of parallel computing, distributed computing, and grid computing. It is the combination and evolution of virtualization, utility computing, Software – as –a-Service(SaaS), Infracture-as-a-Service(IaaS), Platform-as-a-Service(PaaS) and Data-as-a-Service(DaaS) (Santosh Kumar, 2012). "Cloud is a Parallel and Distributed computing system of a collection of inter-connected and virtualized computer based on service level agreements (SLA).

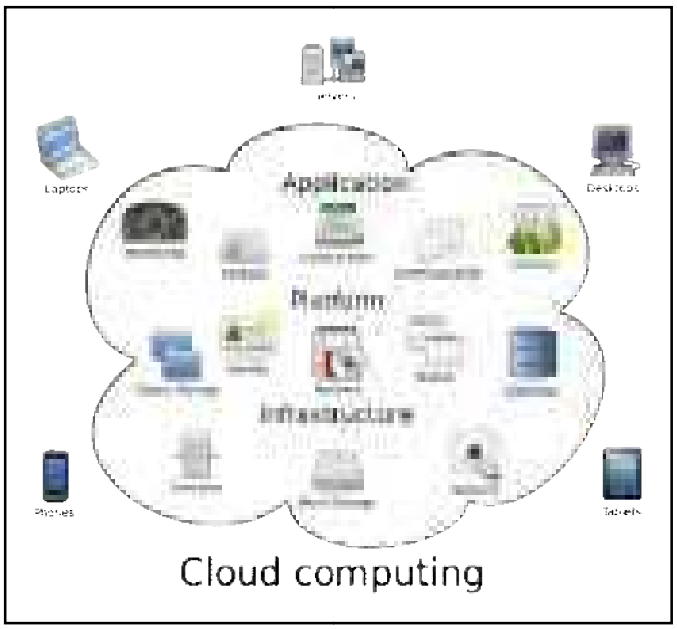

Fig. 4. Cloud Computing

Forrester defines cloud computing as

"A pool of abstracted, highly scalable, and managed compute infrastructure capable of hosting end-customer applications and billed by consumption."

Fig. 5. Five features of Cloud Computing

Cloud Computing architecture

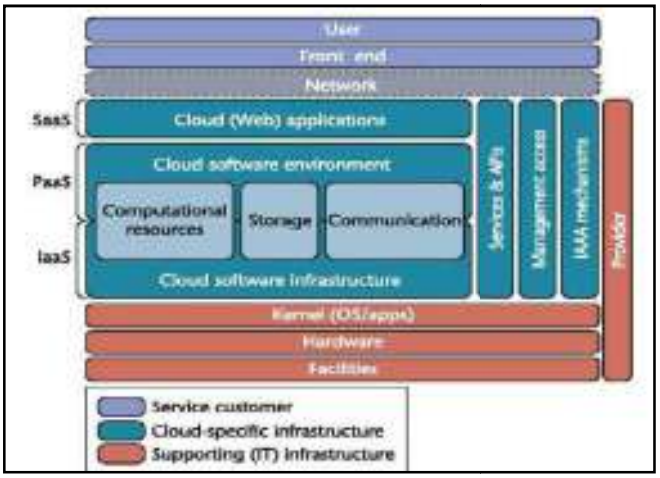

Fig. 6. The Cloud reference architecture

The Fig. 6 shows a cloud reference architecture (Santosh Kumar, 2012), that makes the most important security cloud components explicit and provides an abstract overview of cloud computing for security issue analysis.

The services (http//www.Dolcera.com/wiki/ondex.php?title=cloud_computing#cloud_computing_comparison_of_different_vendors) provided by cloud provides are –

- SaaS – Software as a Service Network-hosted application. (By Google Apps, Salesforce.com)
- DaaS – Data as a Service Customer queries against provider's database. (By Google Big Table, Amazon simple DB)
- PaaS– Platform as a Service Network – hosted software development platform. (By Windows Azure, Google App Engine)
- IaaS – Infrastructure as a Service Provider hosts customer VMs or provides network storage. (By Amazon web service EC2, Gogrid, Rackspace)
- IPMaaS – Identity and Policy Management as a Service Provider manages identity and/or access control policy for customer (By Rightscale, Appistry)
- NaaS – Network as a Service Provider offers virtualized networks (e.g.VPNs)

The concept of Cloud Computing will get cleared from Gig. 7.

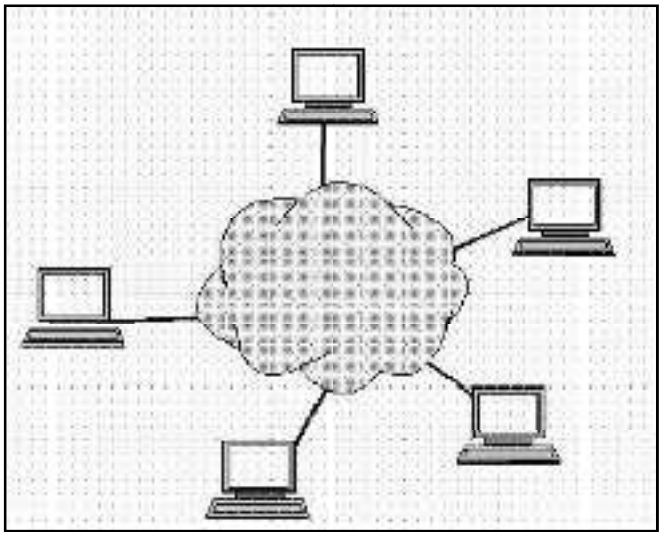

Fig. 7. Cloud Computing

Cloud Computing Types

Public, Private and Hybrid Cloud

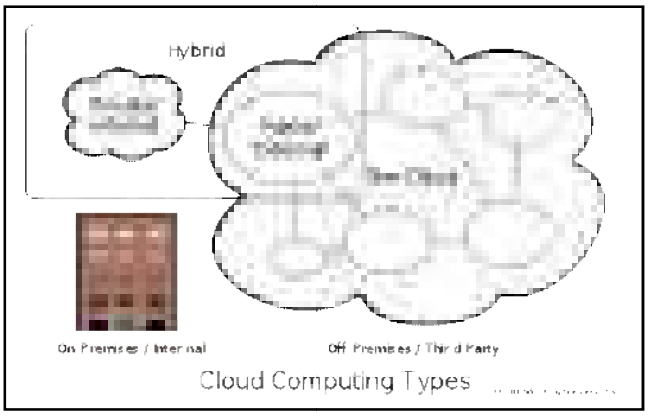

Fig. 8. Cloud computing Types

Public Cloud

Public clouds are owned and operated by third parties; they deliver better economies of scale to customers, as the infrastructure costs are spread among a mix of users, giving each individual client an attractive low-cost, "Pay-as-you-go" model. One of the advantages of a Public cloud is that they may be larger than an enterprises cloud, thus providing the ability to scale seamlessly, on demand.

Private Cloud

Private clouds are built exclusively for a single enterprise. They aim of Private Cloud is to address concerns on data security.

There are two variations to a private cloud:

- **On-premise Private Cloud:** also known as internal clouds are hosted within one own data center.
- **Externally hosted Private Cloud:** This type of private cloud is hosted externally with a cloud provider.

Comparism between Grid and Cloud Computing:

Grid Computing	Cloud Computing
Cha. Of Grid Computing • Loosely coupled (Decentralization) • Diversity and Dynamism • Distributed Job Management and scheduling(http;//www.jatit.org/research/introduction_grid_computing.html)	Cha. Of Cloud Computing • Dynamic computing infrastructure • It service-centric approach • Self-service based usage model • Minimally or self-manged platform • Consumption-based billing
In grid computing, the computers do not have to be in the same physical location 7 can be operated in dependently. As far as other computers are concerned each computer on the grid is a distinct computer.	In cloud computing, the computers need not to be in the same physical location.
The computers that are part of a grid can run different operating systems and have different hardware.	The memory, storage device 7 network communications are manged by the operating system of the basic physical cloud units. Open source software like LINUX can support the basic physical unit management and virtualization computing.
Grid is inherently distributed by its nature over a LAN, WAN.	Clouds are mainly distributed over MAN.

Areas of Grid Computing(http;// www.jatit.org/research/introduction_grid_computing.html)
• Predictive Modeling and Simulations
• Engineering Design and Automation.
• Energy Resources Exploration
• Medical, Militry and Basic Research Visualization
	Areas of Cloud Computing
	• Banking
	• Insurance
	• Weather Forecasting
	• Space Exploration
	• Software as a service
	• Platform as a service
	• Infrastructure as a service
	• Data as a service

Any Std. OS(dominated by Unix)	A hypervisor(VM) on which multiple Oss run
Benefits of Grid Computing (Shruti, 2013) • Exploiting underutilized resources • Parallel CPU capacity • Virtual organization for collaboration and virtual resources • Access to additional resources • Reliability • Management	Benefits of Cloud Computing (Usha Albuquerque, 2017) • Flexibility • Disaster recovery • Automatic Software updates • Free capital-expenditure • Work from anywhere • Document control • Security

Hybrid Cloud

Hybrid Clouds combine both public and private cloud models. The Hybrid cloud environment is capable of providing on-demand, externally provisioned scale.

Advantages of Cloud Computing

Shared Resources: It shares resources to provide the services to multiple users.

- **Pay-As-You-Go:** Users only need to pay those resources which are used by them. They can demand for more resources if they required.
- **Better Hardware Management:** It is easy for cloud service provider (CSP) (provider.techtarget.com/ definition/cloud-provider.) to manage the hardware easily because all computers run the same hardware.

Applications of Cloud Computing

Following are some applications of cloud computing (Zhang, 2010)

- Cloud computing provides dependable and secure data storage center.
- Cloud computing can realize data sharing between different equipments.
- The cloud provides nearly infinite possibility for users to use the internet.
- Cloud computing does not need high quality equipment for the user and it is easy to use.

Benefits of Cloud Computing

The cloud computing is the next big future in computing. It has many benefits like better hardware management. It also provides better and easier management of data, because all data is located on central server so that administrator can control who have access to files (Indu Gandotra, 2011). It also reduces runtime and response time, minimizing the purchasing and deployment of physical infrastructure.

Conclusion

Cloud computing is a new technology of computer network, providing the web services at lower comparing to normal techniques. It contribute to improve the service in other related technologies like

Grid Computing, Cluster Computing
Utility Computing / Automatic Computing
Distributed Computing

Cloud computing is growing part of IT. It has the potential to become a favorite in promoting a secure, virtual and economically viable IT solution in the future. EUCALYPTUS is an open source software framework for cloud computing.
In this way we can say, that fifth generation of the Computing in the form of Cloud Computing has been already started.

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Review on social security attacks on online social networking for Rumors Blocking

Mrs.Shita.M.Mohod Dr.Swati S. Sherekar Dr.V.M.Thakare Dr. N.B.Raut

Abstract- **An online social media is a big platform to share thoughts, ideas and knowledge. Now a days the day life strees with social platform and end on it as well this will become big media of communication. This media will share the good as well as bad thoughts.In this rumor gets spread with the speed of light. So it is necessary to block or filter the media to spreading the rumors, for that the activities done due to rumors can be stop. People from different geometric locations to talk, share photos, ideas and interests, or make new friends as a virtual community is a website on the internet that serves as an ultimate location for. Online social network increase in security treats and rumors with the rapid increase in popularity. By exploiting user's privacy, identity and confidentiality the intruders and attackers are able to outsmart the security measures by using several techniques. In social networking sites users may be unaware of the existence of these rumors. In this paper we proposed different types of attacks to fight against rumors on social network. In this paper we study an overview and classification of Sybil, Malware, Distributed Denial-of-service(DDOS) and Spam attacks.**

Keywords- **Attacks, OSN, DDOS, Social Security Network, Rumor Blocking**

I. INTRODUCTION

With the rapid increase in online Internet users, an online social network such as Twitter, Facebook and Whatsapps. Due to this with more terrible effects rumors can spread faster. In real world situation, Rumors exist in almost every domain of society. We study different types of attacks to fight against rumours on social network.OSN services handle user's information and manage all users activities in the social network. For the correct functioning of services and maintaining a profitable business model OSN's are responsible. OSN's may be translate into reputation damage Service due to following attacks. We classify the four types of attacks those are Sybil,DDoS,Spam and Malware. we also discuss merits and demerits with suitable protocols, techniques, Layers and varient parameters.

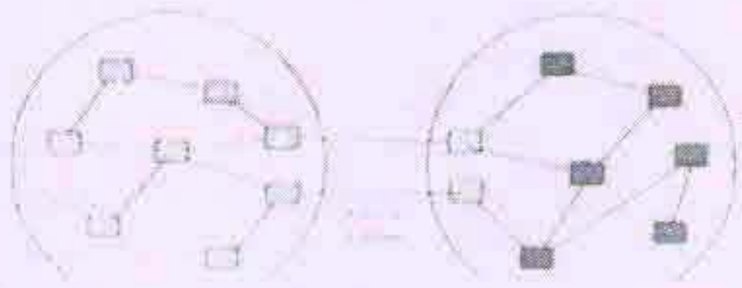

Figure 1: Sybil Attacks

In the Sybil attack, the malicious user claims multiple identities to compromise the whole network. Sybil attacks can be used to access resources or to break the trust mechanism behind a P2P network. The assumption that a P2P network is built on each entity in the network which holds a single identity. With a single entity or with no entity, Sybil attack occurs due to many bogus identities at all. Using Sybil identities, an adversary may provide false opinions for his evil benefits, limit the amount of resources reaching each node, break the trust mechanism in a P2P network and may even cause a Denial-of Service attack(DDoS)[1].digital signatures and digital analyzers were used to mitigate the Sybil attacks[2]. Much effort has gone into the study of trust relationships in social networks [1][2][3][5] and community based schemes to reduce the influences of Sybil attacks [6][7].

2. TYPES OF ATTACKS

2.1Classification of Sybil attacks

(i) Direct vs. In-Direct communication

The attacker must consider the type of communication between honest nodes and Sybil nodes [2][5]. If the communication between honest node and Sybil node is direct, i.e. if the attacker can directly communicate with the honest node using fake identities, it is a case of direct communication. However, if the attacker has to use his rightful or genuine identity to communicate with the honest node, and then divert the Sybil data to the honest node via the valid node, it is the case of indirect

communication.In direct communication, attacker has easy task to instigate Sybil attacks and it is also more difficult to detect such attacks.

(ii) **Busy vs. Idle:** In a P2P network, normally, only few Sybil identities participate in the network while the others remain idle [2]. The power of the Sybil attacker comes from the number of identities he or she holds. If an attacker could afford to get fake identities easily, he or she can make the identities appear more realistic by making them leave and join the network multiple times pretending as an honest node [5].

(iii)Simultaneous vs. Non Simultaneous A simultaneous attack can be performed by involving all the Sybil identities simultaneously or a single physical node can change its identities in regular time slots to appear like all the identities are involved simultaneously. In non-simultaneous attack, an attacker may bring all his identities into the network slowly over a period of time involving only few identities each time. This can be done by pretending that one identity is leaving the network while the other identity is joining the network. As honest identities generally tend to leave and join the network number of times, the malicious node won't be suspected if they pretend to leave or join the network now and then using different identities[8].

(iv) **Insider vs. Outsider** The impact of the Sybil attack depends on whether the attacker is inside or outside the distributed network. If the adversary is part of the network and holds at least one real identity, then the attacker is called an Insider, otherwise he or she is an outsider. An insider may introduce many fake identities, and pretend to communicate with other nodes using his fake identities. However, for an outsider, it is difficult to introduce Sybil identities into the network.

2.2 Distributed Denile-of-service:

A distributed denial-of-service (DDoS) attack occurs when multiple systems flood the bandwidth or resources such as a server, web site or other network resource. The flood of incoming messages, resource requests to the target system forces it to slow down. Exploited machines can include computers and other network resources such as IoT devices. In DDoS attack, the attacker begins by exploiting a flaws in a system that can leave it open to attack and making it the DDoS master. The flaws in a system also called vulnerability. A computer or networked device under the control of an intruder is known as a Botnet [10]. The person in control of a botnet is sometimes referred to as the botmaster (that term has also historically been used to refer to the first system "recruited" into a botnet because it is used to control the spread and activity of other systems in the botnet).Botnets can be comprised of almost any number of bots, botnets with tens or hundreds of thousands of nodes have become increasingly common, and there may not be an upper limit to their size.

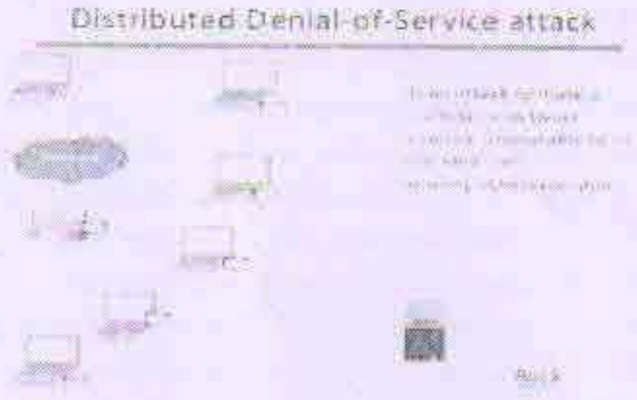

Figure2. DDOS

2.2.1 Classification of DDoS attacks:-

(i) Volume Based Attacks. The attack's goal is to saturate the bandwidth of the attacked site and Magnitude. Volume based attack include UDP floods, ICMP floods, packet floods with bandwidth. The inundation of packets at the target causes a denial of service. The internet of things (IoT) may be useful to legitimate users in some cases [9], they are even more helpful to DDoS attackers. The devices connected to IoT include any appliance into which some computing and networking capacity has been built, and, all too often, these devices are not designed with security in mind[9].For example, for attackers, devices are often shipped with hard-coded authentication credentials for system administration, to log in simply.some other cases, the authentication credentials cannot be changed. Devices also often ship without the capability to upgrade or patch device software, further exposing them to attacks that leverage well-known vulnerabilities. Internet of things bonnets are increasingly being used to wage enormous DDoS attacks[9].

2.3 Spam Attack

Spam can spread out in any information systems like emails, web, social network sites, and blogs or in review platforms. it is an endless repetition of worthless text or image. The concept of web spam was introduced in 1996 [11] and it soon become key challenges for search engine industry [12].Nowadays the major search engine companies have

identified adversarial information retrieval [13] as top priority because of multiple negative effects caused by spam, and also the appearance of new challenges in the field of research. In the first spam the quality of research spoils and prevents the genuine websites of revenue that might earn in the absence of spam. Second it weakens the trust of user in a search engine provider which is a notable issue since the user can easily continue his search form one search engine to other. In Spam to send out unrequested or unwanted messages in bulk, the electronic messaging system to be used.

Figure 3:Spam Attacks

2.3.1Classification of Spam Attack

i) Social network spam: The development of social networking site become very high in the past few years.The people communicate with their friends and chat or share multimedia contents with them. Sites like face book, twitter are constantly among top 20 most viewed websites on the internet [13].

People spent more time on social network compared with other sites. The increasing popularity of social networks allows them to collect a huge amount of personal information about the users, their friends, habits and also their wealth information. In social network a person can reach any person which is attracted by the spiteful parties.As for Twitter, [12] ran an experiment on Twitter spam. Regarding the drawbacks in Bayesian spam filter an user-friendly spam filter called Social network Aided Personalized and effective spam filter (SOAP) is used.social closeness spam filtering, social interest based spam filtering, and adaptive trust management.

ii) **Email spam:** The most common communication in the internet is using email communication. With the vast growth in email and its popularity unsolicited e-mail (spam) also emerged very quickly with almost 90% of all email messages. i.e., over 120 billion of these messages are sent each day [12]. The cost of sending these e-mails is very close to zero being easy to reach a high number of potential consumers [13]. In this context, spam consumes resources, time spent reading unwanted messages, bandwidth, CPU, disk, being also used to spread malicious content. The email system design can easily be exploited by spammers who send inaccurate information. All email on the Internet is sent via a protocol called Simple Mail Transfer Protocol ("SMTP").SMTP is designed to capture information about the route that an email message travels from its sender to its recipient. In actuality, the SMTP protocol provides no security, email is not private, it can be altered en route, and there is no way to validate the identity of the email source.

iii) Image spam: Image spam have been proliferated through emails which contain the text of the spam message in a human readable image instead of the message body. The spam message into images will be embeded as email attachments. Textual content performed by spam filters, including automatic text classifiers becomes the goal for spam to circumvent the analysis of emails. Since attached images are displayed by default by most email clients, the message is directly conveyed to the user as soon as the email is opened. The simplest kind of image spam can be viewed as a screen shot of a plain text written using a standard text editor.

iv) Click spam. In click spam, the spammers generate fraud clicks and make the control function towards their websites. To achieve the goal spammers submit queries to search engine and click on the links point to the target pages [12, 13]. Online advertising is other incentive for spammers to generate fraudulent clicks [13]

V) Content spamming.In content spamming changing the logical view that the search engine has over the page contents. An example of content spamming is keyword stuffing which involves placement of keywords within the webpage to raise the keyword count.

Malware Attack

Malware does the damage after it is implanted or introduced in some way into a target's computer and can take the form of executable code, Script, active content and other software[14].The code is described as computer viruses, worms, Trojan Horses, Spyware[15]. The term

malware comes from combining the two words malicious and software, and to be used to indicate any unwanted software, any code added, changed, or removed from a software system.[16].The purpose of Malware is to cause damage or penetrate users computer for the purpose of hacking personal data for illegal activity such as financial crimes. Many DoS viruses, and the Windows Explore Zip worm, are designed to

demolish files on a hard disk, or to corrupt the file system by writing void data to them.

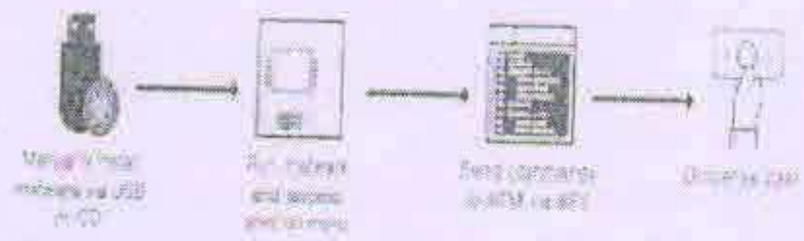

Figure 4: Malware Attacks

2.4.1 Classification of Malware Attack

Several malware classifications have been issued so far, depending on some of their characteristics. The purpose of such classifications is to facilitate the tracking of authorship, correlating information, identifying new variants [17]. However, The classification made, is to categorize the major common malware types into groups depending on the network and web usage.

i) Network-based Malware

Spyware is a kind of malware that is installed secretly on a user computer for the purpose of collecting information about users without their knowledge [17]. Even reputable vendors of software like Microsoft and Google, intentionally, collect information of their users using spywares [18].

Cookies are some information stored on user's computer by their web browsers. The main purpose of cookie is to authenticate users depending on the information stored in, storing site preferences and server-based session [17].

Trojan horse is a code that appears to be a useful program, but actually it steals information or corrupts data [17, 18].

Botnet is a collection of infected computers (contains bot software embedded in it) that have been taken over by hacker and used to perform malicious functions, without the hackers having to log into the client's computer. Botnet can make DoS attack as many clients' bots, under control of hacker bot, having a role of attack [19, 20].

ii) Ordinary Malware

Virus is any software code that has the ability to replicate itself, during infection, into any other application software or a document. Viruses can do harmful functions on a user machine; it can make destruction to the whole system from infected device to uninfected one [18, 19, 20].Worm is any software code that has the ability of self replicating on victim computer. Worms are independent, they don't need for a host program to start lifecycle [20]

Layers	Network	Transport, Application	Applic ation	Network
Techni ques	Light Weight Sybil Attack Detection	Defence techniques	Rule Based scoring system	Signature and Detection
Metho ds	Robust,Li ghtwei ght	Artificial Neural Network	Spamm ers	Pre-pending,En dding,Post pending
Virus Activa ted	Worm Rumor(B ogus	Bomet I	Worms Repetit ion of	Trojan Horse
Mode of Attack s	Identities)	ntruder	worthle ss text or image	Intrusive Code
Protoc ol	P 2 P	UDP,TCP/I P,HTTP, SMURF	SMTP, VOIP	UDP,HTTP,S OCKS 4/5
Merits	i)Efficien t in large overhead ii)No clock synchroni zation	i i) Detecting and stopping a DDoS attack at the source providers. ii) minimum damage is done on legal traffic	i) In a short period of time it is essential to send as many messages as possible ii) Transitio nal period is the only one service need to be maintain ed	i) Protection from Phishing Attacks. ii) Provides Robust Web Protection.

			instead of two parallel running services	
demerits	i) reliability is lesser ii) May encourage attackers economically	i) Sources are widely distributed across the network and a single source behaves like a normal traffic due to this it become difficult to detect DDoS attack at source end. ii)The difficulty of deploying system at the source end.	i) Sending Email capacity become limitted. ii) Analyzing the messages to determine if they contain spam.	i) Security defects in software ii)Insecure design or user error.

III. Conclusion

Social security attacks are needed to fight against rumors blocking on social network. In this paper, we study how social network security attacks occur to fight against rumors on social network and their classification with variant parameters. In Sybil attack, an intruder may introduce many unauthorised identities and to communicate with other nodes using unauthenticated identities. For an outsider it is difficult to introduce sybil identities into the network. In DDoS multiple computer systems attacks a object such as server, website or other network resources and exploiting a vulnerability in one computer system and making it the DDoS master. Using SMTP, VoIP protocols, Spam is essential to send many messages in short period of time. There is an endless repetition of worthless text, lines, videos and images. Spam can spread out in any information system like E-mails, Web, Social Network Sites.Using malware attack any code added, changed or removed from a software system by intentionally causing harm or to disturb the internal function of the system that encompasses viruses, Trojans and other intrusive code. The purpose of such classification is to facilitate the tracking of authorship., correlating information, denitrifying new varients.In future to avoid rumor blocking occurance on social network we needed social security attacks in this direction.

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Study of Security Challenges in Multilayered Structure and Various Attacks on IOT

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Abstract- **Internet of Things (IoT) is one of the most buzzing and discussed topic in research field today. Some of the researchers are also looking future of the world in this technology. Since then significant research and development have taken place on IoT, however various vulnerabilities are observed which shall keep IoT as a technology in danger. Internet of Things (IoT) has been a massive Advancement in the Information and Communication Technology (ICT) .It is projected that over 50 billion devices will become part of the IoT in the next few years. Security of the IoT network should be the fore most priority. In this paper, we evaluate the security challenges in the six layers of the IoT architecture. IoT has no uniform architecture and there are different kinds of attacks on the different layers of IOT such as unauthorized access to tags the malicious node injection attack, sinkhole attack, worm attack and side-channel attack. IoT devices are more vulnerable to attacks because it is simple and some security measure cannot be implemented furthermore, important security technologies like encryption are also analysed in the IoT context. Finally, as per the need of our conveniences the present study discusses about various security attacks on different layers of IoT, classify them and finding the most prominent attacks in IoT and highlight the future research directions within the IoT architecture and help to promote the development of IoT.**

Keywords- **Internet of Things (IOT), layers architecture, Security, IOT Attacks**

I. INTRODUCTION

With the recent advancement in technology a potential innovation, Internet of Things is coming down the road which is growing as a global computing network where everyone and everything will be connected to the Internet [1]. Internet of Things is growing rapidly and the possibilities it can form are infinites. The number of machines requires internet services are increasing every day. The concept of allowing interaction between intelligent devices is a recent technology but the technologies composing the Internet of Things are goes back [2]. Internet of Thing is the approach of gaining data from different devices operated on different platform, and uniting them on any virtual platform existing [3].Internet of things ages back to 1982 when a modified coke machine was connected to the Internet. It has an ability to report the numbers of drinks contained within and that whether the drinks were cold or not [4]. In 1999, Bill Joy passed information about machine to machine communication [5]. In 1999, Kevin Ashton suggested the term "Internet of Things" to describe a communication between IoT comprises of a network of highly diverse digital objects interacted with each other and with humans too. It provides a sensor network with communication system, store and manage the information, provides access and also handles the privacy protection and data security problems [3]. Comparing the research aspects on security in IoT to security in Internet, former is the way complex than the later and therefore needs the significant attention of the researcher and a more precise research methodology and tools should been devices with the help of the internet [6].

II. Architecture of Internet of Things

More than 25,000,000,000 devices are expected to be interconnected by 2020 [9] which is a very large number so the current architecture of Internet with TCP/IP protocols, cannot manage a network as big as Internet of Things, hence to support that huge IoT network we need a new architecture that has an ability to handle various Quality of Service (QoS) and security issues in addition it has also capability of handling an existing network application. Without addressing suitable privacy promise, Internet of Things is not expected to be approved by many. Therefore security of data and isolation of users are crucial challenges for Internet of Things for advance growth of Internet of Things, a number of "*multilayered security architectures*" are proposed. Wang Chen has proposed a 3 level architecture of Internet of Things while Hui Suo proposed a 4 level architecture. Miao Wu has proposed a 5 layered architecture using Internet and telecommunication management networks architectures based on TCP/IP and TMN models individually. Similarly a 6 layered architecture was also projected based on the network hierarchical structure. So basically it has six layers as shown in the figure1

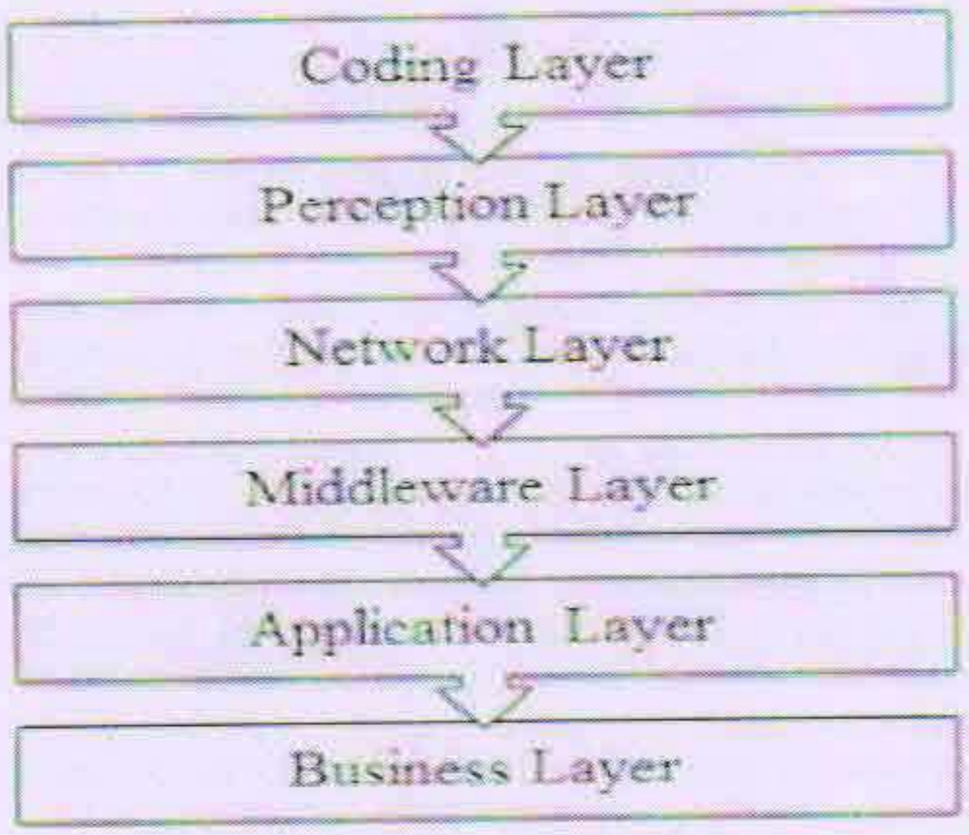

Figure-1 Six-Layered Architecture of Internet of Things

2.1 Coding Layer

Coding layer is the base of Internet of Things which gives essential identification to the devices that are part of Internet of Things. In this layer, each device is assigned with "*unique ID*" which makes it easy to distinguish the devices [2].

2.2 Perception Layer

Perception layer of Internet of Things, which provides a physical meaning to each device. It consists of data sensors in different forms which could sense the humidity, temperature, location and speed of the device. This layer collects the information of the device from the sensor connected with them and translates the information into digital signals which is then delivered onto the Network Layer for advance action.

2.3 Network Layer

The objective of Network Layer is accept the useful information in the form of digital signals from the Perception Layer and transfer it to the processing systems in the Middleware Layer through the trans-mission mediums like Bluetooth, WiFi, Zigbee, WiMaX, 3G, GSM, etc with protocols like IPv6, IPv4, DDS, MQTT, etc.

2.4 Middleware Layer

Middleware layer processes the data expected from Network Layer [2]. It contains the technologies like Ubiquitous computing, Cloud computing which provides a direct access to the database to record all the essential information in it. Using some Intelligent Processing Equipment, the information is processed and a fully automated action is taken based on the processed results of the information.

2.5 Application Layer

Application layer recognizes the applications of Internet of Things for all types of production, based on the administered data. Applications promote the advance development of Internet of Things so this layer is very useful in the huge scale development of Internet of Things network. The Internet of Things applications could be smart transportation, smart homes, smart planet etc.

2.6 Business Layer

Business Layer controls the services of Internet of Things and application and is liable for all the study related to Internet of Things. It makes different business models for different business strategies [1].

III. Different Security Attacks In IOT

In figure 1, a common IoT architecture is given. According to many researchers [4], IoT technology works on three layers perception layer, network layer and application layers as shown in Figure 1. Perception Layer involves various types of data sensors like RFID, Barcodes or any other sensor network. The aim of this layer is to obtain information from the environment by using sensors and then send it to the network layer. The aim of network layer is to transmit the data collected from the perception layer to any specific information processing system through internet, mobile network or any other kind of reliable network. The aim of the IoT of developing smart environment is accomplished at the application layer. The security of IoT is a big challenge because of complexity, heterogeneity and a large number of interconnected resources. The adversary can perform the attack on IoT system by damaging or tampering some node i.e. physical vulnerability, or from within its network by using faults in routing protocol and other network related protocol, or by using malicious program and by breaking encryption strategy i.e. encryption attack. Based on these vulnerabilities we classify the attack in four categories, as physical attack, network attack, software attack and encryption attack as shown in Figure 2. From each category, we considered one attack that is most dangerous from all the attack of that category. From physical attack, malicious node injection attack has been the dangerous attack. Since it is not only stopping the services but also modify the data. From network attack, sinkhole attack is the most risky attack. It not only attracts all the traffic towards the base station, but also the attacker can initiate other threats such as selective forwarding, altering or dropping the packets. From software attack, we select worm attack as most unsafe. Worms are probably the most destructive and dangerous form of malware on the internet. It is the self-replicating program which harms the computer by using security holes in networking software and hardware. It can delete the files in system, steals the information like passwords, they can also change the passwords without your notice, it causes the lockouts, etc.

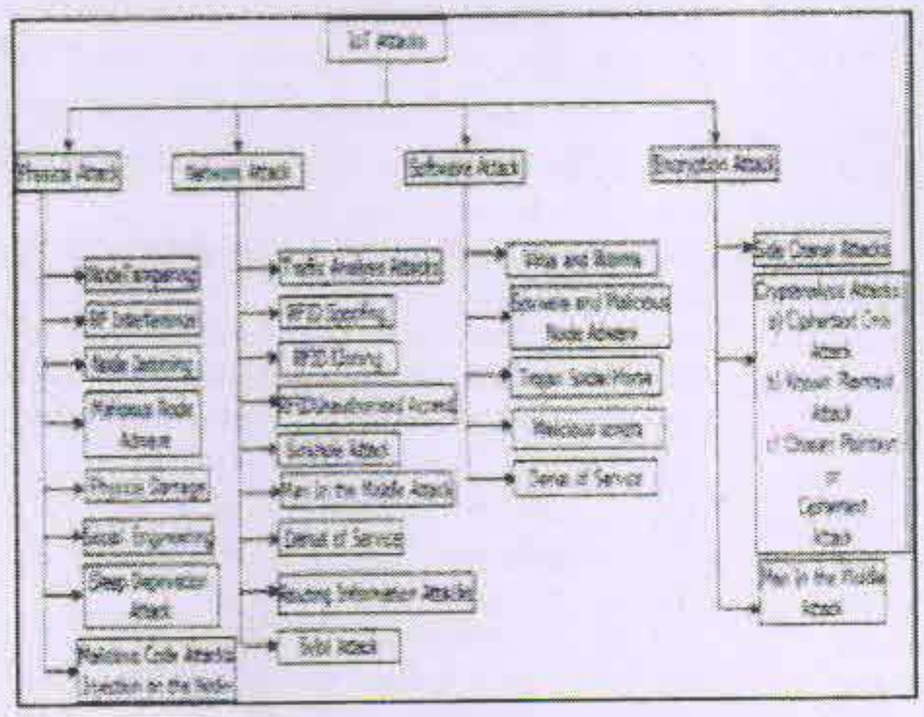

Fig. 2 IoT and its security attacks

From encryption attack, side channel attack is the most difficult to handle. It is very difficult to detect because attacker uses the side channel information to perform the attack [22].

IV. Classifications of IOT Attacks

4.1 Physical Attacks

Physical attacks are concentrated on hardware devices in the system.

4.1.1 Node Tampering: In this attack attacker physically alters the compromised node and can obtain sensitive information such as encryption key [21].

4.1.2 RF Interference on RFIDs: The attacker performs Denial of service attack by sending noise signals over radio frequency signals. These signals are used for RFID"s communication [22].

4.1.3 Node Jamming in WSNs: By using jammer the attacker can disturb the wireless communication. It causes Denial of service attack [21].

4.1.4Malicious Node Injection: In this attack, attacker physically injects a new malicious node between two or more nodes. It then modifies the data the passes the wrong Information to the other nodes. The attacker uses the multiple nodes to perform malicious node injection attack. The adversary first inserts a replica of the node B. After that, inserts other malicious nodes (node M1). Both these nodes work together to execute the attack. Thus collision is occurring at the victim node. Because of these, the attacked node cannot receive send any packet. Hence, the conclusion of watchdog nodes might be affected by incorrectly announcing the attacked node (the legitimate node) as acting maliciously. To prevent this attack, we use a monitoring verification (MOVE) scheme. It can check the monitoring node(s)" result and correctly identify any malicious behaviour. According to the acknowledgment, the verifier node will decide whether the node is malicious or not.

4.1.5 Physical Damage: The attacker physically harms components of IoT system and it results in Denial of service attack.

4.1.6 Social Engineering: The attacker physical interact manipulates users of an IoT system. The attacker obtai sensitive information to achieve his goals.

4.1.7 Sleep Deprivation Attack: The aim of the attacker is t use more power that results in shutting down of nodes [23].

4.1.8 Malicious Code Injection: The adversary physicall introduces a malicious code into the node of IoT system. Th attacker can get full control of IoT system [23].

4.2 Network Attacks

These attacks are focused on the network of IoT system.

4.2.1 Traffic Analysis Attacks: The attacker intercepts and examines messages to obtain network information [21].

4.2.2 RFID Spoofing: An adversary spoofs RFID signal Then it captures the information which is transmitted from RFID tag. Spoofing attacks give wrong information whic seems to be correct and that the system accepts [22].

4.2.3 RFID Cloning: In this attack, adversary copying da from pre-existing RFID tag to another RFID tag. It does n copy original ID of RFID tag. The attacker can inser on data or control the data passing via the cloned node [17].

4.2.4 RFID Unauthorized Access: If the correct authentication is not provided in the RFID systems then the adversary can observe, alter or remove information on nodes.

4.2.5 Sinkhole Attack: In a sinkhole attack an adversa compromises a node inside the network and performs t attack by using this node. The compromised node sends t fake routing information to its neigh boring nodes that it h the minimum distance path to the base station and then attrac the traffic. It can then alter the data and also drop t packets[25].

In paper [22] gives the simple technique to identify sinkhc nodes. In proposed technique, when a node send a packet to neigh boring node it creates the entry of hop distances and in its database. It then computes the average hop-count exce minimum hop-count and compares average and minim value. If this minimum value is too small as compared to t average hopcount, then it is vulnerable to sinkhole attack.

4.2.6 Man in the Middle Attacks: The attacker internet intercepts the communication between the two nod They obtain the sensitive information by eavesdropping.

4.2.7 Denial of Service: An attacker floods the network w large traffic so that services are unavailable to its intenc users.

4.2.8 Routing Information Attacks: In this attack, the attacl can make the network complex by spoofing, modifying sending routing information. It results in allowing or dropp packets, forwarding wrong data or partitioning the network.

4.2.9 Sybil Attack: In this attack, malicious node that takes identities of multiple nodes and acts as them. For e.g. Wireless Sensor Network, voting system single node can v many times.

4.3 Software Attacks

The attacker performs the attack by using virus, worm, spyware, adware etc. to steal data, deny the services, etc.

4.3.1 *Phishing Attacks:* The attacker obtains the private information like username, passwords by email spoofing and by using fake websites.

4.3.2 *Virus, Worms, Trojan horse, Spyware and Aware:* An adversary can damage the system by using malicious code. These codes are spreads through email attachments, downloading files from the Internet. The worm has the ability to replicate itself without any human action. We can use worm detector, anti-virus, firewalls, intrusion detection system to detect the virus.

The paper [17] combines anomaly and signature detection with honeypot to protect the system from worms. This hybrid scheme takes the advantage of honeypot and anomaly signature detection and provides the protection against worms.

4.3.3 Malicious Scripts: By injecting malicious script the attacker can gain access to the system.

4.3.4 Denial of Service: The attacker blocks the users from the application layer by denying services[10].

4.4 Encryption Attacks

These attacks depend on destroying encryption technique and obtain the private key.

4.4.1 *Side-channel Attacks:* The attacker uses the side channel information that is emitted by encrypting devices. It is neither the plaintext nor the cipher text, it contains information about power, the time required to perform the operation, faults frequency, etc. Attacker uses this information to detect the encryption key. There are different types of side channel attack such as timing attacks, Simple and Differential Power Analysis, and Differential Fault Analysis Attacks [21]. Here, we consider timing attack. Timing attacks are dependent on the time require for executing operations. It gives the information of the secret keys. By using this information an attacker can find fixed Diffie-Hellman exponents, factor RSA keys, and break other cryptosystems [21]. Cryptosystems process different inputs in different time. Because of branching and conditional statements, RAM cache hits, processor instructions that run in non-fixed time, etc. Timing computations are providing to a statistical model. It provides the guessed key bit to a certain extent of assurance.

Cryptanalysis of a Simple Modular Exponentiation:

Diffie-Hellman and RSA operations involve calculation of R = y mod n, where n is public and y can be obtained by a listener. The adversary wants to search the secret key x. To perform the attack, the victim must calculate yx mod n for many values of y, where y, n, and the estimation time are known to the adversary and x remains the same. The needed data and timing computation might be gained by secretly listening on an interactive protocol. Hence, an adversary could see the messages received by the target and calculate the time required to respond to each y. A common method to stop timing attacks is to perform all operations in such a way that they take absolutely the same amount of time by adding delay. Sometimes this is difficult.

4.4.2 Cryptanalysis Attacks: In this attack, the adversary obtains the encryption key by using either plaintext or cipher text. Based on methodology used, there are different types of cryptanalysis attacks.

4.4.2.1Cipher text Only Attack:

In this the attacker can access the cipher text and determine the corresponding plaintext.

4.4.2.2 Known Plaintext Attack: In this method, the attacker knows the plaintext for some parts of the cipher text. The aim is to decrypt the remaining part of the cipher text utilizing this information.

4.4.2.3. Chosen Plaintext Attack:

The attacker gets to choose what plaintext is encrypted and find the encryption key.

4.4.2.4 Chosen Cipher text Attack:

By using the plaintext of chosen cipher text the attacker can find the encryption key.

4.4.2.5 *Man in the Middle Attacks:*

When two users are interchanging the key the attacker intercepts the communication and obtains the key [25].

V. Analysis of Different IOT Attacks:

Table1: Comparison of IOT Attacks[13][25]

Classifications Types/parameters	Malicious Node Injection Attacks	Sinkhole Attacks	Worm Attack	Side-channel Attack
OSI Layer	Physical[11]	Network[12]	Application[12]	Application, physical[1]
Attack Type	Active –As the attacker compromise the node[16]	Active -As it provides the wrong information those results in packet dropping [15].	Active -As it modifies the files [13].	Passive-As the attacker can find encryption key by using the side channel information [1].
Attacker Location	External, Internal	External	Both	Internal
Attack Threat	Availability -due to collision at the victim node it cannot Transmit the packet [18].	Availability, Confidentiality -As all the data is attracted to the Compromised node [5].	Availability, Integrity, Authenticity -As it can delete, modify the data	Confidentiality, Integrity-by using side channel information it can find the encryption key [1].
Damage Level	High -As it can modify the data and pass the wrong info to other nodes [15].	High -As all data is flowing through Compromised node the attacker can do anything with packet [15].	High -As it can delete files, mail Documents [14].	High-As the attacker can obtains the secret key without detecting [1].
Detection Chances	Low -As it is replica (clone) of legitimate node [18].	Difficult -To detect when it is near to base Station [25].	Anti-virus can identify it [13].	Negligible because adversary uses side channel information [19].
Possibility of Prevention	Yes - If we could avoid replication attack [21].	Yes -if node authentication is provided [14].	Yes -by avoiding suspicious sites, files [13].	Yes –By using preventive methods [19].
Attacks Based on	Inserting Malicious Node [21].	Routing [19].	Malicious Code [13].	Side-channel information[19]

Vulnerability	Wireless Nature and Hidden Node Problem [21].	Node Authentication is not provided [14].	Not following Security Policies [13].	Side-channel information[19]
Existing solutions and their limitations	Not Possible to detect if more than two nodes are malicious, Consumes power because of over hearing [21]	When Malicious Node near to The base station (1 or 2 hop distance), Algorithm cannot accurately detect sinkhole node[18]	New worms are created everyday [13]	Affect the performance of the system [20].

VI. Conclusion

IoT has been a hot research topic for the last few years and like other revolutionary technologies, it also faces many challenges, most significant of which are the security and privacy threats. In this paper, we described the working of six layers of IoT (Coding layer, Perception Layer, Network Layer, Middleware (Processing) Layer, Application Layer, and Business Layer) and then we explored the security loopholes that can be exploited in these layers. As IoT uses network architecture which is similar to traditional network architecture for communication among different devices, flaws of traditional network architecture is also inherited in it. With the development of IoT, many kinds of attacks also have been invented to breach the security of IoT devices. Researchers have proposed different solutions on these attacks to tackle it. However implementation of all these security measures and techniques together consumes computation as well as battery power of devices which is not acceptable for IoT technology and its devices. There is a need of a security mechanism which handles maximum security. Problems but it should be light weight and robust for fit for IoT technology. Many of the attacks on IoT have been discussed and classified above. Some of these attacks can be avoided by just keeping some security precaution while the development of any application like checking node identity while communication or using devices which are difficult to tamper. However some attacks which are known,which are difficult to detect or prevent, there has been a need to find asecure and efficient solution. IoT is an extension of Internet, which brings new security challenges in multi-layered structure. The proposed IoT architectures are under various attacks on different layers, such as Physical attack, Network attack, software attack and encryption attack. There should be universal standards in architecture and security challenges. They can be helpful to promote the development and adoption of IoT .only in this way, can IoT develop better and can we achieve more benefits from the technology.

7.

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8. Internet of Things Security Architecture: Challenges and Issues

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Abstract

Wireless communication networks are highly prone to security threats. The major applications of wireless communication networks are in military, business, healthcare, retail, and transportations. These systems use wired, cellular, or adhoc networks. Wireless sensor networks, actuator networks, and vehicular networks have received a great attention in society and industry. In recent years, the Internet of Things (IoT) has received considerable research attention. The IoT is considered as future of the internet. In future, IoT will play a vital role and will change our living styles, standards, as well as business models. The usage of IoT in different applications is expected to rise rapidly in the coming years. The IoT allows billions of devices, peoples, and services to connect with others and exchange information. Due to the increased usage of IoT devices, the IoT networks are prone to various security attacks. The deployment of efficient security and privacy protocols in IoT networks is extremely needed to ensure confidentiality, authentication, access control, and integrity, among others. In this paper, an extensive comprehensive study on security and privacy issues in IoT networks is provided. In this paper, the in-depth meaning of Internet of Things (IoT) was explained. The role it contributes to our daily lives was described. The reason why security and privacy are the biggest challenges facing Internet of Things was given. Confidentiality, integrity and availability of IoT were analyzed.

Keywords : Internet of Things (IOT), Security issues in IoT, privacy, IoTAttacks, Confidentiality, Availability, Integrity.

1. Introduction

In a digital world, everything is being connected to the internet, from humans to electronic devices, objects and animals. The connections of those objects to the internet, which exchange and monitor data each other without the intervention of human being, is call as Internet of Things. The number of those connected objects will reach 80 billion in 2025[1]. IoT has helped companies to deliver outstanding Customer services, to enter a new market, and even to develop new business models. However, privacy and security are the biggest challenges facing IoT. Many IoT devices have vulnerabilities such as lack of strong encryption or no encryption at all. Few years ago, some companies implemented IoT in their systems, later they discovered that data were being send in clear text. That means an attacker could capture data and analyses them. That might be the bad news for the entire organization because attackers will have access to all data being sent in clear text, hence the lack of confidentiality. There is no doubt that the raise of IoT has lent a hand to the increase number of security-attacks [2]. Before IoT, there were some few security attacks, but observe how security attacks are growing faster, it grows exponentially with respect to that increase is almost at the same rate of IoT. All those factors made IoT to experience a rapid growth and popularity. How the number of connected devices is increasing exponentially in the following Figure 1 [3].

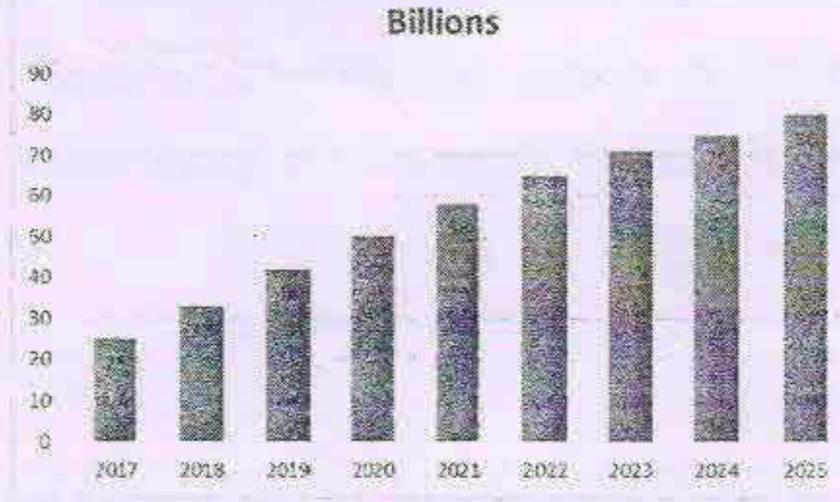

Figure 1: Connected devices in billion from the year 2017 to 2025.

2. Current Background Overview of IOT

A. From manufacturers to consumers

From manufacturers to consumers, IoT has played a tremendous role. Healthcare devices are nowadays being implemented with IoT capabilities that enable medical doctors to remotely

application installed on a smartphone or any computer. That helps the owners to control their entire home remotely whenever they want wherever they are [4].

B. Security and Privacy challenges in IoT

IoT has contributed a lot in different areas such Business infrastructure, industrial control systems where the entire factory can be connected to the internet be controlled via smartphone. Despite all mentioned achievements, security and privacy remain a big challenge in IoT. IoT is exposed to larger attack surface [4].

• Many IoT systems have both hardware and

Software vulnerability that remain unpatched. If a hacker exploits those vulnerabilities, there will be zero-day attacks. That could be a disaster for the entire organization, it will be hard to mitigate those attacks because the manufacturers were not aware of vulnerabilities [5].

• IoT is exposed to larger attack surface. Because devices are connected each other, many attacks are possible not to one device but to the entire network [6].

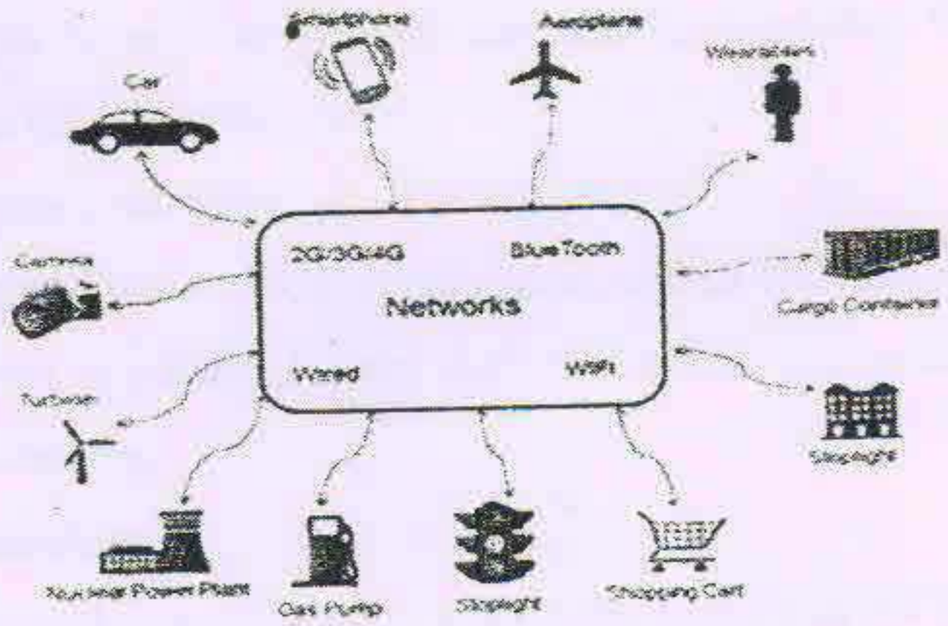

Figure 2: Example of IoT System [3].

3. SECURITY and PRIVACY CHALLENGES

The era of IoT has changed our living styles although the IoT provides huge benefits, it is prone to various security threats in our daily life. The majority of the security threats are related to leakage of information and loss of services. In IoT, the security threats straight forwardly are affecting the physical security risk. The IoT consist of different devices and platform with different credentials, where every system needs the security requirement depending upon its characteristics [4, 5].

The privacy of a user is also most important part because a lot of personal information is being shared among various types of devices [4, 5]. Hence a secure mechanism is needed to protect the personal information. Moreover, for IoT services, there are multiple types of devices that perform communication using different networks. It means there are a lot of security issues on user privacy and network layer. User privacy can also be uncovered from different routes. Some security threats in the IoT are as follows:

1) E2E Data life cycle protection:

To ensure the security of data in IoT environment, end-to-end data protection is provided in a complete network. Data is collected from different devices connected to each other and instantly shared with other devices.

2) Secure thing planning:

The interconnection and communication among the devices in the IoT vary according to the situation. Therefore, the devices must be capable of maintaining security level. For example, when local devices and sensors used in the home-based network to communicate with each other safely, their communication with external devices should also work on same security policy [6].

3) Visible/usable security and privacy:

Most of the security and privacy concerns are invoke by misconfiguration of users. It is very difficult and unrealistic for users to execute such privacy policies and complex security mechanism. It is needed to select security and privacy policies that may apply automatically [7].

4. CIA Triad in IOT

IoT will reach its full potential and full popularity only if interactions between connected devices fulfils the fundamental security model which is known as CIA triad (Confidentiality, Integrity, and Availability)

A. Confidentiality

IoT manufacturers and vendors must make sure that data being transmitted in connected devices will be accessed only by authorized people, i.e. consumers. But confidentiality has remained a challenge to IoT because so many devices were discovered exchanging data in clear text in IoT system [8].

B. Integrity

Data being transmitted among IoT systems must remain unchanged during the entire life cycle.

C. Availability

Availability in critical devices must be 99.999%, i.e. the downtime will be as minimal as possible.

D.IoT Challenges

The IoT improve the communication between devices but still, there are issues related to the scalability, availability and response time. Security is a concern where the data is securely transmitted over the internet. While transporting the data across international border, safety measure. Among different security challenges, the most important challenges relevant to IoT are discussed.

1) Data Privacy: Some manufacturers of smart TVs collect data about their customers to analyse their viewing habits so the data collected by the smart TVs may have a challenge for data privacy during transmission [9].

2) Data Security: Data security is also a great challenge. While transmitting data seamlessly, it is important to hide from observing devices on the internet.

3) Insurance Concerns: The insurance companies installing IoT devices on vehicles collect data about health and driving status in order to take decisions about insurance.

4) Lack of Common Standard: Since there are many standards for IoT devices and IoT manufacturing industries. Therefore, it is a big challenge to distinguish between permitted and non-permitted devices connected to the internet [10].

5) Technical Concerns: Due to the increased usage of IoT devices, the traffic generated by these devices is also increasing.

6) Security Attacks and System Vulnerabilities: There has been a lot of work done in the scenario of IoT security up till now. The related work can be divided into system security, application security, and network security [11].

a) System Security: System security mainly focuses on overall IoT system to identify different security challenges, to design different security frameworks and to provide proper security guidelines in order to maintain the security of a network [12].

b) Application security: Application Security works for IoT application to handle security issues according to scenario requirements [13].

c) Network security: Network security deals with securing the IoT communication network for communication of different IoT devices. In the next section, the security concerns regarding IoT are discussed. The security attacks are categorized into four broad classes [13].

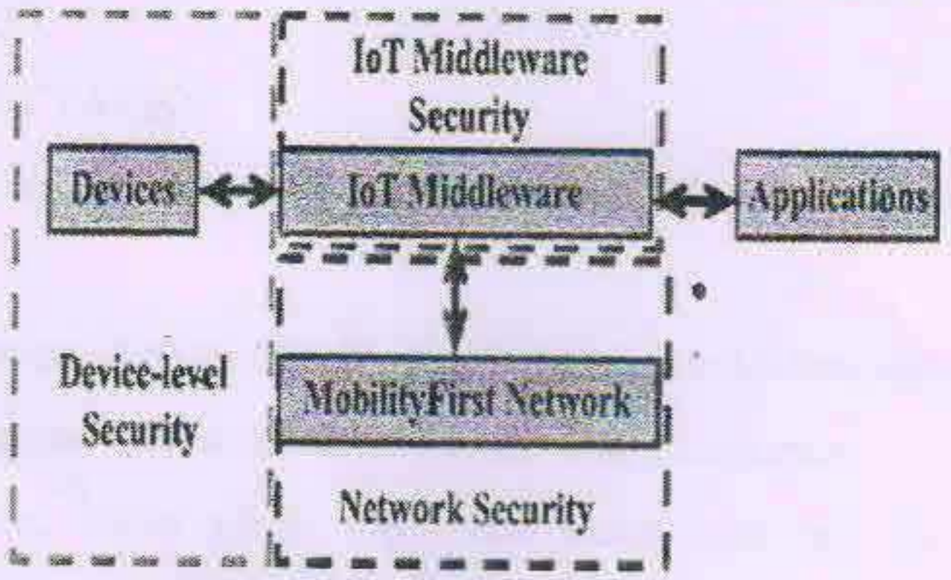

Figure 3: IoT Security Architecture.

5. Analysis of Different Types of Attacks and Possible Solutions

In IoT, all the devices and people are connected with each other to provide services at any time and at any place. Most of the devices connected to the internet are not equipped with efficient security mechanisms and are vulnerable to various privacy and security issues e.g., confidentiality, integrity, and authenticity, etc. For the IoT, some security requirements must be fulfilled to prevent the network from malicious attacks [14]. Here, some of the most required capabilities of a secure network are briefly discussed.

1. Resilience to attacks

The system should be capable enough to recover itself in case if it crashes during data transmission.

2. Data Authentication

The data and the associated information must be authenticated. An authentication mechanism is used to allow data transmission from only authentic devices.

3. Access control

Only authorized persons are provided access control.

4. Client privacy

The data and information should be in safe hands. Personal data should only be accessed by authorized person to maintain the client privacy. Different levels of attacks are categorized into four types according to their behaviour and propose possible solutions to threats/attacks [15].

1) Low-level attack

If an attacker tries to attack a network and his attack is not successful.

2) Medium-level attack

If an attacker/intruder or an eavesdropper is just listening to the medium but don't alter the integrity of data.

3) High-level attack

If an attack is carried on a network and it alters the integrity of data or modifies the data.

4) Extremely High-level attack

If an intruder/attacker attacks on a network by gaining unauthorized access and performing an illegal operation, making the network unavailable, sending bulk messages, or jamming network.

6. Classification of IOT

SECURITY ATTACKS

An action that compromises the security of data. The security attacks can be divided in to two types [16, 17].

1. Active Attacks: Active attacks involve some modification of the data stream or the creation of false stream and can be subdivided into four categories:

a) Masquerade: Takes place when one entity pretends to be a different entity. A masquerade attack usually includes one of the forms of active attack.

b) Replay: Replay involves the passive capture of a data unit and its subsequent retransmission to produce an unauthorized effect.

c) Modification of Messages: Simply means that some portion of a legitimate message is altered, or that message are delayed or reordered, to produce an unauthorized effect.

d) Denial of Service: The denial of service prevents or inhibits the normal use or management of communications facilities. This attack have a specific target; for example, an entity may suppress all messages directed to a particular destination.

2. Passive Attacks: Passive attacks are in the nature of eavesdropping or monitoring of transmission. This attack is divided into following categories:

a) Release of message content: For a release of message content, a telephonic conversation E-mail message or a transferred file may contain confidential data. A passive attack

monitors the contents of the transmitted data. When the message are exchanged neither the sender nor the receiver is aware that a third party may capture the messages.

b) Traffic analysis: Traffic analysis is a special type of inference attack technique that looks at communication patterns between entities in a system. Traffic analysis is the process of intercepting and examining messages in order to deduce information from patterns in communication.

7. Analysis and Discussion

An Active attack attempts to alter system resources or affect their operation. Active attack involve some modification of the data stream or creation of false statement. Ensure both confidentiality and integrity of data. To maintain data confidentiality, symmetric encryption can be applied. The attacker intercepts the connection and modifies the information. Effects confidentiality and integrity of data. Always causes damages to the system. A Passive attack attempts to learn or make use of information from the system but does not affect system resources. The goal of the opponent is to obtain information is being transmitted. Ensure confidentiality of data do not allow an attacker to fetch information using symmetric encryption techniques. In which an intruder attempts to alter data on the target system or data en-route for the target system. Usually breach data confidentiality and involves probing for network information [18].

"Active "in which an intruder initiates commands to disrupt the network's normal operation. While "Passive" when a network intruder intercepts data traveling through the network.

On the other hand, it is quite difficult to prevent active attacks absolutely, because of the wide variety of potential physical, software, and network vulnerabilities. Instead, the goal it is to detect active attacks and to recover from any disruption or delays by them. The detection has a deterrent effect; it may also contribute to prevention. So, the threat level of Active attacks is high and modification of stream / data or its false creation, difficult to prevent, focus is on detection and recovery. While Passive attacks is low and difficult to detect, no alteration of data, focus on prevention.

Summary of Different Types of IOT Attacks

Table1: Comprehensive Study of IOT Attacks Along With Their Level, Nature, Detection technique, Prevention method, limitations and Experiment derived [18,19].

Category of Attacks	Attacks Type	Layer	Threat Level	Behavior	Detection Technique	Prevention Method	Parameter used	Limitations	Experiment derived
Active Attacks	Masquerade	Network	High	Is a disguise.	Profiling-based detection approach	To create innovative algorithms that can efficiently detect the suspicious action	1.Stolen passwords and logons 2.Steal sensitive data	To gain greater privileges than they are authorized for.	The attacker pretends to be an authorized user of a system.
	Replay	Network	Medium	In which a valid data transmission is maliciously or fraudulently repeated or delayed	1 Strong digital signatures with timestamps. 2 Random session keys with time bound and process bound.	1.One-time password 2. Generating a Session-ID and a component number.	1 Login Authentication 2 IP Packet Substitution.	A valid data transmission is maliciously.	Can be prevented by tagging each encrypted component with a session ID and a component number.
	Modification of messages	Application	Extremely high	Data en route to the target	It cause duplication of logon procedure and capture the user password	1. Alters packet header addresses	Intrusion Detection techniques	Modify the numbers in an electronic bank transfer.	Communication delay occurred between sender and receiver.
	Denial of service	Application	Extremely High	Malicious user may modify the packet or resend a packet again on	1. Activity Monitoring.	Some or all legitimate requests from being fulfilled	1. Real time response detection mechanism	Flood a target system or resource.	Apply cryptographic techniques to ensure security of network.

				network.						
Category of Attacks	**Attacks Type**	**Layer**	**Threat Level**	**Behavior**	**Detection Technique**	**Prevention Method**	**Parameter used**	**Limitations**	**Experimental derived**
Passive Attacks	**Release of message content**	Multi-Layer	Low to Medium	Alteration and eavesdropping are the example of this attack.	1 Tamper detection.	1. Using a mutually trusted certificate authority. 2. Mutual-Authentication	1 DSL Modems. 2 WiFi base stations. 3 Router	1 Newly generated server key. 2 Generate trusted authority certificate.	Apply data confidentiality and proper integration on data to ensure integrity.
	Traffic analysis	Physical	Low to Medium	The information content may be lost by an eavesdropper that silently senses the medium	Network Monitoring software(a Sniffer)	Using personal firewales,updated antivirus software, and virtual private networks	1Athentication tokens. 2.Sending Sensitive data 3 .Power splitting and jamming	Unsecured network communications. Public wiFi networks	Apply encryption on all the devices that perform communication.

7. Conclusion

In this paper, IoT was explained considering its contributions to the people all over the world.IoT has been proven to be a beneficial technology to both manufacturers and consumers. Challenges facing IoT were demonstrated. Confidentiality, Availability and Integrity of IoT were analyzed as the fundamental of security model that need to be followed to minimize attacks in IoT. The main emphasis of this paper was to highlight major security issues of IoT particularly, focusing the security attacks and their countermeasures. Due to lack of security mechanism in IoT devices, many IoT devices become soft targets and even this is not in the victim's knowledge of being infected. In this paper, the security requirements are discussed such as confidentiality, integrity, and authentication. In this Survey, six different types of attacks are categorized as low-level attacks, medium-level attacks, high-level attacks, and extremely high-level attacks along with their nature or behavior as well as suggested solutions to encounter these

attacks are discussed. Considering the importance of security in IoT applications, it is really important to install security mechanism in IoT devices and communication networks. Moreover, to protect from any intruders or security threat, it is also recommended not to use default passwords for the devices and read the security requirements for the devices before using it for the first time. Disabling the features that are not used may decrease the chances of security attacks. Moreover, it is important to study different security protocols used in IoT devices and networks.

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Factors Affecting Segmentation of Web Pages Using Web Content Mining

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Abstract—

Web is a treasure of information and data, where large amount of data is available in different formats and structures. Finding the useful data from the web is a complex task. the above problem has given rise to the development of web content mining. Extraction of Information has become an important task for discovering useful knowledge or information from the Web Pages. But On the Internet web pages contain several items that cannot be classified as the informative content. Maximum clients and end users search for the informative content, and don't interest in non-informative content. With the informative content, web pages commonly have blocks that are not the main content blocks and are called the non-informative blocks or noise. For getting the informative content, first we do the segmentation of web pages into differ blocks such as main content, title, heading header footer etc. Various factors are to be considering in segmentation of web pages for content extraction from web pages using web content mining. The main objective of this paper is to eliminate the non-informative content blocks by doing segmentation of web pages using web content mining techniques. In the paper we prepared techniques, factors for segmentation for content extraction.

Keywords-content extraction, information extraction, web content mining, web segmentation, informative blocks

Introduction:

Use of internet and World Wide Web (WWW) has become as first source of information for everyone, but the World Wide Web has been exponentially increases [1, 2] It resulted in difficulties for individual user to process all these information. With the increasing of web usage, the content available on web becoming more mature, and its presentation even more sophisticated. In Presentation, creators placing different pieces of information on web pages for different purpose to the end-user. The information must appear coherent to users who browse the web page. These pieces have carefully-placed visual and other clues that cause most users to sub consciously segment the browser-rendered page into semantic regions, each with a different purpose, functionality, and content. From the web, it is difficult task to find, retrieve and identify dissimilar information elements. In addition with the main content present web pages contains a bunch of textual elements such as text ads, snippet previews of related documents, legal disclaimers, navigation menus, user comments etc. Separating these different elements and classifying them into relevant and non-relevant parts is important for high-class results.web page segments are left navigation menu bar, site-specific banner that might be at the top, navigation footer, links and abstracts of related web pages, banner and other forms of advertisement scattered

throughout a page, copyright notices, terms of service, and contact information, and last but not the least, the actual content itself. It also depends on how the creator of the web page chose to organize it, the content might itself be represented by multiple segments. Method to divide a Web page into visually and semantically cohesive pieces is called web page segmentation. There is a huge no. of benefits and potential for web applications using web page segmentation. Web Page segmentation is of extreme importance when information is to be extracted omitting the noise from web pages [4]. Web page segmentation distinguishes informative and non-informative content on a web page; they can also differentiate between different types of information. Consider a multiword query whose terms match across different segments in a page, this information can clearly be useful in adjusting the relevance of the page to the query. Identification of segments also plays an essential role in displaying web pages on screen-space constrained devices such as smart phones, PDAs etc [5]. We consider three input application areas for web page segmentation: (1) De-duplication. Matching content information may be presented using different web page layouts. (2) Content Extraction. Besides the obvious Benefits for Web-based news clipping etc., removing template noise might also increase classifier performance. (3) Keyword-based Web search. A page should be regarded less relevant to the query if the matched term only occurs in a template segment. Different types of segmentation consist of DOM based segmentation and vision based segmentation. The page segmentation problem has been addressed from many different perspectives. Many methods and techniques used different approaches such as DOM based, Vision Based, Text based, and Hybrid etc. [12].

Literature Review:

Today, the most frequently used segmentation algorithm is Vision-based Page Segmentation (VIPS), proposed by [3] from Microsoft Research. The vision-based method utilizes visual clues in a Web page. VIPS utilizes many visual cues such as element size, background color, font size and etc. to build a visual partition tree of a web page. Each node in the tree is a visual block of the web page. Yang proposed the VIPS (Vision-based Page Segmentation) algorithm by considering vision information and heuristic rules to identify blocks [6]. VIPS approach focus on segmentations of web pages and informative block detection algorithms [3]. Row column splitting indicator helps us provide an easy to use partition granularity value which solves the difficulty of choosing an appropriate Degree of coherence value in VIPS algorithm. Manjusha Annam et al [7] state Entropy based Informative Content Density approach for efficient web content Extraction. This paper proposed a web content extraction technique build on Entropy based information content Density algorithm. The proposed EICD algorithms initially analyses higher text density content. The Page information density (PID), Tag information density (TID) and content ratio (CR) calculated. EICD is to utilize the information entropy for representing the knowledge that correlates to the amount of informative content in a page. Dr.Anna saravanperumaem et al [5] provides a simple but effective approach named layout based detachment approach (LBDA). Using this approach we removes the irrelevant information like header, footer content, navigation bars and other noisy image and extract the main content from the web page. It can eliminate noise and extract the main content blocks from web. Ranking the Relevance and Evaluation of Search Results through Web Content Mining is stated by G. Poonkuzhali, [1]. Correlation algorithm is studied for web content mining and correlation method for relevance ranking and normalized discounted cumulative gain for useful

evaluating this ranking method. The search results obtained through this approach is accurate and time consuming. V. Bharanipriya et al [2] presented a paper web content mining tools a comparative study. It was mainly focused on one of the categories of Web mining namely Web Content Mining and its various tasks. After studying of different techniques of WCM it observed that Screen scraper is not user friendly and some of these tools seem to be applicable for email data mining. Rajkumar et al. [13] presents a new method that segments web pages based on either reappearance based scheme, by recognizing reappearance tag pattern from the DOM tree structure of a web page Ruipe et al. [14] proposed a method that analyzes semantically the content of web page in order to extract the textual contents.

Factors For Segmentation

DOM-based and layout-based is the accepted web page segmentation algorithms. Web page based on the Document Object Model is considered for tag information used to divide a web page using DOM based segmentation. The DOM has a tree structure in which each node contains one of the components from an HTML tag. Web pages split using some relatively simple DOM nodes such as the <P>, <TABLE>, and <UL> nodes for further conversion or summarization. The <TABLE> node and its offspring to be a content block and use entropy-based approach to determine the informative ones. Nodes such as <TABLE> and <P> are not only used for content organization but also for layout presentation. The layout-based segmentation method uses layout information after rendering, assuming that similar content blocks are located close to each other and have similar shapes. This Web page segmentation method is comprised of three steps: (1) dividing a Web page into minimum blocks, (2) classifying the blocks into title blocks or non-title blocks, and (3) combining the blocks into Web content chunks based on title blocks. In DOM based segmentation main factor that affect the segmentation is tag and its structure. Depending on tag we calculate precision and recall for result consideration.

In EICD technique we used factors like No. of characters of node, No. of informative pages and No. of informative tags. The Text Density and Entropy factors are considered. Others factors considering for EICD approach are page information density (PID) and tag information density (TID). Page information density is the number of web page classified as informative in a given set of pages. These metrics are calculated using the following equations.

PID= (No of informative pages)/ (Total number of pages in dataset)

TID= (No of informative tags)/ (Total number of text content tags)

The content ratio is a measure to define the count of nodes which are high text content threshold condition for different values of α.

Content Ratio= (No of nodes satisfied threshold)/ (Total number of nodes)

In LBDA (Layout based detachment approach) No. of Relevant terms and precision Factors are used. The Time and memory factors are considered. As per the LBDA Based segmentation perform operation through the system and collected the results. Number of relevant and irrelevant pages related to the given keyword is the key issues for segmentation. Others parameter like f-Measure, Precision and recall, F-measure, Goodness are consider for segmentation that affect segmentation.

Conclusion

To conclude, paper discusses various segmentation methods for web content extraction with the factors affecting segmentation of web pages. In the future more research will be needed for efficiency and accuracy of information extraction for better results using segmentation.

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Discrimination at work place

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Abtract- Women are enjoying more freedom today and have joined the work as doctors, lawyers, teachers, designers, truck drivers and in many other professions. But discrimination against women still exists in various forms, particularly at the workplace. Women should know their rights as a worker and take responsibility to stop rights violations at the workplace.

Keywords- Discrimination, Legislation, Sexual harassment

According to Hindu mythology, the Manusmriti is the word of Brahma. In Manu's set of laws, women were treated on par with slaves or Shudras. It means from the ancient time, our society is male dominating or supremacy of the men over the women. Another sign of the lower status of women was the practice of monogamy for the wife while the husband was free to have several wives. They were targeted of various types of violence and discriminatory practices done by men.

Now the time is changing. From the last five decades, the women are actively participating at the workplace with the role of housewife, mother, and care taker. Many women are making her career in the field of interest. They want to become self- independent. She shows aptness and assiduity in her work whether she may at home or at workplace. One thing is cleared that women are striving to gain equality in the work.

But even today, women are not treated the same as men. One area where this oppression shows is the 'equal pay for equal jobs'. Another area in which women are inconvenient at the workplace is through discrimination. Discrimination can be an uncomfortable situation for the women concerned. There are two types of discrimination- indirect and direct. Indirect discrimination may contain a woman being neglected for the promotion or an employee displaying improper sexual matter or allotment of more work at the workplace. On the other hand, direct discrimination may include a women being took out from her employment during pregnancy, or being excluded from after work group events.

Another major area where being the women have been suffered at the workplace is sexual harassment. Sexual harassment is the direct sign of sex discrimination and mostly the sexual discrimination is occurred where the women having lower paying jobs. The sexual harassment or sexual discrimination at workplace creates tensions that make the women doing job more difficult. Thus the condition of working women is particularly vulnerable. They need equal treatment and special protection under the laws. To protect the working women, many legislative provisions have been provided in almost all labour statutes which address the problems of women labour in their employment situation. The Second National Commission on labour, 2002 has also justified the protective discriminatory legislation by recommending that all such legislations are necessary for women workers.

There are a provision for protection of women under labour laws such as- The Factories Act- 1948, The Employees' State Insurance Act- 1948, The Maternity Benefit Act-1961, The Equal Remuneration Act- 1976, The Workmen Compensation Act- 1923, The Minimum Wages Act- 1948, National Rural Employment Guarantee Act- 2005, The Contract Labour (Regulation and Abolition) Act-1970 and Sexual Harassment of Women at Workplace (Prevention, Prohibition and Redressal) Act, 2013.

These legislations in the Indian labour laws regulates the employment in dangerous occupations, prohibition of night work, restriction on carriage of heavy loads, wages, health, gratuity, maternity relief, equal pay for equal work, social security, provision of creches and other welfare facilities etc. These labour laws for women have been classified into three categories such as (1) Measures in regard to health, safety and welfare (2) Social security measures (3) Wage protection. Everyone should know

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about these laws. Our constitution provides all women workers health, safety and welfare.

Conclusion- India presents an inimitable set of challenges that are deep-rooted in diverse cultural, religious and social. Thus collective action must be taken towards establishing the equality in gender roles and women in the workplace. By the way, gender inequality is a genuine issue that limits the progress of modern India and our mission is to establish spontaneous and natural workplace for members of all genders. Women's in India has the potential to be powerful community leaders and the responsibility of change lies on every one of us.

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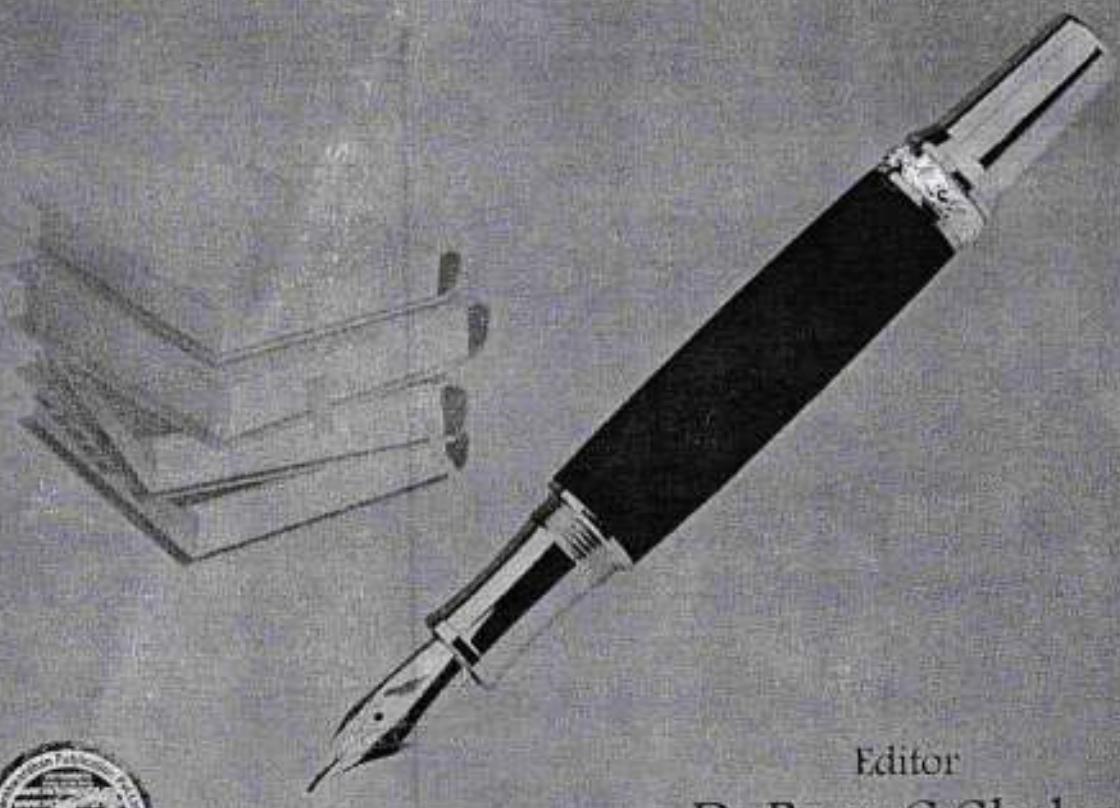

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Dr.Bapu G.Gholap

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slowly in Bangladesh the hawk eyed super powers will try to fish in troubled waters which will be suicidal for India in particular and the entire subcontinent in general. It is thus the geographic factor that has played a determining role in shaping the bi- lateral relations.

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Socialite Evenings: A Chronicle of Karuna's journey towards emancipation as a new woman

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Abstract:

Women have always been given a subordinate role in the family system of India. They have been fighting a perennial battle against their counterparts for their dominance and to avail equal status. But women can carve a niche for themselves if they are strong in mind and body, and bold enough in their outlook to put their traditional identity and nature of submissiveness aside.

This paper discusses the journey of Karuna from assertion to emancipation in the maiden novel **Socialite Evenings** by Shobha De. A middle class girl, Karuna dreams of being a part of the upper class society, who rebels against her family and tries to create an independent world of her own. The novel is about the journey of a prominent Bombay socialite Karuna from a middle class girl to a self-sufficient woman. Making a feminist approach, the novel gives us the picture of the marginalization of the Indian women at the hands of their husbands. Many a times Karuna adopts a militant attitude towards her husband as she does not want to be marginalized in a patriarchal society. The portrayal is authentic, being an inside story as the narrator herself

belongs to this class. The novel is a romantic tale, suffused with feminist traits.

Keywords: - Society, patriarchal, emancipation, perennial, submissiveness, militant.

The journey from assertion to emancip ation is symbolic of the winds of social change blowing across the world and intends to focus on "women who are today in a fair way to dethrone the myth of femininity, they are beginning to affirm their independence in concrete ways; but they do not easily succeed in living completely the life of a human being." (Beauvoir,Sex)'.The battle to come out of the shadow of male dominance has been going on for centuries. The fight for autonomy in a male dominated and traditional society is a tough one "but women can find a respectable place for themselves in the society only if they have an intellectually strong mind to put aside all traditional factors and come out of the Sita-Savitri image and the tradition of submissive ness." (Shirwadkar, Image of Woman...p.55)

Shobha De's first novel - **Socialite Evenings** deals with the story of a middle class girl Karuna who wants to rise above her ranks. She is not ashamed of her sexuality and does not miss any opportunity to cut down to size her male counterparts. But the tug of war between her role as a house maker and her desire for individual freedom and happiness creates a problem for her. The novel describes her journey where she reaches the cross- roads. Her dilemma is to go back to her old life or to be a part of the elite world. Though they have discarded the old order, but have not been able to carve out any new concrete niche for themselves. Finally, the realization is there that individual freedom is just a myth and not a reality.

Indian fiction in English has been enriched by several talented women novelists including Kamala Markandaya, Anita Desai, Nayanatara Sahyagal, Attai Hosain, Santhara marau, Shashi Deshpande and Shobha De. They have a women perspective on the world. They have written about Indian women, their struggle, their suffering and their awkward position, keeping in view their image and role which the society has created. Their chief contribution consists of their exploring the moral strength of women characters and their struggle with challenges in creating their own identity.

Shobha De is a prolific writer born in Maharashtrian Brahmin Family in Mumbai,she writes about the high-flying upperclass society of India. She has dealt with issues related to woman.To project urban culture, she has changed traditional picture of enduring, submissive and self-sacrificing women with a new picture of bold and liberated urban women. Shobha De is renowned for bold and frank style of writing. She explored the lives of bored housewives and their loveless rich husbands and family. Her novels mirror the life styles of the elite and the middle classes of urban world.

Socialite Evenings is Shobha De's first novel published in 1988. The novel portrays Mumbai high society and explores the lives of bored rich housewives trapped in loveless marriages and engaging in ill-fated, extra-marital affairs, smug selfish husbands, fashionable parties, false spiritual leaders, and a portrait of general moral, spiritual and intellectual bankruptcy and decadence of the elite who have traded their traditional culture for westernization and modernization. In the novel, Karuna the main protagonist and narrator caught up in a drab, boring life that she seeks to escape by writing memoirs. Her memoirs are successful and she achieves a measure of fame and pride in herself as she becomes an active socialite and eventually uses her new found prominence as celebrity to get herself a position as an advertising copy writer and creator of a television series.

In the novel **Socialite Evenings** Karuna is the main protagonist. She is all agog to break-out of such thralldom which compels her to

assume the status of the other. A problem child both at home and at school, she declines a dog the traditional path of etiquette and manners. At home, she refused to cower before elders and at school she wore her sash hipster style. As she grows in age there develops in her the emotional urge to identity with the outside world, the modern crowd, the bewitching and fascinating world of affluent girls who had the lewd and clandestine world of modeling with her secret assignment as the Terkosa Girl. Throughout the novel Karuna figures as a woman who asserts her feminine psyche through protest and defiance. She figures as a woman, not victim. Shobha De deals with the sullenly skewed of art. We do not have here the stereotypes associated with male artistic representations of women. Karuna's initiation into the fashionable world of modern life begins at Anjali's fancy place in Malabar Hill. But Anjali accuses Karuna of bitchiness and lechery, her insatiable appetite for sex. This is borneout when Karuna dates with the New Delhi ad film-maker in London. Further her stay in the United States gives her a feeling of superiority and makes her assertive. Karuna, with all her attempts at ego assertion, refuses subscription to stereotypes, to succumb to the hegemony of the malist culture.

Socialite Evenings gives us the image of new women at the hands of their husbands. ShobhaDe's is the picture of women not only as protagonists but also as motivating factors in society, initiating and regulating their own lives as well as the lives of others in the voluptuously fascinating world of Bombayites, its enticing glitter and glamour enamoring many a Karuna to its ensnaring and captivating gossamer. Karuna's marriage is a failure since it is loveless, joyless and bridgeless. There is no under standing between the husband and the wife. She feels that she has married "the wrong man for the wrong reasons at the wrong time. Her husband is just the average Indian husband, unexciting, uninspiring, untutored. He was not made for introspection. The average Indian woman's conjugal life is to her an exhausted generation of wives with no dreams left and marriage is like a skin allergy, an irritant.But she is not afraid to face this irritant, this allergy. She boldly and defiantly encounters it, for she realizes "marriage is nothing to get excited or worried about. It is just something to get used to" (De, Socialite, p.68) and she gets used to this stereotyped social institution in the course of time. She detests the stand-offish and callous attitude of the husbands who often kept themselves busy in drab monotonous activities – like reading and business pages of The Times of India. But despite these laxities, a husband was above all, a sheltering tree, a rock to the wife. They were not wholly bad or evil and the wife as a woman was only peripheral being, Karuna says:

> We were reduced to being marginal people. Everything that mattered to us was trivialized. ...roof over our head and four square meals a day. (De, Socialite, p.69)

The subordination of women as housewives stems from a castration-panic on the part of the husband. The Indian male is presented by Shobha De as a person "terribly threatened by self-sufficient women."(De, Socialite, p.69) He is inadequate and incomplete as a husband since he lacks the traits of an ideal husband. Fear of the loss of domination and control over the self-affirming wife makes him resort to several defense mechanisms. One of these strategies is his male chauvinism and power-assertion ventilating in bullying and committing atrocities upon his wife. But his stupid self-conceit and ego restricts a free exchange of views among sexes. Karuna inquisitively wonders: "how could he communicate anything at all to men who perpetually sat reading pages of The Times of India while concentratedly picking their noses ?" (p.69)

Karuna learns from Ritu, whom she

chances upon at a finance director's party that "men like dogs could be conditioned through reward and punishment." (p.87). But could she condition her husband in the like manner. But she was fed up with her husband's compulsive socializing, his horrible safari suits and the gum he constantly chewed. She could not turn to anything in such a boring milieu save her books and her fantasies. Crosswords and newspaper chess were other alternatives to utter boredom. She realizes that despite her little acts of protest, she is "a well-trained Indian wife" (p.54) but she shares the same rational human nature as men do. Karuna is not "the toy of man, his rattle," which "must jingle in his ears whenever, dismissing reason, he chooses to be amused."(Surendran, Another De..., p.12)

The subordination of women in the malist culture is symptomatic of hierarchization of socio-moral values between the sexes. It symbolizes the polarity between activity and passivity, between meek obedience and defiance. Helene Cixous observes: "A male privilege can be seen in the opposition between activity and passivity. Traditionally, the question of sexual difference is coupled with the same opposition: activity/passivity." Women are often the symbols of passivity.Helene Cixous further maintains: "Either the woman is passive; or she doesn't exist. What is left is unthinkable, unthought of. She does not enter into the opposition, she is not coupled with the father who is coupled with the son." (p.288)

Woman is thus reduced to matter, a mere object. This reduction of woman to matter or a commodity is in the main a phallocentric pattern. Karuna's husband treats her as matter, a mere object subjected to his own will. Karuna's humorously sarcastic approach to her problems in the patriarchal male culture apparently deconstructs the traditional gender hostility used to elaborate the polarities of connubial ties. Karuna undermines male superiority. She loathes her husband's dwelling in "post-mortems." (p.186) She makes an ingenuous declaration about her inner urge to express herself through love:

"I love this friend of yours, and I want to be with him in Venice. There is a good chance ...It's the Taurean in me that's surfacing these days. Treat this as a short-term mania that will wear itself out." (p.186)

It is clear that Karuna has just a formal relationship with her husband. Intimacy between the husband and wife is lacking for Karuna who never calls her husband by his name but derogatorily as 'Black Label.' Shobha De resorts to the technique of manipulating language in order to deconstruct the male ego: "the fact that his wife had taken a lover excited him. resisting – it would have only consumed more time." (p.188)

Shoba De in her long narration depicts the pathetic story of Karuna and her incessant struggle tobe free from the dominance of her husband and her journey towards emancipation; she also has added the other female character such as Anjali, Ritu and Gul. They faced a dilemma which is the outcome of their own undoing, their blind urge to emulate the elites and in this process they are uprooted and wandered aimlessly in the jungle fully of female devourers. In the beginning, these women discard the social norms and march ahead on the path of emancipation and liberation and once they achieved their desire, they find themselves all alone and feel lost. With no support and no clear path outlined for them, disillusionment sets in and plunges them into dilemma, now they have two choices to make- either to come back to their roots or to continue suffering.

Women in Shobha De's novels symbolize the overpowering materialism and the lack of spirituality that characterizes modern age. With the crumbling of moral and ethical values there is an inner conflict which drives the modern Indian women to seek shelter in different identities for momentary solace. One of the most

notable features of these women is they lack an identity. But the whole blame cannot be laid on women only because in ShobhaDe's novels there are type of men who use and abuse women and then discard them. In **Socialite Evenings** one encounters a liberal Indian husband who allows his Indian wife to go abroad and get herself screwed once for all as the last gesture of good will. From the individual, it comes to the family. It is the family which is the centre of deviance. Subhash Chandra regards family's disintegration is the instrument of degeneration of Socialite Evenings.

Thus ShobhaDe's novel **Socialite Evenings** shows the image of new woman against predatory male-dominated society. But her vamp ideology of feminism provides no redemption for the deviant and fallen women who in their frantic struggle to escape male-domination and attain individuality, meet with failure and are victimized in one way or the other. In enacting the drama of seduction and betrayal in her foray against patriarchal structures, the glamorous vamp in De's novels, may end up being as seductively treacherous to women as to men. A woman in Indian society marries not just the man but also his family and subsequently loses her identity in marriage, relinquishes her freedom and sets about pleasing everybody. But the new generation of women with their new-found release from matrimonial bondage adopts different perspectives, and revolt against the old order. De's women are such liberated individuals in search of a niche in their lives.

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INTERTEXTUALITY IN RUSKIN BOND: BRIDGING THE GAP BETWEEN FACT AND FICTION

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ABSTRACT

The fact that Ruskin Bond's literature is autobiographical in nature has been widely established. He can easily be tented as one of the most self-indulgent writers who have always fed on his life- people, places and experiences- to sustain the writer in him. Most of Bond's writings have taken roots in his biography- in its broad sense. There are some distinctive features -stylistic as well as thematic- which make his writings uniquely subjective and biographical in nature. Some characters, themes, settings and philosophy return again and again in his stories, essays and novellas in different contexts. Many of these characters are drawn on real life persons; the themes and settings could also be easily traced to the writer's biography. These recurrent appearances of the certain characters, themes and settings can be taken as instances of intertextual borrowings. Such intertextual references in Bond's case assume the shape of the bridge between author's life and his art. This paper aims at locating the intertextual sources in the works of Ruskin Bond in order to prove their relation to his biography. Ruskin Bond having remained unmarried adopted a family of his former help. So in a way he has been successful in seeking union with mankind as he has been living with Prem Sing and his family-just as Rusty tried to do the same while living in Room on the Roof with Kishen and Menna Kapoor or sharing a room with Suraj and Kamla the prostitute in Delhi is Not Far. The names have changed, contexts may have become different but the characters, their mind, heart and soul have remained the same.

The fact that Ruskin Bond's literature is autobiographical in nature has been widely established. He can easily be tented as one of the most self-indulgent writers who have always fed on his life- people, places and experiences- to sustain the writer in him. Most of Bond's writings have taken roots in his biography- in its broad sense. There are some distinctive features -stylistic as well as thematic- which make his writings uniquely subjective and biographical in nature. Some characters, themes, settings and philosophy return again and again in his stories, essays and novellas in different contexts. Many of these characters are drawn on real life persons; the themes and settings could also be easily traced to the writer's biography. These recurrent appearances of the certain characters, themes and settings can be taken as instances of intertextual borrowings. Such intertextual references in Bond's case assume the shape of the bridge between author's life and his art.

This paper aims at locating the intertextual sources in the works of Ruskin Bond in order to prove their relation to his biography. Ruskin Bond wrote his first novel at the age of 17 and since then he has been making his living by writing books. He published his first

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autobiographical work in 1989. Three more works, autobiographical in nature, followed till 2002. Apart from his interviews these four volumes can be taken as the only 'unadulterated' sources for looking into writer's personal life. The very first work *The Room on the Roof* (hereafter referred to as *The Room)* set the mood and tone for Bond's future writings. Bond certainly has come a long way as a writer, since his first book written as a teenager. But the basic fabric of his writing remained the same. *The Room* was set against the backdrop of his own teenage life. The setting, the characters and the incidents have so much common to the writer's life that it can be easily taken as an autobiographical writing. However the writer has blended the reality of his life with fiction so cleverly that at times it becomes impossible to distinguish one from the other. The teenager Ruskin did certainly live in the room on the roof, But this one piece of reality has been weaved into the fabric of his imagination. After his quarrel with his mother, he decided not to live with her. So he was a given a room on the roof. In his novel he fictionalized it as a room given to Rusty by a Mrs. Kapoor for giving her son tuitions. Rusty, the teenager protagonist, left Mr. John Harrison's house, after beating the guardian for torturing him. After spending a few days on street he shifted to the room on the roof. Here his guardian John Harrison is a fictional character. But he is drawn in such a way as to remind us of his headmaster at Bishop Cotton School and his stepfather. In this context Meena Khorana writes: "Bond admits that Mr. Harrison's character is based on the people he had resented as a teenager: his stepfather, his uncle in Jersey, and Mr. Fisher, the teacher and headmaster at Bishop Cotton School" (35). Mr. Harrison's character returns again in number of stories with only the cosmetic changes like the name, and its relationship with the protagonist.

In the story *A Job Well Done* Mr. Harrison reappears as Major Summerskill, the stepfather who hates the boy for being "too soft" (*Collected Fiction* 103) Here when we read the story, we can't help but thinking about the novel *The Room*. We don't have to understand the character of Suimerskil1 as his initial description connects him to Mr. Harrison whom we already knew. "The 'Major Sahib' was my stepfather, Major Summerskill. A tall, hearty, back-slapping mart, who liked polo and pig-sticking. He was quite unlike my father... The Major said I would become a dreamer if I read too much and took the books away. I hated him..." (103). We are instantly reminded of Mr. John Harrison who ".. felt only contempt for the (good lady's) buoyancy of spirit, "Harrison tells the lady that the boy "dreams too much" (550). These descriptions borrowed from the two different texts, if read simultaneously, convinces us of what Julia Kristeva says about the notion of intertextuality. "The notion of intertextuality replaces the notion of intersubjectivity" (Kristeva 69) Here we don't form the impression of Sumrnerskill by reading about him; we are transported back to the character of Harrison. We realize that meaning is not transferred directly from the writer but from the certain preconceived and established understanding of the reader based on the earlier text. Secondly the character of Mr. Harrison is also a result of author's real life experiences of some individuals. In short, we may prove that a fine blending of fact and fiction has been achieved by the author through a subtle use of intertextuality.

The similar technique seemed to have shaped most of the characters, themes, setting and philosophy in the writings of Ruskin Bond. The principal characters like Rusty the teenage boy, his mother and the stepfather certainly come out as the archetypes of Bond's fiction. Most of the time these characters remain faithful to their original counterparts as revealed through Bond's autobiographical volumes. However even the minor characters like Ganpati

the beggar, Seth Govindram, Mrs. Meena Kapoor, her son Kishan, the young prostitute Kamla and his friends also appear in more or less the same way with some contextual changes. Mrs. Meena Kapoor in *The Room* "was a capable person, still young, a charming hostess; and in her red sari and white silk jacket, her hair plaited and scented with jasmine, she looked beautiful." (CF 584) Rusty much younger than Meena, falls in love with her. He, as inexperienced teenager,, gets seduced and "intoxicated" by the charming beauty of his pupil's mother. We are reminded of Meena when we are told about Leela, another woman in her early thirties. In the short story, *His Neighbour wife*, "Leela was a most attractive woman... I was her junior by about five years and she called me her 'younger brother" (40).

This typical character of a woman marrying or romancing a younger boy has a peculiar biographical background. Bond while in his early thirties fell for a girl of seventeen "Sashi Kishore" (MK86). He could not marry her due to the age difference and cultural differences. Apart from this unfulfilled love affair "Bond was romantically involved with a couple of women" (86). So in a way Bond, while portraying these, characters, was gratifying his own unfulfilled desires through them. Here we may say that Bond was bridging the gap between the reality and imagination by blending the fact so tactfully with fiction. Meena Khorana's observes: "He is loyal to his characters (just as he is loyal to his friends and neighbours), hence the same characters or character types (sometimes with different names) appear in several stories, essays and novels" (60).

Sashi Kishore was Bond's neighbor when he was living in Delhi. She appeared as Sushila in his short story called, *Love is a Sad Song*. The protagonist is a writer like him who tried everything to marry the girl. But she chooses a bank officer over the writer. The teenager Sushila returns in another story *Time stops at Shamli* as a mature married woman. She has grown to be "the liberated woman, free from compunctions and taboos" (Haider 86). That is why she is very much willing to have extramarital relations with the writer, as she has been struggling in her "incompatible marriage" (MK 86). Here we do not have proof to further link Sushila's response to Bond's teenager sweetheart. However the intertextual pattern of the character further moves on the thematic level. Seeking emotional and spiritual liberation through sexual relations has been the recurrent theme in the literature of Ruskin Bond. The novels. like *The Room, Delhi is Not Far, The Sensualist* have the principal characters indulging in extramarital affairs to find either his "true identity" (MX 87) or to explore "the unsuspected depths of feeling and passion" (CF 72). Both the male and female characters use extramarital sex as a medium to find some meaningful companionship. Secondly most of the time, they are found to be simply responding to the bare needs of the flesh. Mrs. Meena Kapoor responded to the young boy's kiss when she was being neglected by her drunkard husband. The young boy living on his own simply fell in love with the mature woman. The entire incident of the love between a woman and a young boy has been narrated in the most mailer-of-the-fact manner, retaining purity of the relationship. While on the picnic Meena and Rusty were alone listening to the "silence" of the dense forest. A sudden sharp shrieking of the bird made the boy hold Meena tightly as if to protect her; he didn't release her even after realizing the truth of the shriek-

> *But he was unable to release his hold, and she made no effort to free herself. She laughed into his face and her eyes danced in the shadows. But he stifled her laugh with his lips, it was a clumsy, awkward kiss, but fiercely passionate, and*

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Meena responded, tightening the embrace, returning the fervor intoxicated with beauty and sweetness, Meena with freedom and the comfort of being loved. (CF 612-613)

The narrator's bisexual relationship with his friend Suraj and Kamala the prostitute, seeks both physical gratification and the emotional solace the young author needed when living alone on his own. Such relationships found in all these novels and in number of stories prove the intertextual borrowing occurred on the thematic level in the writings of Ruskin Bond.

On the thematic level the biographical linkages of the intertextual borrowings related to the extramarital affairs are easy to be traced. Bond is more of a true naturalist in almost all the aspects of life. So most of his love stories involve "the carefree and natural love between a male and a female" (MK 84). As is the case with him in his personal life, the male protagonists in his love stories remain unrewarded though they might have had sexual relations. The stories like, *The Time Stops at Shamli, Love is a Sad Song, The Night train at Deoli, The Girl from Copenhegan* have the heroes waiting forever for the consummation of their relationship.

One of his most controversial novels, *The Sensualist: A Cautionary Tale* gives us the author's take on the sexual passion. He prefers "the unbridled enjoyment of sensual pleasures "over" the total abstinence or renunciation of the world" (87). Most of his characters share this same primal belief that physical passion can help man come face to face with his true self. Rusty's encounter with Meena gave him a new confidence to pursue his interests on his own with fierce passion. Archetypal analysis of the novel *The Sensualist*, give us the sense of conflict between unbridled passion of primal nature and civilized thinking of "control of the matter over mind" (87). The two male protagonists the Pilgrim and the Ascetic are the two sides of the same personality at the end of the novel, the later being proven to be the shadow of the former. The Pilgrim decides to go in search of 'the hill woman' who had stolen his (Ascetic's) manhood. This for him is the only way to leave "...my dead self in the cave and continue my search for the perfect stranger in the night" (CF 946). The similar kind of echoes can be found in the novels like *Delhi is not Far, The Room* and the stories like, *The Time Stops at Shamli, The Night Train at Deoli and others.* After having slept with prostitute Kamla in presence of his friend Suraj, the young protagonist confesses: "I have been seeking through sex something beyond sex- a union with all mankind" (CF 805). His search to have union with the mankind continues in these stories through the unfulfilled relationships with Sushila, the girl selling baskets, Sashi, Meena and others. His unfulfilled relationships are symbolic of the unbridled physical passion that cannot be quenched in one lifetime These intertextual references offer us a glimpse into author's personal life. His failed relationships with women can be taken as part of his attempts to "seek union with all mankind." Ruskin Bond having remained unmarried adopted a family of his former help. So in a way he has been successful in seeking union with mankind as he has been living with Prem Sing and his family-just as Rusty tried to do the same while living in *Room on the Roof* with Kishen and Menna Kapoor or sharing a room with Suraj and Kamla the prostitute in *Delhi is Not Far*. The names have changed, contexts may have become different but the characters, their mind, heart and soul have remained the same.

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BABY HALDER'S "A LIFE LESS ORDINARY": AN EXTRAORDINARY AUTOBIOGRAPHY

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ABSTRACT

Baby Halder, formerly a domestic worker and now a writer, is the author of three memoirs. Her first book, Aalo Aandhare (2002), written in Bengali, is the first account of a domestic help from India. It has been translated into 25 languages. Baby Halder's story is extraordinary precisely because domestic workers' realities are so invisible in middle and upper-class peoples' everyday consciousness. Halder battled enormous odds, a single mother of three, at the age of 25. Her autobiography, written alongside her job as a domestic worker, is a bestseller and has been translated into twenty-one languages. Written without a trace of self-pity, A Life Less Ordinary is a shocking look deep inside a world of poverty and subjugation that few outsiders know about—and an inspiring true story of one remarkable woman's strength, courage, and determination to soar above her circumstances. The present paper reveals the courageous character of Baby Halder , the champion who comes out with triumph.

INTRODUCTION

Article 2 of the universal declaration of Human rights states: " Everyone is entitled to all the rights and freedom set forth in this declaration, without distinction of any kind, such as race, color, sex, language, religion, political or other opinion, national or social origin, birth or other status"

India, as an ancient country has seen many upheavals both natural and man- made. In early Vedic era, equal opportunities s of education for women is mentioned. But later on Manu openly played a degenerating role in lowering women's status. In addition to this, frequent invasions from the other parts of the world also kept changing the position of women in Indian society. They were considered as a commodity or a prize of war. They were deprived of the changes in the society. On the emergence of women like Meerabai from Bhakti Movement, general position of women's education was restricted only to listening to Kathas and kirtans.

During the Mughal empire, nothing much has been done in this field except to provide access to education to women of elite class. Whenever the society was in flux, the most affected and suppressed class was the women. The social norms and prejudices became more tenacious against the women. But with the advent of British people, some changes were being brought from the West. Some literate Englishmen and enlightened Indians like Raja Rammohan Roy, Ishwarchand Vidyasagar, Mahtma Jotiba Fule worked very hard to start educational institutions for girls. Mahatma Jyotiba Fule an ardent lover of humanity started first girls school in the house of Mr. Bhide in 1848 in Pune. This school was meant for girls from the poor as well as rich classes. Girls from untouchable classes were also admitted and education was imparted to them. This rumor of girls school spread all over Pune and some parts of the country too. In the later half of the 19th century the efforts of these philanthropists resulted in the realization by the emergent Bengali " Bhadralok" to impart a certain measure to educate their women folk. The heroine of this article Baby Halder is the outcome of such a long lasted strife against the existing social systems.

The story of Baby Halder's life is an extraordinary lesson in courage and survival. It is a story of a young domestic worker who has battled poverty, hardship and violence. A strenuous life story with storms and woos. She only used to sob and go ahead with courage and strength. Nobody, even her father, step mothers, brothers and relatives helped her to come out of the miseries and agony in her life. The sufferings which are found in her story are beyond imaginations and tolerance.

A small girl of hardly eleven years leaves her home with her small brother from Dhanbad to Durgapur to her Jetha (Brother of her father). Stayed there and joined school. She wants to learn. She joins school. No books and other aids for learning but an utter desire and urge for education

pushed her upto higher class in school. Her father was in army once upon a time, after his retirement came back and joined some other jobs. He could not provide financial support to family. He did not take care of his wife and children. Finally his wife along with his younger son, a child of 3 years leaves his house without telling anyone around her. In this situation Baby's elder sister (Didi), Baby and one younger brother Hemraj became like orphans.

Baby's story is a story of hardships and acute poverty. Story begins from her childhood. Her father got her elder sister (Didi) married with a person who was a bad man. He used to beat her often. Her Didi could not resist much and finally one fine morning committed suicide. Being a paternal society nobody in the family could oppose him. Baby was left alone with her brother for further suffering. After going through a lot of hardships with two steps mothers who ill treated Baby. No good food and sufficient clothes were served to her. But still baby continued to learn.

One day Baby was in her Mashi's house she found her bed and clothes wet with blood. She started weeping. She didn't understand what was happening to her. She was very much frightened and started weeping. Pishi Mashi convinced her and added one more burden that now she was no more a small girl. But as Baby was very courageous she used to play with boys. She loved to play all the boys games. She used to run very fast, swim very swiftly and so on.

The tragic story of her life has taken a second bad turn when she was eleven and half years. Her father got her married to a man of twenty six years. As her father and other relatives were negotiating her marriage, Baby was unable to understand the situation. She anyhow was not prepared for the marriage. Her marriage was settled with a man named Shankar, a son of a potter.

Shankar who was a mere worker having a small house of mud. He spoke lie while fixing the marriage that he has no father or mother and he is all alone. But he has a family at a small village. As per nature's law Baby became pregnant and conceived a son in the hospital. Despite pains and labor for three to four days her husband did not turn up to see her or did not care for her at all. He used to come from work, used to eat and go to sleep. He was very cruel and selfish. For him a woman was only a means of enjoyment. He never used to give her money for home expenses. On top of it he was very much suspicious about his wife and never allowed her to speak to neighbors like Shanti and her sisters who were kind enough to her. Actually Baby liked to see cinemas, jatras and participate in the pooja of Kali but Shankar always forbidden her from all these activities. If she failed to obey him, he would beat her like animal. He never pitied her. Once when she was carrying four months child in her womb, Shankar beat her so brutally that she got aborted. She went to her father's house with the determination of not going back to Shankar's house ever but she was helpless. As her stepmother didn't like her staying in the house. So her father insisted her to go back to her house.

Baby comes to her husband's house to live together, but her husband was very much reserved type of a man. They did not have any cordial relations. He never used to give her money. She was totally dependent on him. This dependency and despondency made her a slave of Shankar. She remained pregnant again and gave birth to a son. Still she had to survive in the same hopeless conditions. There was no improvement in the relations of husband and wife.

Baby, as a woman, a wife and as a mother had tried to resist and revolt against the situation many times. Her struggle for searching her identity, for her freedom and liberty was going on relentlessly. But Shankar had no sympathy for her. When she quarreled for justice, he used to beat her cruelly. She became desperate and left all hopes of cordial relations with her husband. She conceived one more daughter in such a tense relations. Living with such an inhuman and callous man was getting critical day by day. One day Shankar fought with her very badly and beat her horribly before her children. Children were terribly frightened to see this. Baby decided to stop the farce.

On the next morning, with an air of finality, Baby went to her father's house along with her children and declared that she will never go back to her husband's house. Her father didn't like this. He tried to explain to her that her husband's house is the only destination for her. She demanded few money to her father and address of her brother and got the railway tickets. With all sorts trouble she reached Faridabad to her brother's house. Baby's sister-in-law didn't like this addition to her family. She along with her three children had her dinner and next morning went in search of another room which was near her brother's house. She requested him to search for some work for her so that she can pull on her expenses. Moreover she wanted her children to learn. It had been her dream that

the children should go to a school. After two days she found a work. She requested a small place to live with her children. Memsab was very unsympathetic with her all the times. She used to keep her busy for the whole day. Baby hardly got any time to spare with her children. Memsab used to love her dog' more than maid servant. Baby felt very bad and left her job.

Baby Halder started working in the house of Dr. Prabodhkumar Shrivastav. He used to give her Rs. 500 per month. He was very kind hearted man. He used to give her fatherly and brotherly treatment in the house. He never treated her like a servant. He asked her to bring her children there in his house only. He gave one room for them. As her school going children were small he used to ask Baby to take milk for her children. He was living there with his sons. One day she went up-stairs which happened to be a study room of Dr. Prabodhkumar. She started cleaning the bookshelves and books very carefully and neatly. Her busy hands would go slow as she dusted the books. During this she picked up one book and started reading it. She didn't know Dr. Prabodhkumar was also present in the study room at that time. He was very much surprised to see her reading a book. He asked, "Do you read?" and she kept quiet for a while. She looked so guilty as if he had caught her hand in the biscuit tin. Thereafter Dr. Prabodhkumar encouraged her to read and write at her leisure time. One day he asked her to show what she wrote. She handed over the papers to him. He read all those papers and sent to his friend to go through. His friend liked the story very much and asked Dr. Prabodhkumar to publish it. Dr. Prabodhkumar belonged to a literary family. His grandfather Munshi Premchand was one of India's best known writers whose novels and short stories brought out a social reform in the early 20th century.

Here Dr. Prabodhkumar, her dada, worked as a source of inspiration in Baby Halder's life. He encouraged her to read and write. As a servant Baby entered his house, he treated her sympathetically like his daughter and behaved like a good human being, a true Samaritan. As the days passed the result came out in the form of a book, "A life less Ordinary " (Published in Hindi and Bengali as 'Aalo Andhari', from which means 'darkness to light')

During an interview 'If You will.....U Can.....Baby Halder proved it' which was telecasted on Delhi Doordarshan in a programme called 'Stree Shakti', Baby Halder shared one incident in which she said when she used to clean the bookshelf at her dada's house she came across a book written by Mahashweta Devi which depicted a pathetic story of a suppressed woman who undergoes the ordeal of life, wins in life by creating her own identity. Baby was overwhelmed to read this experience. She was also highly inspired by these words of encouragement. Coincidentally Mahashweta Devi, the great Champion of Women's Freedom Movement in India read Baby Halder's Autobiography and wrote her comment," A story of courage and grace.....a book worth waiting for."

Our Former Prime Minister, Pandit Jawaharlal Nehru said that until and unless our male and female are suppressed under the dominance of some power they cannot find themselves independent and free by any law or rule. Economic dependence is the main reason of backwardness of Indian women. They are never free as long as they are not economically self- reliant.

CONCLUSION

Baby Halder's book is miraculous and an inspiration to all of us. It gives the message to the reader's that Education brings rays of happiness and prosperity in one's life. She is a woman with perseverance, self respect and resilience. She showed the courage to fight against all odds in life and worked as a torch bearer, bringing light of hopes and spirit not only for herself but also for all the women folk in India who are fighting the battles of life, searching for their own identity in the darkness. She underwent the ordeal of life only to prove herself. Of course in this rigorous journey of adversity Mr. Prabodhkumar, her dada, played the role of a lighthouse which stands firm to show light and gives right direction to the ship that loses path during the voyage.

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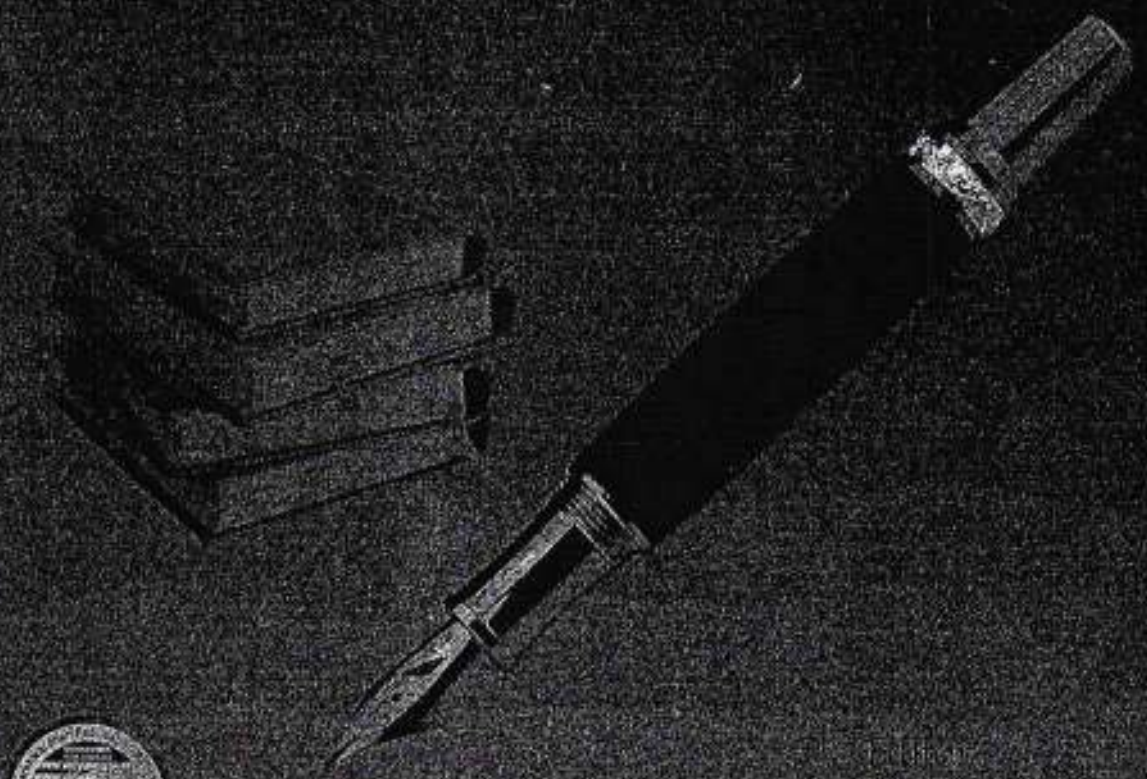

Dr Bapu G Ghotkar

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There have been many disputes about whether it should be accepted or not without solid decisions of its acceptance or not. The question of evaluating the act of death in the variety of methods prevalent is often intricate, thus contemporary debate on euthanasia being morally valid is continual throughout the world. It has been studied that, all over the world that philosophies and religion plays a central character in determining ethical standing of euthanasia. While active euthanasia is not easy to be implemented, it is not impossible to secure passive euthanasia. It appears to be ethically acceptable.

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A Married Woman: an analysis in Feminist Perspective

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Abstract: Manju Kapur, an internationally famous Indian woman novelist has written five novels. She reveals the life of women, their oppression as well as their struggle for rights, survival and quest for identity. In this paper, efforts have made to analyze Manju Kapur's novel **A Married Woman**, from the feminist point of view. Indian writers have made a significant contribution in enriching the novel as a genre. Despite all challenges and problems Indian English novel has carved a niche of its own. Many of the female writers during post independent era have used their pens to delineate Indian women in new perspective. They have mainly focused on the issues related to woman such as self-reliance, financial independence, self-respect and above all their emancipation from the male dominance.

Feminism is rational movement that advocates for seeking equal political, economic and social rights for women. It focuses on women's woes and sufferings all over the world, and struggle for eradicating gender inequality prevailing in the society. The major component of the feminist theory is to challenge the patriarchal beliefs for attaining independence and individuality. The first feminist movement started from Britain and gradually, it took the shape of a global association. Anita Desai, Nayantara Sahgal, Manju Kapur ,Shashi

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Despande, Shobha De and others are writers who observed the gender issues which marginalize and oppress women in the patriarchal society. These writers protest the repression and suppression of women. This paper discusses issues related to women's identity, self-respect, their role in decision making and above all spirit of gender equality from feminist point of view as reflected in A **Married Woman,** a novel by Manju Kapur.

Key word: Feminist, Feminism, independence, movement

Manju Kapur like that of her contem porary female writers described human psyche and the plight of female world. **A Married Woman** is the story of an artist whose canvas challenges the constraints of middle class existence. The story is simple-a married woman struggles to keep her identity. The novel centers round a middle class Delhi-based Hindu family. Hemant, an America-returned Delhi business man, married Astha Bhadra, a middle-class educated Hindu girl. Initially their married life runs smooth and they have two children, a daughter Anuradha and a son Himanshu. Their traditional marriage is soft, sound and healthy till Astha meets Aijaz Khan. The death of the Aijaz Khan scattered her world. Then Astha is encountered with Pipeelika, the widow of Aijaz. Pipeelika is a qualified Hindu girl. She is an M.A. in Economics and Sociology. Astha and Pipeelika is probably a lesbian couple. Their love relationship reaches a climax when Pipeelika flies to the US for her Ph.D. Manju Kapur is determined that the new, educated Indian woman has the ability to decide her priorities for self-discovery. She has visualized the emerging image of the educated Indian woman symbolically represented by Astha.

The novel is the story of well educated woman, Astha. She is traditionally well brought up daughter by her parents. But, in an Indian conventional family, a girl is a liability to the parents. It is a middle class family who struggle in their life for children and everything. Astha gets admitted in the college. Her father was in favor of her higher education. During her college days she was attracted towards Bunty. Her first love disappears when she received the letter from Bunty which reveals that he is not able to meet her further. In fact, she never spoke openly about her love. With this letter everything comes to an end in her life. It is very hard to imagine the condition of Astha's heart that aches inside. In the process she dates with a couple of young men of her own choice like her western counter parts, marries a man of her parents' choice and discovers the joys of intimacy with her husband, begets children, yet grows distant from him ,and struggles to become a painter. Much against her husband and her other family members she becomes a social activist, and falls in love with a woman, and finds herself –sort of, more. She reflects the middle class values and seems to enjoy her mental bliss for a long time but gradually experiences that there is something certainly lacking in her life. She suffers from a sense of incompleteness, suppression and agony which is further provoked by her involvement into the outer world of upheaval and protest.

This novel can be read at the feministic level as it has dealt with many issues related to the female world. Manju Kapur is in one of her interviews reveals her views: "I am a feminist. And what is a feminist? I mean I believe in the rights of women to express themselves in the rights of women to work. I believe in equality, you know domestic equality, legal equality. I believe in all that. And the thing is that women don't really have that-you know even educated women, working women. There is a trapping of equality but you scratch the surface and it is not really equal (Unheard Melodies, p.4).

The female protagonist Astha who is the daughter of a cultured father and an orthodox mother, has an earnest desire for passive co-existence in the family. But she is dominated

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against and discriminated at her-in-law's house. There, she is made-up to have a willing body at night, a willing pair of hands and feet in the day and a submissive mouth. Her marriage with Hemant, does not show to be based on mutual co-operation and appreciative. She is duty-bound to be a stable wife and sacrificing mother, like a sacred cow in the position of married woman. It traps to her bodily exploitation and emotional hunger. Being depressed of her emotional discharge, she recklessly seeks for it and drives to a "substitute-husband" (Rationale, p.110), lesbianism. Astha, has stamped out a self-governing life of the woman for self-fulfillment and advocated for inter-religious marriage and female-female relationship divergent to the patriarchal norms of traditional society. Astha had the passions or infatuations of a teenager like any other girl. But those infatuations are turned into oblivion. She has to set up a diverse life after her marriage with Hemant. She is cynical with her husband's love for her family relationships are not right with her. Her mother-in-law likes her to be a stable and sacrificing woman like customary wives and mothers. She is constantly under stress of work and suffocating with her responsibilities to meet everybody's need. She is "always adjusting to everybody's need" (AMW, p.227). She senses that a married woman's status in the family is always dependent on her husband. She is torn between her responsibility and socio-religious perception. She has no emotional free will from the domestic relationships. She is exhausted of her responsibility and thinks "A tired woman cannot make wife good" (AMW, p. 154). She is reeling under the pressure and dejection of a married woman who is no better than an unpaid servant. She has to give pleasure to her husband and for pleasing him; she must be "A willing body at night, a willing pair of hands and feet in the day and an obedient mouth" (AMW, p. 231). She is marginalized in her own family by sadistic social atmosphere. She thinks of freedom from stress and depression. She thinks of a fine job thinking that "with good job comes independence" (AMW, p. 4) so, she joins as a teacher but this job also does not keep her free from distress and trauma of discrimination.

Indian Society prefers a baby-boy rather than a baby-girl. "Manju Kapur gently digs at the Indian attitude of preferring a baby-boy to a baby-girl in the novel" (Rationale, p. 107). Astha s family proves that their need of baby-boy by their superstitional belief, "When her daughter Anuradha was four, Astha conceived again. Her mother brought in a poojari to perform special pooja to propitiate the gods to grant them a boy for Astha" (Rationale, p. 107). Having given birth to Himanshu a son, she does not feel substandard to anyone in the society and the family members are thankful to her because they feel "the family is complete at last" (AMW, p. 68). Astha also feels happy about her motherhood like a married woman but she does not like the gender discrimination. She is much traumatized at the uninterested response of members of the family and society at her daughter, Anuuradha's birthday. But she obtains an appraisal and sanction of motherhood after the birth of her son—Himanshu. She abhors such a false notion and discrimination between a daughter and a son, such an outlook of Indian traditional society is injurious to equal status of women who "feel caught up in the web of daily life"(AMW, p.84) and fall a victim to tension and depression that is "the disease of modern life"(AMW, p.76). The narrow-minded socio-cultural tradition is responsible for such a dilemma of women in our society "Where we must recognize the critical role played by popular culture in reinforcing prejudices against women". It gives women to be broadminded like earth instead of conveying them equal status like men. Manju Kapur has responded harshly against unequal treatment of women in our family and society. The perception of male dominant patriarchal society that women should

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Only economic freedom is not enough for them. socio-religious culture has to accept their individuality. The researchers have to permit her to let her be what she decides and let her have the integrity which has been ignored to her for ages. They can no longer remain submissive, subjugated and discriminated. In Astha-Aijaz-Pipee episode, religion has been decreased. Aijaz himself is a secular and open-minded Muslim. He is connected with a theatre group which works for the awakening of society. Pipee also runs an N.G.O. and Astha is also shown connected with a Manch. Her paintings also help in carrying out a new type of political consciousness. There are no embarrassments for matters such as lesbianism, extra marital relationship etc. A post–modernistic trend has been seen by the novelist through this novel. In short, Manju Kapur is a feminist by vocationand by practice. Her female protagonist, Astha has represented her all ideas lurking in her mind to exhibit her ideology as far as the emancipation of female world is concerned.

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14

Relationship Between Economics and Sociology

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Abstract:

There is a relationship between economics and sociology. These are long established, as is the interest in sociology shown by some economists. We need only recall the role played in both disciplines by Vilfredo Pareto at the turn of the last century. We will not attempt to summarize the history of these relations, however, which are often presented as conflicted, or even define the frontier between economics and sociology. It is well known that the two disciplines are distinguished as much by their methods as their focus of study; it is easy to think of points of contact between them, such as social reference points in motives for economic behavior or intervention of "non-market," social relationships in business, government, and sometimes even in the market itself. In this article, an attempt is made to discuss the relationship between economics and sociology in general and the major difference between both sociology and economics.

Keywords: Economic sociology, social conse quences of economic exchanges, social associations, economic welfare, etc.

Introduction:

The drive to understand the evolution of human society in all its dimensions is one that comes naturally; it has always been and remains a deeply-rooted motivation for historians,

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Kantowski-Sachs Bulk Viscous String Cosmological Model in $f(R, T)$ Gravity with Time Varying Deceleration Parameter

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Abstract- We propose a specially homogeneous and anisotropic Kantowski-Sachs string cosmological model with bulk viscosity in the framework of $f(R, T)$gravity by considering two cases (i) the special form and (ii) linearly varying deceleration parameter. To obtain a deterministic solution of the field equation we have been used some physical plausible condition. In this theory, cosmological model is presented in both cases. Also some important features of the models, thus obtained, have been discussed.

Keywords: $f(R, T)$*gravity, bulk viscous fluid, cosmic string, deceleration parameter.*

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Abstract- We propose a specially homogeneous and anisotropic Kantowski-Sachs string cosmological model with bulk viscosity in the framework of $f(R,T)$ gravity by considering two cases (i) the special form and (ii) linearly varying deceleration parameter. To obtain a deterministic solution of the field equation we have been used some physical plausible condition. In this theory, cosmological model is presented in both cases. Also some important features of the models, thus obtained, have been discussed.

Keywords: $f(R,T)$ *gravity, bulk viscous fluid, cosmic string, deceleration parameter.*

I. Introduction

In the light of the recent discovery of the accelerated expansion of the universe [1-3]. However, final satisfactory explanation about physical mechanism and driving force of accelerated expansion of the universe is yet to achieve as human mind has not achieved perfection. It is known that a point of universe is filled with dark energy. It has been addressed by various slow rolling scalar fields. It is supposed that the dark energy is responsible for producing sufficient acceleration in the late time of evolution of the universe. Thus, it is much more essential to study the fundamental nature of the dark energy and several approaches have been made to understand it. The cosmological constant is assumed to be the simplest candidate of dark energy. It is the classical correction made to Einstein's field equation by adding cosmological constant to the field equations. The introduction of cosmological constant to Einstein's field equation is the most efficient way of generating accelerated expansion, but it faces serious problems like fine tuning and cosmic coincidence problem in cosmology [4, 5]. Quintessence [6], phantom [7], k-essence [8], tachyons [9], and Chaplygin gas [10] are the other representative of dark energy. However, there is no direct detection of such exotic fluids. Dark energy can be explored in several ways, and modifying the geometric part of the Einstein-Hilbert action [11] is treated as the most efficient possible way. Based on its modifications, several alternative theories of gravity came into existence. Modified theories of gravity are attracting more and more attention of cosmologists because of the fact that these theories may serve as the possible candidates for explaining the late time acceleration of the universe. Some of the modified theories of gravity are (T), (R), (G), and (R, T) gravity. These models are proposed to explore the dark energy and other cosmological problems. Sharif and Azeem [12] discussed the Cosmological evolution for dark energy models in (T) gravity. Jamil et al. [13] have studied the stability of the interactive models of the dark energy, matter, and radiation for a FRW model in (T) gravity. Generalized second law of thermodynamics in (T) gravity with entropy corrections has been studied by Bamba et al. [14]. Recently, Harko et al. [15] developed another modified gravity known as $f(R,T)$ gravity. In this theory, the gravitational Lagrangian is given by an arbitrary function of the Ricci scalar R and of the trace of T of the stress energy tensor. In this paper, we concentrate on (R, T) gravity, with $f$being in this case a function of both R and T, manifesting a coupling between matter and geometry. Before going into the details of (R, T) gravity, The field equations of $f(R,T)$ gravity obtained from the action

$$S=\frac{1}{16\pi}\int\left[f(R,T)+L_m\right]\sqrt{-g}\,d^4x, \qquad (1)$$

where $f(R,T)$is an arbitrary function of the Ricci scalar R, T is the stress energy tensor T_{ij} of matter and L_m is the matter Lagrangian density, are given by

$$R_{ij}-\frac{1}{2}g_{ij}R=8\pi T_{ij}+2f'(T)T_{ij}+\left[2pf'(T)+f(T)\right]g_{ij}. \qquad (2)$$

Studies of cosmic strings and bulk viscosity are crucial as they play an important role in structure formation of the early stages of evolution of the universe. Cosmic strings are one dimensional topological defects, which may be formed during symmetry breaking phase transition in the early universe along with other defects like domain walls and monopoles. Bulk viscosity driven

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inflation is primarily due to the negative effective pressure which may overcome the pressure due to the usual gravity of matter distribution in the universe and provides an impetus for rapid expansion of the universe. Hence construction of bulk viscous string cosmological models have received considerable attention of research workers in the field. Many authors have investigated the astrophysical and cosmological implications of the (R, T) gravity [16–19]. Jamil et al. [20] have reconstructed some cosmological models for some specific forms of (R, T) in this modified gravity. Shamir et al. [21] obtained exact solution of anisotropic Bianchi type I and type V cosmological models whereas Chaubey and Shukla [22] have obtained a newclass of Bianchi cosmological models using special law of variation of parameter. Using a decoupled form of (R, T), that is, $(R, T) = (R) + (T)$ for Bianchi type V universe, Ahmed and Pradhan [23] have studied the energy conditions of perfect fluid cosmological models and Yadav [24] obtained some string solutions. Pawar and Solanke [25] have studied cosmological model filled with perfect fluid source in (R, T) gravity. Pawar and Agrawal [26] have obtained the solutions of dark energy cosmological model in the framework of the (R, T) theory of gravity. Recently Pawar et al. [27] have explored two fluid cosmological models in (R, T) theory. Mishra and Sahoo [28] solved the field equations of Bianchi type-VI*h* cosmological model in presence of perfect fluid in f (R,T) gravity. Sahoo and Mishra [29] studied Kaluza–Klein dark energy model in form of wet dark fluid in this theory. Reddy et al. [30] presented Kantowski-Sachs bulk viscous string model in (R, T) theory. Recently, Naidu et al. [31], Kiran and Reddy [32], and Reddy et al. [33] discussed the Bianchi type-V, Bianchi type-III, Kaluza-Klein space time with cosmic strings, and bulk viscosity in $f(R, T)$ gravity, respectively. Caroll et al.[34], Nojiri and Odintsov [35-37] and Chiba et al.[38] are some of the authors who have investigated several aspects of *f (R)* gravity. Recently, Adhav [39] has obtained Bianchi type-I cosmological model in *f (R,T)* gravity. Reddy et al.[40, 41] have discussed Bianchi type-III and Kaluza-Klein cosmological models in *f (R,T)* gravity while Reddy and Shantikumar [42] studied some anisotropic cosmological models and Bianchi type-III dark energy model, respectively, in *f (R,T)* gravity. Subsequently Kiran and Reddy [43] established the non-existence of Bianchi type-III bulk viscous string cosmological model in *f (R,T)* gravity. Recently, Naidu et al. [44] presented Bianchi type-V bulk viscous string model in *f (R,T)* gravity while Reddy et al. [45] have obtained the same in Saez-Ballester theory. We describe some important features of the (R) gravity. The recent motivation for studying (R) gravity came from the necessity to explain the apparent late-time accelerating expansion of the universe. Detailed reviews on (R) gravity can be found in [46–49]. Thermodynamic aspects of (R) gravity have been investigated in the works of [50, 51].

Inspired by the above investigation and discussion, in this paper we investigate the role of variable deceleration parameter in Kantowski-Sachs space time with bulk viscous string and $f(R, T)$ gravity. The plan of this paper is as follows: In sec. 2, we derive the field equations of $f(R, T)$ gravity in Kantowski-Sach space-time when the matter source is bulk viscous fluid with on dimensional cosmic strings. In Section 3, we find the solution of the field equations and the model. Some physical and kinematical properties of the model are discussed in section 4. Concluding remarks are presented in section 5.

II. Metric and Field Equations

The Spatially homogeneous and anisotropic Kantowski-Sachs space-time in the form

$$ds^2 = dt^2 - A^2 dr^2 - B^2\left(d\theta^2 + \sin^2\theta\, d\phi^2\right), \quad (3)$$

where A and B are the cosmic time t only.

The energy momentum tensor for a bulk viscous fluid containing one dimensional cosmic string is considered as

$$T_{ij} = \left(\rho + \bar{p}\right)u_i u_j - \bar{p} g_{ij} - \lambda x_i x_j, \quad (4)$$

$$\bar{p} = p - 3\xi H, \quad (5)$$

where ρ is the rest energy density of the system, $3\xi H$ is usually known as bulk viscous pressure, H is Hubble's parameter, p is the pressure and λ is the string tension density. Also $u^i = \delta_4^i$ is the four velocity vector, which satisfies

$$g_{ij}u^i u_j = -x^i x_j = 1, \qquad u^i x_i = 0 \quad (6)$$

Here, we also consider $\rho, \bar{p}, \lambda$ as functions of cosmic time t only.

Now, by adopting commoving coordinates the field equations (2) of $f(R, T)$ gravity for the metric (3), with the help of eqs. (4)-(6), for the particular choice of the function

$$f(T) = \mu T \quad (7)$$

where μ is constant, can be written as

$$2\frac{\ddot{B}}{B} + \frac{\dot{B}^2}{B^2} + \frac{1}{B^2} = \bar{p}(8\pi + 3\mu) - \lambda(8\pi + 3\mu) - \mu\rho \quad (8)$$

$$\frac{\ddot{A}}{A}+\frac{\ddot{B}}{B}+\frac{\dot{A}\dot{B}}{AB}=\bar{p}(8\pi+3\mu)-\mu\lambda-\mu\rho \quad (9)$$

$$2\frac{\dot{A}\dot{B}}{AB}+\frac{\dot{B}^2}{B^2}+\frac{1}{B^2}=\mu\bar{p}-\rho(8\pi+3\mu)-\mu\lambda \quad (10)$$

where an overhead dot indicates differentiation with respect to t.

Spatial volume and the scale factor for the metric (3) are respectively, defined by

$$V=AB^2 \quad (11)$$

$$a=(AB^2)^{\frac{1}{3}} \quad (12)$$

The physical quantities which play a significant role in the discussion of cosmological models are expansion scalar θ the mean anisotropy parameter A_h and shear scalar σ^2 which are defined as

$$\theta=3H=3\left(\frac{\dot{A}}{A}+2\frac{\dot{B}}{B}\right) \quad (13)$$

$$3A_h=\sum_{i=1}^{3}\left(\frac{\Delta H_i}{H}\right)^2,\ \Delta H_i=H_i-H,\ i=1,\ 2,\ 3 \quad (14)$$

$$\sigma^2=\frac{1}{2}\sigma^{ij}\sigma_{ij}=3{A_h}^2-H^2 \quad (15)$$

where H is the mean Hubble parameter.

III. Solutions of the Field Equations

The field equations (8)-(10) reduce to the following two independent equations:

$$\frac{\ddot{A}}{A}-\frac{\ddot{B}}{B}-\frac{\dot{B}^2}{B^2}+\frac{\dot{A}\dot{B}}{AB}-\frac{1}{B^2}=(8\pi+2\mu)\lambda \quad (16)$$

$$\frac{\ddot{A}}{A}+\frac{\ddot{B}}{B}-\frac{\dot{B}^2}{B^2}-\frac{\dot{A}\dot{B}}{AB}-\frac{1}{B^2}=\bar{p}(8\pi+2\mu)+\rho(8\pi+2\mu) \quad (17)$$

Here there are two equations involving five unknowns. Since the field equations are highly nonlinear for the complete determinacy, we need extra conditions among the variables. We consider these conditions in the form case (i) and case (ii) as defined below

(i) The scalar expansion θ in the model is proportional to the shear scalar σ^2 which yields

$$A=B^m \quad (18)$$

where $m\neq 1$ is a constant, takes care of anisotropy of the space-time (Collins et al. [52])

(ii) The combined effect of the proper pressure and the bulk viscous pressure for barotropic fluid can be written as

$$\bar{p}=p-3\xi H=(\varepsilon_0-\gamma)\rho,\quad 0\leq\varepsilon_0\leq 1,\ \ p=\varepsilon_0\rho \quad (19)$$

where ε_0 and γ are constants.

Case (i)

The case (i) consists of (i), (ii) and special form of deceleration parameter [53]

$$q=-1+\frac{\beta}{1+a^{\beta}} \quad (20)$$

where $\beta>0$ is a constant and a is a scale factor of the metric.

In this case, we have discussed the solution of the field equations by considering the extra conditions as above.

The Hubble parameter H is defined as $H=\frac{\dot{a}}{a}$ and from (20) we obtained

$$H=\frac{\dot{a}}{a}=a_1\left(1+a^{-\beta}\right) \quad (21)$$

where a_1 is a constant of integration.

Integrating (21) and using the initial conditions $a=0\ at\ t=0$ we have found

$$a=\left(e^{a_1\beta t}-1\right)^{\frac{1}{\beta}} \quad (22)$$

The scale factor of metric (3) is defined as

$$a=(AB^2)^{\frac{1}{3}} \quad (23)$$

With the help of (18), (22)and (23), we have found

$$A=\left(e^{a_1\beta t}-1\right)^{\frac{3m}{\beta(2+m)}} \quad (24)$$

$$B=\left(e^{a_1\beta t}-1\right)^{\frac{3}{\beta(2+m)}} \quad (25)$$

Using (24) and (25), the metric (3) can be written as

$$ds^2 = dt^2 - \left(e^{a_1\beta t} - 1\right)^{\frac{6m}{\beta(2+m)}} dr^2 - \left(e^{a_1\beta t} - 1\right)^{\frac{6}{\beta(2+m)}} \left(d\theta^2 + \sin^2\theta\, d\phi^2\right) \tag{26}$$

From (16), with the help of (24)-(25) we obtain the string tension density λ as

$$\lambda = \frac{1}{(8\pi + 2\mu)} \left\{ \frac{(m-1) m_1 e^{a_1\beta t}}{\left(e^{a_1\beta t} - 1\right)} \left[\beta \left(1 + \beta_1 \frac{e^{a_1\beta t}}{\left(e^{a_1\beta t} - 1\right)} \right) + \frac{m_{11} e^{a_1\beta t}}{\left(e^{a_1\beta t} - 1\right)} \right] - \frac{1}{\left(e^{a_1\beta t} - 1\right)^{\frac{6}{\beta(2+m)}}} \right\} \tag{27}$$

where $m_1 = \dfrac{3a_1^2}{(2+m)}$, $\beta_1 = \dfrac{3}{\beta(2+m)} - 1$, $m_{11} = \dfrac{3(m+1)}{\beta(2+m)}$

From (17), with the help of (19) and (25), we obtained the rest energy density ρ as

$$\rho = \frac{1}{(8\pi + 2\mu)(\varepsilon_0 - \gamma + 1)} \left\{ \frac{m_1 e^{a_1\beta t}}{\left(e^{a_1\beta t} - 1\right)} \left[(m+1)\beta \left(1 + \beta_1 \frac{e^{a_1\beta t}}{\left(e^{a_1\beta t} - 1\right)} \right) + \frac{3\left(m^2 - 2m - 1\right) e^{a_1\beta t}}{(2+m)\left(e^{a_1\beta t} - 1\right)} \right] - \frac{1}{\left(e^{a_1\beta t} - 1\right)^{\frac{6}{\beta(2+m)}}} \right\} \tag{28}$$

From (19), with the help of (28), we have obtained the total pressure $\overline{p}$, proper pressure p and the coefficient of bulk viscosity ξ as follows:

$$\overline{p} = \frac{(\varepsilon_0 - \gamma)}{(8\pi + 2\mu)(\varepsilon_0 - \gamma + 1)} \left\{ \frac{m_1 e^{a_1\beta t}}{\left(e^{a_1\beta t} - 1\right)} \left[(m+1)\beta \left(1 + \beta_1 \frac{e^{a_1\beta t}}{\left(e^{a_1\beta t} - 1\right)} \right) + \frac{3\left(m^2 - 2m - 1\right) e^{a_1\beta t}}{(2+m)\left(e^{a_1\beta t} - 1\right)} \right] - \frac{1}{\left(e^{a_1\beta t} - 1\right)^{\frac{6}{\beta(2+m)}}} \right\} \tag{29}$$

$$p = \frac{\varepsilon_0}{(8\pi + 2\mu)(\varepsilon_0 - \gamma + 1)} \left\{ \frac{m_1 e^{a_1\beta t}}{\left(e^{a_1\beta t} - 1\right)} \left[(m+1)\beta \left(1 + \beta_1 \frac{e^{a_1\beta t}}{\left(e^{a_1\beta t} - 1\right)} \right) + \frac{3\left(m^2 - 2m - 1\right) e^{a_1\beta t}}{(2+m)\left(e^{a_1\beta t} - 1\right)} \right] - \frac{1}{\left(e^{a_1\beta t} - 1\right)^{\frac{6}{\beta(2+m)}}} \right\} \tag{30}$$

$$\xi = \frac{\gamma\left(e^{a_1\beta t} - 1\right)}{9a_1(8\pi + 2\mu)(\varepsilon_0 - \gamma + 1)e^{a_1\beta t}} \left\{ \frac{m_1 e^{a_1\beta t}}{\left(e^{a_1\beta t} - 1\right)} \left[(m+1)\beta \left(1 + \beta_1 \frac{e^{a_1\beta t}}{\left(e^{a_1\beta t} - 1\right)} \right) + \frac{3\left(m^2 - 2m - 1\right) e^{a_1\beta t}}{(2+m)\left(e^{a_1\beta t} - 1\right)} \right] - \frac{1}{\left(e^{a_1\beta t} - 1\right)^{\frac{6}{\beta(2+m)}}} \right\} \tag{31}$$

a) Some Physical Properties of the Model

Some physical properties of the model are given below, which have crucial role in the discussion of cosmological models are the spatial volume V, scalar expansion θ, The Hubble's parameter H, shear scalar σ^2 and mean anisotropy parameter A_h, for the model (26) the above quantities are given by

$$V = \left(e^{a_1\beta t} - 1\right)^{\frac{3}{\beta}} \tag{32}$$

$$\theta = \frac{9a_1 e^{a_1\beta t}}{\left(e^{a_1\beta t} - 1\right)} \tag{33}$$

$$H = \frac{3a_1 e^{a_1\beta t}}{\left(e^{a_1\beta t} - 1\right)} \tag{34}$$

$$3A_h = \frac{6 + 4m + 2m^2}{(2+m)^2} \tag{35}$$

$$\sigma^2 = \frac{\left(6 + 4m + 2m^2\right)^2}{3(2+m)^4} - \frac{9a_1{}^2 e^{2a_1\beta t}}{\left(e^{a_1\beta t} - 1\right)^2} \tag{36}$$

In this model we observed that at initial epoch the values of energy density ρ, proper pressure p, total pressure $\overline{p}$, coefficient of bulk viscosity ξ, and Hubble prarmaeter H are very high and these quantities gradually decreases with the evolution of time; and as $t \to \infty$, $\rho, p, \overline{p}, \xi, H \to 0$. Spatial volume increases with the evolution of time; that is $t \to \infty$, $V \to \infty$, when $t = 0$ spatial volume vanishes and the expansion scalar is infinite. Which shows that the universe starts evolving with zero volume. The scale factor vanishes at $t = 0$ and hence the model has a point singularity at the initial epoch. As t increases, the scale factor and the spatial volume increases but the expansion scalar decreases. Anisotropy parameter is constant which shows that model is model remains anisotropic

throughout the evolution of the universe. It is noted that bulk viscosity in the universe decreases with time so that, we obtain, inflationary models. In this model as t increases string tension density λ increases slowly.

Case (ii)

The case (ii) consists of (i), (ii) and special form of deceleration parameter [54]

$$q = -kt + n - 1 \tag{37}$$

From (37) we have Akarsu and Dereli [54]:

$$= {}_1 \exp\left[\frac{2}{\sqrt{n^2 - 2c_1 k}} \arctan h\left(\frac{kt - n}{\sqrt{n^2 - 2c_1 k}}\right)\right] \qquad for\ k > 0 \quad n \geq 0 \tag{38}$$

And $a = \begin{cases} k_2 (nt + c_2)^{\frac{1}{n}} & for\ k = 0 \quad n > 0 \\ k_3 e^{c_3 t} & for\ k = 0 \quad n = 0 \end{cases}$

where $k_1, k_2, k_3, c_1, c_2, c_3$ are constants of integration. The last two values of a give the constant deceleration parameter. So we neglect these values of a as $q = cons \tan t$ is studied by earlier researcher. Thus we focus on the first value of scale factor.

The scale factor a can also be expressed as follows for $n > 1 \quad c_1 = 0$

$$a = k_1 \exp\left[\frac{2}{n} \arctan h\left(\frac{kt - n}{n}\right)\right] \tag{39}$$

$$a = k_1 e^{\left[\frac{2}{n} \arctan h\left(\frac{kt}{n} - 1\right)\right]}$$

With the help of (18), (23) and (39) we have obtained

$$A = k_1^{\frac{3m}{(2+m)}} \exp\left[\frac{6m}{n(2+m)} \arctan h\left(\frac{kt}{n} - 1\right)\right] \tag{40}$$

$$B = k_1^{\frac{3}{(2+m)}} \exp\left[\frac{6}{n(2+m)} \arctan h\left(\frac{kt}{n} - 1\right)\right] \tag{41}$$

From (16), with the help of (41), we found the string tension density as

$$\lambda = \frac{1}{(8\pi + 2\mu)} \left\{ \frac{k_{11}}{(2n - kt)^2 t^2} [kt + k_{12} + k_{13}] - \frac{1}{k_1^{\frac{6}{(2+m)}} \exp\left[\frac{12}{n(2+m)} \arctan h\left(\frac{kt}{n} - 1\right)\right]} \right\} \tag{42}$$

where $k_{11} = \frac{12(m-1)}{(m+2)}, \quad k_{12} = \frac{3}{(m+2)} - n, \quad k_{13} = \frac{3(m+1)}{(m+2)}$

From (17), with the help of (19) and (42), we found the rest energy density ρ :

$$\rho = \frac{1}{(8\pi+2\mu)(\varepsilon_0-\gamma+1)}\left\{\frac{4k_{13}}{(2n-kt)^2t^2}[kt+k_{12}+k_{14}]-\frac{1}{k_1^{\frac{6}{(2+m)}}\exp\left[\frac{12}{n(2+m)}\arctan h\left(\frac{kt}{n}-1\right)\right]}\right\} \quad (43)$$

where $k_{14}=\frac{3(m^2-2m-1)}{(m^2+3m+2)}$.

From (19), with the help of (43), we obtained the total pressure $\bar{p}$, proper pressure p and the coefficient of bulk viscosity ξ as follows:

$$\bar{p} = \frac{(\varepsilon_0-\gamma)}{(8\pi+2\mu)(\varepsilon_0-\gamma+1)}\left\{\frac{4k_{13}}{(2n-kt)^2t^2}[kt+k_{12}+k_{14}]-\frac{1}{k_1^{\frac{6}{(2+m)}}\exp\left[\frac{12}{n(2+m)}\arctan h\left(\frac{kt}{n}-1\right)\right]}\right\} \quad (44)$$

$$p = \frac{\varepsilon_0}{(8\pi+2\mu)(\varepsilon_0-\gamma+1)}\left\{\frac{4k_{13}}{(2n-kt)^2t^2}[kt+k_{12}+k_{14}]-\frac{1}{k_1^{\frac{6}{(2+m)}}\exp\left[\frac{12}{n(2+m)}\arctan h\left(\frac{kt}{n}-1\right)\right]}\right\} \quad (45)$$

$$\xi = \frac{\gamma t(2n-kt)}{18(8\pi+2\mu)(\varepsilon_0-\gamma+1)}\left\{\frac{4k_{13}}{(2n-kt)^2t^2}[kt+k_{12}+k_{14}]-\frac{1}{k_1^{\frac{6}{(2+m)}}\exp\left[\frac{12}{n(2+m)}\arctan h\left(\frac{kt}{n}-1\right)\right]}\right\} \quad (46)$$

b) Some Physical Properties of the Model

Some physical properties of the model are given below, which have significant role in the discussion of cosmological models are the spatial volume V, scalar expansion θ, The Hubble's parameter H, shear scalar σ^2 and mean anisotropy parameter A_h, the above quantities are given by

$$V = k_1^{3}\exp\left[\frac{6}{n}\arctan h\left(\frac{kt}{n}-1\right)\right] \quad (47)$$

$$\theta = \frac{18}{t(2n-kt)} \quad (48)$$

$$H = \frac{6}{t(2n-kt)} \quad (49)$$

$$3A_h = \frac{6+4m+2m^2}{(2+m)^2} \quad (50)$$

$$\sigma^2 = \frac{(6+4m+2m^2)^2}{3(2+m)^4} - \frac{9a_1^{\,2}e^{2a_1\beta t}}{(e^{a_1\beta t}-1)^2} \quad (51)$$

In this model the energy density ρ, proper pressure p, total pressure $\bar{p}$, coefficient of bulk viscosity ξ, and Hubble prarmaeter H gradually decrease with the evolution of time. Spatial volume increases with evolution of time, after that it also diverges. Anisotropy parameter is constant so the model is anisotropic model throughout the evolution of the universe. In this model cosmic string decreases as t increases.

IV. Concluding Remarks

In this paper we have studied the Kantowski-Sachs bulk viscous string cosmological model in $f(R,T)$ theory of gravity with variable deceleration parameters. According the choice of deceleration parameter (20) and (37) we have presented two

cosmological models. The observations of both the models are as follows:

- It is observed that in the first case the model has point singularity at the initial epoch. In the second case there is no point type singularity.
- In both the model as $t \to \infty \; then \; \rho, p, \overline{p}, \xi, H \to 0$
- In both cases the mean anisotropy parameter $A_h \neq 0$ the model do not approach isotropy and it is time independent in which gives the indication that the anisotropy in expansion rates is maintained throughout the cosmic evolution.
- In the first model The spatial volume is zero at $t = 0$ and the expansion scalar is infinite, which suggest that the universe starts evolving with zero volume at $t = 0$, i.e. we have big bang scenario.
- We observed that the type of time variations of deceleration parameter considered here affect the nonexistence of cosmic string in this model. Hence the consideration of variable deceleration parameter contribute towards the existence of cosmic strings in the theory of Kantowski-Sachs space time.

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blissful experiences. On the other hand neglect of any of the three aspects (i.e. body, mind & spirit) of health result in imbalance and disharmony in the being and the person carries negative health.A good deal of studies have been done to indicate the short and long term effects of the yogic practices on psycho physiological functioning and their role in the prevention and management of different health problems. The selected yogic practices have a favorable conditioning effect on various physiological systems. The different meditational practices have relaxing and rejuvenating effects on the respiratory, circulatory and nervous system. As a result yogic practices have been found useful in preventing and managing disorders related to the body systems.

Meaning of Yoga

The word "Yoga" comes from "Yuj" root in Sanskrit which means union or joining together. When a man develops a relationship with another that relationship is also known as yoga. According to general language, three meanings of Yoga are Jodna, Samadhi and sanyama. So it is clear that Yoga word is multi meaning.

Definitions of Yoga

*Oxford Dictionary defined it "a Hindu system of Philosophic meditation and asceticism designed to affect the reunion of the developed soul with the Universal sprit"

*According to swami Vivekananda "Each soul is potentially divine. The goal is to manifest this divinity within, by controlling Nature- external and internal. Do it either by work or worship, psychic control or philosophy, by one, or more, or all of these and be free"

*According to Bhagvad Gita. "This Yoga must be followed with faith, with a strong and courageous heart"

The stages of Yoga

The right means are just as important as the ends in view. Patanjali enumerates these means as the eight limbs or stages of Yoga for the quest of the soul. They are

1. Yama (Universal morall commandments)
2. Niyama (Self-purification by discipline)
3. Asana (Physical Posture)
4. Pranayam (rhythmic control of the breath)
5. Pratyahara (with drawl of sense organs)
6. Dharana (Concentration)
7. Dhyana (Meditation) - :
8. Samadhi (a state of super consciousness)

Yoga as a Science:

Yoga is a complete science of life and although ancient one, has become popular only in recent past. It is a scientific method for exercising and relaxing to ease the tensions and stress of modern day living. Yoga is one of the techniques which help the development of physical and mental health of a person. The science of Yoga has a very wide spectrum as regards its application. In India and any other developed countries yoga is included as a discipline in the curriculum of education.

Yoga is a science which combines body movements that coordinates with mind, posture and breathing techniques which produces the best results for healthy living. Today Yoga is gaining popularity due to its possible application to various fields of human interest i.e., health cure and prevention of sports injuries, sports performance, development of physical fitness. Yoga is recognized as a system which promotes an integral development of body and mind. Yoga and Physical Fitness

Problems of Modern Life Style

Uncountable problems are created by present day's life style. The following are the three main problems which are the root cause for others problems and risk

- Stress.
- Cardiac problems
- Obesity

The problems accumulated at the body level as stiffness of joints and spasms of muscles can be released by the practice of yogasanas which are congenial posterns of the body. Yoga in itself is a science of health management rather than a method of treatment. When yoga is combined with certain healing and therapeutic modalities, it increases health, general wellbeing and longevity. It does this by removing tension, calming the mind and improving vitality. Yoga generally enhances our lives on all levels.

Today's life style stress, Cardiac Problems and obesity is the burning problems and risk.

Stress.

Stress (roughly the opposite of relaxation) is a medical term for a wide range of strong external stimuli, both physiological and psychological, which can cause a physiological response called the general adaptation syndrome, first described in 1963 by Hansselye in the journal "Nature". It can be understood as tension: (Psychology) a state of mental or emotional strain or suspense.

Stress is the body's physical, mental and chemical reactions to circumstance that frighten,

excite, confuse, challenge, surprise, anger, endanger or irritate. The events that cause stress may be good or bad.

While many people have always thought of yoga as some mystic Hindu practice, that image is rapidly disappearing-almost as fast as the stressed of our modern lives are increasing. The American Academy of Family physicians has noted that stress related symptoms promptheart decease and 60 millions have hypertension.

Obesity

It may be defined as excess Wight or deposition of excess fat on body, which leads various diseases like diabetes, heart diseases, hypertension, lowered pulmonary function, lowers life expectancy.

Obesity, obviously, is a curse and a serious disease by itself. If you donot modify your life style and choose the right food on a regular basis, the weight you lose on any diet will come right back. Almost 70 per cent of those who diet, regain their lost weight within a year, and have to diet all over again. Constant losing and gaining of weight in the battle of bulge is fur sting and demoralizing. It often leaves serious psychological sears. You can help yourself to be fit and not fat.

Yoga a way to Balanced Life

Health is the foundation on which rests the happiness of the people and the strength of nation. Yoga is *a* science that regulates the physical and physiological behavior of an individual. Regular practice of Yoga will develop physical fitness and keep the ailments away and also it gives the mental power. Some of the advantages of Yoga are:

- It's a traditional system of practice, coordination, both mind and body, which is ultimately needed for the today's modernized society.Yoga plays a vital role determining the individual's physical and mental fitness.
- Unlike some allopathic medicines, Yoga practice has no side effects.
- Regular practice of yoga prevents occurrence of many diseases of modernized life style.

two-third of the office visits to family Physicians Exercise and alternative therapies are now commonly prescribed for stress-related complaints and illness. Even a recent issue of consumer Reports suggests Yoga for stress relief.

Practicing Yoga can alter your *brain* chemistry. Some yoga positions in particular are effective in stimulating the pituitary gland to release endorphins and to reduce the level of cortisol (the stress hormone.)

Asanas greatly influence the functioning of the endocrine system. We know the important role the endocrine glands play during stress adaptation, by secreting the stress hormones. There is such an intaricate. relationship between the glands that one malfunctioning gland can cause the disruption of the whole system.

Cardiac Problems

Heart is said to be most sensitive to emotional stress. During stress period, the vessels of the visceral organs are tightened and amount of blood flow to the muscles is increased. By restricting the tiny vessels to visceral organs, the heart is pressed to work harder, when heart beats faster, the blood pressure rises. If the emotional stress persists blood pressure remains consistently high leading to stroke and other cardiovascular disease.

Yogic practice help to prepare a healthy body and mind trained in such a way that a necessary equilibrium is established in over all functions. It is short of recondition of physiological mechanism of body as a whole. The effectiveness of Yoga in controlling hypertension by removing stress related disorders.

Conclusion:

1. Yogic Science fruitful field for fundamental and applied research and teaching at higher levels by behavioural scientist, particularly psychologistic.

2. It is important that indigenous knowledge of yoga and yoga psychology is suitably incorporated as an integrated aspect of life in our routine.

3. Yoga is good for everyone so people of all professions, cultures, religions and socio-economic strata adopt yogic lifestyle and attain an inspired vision for future.

4. Yogic life style has the potential to harmonize the emotional life of the individual and helps one to gear up for the inner journey of the everlasting contentment. Yoga is a complete science of life and although ancient one, has become popular only in the recent past. It is a scientific methods for exercising and relaxing to ease the tension and stresses of modern day living. To conclude this, I would strongly recommend suggest yoga as one of the preventive & social medicines of westernized society.

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अर्थतज्ज्ञ लोकमान्य टिळक

डॉ. देवेंद्र रंगाचार्य
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प्रस्तावना :

हिंदुस्थानचा स्वातंत्र्य लढा चालू असतानाच हिंदूस्थानच्या आर्थिक परिस्थितीविषयी नेते मंडळी व अर्थतज्ज्ञ विचार करत होते. देशाच्या अर्थव्यवस्थेसंबंधी सखोल विचार करण्यातं दादाभाई नौराजी, न्यायमूर्ती रानडे, नामदार गोखले, रोमेशचंद्र दत्त आघाडीवर होते. तर्खडकर, जोशी आदी प्रभुतीनीही देशाच्या आर्थिक दुरावस्थेविषयी विचार व्यक्त केले जाते. परंतु हे सर्व थोर विचारावंत नेते मवाळ होते. सरकारच्या चांगुलपणावर त्यांचा भरवसा होता. सनदशीर लढ्यावर त्यांचा विश्वास होता. अशा परिस्थितीत हिंदुस्थानला आक्रमक खंबीर नेतृत्वाची गरज होती अन ती लोकमान्य टिळकांच्या रुपाने पुरी झाली. आपल्या जहाल नेतृत्वाने त्यांनी भारतीयांना आकर्षित केले. संपूर्ण स्वराज्याची मागणी करत असतानाच त्यांनी ब्रिटीशांच्या आर्थिक धोरणाचे वाभाडे काढले. त्यांचे केसरीमधील लेख, त्यांची काँग्रेसच्या व्यासपिठावरील भाषणे व इतर लेखन हे टिळक उत्तम अर्थतज्ज्ञ असल्याचे सुचित करतात. हिंदुस्थानच्या प्रगतीसाठी पाश्चात्य आर्थिक धोरण उपयोगी नसून, या देशाच्या धार्मिक, आध्यात्मिक विचारणामधूनच त्यासाठी उपाय शोधला पाहिजे या विचारांवरच त्यांची आर्थिक राजकीय नीती उभारलेली होती. लोकमान्यांनी वेळोवेळी व्यक्त केलेल्या अर्थविषयक विचारांची ही एक झलक.

हिंदुस्थानच्या दारिद्रयाची कारणे :

अर्थव्यवस्थेविषयी विचार करताना आपल्या दारिद्रयाची कारणे कोणती हे आपणास समजले तरच त्यावर योग्य उपाय करता येतील. या मूलभूत समस्येबद्दल विचार करतांना टिळक लिहीतात 'देशाची विपन्नावस्था होण्यास मुख्य तीन कारणे असतांत.'

१) देशातले लोक सुस्त, निरुद्योगी व अज्ञान असल्यामुळे त्यांच्याकडून मुळीच किंवा व्हावी तितकी संपत्ती उत्पन्न होत नाही.

२) कदाचित ते उत्पन्न करत असतील, पण ते दुसरेच कोणीतरी काढून नेत असेल.

३) ते जितके उत्पन्न करतात तिच्यापेक्षा व्यय करणारे अधिक निपजत असतील. आमच्या भाग्यशाली भरतखंडात तिन्ही कारणे पूर्ण वास करत आहेत. आम्हाकडून व्हावे तितके उत्पन्न होत नाही. झालेल्याचा बराच भाग बाहेर जातो आणि प्रतिवर्षी उत्पन्न करणाऱ्या संख्येपेक्षा ती मटकावणाऱ्यांची संख्या झपाट्याने वाढत आहे. (भारताच्या लोकसंख्या वाढीच्या गंभीर प्रश्नाकडे लक्ष वेधणारे टिळक हे पहिले पुढारी असावेत) दुर्देवाने आज शे-सव्वाशे वर्षानंतरही लोकसंख्येच्या या समस्येमुळे देशाची प्रगती अपेक्षित वेगाने होत नाही.

दारिद्रय दुर करण्याचे उपाय :

१) मुलद्रव्ये पुष्कळ उत्पन्न केली पाहिजेत. मुलद्रव्यांची उत्पत्ती अधिक होण्यास खाणीचा शोध व शेतकी सुधारणा हे उपाय केले पाहिजेत. म्हणजेच नैसर्गिक संपत्तीचा शोध घेऊन तिचा उपयोग करणे (भारताला स्वातंत्र्य मिळून ६७ वर्षे झाली असून सुद्धा आजही आपण देशाच्या नैसर्गिक साधनसंपत्तीचा संपूर्ण शोध घेऊ शकलेलो नाही)

२) या सामग्रीचा उपयोग करण्यासाठी लागणारे ज्ञान, कौशल्य, यांत्रिक कलेतील निष्णातता (कुशल इंजिनियर्स, तंत्रज्ञ) प्राप्त करण्यासाठी आपल्या विद्यार्थ्यांना युरोप, अमेरिका, जपान येथे पाठवावे.

३) यासाठी लागणाऱ्या पैशाची तजवीज करण्यासाठी संस्थानिकांनी पुढाकार घ्यावा. विद्यार्थ्यांना शिक्षणासाठी अल्प दराने पैसे देऊन नंतर तो विद्यार्थी कमावता झाल्यानंतर त्याने हप्त्याने कर्जाची परतफेड करावी.

४) मजुरी व कच्चामाल या आपणास अनुकूल असलेल्या घटकांचा योग्य उपयोग.

औद्योगिक पारतंत्र्य :

परकीय राज्य हे आपल्या देशाच्या सर्व समस्यांचे मूळ होते. राजकीय, धार्मिक व सामाजिक पारतंत्र्याबद्दलल समाजामध्ये खल होत आहे. परंतु या पारतंत्र्यांचा अविभाज्य भाग असलेल्या औद्योगिक पारतंत्र्याबद्दल मात्र पाहिजे तितकी चर्चा होत नाही. याबद्दल टिळकांनी खंत व्यक्त केली होती. औद्योगिक पारतंत्र्याबद्दल जनता पुरेशी जागरुक नसल्यामुळे आपल्या देशाची आर्थिक अवनती वेगाने होत आहे याकडे टिळकांनी लक्ष वेधले होते. युरोपातही औद्योगिक क्रांती होण्यापूर्वी सर्व कामे हातानेच केली जात. परंतु तेथे झालेल्या औद्योगिक क्रांतीमुळे अगदी थोड्या अवधीत मालाचे प्रचंड प्रमाणात उत्पादन होऊ लागले. युरोपातील या क्रांतीचा लाभ आपल्यालाल उठवता आला नाही. आपल्या या अपयशाची कारणमीमांसा टिळकांनी येणेप्रमाणे केली.

१) आपला देश अतिविस्तीर्ण व अतिसुपीक आहे

२) सर्वसाधारण भारतीयांची निवृत्ती मार्गाकडील प्रवृत्ती

३) शेकडो वर्षाची परकीय सत्ता

४) या देशाचे हवापाणी

५) सर्वसामान्य लोक ठेविले अनंते तैसेची रहावे अशा अल्पसंतुष्ट वृत्तीचे आहेत (म्हणूनच टिळकांनी गीतारहस्याद्वारे भारतीयांना कार्यप्रवृत्त करण्याचा प्रयत्न केला.

आपल्या आजारी अर्थव्यवस्थेचे निदान करतांना लोकमान्य म्हणतात, युरोपात मोठ्या प्रमाणावर मालाची निर्मिती होत आहे. यंत्राच्या या राक्षसी सामर्थ्यामुळे आपला हस्तव्यवसाय हतबल झाला आहे. तशातच आपल्याकडील भांडवलाची कमरता, तंत्रज्ञानाची वानवा यामुळे आपण उद्योगधंद्यात प्रगती करु शकत नाही. आपल्याकडे उद्योगधंदे नसल्याकारणाने नफारुपी भांडवल जमा होत नाही, तसेच उद्योगधंदे नसल्यामुळे तंत्रशिक्षणाकडे लोकांचे दुर्लक्ष होत आहे. याउलट ही दोन्हीही साधने नसल्यामुळे उद्योगधंद्यांत वाढ होत नाही. अशा तऱ्हेने आपली अर्थ व्यवस्था एका दुष्टचक्रांत (Viscious Circle) सापडली आहे. परंतु हताश न होता या समस्येवर मात केली पाहिजे. टिळकांनी यावर सूचवलेली उपाययोजना ही एखाद्या कसलेल्या अर्थतज्ज्ञाला साजेशी आहे.

टिळकांचे उपाय

१) छोट्या उद्योगांना प्रोत्साहन देणे

२) औद्योगिक शिक्षणाची कास धरणे

३) आवश्यकता असेल तेथे परदेशी तंत्रज्ञास नोकरीस ठेवणे.

४) परदेशांतून व्याजाने पैसे घेणे

टिळक म्हणत भांडवल उभारणीचे काम श्रमसंयोगाने किंवा सहकारी तत्वावर (को.ऑपरेशन आणि को ऑपरेटिव्ह सोसायटया) होऊ शकते. वैयक्तिक स्तरावर उद्योग सुरु करणाऱ्यास त्या व्यवसायासंबंधी मनःपूर्वक प्रेम पाहिजे तसेच ती व्यक्ती शिक्षणामुळे सुसंस्कृत असून, प्रामाणिक पाहिजे हे त्यांनी आग्रहपूर्वक सांगितले. (आजच्या कर्ज पुरवठा करणाऱ्या आधुनिक संस्थानही नेमक्या याच गोष्टींचा म्हणजे कर्जदाराच्या चारित्र्य, सामर्थ्य आणि क्षमता यांचा अग्रक्रमाने विचार करतात हे येथे मुद्दाम लक्षात घेतले पाहिजे).

ब्रिटींशाची आर्थिक नीती :

व्यापाराच्या सहाय्याने हिंदुस्थानात आलेल्या ब्रिटीशांनी येथील अनागोंदीचा पुरेपूर फायदा उठवत संपूर्ण हिंदुस्थान आपल्या ताब्यात घेतला. तत्कालिन आधुनिक शस्त्रास्त्रांनी युक्त असे शिस्तबद्ध सैन्य व व्यापारी धूर्तता यांच्या जोरावर त्यांनी आपले राज्य स्थिर केले. येथे इंग्रजी शिक्षणाची सुरुवात करुन त्यांनी आपल्या सैन्यांच्या व मालाच्या सुलभ वाहतुकीसाठी रेल्वेचे जाळे पसरवण्यास सुरुवात केली. पोस्ट खाते व तारायंत्रे यांच्या साह्याने जलद संपर्क सोय केली. इंग्रजांनी केलेल्या विविध सुधारणांमुळे आणि निर्माण झालेल्या राजकीय स्थैर्यामुळे अनेक लोक इंग्रजांचे गुणगान करु लागले. परंतु इंग्रज राज्यकर्ते अत्यंत कावेबाजपणे आपल्या देशाची पद्धतशीर लूट करत आहेत हे टिळकांनी वेळोवेळी दाखवून दिले. उदा. स्वतःच्या देशातील कापड धंद्याला ऊर्जितावस्था यावी यासाठी त्यांनी या देशात तयार होणाऱ्या जाड कापडावर शेकडा साडेतीन टक्के कर बसवला, तर इंग्लंडमधून आयात केल्या जाणाऱ्या तलम कपड्यावरील कर पाच टक्क्यावरुन साडेतीन टक्क्यांवर आणला. परिणामस्वरुप ब्रिटीश माल वापरणाऱ्या श्रीमंत लोकांचा फायदा झाला तर जाडेभरडे सुती कपडे वापरणाऱ्या गरीब जनतेचा तोटा झाला.

संदर्भग्रंथ :

१) लोकमान्य टिळक आणि क्रांतीकारक, व.दि. फडके
२) लोकमान्य ते महात्मा, डॉ. सदानंद मोरे, राजहंस प्रकाशन, पुणे.
३) लोकमान्य टिळक यांचे चरित्र, नरसिंह चि.केळकर, रिया पब्लीकेशन, कोल्हापूर.

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SWATIDHAN PUBLICATIONS

Indian Art and Architecture

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India is well-known in the world due to its cultural heritage, art and architecture. Ancient Indian civilization is remarkable in various feiid like language, literature, science, technology, art and architecture.

Following is the area of Art and Architecture achievement in India.

Indus valley civilization-

Urban civilization having the knowledge of urban structure.

Indian art contains various form such as plastic, visual art, textile etc. Indian arts exposed the symbol of religion like Hinduism, Buddhism, Jainism and Islam.

Indus valley civilization consisting different type of arts like dancing girl in Mohenjo-Daro seals, yoga pose, idol of Pashupati, figure of Lord Shiva etc.

Mauryan art (340 BCE – 232 BCE)-

Monumental art is famous related to Mauryan art. Indian rock architecture, Ashoka pillars, Emblem of India etc are remarkable achievements in the area of art.

Buddhist art –

There are many sites scattered in India which explorer the art in Buddhism. Sanchi, Bharut, Amravati, and Ajanta, caves are the main example.

Gupta Art-

Jain religion art found in northern part of India.

Dynastic of South Asia

is full of Badami caves, shore temples, Shiva and Nataraj sculpture, Temple of Khajuraho is considered as a world heritage.

Akabarnama, Jama Masjid, Taj Mahal, etc art and painting is the part of Mogul art. Charminar, Golkumbha are the symbol of Deccan art of south. Central India Later on in British Kingdom also has great impact on Indian art. Super wall painting, natural maintaining, jewelry, temple art, folk and tribal art etc are the various types of Indian art.

The Indian Art has many aspects to explore the various chapter of Indian culture.

Following are some of Indian art forms-

Visual Arts

1. Lalit Kala Akadami (National Academy of Fine Arts established 1954 in New Delhi. Basically it promotes painting, sculpture, print making and ceramics. It also organizes the exhibitions on contemporary Indian Arts.

Performing Art

Types of performing art.

1. Music
2. Dance

3. Theatre
4. Literature

Institution of Arts -

1. Sahitya Academy
2. National School of Drama
3. Lalit Kala Academy
4. Sangit Natak Academy

There is a provision to award and sponsor the various fellowship, scholarship and grants for promotion of Indian Art. Archeological survey of India (ASI) also plays an important role to present the Indian art. Department of culture and ministry of tourism maintain conservation and perseverance of centrally protected monuments and museums, libraries, etc.

Indian art is most traditional and has the oldest history in the world with highly realistic approach.

Literature and architecture, philosophy are the main components of Indian art. Sacred and holiness is the main immortal part of Indian art.

Following are some of the feathers of Indian art-

1. Earth, water, fire, air, sky are the main symbols in Indian art
2. Cuisine, trip, rangoli fresco, mosaic, sketch etc are the various medium of Indian art
3. Oldest, spiritual and uniqueness are different than other culture.
4. Remarkable about food, language, festivals, religion, epic, sculpture, painting, agriculture, clothing, music, dance etc expose **'unity in diversity'**.
5. Performing dance, sports, literature, and films along with recreation, education are inserted as Indian Art,
6. Heritage of Ayurveda, yoga, culture, folkdances, handcrafts and artefacts are universal things related to Indian art.
7. Indian culture is 5000 years old culture having richness of an ancient heritage and contemporary art.
8. Beliefs, purans, costumes, traditions also reflect in Indian art.

Indian Architecture

The architecture of India is deeply inserted in history, culture, religion, and civilization. Indian architecture explores the various feathers of the stages.

In the early middle era, Vijayanagar kingdom was well-known in south India. Chankya, Hoyasala, Pandya and Chola styles provided best, simplest, and attractive art of India. Qutub Minar, Red fort, Fatepur Sikri, Taj Mahal are the achievement of Islamic architecture and Mogul era around (1526 AD-1857 AD)

Ellora in Western India, Khajuraho in central India, Konark in South India are remarkable achievement in the architecture of India. Indian architecture represents the diversity of Indian culture.

Following are the some of the fantastic evidence of Indian architecture-

1. Lingraja Temple – 100 A.D.
2. Mukteshwar Temple
3. Jagnath Temple- Puri
4. Sun Temple- Pattadakkal
5. Parasnath Temple- Konark
6. Somnathpur Temple
7. Shore Temple Mahabalipuram
8. Brihadishwara Temple- Tanjore
9. Meenakshi Temple- Madurai
10. Hampi-Karnataka

Conclusion-

Indian architecture is a symbol of pluralistic and unique approaches. Temples, building, paintings in this duration has special and unique attraction in the world. It also explores the culture and living standard of the region. Different types of Indian architecture styles express the space and time in history. Glaciers of Hindus and Islam's, ancient, cave rock and temple etc are the main examples of Indian architecture.

Indian architecture preserves and creates variedness, beautifully and blended monumental scripts architecture style.

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HEMATOLOGICAL RESPONSES TO ENDOSULFAN TOXICITY IN THE INDIAN GARDEN LIZARD, *CALOTES VERSICOLOR*

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ABSTRACT

The organochlorine insecticide, endosulfan is widely used in crop field as well as for garden plants to control insects. The Calotes, common habitant of garden, is unknowingly affected by such insecticides. Hematological parameters vary in response to different toxicants in different animals. Considering this the present study was undertaken to evaluate the effect of endosulfan on some hematological parameters of Indian garden lizard, Calotes versicolor. Endosulfan (2.5 µl) was introduced orally to it at 24, 48, 72 and 96 hrs. It was observed that hemoglobin declined gradually throughout the experimental period than that of control. The lymphocytes decreased suddenly at early phase of 24 hours and then increased after 48 hrs. in experimental lizards, but could not increase beyond the lymphocyte count of control throughout the experimental period. Eosinophils, red blood cells and total leucocytes decreased gradually upto 96 hours than that of control after exposure to endosulfan.

KEYWORDS: *Hematological indices, Endosulfan, Calotes versicolor.*

INTRODUCTION:

The pesticides developed for human welfare are being considered as the most disastrous factors in producing harmful effect in environment and have become the serious sources of pollutant (Rameshwarsing, 2004). The regular utilization of large quantities of these pesticides into environment creates a pesticide pollution which constitutes the most dangerous health hazards on non-target organism. Reptiles have been reported to be more sensitive to the effects of these pesticides than are birds and mammals (Davidson *et al.*, 2002). Some studies established that the reptiles face many impact from human activities (Khan and Law, 2005). Hall (1980) reviewed several studies showing deaths of lizards and other reptiles following use of organochlorine pesticides, especially DDT, Dieldrin, Endrin, and Heptachlor and reported widespread mortality in two lizard populations following application of Heptachlor. Alterations in hematological parameters due to water pollutants are well established (Radha *et al.*, 2005; Sah *et al.*, 2006; Gupta *et al.*, 2007). Reduction in erythrocytes is reported in *Labeo rohita* exposed to sub lethal concentration of Nuvan and it became anemic (Wedemeyer *et al.*, 1984). The hematology of fingerlings of *L. rohita* exposed to two sublethal concentrations i.e. 10.3 ppm and 2.06 ppm of Nuvan was studied by Das and Mukhaerjee (2001), and it was found that there was reduction in total erythrocytes count and hemoglobin percentage. Total counts of erythrocytes and hemoglobin were decreased and leucocytes were increased in endosulfan treated group of rats and differential counts of leucocytes showed significant increase in basophils and monocytes (Das *et al.*, 2010). Possible impacts on lizards include direct poisoning from eating (or licking) poisoned bait and secondary poisoning from eating dead, dying, or disorientated insects contaminated with insecticides. The impact of pesticides on reptiles exposed to it is by many routes but perhaps the most common route is agricultural practices which affect natural habitat in several ways. As endosulfan is a worldwide used synthetic insecticide that has an important role on management of pests in agriculture, the present work was undertaken to determine the effect of endosulfan on the hematological parameters of *Calotes versicolor* which can be a promising procedure for use in biomonitoring programmes to diagnose pesticide exposure of wild populations.

The pressure on land in India is constantly mounting due to rapidly increasing need of providing food to the ever increasing population. Owing, the limited scope for exploitation of unused land for agriculture, the solution lies in intensive and extensive cultivation to increase production and productivity. Pesticides may continue to play an essential role to ensure an adequate supply of food to meet the need of human beings.

Keeping the above references in mind, it is evident that, despite the pesticide poisoning incidents all over the world, no effective protective and preventive steps are implied. The no. of deaths has kept arising. Although many physiological causes for poisoning have been reviewed by scientists, root cause for the poisoning is still not evident. This is our small attempt to search to farmers in rural areas for finding the root causes of pesticide poisoning.

METHOD AND MATERIALS

Yavatmal district has a population of 2,07,7144, from this population 53% are directly involved with agriculture. The survey was conducted in different villages of district Yavatmal. The survey included villages from tehsil Ner, Mahagaon, Pusad, Darwha, Arni and Umarkhed. The villages undertaken our survey are Kali (Tq. Mahagaon), Shilona (Tq. Pusad), Sarkinhi (Tq. Mahagaon), Malkinhi (Tq. Mahagaon), Kapshi (Tq. Ner).

The survey was conducted from 25th September 2017 to 15th February 2018. Primary data were collected by cross sectional guided questionnaire and observations on spot. The survey included 30 to 40 farmers that were engaged in pesticide application practices and also includes visits to family member of farmer which were died due to pesticide poisoning. The questionnaire consists of closed and open ended questions. Secondary data were collected by the Shri Vasantrao Naik Government College and Hospital Yavatmal.

When poisoning were assessed, the interviewed person was asked if he had fallen ill during the past months or years and if he answered yes, then he was asked to specify the systems in details.

OBSERVATION AND RESULT

In our survey Separate questionnaire was asked to the farmers of different villages of Yavatmal district. As Maharashtra is famous for its traditional crops like Cotton, Tur, Soya bean, most no. of pests are attacked on these crops which requires pesticides as a pest control. On the basis of answers given and interactions with the farmers in selected areas, list of pesticides is prepared which are mostly used. The table below indicates the list of most used pesticides.

Pesticides	Chemical group
Polo	Diafenthiuran
Profex super	Profenofos + Cypermethrin
Police	Imidacloprid + Fipronil.
Monocil	Monocrotophos.

Table:- Different pesticides used by farmers and their chemical groups.

All the farmers usually use mixture of two to four pesticides in one spray. During the interviews, majority of the farmers stated that using mixture of pesticides makes the dose even stronger and effective while some believed that single dose proves less effective. It was also noted down that the person who sprays pesticide prefers making the formulations on his own or as told by experienced farmers. Farmers stated that the doses depend on the amount of attack of pests but usually the whole bottle of pesticides is used at once. There was no standard method preferred for making formulations.

All the farmers of cotton field usually sprays on cotton once a week in one field. But they undertake hired spraying work in other farmer's field. Farmers stated that on an average, they spray 8 hours per day. It

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was observed that the farmers who spray pesticides usually spray whole day i.e. in hot and humid conditions.

When we asked about time from which they apply pesticides, they responded that all of them spray pesticide from about 8-9 years and had poisoning after prolonged use of pesticides. They also stated that the symptoms of pesticide poisoning didn't arrive early.

It was noted that while applying pesticides, there were lot of difficulties faced by the farmers, among these difficulties common answers were increased height of cotton crop which is the probable cause of inhalation poisoning, also direction of wind played important role for entering the human route through nasal track. It was also noted that most of the farmers don't use any protective equipments while applying the pesticides in the fields.

According to answers given by the farmers general symptoms observed and their extent is given in table below

S.N	Symptoms	Prevalence (%)
1.	Headache	88%
2.	Dizziness	70%
3.	Blurred vision	73%
4.	Difficulty in Breathing	89.4%
5.	Skin rashes	67%
6.	Vomiting	55%
7.	Irregular heart beat	47%
8.	Excessive Sweating	84.6%
9.	Eye rashes	47 %

Table 2: Occurrence of symptoms with their prevalence

From the survey it was evident that there are very few farmers who use protective equipments. It was observed that there is direct relationship between no. of protective equipments used and occurrence of symptoms. The graph below shows relationship as no. of symptoms are more when there is less use of protective equipments.

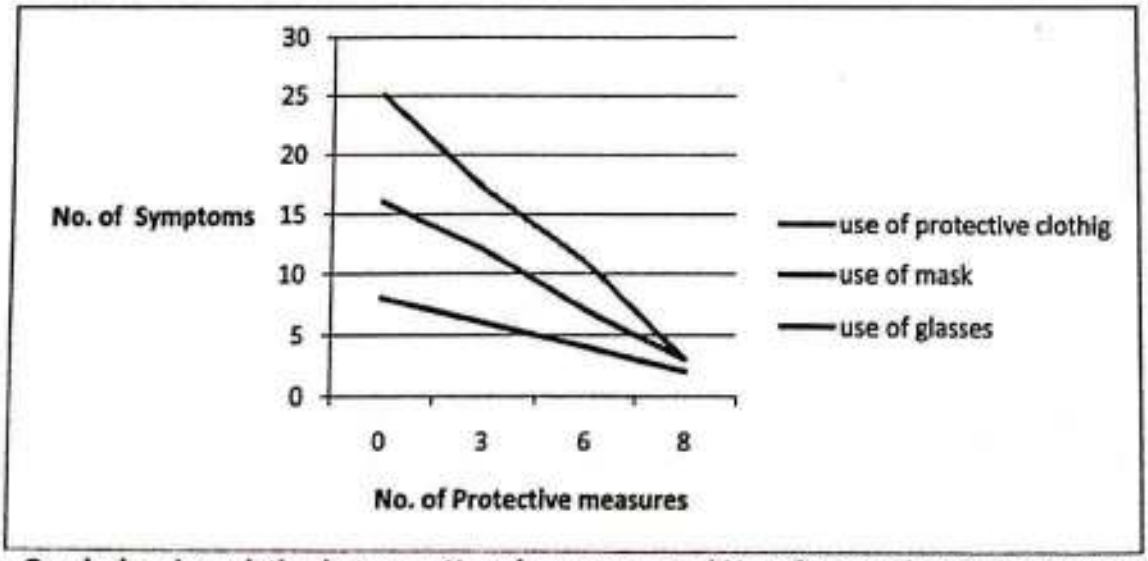

Fig: Graph showing relation between No. of symptoms and No. of protective equipments used.

It was observed that due to lack of education and awareness, most of the farmers had very little knowledge about the toxicity and safe handling of pesticide. This was thought to be one of the important

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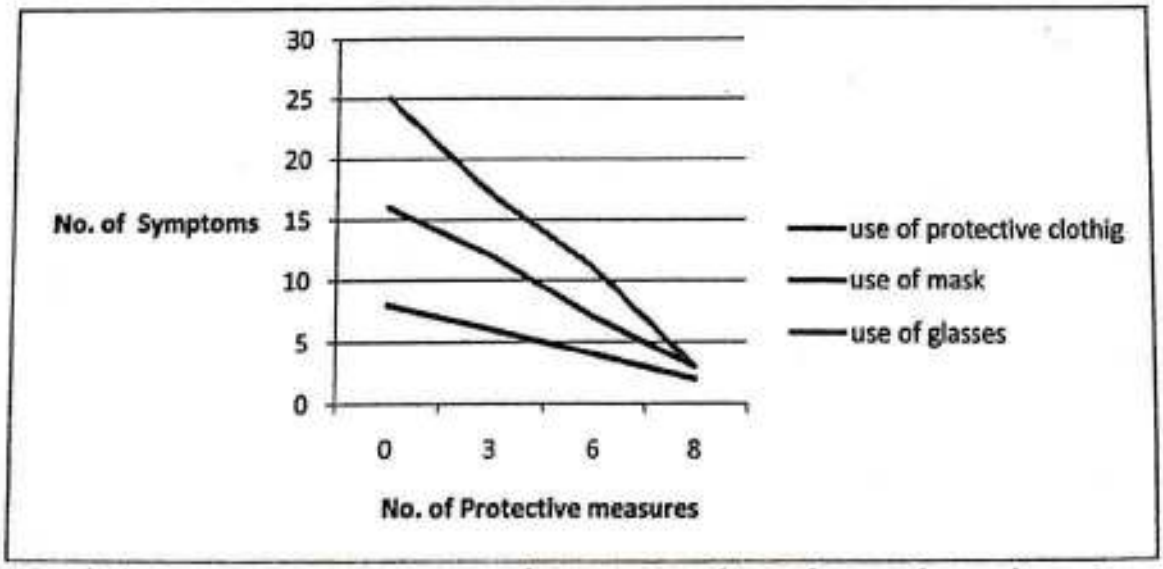

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It was observed that due to lack of education and awareness, most of the farmers had very little knowledge about the toxicity and safe handling of pesticide. This was thought to be one of the important

reason for increasing cases of poisoning as 95% of the farmers who spray pesticides stated that they didn't even knew how to read the instruction on user manual.

DISSCUSSION

The approach of face to face questionnaire and direct interaction with the affected as well as the daily sprayers was made to assess the common reasons behind this much extent of pesticide poisoning.

Despite the fact that most of the farmers were aware about the health hazards associated with pesticide spraying, they avoided the use of personal protective equipments. A higher percentage of farmers said that they received instructions from agriculture shop or neighbor but the dilemma is that there was no training or workshop regarding the safe practices. With regarding to no. of hours spent for application of pesticide, the study found that most of the farmers used to spray about 7-8 hours/day according to the answers provided by them. The finding of this study was quite similar to the study conducted by Jensen *et al.*, (2011) who concluded that symptoms of pesticide poisoning were related to no. of hours spraying and no. of personal protective equipments used.

From this survey it was also reported that Organophosphate was the most impactful pesticide leading to increasing no. of affected persons. Similar study was conducted by Antonijevic (2007), who concluded that Organophosphates are deterious to target as well as non target organisms.

CONCLUSION

From this survey based analysis of the extent of pesticide poisoning amongst pesticide spraying people in different villages of Yavatmal district, it is evident that most of the reported health effects were observed due to lack of knowledge about safe handling of pesticides. Although farmers had awareness about the danger of pesticides, but no protective measure were used by them, which proved to be the main reason behind inhalation and contact poisoning.

Most of the farmers were uneducated and reading the instruction manual was not possible. Spraying the pesticides without knowing the proper dose proved to be one of the main reasons for poisoning. The first priority for reducing the no. of pesticide poisoning cases must be to effectively phase out the most hazardous pesticides from the market. Proper knowledge and Education amongst pesticide sprayers for the proper use of pesticides is the need of hour. This can be achieved by awareness among farmers towards proper use of pesticides by conducting seminars and workshops by the agriculture department of that particular area.

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ENDOSULFAN AND PARATHION INDUCED EFFECT ON LIVER AND KIDNEY OF GARDEN LIZARD *CALOTES VERSICOLOR* IN RESPECT OF METABOLITE: GLUCOSE AND PROTEIN

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ABSTRACT:

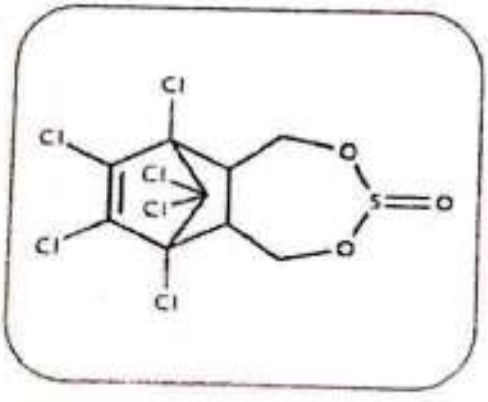
The present study highlights the effect of endosulfan (2.5µl) and parathion (3µl) on kidney and liver of Calotes versicolor. A moderate decrease in kidney protein was found in Calotes versicolor treated with endosulfan and parathion. A significant decrease were noted in liver protein in endosulfan treated Calotes for 24 and 48 hours but statistically non significant changes were found in rest of the exposure periods under the treatment of both pesticides. A significant decrease were noted in liver glucose except 24 & 48 hours whereas non significant decrease was noted in kidney glucose.

KEYWORDS – *Induced effect, endosulfan and parathion, Calotes versicolor.*

INTRODUCTION

Pesticide and related chemical destroy the delicate balance between species that characterizes a functioning ecosystem. Fish, bird and wildlife that live in direct contact with environment subject to pesticide exposure are sentinel species (Kegley *et al.*, 1999) A number of wildlife species can be affected by pesticides used in a agricultural field because of their effect on physiological functions of all kind of animals. Due to human activities and involvement in an effort to increase agricultural product and the use of indiscriminate pesticides, approximately 25% of reptiles and 20% of amphibians are listed as threatened (Hilton-taylor, 2000).Organophosphate and Carbamate are widely used and have a variety of lethal and sublethal effect on non target wild life (Parson *et al.*, 2000). A lot of work has been done on the effect of pesticides on amphibians and reptiles by Antony and Ramalingham (1990); Balasundaram and Selvarajan (1990); Alvarz *et al.*,(1995); Pauli and Money (2002). There has been great deal on interest in reptiles and amphibians ecotoxicology. Some work has been reported by Khan *et al.*, (2003) about the reduction of cholinesterase activity and protein content in *Calotes versicolor* due to pesticides. In present study the effect of endosulfan and parathion on glucose and protein content of liver and kidney of *Calotes versicolor* is observed.

MATERIAL AND METHODS



Local *Calotes* were collected from the field irrespective of sex. They were kept in a aquarium for seven days before the experiment. During captivity food and water were provided in the aquarium. Two groups of six experimental animals were exposed to the predetermined dose of (LC50 for 96 Hrs.) endosulfan (2.5µl) and parathion (3µl) separately was introduced orally to the *Calotes* (single pesticide per 6 animals).A batch of unexposed lizard were also maintained in same laboratory condition. After 24, 48, 72 and 96 hours animals were

rificed and glucose and protein content was estimated from liver and kidney of these animals.

OBSERVATIONS

Table No. 1.

Effect of sub lethal concentration of endosulfan (2.5µl) and parathion (3µl) on kidney and liver protein (gm/dl) level of *Calotes versicolor*

Exposure periods	Tissue	Control	Experimental	
			Endosulfan	Parathion
24 Hrs.	Liver	4.1+0.260	2.8 + 0.219 ** (-31.7)	2.5+0.089** (-39.00)
	Kidney	3.8+0.089	2.6+0.148** (-31.57)	2.7+0.141** (-28.94)
48 Hrs.	Liver	4.2+0.173	2.1+0.219** (-50)	2.0+0.167** (-52.3)
	Kidney	3.7+0.14	2.1+0.118** (-43.24)	1.8+0.089** (-51.35)
72 Hrs.	Liver	3.7+0.194	3.3+0.757NS (-10.87)	2.6+1.007 NS (-3.18)
	Kidney	3.8+0.089	1.7+0.178** (-55.26)	1.5+0.089** (-60.52)
96 Hrs.	Liver	3.8+0.2)	3.4+0.118 NS (-10.52)	2.8+0.963 NS (-26.3)
	Kidney	3.9+0.141	1.10+0.148** (-71.79)	1.2+0.077** (-69.23)

Table No:-2

Effect of sub lethal concentration of endosulfan (2.5µl) and parathion (3µl) on kidney and liver Glucose (gm/dl) level of *Calotes versicolor.*

Exposure periods	Tissue	Control	Experimental	
			Endosulfan	Parathion
24 Hrs.	Liver	125.6±1.368	121.5 ± 4.037** (-3.26)	123.5±2.58* (-1.67)
	Kidney	116.5±1.378	114.3±2.277^{NS} (-1.89)	113.1±2.927^{NS} (-2.91)
48 Hrs.	Liver	124.3±4.71	119.3±1.81** (-4.02)	122.6±2.58** (-1.36)
	Kidney	116.3±1.033	115.5±0.84^{NS} (-0.68)	112.8±2.00^{NS} (-3.00)
72 Hrs.	Liver	125.3±5.988	117.8±4.490* (-5.98)	122.0±2.607* (-3.18)
	Kidney	116.0±1.095	113.8±1.169* (-1.89)	112.3±2.339* (-3.18)
96 Hrs.	Liver	125.5±6.12	116.3±4.63 ** (-7.33)	121.8±2.92** (-26.3)
	Kidney	116±0.984	113.6±2.066* (-2.06)	113.1±2.92** (-2.5)

ues are mean ± SD of six observations
Non Significant,
ues are significant at *P<0.05, **P<0.01

RESULT AND DISCUSSION

Under the effect of endosulfan and parathion kidney protein was found to decrease moderately. Liver protein was found to decrease moderately in 24 and 48 hours of exposure periods but later no significant decrease were noted in protein content due to the same treatment for 72 and 96 hrs. Liver glucose was found to decrease significantly in most of the exposure periods except 24 & 48 hrs. Whereas there was non significant decrease noted in kidney glucose under the treatment of both pesticides. The result of present investigation indicate that the influence of both pesticides on the liver and kidney of *Calotes versicolor* reduce the level of protein. Similar results were also observed by Khan *et al.*, (2002) in kidney and liver protein of *Calotes versicolor* and frog *Rana tigrina* due to the treatment of cypermethrine. Khan, (2005) noted inhibition in the activity of cholinesterase in liver and kidney of *Calotes versicolor* due to the treatment of cypermethrine and Malathion. Deli and Kiss, (1988) observed a muscle damaging effect in Chicken embryo when treated with parathion and methyl parathion. They suggested that this muscle damaging effect of organophosphate insecticide may be related to the decrease of tissue content of certain cytoskeletal protein. Age dependant toxic effect of endosulfan was observed by Kiran and Verma (1988) in different age groups of rat. They observed a maximum depletion of liver glycogen and maximum inhibition of brain cholinesterase activity in 365 days old animal. Kaur and Dhanju (2005) studied toxic effect of three oraganophosphate: Monocritophus, Dimethote and methyl parathion on the ovaries of albino rat, they noted significant decrease in the concentration of cytoplasmic as well as membrane bound protein cholesterol.

Tilak *et al.*, (1999) suggested that the decrease in protein content in the kidney and liver of fish, *Labeo rohita* due to the interference of pesticides in protein metabolism and according to them when the fish exposed to pesticides stress the tissue were actively involved in deamination leading to protein depletion. A significant decrease in kidney carbohydrate was noted by Kumari and Kumar (1997) in the fish *Channa punctatus* and they augmented that this decreased kidney glucose may be due to increased glycogenolysis under the pollutant stress. Decreased liver glucose of endosulfan treated *Heteropneustes fossilis* was observed by Shrivastava and Singh (1997) and according to them this decrease was probably due to acceleration of TCA cycle, along with elevated glycogenolysis and gluconeogenesis to meet the excessive energy demand during pesticide stress condition. Shrivastsva and Singh (1997) also observed consistent depletion in the amount of glucose in liver of *Heteropneustes fossilis* under the treatment of endosulfan. Sharma (1999) noted a reduced protein level in the liver of fish *Clarius batracus* when treated with pesticide Carbaryl. Dhapate *et al.*, (2006) noted a reduction in kidney and muscle protein of the fish *Clarius batrachus* due to the treatment of endosulfan. Rajyashree (1996) also observed decline in protein level in liver during Carbamide exposure to *Labeo rohita* and augmented that this decrease due to the physiological adaptability of fish to compensate to pesticide stress.

In the present investigation the exposure of *Calotes* to endosulfan and parathion toxicity resulted into moderate decrease in kidney and liver protein which is similar to the findings of other investigators cited above. Thus we can argue that the exposure of toxicity of both pesticides brings hepatocellular damages and inhibition of protein synthesis in liver, which finally resulted into decreased in liver protein level, Secondly this reduced protein content of liver may be attributed to stress mediated mobilization of this compound to fulfill the increased demand for energy to cope with the detrimental condition imposed by the pesticides. Because to overcome the stress, animal required high amount of energy and this energy demand might have led to the stimulation of protein catabolism which finally resulted in to decline in liver protein level. The resulted decrease in protein content of kidney may be due to increased proteolytic enzymes activity for the breakdown of tissue protein into amino acid in this condition of endosulfan and parathion stress.

Glucose is the major fuel of most organisms and it can be mobilized from glycogen in the time of demand to meet day to day energy requirement. Thus we can conclude that the resulted significant decrease in kidney glucose may be due to its high utilization to meet the energy demand during stress of both pesticides endosulfan and parathion. Decreased liver glucose may be due to elevated glycogenolysis and gluconeogenesis to meet the excessive demand of energy to compensate the stress of both pesticides.

RESULT AND DISCUSSION

Under the effect of endosulfan and parathion kidney protein was found to decrease moderately. Liver protein was found to decrease moderately in 24 and 48 hours of exposure periods but later no significant decrease were noted in protein content due to the same treatment for 72 and 96 hrs. Liver glucose was found to decrease significantly in most of the exposure periods except 24 & 48 hrs. Whereas there was non significant decrease noted in kidney glucose under the treatment of both pesticides. The result of present investigation indicate that the influence of both pesticides on the liver and kidney of *Calotes versicolor* reduce the level of protein. Similar results were also observed by Khan *et al.,* (2002) in kidney and liver protein of *Calotes versicolor* and frog *Rana tigrina* due to the treatment of cypermethrine. Khan, (2005) noted inhibition in the activity of cholinesterase in liver and kidney of *Calotes versicolor* due to the treatment of cypermethrine and Malathion. Deli and Kiss, (1988) observed a muscle damaging effect in Chicken embryo when treated with parathion and methyl parathion. They suggested that this muscle damaging effect of organophosphate insecticide may be related to the decrease of tissue content of certain cytoskeletal protein. Age dependant toxic effect of endosulfan was observed by Kiran and Verma (1988) in different age groups of rat. They observed a maximum depletion of liver glycogen and maximum inhibition of brain cholinesterase activity in 365 days old animal. Kaur and Dhanju (2005) studied toxic effect of three oraganophosphate: Monocritophus, Dimethote and methyl parathion on the ovaries of albino rat, they noted significant decrease in the concentration of cytoplasmic as well as membrane bound protein cholesterol.

Tilak *et al.,* (1999) suggested that the decrease in protein content in the kidney and liver of fish, *Labeo rohita* due to the interference of pesticides in protein metabolism and according to them when the fish exposed to pesticides stress the tissue were actively involved in deamination leading to protein depletion. A significant decrease in kidney carbohydrate was noted by Kumari and Kumar (1997) in the fish *Channa punctatus* and they augmented that this decreased kidney glucose may be due to increased glycogenolysis under the pollutant stress. Decreased liver glucose of endosulfan treated *Heteropneustes fossilis* was observed by Shrivastava and Singh (1997) and according to them this decrease was probably due to acceleration of TCA cycle, along with elevated glycogenolysis and gluconeogenesis to meet the excessive energy demand during pesticide stress condition. Shrivastsva and Singh (1997) also observed consistent depletion in the amount of glucose in liver of *Heteropneustes fossilis* under the treatment of endosulfan. Sharma (1999) noted a reduced protein level in the liver of fish *Clarius batracus* when treated with pesticide Carbaryl. Dhapate *et al.,* (2006) noted a reduction in kidney and muscle protein of the fish *Clarius batrachus* due to the treatment of endosulfan. Rajyashree (1996) also observed decline in protein level in liver during Carbamide exposure to *Labeo rohita* and augmented that this decrease due to the physiological adaptability of fish to compensate to pesticide stress.

In the present investigation the exposure of *Calotes* to endosulfan and parathion toxicity resulted into moderate decrease in kidney and liver protein which is similar to the findings of other investigators cited above. Thus we can argue that the exposure of toxicity of both pesticides brings hepatocellular damages and inhibition of protein synthesis in liver, which finally resulted into decreased in liver protein level, Secondly this reduced protein content of liver may be attributed to stress mediated mobilization of this compound to fulfill the increased demand for energy to cope with the detrimental condition imposed by the pesticides. Because to overcome the stress, animal required high amount of energy and this energy demand might have led to the stimulation of protein catabolism which finally resulted in to decline in liver protein level. The resulted decrease in protein content of kidney may be due to increased proteolytic enzymes activity for the breakdown of tissue protein into amino acid in this condition of endosulfan and parathion stress.

Glucose is the major fuel of most organisms and it can be mobilized from glycogen in the time of demand to meet day to day energy requirement. Thus we can conclude that the resulted significant decrease in kidney glucose may be due to its high utilization to meet the energy demand during stress of both pesticides endosulfan and parathion. Decreased liver glucose may be due to elevated glycogenolysis and gluconeogenesis to meet the excessive demand of energy to compensate the stress of both pesticides.

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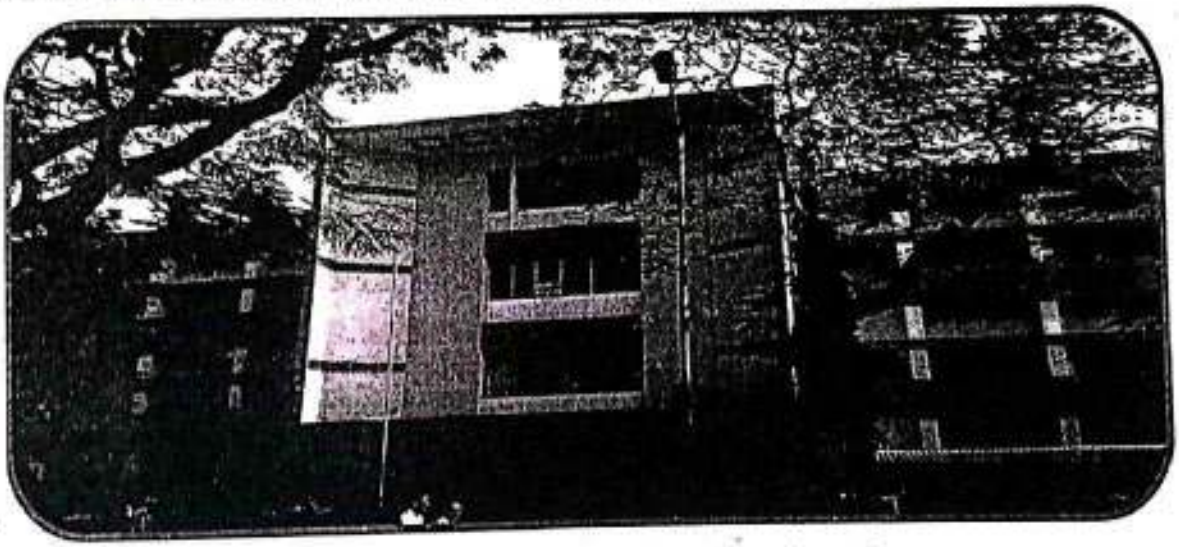

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आधुनिक काळातील : भारतीय स्त्री

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राज्यशास्त्रविभागप्रमुख, कला व विज्ञान महाविद्यालय. कु–हा,
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आधुनिक काळातील भारतीय स्त्रीचा विचार करण्यापूर्वी निरनिराळ्या कालखंडातील भारतीय स्त्री चा अभ्यास प्रथमतः करणे आवश्यक आहे. स्त्रीयांना स्वातंत्र देवूनही स्त्री म्हणजे पापाची खाण आहे. अशी जुनी समजूत होती. वैदिक काळापासून स्त्रीयांचा इतिहास पाहता, स्त्री स्वातंत्र व स्त्री शिक्षण हा बराच वादग्रस्त असा विषय राहिला आहे. स्वतः स्त्री जागृत नसल्यामुळे व पुरुषी वर्चस्वामुळे स्त्री ही स्वातंत्र व शिक्षणापासून बरीच दुर राहिलेली दिसते. पुरुषप्रधान संस्कृतीत स्त्रीचे स्थान पुरुषांच्या बरोबरीचे आहे ही कल्पनाच पुरुष वर्गाला मान्य होण्यासारखी नव्हती. आजही आधुनिक काळाचा विचार करता मुलांसाठी वेगळी वागणूक व मुलींसाठी वेगळे नियम मोठ्या प्रमाणात दिसून येतात. त्याला काही अपवाद सुद्धा आहे. परंतू त्यामुळे सामाजिक जिवनात फार मोठे परिवर्तन झाले असे म्हणता येत नाही.

निरनिराळ्या कालखंडातील स्त्रियांची स्थिती :

भारतीय इतिहासाचा विचार करता, स्त्रियांच्या कालखंड खालीलप्रमाणे अभ्यासिले जावू शकतात.

अ) वैदिक कालखंड, ब) उत्तर वैदिक कालखंड, क) स्मृती युग, ड) 19 वे शतक, इ) वर्तमानातील भारतीय स्त्री या कालखंडाच्या थोडक्यात गोषवारा खालील प्रमाणे करता येईल.

अ) वैदिक कालखंड : वैदिक साहित्यावरुन असे दिसुन येते की, या कालखंडामध्ये स्त्री–पुरुष समानता असल्याचे दिसून येते. शिक्षण, विकास, संपत्ती याबाबतीत स्त्रीयांना पुरुषा इतकाच दर्जा होता. वैदिक कालखंडातील समाज पुरुषप्रधान असला तरी या कालखंडात स्त्रियांना महत्वाचे व मानाचे स्थान होते.

ब) उत्तर वैदिक कालखंड : इ.स. पुर्व 600 ते इ.स. 300 या उत्तर वैदिक कालखंड म्हणुन इतिहासात समजला जातो. या कालखंडामध्ये स्त्रियांचा दर्जा खालावलेला दिसुन येतो. तसेच स्त्रियांना लिहिण्या वाचनाची योग्य संधी मिळालेली दिसत नसुन शिक्षणाचा स्तर घसरुन 'चुल व मूल' ही संकल्पना प्रकर्षाने उदयास आलेली दिसून येते. याच कालखंडामध्ये 'बालविवाह' प्रथेचा उदय झाल्याचे प्रकर्षाने दिसून येते.

क) स्मृती युग : हा कालखंड प्रामुख्याने रामायण, महाभारताचा कालखंड या नावाने प्रचलित आहे. त्या काळात स्त्रियांची परिस्थिती अधिकच हिन झालेली दिसून येते. विवाहाचे वय हे दहा ते बारा वर्ष असे

या कालखंडातील साहित्यावरुन दिसून येते. पत्नीने पतीधर्म पाळावा, पतीसेवा हेच स्त्रिचे कर्तव्य आहे. स्त्री ही मानसिकदृष्टया पुरुषापैकी कमकुवत आहे. ही धारणा बनली.

ड) एकोणविसावे शतक : एकोणविसावे ते शतक हे स्त्रियांच्या उत्थानाकरीता महत्वाचे ठरले. कारण एकोणविसावे व्या शतकात इंग्रजी राजवट अस्तित्वात होती. इंग्रजी राजवटीने बालविवाह, सतीप्रथा, केशवपन, या विरोधात कडक कायद्यांची तरतुद केल्यामुळे या कालखंडात स्त्रीयांवर होणा–या अत्याचाराला कायद्याचे बळ मिळाले. तसेच या काळात ईश्वरचंद विद्यासागर, ॲनी बेझंट, राजा राममोहन रॉय, महर्षी कर्वे इत्यादी समाजसुधारकांनी स्त्रियांच्या स्थितीत सुधारणा करण्याचा प्रयत्न केला. त्यामुळे भारतीय स्त्रियांच्या बाबतीत भविष्यात अनुकुल वातावरण निर्मिती होण्यास मदत झाली.

एकोणविसाव्या शतकानंतर स्त्री सुधारणाच्या दृष्टीने वातावरण निर्माण झाल्यामुळे छत्रपती शिवाजी महाराज, शाहु महाराज, महात्मा फुले, सावित्रीबाई फुले, डॉ. बाबासाहेब आंबेडकर अशा अनेक समाजसुधारकांनी आधुनिक काळातील स्त्रियांना गतिमान करण्याचे कार्य केले. डॉ. बाबासाहेब आंबेडकरांनी तर स्त्रियांवर अन्याय करणारे, स्त्रि पुरुषामंध्ये असमानता दर्शविणारे, स्त्रियांना जनावरांप्रमाणे वागणूक देणारे, स्त्रियांच्या प्रगतीला गालबोट लावणारे अशा 'मनुस्मृती' चे दहन करुन स्त्री उच्चाटनाचा मार्ग मोकळा केला. डॉ. बाबासाहेब आंबेडकरांनी घटनेमध्ये स्त्रियांच्या बाबतीत अनेक महत्वाचे कायदे केल्यामुळे आधुनिक भारतातील स्त्री ख–या अर्थाने स्वातंत्र्याचा आनंद घेत असल्याचे दिसून येते. आज आधुनिक भारतातील स्त्री ही सर्वच क्षेत्रामध्ये प्रगती करतांना दिसून येते. शिपाई ते राष्ट्रपती, ॲटोचालक ते पायलट अशी विविध क्षेत्रे पादांकांत करीत आहे. त्यामुळे आधुनिक भारतीय स्त्रीचं जीवनमान उंचावण्यास मदत होत आहे. आज भारतीय स्त्रीची, कौटूंबिक व वैवाहिक स्थिती, शैक्षणिक क्षेत्र, आर्थिक क्षेत्र, सामाजिक क्षेत्र, राजकीय क्षेत्रात आपली बुद्धिमत्ता व कार्यकौशल्य प्रगट करुन आपली योग्यता सिद्ध केलेली दिसुन येते.

एकंदरीत भारतीय स्त्रीची प्रगती ही विकसित दिसत असली तरी, स्त्रियांच्या बाबतीत तीन प्रमुख अडथळे दिसून येतात. ते म्हणजे शहरी – ग्रामीण भेदभाव, वर्णभेद, लिंगभेद इत्यादी. आज भारतीय स्त्रीया पुरुषांच्या बरोबरीने त्यांच्या खांद्याला खांदा लावून सर्वच क्षेत्रामध्ये वाटचाल करीत असतांना स्त्रीला आजही लैगिंक अत्याचारापासून पाहिजे तशी मुक्ती मिळालेली नाही. कामाच्या ठिकाणी लैगिंक अत्याचाराचे प्रमाण वाढलेले दिसुन येते, आजही भारतीय स्त्री कामानिमित्त बाहेर जात असतांना तिला असुरक्षिततेची जाणीव होते. तिच्याकडे आजही उपभोगाचे साधन या दृष्टीने पाहिले जाते.

स्त्री –पुरुष समानता ही तत्वे नुसते मान्य करुन चालणार नाही. तर त्या तत्वांची सामाजीकरण करणे गरजेचे आहे. त्यासाठी कुटूंब, शाळा, समाज या सर्वांचे सहकार्य मिळून त्यांचा प्रचार व प्रसार करुन समाजात जनजागृती करणे स्त्रीयांना अपेक्षीत आहे. या सर्वांतून सहकार्य, स्वातंत्र, व सुरक्षेची हमी मिळाल्यास तरच भारत एक प्रगतीशिल राष्ट्र म्हणून आपली ख्याती संपुर्ण विश्वात मिळविल्याशिवाय राहणार नाही.

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"ROOT CAUSES OF PESTICIDE POISONING AMONG FARMERS IN DIFFERENT VILLAGES OF YAVATMAL REGION"

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ABSTRACT

India is currently the largest manufacturer of pesticides and the second largest producers of agrochemicals in Asia, out of 145 pesticides registered in India, 85 are of technical grade and are locally produced. Multiple cases of pesticide poisoning were reported in India causing Deaths mostly among farmers. This cross sectional study was conducted among the farmers of different villages in Yavatmal district during the period of 25th September 2017 to 15th February 2018 to know the root cause of pesticide poisoning. From this survey based analysis it was evident that most of the reported health effects were observed due to lack of knowledge about safe handling of pesticides. Although farmers had awareness about the danger of pesticides, but no protective measure were used by them, which proved to be the main reason behind inhalation and contact poisoning.

KEYWORDS: *Pesticides, Poisoning, Knowledge, Survey, Yavatmal.*

INTRODUCTION

Many farmers in India have an impression and belief that if pesticides are used in excess, pests can be controlled quickly to get more protection from pests and high yields. In India, the sale, dosages and uses of many of these pesticides is not very well regulated. According to official estimates, Pesticide poisoning is directly responsible for the death of at least 10,000 people every year and these deaths are mostly of poor people, who are not reported or are under- reported (Gupta, 2004). Pesticides are the chemicals that are designed to kill member of one species i.e. insect's pests, but it is often found that members of different species are also affected including humans. Pesticides come under the category of economic poisons, a general term to describe chemical agents the use of which is acknowledged to confer benefits that outweigh the harmful consequences that may be associated with their use (Aiyar, 2003).

The world health organization stated that there are 3 million cases of pesticide poisoning each year and up to 2, 20,000 deaths, primarily in developing countries (W.H.O. 2016). Gupta (2017) analyzed the pesticides exposure scenario in India and concluded increasing cases of pesticide exposure were found.

Jeyaratnam *et al.*, (1987) investigated the extent of acute pesticide poisoning amongst agricultural communities in Indonesia, Malaysia, Sri Lanka and Thailand and confirmed that the existence of the problem was due to the inadequate knowledge of safe practices in the use of pesticides and the lack of personal protective equipments use by farmers in hot and humid conditions.

India is currently the largest manufacturer of pesticides and the second largest producers of agrochemicals in Asia, out of 145 pesticides registered in India, 85 are of technical grade and are locally produced from which, Insecticides (73%) dominate the market.

MATERIALS AND METHODS

Calotes were collected from the nearest agricultural field without regard of sex. They were kept in cages, acclimatized for two weeks in laboratory conditions before the experiment and fed with insects during and before the experiment. The Endosulfan (2.5µl) was introduced orally to the *Calotes*. A batch of untreated lizard was also kept for comparison as control without administration of endosulfan. At 24, 48, 72, and 96 hrs. the blood was drawn from both control and experimental groups from the orbital sinus with the help of glass capillary tube for analysis of eosinophils, lymphocytes, monocytes, neutrophils, RBC and hemoglobin percentage.

RESULTS

Alterations in hematological parameters of *Calotes versicolor* after exposure to Endosulfan

Parameters	Groups	Periods of Exposure			
		24 Hrs.	48 Hrs.	72 Hrs.	96 Hrs.
Hemoglobin (gm/dl)	Control	7.7±0.374	7.6±0.316	7.5±0.489	7.4±0.435
	Experimental	5.4±0.352** (-29.8)	5.1±0.556** (-32.8)	4.3±0.624** (-42.6)	4.2±0.331** (-76.1)
Eosinophil %	Control	10.6±1.213	9.5±1.048	10.3±1.633	10.8±0.983
	Experimental	7.8±1.189* (-26.41)	5.6±0.819** (-41.05)	3.5±1.048** (-66.01)	2.3±0.9** (-78.70)
Lymphocytes%	Control	6.0±2.0	5.1±1.69	5.5±2.345	5.6±1.833
	Experimental	2.6±2.18** (-56.66)	3.8±1.685 NS (-25.49)	4.1±1.691 NS (-25.45)	3.6±1.833** (-35.71)
Monocytes %	Control	1.6±0.521	1.8±0.409	1.5±0.547	1.5±0.707
	Experimental	0.83±0.752* (-48.1)	0.66±0.515** (-63.3)	0.5±0.836** (-66.6)	0.33±0.505** (-78)
Neutrophils %	Control	3.8±1.685	3.3±1.319	3.6±1.166	3.5±1.870
	Experimental	2.1±1.691** (-44.73)	2.8±1.68 NS (-15.15)	2.6±1.833 NS (-27.77)	2.5±1.224 NS (-28.57)
Red Blood Cells (Million/mm3)	Control	1.20±0.044	1.21±0.051	1.21±0.037	1.19±0.037
	Experimental	1.37±0.052* (14.16)	1.17±0.037 NS (-3.30)	1.13±0.046 NS (-6.61)	1.10±0.04 NS (-7.56)
Total Leucocytes count(cu.mm. In thousands)	Control	5.69±0.043	5.68±0.151	5.67±0.309	5.68±0.122
	Experimental	5.63±0.130 NS (-1.05)	5.59±0.026 NS (-1.58)	5.53±0.137 NS (-2.46)	5.50±0.167**(-316)

Values are mean ± SD of six observation NS- Not Significant Values are significant at *P<0.05, ** P<0.01
Values in parenthesis expresses percentage difference.

DISCUSSION

The toxicity of endosulfan varies depending upon the route of administration, vehicle, species and sex of animal. (Dikshith *et al.*, 1988). The experiments conducted on sexually matured male rats to determine the effect of endosulfan on the hematological and haemochemical parameters of albino rats fed with 5 mg/kg body weight endosulfan in mixed food stuff for 42 days revealed decreased total counts of erythrocytes and hemoglobin, whereas leucocytes were increased in treated group (Das *et al.*, 2010). In our experiment significant decrease was found in hemoglobin percent in *Calotes* in all the exposure periods treated with endosulfan. The percent changes in hemoglobin over the control were 29.8, 32.8, 42.6 and 76%. The decrease in hemoglobin percent may be due to the disruptive action of the pesticide on the erythropoetic tissue. Solanke and Singh (2000) also reported declination in hemoglobin percent in Rat, *Rattus rattus* when exposed to thidon 53EC and postulated that this decrease may be due to haemolysis, hemorrhage and reduced erythropoiesis resulted due to the stress of endosulfan. In our investigation a reduction in R.B.Cs. number was observed but statistically it was nonsignificant. Compared to control, decrease was noted in R.B.Cs. count at 48, 72 and 96 hrs., but a slight increase was observed at 24 hrs. Thus it can be concluded that the decreased hemoglobin percent may be due to

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the reduced number of R.B.Cs. Sayim *et al.*, (2005), also reported decrease in mean corpuscle volume, hemoglobin, RBCs count and mean corpuscular hemoglobin, whereas no statistically significant increase in WBCs count, but significant increase in number of lymphocytes and monocytes in hematological analysis of rats when orally administered with synthetic pyrethroid insecticide, cypermethrine (150 and 300 mg/kg for 28 consecutive days). This decrease in R.B.Cs. count was suggested due to disrupted erythropoiesis due to pesticidal stress. Johal and Garwal (2004) studied toxicity of Carbaryl on *Channa punctatus* and recorded a general decrease in R.B.Cs count suggesting metabolic stress. Thus it may concluded that decrease in R.B.Cs due to disrupted erythropoiesis caused by stress of Endosulfan and slight increase in initial exposure periods may be justified for increased demand of energy during the experimental period.

Statistically no significant changes were noted in total leukocytes count in all the exposure periods but slight decrease in all the exposure periods may be due to the leucocytopenia exerted by endosulfan stress. A significant decrease was noted in neutrophil percent of treated *Calotes* in our study. Dikshith *et al.*, (1982) noted a reduction in neutrophil percent after repeated oral administration of Quinalphos to male goat. Similar result was also recorded by Rajini *et al.*, (1987) in Albino rat after the treatment of Primiphos which causes an adverse effect on normal functioning of the bone marrow or changes in the varied factors responsible for normal leucocyte balance. Thus, it can be concluded that the endosulfan interfere in the normal physiology of neutrophils. Mandal and Lahiri (1985) noted a significant decrease in lymphocyte number in blue rock pigeon after the treatment of Sumithion.

In our studies, also a significant decrease was noted in Lymphocyte percent in *Calotes*. Lymphocyte percent was decreased sharply at early period of 24 hours and later increased steadily in endosulfan administered lizards but could not increase than that of control group. Thus the resulted lymphocyte count may be justified due to immunosupression caused by endosulfan toxicity. The assessment of the acute toxicity (96-h LC50 median value of 2.6 µgl.) and physiological parameters after exposure to 0; 0.25; 1; 2; 3; 4 and 16 µgl. endosulfan for 96 h under semi-static conditions in a freshwater perciform fish, *Cichlasoma dimerus* was done by Da Cuña *et al.*, (2011) and found decrease in erythrocyte mean corpuscular volume and mean corpuscular hemoglobin concentration in exposed fish suggesting a state of anemia. Rehaman (2006) observed decrease in lymphocyte count in Endosulfan treated fish *Cyprinus carpio* where the red blood cell population was observed to be declined by 20% at 120 hr. and by 45.2% at 240 hr. of endosulfan exposure. The hemoglobin levels were also depressed by 32.2 % at 120 hr. and 64.3 % at 240 hr exposure. The decrease of 24.6 % of counts of small lymphocytes was noted at120 hr. which further declined 52.6%, at 240 hr. The counts of large lymphocytes were found to be lowered in endosulfan-affected fish by 19.5 at 120 hr, and 65.9% at 240 hr. Suppression of the basophil numbers was observed at 120 hr and by 37.9% at 240 hr of endosulfan treatment. Attenuation of neutrophils was 9.4%; not significant at 120 hr. and 12.5% at 240 hr. of the pesticide exposure. The eosinophils were diminished by 30.4% at 240 hr. The thrombocyte was the only blood parameter studied showing elevated counts (9.5%) a 120 hr. The monocytes were depressed by 11.7% at 120hr and by 29.5% at 240 hr in endosulfan-exposed fish.

In our findings a moderate decrease was noted in eosinophil percent in *Calotes* and notable changes were recorded in monocyte count after the treatment of endosulfan in all the exposure period. Dikshith, *et al.*, (1982) observed a decreased monocyte count after oral treatment of Quinalphos to male goat. Nath and Banarjee (1999) also recorded a low count of monocyte in *Heteropneustes fossilis* due to toxicity of Rogor. Omoyakhi *et al.*, (2008) observed a progressive decrease in monocyte percent in growing rabbit due to the treatment of Acetellic dust. Mandal and Lahiri (1985) also observed a gradual decrease monocyte percent in pigeon *Columbia livia* exposed to Sumithion. According to them this decreased eosinophilic count may be due to splenic immunosupression caused by pesticidal stress. The above findings support our investigation and can be concluded that Endosulfan exert stress on eosinophils and moncytes count via suppressed leucocytes.

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ORIGINAL RESEARCH

Design of novel amyloid β aggregation inhibitors using QSAR, pharmacophore modeling, molecular docking and ADME prediction

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Abstract
The inhibition of abnormal amyloid β (Aβ) aggregation has been regarded as a good target to control Alzheimer's disease. The present study adopted 2D-QSAR, HQSAR and 3D QSAR (CoMFA & CoMSIA) modeling approaches to identify the structural and physicochemical requirements for the potential Aβ aggregation inhibition. A structure-based molecular docking technique is utilized to approve the features that are obtained from the ligand-based techniques on 30 curcumin derivatives. The combined outputs were then used to screen the modified 10 compounds. The 2D QSAR model on curcumin derivatives gave statistical values $R^2 = 0.9086$ and SEE = 0.1837. The model was further confirmed by Y-randomization test and Applicability domain analysis by the standardization approach. The HQSAR study ($Q^2 = 0.615$, $R^2_{ncv} = 0.931$, $R^2_{pred} = 0.956$) illustrated the important molecular fingerprints for inhibition. Contour maps of 3D QSAR models, CoMFA ($Q^2 = 0.687$, $R^2_{ncv} = 0.787$, $R^2_{pred} = 0.731$) and CoMSIA ($Q^2 = 0.743$, $R^2_{ncv} = 0.972$, $R^2_{pred} = 0.713$), depict that the models are robust and provide explanation of the important features, like steric, electrostatic and hydrogen bond acceptor, which play important role for interaction with the receptor site cavity. The molecular docking study of the curcumin derivatives elucidates the important interactions between the amino acid residues at the catalytic site of the receptor and the ligands, indicating the structural requirements of the inhibitors. The ligand–receptor interactions of top hits were analyzed to explore the pharmacophore features of Aβ aggregation inhibition. The Aβ aggregation inhibitory activities of novel chemical entities were then obtained through inverse QSAR. The newly designed molecules were further screened through machine learning, prediction of toxicity and nature of metabolism to get the proposed six lead compounds.

Keywords Alzheimer's disease · *Curcuma longa* · 2D-QSAR · 3D-QSAR · Molecular docking

Introduction

Alzheimer's disease (AD), a devastating neurodegenerative disease, remains epidemic for public health in the twenty-first century (Alzheimer's Association 2017). AD is characterized by the disintegration of the nervous system, which results in episodic memory problems leading to abnormal behavior and is the leading cause of dementia (Citron 2010). The presence of the extracellular deposits of misfolded and aggregated amyloid-β (Aβ) peptides in the brain is widely considered to be critically concerned in the progression of AD (Hardy and Selkoe 2002; Jack et al. 2010). The sequential enzymatic actions of β-secretase and γ-secretase result in the proteolytic cleavage of amyloid precursor protein (APP) (Selkoe 1997). The formation of Aβ is a two-step process which involves the cleavage of APP by BACE1 to form a β-secretase derived C-terminal fragment of APP, followed by an action of γ-secretase to generate Aβ isoforms ranging from 37 to 42 amino acid residues. $Aβ_{40}$ is the most abundant isoform, whereas the Aβ, which is mainly associated with AD pathogenesis, is aggregated $Aβ_{42}$ (Selkoe 1994; Golde et al. 2000). Thus in AD, Aβ monomers form undesirable Aβ aggregates of long insoluble fibrils. They aggregate in the extracellular deposits known as senile plaques. These abnormal changes in Aβ induce abnormal hyperphosphorylation of tau and tangle formation as well as neuronal loss, bringing about cognitive impairment (Haass and Selkoe 2007). The

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inhibition of abnormal Aβ aggregation is considered as one of the most important etiological agents and is an attractive therapeutic target to control AD (Xiao et al. 2015).

Curcumin is a bioactive phenolic compound present in the rhizome of *Curcuma longa* L. (Zingiberaceae). Curcumin exhibits various biological and pharmacological activities like anti-inflammatory (Jin et al. 2014), antioxidant (Nishikawa et al. 2013), antimicrobial (Dubey et al. 2008), anti-fungal (Nguyen et al. 2014), and antibacterial activities (Negi et al. 1999). Moreover, various in vivo and in vitro experiments reveal the effects of curcumin on treating or preventing AD pathology (Caesar et al. 2012; Garcia-Alloza et al. 2007; Hamaguchi et al. 2009; Ma et al. 2013). One of the most significant features of curcumin is that it directly inhibits the formation and extension of fibrillar Aβ aggregates and also destabilizes preformed fibrillar Aβ aggregates (Ono et al. 2004). It was reported that chronic dietary curcumin lowered Aβ deposition in Alzheimer Transgenic Mouse (Lim et al. 2001). Some researchers have reported that AD model mice treated with curcumin displayed a reduction in Aβ accumulation in the brain (Begum et al. 2008; Yang et al. 2005a, b). The unique benefit of the curcumin is that it is nontoxic to human even with high dosage (Sharma et al. 2001).

Nowadays, the in vitro assessment of Aβ aggregation inhibitors is still a time consuming and labor intensive task. So we are interested in identifying potential novel leads as Aβ aggregation inhibitors using techniques based on Computer Aided Drug Design (CADD). (Kapetanovic 2008). Molecular modeling in combination with Quantitative Structure–Activity Relationship (QSAR) is used to test the activity of a ligand and the type of interaction into the active site of the protein (Elfiky and Elshemey 2016; Saleh 2015; Aswathy et al. 2017).

The ligand-based molecular modeling techniques used are Pharmacophore mapping and QSAR analysis. The pharmacophore model gives information regarding hydrophobic properties, hydrogen binding properties (acceptor or donor) and aromatic functionality of the compounds in the dataset. The 3D-QSAR studies, which include CoMFA (Cramer et al. 1988) and CoMSIA (Klebe et al. 1994), cover an entire force field around a molecule instead of only spotlighting the pharmacophoric information (Cruciani and Watson 1994). Various properties like electrostatic, steric, hydrophobic and hydrogen-bond donor/acceptor factors were considered in 3D-QSAR for the force field calculations which give the best results when target-recognizing ligands share a unique structural scaffold (Ballante and Ragno 2012; Shibi et al. 2015; Jisha et al. 2017). Molecular docking studies have been extensively employed to identify the exact conformation of ligands in the precise location of the binding cavity of a protein receptor molecule (Lengauer and Rarey 1996). It also predicts the affinity between the ligand and the active site residues of the protein receptor. Therefore, these can be useful to find out the best lead molecule and their further modification by rational drug design approach. On this ground, we chose 30 curcumin derivatives with Aβ aggregation inhibition values reported by Yanagisawa et al. (2015) for the present study.

Materials and methods

Dataset preparation

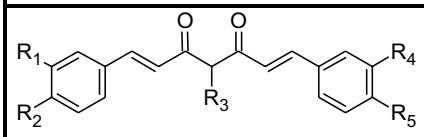
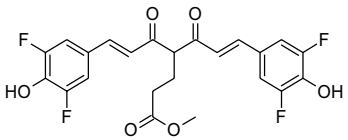
A desirable set comprising 30 structurally diverse compounds which inhibit abnormal Aβ aggregation has been considered for the study. In this study, the IC_{50} values of these compounds were converted to pIC_{50} ($-\log IC_{50}$). The structures of the compounds along with their pIC_{50} values are specified in Table 1. The compounds were divided into 80% training and 20% test sets. While dividing datasets, a wide range of activity data was confirmed in training as well as test sets. The inhibitory activities on Aβ aggregation (pIC_{50}) have been used as the dependent variables for doing QSAR studies.

Calculation of descriptors

Using powerMV software, about 179 descriptors, which include Pharmacophore fingerprints, weighted burden number and eight drug-like properties were computed for the development of 2D-QSAR analysis. Using PAdel-Descriptor, about 15,345 descriptors were also calculated (Yap 2011). In addition, by employing the QuaSAR module of Molecular Operating Environment (MOE), a total of 365 descriptors belonging to three classes: 2D descriptors, which use the atoms and connection information of the molecules, external 3D (x3D), which uses 3D coordinate information with an absolute frame of reference and internal 3D (i3D), which uses 3D coordinate information about each molecule, were calculated. Thus a total pool of 15,889 descriptors was generated for this study.

The pool of 15,889 descriptors was then reduced to 1495 by removing those descriptors that have the same value for 90% of the dataset using "General" descriptor selection algorithm. It is further reduced to 137 by eliminating descriptors highly correlated using "CORCHOP" descriptor selection algorithm. Finally by applying subjective selection using Genetic algorithm method, the pool of descriptors was eventually reduced to six. These six descriptors were used to build the 2D-QSAR model.

Table 1 Molecular structures and corresponding experimental pIC_{50} values of the curcumin derivatives

ID	R_1	R_2	R_3	R_4	R_5	pIC_{50}
						
1	CH_3O	HO	H	CH_3O	HO	5.6990
2	CF_3O	HO	CH_3	CF_3O	HO	5.4949
3[a]	CF_3O	HO	H	CF_3O	HO	5.5850
4	CF_3O	HO	$CH_3O–CO–CH_2–CH_2$	CF_3O	HO	5.3565
5	CF_3O	HO	$HOOC–CH_2–CH_2$	CF_3O	HO	5.0862
6	CF_3O	HO	$CH_3O–CO–CH_2$	CF_3O	HO	5.2441
7[a]	CF_3O	HO	$CH_3O–CO–CH_2–CH_2–CH_2$	CF_3O	HO	5.4559
8	CF_3O	HO	$CH_3–CH_2–O–CO$	CF_3O	HO	5.8861
9	CF_3O	HO	$CH_3–CH_2O–CO–CH_2–CH_2$	CF_3O	HO	5.4202
10	CF_3O	HO	$(CH_3)_3C–O–CO–CH_2–CH_2$	CF_3O	HO	5.1871
11	CF_3O	HO	$(CH_3)_2CH–O–CO–CH_2–CH_2$	CF_3O	HO	5.4089
12						5.2291
13	CF_3O	HO	$(CH_3)_2$	CF_3O	HO	3.9931
14	CF_3O	CH_3O	CH_3	CF_3O	CH_3O	3.7905
15[a]	CF_3O	HO	$CH_3O–CH_2–O–CH_2–CH_2–CH_2$	CF_3O	HO	5.3010
16	CF_3O	$CH_3O–CH_2–O$	$CH_3O–CO–CH_2–CH_2$	CF_3O	$CH_3O–CH_2–O$	4.3270
17[a]	CF_3O	$CH_3O–CH_2–O$	$(CH_3)_3C–O–CO–CH_2–CH_2$	CF_3O	$CH_3O–CH_2–O$	3.6925
18	CH_3O	HO	$CH_3O–CO–CH_2–CH_2$	CH_3O	HO	5.4949

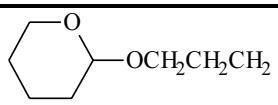
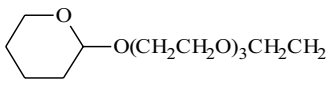
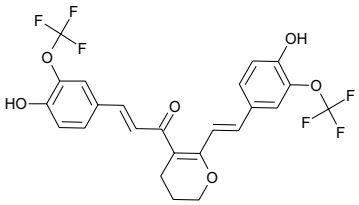
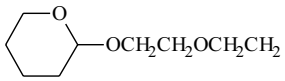
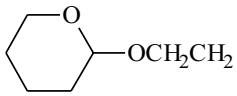
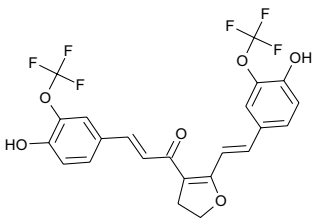
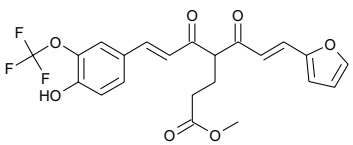
2D QSAR study

In the present work, the multiple linear regression (MLR) based QSAR model was developed, to obtain specific information regarding the contribution of different structural and physicochemical characteristics of the compounds towards the inhibitory activity.

Validation of 2D-QSAR model

The leave-one-out (LOO) cross-validation method was used as an internal validation tool to check the predictive ability of the built 2D-QSAR model (Tetko et al. 2001). The internal predictabilities of the model were verified by LOO cross-validated regression coefficient (Q^2). Internal validation parameters like standard error of estimate (SEE), the square of correlation coefficient (R^2), adjusted R^2 (R^2_A), variance ratio (F) and predicted residual sums of squares standard deviation (PRESS) were used, along with parameters like r^2_m(LOO) and $\Delta\, r^2_m$(LOO) (Roy et al. 2015a, b). For external validation, the parameter R^2_{pred} was used, to verify the predictive ability of the model on the test set. External validation parameters (without scaling) like r^2,

Table 1 (continued)

19	CF_3O	HO		CF_3O	HO	5.5086
20	CF_3O	HO		CF_3O	HO	5.0315
21[a]						4.9101
22	CF_3O	HO	$HO–(CH_2–CH_2–O)_3–CH_2–CH_2$	CF_3O	HO	4.7328
23	CF_3O	HO	$(CH_3)_2N–CO–CH_2–CH_2$	CF_3O	HO	5.3010
24[a]	CF_3O	HO		CF_3O	HO	5.1871
25	CF_3O	HO	$HO–CH_2–CH_2–O–CH_2–CH_2$	CF_3O	HO	5.1549
26	CF_3O	HO		CF_3O	HO	5.2441
27						5.6026
28	CH_3O	HO	H	CH_3O	$CH_3O–CO–CH_2–O$	5.8539
29	CH_3O	HO	H	CH_3O	$HOOC–CH_2–O$	5.5086
30						5.1871

[a]Test compounds

r_0^2, Concordance Correlation Coefficient (CCC), Q_{F1}^2, Q_{F2}^2, Q_{F3}^2 were also used. Golbraikh and Tropsha (2002) metrics were also found out. Y-randomization technique and Applicability domain analysis were also performed for the MLR model to ascertain the robustness, significance, and reliability of the 2D-QSAR model (Tropsha et al. 2003). The parameter $^cR_p^2$ was taken into consideration as the validation parameters for the Y-based randomization test (Ojha and Roy 2011).

HQSAR

Hologram QSAR (HQSAR) module available at SYBYL-X software v.1.3 was used for the generation of HQSAR models (Sybyl 1.3, Triops Inc, St). A predefined set of rules was used to have a molecule into a molecular fingerprint that encoded the frequency of occurrence of different molecular fragment types. Then the molecular fingerprint was cut into strings at a fixed interval as specified by a hologram length (HL) parameter. All of the generated strings were

hashed into a fixed length array. HQSAR does not necessitate 3D alignment for model generation. HQSAR uses different parameters such as atom count, hologram length, and fragment distinction, which are the most important factors involved in the model development. 21 different models were derived using the default fragment size (4–7 atoms) and various combinations of fragment distinctions (A-atoms; C-connections; B-bonds; H-hydrogen; Ch-chirality; DA-donor and acceptors of hydrogen bonds).

3D-QSAR

Molecular modeling and alignment

The partial atomic charges for electrostatic contribution were calculated by the method of Gasteiger–Hückel. Tripos force field was employed for optimization and energy minimization of the compounds with the convergence criterion of 0.01 kcal/mol Å. The most active molecule, compound 8, which has the minimum energy conformation, was selected as a reference molecule (Fig. 1). The remaining compounds were aligned on it by the common substructure alignment.

CoMFA model

The CoMFA model illustrates steric (S) and electrostatic (E) features of the scaffold for showing the selective inhibition of the target. The S and E fields were calculated at each lattice with a grid size of 2 Å. A sp^3 hybridized carbon atom was used with +1 charge serving as a probe atom. Column filtering was set to 1.0 kcal/mol to reduce noise and improve the outcomes of the built model. The cut-off value for steric and electrostatic fields was set to 30 kcal/mol.

CoMSIA model

The CoMSIA model helps to understand the hydrogen bond acceptor (A) and donor (D), the hydrophobic (H) features in addition to the 'S' and 'E' features. The same lattice box utilized for the creation of the CoMFA model was also employed during the CoMSIA calculation. CoMSIA descriptors were calculated based on a sp^3 hybridized carbon as a probe atom with +1 positive charge, +1 hydrophobicity, +1 hydrogen bond donor and +1 hydrogen bond acceptor at each lattice and grid spacing of 2.0 Å.

Validation of 3D-QSAR models

The partial least squares (PLS) were adopted for the regression analysis to build the 3D-QSAR equations. The optimal number of components and the cross-validation correlation coefficient (Q^2) were determined by leave-one-out (LOO) cross-validation procedures. Then, the non-cross-validated analysis was performed to calculate the non-cross-validation correlation coefficient (R^2), SEE and F value.

The predictive abilities of the 3D-QSAR models were identified by a test set of 6 compounds, and their pIC_{50} values were predicted using the following Eq. (1):

$$R^2_{pred} = 1 - \frac{\sum(Y_{predicted} - Y_{observed})^2}{\sum(Y_{observed} - Y_{mean})^2} \quad (1)$$

where $Y_{predicted}$, $Y_{observed}$ and Y_{mean} are predicted, actual and mean values of the activity, respectively. $\sum(Y_{predicted} - Y_{observed})^2$ is the predictive sum of squares (PRESS).

Generation of a pharmacophore model

Using the MOE pharmacophore consensus search module, a pharmacophoric model was generated to highlight the most important key features shown by each group of compounds belonging to the dataset. It was comprised of four different annotation points such as H-bond donor, H-bond acceptor, hydrophobic and aromatic features.

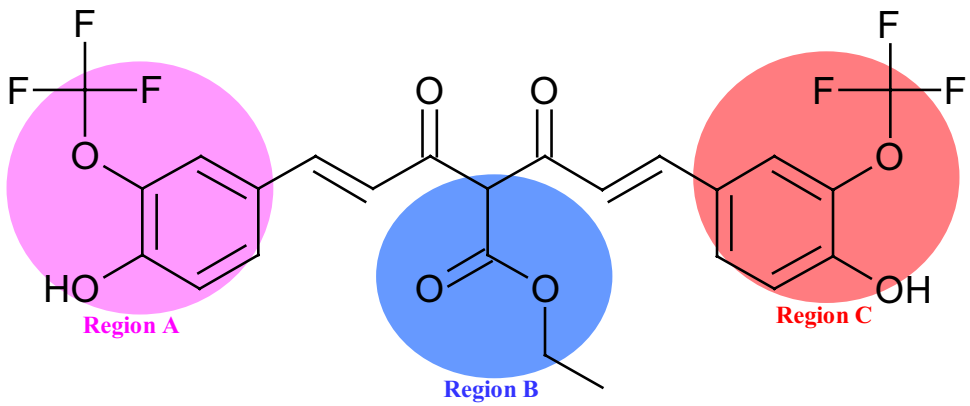


Fig. 1 Structure of the template compound (8) and the three regions A, B and C

Molecular docking

Primary and secondary structure prediction and validation of the protein molecules

For physico-chemical characterization, theoretical isoelectric point (pI), total number of positive and negative residues, aliphatic index (AI) (Ikai 1980), instability index (II) (Guruprasad et al. 1990), extinction co-efficient (EC) (Gill and Von Hippel 1989) and grand average hydropathy (GRAVY) (Kyte and Doolittle 1982) were computed using the Expasy's ProtParam server (Gasteiger et al. 2005).

The secondary structural features of the proteins were studied using Self-Optimized Prediction method With Alignment (SOPMA) (Geourjon and Deléage 1995). It give details of Alpha helix, Pi helix, Beta bridge, Extended strand, Beta turn, Bend region, Random coil and Ambiguous states.

Protein–ligand molecular docking analysis

Molecular docking studies representing the correct conformation of the curcumin derivative in protein binding sites was performed using MOE (Chemical Computing Group Inc, Montreal, Quebec, Canada). The 3D structure of the protein complex was downloaded from the Protein Databank (http://www.rcsb.org) with the PDB ID 2BEG (Lührs et al. 2005). This structure was 3D protonated and energy minimized in a MMFF94x force field to a gradient of 0.0001 kcal/mol/Å (Halgren 1996). The active site of the protein molecule was generated using the MOE-Alpha site finder. Then the dummy atoms were created from the obtained alpha spheres. The default settings for all of the parameters including Ligand Placement (Triangle Matcher) and Rescoring (London dG) were found to be suitable for reproduction of the ligand–receptor complexes. After molecular docking, LigX feature of MOE was used to locate the hydrogen bonding interactions between ligand and receptor protein. The top scoring ligand poses from each docking run were used for calculation of binding energy.

Machine learning model

In machine learning approach, predictive models were generated with the help of a set of known active compounds and their extracted properties were used to predict the activity of unknown compounds (Wahi et al. 2015). In the present study, random forest (RF) was employed as a classifier (Shibi et al. 2016). RF is chosen as the classifier, due to its suboptimal performance in cases of strongly unbalanced data (Dong et al. 2015; Hsu et al. 2015; Janitza et al. 2013). The RF algorithm parameters include a forest of ten classification trees with ten attributes randomly selected for splitting at each node, and predictions are based on a majority vote. The WEKA (Waikato University, Hamilton, New Zealand, v3.7), data mining software, was used for the classification. It contains tools for data pre-processing, regression, clustering, association rules, classification, and visualization. The PubChem bioassay dataset AID 647 was selected for model generation which contains 1420 actives and 820 inactives. The machine learning based classification model was generated using training set (80%) and the quality of the generated model was assessed through test set (20%) with tenfold cross validation. Sensitivity, specificity, accuracy and receiver operating characteristic (ROC) were used to understand the performance of the classifier. True positive rate (TPR) or sensitivity is defined as the ratio of true actives, correctly classified as active. True negative rate (TNR) or Specificity is defined as the ratio of true inactives, correctly classified as inactive. The overall effectiveness is assessed by the accuracy.

Prediction of metabolic behavior and ADME properties of the virtual molecules

The metabolic information about compounds in the drug discovery pipeline is critical because of the fact that an extensive first-pass metabolism can result in low bioavailability. Metabolism that occurs too rapidly causes a short therapeutic window requiring a frequent dosing schedule. On the contrary, metabolism that proceeds too slowly can cause an accumulation of the drug molecule in the body which could result in an increase in the risk of toxic effects.

The cytochrome P450s (CYPs) are heme-thiolate enzymes that can metabolize a variety of xenobiotics. There are 57 CYP isoforms in humans, out of which five CYP isoforms, CYP3A4, 2D6, 2C19, 2C9, and 1A2, are accountable for ~ 90% of drug metabolism. Molecular docking method can be utilized to identify the binding conformations of the curcumin derivatives into the site of CYP enzymes (Mannu et al. 2011).

The crystal structures of human CYP3A4 in the unliganded form (1WOE) (Chatake et al. 2005) and bound to substrate (1WOF) (Yang et al. 2005a, b) are downloaded from Protein Data Bank. The protein 1WOE is a wild-type enzyme, except that the N-terminal membrane insertion peptide has been removed to increase solubility for crystallization. There was no substrate or inhibitor bound in the active site of this crystal structure.

In vitro human intestinal absorption (HIA), Caco2 and blood brain barrier (BBB) penetration values were obtained using web based PreADMET program (https://preadmet.bmdrc.kr/).

Results and discussion

2D-QSAR

The Aβ aggregation inhibitory activities of the molecules are mainly dominated by the type of substituent and the substituted positions on curcumin framework. Therefore, 2D QSAR technique can exert its advantages on discovering the dependence of activity on their molecular structures.

A 2D QSAR model was developed through the MLR analysis and the obtained model is depicted in the Eq. (2).

$$\begin{aligned} pIC_{50} = {} & 5.17173(\pm 0.03835) - 5.687(\pm 0.60642)MDEC - 44 \\ & + 1.29883(\pm 0.2094)WK.eneg - 0.20612(\pm 0.1117)ExtFP728 \\ & - 0.36098(\pm 0.09881)GraphFP295 + 1.20961(\pm 0.12137)GraphFP912 \\ & + 0.0091(\pm 0.0057)PEOE\_VSA + 4 \end{aligned} \quad (2)$$

The negative coefficient of the ***MDEC-44*** in the model suggests that a lower value favors the biological activity. ***MDEC-44*** is Molecular distance edge between all quaternary carbons. Similarly, ***ExtFP728*** and ***GraphFP295*** also show negative contribution. ***WK.eneg*** is Non-directional WHIM, weighted by Mulliken atomic electronegativities and the descriptor, ***GraphFP912*** show positive contribution to the biological activity.

$SEE = 0.1837$; $R^2 = 0.9086$; $R^2_A = 0.8763$; PRESS = 0.5734; F = 28.162; $r^2 = 0.8987$; $r^2_0 = 0.8098$; $Q^2_{F1} = 0.8211$; $Q^2_{F2} = 0.8073$; $Q^2_{F3} = 0.7062$; CCC = 0.8656; $|r^2_0 - r'^2_0| = 0.2576$, $[(r^2 - r^2_0)/r^2] = 0.0989$, $[(r^2 - r'^2_0)/r^2] = 0.3856$, $k = 0.9939$, $k' = 1.0032$; Average $r^2_{m(test)} = 0.5063$; $\Delta r^2_{m(test)} = 0.2421$ indicate a good predictive capability.

Since the $R^2_{m(Overall)}$ value is 0.712 and is more than 0.6, indicates the acceptable overall fitting of the developed model. The predicted versus experimental pIC_{50} values are shown in Fig. 2a. The predicted Aβ aggregation inhibitory activities of the developed model obtained are shown in Table 2.

The robustness of the built 2D-QSAR model was further assessed by applying Y-randomization test. The test is carried out by shuffling the biological activity (pIC_{50}) at 100 random trials for the same number of training set molecules, and the new QSAR models have low R^2 values in the range from 0.033 to 0.573 and Q^2 values in the range of − 0.537 to − 0.243. But the R^2 and Q^2 value of the 2D-QSAR model is significantly greater ($R^2 = 0.908$; $Q^2 = 0.747$). Also, for an acceptable QSAR model, the average correlation coefficient (R_r) of randomized models should be less than the correlation coefficient (R) of the non-randomized model. The extent of the difference in the values of the mean squared correlation coefficients of the randomized (R^2_r) and that of the non-randomized (R^2) models is reflected in the value of $^cR^2_p$ parameter. The value of $^cR^2_p$ should be more than 0.5 for passing Y-randomization test.

$$^cR^2_p = R \times \sqrt{R^2 \times R^2_r} \quad (3)$$

Since the $^cR^2_p$ value obtained is 0.780, the Y-randomization test was passed for our model.

Applicability domain plays a vital role in checking the reliability of the QSAR models by filtering the chemical structures that cannot be tolerated by the model. We have used applicability domain using standardization approach which uses the molecular descriptors used to build the

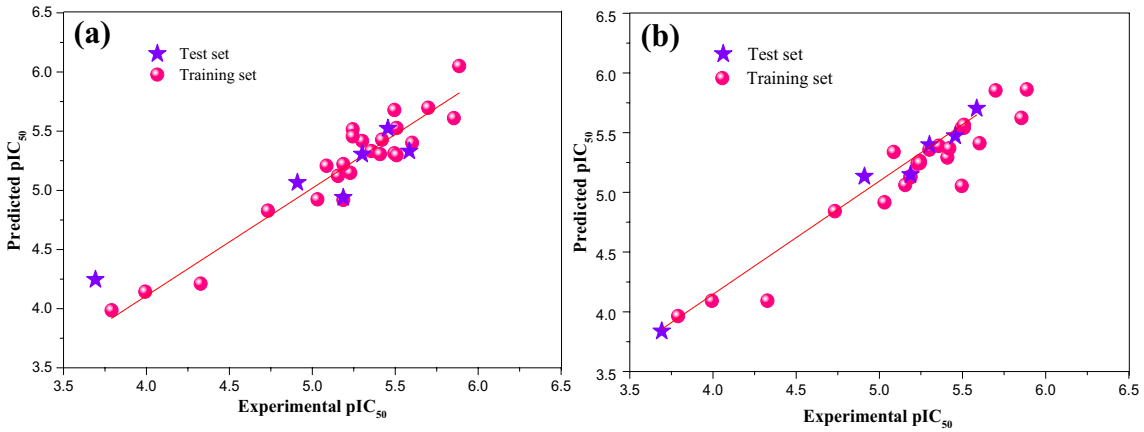


Fig. 2 Correlations between actual and predicted pIC_{50} in the training and test sets for **a** 2D QSAR and **b** HQSAR

Table 2 Experimental and predicted activities (pIC_{50}) of the compounds

Compounds	Actual pIC_{50}	Predicted pIC_{50}			
		2D QSAR	HQSAR	CoMFA	CoMSIA
1	5.699	5.698	5.854	5.384	5.395
2	5.495	5.312	5.054	5.412	5.445
3[a]	5.585	5.331	5.703	5.407	5.414
4	5.357	5.332	5.390	5.343	5.304
5	5.086	5.208	5.339	5.345	5.372
6	5.244	5.516	5.246	5.314	5.283
7[a]	5.456	5.523	5.472	5.365	5.328
8	5.886	6.050	5.862	5.417	5.462
9	5.420	5.428	5.369	5.347	5.324
10	5.187	4.919	5.135	5.304	5.296
11	5.409	5.306	5.293	5.345	5.322
12	5.229	5.148	5.241	5.368	5.386
13	3.993	4.144	4.092	4.172	4.158
14	3.791	3.987	3.964	3.426	3.431
15[a]	5.301	5.305	5.398	5.378	5.419
16	4.327	4.212	4.093	4.786	4.747
17[a]	3.693	4.246	3.838	2.987	2.996
18	5.495	5.679	5.541	5.375	5.359
19	5.509	5.296	5.541	5.405	5.455
20	5.032	4.924	4.916	5.284	5.268
21[a]	4.910	5.065	5.134	5.266	5.307
22	4.733	4.828	4.843	5.139	5.083
23	5.301	5.417	5.359	5.353	5.359
24[a]	5.187	4.939	5.147	5.338	5.382
25	5.155	5.122	5.062	5.304	5.297
26	5.244	5.456	5.262	5.310	5.307
27	5.602	5.401	5.411	5.395	5.406
28	5.854	5.610	5.624	5.453	5.467
29	5.509	5.526	5.564	5.424	5.437
30	5.187	5.222	5.126	5.337	5.382

[a]Test compounds

QSAR model and to predict activity values (Roy et al. 2015a, b). If the training set of the compounds contains properties very dissimilar to the rest of the compounds, then these compounds are considered as X-outliers. In the test set, molecules which are not similar to any of the training set of molecules are considered outside the applicability domain. In our 2D-QSAR model, no compound from the training set or test set was found as X-outlier. As all the compounds of the dataset used to develop 2D-QSAR model fell inside the domain of applicability, our model was not obtained by mere chance.

HQSAR

A total of 21 HQSAR models were constructed by varying the fragment distinction and maintaining the default fragment size (4–7 atoms) with the endeavor of evaluating the influence of the descriptors on the robustness of the models (Table 3). For each constructed model, we also accessed the influence of the hologram length (HL) by building models varying HL as 53, 59, 61, 71, 83, 97, 151 199, 257, 307, 353 and 401 bins. All constructed models showed acceptable LOO validation coefficients (Q^2) indicating that the HQSAR method is suitable to generate robust statistical models. According to the highest Q^2 value, the best HQSAR model was constructed with A/B/C/Ch. The model had a higher Q^2 value and lowered standard error of prediction (SEP) than the two second best models (A/C/DA and A/B/C/H/Ch/DA).

The model A/B/C/Ch was subjected to external validations employing the test set of compounds. The predicted pIC_{50} values for all test set of compounds showed a residual error lower than 1 log unit. The predictive potential for the test set (R^2_m) is equal to 0.910 and the predictive potential for all compounds ($R^2_{m\,overall}$) is equal to 0.849. The graphical plot of predicted versus actual pIC_{50} values is represented in Fig. 2b. The predicted Aβ aggregation inhibitory activities of the developed model A/B/C/Ch are shown in Table 2.

Contour maps of the HQSAR analysis (Fig. 3) show the different colors of the atoms or fragments, which determine the overall contribution to the activity profiles of the molecules. The contributions of (i) red colour indicates a bad contribution less than −0.244 (ii) red–orange color indicates a bad contribution ranging from −0.244 to −0.146, (iii) orange color ranges from −0.146 to −0.098 (iv) the white color indicates an average contribution ranging from −0.098 to 0.0303, (v) a yellow color indicates a good contribution of 0.0303 to 0.045, and (vi) the green color signifies the maximum contribution of 0.076 and above. The most significant green contribution is observed in the benzene ring (Fig. 3). Backbone alkyl chains also depict the average contribution as per the most active compound. The contour map of the least active compound 17 is assigned red-orange and yellow color, indicating the most unfavorable fragment contributing to the activity and has a negative impact towards the inhibitory activity.

CoMFA analysis

CoMFA study analysis is implemented by the most potent ligand compound 8, used as a template to align all the ligands. The training set is used to build the CoMFA model. The statistical parameters derived from the CoMFA studies are provided in Table 4. The developed CoMFA model has a cross-validated Q^2 of 0.687, with five Optimum Number of Components (ONC), a

Table 3 Statistical results of the 21 initial HQSAR models obtained from the variation of the fragment distinction and maintaining the default fragment size (4–7 atoms)

Fdist	Q^2	SEP	R^2_{ncv}	HL	PCs	R^2_{pred}
A/B/C	0.543	0.353	0.928	257	5	0.423
A/B/H	0.549	0.408	0.921	61	6	0.317
A/C/H	0.446	0.428	0.876	151	4	0.489
A/B/Ch	0.439	0.455	0.948	353	6	0.386
A/C/Ch	0.550	0.349	0.942	97	5	0.138
A/B/DA	0.512	0.424	0.943	83	6	0.168
A/C/DA	0.609	0.380	0.946	257	6	0.423
A/B/C/H	0.438	0.431	0.852	307	4	0.861
A/B/C/Ch	**0.615**	**0.306**	**0.931**	**257**	**5**	**0.956**
A/C/H/Ch	0.434	0.432	0.878	151	4	0.909
A/C/H/DA	0.565	0.400	0.954	53	6	0.538
A/B/H/Ch	0.484	0.413	0.812	59	4	0.848
A/B/C/DA	0.577	0.384	0.917	59	5	0.948
A/H/Ch/DA	0.542	0.400	0.897	199	5	0.891
A/B/Ch/DA	0.502	0.417	0.934	401	5	0.418
A/B/H/DA	0.527	0.406	0.936	257	5	0.898
A/B/C/H/Ch	0.424	0.436	0.851	307	4	0.887
A/B/C/Ch/DA	0.568	0.388	0.910	401	5	0.948
A/B/H/Ch/DA	0.522	0.408	0.916	307	5	0.876
A/B/C/H/DA	0.578	0.373	0.912	83	4	0.899
A/B/C/H/Ch/DA	0.585	0.370	0.915	83	4	0.904

Selected model is given in bold

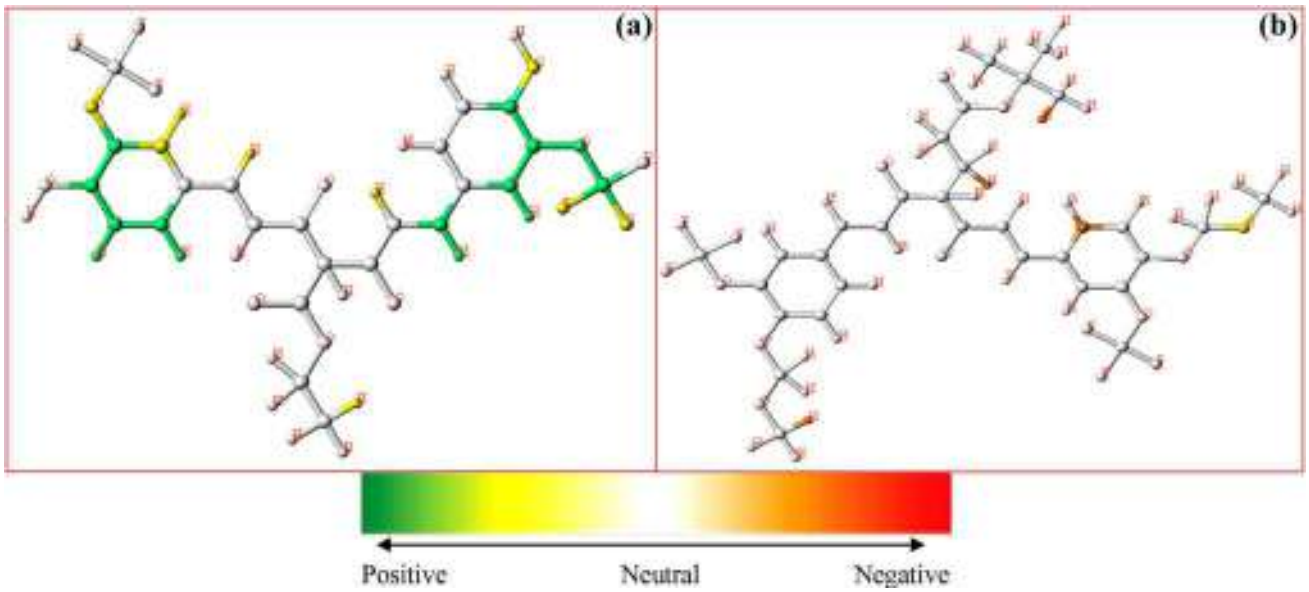


Fig. 3 Contribution map generated by HQSAR model

non-cross-validated R^2_{ncv} of 0.787, F-value of 181.42 and low SEE of 0.246. Thus the resulted CoMFA model is statistically significant in depicting the novel curcumin derivative's inhibitory activities.

The predictive ability of the developed model is assessed by a test set of six ligands. The estimated predictive correlation coefficient (R^2_{pred}) of the CoMFA model on the test set is 0.731.

The calculated pIC_{50} values of the compounds for the CoMFA model are listed in Table 2. The correlation between the experimental pIC_{50} and the calculated ones for the CoMFA model is displayed in Fig. 4. Most of the ligands

Table 4 Statistical results of CoMFA and the best CoMSIA models

	CoMFA	CoMSIA (Model 6)
[a]Q^2/ONC	0.687/5	0.743/3
[b]R^2_{ncv}	0.787	0.972
[c]SEE	0.246	0.094
[d]R^2_{pred}	0.731	0.713
F value	181.420	230.975
Field contribution		
Steric	55.4	19.7
Electrostatic	44.6	52.0
H-bond acceptor	–	28.3

[a]Cross-validated correlation coefficient

[b]Non cross-validated correlation coefficient

[c]Standard errors of estimate

[d]Predicted correlation coefficient for the test set

are located on or nearer to the trend line ($R^2 = 0.798$) specifying that the predictive power of the developed model is good. The analysis of statistical results from CoMFA and graphical output (Fig. 5a) of the correlation analysis reveals that the predicted pIC_{50} values are in line with the experimental pIC_{50}.

The higher contributions of electrostatic field (55.4%) than the steric field (44.6%) demonstrate that the electrostatic field is more dominant than the steric field to the inhibitory activity for CoMFA model.

CoMFA contour plots

The information about the steric and electrostatic fields surrounding the molecule can be acquired from the polyhedral contour plots. The contour plots show the regions in 3D space where the variation of the molecular fields is highly related to the corresponding changes in biological activity. The contour plots showing various fields' contribution of

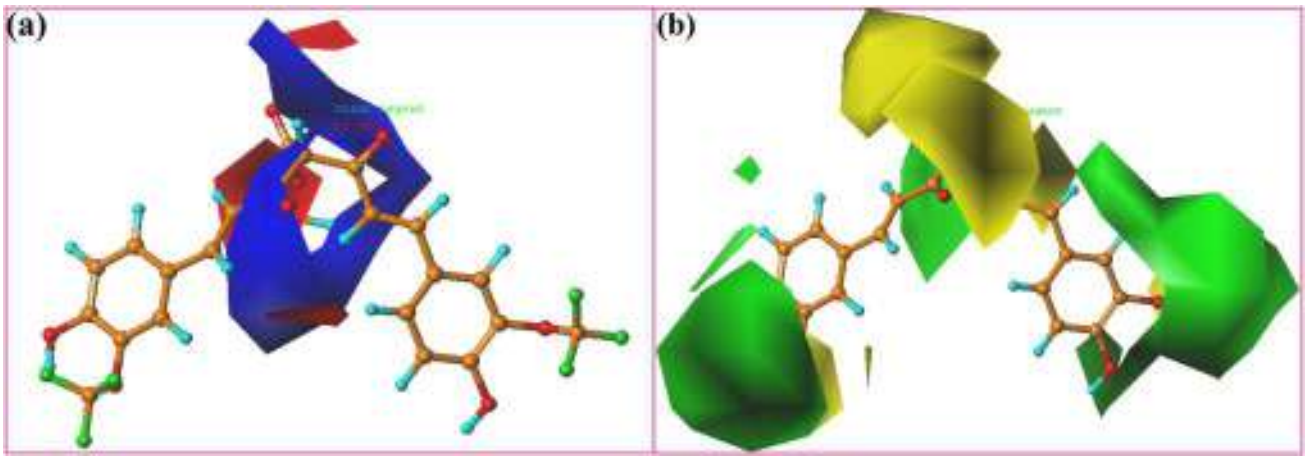


Fig. 4 Contour maps of CoMFA: **a** electrostatic and **b** steric based on compound 8

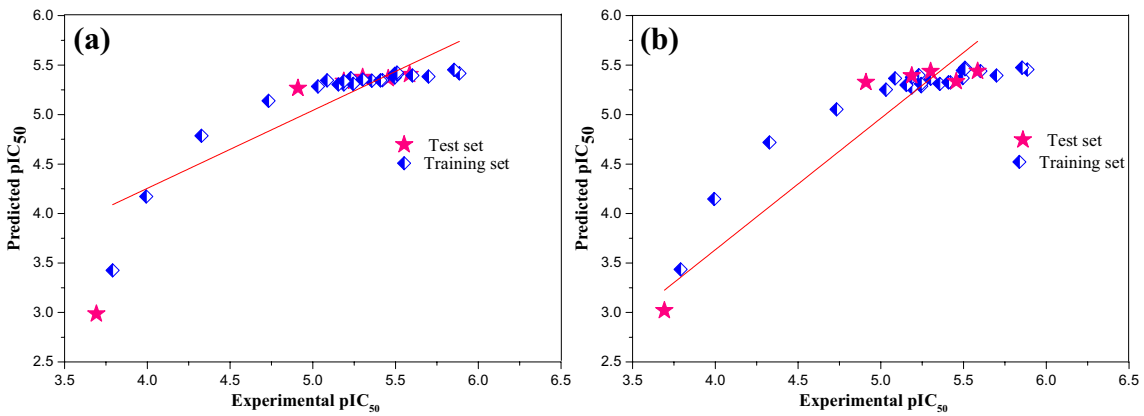


Fig. 5 Correlations between actual and predicted pIC_{50} in the training and test sets for **a** CoMFA and **b** CoMSIA models

CoMFA model is demonstrated with the template compound 8. Figure 4 represents the steric and electrostatic contour plots of CoMFA respectively. The favorable and unfavorable steric interactions are shown in green and yellow colored polyhedrons (80 and 20% contributions) respectively, while the favorable electropositive and electronegative interactions are given in the blue and red polyhedron (80 and 20% contributions) respectively. 3D color contour plots offer valuable contributions for the change in the design of new ligands.

Steric contour maps (Fig. 4a) indicate that if the bulky groups of the compounds are oriented towards the green region, then it can increase the biological activity. The opposite is true for yellow contours. In template compound 8, which is the most active compound, the contour map shows three large green contours around regions A, B and C, while these regions also show small yellow contours around regions A and C, and large contour around region B, indicating that bulkier substituents are not favorable in these regions. A favorable steric contour around region C can be supported with the good inhibitory potency ($pIC_{50} = 5.854$) shown by compound 28, having bulky $CH_3O–CO–CH_2–O$ group when compared with compound 1 ($pIC_{50} = 5.699$). The $(CH_3)_3C–O–CO–CH_2–CH_2$ group attached in the region B of compound 10 is embedded in the yellow region, and the $CH_3O–CO–CH_2–CH_2$ group in the same region of the compound 4 seems partially embedded in the yellow contour. Thus compound 4 shows highest activity ($pIC_{50} = 5.357$) than compound 10. Compounds 20 and 24 with pIC_{50} value of 5.032 and 5.187, respectively, have poor activity due to the presence of the bulkier groups in the region B oriented in the yellow region. Similarly, for compound 17 ($pIC_{50} = 3.692$), compound 22 ($pIC_{50} = 4.733$), and compound 10 ($pIC_{50} = 5.187$), having bulkier groups at the B region oriented towards the yellow region indicates poor activity for these compounds.

Electrostatic contour maps are shown in Fig. 4b, wherein the blue area specifies the favorable region for electropositive groups and the red area specifies an unfavorable region for electropositive groups. There are 80 and 20% contributions to favorable and unfavorable areas, respectively. Electrostatic contour maps show that the red contour is present over the $HOOC–CH_2–CH_2$ group in the region B of the compound 5 with low activity value of $pIC_{50} = 5.086$. Compound 23 ($pIC_{50} = 5.301$) showed good inhibitory activity due to the blue contour present around the $(CH_3)_2N–CO–CH_2–CH_2$ group at the B region of the compound. Compounds 18 and 7 ($pIC_{50} = 5.495$ and 5.456, respectively) showed good inhibitory activity due to the red region present over the electronegative oxygen of the carbonyl group of these compounds. Electronegative oxygen of the carbonyl group and hydroxyl group were oriented towards the blue contour, indicating poor activity of compound 22 ($pIC_{50} = 4.733$) and compound 16 ($pIC_{50} = 4.327$), respectively. Compounds 20, 24 and 26 ($pIC_{50} = 5.031$, 5.187 and 5.244, respectively) contain electronegative oxygen atom oriented towards the blue region, showing lower activity.

CoMSIA analysis

Different combinations of 5 fields (S, E, D, A and H) are combined to generate a total of 16 CoMSIA models. The statistical results of the constructed 16 CoMSIA models are summarized in Table 5. Out of these we selected the model 6 as it has Q^2 value greater than 0.5, high F value, high R^2_{ncv} when compared to other models.

The statistical results of the CoMSIA studies are listed in Table 4. The generated CoMSIA model illustrated a Q^2 LOO value of 0.743 (> 0.5) by three components. The non-cross validated PLS analysis with the ONC = 3 gave a non-cross-validated R^2 ($R^2_{ncv} = 0.972$), a test set R^2 ($R^2_{pred} = 0.713$), SEE = 0.094, F value of 230.975, steric = 19.7%, electrostatic contribution = 52.0% and H-bond acceptor contribution = 28.3%. The obtained high R^2_{ncv}, Q^2 and F values along with the lower SEE_{ncv} indicated the satisfactory predictive ability of the derived model. The pIC_{50} values predicted by the CoMSIA model are listed in Table 2. Figure 5b demonstrates the correlation between experimental and predicted pIC_{50} values by the CoMSIA model.

CoMSIA contour plots

The steric, electrostatic and H-bond acceptor contour maps derived from the CoMSIA model based on the reference compound 8 are shown in the Fig. 6. As shown in Fig. 6a, a large yellow contour is present near regions B, indicating that the bioactivity of molecules is influenced by the introduction of bulky groups near these regions. The inhibitory activity would be decreased by the introduction of bulky groups in the B region, such as compounds 17 and 16 where the use of bulky groups ($(CH_3)_3C–O–CO–CH_2–CH_2 > CH_3O–CO–CH_2–CH_2$) resulted in lower pIC_{50} values ($3.693 < 4.327$). This can also be observed by the comparison of molecules 22 (substituted by $HO–(CH_2–CH_2–O)_3–CH_2–CH_2$ with pIC_{50} value of 4.733) and 25 (substituted by $HO–CH_2–CH_2–O–CH_2–CH_2$ with pIC_{50} value of 5.155). This can also be observed by a comparison of compounds 9 (substituted by $CH_3–CH_2O–CO–CH_2–CH_2$ with pIC_{50} value of 5.420) and 11 (substituted by $(CH_3)_2CH–O–CO–CH_2–CH_2$ with pIC_{50} value of 5.409).

Two large green contours are found in the regions A and C, which shows that bulky groups at these regions would lead to increase the inhibitory activity. In compound 28, the green region covers the $CH_3O–CO–CH_2–O$ group at the region C, which can be supported with the good inhibitory potency ($pIC_{50} = 5.854$) shown by compound 28. For

Table 5 Statistical parameters of CoMSIA models

Model	Descriptors	$R^2_{LOO}(Q^2)$/ONC	R^2_{ncv}/SEE_{ncv}	F value	$R^2_{m\ (overall)}$	R^2_{pred}
1	S, D and A	0.661/1	0.802/0.238	88.968	0.7763	0.7092
2	S, H and A	0.718/3	0.974/0.091	245.649	0.8182	0.5971
3	E, D and H	0.674/1	0.807/0.235	91.854	0.7748	0.7219
4	E, A and H	0.683/1	0.807/0.234	92.100	0.7729	0.7174
5	S, E and H	0.692/3	0.963/0.108	173.486	0.8248	0.6131
6	**S, E and A**	**0.743/3**	**0.972/0.094**	**230.975**	**0.7773**	**0.7127**
7	S, E and D	0.673/1	0.807/0.235	91.907	0.7779	0.7167
8	D, A and H	0.660/1	0.802/0.237	89.359	0.7735	0.7135
9	D, A and E	0.672/1	0.811/0.232	94.306	0.7804	0.7210
10	S, D and H	0.664/1	0.790/0.245	82.890	0.7692	0.7114
11	S, E, D and A	0.698/1	0.820/0.227	99.913	0.7787	0.7194
12	S, E, D and H	0.699/1	0.816/0.229	97.252	0.7856	0.7228
13	S, E, A and H	0.726/3	0.944/0.132	112.754	0.8326	0.6382
14	D, A, H and S	0.690/1	0.812/0.232	94.753	0.7851	0.7119
15	D, A, H and E	0.697/1	0.819/0.227	99.511	0.7867	0.7036
16	S, E, D, A and H	0.714/1	0.827/0.222	105.027	0.7913	0.7197

Selected model is given in bold

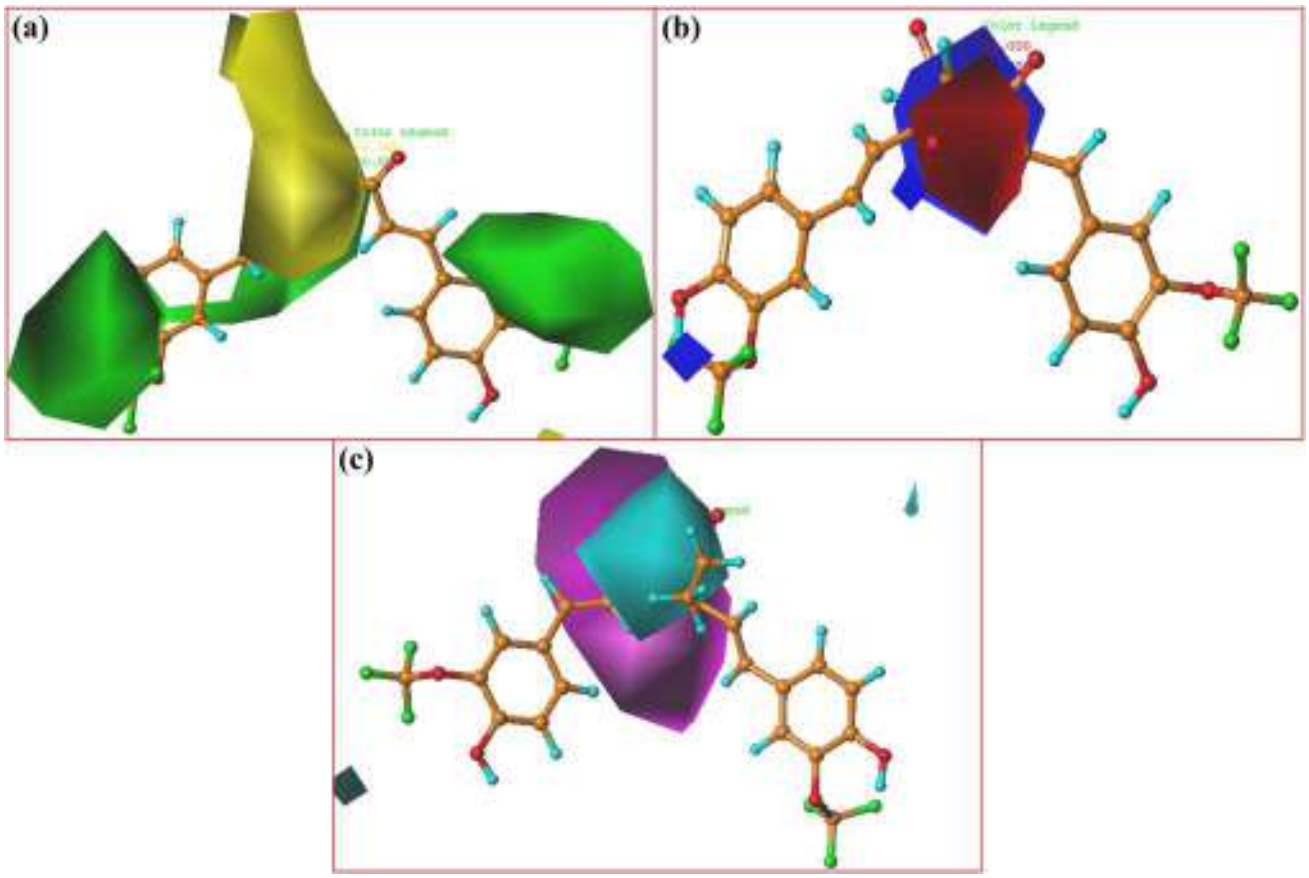


Fig. 6 Contour maps of CoMSIA: **a** steric; **b** electrostatic and **c** H-bond acceptor based on compound 8

instance, the agonist activity of compounds 29 (substituted by HOOC–CH_2–O–) and 18 (substituted by –OH) was varied in the order: 18 < 29. This can also be observed by comparing molecules 16 (having CH_3O–CH_2–O group at regions A and B) and 14 (having CH_3O group at regions A and B), where using a bulky group influenced the outcome of pIC_{50} values (4.327 > 3.790).

Electrostatic contour maps are displayed in Fig. 6b, wherein the blue region designates the favorable region for electropositive groups, and the red region designates an unfavorable region for electropositive groups. There are 80 and 20% contributions to favorable and unfavorable areas, respectively. Electrostatic contour maps show that a medium red contour and a medium blue contour is present over the region B. The compound 5 (pIC_{50} = 5.086) showed good inhibitory activity due to the red region present over the oxygen of the carboxyl group, when compared with compound 14 (pIC_{50} = 3.790). Electronegative oxygen of the hydroxyl group was oriented towards the blue contour, indicating poor activity of compound 22 (pIC_{50} = 4.733). Compounds 7 and 9 (pIC_{50} = 5.456 and 5.420, respectively) contain an electronegative oxygen atom at the region B oriented towards the red region, showing higher activity. In compound 17 (pIC_{50} = 3.693) the electronegative oxygen of carbonyl group is oriented towards the blue region, justifying the poor activity of the compound.

H-bond acceptor contour maps are shown in Fig. 6c, wherein the magenta region shows the favorable region for H-bond acceptor groups and the cyan region shows an unfavorable region. Almost 80 and 20% contributions to the favorable and unfavorable region, respectively, are shown. The significantly increased potency of compound 23 (pIC_{50} = 5.301) may be explained by its atom N as the H-bond acceptor at the region B is oriented towards the magenta contour compared to molecule 14 (pIC_{50} = 3.790) with a CH_3 group at the same position. In fact, compounds with significant activity, for instance compounds 18 (pIC_{50} = 5.495), 7 (pIC_{50} = 5.456), 9 (pIC_{50} = 5.420), 11 (pIC_{50} = 5.409), 4 (pIC_{50} = 5.237) and 15 (pIC_{50} = 5.301), all have such H-bond acceptor groups at the region B, oriented towards the magenta contour map, which are consistent with this contour implication. The compounds 13 (pIC_{50} = 3.993) and 14 (pIC_{50} = 3.790) exhibits reduced inhibitory affinity as these compounds do not have the H-bond acceptor.

Pharmacophore analysis

A pharmacophore is an incorporation of steric, electrostatic, H-bond donor, H-bond acceptor and hydrophobic characteristics that were necessary to ensure the optimal molecular interactions with the biological target. Ten structurally diverse curcumin derivatives with high inhibitory activity were used for developing pharmacophore model. Results indicated that pharmacophore model generated have the following requirements: two hydrophobic & aromatic features, two hydrogen bond donor function, and one hydrogen acceptor function as seen in Fig. 7.

Molecular docking

Primary and secondary structure prediction and validation

Isoelectric point (pI) value is the pH at which a protein is stable and compact has no net charge. The computed pI value of 2BEG (5.31) is less than 7 (pI < 7) indicated that these proteins were acidic. The II value provides an assessment of the stability of protein and when the value is smaller than 40, the protein is predicted as stable and when the value is above 40, the protein is predicted to be unstable. The II value for the protein 2BEG is found to be 18.17 suggesting that 2BEG is stable.

The AI is defined as the relative volume of a protein occupied by aliphatic side chains and is a positive factor for the increase of thermal stability of globular proteins. AI for 2BEG is found to be 97.38. The very high AI values of

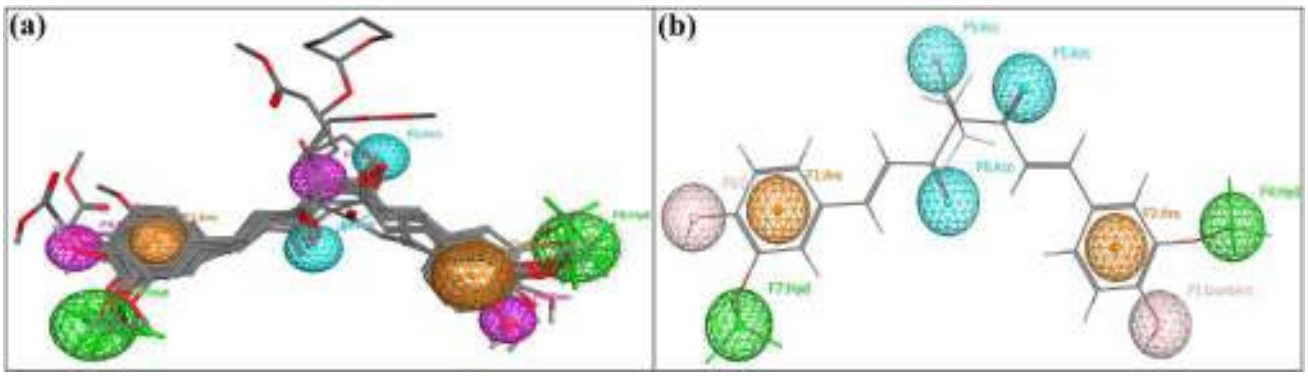


Fig. 7 Pharmacophore models **a** of all the 30 curcumin derivatives **b** most active compound 8

the protein indicate that the protein may be stable for a wide temperature range.

The secondary structures analysis of the protein predicted by SOPMA shows that, the percentages of random coils were more in the protein molecule. The conformational entropy associated with the random coil state contributes to the energetic stabilization of the protein and accounts for much of the energy barrier to protein folding.

Protein–ligand molecular docking analysis

In the present study, the binding mode for 30 curcumin-based molecular hybrids in the active site of the protein structure 2BEG was explored using molecular docking studies. The optimal conformations of these compounds when docked were identified. The active site of the protein 2BEG contains the highly conserved residues. To further elucidate the interaction mechanism, we selected the most potent compound 8 and least potent compound 17, Aβ aggregation inhibitor to perform the deeper docking study and discussion.

The results of the molecular docking studies are summarized in Table 6. These docking results clearly indicate that the most active compounds in the study exhibited significant binding affinities towards the active site of the protein (− 12.250 to − 11.110 kcal/mol), and the energy ranges are comparable to the Aβ aggregation inhibitor.

Molecular design of novel chemical entities

The detailed analysis of 2D-QSAR, HQSAR, 3D-QSAR, Pharmacophore and Molecular docking studies empower us to identify structural requirements for the observed inhibitory activity. According to the information derived from 2D-QSAR, HQSAR, 3D-QSAR, pharmacophore and molecular docking studies, some important facts about the chemical structures requirement was presented to examine the effect of each kind of group as the substituent for regions A, B and C on the inhibitory activity. The HQSAR result shows that the presence of hydroxyl group and oxygen would enhance the inhibitory activity. So it is retained in some of the molecules. 3D-QSAR studies indicate that the presence of bulky groups at regions A and C were considered to enhance the activity. However, the presence of bulky groups at region B would decrease the activity. Molecular docking studies demonstrate that the presence of hydroxyl and carbonyl groups increases the interaction with the active site of the protein moiety. Also, the presence of oxygen atom increases the inhibitory activity of the molecules. Based on these, some novel chemical entities were designed.

For predicting their biological activity, 2D-QSAR model is applied to these new molecules and the corresponding results are listed in Table 7. The descriptors of the newly designed virtual molecules were calculated using PaDEL-Descriptor and MOE softwares. The results show that the eight compounds, M(1), M(2), M(5), M(6), M(7), M(8), M(9) and M(10) show predicted biological activity values higher than before, indicative of their good inhibitory activity. Therefore it is expected that these compounds perhaps should be regarded as the good candidate molecules for experimental synthesis.

Table 6 Molecular docking scores (kcal/mol) of the active molecules in the binding site of the protein 2BEG

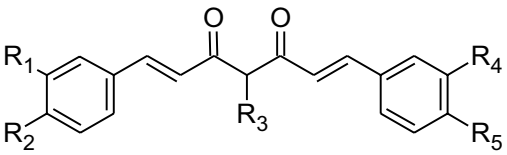
Compound ID	E_score (kcal/mol)
5	− 11.5212
6	− 11.1483
11	− 11.9898
15	− 11.1105
16	− 11.3656
21	− 12.2503
23	− 11.4561
25	− 11.1258
29	− 12.2175

Data mining

Data mining techniques can examine the main useful patterns emerging from a set of data. Machine learning (ML) technique can be effective in generating a model out of such data, and the model can be further used to predict the activity any molecule present in a set of selected molecules. This provides good results and accurate information which can be helpful for solving many of the health-related problems. An understanding of the structural features of a set of molecules may thus throw light on the factors that are characteristic of the activity of the molecules.

WEKA (Waikato Environment for Knowledge Analysis) 3.7.3 with ML method was used to screen and to recognize the Aβ aggregation inhibitory activity of the newly designed curcumin derivatives (Frank et al. 2005). The process of classification requires building a classifier (model) which is a mathematical function that assigns class (e.g., active/inactive) labels to instances defined by a set of attributes (e.g., descriptors). The active (n = 1420) and inactive (n = 820) molecules present in the AID 647 dataset downloaded from PubChem were used for the development of classification models. For each molecule, 179 different molecular descriptors were computed using the software called powerMV. The Random Forest (RF) algorithm of WEKA gives high accuracy and time efficiency for predictive data modeling and is regarded as the best classifier (Sajeev et al. 2013; Seal et al. 2012). Therefore in the present study, we tested the activity of the novel chemical entities' using the classifier

Table 7 Predicted pIC_{50} values of novel chemical entities using inverse QSAR

ID	R_1	R_2	R_3	R_4	R_5	Predicted pIC_{50}
						
M(1)	$(CH_3)_3O$	HO	$(CH_3)_2CH–CH(NH_2)–CO–O$	$(CH_3)_3O$	HO	6.5814
M(2)	$(CH_3)_3O$	HO	$C_6H_5–CO$	$(CH_3)_3O$	HO	6.5314
M(3)	$(CH_3)_3O$	$(CH_3)_3O$	$(CH_3)_3C–CH_2–CH_2$	$(CH_3)_3O$	$(CH_3)_3O$	5.4683
M(4)	$(CH_3)_3C$	$(CH_3)_3C$	$(CH_3)_2N(CH_3)$	$(CH_3)_3C$	$(CH_3)_3C$	5.5780
M(5)	$(CH_3)_3O$	HO	$CH_3–CH_2–C_6H_5$	$(CH_3)_3O$	HO	6.5886
M(6)	$C_6H_{11}O$	HO	CH_3	$(CH_3)_3O$	$C_6H_{11}O$	6.8062
M(7)	$((CH_3)_2CH)_3CO$	HO	$CH_3–CH_2$	$((CH_3)_2CH)_3CO$	HO	6.5836
M(8)	$((CH_3)_2CH)_3CO$	CH_3O	$CH_3–CO–O–$	$((CH_3)_2CH)_3CO$	CH_3O	5.9633
M(9)	Cl_3O	CH_3O	$CH_3–CO–O–$	Cl_3O	CH_3O	5.9396
M(10)	Cl_3O	CH_3O	$CH_3–CH_2$	Cl_3O	CH_3O	6.7362

based on RF. Using the tenfold cross-validation (CV), the RF classifier was evaluated. A cross-validation is a standard tool in analytics, which helps to develop and fine-tune data mining models. The model was used by taking 80% of the data as the training cum validation set and 20% of data as an independent test set.

Data mining results show that out of the ten novel chemical entities, molecules M(1), M(2), M(3), M(4), M(5), M(7), M(8) and M(9) were active. The model displayed better statistical indices like 63.24% accuracy, 84.8% sensitivity, specificity 30.2%, 63.2% BCR (Balanced Classification Rate). This model achieves a precision of 61.6% and recall of 63.2%. The classifier achieved an F-measure of 0.601 and ROC area of 0.644.

Prediction of site of metabolism and ADME properties

In drug design process, the information of site of metabolism (SOM) is vital to mitigate the toxicity issues and to improve the metabolic behavior of a molecule. For metabolite identification, we have used the Toxtreev2.6.13 software. The methylene group ($–CH_2–$) in between two carbonyl groups is ranked as the best SOM in most of the compounds M(2), M(5), M(7), M(8) and M(9). This SOM involves aliphatic hydroxylation reaction for metabolism. For the compound M(1), the methylene group attached to the $–NH_2$ group is ranked as the best SOM. In compound M(2), the double bonds of the benzene ring adjacent to the oxygen atom are regarded as the SOM with the second rank and the metabolism occurs through aromatic hydroxylation. In compound M(4), the alkyl groups attached to the N atom, are considered as SOM with highest ranks. It undergoes *N*-dealkylation reaction. This site undergoes *O*-dealkylation reaction. In compounds M(8) and M(9), the $–CH_3$ of the methoxy group is regarded as the SOM with second position. This site also undergoes *O*-dealkylation reaction for metabolism.

The ADME properties of the selected six compounds were studied using web based PreADMET program. It gives the details of properties such as HIA rate, BBB penetration and in vitro Caco-2 cell permeability (nm/s). The predicted values of these properties are shown in Table 8.

The BBB penetration values give us an idea whether a compound can pass across the BBB or not. A compound having BBB value > 2.0 is considered as highly absorbing to CNS (Central Nervous System), that with the value 2.0–0.1 is considered as with middle absorption to CNS and that with the value < 0.1 is to be considered as low absorbing to CNS (Ma et al. 2005; Ajay et al. 1999). The result showed that the compounds M(5) and M(7) have high absorption to CNS and the compounds M(1), M(2), M(8) and M(9) have middle absorption to CNS.

Table 8 ADME properties for novel chemical entities

Compound ID	M(1)	M(2)	M(5)	M(7)	M(9)	M(8)
BBB	0.1434	0.7918	4.8833	10.4024	0.9439	0.2978
Caco2	21.9193	36.4299	46.0038	51.4046	56.2054	22.8121
HIA	94.1330	95.7125	96.2881	96.5479	97.7153	98.0645

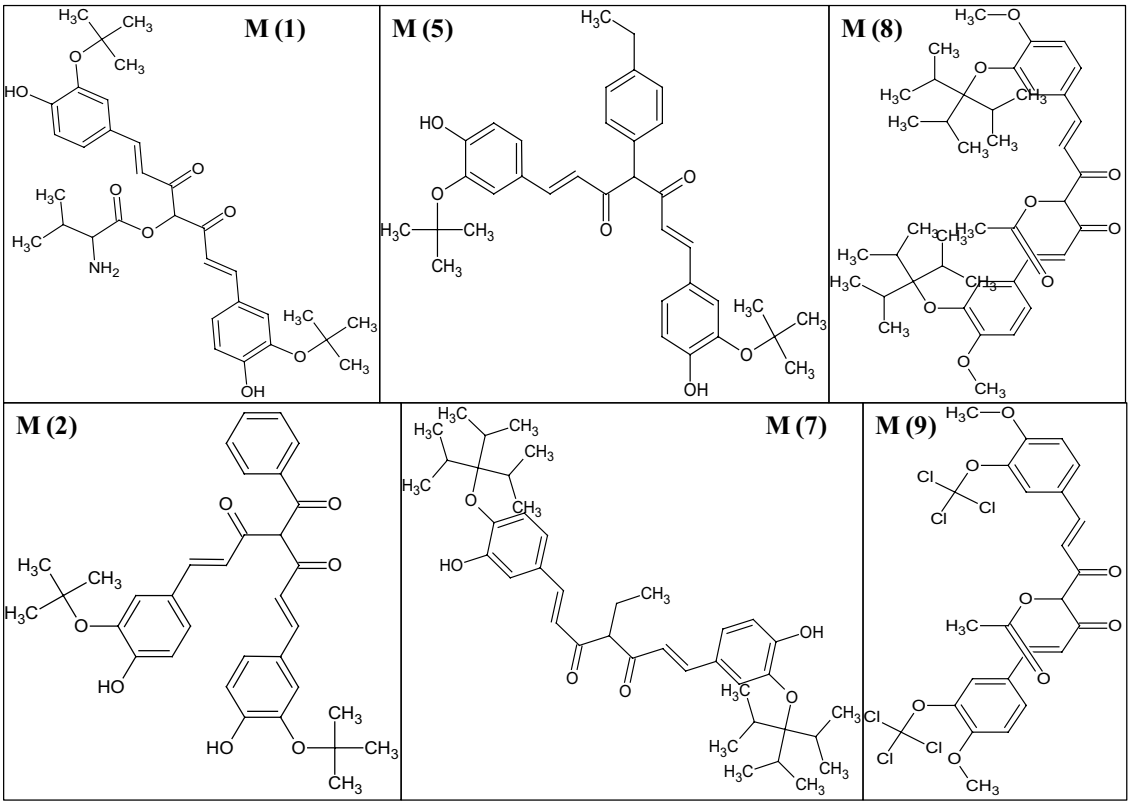


Fig. 8 Structures of the lead molecules

For understanding the intestinal absorption of the compounds under study, several in vitro methods have been used. Caco-2 cell permeability is suggested as a dependable in vitro model for the prediction of oral drug absorption. For a low permeable compound, Caco-2 value should be less than 4; while for a middle permeable one the value should be between 4 and 70; and one with more than 70 is considered as a highly permeable compound (Yamashita et al. 2000). In this study, the result demonstrated that the compounds M(1), M(2), M(5), M(7), M(8) and M(9) have moderate cellular permeability against Caco-2 cells.

The HIA data is the summation of absorption evaluated from the ratio of cumulative excretion and bioavailability. The HIA value for poorly absorbed compounds is between 0 and 20%. For a moderately absorbed compound, the HIA value is 20–70%, and for the well-absorbed compounds, the HIA value ranges from 70 to 100% (Zhao et al. 2001). In this study, we obtained very good HIA values for the compounds M(1), M(2), M(5), M(7), M(8) and M(9).

Molecular docking studies were carried out to propose the binding pose for the identified hit compounds in the binding site of CYP3A4, which would lead to helpful insights for the development of new medications. Here, we present the molecular interactions of Aβ aggregation inhibitors with CYP3A4 using an in silico docking study. CYP3A4 is a complex heme-containing enzyme. It metabolizes more than 50% of the administered drugs. It is the isozyme most implicated in drug-drug interaction profiles (Gibbs and Hosea 2003). The active site of the CYP3A4 enzyme is larger and considerably flexible. The results show that the molecules are not tightly locked into the CYP3A4 active site. They can dissociate and rebind during different stages of the metabolism cycle.

Molecular docking studies of the 10 new virtual active compounds were also performed in the binding pocket of the protein 2BEG. These docking results clearly indicate that the new virtual active compounds in the study exhibited significant binding affinities towards the active site of the protein (− 12.625 to − 10.1492 kcal/mol), and the energy ranges are comparable to the Aβ aggregation inhibitor activity.

Thus compounds M(1), M(2), M(5), M(7), M(8) and M(9) (Fig. 8) are selected as the lead molecules metabolise through aliphatic hydroxylation, aromatic hydroxylation, *N*-dealkylation, and *O*-dealkylation reactions.

Conclusion

In the current study, an effort has been made by extracting the relevant properties of a known Aβ aggregation inhibitory activity set and extrapolating this knowledge to develop predictive cheminformatic models for the classification, identification, and prioritization of new Aβ aggregation inhibitors. For the purpose, a series of 30 curcumin derivatives which are reported as potent Aβ aggregation inhibitors were selected to develop various QSAR and pharmacophore models. The established 2D and 3D-QSAR models showed significant statistical quality and excellent predictive ability. To verify the reliability of the models, the inhibitory activities were evaluated and predicted. Molecular docking analyses of the representative inhibitors were performed to determine the binding modes of the inhibitors at the active site of the protein molecule 2BEG. Based on the QSAR and molecular docking results, some new potent inhibitors were designed, and their activities are then predicted using an inverse QSAR technique. These molecules were further filtered using data mining techniques by Weka, ADME properties were evaluated and the binding interactions understood by molecular docking studies. This resulted in the selection of six lead molecules, M(1), M(2), M(5), M(7), M(8) and M(9). Finally, our in silico results provide compelling evidence for the utility of curcumin derivatives as a preventive medication for neurodegenerative diseases such as $A\beta_{1\text{-}42}$ induced AD. Further investigations are necessary to examine the mechanisms of these molecules and their in vivo effect. Yet, the results of the present study open up the possibility that these derivatives can be developed as promising therapeutics to reach to advanced studies for treatment against Alzheimer's disease.

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GROWING CYBERCRIMES, THREATS WITH RANSOMWARE

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ABSTRACT

Cybercrime are growing day to day. It's a new year, and we are poised again for another round of malicious, often successful cyberattacks, many of which will draw upon ever more sophisticated technology. And some of which will be surprisingly deceptive. Onion-layered attacks are just one of a number of challenges we see unfolding this year in the cybersecurity arena. As early stage venture capitalists specializing in cybersecurity investing, it is our business to know the biggest and potentially costliest cyber-trends on the horizon and to painstakingly scrutinize, vet and then invest in select startups to remedy the problem.

Trends In Cybercrime

Here are seven trends :

1. Targeted spear phishing: The easiest way for a cybercriminal to access valuable data is often by tricking persons into divulging their user names and passwords. This is easier than writing sophisticated computer code. What is new about phishing attacks is the targeting of high-level executives and others with a high security clearance. Educating targets is insufficient. What is also needed is real-time monitoring and scanning systems with blocking capabilities.

2. Ransomware: This is malware that steals something from the computer user and demands a ransom to return it. One piece of ransomware, the recent CyrptoWall v3, which often exploits social engineering techniques, has cost hundreds of thousands of users globally more than $325 million so far, according to the Cyber Threat Alliance.

There are essentially two types of ransomware. One locks a computer system and tricks the user into believing that a ransom payment is required to unlock it. Generally, no harm is done to the system and no information is stolen. The other, more serious type of ransomware encrypts files on a system's hard drive and requires a ransom payment to get the keys to decrypt the files. It is very difficult, if not impossible, to break the encryption, and information is sometimes lost during these attacks. One variant of this ransomware encrypts not only hard drive files, but also the network-shared data, potentially targeting more users.

3. Continuation of porous defense against malicious insiders: Surprisingly, many attacks have an insider component, even if it is just some sort of mistake. Among other things, insiders erase router configurations and make unauthorized rule changes to firewalls. Because it is sometimes difficult to distinguish these malicious steps from normal service outages, some situations persist for weeks before the start of a formal investigation.

Remedying the problem in this particular case is usually more a matter of accountability than technology. Bad password policies, for example, continue to compromise employee termination procedures. When a system or network administrator leaves an organization, disabling their personal accounts doesn't always limit their ability to cause damage. Sometimes former ill-willed employees can still access shared company accounts.

4. Sophisticated hackers target geopolitical conflicts as cyberskills become more democratic: In the recent past, cyberattackers focused on entities on both sides of the Russia-Ukraine conflict. Other attacks targeted Hong Kong protests, territorial disputes in the South China Sea, and Israeli military operations in Gaza. This is certain to increase as a tool of foreign policy objectives. As it does, industrial control systems supporting national infrastructure also become targets.

5. Poor security basics undermine corporate risk management: When a corporation or other organization is the target of a cyberattack, it must work hard to learn from the episode. Among other things, it must profile the culprits, learn their modus operandi, and adopt strong countermeasures. Even so, entities must also do something simpler and more important—master and rigorously implement security basics.

Far too many organizations have yet to do so. They still don't manage passwords properly and do not require two-factor authentication. In addition, most corporations still have too many unpatched vulnerabilities that will be exploited and accept too many web security flaws.

6. Hacker expertise continues to grow: Hackers have become extremely skilled, highly specialized and

increasingly global, and this trend will keep growing. Predictably, many hackers concentrate on finding exploits in software. When successful, they think big, not small. Rather than use the knowledge they have acquired, they often sell their work to others who specialize in packaging exploits and running them through botnets. Making matters worse, many rent their botnets to still other hackers.

7. Cyber information sharing and collaboration will increase: Rapid information sharing between the government and the private sector helps block cyberthreats before significant damage occurs. Fortunately, The Department of Homeland Security is on the case via its Cyber Information Sharing and Collaboration Program (CISCP). Information shared via CISCP allows participants to better secure their networks and helps support the shared security of CISWCP partners. There is room for improvement, of course, because the government and private sector need to build more trust in each other. One example of insufficient trust is the apparent stalemate between the government and Silicon Valley regarding adoption of a "back door" encryption key.

Ransomware

Ransomware is computer malware that installs covertly on a victim's device (computer, smartphone, wearable device, etc), executes a cryptovirology attack that adversely affects it, and demands a ransom payment to decrypt it or not publish it. Simple ransomware may lock the system in a way which is not difficult for a knowledgeable person to reverse, and display a message requesting payment to unlock it. More advanced malware encrypts the victim's files, making them inaccessible, and demands a ransom payment to decrypt them. The ransomware may also encrypt the computer's Master File Table (MFT) or the entire hard drive. Thus, ransomware is a denial-of-access attack that prevents computer users from accessing files, since it is intractable to decrypt the files without the decryption key. Ransomware attacks are typically carried out using a Trojan that has a payload disguised as a legitimate file.

Encrypting Ransomware

The first known ransomware was "AIDS" (also known as "PC Cyborg"), written in 1989 by Joseph Popp. Its payload hid the files on the hard drive and encrypted their names, and displayed a message claiming that the user's license to use a certain piece of software had expired. The user was asked to pay US$189 to "PC Cyborg Corporation" in order to obtain a repair tool even though the decryption key could be extra... the code of the Trojan. Popp was declared unfit to stand trial for his actions, but he pro... donate the profits from the ... fund AIDS research.

The notion of using public key cryptography ... attacks was introduced in 1996 by Adam ... and Moti Yung. Young and Yung showed ... AIDS Trojan was ineffective due to ... of symmetric cryptography, since the decryp... can be extracted from its code, and implem... experimental proof-of-concept cryptov... a Macintosh SE/30 that used RSA and ... Encryption Algorithm (TEA) to hybrid ... victim's data. Since public key crypto is u... cryptovirus only contains the *encryption* ... attacker keeps the corresponding *private* decry... private. Young and Yung's original cryp... cryptovirus had the victim send the ... ciphertext to the attacker who deciphers it and ... the symmetric decryption key it contains to ... for a fee. Long before electronic money existe... and Yung proposed that electronic money ... extorted through encryption as well, stating ... virus writer can effectively hold all of the ... ransom until half of it is given to him. Even ... money was previously encrypted by the user, ... use to the user if it gets encrypted by a cryp... They referred to these attacks as being "cry... extortion", an overt attack that is part of a larger ... attacks in a field called cryptovirology ... encompasses both overt and covert attacks.

Some ransomware strains have used pro... to Tor hidden services to connect to their comm... control servers, increasing the difficulty of ... exact location of the criminals. Furthermore ... web vendors have increasingly started to ... technology as a service.

Symantec has classified ransomware to be a ... dangerous cyber threat.

Non-encrypting Ransomware

In August 2010, Russian authorities arrested ... individuals connected to a ransomware Trojan ... WinLock. Unlike the previous Gpcode ... WinLock did not use encryption. Instead, it ... trivially restricted access to the system by ... pornographic images, and asked users to ... a premium-rate SMS (costing around US$10) ... a code that could be used to unlock their machine. ... In 2011, a ransomware Trojan surfaced that ... the Windows Product Activation notice, and ...

increasingly global, and this trend will keep growing. Predictably, many hackers concentrate on finding exploits in software. When successful, they think big, not small. Rather than use the knowledge they have acquired, they often sell their work to others who specialize in packaging exploits and running them through botnets. Making matters worse, many rent their botnets to still other hackers.

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Encrypting Ransomware

The first known ransomware was "AIDS" (also known as "PC Cyborg"), written in 1989 by Joseph Popp. Its payload hid the files on the hard drive and encrypted their names, and displayed a message claiming that the user's license to use a certain piece of software had expired. The user was asked to pay US$189 to "PC Cyborg Corporation" in order to obtain a repair tool even though the decryption key could be ex... the code of the Trojan. Popp was declar... unfit to stand trial for his actions, but he ... donate the profits from the ... fund AIDS research.

The notion of using public key cryptogra... attacks was introduced in 1996 by Adam ... and Moti Yung. Young and Yung showed ... AIDS Trojan was ineffective due to ... of symmetric cryptography, since the dec... can be extracted from its code, and impl... experimental proof-of-concept crypto... a Macintosh SE/30 that used RSA and ... Encryption Algorithm (TEA) to hybrid ... victim's data. Since public key crypto is ... cryptovirus only contains the *encryption* ... attacker keeps the corresponding *private* dec... private. Young and Yung's original cr... cryptovirus had the victim send the ... ciphertext to the attacker who deciphers it a... the symmetric decryption key it contains b... for a fee. Long before electronic money exis... and Yung proposed that electronic money ... extorted through encryption as well, stating ... virus writer can effectively hold all of ... ransom until half of it is given to him. Even ... money was previously encrypted by the user ... use to the user if it gets encrypted by a cr... They referred to these attacks as being "... extortion", an overt attack that is part of a larger ... attacks in a field called cryptovirology ... encompasses both overt and covert attacks.

Some ransomware strains have used ... to Tor hidden services to connect to their com... control servers, increasing the difficulty of ... exact location of the criminals. Further... web vendors have increasingly started to ... technology as a service.

Symantec has classified ransomware to be ... dangerous cyber threat.

Non-encrypting Ransomware

In August 2010, Russian authorities arre... individuals connected to a ransomware Trojan ... WinLock. Unlike the previous Gpcode ... WinLock did not use encryption. Instead, ... trivially restricted access to the system by ... pornographic images, and asked users ... a premium-rate SMS (costing around US$10) ... a code that could be used to unlock their machi... In 2011, a ransomware Trojan surfaced that ... the Windows Product Activation notice, and ...

users that a system's Windows installation had to be re-activated due to " victim of fraud". An online activation option was offered but was unavailable, requiring the user to call one of six international numbers to input a 6-digit code. While the malware claimed that this call would be free, it was routed through a rogue operator in a country with high international phone rates, who placed the call on hold, causing the user to incur large international long distance charges.

In February 2013, a ransomware Trojan based on the Stamp.EK exploit kit surfaced; the malware was distributed via sites hosted on the project hosting services SourceForge and GitHub that claimed to offer "fake nude pics" of celebrities. In July 2013, an OS X-specific ransomware Trojan surfaced, which displays a web page that accuses the user of downloading pornography. Unlike its Windows-based counterparts, it does not block the entire computer, but simply exploits the behavior of the web browser itself to frustrate attempts to close the page through normal means.

In July 2013, a 21-year-old man from Virginia, whose computer coincidentally did contain pornographic photographs of under aged girls with whom he had conducted sexualized communications, turned himself in to police after receiving and being deceived by ransomware purporting to be an FBI message accusing him of possessing child pornography. An investigation discovered the incriminating files, and the man was charged with child sexual abuse and possession of child pornography.

Leakware (also called Doxware)

The converse of ransomware is a cryptovirology attack that threatens to publish stolen information from the victim's computer system rather than deny the victim access to it. In a leakware attack, malware exfiltrates sensitive host data either to the attacker or alternatively, to remote instances of the malware, and the attacker threatens to publish the victim's data unless a ransom is paid. The attack was presented at West Point in 2003 and was summarized in the book Malicious Cryptography as follows, "The attack differs from the extortion attack in the following way. In the extortion attack, the victim is denied access to its own valuable information and has to pay to get it back, where in the attack that is presented here the victim retains access to the information but its disclosure is at the discretion of the computer virus". The attack is rooted in game theory and was originally dubbed "non-zero sum games and survivable malware". The attack can yield monetary gain in cases where the malware acquires access to information that may damage the victim user or organization, e.g., reputational damage that could result from publishing proof that the attack itself was a success.

Mobile Ransomware

With the increased popularity of ransomware on PCs, there has also been a significant increase in the volume of ransomware affecting smartphones, particularly Android devices. (iOS devices are protected by Apple Inc.'s restrictions of what applications they allow on the iOS App Store.)

Unlike ransomware on desktop computers, where encrypting ransomware is more widespread than non-encrypting ransomware, mobile devices have almost no encrypting ransomware because most of the crucial data is stored in clouds. When data is backed up in cloud storage, there is no need to pay a ransom. For this reason, non-encrypting ransomware (or 'blockers', because they block access to the device) are much more popular on mobiles.

Mobile ransomware usually spreads by pretending to be a legitimate app in third party stores, however, they can also spread through other means such as infected emails, and unsecure websites. They act by overlaying the interface of every app with the malware's own, which prevents the user from using any application. Blockers are also more effective on mobile devices because the hard drive is usually soldered onto the motherboard, whereas on PCs one could simply unplug the hard drive from the infected PC and use another PC to retrieve its data. One thing that is unique to mobile ransomware is that it can hijack the phone's PIN and use the device's own security against the user. To protect a phone from ransomware, one can either scan for malware on the phone regularly, and avoid suspicious links and applications.

Conclusion

Cybercrime is increasing so fast and in year 2017 it may be doubled. Ransomware is a malware which creates problems to government and non-government organizations. Using cybersecurity, cybercrimes can be resolved. This can control the number of malware that creates problem to computer and other systems.

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EXPLORATION, ASSESSMENT AND ETHNOBOTANICAL STUDIES OF TRIBE KORKU INHABITED IN MELGHAT FOREST AREA OF AMRAVATI, MAHARASHTRA, INDIA

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ABSTRACT: Melghat forest is rich in biodiversity of medicinal plants and this area is inhabited by scheduled tribe Korku. The purpose of the present study was to record the ethnobotanical knowledge of korku tribe using these wildly growing medicinal plants and the survey was conducted during the years 2014-2017. Forty eight plant species belonging to thirty four families which are extensively being used as medicinal plants as well as for food were collected and their traditional usage by korku tribe were studied. The botanical name, family, vernacular name, Flowering periods, Voucher specimen, date of collection, Precise GPS Location, Height above Sea level, Life form, Abundance, Frequency Citation, Relative Frequency Citation index, parts used, Drug formulation & dosage to cure various ailments are discussed in this study. The indigenous extraction and drug formation practices recorded in the present study can be tested and standardized on scientific scale. This study will be helpful in providing awareness about harvesting these medicinally important plants in a conservative manner.

KEYWORDS: Melghat Forest, Korku, Indigenous knowledge, Statistical methods.

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1.INTRODUCTION

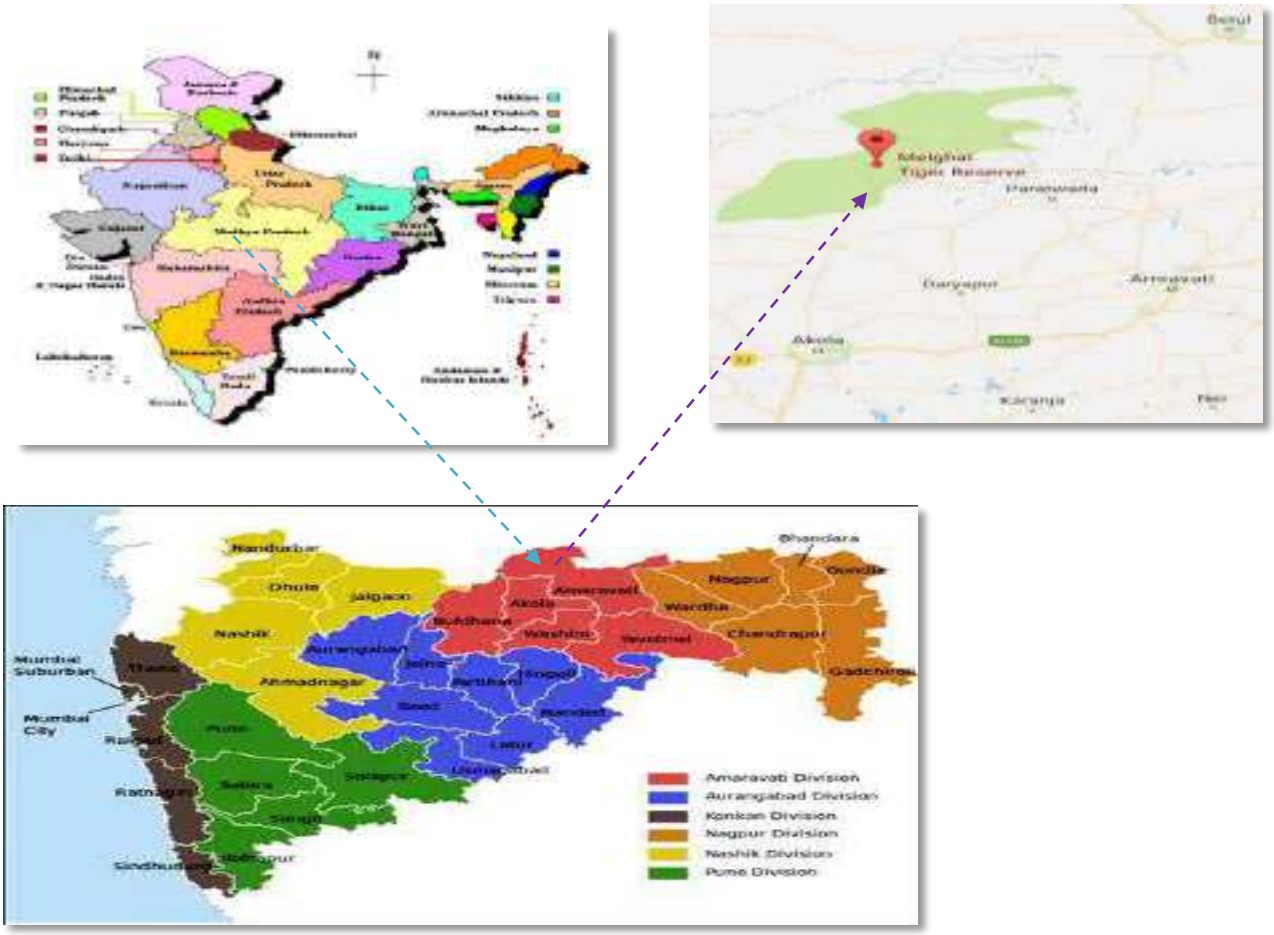
Forest structure and floristics knowledge are necessary for the study of forest dynamics, animal – plant interactions and cycling of nutrients. As life support system forests are the most important component on the earth. These days Biodiversity has always remained the topic of hot debate and discussion. Biodiversity conservation strategy needs strong basis of Biodiversity Assessment. Until and unless we know what is our biodiversity, we can't decide what is to be conserved and how. As far as plants are concerned most of the region of the country are floristically explored – are continuously being explored - and to good extent we have idea about our species wealth [1]. Besides the detailed assessment of floristic diversity of area of conservation, whether they are endemic, endangered or medicinally important plant species, the causes of forest destruction are also equally important in assigning conservation values. Plants have now been used as traditional medicines from about more than five thousand years for curing, suppressing, and prevention of diseases of humans [2]. Ancient methods of using plants for various diseases is known as herbal medicine which refers to the use of different parts of the plant for medicinal purposes [3]. The herbal medicines are considered to be of great importance among different indigenous and rural communities in many developing countries [4]. Herbal drugs constitute only those traditional medicines which primarily use medicinal plant preparations for therapy [5]. According to WHO, traditional medicines is therapeutic practices which have an existence from more than hundreds of years [6]. Analyses of published information on medicinal plants used by the six major systems of medicine in India are as; 1250-1400 plants in Ayurveda [7]; 342 plants in Unani; and 328 plants in Siddha; 4671 in Folk; 482 in Homoepathy; 1106-3600 plants in Tibetan Medicine [8]. Even most world population belonging to developing countries are still dependent on these traditionally used medicinal plants for their health care [9]. The information about the usage and importance of these medicinal plants was discovered by local tribal communities. Due to the rich biodiversity of Melghat forest certain scheduled tribes are inhabited in this area which includes ‘Korku’, ‘Gond’, ‘Nihal’, ‘Balai’ and ‘Gaoli’ etc but majority of population and area is covered by Korku tribe while as percentage of other tribes is limited [10]. According to official website of Melghat Tiger Reserve, Korku’s had been drawing their sustenance from a period of almost one century from the forests of this area and are mainly engaging themselves in forest produce harvesting. This tribe has very important role in providing laborers for development works and forest conservation. They have acquired skills which are required for harvesting these forest products which are later processed and send to markets as forest products. The main purpose of this survey is that it can be very important for research students dealing with medicinal plants. Some already studied plants of this area have shown that nutritional value of those plant foods is quite high, as they contain greater amounts of vitamins, minerals, carbohydrates, protein, and fat than cultivated plant foods. Taking these perspectives in consideration, the exploratory study for the study of plants with medicinal use was carried out within

korku tribe inhabiting in the Melghat forest. This area being hilly in character, tribal people are mostly relying on the plants or plant derived products for the basic health care and foods. Most of the human ailments and veterinary diseases are cured by prescriptions of local bhagat (vaidoo) and elderly people with the help of herbal products.

2. MATERIALS AND METHODS

Demography

The Melghat area is in the Northern part of Amravati District of Maharashtra State and was declared a tiger reserve in 1974. The total area of the biosphere reserve is around 1677 km^2. The forest vegetation is tropical dry deciduous in nature. The study was done in the Korku tribe which reside in Melghat area at coordinates 21° 26′45″N and 77°11′50″E which is also shown by map in "Figures 1, 2, &3".



Figures 1, 2, & 3: Map of India showing Maharashtra State in which study area Melghat Forest Area has been shown

Methodology

The study was planned in the beginning of the May 2014 - January 2017 to investigate and enumerate the flowering plant which are used by people of korku tribe in their routine health care system to cure various ailments. Nature of ailments was identified with the help of elderly tribal healers of the particular area. Seven trips were done to the understudy area during investigating time

period (May & September, 2014; March & November, 2015; November & December, 2016; January, 2017) by all the authors from time to time in order to record the diversity and ethnic knowledge of the plant diversity found in the understudy area. For collection of data questionnaire, semi-structured interviews and direct observations were done [11]. Before each interview, researchers and the informants signed a Prior informed consent (PIC) according to Kyoto protocol concerning the intellectual property rights (IPR) of local inhabitants and plant resources of the area. The sole purpose of this study was designed for unveiling the precious wealth of indigenous knowledge. The information about local name, part used and methodology of usage from the korku tribe was noted during the survey [12]. During observation field notes were recorded in field notebooks and voucher specimens of these species were collected. The collected specimens were processed using usual taxonomic methods of drying and mounting [13] and herbarium were prepared by standard methods [14]. The specimens were identified with the help of existing literature [15],[16],[17],[18],[19] and authorized taxonomist of the area. These collected specimens have been preserved in the herbarium of Department of Botany, Vidyabharati Mahavidyalaya College, Amravati (M.S.). The plants were classified according to the classification of Bentham and Hooker (1862-1883) [20] and their botanical name, local name, family, flowering phonology, altitudinal range, life form representation, part used and methodology of using these parts (wherever necessary) and most frequently treated diseases. The plants in this survey were classified into herbs, shrubs, trees and climbers using the Raunkiar's (1934) [21] life form classification system. Data documented during the ethnobotanical survey was entered on a Microsoft excel database and analyzed to determine the proportions of different variables. Relative Frequency of Citation (RFC) of reported species was also determined by using formula;

$$RFC=FC / N \ (0<RFC<1)$$

This index shows the local importance of each species and it is given by the frequency of citation (FC, the number of informants mentioning the use of the species) divided by the total number of informants participating in the survey (N), without considering the use-categories [22], [23],[24].

3. RESULTS AND DISCUSSION

The local inhabitants have learnt to utilize plants for treating various diseases. Thus there is a vast list of plants used by this tribe but some important wildly growing forty eight plant species belonging to thirty four families which are extensively being used to cure various ailments are given in "Table 1". In the present study, a total of 51 persons were interviewed among which 20 were males and 31 were females. The informants were divided into four age groups; (1) 12-20 years; (2) 20-35 years; (3) 35-65 years and (4) above 65 years old. Age group of 35-65 years old comprised the most informants. 6 drug formulations practices or recipes formulations were harvested from 1st age group, 29 from 2nd age group, 23 from 3rd age group and 43 from 4th age group. Present study was unique in comparison to the previous ethnobotanical studies all around the world as we interviewed first

time the female community of the korku tribe residing in Melghat tiger reserve of Amravati, Maharashtra. In this area, the females of the said community are traditional and very conservative in talking to males (strangers or outsiders) except their close relatives within the community. Authors were assisted by an elderly woman of the same community for interviewing these females within their houses. This strategy was adopted for the purpose of the data collection from female informants and also to compare their indigenous knowledge with male members of the same community. Other purpose was to know their interest regarding the use of medicinal plants to treat different ailments. The aim of the data collection was explained to the local inhabitants and then semi-structured questionnaire based interviews were carried out. The inhabitants of the korku community were requested to share the knowledge of utilizing these medicinal plants in their local language in order to collect the detailed information which was converted to common tongue by a member (*Mama*) of the same community. It can be assumed from this study, that most members of the community generally rely on traditional herbal medicines due to easy availability and rich diversity of medicinal plants in the area. It is noted during the survey, that the female informants in comparison to male members have a significant knowledge about the preparation and administration of herbal drugs which reflect their role in house hold management and disease treatment in order to keep the family healthy. However, the technique for diagnosis of the various ailments is very primitive in the tribe. Different diseases are being diagnosed on the external characters of the patient by these elder men and women of the tribe. Color of the tongue, eyes, cold and hot conditions of the body are common indicators which are being used to understand the patient's problem. The specimens studied, their assessment and ethnobotanical usage are given in the Table 1. The study was undertaken for the first time in the understudy tribe and the results revealed that Korku tribe is good in plant based ethno-medicine. The gender, related age group from which the knowledge was harvested and number of recipes has been presented in "Figure 4". During the field work of the present study, 48 plant species belonging to 44 genera and thirty four families were collected. The complete inventory of ethnoflora consisting of taxon name, with their family, Local name / vernacular name, flowering period, voucher specimen number, date of collection, life form, abundance, Frequency citation, Relative frequency of Citation, part used, mode of administration and dosage has been recorded in the present study shown in "Table 1". The best represented families are Ceasalpinaceae (four species), Euphorbiaceae (3 species) while as Liliaceae, Anacardiaceae, Papilionaceae, Zingiberaceae, Lamiaceae, Moraceae, Lythraceae, Myrtaceae, Rhamnaceae each represented by two species and other 23 families with one species each. Some of the species were commonly found in the study area while as some the species showed different abundance patterns. However, we can also state that, more commonly a plant taxon found in an area, the greater will be the probability of its popular use. In accordance with the life form, tree species (26) were the highest followed by herbs (17), shrubs (4) and climbers (1) as shown in "Figure 6". This is not surprising as the area is deciduous

forest type in which dominant vegetation is Trees followed by the growth of herbs in rainy monsoons. The findings of this study indicate that aerial parts (67.54%) were mostly used, followed by the usage of underground parts (29.87%) and whole plants (2.59%) for the formulations of recipes shown in "Figure 8". The present study also shows that the area has vast medicinal flora with major potential to cure many diseases. Both fresh and dried parts are used for making drugs in crude form. Mostly, the drugs are prepared in the form of paste, tablets, powder, latex, decoction, and even as extracts shown in "Figure 7". The dosage and mode of administration against different ailments is subject to approximation during treatment procedure. The ailments which were cured by these under study plants are anti-emetic, skin diseases, cough, menstruation disorders, stomach pains, cholera, indigestion, muscle pains, rheumatic pains, Diabetes, anti-fertility, breast ulcers, gastric disorders, ophthalmic disorders, Blisters, jaundice, headache, paralysis, etc. The study also gives the approximate GPS location where these medicinal plants can be collected and harvested as well as can be protected from unsustainable harvesting or over harvesting in that area. The photographs taken during the data collection (interviewing the informants and collection of plant specimens) are presented in Photoplate 1 and Photoplate 2 & 3 show the digitalized pictures of some important species of the area.

Some plant species of this study area are widely distributed in other parts of country as they have wide adaptability for different ecological zones. Among all medicinal plants reported in present study *Syzygium cumini, Ficus religiosa, Euphorbia hirta, Butea monosperma, Sterculia urens, Hemidesmus indicus, Emblica officinalis, Cassia fistula* and *Aegle marmelos* have high RFC values which indicates that these are well-known plants of the korku tribe. Findings of the present study are in contrast to most of the previous ethnobotanical studies where different plant species are being reported with respect to their preference use [13, 25, 26, 27]. The other most cited medicinal plants based on RFC data includes *Acalypha indica L., Cayratia auriculata, Chlorophytum tuberosum, Costus speciosus, Dendrocalamus strictus, Colebrookea oppositifolia, Lagerstroemia parviflora, Madhuca indica, Miliusa tomentosa, Wrightia tinctoria, Zizipus xylopyra, Anisochilus carnosus.*

Table 1: Exploration, Assessment and Ethnobotanical Usage

Botanical name / Family/ Vernacular name / Fls & frts./ Voucher specimen No./ Date of Collection	Location / Height above Sea level	Life Form	Abundance	FC	RFC	Part/s Used	Methodology of Usage/ Formulation of Recipes and Disease Treated
Acalypha indica L. / Euphorbiaceae/ Khajoti/ Throughout the year. (NAW-1361)/ 07-05-14	N-21^0.28.234_ E-077^{0}23.326 897m	S	1	17	0.33	Roots Leaves	Roots ground with black peper (*Piper nigrum*) and the extract orally administered as an anti-emetic. Leaves with turmeric (*Curcuma longa*) ground in to fine paste applied for skin diseases.
Achyranthes aspera L. / Amaranthaceae/ Agahada / Throughout the year. (NAW-1362) 03-09-14	N-21^0.28.273_ E-077^{0}24.267 667m	H	1	14	0.27	Roots	Root ash with honey used medicinally to relieve cough. Root extract used for normal delivery.
Aegle marmelos (L.) Correa / Rutaceae Bela / Fls.: May June; Frts: Oct.–Nov. (NAW-1363) 22-03-15	N-21^0.28.296_ E-077^{0}24.291 667m	T	3	20	0.39	Stem Leaves Fruits	Stem bark ground with black pepper (*Piper nigrum*) and the filtered extract administered for cholera (2 spoonful s thrice a day for 3 days) Extract from stem bark ground with *Saccharum officinarum* administered for chest pain (5 spoonfuls thrice a day for 2 days). Leaf juice poured in to paste and applied on head and also taken internally for cooling the body. Fruits edible use medicinally in gastric disorder.
Asparagus racemosus Willd. / Liliaceae/ Shatavari. / Fls, & frts. : Oct .- Dec./ (VBMV-1739) 03-09-14	N-21^0.28.815_ E-077^{0}23.931 634m	H	3	15	0.29	Tuber	Tuber crush with turmeric (*Curcuma longa*) and the filtrate administered for chest pain and stomach pain (2 spoonfuls twice for three days). Also tuber chewed to stop dehydration.

Bauhinia racemosa Lam. / Caesalpinaceae /Bhusa / Fls .: Apr – June ; Frts, : Nov - Jan. (NAW-1364) 22-03-15	N-21^0.28.827_ E-077^{0}23.034 628m	T	3	12	0.23	Roots Stem Leaf	Root bark crushed and the filtrate administered for diarrhea by 5 spoonfuls twice a day for 5 days. Stem bark crushed and filter mixed with goats milk administered orally for epilepsy by kurku. Tender leaf juice poured in to eyes (2drops) for ophthalmic infections and tender leaves and fruits used as vegetable.
Bauhinia vahlii Wight & Arn. / Caesalpinaceae Mahul / Fls: June - Aug ; Frts: Dec - Jan./ (NAW-1365) 11-12-16	N-21^0.28.300_ E-077^{0}24.195 699m	T	2	16	0.31	Stem Fruits	Decoction of bark is used to treat jaundice. Fruits are used as vegetable or eaten raw and used to cure infertility.
Bombax ceiba L. / Bombacaceae Katasavar / Fls: Feb; Frts: Mar. (NAW-1366) 11-12-16	N-21^0.28.447_ E-077^{0}23.954 685m	T	4	13	0.25	Root Stem bark	Root bark crushed with garlic (*Allium sativum*) and the extract administered (Spoonfuls once a day for 5 days after menstruation) for menstrual disorders. Stem bark ground with urine of infant and paste mildly heated and applied on blisters and ulcers.
Buchanania lanzan Spreng./ Anacardiaceae Charodi / Fls: Jan - Feb; Frts.: Apr- May (NAW-1367) 24-03-15	N-21^0.28.423_ E-077^{0}23.848 677m	T	4	8	0.15	Stem bark	Stem bark ground with soaked rice (*Oryza sativa*) and the filtrate administered for chest pain by kurku 2 spoonful twice a days for 5 days. Stem bark paste mixed with castor oil (*Ricinus communis*) and applied on boils and ulcers.
*Butea monosperma (*Lam.) Taub. / Papilionaceae Palas / Fls & Frts.: Feb - Mar./ (NAW-1368) 24-12-16	N-21^0.28.818_ E-077^{0}23.996 629m	T	1	24	0.47	Stem bark	Stem bark crushed with oil (*Sesamum indicum*) and the filtrate administered for antifertility (One spoonful twice a day for 7 days after menstruation).

Cayratia auriculata (Roxb.) Gamble / Vitaceae Kumbli / Fls.& Frts.: Sep-Nov./ (VBMV-1740) 24-11-16	N-21^0.28.837_ E-077^{0}23.082 624m	H	2	16	0.31	Leaves	Leaves ground with turmeric (*Curcuma longa*) and the paste applied externally for chicken pox and is also used to feed domestic cattle.
Chlorophytum tuberosum (Roxb.) Baker Liliaceae/ Musli / Fls.: June & frts.: Sep (VBMV-1523) 03-09-14	N-21^0.28.900_ E-077^{0}23.187 622m	H	4	16	0.31	Tubers Leaves	Tubers collected by tribal people and are good demand from traders as they are sweet in taste and also used against indigestion. Leaves used as vegetable.
Cissampelos pareira L./ Menispermaceae Pahadmul / Fls.: Aug-Oct; Frts.: Oct. Nov. (VBMV-1488) 20-11-16	N-21^0.28.455_ E-077^{0}23.848 685m	C	3	12	0.23	Tubers Leaves	Tuber extract mixed with a pinch of salt administered for chest pain and stomach pain. 2 spoonfuls thrice a day till cure. Leaves crushed with that of *Andrographis paniculata* and *Pongamia pinnata* and the extract given orally to kill intestinal worms (3 spoonfuls thrice a day for 3days).
Costus speciosus (J. Koenig) Sm. / Zingiberaceae/Jangli adrak / Fls: Aug; Frts: Nov./ (VBMV-1742) 04-09-14	N-21^0.28.489_ E-077^{0}23.824 685m	H	3	15	0.29	Rhizome	Rhizome ground with *Pennisetum americanum* (bajra) and formulated as tablets (eaten continuously for almost 21 days) for muscular rheumatism (waat).
Curcuma pseudomontana J. Graham / Zingiberaceae Kuksuma root / Fls & Frts. July-Aug. (VBMV-1028) 22-05-14	N-21^0.28.507_ E-077^{0}23.811 685m	H	3	10	0.19	Roots Tubers	Root powder one spoonful twice a day with milk use in tuberculosis (T.B). Tuber extract administered for jaundice (2 spoonfuls twice a day till cure). Warm tuber paste applied on body swelling and on head for cooling effect. Boiled tubers ground with a pinch of salt and given orally for increased lactation.
Dendrocalamus strictus (Roxb.) Nees / Poaceae/ Katbans / Flower not seen. (VBMV-1034) 04-05-14	N-21^0.28.893_ E-077^{0}23.152 627m	T	1	18	0.35	Leaves Grains	Tender leaves boiled, cooled and tied over the eyes for sores. Tender sprouts used as vegetable. Grains boiled and eaten.

Desmodium gangeticum (L.) DC. / Papilionaceae Chikum ghass / Fls & Frts: Oct- Nov./ (VBMV-1746) 24-11-16	N-21^0.28.886_ E-077^{0}23.286 632m	H	3	12	0.23	Roots	Roots ground with garlic (*Allium sativum*) and made in to pills and administered for epilepsy by korku 2-3 pills twice a day till cure.
Dioscorea hispida Dennst. / Dioscoreaceae/ Baichan / Fls & Frts.: Sep. Nov. (NAW-1296) 20-11-16	N-21^0.28.892_ E-077^{0}23.247 630m	H	2	14	0.27	Tubers	Tubers kept in running water for a day and boiled with the leaves of tamarind and water filtered then cooked and eaten.
Cassia fistula L. / Caesalpinaceae Amaltas / Fls.: May – Aug; Frts.: Oct - Feb. (VBMV-1366) 20-11-16	N-21^0.28.524_ E-077^{0}23.785 659m	T	1	22	0.43	Stem Leaves	Tender leaves cooked with juice of tamarind eaten as vegetable and also used as a purgative. Stem bark pieces tied together and worn as necklace for malarial fever. Tender leaves ground with turmeric and this paste is applied for skin diseases.
Cassia obtusifolia L. / Caesalpinaceae/ Tarota / Fls, & Frts. : Aug.- Nov. (VBMV-1365) 22-11-16	N-21^0.28.497_ E-077^{0}23.661 654m	S	3	8	0.15	Whole Leaves	Whole plants crushed and the extract administered for epilepsy (two spoonfuls once a day for 15 days). The leaf paste applied for cuts, wounds and scorpion stings. Tender leaves used as vegetable.
Clerodendrum serratum (L.) Moon / Verbenaceae Bharanga / Fls-Frts.: Sep.- Dec (NAW-1531) 09-05-14	N-21^0.28.902_ E-077^{0}23.352 648m	S	2	9	0.17	Roots	Roots crushed with that of *Rauwolfia serpentina* and the filtrate administered for fever stomach pain and menstrual disorders (3 spoonfuls once a days for 5 days).
Colebrookea oppositifolia Sm./ Lamiaceae Bhaman / Fls. & Frts.: Dec.- Mar. (NAW-1369) 22-12-16	N-21^0.28.898_ E-077^{0}23.415 657m	S	2	18	0.35	Stem bark Infloresence	Stem bark crushed and the filtrate administered for giddiness (2 spoonfuls twice a day for 3 days). The dried inflorescence used in sorcery.

Curculigo orchioides Gaertn. / Amaryllidaceae Kali musli / Fls. & Frts: June – Sep (VBMV-1750) 22-05-14	N-21^0.28.898_ E-077^{0}23.415 657m	H	3	8	0.15	Tuber	Tuber extract administered for asthma and piles and extract administered for asthma and piles (2 spoonfuls twice a day till cure) and the paste applied on cuts. Raw tuber eaten for dysentery.
Euphorbia hirta L. / Euphorbiaceae/ Dhodhi / Fls. & Frts: Throughout Year/ (NAW-1370) 09-11-15	N-21^0.28.596_ E-077^{0}23.593 646m	H	1	26	0.50	Leaves Latex	Tender leaf extract mixed with sugar administered for dysentery (2 -3 spoonfuls thrice a day). Latex applied on cuts by kurku.
Ficus benghalensis L./ Moraceae/ Wad / Fls.: Feb - June; Frts: Nov.- Jan. (NAW-1107) 08-11-15	N-21^0.28.574_ E-077^{0}23.588 675m	T	2	6	0.11	Latex	Latex applied for breast ulcer.
Ficus religiosa L./ Moraceae/ Piple / Receptacle: Feb –May. (NAW-1108) 08-11-15	N-21^0.28.447_ E-077^{0}23.954 685m	T	2	27	0.52	Stem bark	Stem bark extract mixed with buttermilk administered for paralysis (3 spoonfuls twice a day for 30 days). Branches used in festivals and religious ceremonies.
Adina cordifolia (Roxb.) Hook. f. / Rubiaceae/Haldu / Fls : June-July; Frts. : Feb.-May. (NAW-1373) 22-12-16	N-21^0.28.895_ E-077^{0}23.462 655m	T	2	15	0.29	Root Stem	Root and Stem bark extract mixed with oil of *Sesasum indicum* administered for antifertility (2 spoonfuls thrice a day for 9 days after menstruation).
Hemidesmus indicus (L.) R. Br. Ex Schult. / Periplocaceae Dhodhkadi / Fls . & Frts.: Sep.-Jan. (VBMV-1120) 09-05-14	N-21^0.28.846_ E-077^{0}23.641 675m	H	2	24	0.47	Roots	Roots crushed with garlic (*Allium sativum*) and the extract administered for menstrual disorders (2 spoonfuls twice a day for 5 days). Root powder along with goat milk given orally for impotency and also to tone the health (3-4 spoonfuls once a day for 30 days). Root powder with garlic administered orally as lactagogue.

Holarrhena antidysenterica (Roth) Wall. ex. A. DC. / Apocynaceae Kudda. / Fls.: Apr - July; Frts.: Nov. - Feb. (NAW-1564) 04-05-14	N-21^0.28.888_ E-077^{0}23.573 660m	T	3	12	0.23	Root Stem Latex	Root bark ground with the roots of *Hemidesmus indicus* and the paste made twice a day till cure. Stem bark ground with black pepper and the paste made into pills administered for cough (1-2 pills twice a day for 3 days). Latex applied on cuts.
Lagerstroemia parviflora Roxb. / Lythraceae Landiya / Fls . : Apr.-May; Frts. : Dec.- Jan. (NAW-1142) 08-11-15	N-21^0.28.617_ E-077^{0}23.561 637m	T	2	18	0.35	Leaves	Leaves crushed with that of *Magnifera indica* and *Syzygium cumini* and the filtrate administered for stomach pain. Wood also used for making agricultural implements and house construction.
Lannea coromandelica (Houtt.) Merr. / Anacardiaceae Moin / Fls . : Feb. – Apr.; Frts. : May. - June. (VBMV-1330) 07-01-17	N-21^0.28.607_ E-077^{0}23.459 645m	T	3	16	0.31	Stem bark	Stem bark decoction administered for chest pain gastric trouble and muscle pain (1 spoonful twice a day till cure). Stem bark paste or gum applied on cuts and wounds also used for head ache.
Leea macrophylla Roxb. ex Hornem. / Leeaceae Hattikand / Fls. & Frts. : Oct.-Dec. (VBMV-1156) 09-05-14	N-21^0.28.820_ E-077^{0}23.687 683m	H	3	14	0.27	Root bark Ste	Root bark extract administered orally for stiff joint and rheumatic pains by 2 spoonfuls once a day till cure. Stem bark paste mixed with castor oil mildly heated and applied on cuts and wounds.
Madhuca indica J.F. Gmel. / Sapotaceae Moha / Fls. : Feb.-Mar ; Frts. : June-July. (VBMV-1226) 09-05-14	N-21^0.28.742_ E-077^{0}23.752 707m	T	2	18	0.35	Roots	Root paste applied on abscess boils. Seed cooked and eaten.
Martynia annua L. / Martyniaceae Moha / Fls. & Frts. : Sep.-Nov. (VBMV-1199) 11-12-16	N-21^0.28.710_ E-077^{0}23.797 711m	H	2	12	0.23	Roots Leaves	Roots decoction administered orally for bronchitis by Chenchus. Leaf paste applied over head for cooling effect and headache.

Miliusa tomentosa (Roxb.) J. Sinclair / Annonaceae Humba / Fls. : May-June; Frts. : June - July. (VBMV-1200) 22-11-16	N-21^0.28.497_ E-077^{0}23.661 659m	T	3	16	0.31	Fruits	Fruits edible and Wood also used for making agricultural implements and for house construction.
Mitragyna parviflora (Roxb.) Korth. / Rubiaceae Kalam / Fls . :May.- June; Frts. : Mar.-Apr. (NAW-1203) 07-01-17	N-21^0.28.902_ E-077^{0}23.352 648m	T	2	14	0.27	Stem Leaves	Stem bark crushed with that of *Haldina cordifolia* and the extract administered for peptic ulcers (2 spoonfuls twice a day for 3 days). Stem bark extract missed with jaggery given orally for dysentery (2 spoonfuls twice a day, till cure). Leaf juice poured into eyes for jaundice.
Sida cordata (Burm. f.) Borss. Waalk. / Malvaceae Bhumi / Fls . & Frts. : Aug.- Jan. (VBMV-1146) 24-11-16	N-21^0.28.617_ E-077^{0}23.561 637m	H	2	13	0.25	Leaves	Leaf juice mixed with goats milk administered for paralysis (2 spoonful twice a day till cure). Leaf paste applied for scorpion sting.
Sterculia urens Roxb. / Sterculiaceae Sardol / Fls.: Dec. - Feb; Frts.: Mar. - Apr. (NAW-1376) 03-09-14	N-21^0.28.693_ E-077^{0}23.810 700m	T	3	24	0.47	Stem Gum	Stem bark ground with turmeric, the filtrate mildly heated, and administered for rheumatic pains and peptic ulcers (2 spoonfuls twice a day for 5 days). Gum dissolved in water given orally for cooling the body and also to cure dysentery.
Syzygium cumini (L.) Skeels / Myrtaceae Jamun / Fls . : Apr. – June;Frts. : July.- Aug. (VBMV-1108) 04-05-14	N-21^0.28.632_ E-077^{0}23.867 697m	T	2	34	0.66	Stem Fruits	Stem bark extract administered for leucorrhoea and also for cough (2 spoonfuls twice a day for 5 days). Stem bark ash mixed with niger oil and applied over burns and wounds. Crushed stem bark used as fish-poison. Fruits edible.
Syzygium heyneanum (Duthie) Gamble / Myrtaceae/ Jamon / Fls. : Apr. – June & Frts. : July.-Aug/ (NAW-1344) 04-05-14	N-21^0.28.898_ E-077^{0}23.415 657m	T	3	13	0.25	Fruits	Fruits powder used to control diabetes.

Terminalia chebula Retz. / Combretaceae Hirda / Fls. :Mar. – May Frts.: May.-June. (NAW-1377) 07-01-17	N-21^0.28.895_ E-077^{0}23.462 655m	T	3	14	0.27	Stem Fruits	Fruits ground with the latex of *Ficus racemosa* and the paste applied over for muscle pain and rheumatic pain. Fruit paste mixed with breast milk, administered orally to infants for cough, and also applied on wounds. Crushed stem bark and fruits used as fish-poison.
Wrightia tinctoria R. Br. / Apocynaceae Dodhi / Fls . :Mar.-May; Frts : Oct.-Feb. (NAW-1124) 07-05-14	N-21^0.28.908_ E-077^{0}23.513 655m	T	2	16	0.31	Latex	Latex applied on cuts and also 3-5 drops for preparing instant curd. Bark fiber used for making cordage.
Woodfordia fruticosa (L.) Kurz / Lythraceae Dhin / Fls. : Jan.-Apr & Frts. : Apr.- May (NAW-1378) 07-11-15	N-21^0.28.593_ E-077^{0}23.897 701m	T	3	12	0.23	Stem Leaves	Dried stem bark added to toddy to enhance taste and intoxication. Leaves crushed and mildly heated, gently massaged for rheumatic pain. Leaves boiled in water and taken bath for body pains.
Zizipus xylopyrus (Retz.) Willd. / Rhamnaceae Gorgot / Fls.: Apr. - June & Frts.: Dec. - Jan. (NAW-1286) 07-01-17	N-21^0.28.508_ E-077^{0}23.891 697m	T	2	18	0.35	Stem Fruits	Stem bark paste made into pills and administered orally for cholera by taking 2 pills thrice a day for 2 days. Fruits edible.
Ensete superbum (Roxb.) Cheesman / Musaceae Jangli kela / Fls . & Frts. : Oct. - Jan. (NAW-1287) 04-05-14	N-21^0.28.428_ E-077^{0}23.926 689m	H	3	12	0.23	Roots Fruits	Root powder mix with curd and crystal sugar (1 glass daily) for menstruation problems. Fruits and pithy inner part of stem eaten by local people.
Anisochilus carnosus (L.f.) Wall. / Lamiaceae Chikhal ghass / Fls . & Frts. : Sep.-Nov (NAW-1690) 07-01-17	N-21^0.28.466_ E-077^{0}23.691 692m	H	2	16	0.31	Inflorescence	Inflorescences burnt in a plate and the ash mixed with coconut oil is applied to boils and pimples.
Zizyphus mauritiana Lam. / Rhamnaceae Bor / Fls.: Dec. - Feb & Frts. : Feb. - Apr.	N-21^0.28.632_ E-077^{0}23.513	T	2	14	0.27	Fruits	Tender fruits crushed and the extract administered for diarrhea (2 spoonfuls twice a day for 5 days) and fruit paste applied on head

(NAW-1379) 07-01-17							for cooling effect. Fruits edible.
Emblica officinalis Gaertn. / Euphorbiaceae Aola / Fls.: Feb. - Mar & Frts.: Oct. - Dec. (VBMV-1092) 22-11-15	N-21^0.28.461_ E-077^{0}23.958 691m	T	2	22	0.43	Leaves Fruits	Fruits pickled by korku tribals. Leaf ash mixed with oil applied to burnt skin which prevents black scar formation.
Cyathocline lutea law ex Wight / Asteraceae Piwali Gangawan / Fls &Frts: Feb. – April (NAW/-1380) 04-05-14	N-21^0.28.818_ E-077^{0}23.996 629m	H	4	9	0.17	Roots Whole	Root decoctions are used to relieve stomach pains. Crushed plant is applied on wounds as antimicrobial. Decoctions of whole plant are used as anti-helminthic.

Life Form (Habit of plant): H= Herb; S= Shrub; T= Tree; C= Climber

Abundance: 1 = very common; 2 = common; 3 = uncommon; 4 = rare; 5 = very rare

FC: Frequency Citation

RFC: Relative Frequency Citation

Table No. 2: Definitions of Abundance categories

Value	Category	Definition
1	Very common	Easy to find close to all houses
2	Common	Close to houses, but not always all houses
3	Uncommon	Close to few houses, but very scarce in the natural environment
4	Rare	Hard to find in valleys (inhabited area)
5	Very rare	Hard to find at the scale of the valley

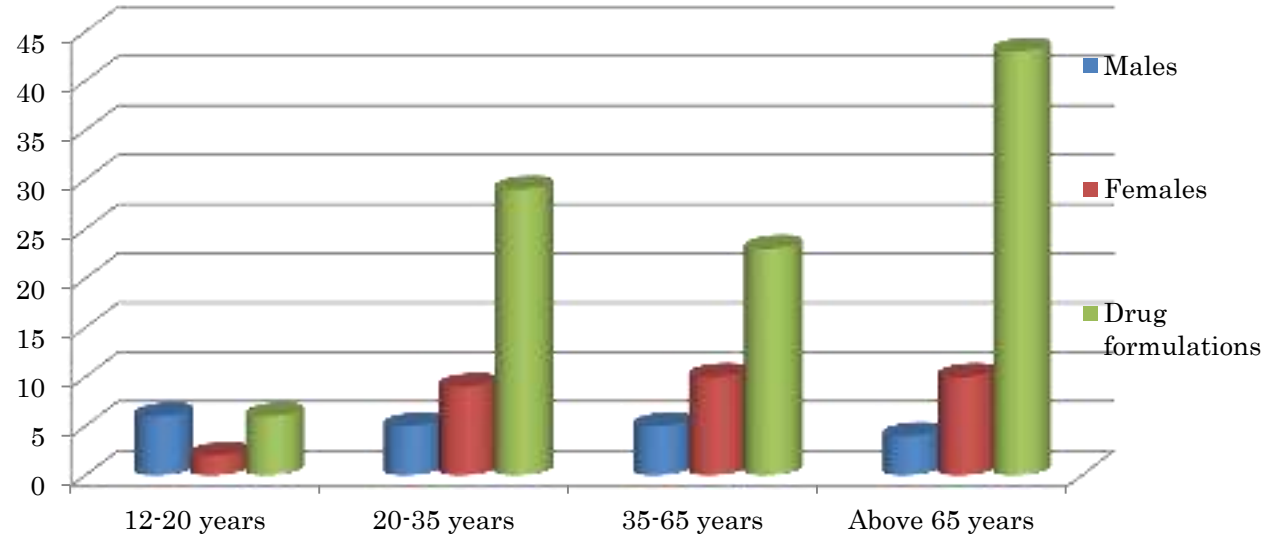


Figure 4: Distribution of gender, age groups and drug formulations of the interviewed informants

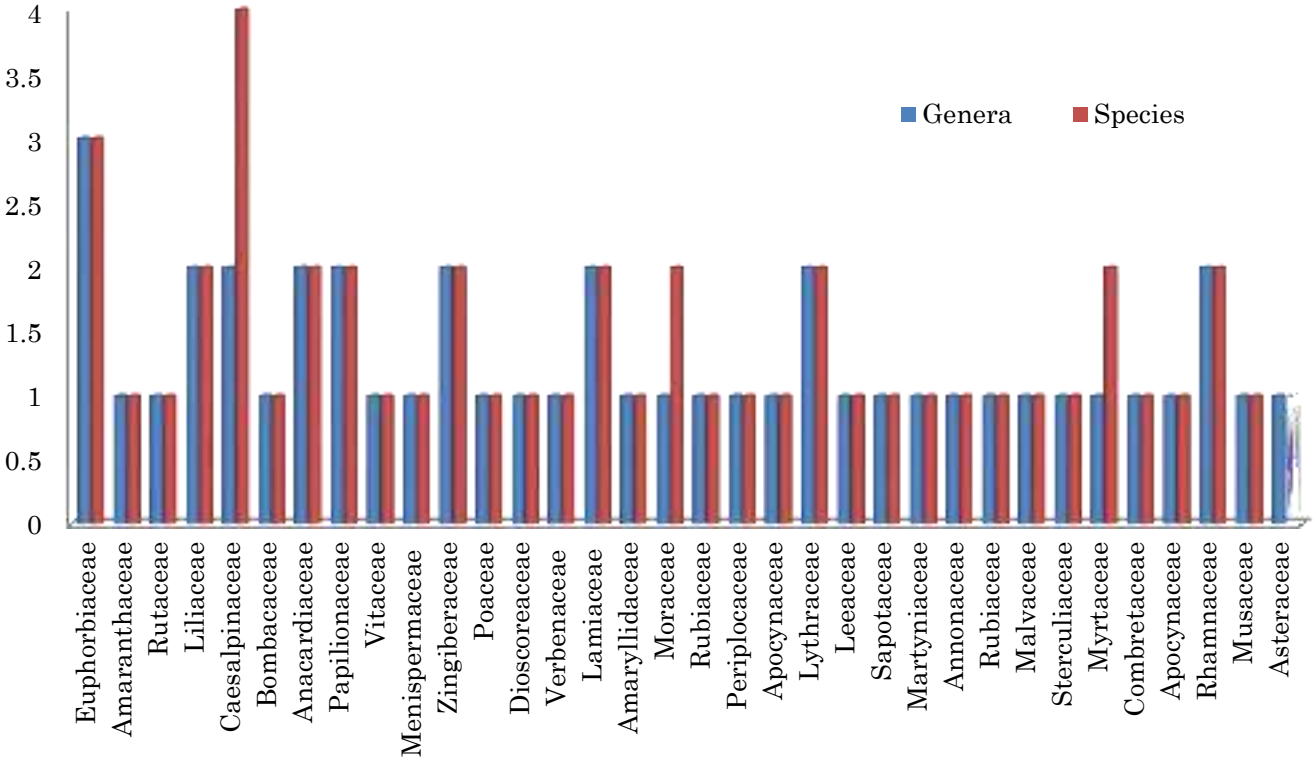


Figure 5 : Familes with their respective genera and species studied

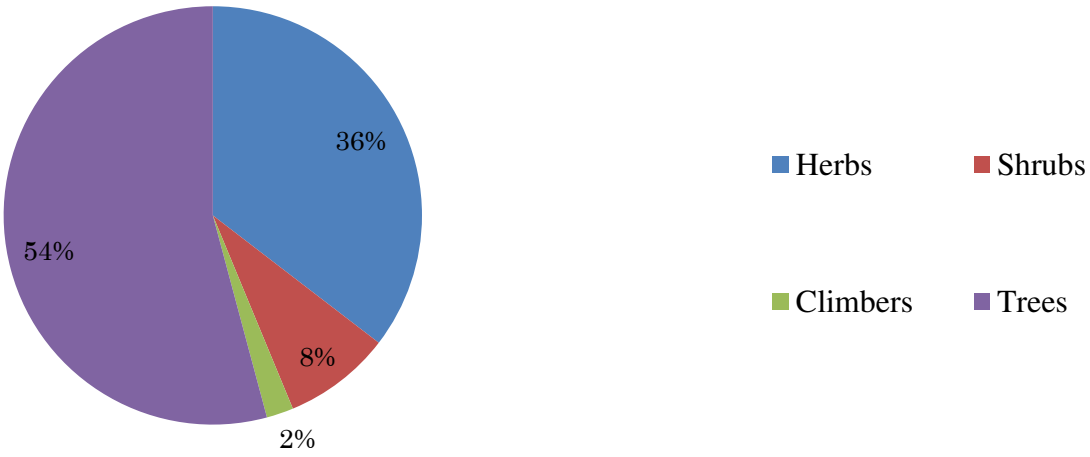


Figure 6 : Life form representation of medicinal plants

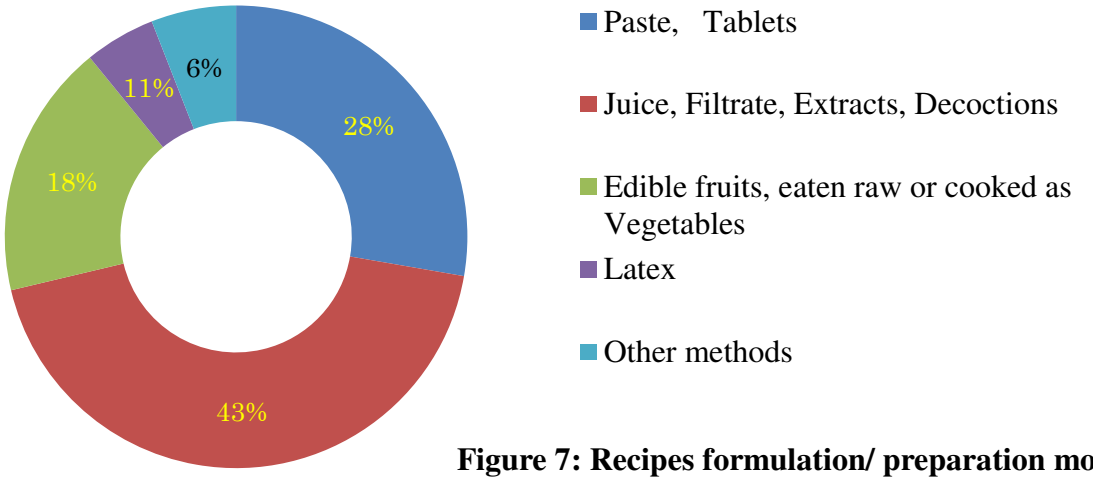


Figure 7: Recipes formulation/ preparation mode

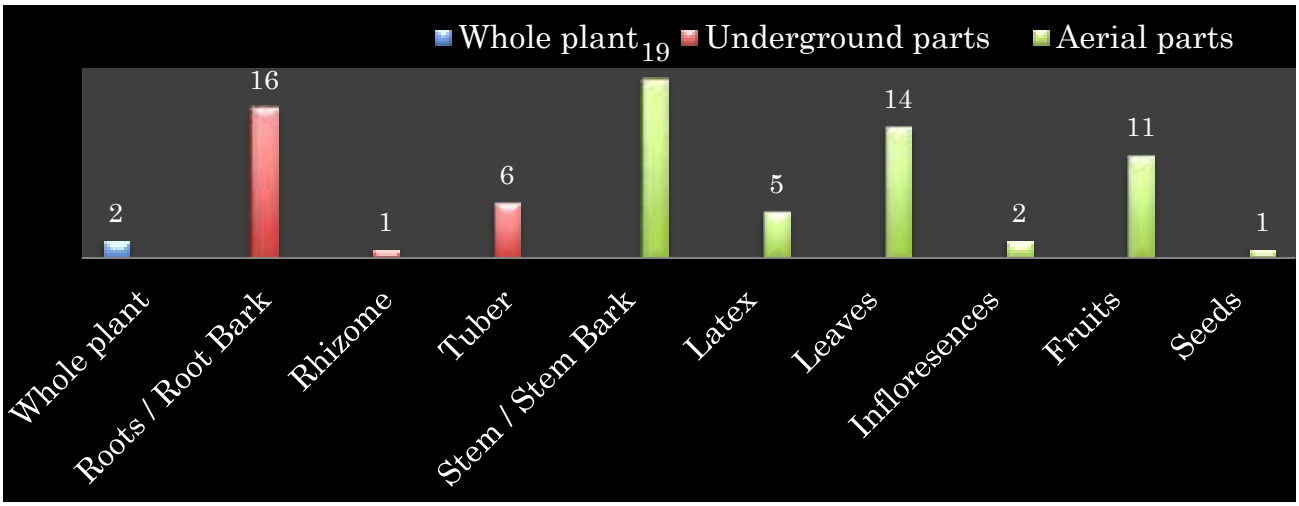


Figure 8: Plant parts used for Herbal drug preparation and Utilization

Photoplate 1

Photoplate 1 showing various pictures of authors taken during the collection and interviewing of the persons of the korku tribe.

Photoplate 2

Bahaunia vahilli

Chlorophytum tuberosum

Clerodendrum serratum

Costus speciosus

Curcilago orchoides

Curcuma pseudomontana

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Photoplate 3

Leae microphylla

Dioscorea bulbifera

Sterculi urens

Wrightia tinctoria

Cyathocline lutea

Butea monosperma

4. CONCLUSION

This study contributed to the establishment of an inventory of plant based medicines used by korku tribe inhabited in Chikhaldara of Melghat Tiger Reserve, Amravati, Maharashtra, India. A total of 51 inhabitants were interviewed during the survey to document the indigenous knowledge about the use of wildly growing medicinal plants. The paper summarizes a adata of 48 plant species used to treat 101 common ailments. RFC values ranked *Syzygium cumini; Ficus religiosa, Euphorbia hirta, Butea monosperma* as top most cited and well known species in the area. A vast number of ailments were cured by this community with the help of these locally growing medicinal plants. The data provided by informants of the korku tribe clearly shows that they are still dependent on the indigenous knowledge of medicinal plants. This novel information has provided rich ethnopharmacological knowledge that will provide basis for new avenues in future for the pharmacological screening of novel natural compounds which can be used to improve healthcare systems. However, detailed pharmacological investigations must be carried out to improve the use of these medicinal plants globally. The study has also provided good information regarding the used plant parts, formulation and dosage which can be used as medicine. It will also provide various socioeconomic dimensions associated with the common people.

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CONFLICT OF INTEREST

The authors declare that they have no competing interests with any author, agency or institution. And no funding was provided by any agency, institution or any individual.

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Cytotoxic Properties of *Curcuma inodora* Blatt. Leaf Against (Miapaca-2) Human Pancreatic Carcinoma Cell Line

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Abstract:

In the present study cytotoxic effect of Curcuma inodora Blatt. aqueous extract of leaf was evaluated on human pancreatic carcinoma cell lines (MiaPaca-2). MiaPaca-2cells were cultured in a DMEM medium and incubated with different concentrations (10, 20, 30, 40 and 50µg/ml)of aqueous extract of Curcuma inodora leaf for 48 hrs. with standard positive control chemotherapeutic agent viz. 5-Flurouracil.Cell viability was assessed by MTT assay.Cell proliferation was measured using a calorimetric method based on the ability of metabolic active cells to cleave the yellow tetrazolium salt MTT to an insoluble purple formazan crystal. The soluble formazan dye was directly quantified using ELISA plate reader. The aqueous extract of Curcuma inodora leaf decreases the viability in malignant cells in a dose dependent manner. The IC_{50} value in MiaPaca-2 cells was determined as 115.29 ± 17.01µg/ml. It may be concluded that Curcuma inodora can cause cell death inMiaPaca-2 cells which can be considered as a promising chemotherapeutic agent in pancreatic cancer treatment.

Keywords: *Curcuma inodora*, leaf, Cytotoxicity, Pancreatic cancer cells, MTT assay, 5-Flurouracil.

Introduction:

In the modern world it has been realized the herbal drugs strengthen the body system specifically and selectively without side effects. The importance of traditional herbal medicinal system has now gained vital importance in developed and underdeveloped countries. India is blessed with rich and diverse heritage of cultural traditions. These traditions are associated with use of wild plants as medicinal herbs.The wild plants offer a good material for studying the phytochemical compounds responsible for curative properties of the plants. In the developing nations, numerous types of wild plants are exploited as a source of food and hence provide an adequate level of nutrition to the inhabitants (Borkataky *et al*., 2013).

Cancer has been thought to be a preventable disease due to its slow development and progression, taking many years to become invasive in a step by- step manner (Yao *et al*., 2011). Such property provides a great opportunity not only for early detection but also for prevention of the disease progression. Over the past several decades, there has been a particular interest in the role of medicinal plant extracts in cancer prevention. Plants are rich sources of chemically diverse compounds, many with beneficial properties to human health. Consequently, about 50% of the anticancer therapeutic agents known are derived from plants (Balunas and Kinghorn, 2005). Chemical compounds were extracted from plant origin such as Taxol and Vinca alkaloids acts to destabilize the microtubules of cancer cells, preventing the rapid proliferation of tumors (Prasain and Barnus, 2007).

Pancreatic cancer (PC) is a highly aggressive human malignancy worldwide with an extremely poor prognosis (Siegel *et al*., 2016). For the majority of the PC patients, the only therapeutic promise is cytostatic treatment using standard chemotherapeutic drugs such as gemcitabine and 5-FU (5-fluorouracil) or their combination (Michl and Gress, 2013). However, the median survival time of PC patients is only about six months mostly due to an almost

complete chemotherapy resistance, and the dismal 5-year survival is currently approximately 2% (Ramfidis *et al*.,2014) Therefore, there is a dire need for both new biomarkers with prognostic and predictive value and newer therapeutic options for this disease. MIA PaCa-2 cell line is a primary tumor currently used in vitro models to study pancreatic carcinogenesis. Natural compounds provided many effective anticancer agents in current use.

Curcuma inodora Blatt. belongs to family-Zingiberaceae, commonly known as scentless turmeric. Traditionally, it is used in the treatment of muscular pain, psychosomatic disorders and constipation. Scentless turmeric is used by the tribal as a hair tonic and to cure wound. Curcuma is the widely used Rasayana in the field of Ayurvedic medicine. Curcumin (diferuloylmethane) is a polyphenol derived from the *Curcuma longa* plant, has several pharmacologic properties under both pre-clinical and clinical conditions (Prasad *et al*., 2014).Tribal uses of *Curcuma inodora* gives an importance to this plant to scientific community and no scientific literature is available to explore the use of anticancer effect of *Curcuma inodora*. Hence, present study was attempted to evaluate the cytotoxic properties of aqueous extract of *Curcuma inodora* leaf in the inhibition of cell proliferation by using MTT assay.

Materials And Methods

Materials

Selection and Collection of Plant: The leaves of *Curcuma inodora* were collected from Melghat region of Amravati District in the month of June to September.

Curcuma inodora Habitat

Identification and Authentication of plants:

The plant was identified with the help of standard floras (Sharma et al., 1996; Dhore, 2002) and authenticated by Taxonomist Dr. S.P.Rothe Professor and Head Department of Botany, Shri. Shivaji Science College, Akola.

Preparation of test solution:

1 gm powder of leaf part was crushed in mortar and pestle by adding 10 ml. DW, then centrifuge at 4000 rpm for 10 min. Concentrations (10-50 µg/ml) were prepared by using supernatant accordingly.

In-vitro Cytotoxic Activity Assay

Cell Line and Culture Medium:

The Human Pancreatic Carcinoma cell (MiaPaCa-2) was procured from the National Centre for Cell Sciences (NCCS), Pune, and Maharashtra. These cells were grown in Dulbecco's Minimum Essential Medium (DMEM) (GIBCO by Life Technologies) which contained, 1.5 g/L sodium bicarbonate,10% fetal bovine serum (GIBCO by Life Technologies) and 1X Antibiotic-Antimycotic solutions (Invitrogen). All cells were maintained at 37°C, 5% CO_2, in a 90% humidified atmosphere in CO_2 incubator (Galaxy Make) Cells were passed after every 5th days. Cells were used in experiments during the linear phase of growth (fig.3.1) and all experiments were carried out in 96 well tissue culture plates. The cytotoxic activity was measured using MTT

(3-(4,5dimethylthiazol- 2-yl)-2,5-diphenyltetrazolium bromide) assay [Berridge MV]. Briefly, 2 X 10^4cells/well were seeded in 96-well microliter plates.

Cell Treatment Procedure

Cells were treated with various working concentrations (10-50 µg/ml) of aqueous extract of leaf and standard anticancer drug i.e. 5-Fluorouracil (5-FU) (10-50 µg/ml) for 48 hours. At the end of incubation period, the medium was replaced by 150µl fresh medium and 50 µl MTT (1mg/mL) was added to each well, followed by an incubation period for a further 4 hours at 37°C. Later, 150 µl of DMSO was added to each well for solubilization of the formazan products. Absorbance was taken at 630 nm using a Bio-Tek microplate reader. The percent cell cytotoxicity was calculated by using the following formula.

$$\% \text{ Cytotoxity} = \frac{(\text{Absorbance of control sample} - \text{Absorbance of treated sample})}{\text{Absorbance of control sample}} X\,100$$

Statistical Analysis

The results are presented as means ± SD of three independent experiments. Statistical differences among means were determined by one way ANOVA. Differences were considered significant at $P<0.05$. The IC_{50} values were calculated using Graph Pad Prism 5.0 (Graph Pad Software Inc., San Diego, CA). Every experiment included a set of negative controls (untreated cultures) and positive control treated with 5-Flurouracil (Standard anticancer drug).

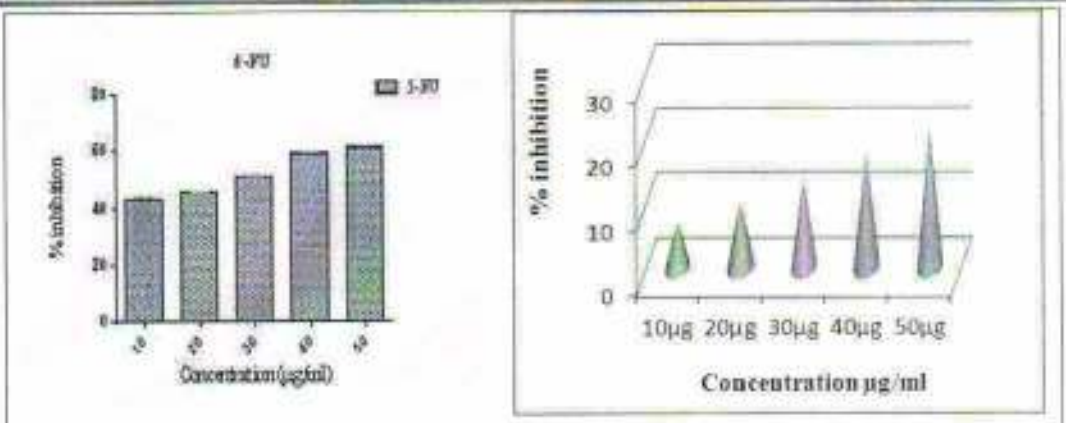
Results And Discussions:

The results for cell growth inhibition by aqueous extracts of the leaf against MIAPaCa-2 cell lines at 10-50µg/ml concentrations is shown in Table 1 and graphically represented in Fig. 1. The aqueous extract of Curcuma inodora leaf was tested in vitro for its potential human cancer cell growth inhibitory effect on MIAPaCa-2 cancer cell line using MTT assay, a non radioactive, fast and economical assay widely used to quantify cell viability and proliferation. In the present study MIA paca-2 cells showed growth inhibition in a dose dependent manner when treated with aqueous extract at concentrations ranging from 10-50µg/ml (Table 1 & Fig.1). The percentage of dead cells for each concentration was found to be 7.14, 10.23, 13.80, 17.85 and 21.66. The 50% cytotoxic effect (IC_{50}) of aqueous extract of Curcuma inodora leaf was found to be 115.29± 17.01µg/ml. The IC_{50} for the 5-FU standard control was found to be 25.9 ±0.68µg/ml.

Table 1: Effect of aqueous extract of Curcuma inodora leaf on growth of MIAPaCa-2 cell line after the incubation for 48 hrs.

*Results are represented as an average of three± replicates[**AQ**-Aqueous extract; 5-FU- 5-Flurouracil]

Conc. (µg/ml)	% inhibition	
	AQ	5-FU
Control	0	0
10	7.14 ± 0.71	43.02 ±1.00
20	10.23 ± 1.79	45.78 ± 0.10
30	13.80 ± 1.09	51.02 ± 0.36
40	17.85 ± 1.88	59.37 ± 0.72
50	21.66 ± 0.82	61.07 ± 0.52
IC_{50}	**115.29 ± 17.01**	**25.9 ± 0.68**



A B

Fig. 1: Cytotoxic effect of aqueous extracts of *Curcuma inodora* leaf on growth of MIAPaCa-2 cells after the incubation for 48 hrs. using MTT assay. (A) 5-FU as standard (positive control) and (B) % inhibition of CU-L extract. Data are represented by mean ± SD (n=3). Statistical significance between untreated and treated cells was determined using one-way ANOVA where $p < 0.05$ verses untreated control cells.[AQ-Aqueous extract; 5-FU- 5-Flurouracil]

The cytotoxicity assay is based on the capacity of mitochondria succinate dehydrogenase enzymes in living cells to reduce the yellow water soluble substrate tetrazolium salt 3-(4,5 dimethyl thiazol-2-yl)-2-5-diphenyl tetrazolium bromide (MTT) into a blue colored i.e. formazan crystals which is measured spectrophotometrically (Masters, 2000; Mosmann, 1983). Since reduction of MTT can only occur in metabolically active cells, the level of activity is a measure of the viability of the cells. The number of cells was found to be proportional to the extent of formazan production by the cells used (Francis and Rita, 1986).In the last few decades, human cancer cell lines have aggregated an accessible, easily usable set of biological model to examine cancer biology (Green, 2003). The utility of cell lines acquired from tumor allows the investigation of tumor cells in a simplified and controlled environment (Arya *et al.*, 2011).

MTT proliferation assay was carried out to determine the growth rate of cells. In this study, the aqueous extract of *Curcuma inodora* leaf has indicated significant growth inhibition on Miapaca-2 cell line. The aqueous extract treatment on Miapaca-2 cells lines showed significant decrease in growth rate compared with control. The qualitative phytochemical analysis of aqueous extract of *Curcuma inodora* leaf detected the presence of carbohydrate and glycosides, protein and amino acids, alkaloids, phenolic compounds & flavonoids, phytosterols, saponins and terpenoids (Ghurde, 2018) which could be responsible for this activity. Flavonoids have been found to possess antimutagenic and anti-malignant effects (Masmaan, 1983). Moreover it has protective effect against cancer by their effect on signal transduction in cell proliferation and angiogenesis.

Conclusion:

The present study revealed that the aqueous extract of *Curcuma inodora* Blatt. leaf was found to be cytotoxic towards human pancreatic cancer cell line in MTT assay. The 50% cytotoxic effect (IC_{50}) of aqueous extract of Curcuma inodora leaf was found to be 115.29 ± 17.01µg/mlmay be due to thebioactive compounds. Hence present study shows the positive

efficacy of Curcuma inodora leaf for cytotoxicity towards MIA PaCa-2 cells thus suggesting the potentialtherapeutic agent in pancreatic cancer treatment in future after animal experimentation.

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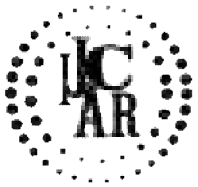

Research Article

METAPHORICAL EFFECTS OF ORGANOPESTICIDES CARBENDEZIM AND MALATHION ON THE GROWTH AND PHYSIOLOGICAL ACTIVITIES OF CYANOBACTERIA *NOSTOC COMMUNE*, VAUCHER INHABITING THE RICE FIELD OF BHANDARA DISTRICT (M.S.)

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A B S T R A C T

The effect of pesticides on Cyanobacteria (*Nostoc* ***commune*** vaucher) has been analyzed in vitro in the laboratory, for which the pure culture of *Nostoc commune* (Voucher) was treated with various concentrations of two pesticides i.e. carbendazim and malathion and its metabolic effect was analyzed using parameters like concentration of proline and protein along with change in biomass production. The result obtained in the study indicates that amount of biomass and extracellular protein was increased with enhancing incubation time as well as with increase in concentrations of pesticides but decline after certain limit. The present data obtained cleared a way that the use of high concentrations and continuous use of organophosphorus pesticide causes detrimental effect on rice field cyanobacteria.

INTRODUCTION

Several unique features of cyanobacteria such as cosmopolitan, pioneer, oxygenic photosynthesis, high biomass yield, growth on non-arable lands and on a wide variety of polluted water sources, generation of useful by-products and bio-fuels by them, enhancing the soil fertility, reducing green house gas emissions, have collectively offered these bio-agents as the precious bio-resource for sustainable development (Thajuddin and Subramanian, 2005). They are phototrophic, and naturally occur in several agro-ecosystems like paddy fields and from Antarctica to Arctic poles (Pandey et. al., 2002). Cyanobacterial biomass is the effective bio-fertilizer source to improve soil health and physico-chemical characteristics such as water-holding capacity and mineral nutrient status of the degraded lands (Nanjappan et. al, 2007.) As a beneficial microbe, cyanobacteria could play a potential role in the enhancement of agriculture productivity and mitigation of GHG emissions (Prasad et. al., 2005). It has been proposed that cyanobacteria could be the vital bio-agents in ecological restoration of degraded land (Singh et al. 1988). Cyanobacteria are the group of photosynthetic organisms which can easily survive on bare minimum requirement of light, carbon dioxide (CO_2) and water (Brouwer et. al. 1999).

The term pesticide covers a wide range of compounds including insecticide, fungicides, herbicides, rodenticides, molluscicides, nematicide, plant growth regulator (PGR) and others. There has been steady growth in the production of technical grade pesticide in India, from 5000 metric tons in 1958 to 102,240 metric tons in 1998. India ranks 10th in the world in pesticide consumption, as its total consumption amounts to about 500 million tons (Lari et. al. 2014). The Indian pesticides market is the 12th largest in the world with a value of US$ 0.6 bn. which is 1.6% of the global market (Hundal B. S., 2006; Lari et. al. 2014,) Despite increasing research efforts toward crop improvement by methods obviating the use of pesticides, agriculture remains heavily dependent on these chemicals (Gadkari, 1988). Cyanobacterial photosynthesis, growth and heterocysts differentiation is reduced or inhibited by herbicides and pesticides, such as, 2,4-D, atrazine, metsulfuron methyl (Berard *and* Benninghoff, *2001*). The biochemical constituents of cyanobactreia depend on the nature of strains, physiological state of the culture & the environment (Mounika et. al. 2018). In correlation with these studies the present analysis was carried out to evaluate the effect of two pesticides i.e. carbendazim and malathion (diethyl (dimethoxy phosphinothioyl) thiobutanedioate) on the growth and physiological activities of cyanobacteria *Nostoc commune* Voucher.

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MATERIAL AND METHOD

Sample collection, isolation and identification

The culture of Nostoc commune was isolated from rice field of Lakhandur (Bhandara), then it was sub-cultured and pure culture of *Nostoc commune* Voucher in vitro was obtained. Microscopic observation and identification was done by spreading isolated culture on glass slide and observing it under high power microscope. Pure forms of cyanobacteria were identified on the basis of morphological characteristics mentioned in Bergey's Manual of Determinative Bacteriology and Bergey's Manual of Systematic Bacteriology, 2nd ed. Vol. 1 (Buchanan and Gibbons, 1994) and Desikachary (1959).

Estimation of proline

Proline is a basic amino acid found in high percentage in basic protein. Free intracellular proline is said to play a role in plants under stress conditions. Though the molecular mechanism has not yet been established for the increased level of proline, one of the hypotheses refers to breakdown of protein into amino acids and conversion to proline for storage. Many workers have reported a several-fold increase in the proline content under physiological and pathological stress conditions. Hence, the analysis of proline in plants has become routine in pathology and physiology division of agricultural sciences (Bates, 1973).

Optimization of Biomass Production

Pure culture of *Nostoc commune* was inoculated in conical flask containing 100 ml BG-11(Andersen, 2005) broth and incubated at 30ºC for 15 days in continuously illuminated chamber at 4000 lux. The best growth medium was selected to carry out further experiments. At the stationary phase, *Nostoc commune* was harvested using centrifugation at 2000 rpm. Biomass was obtained by filtration using Whatman No. 1 filter paper and dried in hot air oven at 50ºC for 2 hrs to remove extra moisture then total biomass was weighed. Same process was followed by control test and pesticide different gradient concentration.

Protein estimation

The Lowry method (Lowry et al., 1951) was used to measure the protein content of the pretreated culture of *Nostoc commune,* The cells were pretreated with aluminum oxide for 5-min to release all the cellular protein followed by crushing. It resulted into total disruption of algal cells and longer periods of milling did not further increase the concentration of protein in the cell homogenates for liquid suspension**.** The obtained extract then analyzed for protein estimation.

Figure 1 Filtration and optimization of Biomass culture of *Nostoc commune*

RESULT

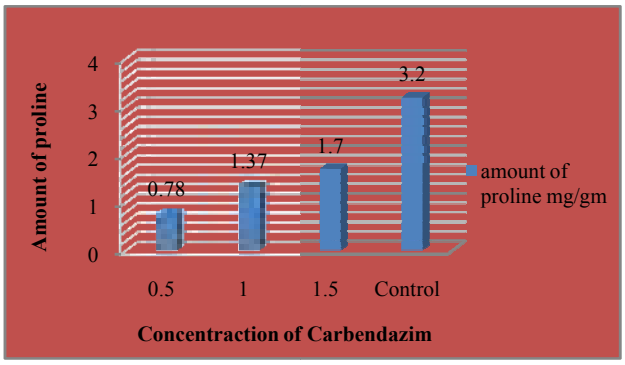

Fig 2 Amount of proline in culture extract of *Nostoc commune* in different concentrations of pesticide Carbendazim, after 15 days incubation

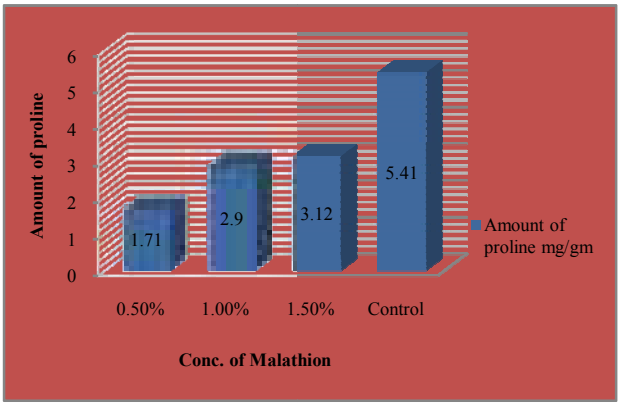

Fig 3 Amount of proline in extract of *Nostoc commune* in different con .of pesticide Malathion after 15 days incubation

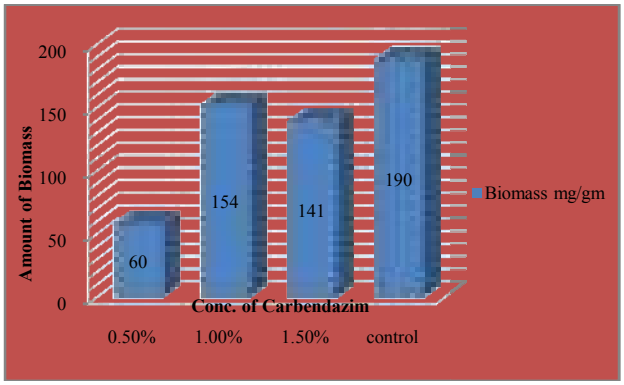

Fig 4 Total biomass estimation of Nostoc commune in different concentrations of pesticide Carbendazim after 15 days incubation

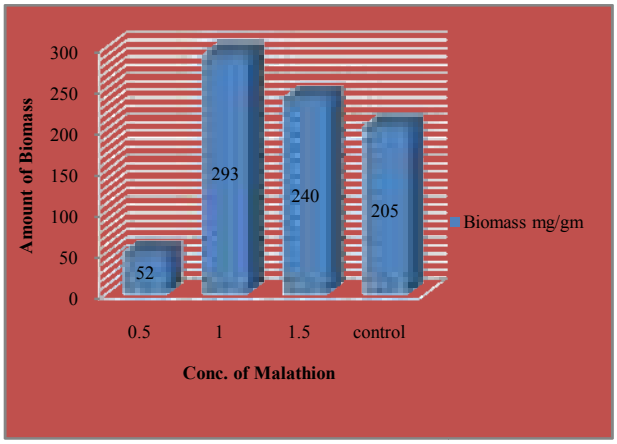

Fig 5 Biomass estimation of Nostoc commune in different concentration of pesticide Malathion after 15 days incubation

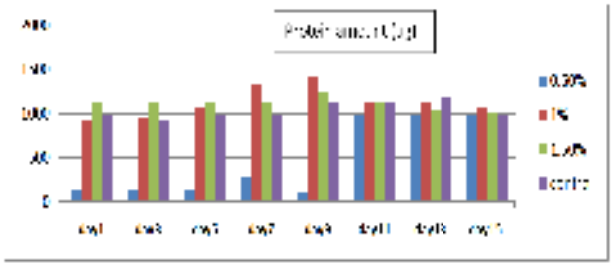

Fig 5 Total proteins in culture of Nostoc commune in different concentration of pesticide Carbendazim during15 days incubation

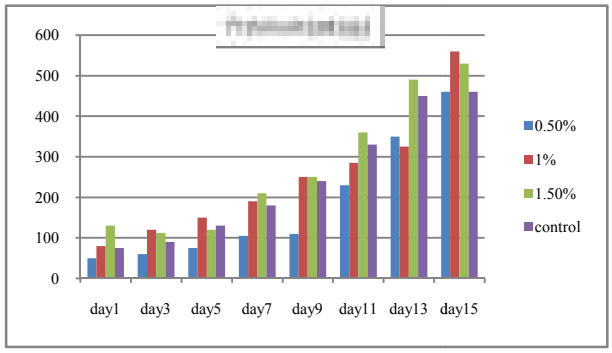

Fig 6 Total proteins in culture of Nostoc commune in different concentration of pesticide Malathion during15 days incubation

The data obtained in the present study reveals that proline content was increased as the concentrations of pesticide enhances but it remains lowered as compare to control of both the insecticides. Proline is a basic amino acid found in high percentage in basic protein. Free proline is said to play a role in plants under stress conditions. Though the molecular mechanism has not yet been established for the increased level of proline, one of the hypotheses refers to breakdown of protein into amino acids and conversion to proline for storage. Many workers have reported a several-fold increase in the proline content under physiological and pathological stress conditions.

The biomass and metabolite estimation of various incubation extract was evaluated using standard protocols and results obtained showed that biomass was increased as incubation period augmented as well as it depends on the concentrations of pesticide. It has been found that minimum biomass i.e. 52 mg was produced in 0.5% concentration of pesticide malathion after 15 days incubation in Nostoc commune. The biomass was maximum i.e. 293 mg at 1.0 conccentration of pesticide during 15 day incubation. Results indicates that amount of proteins was increased up to 15 days incubation time but not significantly. Amount of protein was maximum i.e. 1430 ug at 9th day in carbendazim and 560 ug in malathion treated group respectively.

The biochemical constituents of cyanobactreia depend on the nature of strains, physiological state of the culture & the environment. Rosaleset al.2005, observed significant variation in protein content among the isolated of Nostoc sp. Due to this biochemical variation he could enabled to distinguished between the sub species in several cyanobacterial genera. There are certain factors including pesticide stress, which also influence the protein synthesis (Borbely et al. 1985).

cyanbacteria are nurtured by soil and in spite that most reverend providing health, fertility and microflora to the soil. Because of it exhibit novel properties such as bio indicator and bio-remediator in contaminated agriculture field due to pollutant stress at moderately. But Nosoc commune in general do not resist to a very high concentration of insecticides carbendazim and malathion as it is revealed in present analysis. However the effect of pesticide on the population of nitrogen fixing cyanobacteria in rice fields also depends on other insecticide concentration and flooding of water associated with paddy fields. More detailed field studies are needed, avoiding the use of high application rates more than recommended will likely increase the more tolerant cyanobacteria.

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Arbuscular Mycorrhizal biodiversity associated with *Citrus aurentifolia* from Amravati region

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ABSTRACT

Arbuscular Mychorrhizai fungus is a key component of soil, which associate with root and rhizosphere of soil and create symbiotic association. In the present work, five soil samples were collected from five different sites of Amravati region (Maharashtra) for isolation and identification of AM spores, for this sieves and decanting method were used and observed that all the collected sample were infected by AM fungi but there population varied according to the soil sample, the Chandur Railway and Mardi site having maximum population of Am fungi but the Malkhed site contain very less population. The isolated spore belongs to five Genera which are *Acaulospora, Entrophosphora, Gigospora, Glomus and Scutelospora*. *Glomus* species was observed high amount.

Key words: Citrus plant, Rhizosphere soil, AM spore, AM species.

INTRODUCTION

Arbuscular Mycorrhiza is fungus-root symbiosis that occurs in the vast majority of plants have existed since the Devonian period and might have been essential for the evolution of land plants. Fungal species involved in the formation of arbuscular mychorhiza (AM) with higher plants are worldwide distributed in all terrestrial ecosystems. During the past decade, it has been established that AMF influences soil fertility and thus the growth and development of plant and therefore, these can be an alternative to rising agriculture and fertilizer costs. AMF form a key functional group of soil biota that can contribute towards the ecosystem sustainability and plant productivity (Urcoviche *et al.* 2014). AMF, which belong to phylum Glomeromycota (Schubler *et al*., 2001), Arbuscular mycorrizal fungi (AMF) propagule composition has an important effect on root colonization *(*Klironomos and Hart, 2002*)*. The occurrence of AMF at four soil depths i.e. 8, 15, 23 and 30cm. were studied by and registered more species at 15cm. depth. (Charles *et al*., 2008). The ability of soil to

support AMF population decreased significantly with increased soil depth and the involvement of factor other than soil P^H and moisture content in AMF distribution (Shukla *et al*., 2013).

Arbuscular Mycorrhiza are associate with the root of majority of the land plants, the most important role of Arbuscular Mycorrhiza is that they uptake phosphorus, which is a limiting nutrient in most of the soils (Yao *et al*., 2001; Koide and Schreiner, 1992) and nitrogen (N) and also water from the soil and transport them to the plant root. AM fungi not only uptake the nutrient from the soil but also it enhance the productivity of plant by suppressing plant disease *(*Khaosaad *et al*., 2007*)*, controlling nematode infection *(Elsen et al., 2008)*, stimulation of phytohormones production (Martínez-Medina *et al*., 2011), improve soil texture (Wu *et al*.,2008) and plant tolerance to stress conditions including drought (Pinior *et al*., 2005) and salinity (Hajiboland *et al*., 2010*).* The Biotic and Abiotic factor are greatly affected the diversity and distribution of Arbuscular mycorrhiza *(Mohammad et al. 2003).* The recent experimental study showing that AMF can grow and form spores in vitro, if provided with a carbon source and stimulated by particular bacterial strains (Hildebrandt *et al*., 2006). On global basis, Mycorrhiza occurs in 83% dicot and 79% monocot, whereas all gymnosperms are having Mycorrhizal colonization (Wilcox, 1991). Am fungi are fatty acid heterotrophs(Wewer, 2014) that depend on host deliverd organic carbon (C) in the form of fatty acids (Bravo, 2017, Keymer *et al.* 2017) in order to complete their life cycle.

MATERIALS AND METHODS

Sampling:

The Rhizosphere soil samples of *Citrus aurentifolia* were collected in sterile polythene bags. The collection was carried out in the month of February 2013 from Mardi, Amravati, Chandur Railway, Malkhed and Phora. All soil samples were dried and stored at 4^0C.

Quantitative and Qualitative Estimation of AM fungi:

Different methods are used for counting AM fungal spores. The procedure describe by *(Gaur and Adholeya, 1994)* was used for counting Am spores as it is a simplified method for counting Am fungal spores. In the present study, the wet sieving and decanting technique was used (Gerdemann and Nicolson, 1963) for isolation of AM fungi. Isolated fungi were scanned and mounted on slide in Polyvinyl Lactic Acid as mounting medium. The AM fungi were identified by using standard manual of *(*Schenck and perez, 1990*)* keys of (Morton and Benny, 1990*)* and of (Mehrotra and Baijal, 1994). The Isolated AM fungi were identified by morphology of spores especially on the basis on their wall layer.

Observation:

Qualitative Analysis of AM fungi:

Root and rhizosphere soil sample of *Citrus aurentifolia* from five different sites of Amravati were collected in sterile polythene bags during the month of February 2013.

Quantification Analysis:

The isolated AM fungi from each soil samples were varied according to the soil sample. Soil PH, soil moisture, micronutrients and soil depth all are major factor which effect on AM fungi population. In the present study, found that *Glomus* species in high amount in all the five samples total 18 species, out of 18 species *Glomus aggregatum and Glomus fasciculatum* observed in maximum site then after *Glomus albidum, Glomus arborense, Glomus fecundisporum, Glomus flavisporum, Glomus fulvum, Glomus geosporum, Glomus globiferum, Glomus glomerulatum,* Glomus halon, *Glomus leptotichum, Glomus manihot, Glomus maculosum, Glomus microaggregatum, Glomus verseforme and Glomus pulvinatum* also isolated and identified then *Acaulospora* with 8 species and *Enthrophosphora* and *Gigospora* found very less in number, *Enthrophosphora* Am fungi observed only at site number 1, 3, 5 and *Gigaspora* found in site 1 and 4. The total numbers of AM fungi were recorded during the study in soil sample showing in the Table2.

Quantification analysis show the number of species found in all the sites, one the basis of the above observation following graph is formed, it show the number of spore in each 100g of soil sample.

Table-1. Showing the site number of collected samples and identifies species.

Sr. no.	Site no.	Genera	Species identified
1	S1, S2, S3, S4, S5	*Acaulospora*	*Acaulospora appendicular*
2	S1, S4, S5	*Acaulospora*	*Acaulospora delicate*
3	S2, S4,S5	*Acaulospora*	*Acaulospora bireticulata*
4	S1,S2,S3,S4,S5	*Acaulospora*	*Acaulospora denticulate*
5	S3	*Acaulospora*	*Acaulospora foveta*
6	S2, S4	*Acaulospora*	*Acaulospora lacunose*
7	S1, S3	*Acaulospora*	*Acaulospora laevis*
8	S3	*Acaulospora*	*Acaulospora tuberculata*
9	S5	*Entrophosphora*	*Entrophosphora colombiana*
10	S1, S3	*Entrophosphora*	*Entrophosphora infrequens*
11	S1, S4	*Gigaspora*	*Gigaspora decipiens*
12	S1, S2 ,S4,S3	*Glomus*	*Glomus aggregatum*
13	S1,S2, S4	*Glomus*	*Glomus albidum*
14	S1	*Glomus*	*Glomus arborense*
15	S1, S2, S3, S4, S5	*Glomus*	*Glomus fasciculatum*
16	S1, S3	*Glomus*	*Glomus fecundisporum*
17	S1, S4,S5	*Glomus*	*Glomus flavisporum*
18	S2,S4,S5	*Glomus*	*Glomus fulvum*
19	S2,S4,S5	*Glomus*	*Glomus geosporum*
20	S3,S2	*Glomus*	*Glomus globiferum*
21	S5	*Glomus*	*Glomus citriculata*
22	S3	*Glomus*	*Glomus glomerulatum*
23	S2,S4,S5	Glomus	Glomus halon
24	S1,S3	*Glomus*	*Glomus hoi*
25	S3	*Glomus*	*Glomus leptotichum*
26	S1,S4,S5	*Glomus*	*Glomus manihot*
27	S5	*Glomus*	*Glomus maculosum*
28	S3,S2	*Glomus*	*Glomus microaggregatum*
29	S5	*Glomus*	*Glomus verseforme*
30	S3	*Glomus*	*Glomus pulvinatum*
31	S1,S2,S3,S4,S5	*Scutelospora*	*Scutelospora nigra*
32	S5	*Scutelospora*	*Scutelospora clavispora*

{S1-Chandur railway, S2- Malkhed, S3-Mardi, S4-Amravati, S5- Pohra}

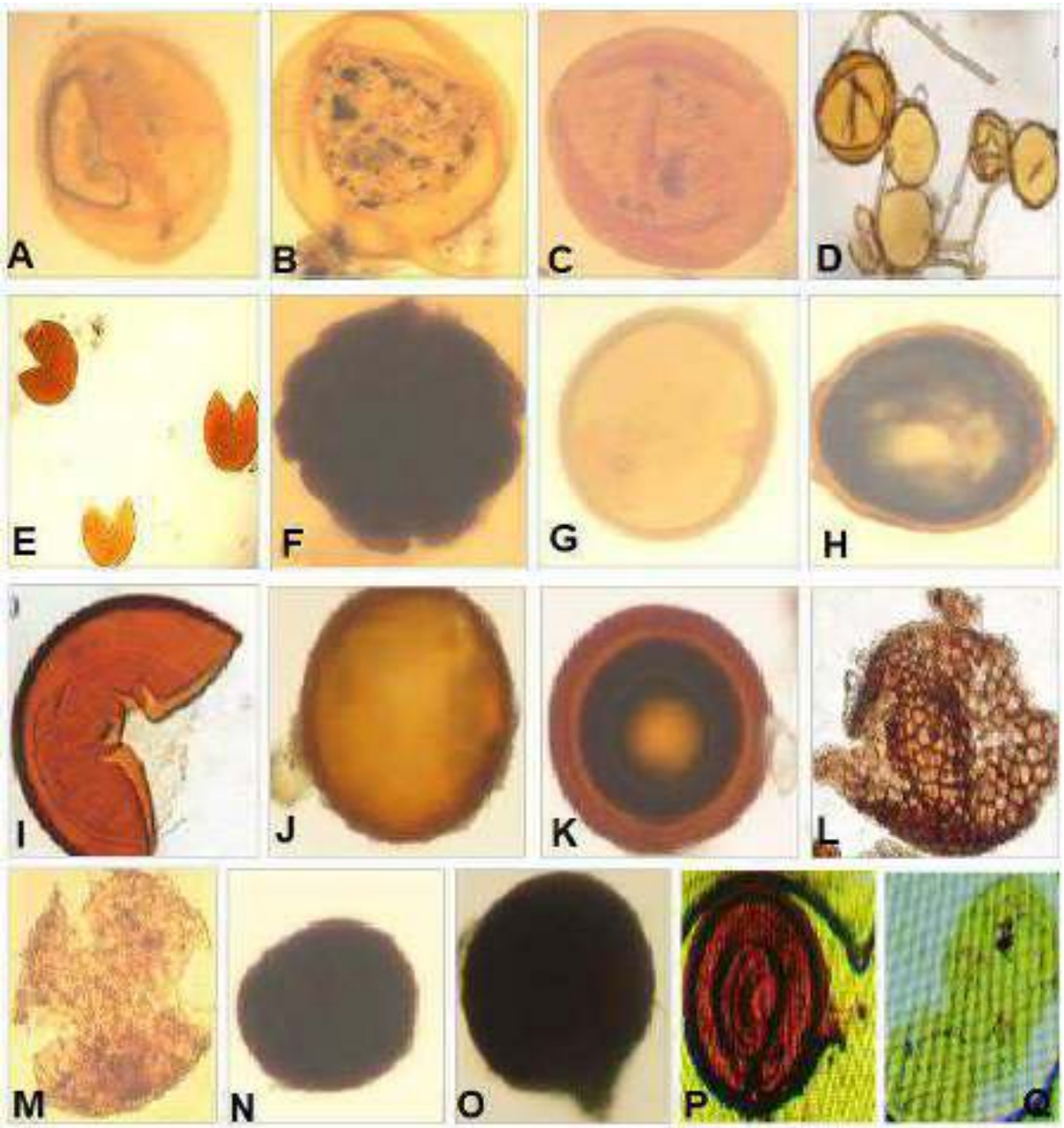

Figure 1 : A, B *Glomus fasciculatum;* **C,D,E:** *G.aggregatum;* **F***: Glomus citriculata;* **G:** *G. dominikii;* **H**- *G.glomerulatum;* **I**- *G.tuberculatum;* **J**: *G.albidum;* **K :**- *A.foveata;* **L, M:** *A. bireticulata;* **N**: *A.sporocarpa;* **O:** *Scutellospora nigra.;* **P :***E.infraquens;* **Q**: *E.colombiane*

Table-2. Total number of AM fungi species as follow

Serial No.	Name of AM Genra	No. of spores found in each Sites Number					No. of Species
		S.1	S.2	S.3	S.4	S.5	
1	*Acaulospora*	4	4	5	5	4	8
2	*Glomus*	8	8	9	8	9	19
3	*Gigospora*	1	-	-	1	-	1
4	*Enthrophosphora*	1	-	1	-	1	2
5	*Scutelospora*	1	1	1	1	2	2

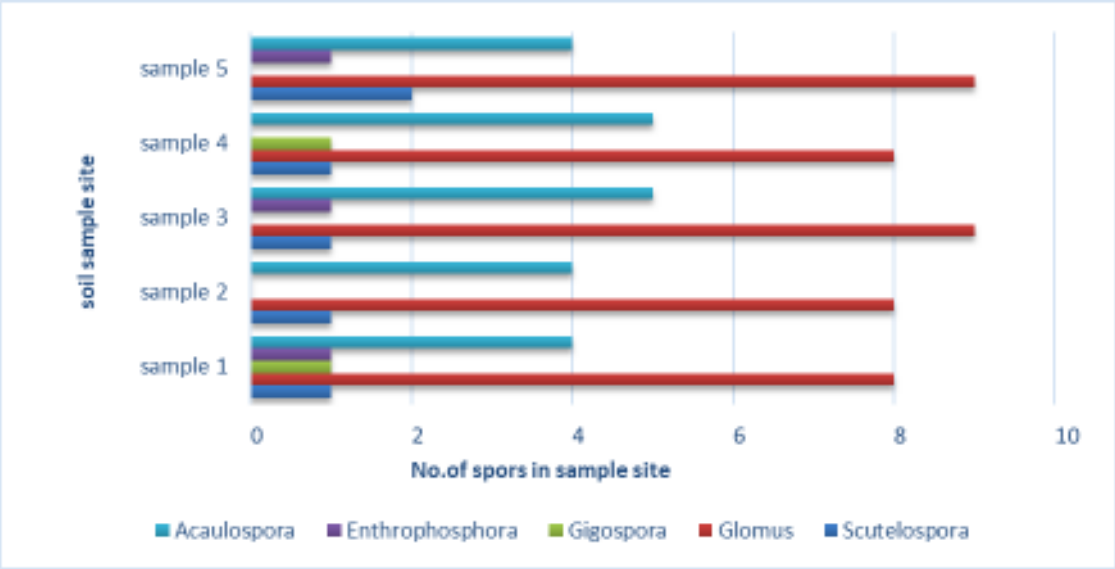

Fig:2. Showing the number of spores found in each soil sample and identified spores in each sample.

Result and Discussion:

An extensive field investigation was carried out in Amravati region, Maharashtra (India), on a *Citrus* plant which belongs to Rutaceae family. The association of AM fungi with *Citrus aurentifolia* plant and their colonization and population in the Rhizosphere is presented in (Table 1). All the sites having low to moderate AM population but in site1 (Chandur railway) maximum population were observed with maximum AMF colonization. More than 102 AM species have so far been reported from India (Manoharachary,C. ,2005). AMF colonization is about 20 % of the fine root segments in *Citrus volkameriana*. A total of 32 AMF species were isolated from rhizospheric soil. Maximum species belongs to *Glomus* (Fig 1-10) and *Acaulospora* (Fig 11-14) isolated species were 19 & 8 in numbers, remaining belongs to *Enthrophosphora, Gigospora* and *Scutelospora* which were 2, 1 & 2 in numbers they were isolated and identified on the basis of their morphological characteristics. Seasonal variation is a major factor in biodiversity of AM fungus was quite evident from the fluctuations of spores in soils (Sampath Kumar, 2001). *Glomus* species were the most commonly found in all type of different soil (Panneerselvam and Thamizhiniyan, 2011; Camprubí and Calvet,1996; Beena *et al.*, 2000; Bhuvaneswari, 2010; Unegbu *et al.*, 2016) and in present work also the major isolated species was belongs to Glomus. *Acaulospora appendicula* and *A. denticulata* were also observed in all five sites. *Gigaspora* spore was frequently observed in the two soils sites (Chandur railway, Amravati), but they were apparently from only one species. The soil sample of village Malkhed (s-2)contains least number of AM spores, the possible reason behind these variation season, age of plant, soil P^H, salinity etc. (Abbott and Robson, 1991; Johnson *et al.*, 1992), whereas Mardi(S3) and Amravati sites (S4)contain the widest variety of AM species. All the five sites of soils exhibit different physico-chemical and microbiological characteristics. Citrus plant mostly contain *Glomus* and *Acaulospora* species in major quantity but absence of other genera or they may be present in low rate is not surprising because sometimes they are not detected at the time of survey of Am fungi, in present survey also found that *Glomus* and *Acaulospora* were present in high rate, (Singh *et al.*,2008). A total 32 species were isolated from all the sites. 19 species belonging to *Glomus*, 8 species from *Acaulospora*, *Enthrophosphora* and *Scutelospora* both were having 2 species and only one species i*n Gigospora. G. fasciculatum* was found in all the five site and *G. aggregatum* found in four site. Similarly *A. appendicula* and *A. denticulate* were found in all the sites.

CONCLUSION

Arbuscular Mycorrhiza is associate with the soil and root of major land plants. AMF is an ecofriendly it increase the soil fertility by up taking phosphorus from the soil and improve plant productivity. AMF is a natural tool so, it is necessary to retain the AM population in soil. In the present study, only few site

having high AM population and that site productivity was good the only reason that site uptake phosphorus compound from the soil, these compound concentration in soil is low but it is soluble phosphorus.

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Embedded System Security

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Abstract:

Security is an important aspect of embedded system design. The characteristics of embedded systems give rise to a number of novel vulnerabilities. A variety of different Solutions are being developed to address these security problems. In this paper, we provide a brief overview of important research topics in this domain.

With the increasing use of embedded devices in our daily life, security threats have also been increasing in a proportional rate. However, ensuring security in the embedded systems has become a great challenge not only for the embedded device experts but also for the manufacturers. The problem especially arises because of the limited hardware and software implementation options for the designers. At the same time, companies are trying to keep the vulnerabilities of the operating system of those embedded devices in secret and they are not relieving any necessary security updates quickly. It has become very urgent to ensure proper security of the embedded systems to save it from any major technological disaster near future. In this paper, we have broadly discussed the structures, characteristics and applications of different embedded devices in our daily life. Beside this, we have also discussed about the different causes of security threats and some of our suggested solutions to protect the systems from the attackers as well that we have found in our research.

Keywords: cryptography, firmware, hackers, microcontroller, real-time constraints, Vulnerabilities

Introduction

An embedded system can be defined as a special type of computer system that performs some specific pre-defined programs which is generally used within a larger scale of electrical or mechanical system. Generally, it is started from small MP3 players to largely complex hybrid vehicle systems. Some other examples of frequently used embedded systems in our daily life are keyboard, mouse, ATM, TV, PDA, cell phone, printer, elevator, smoke detector, DVD player, refrigerator, camera, GPS navigator, radio, TV remote, telephone, game controller, monitor, digital image processor, bar code reader, SD card, washing machine, anti-lock breaking system, blender etc. We use embedded systems especially because of its dependability, efficiency and it meets the real-time constrains

Characteristics Of Embedded Systems:

In general, embedded systems are designed to perform any particular pre-defined task that must meet any real time constraint. The main difference between a computer and an embedded system is a computer is used to perform multiple tasks defined by the user. On the other hand, an embedded system is used to perform a specific task that is pre-defined by the manufacturers. Here, meeting all the real-time constraints is a very important characteristic of an

embedded system. A real-time constraint is divided into two parts. One is hard real-time system and the other is soft real-time system. Hard real-time system means it must meet all its deadlines with a zero degree of flexibility and it is acceptable to be little flexible in the soft real-time system. It is not necessary to be standalone always for the embedded devices. Actually most of the embedded systems are integrated within a large computerized device. Devices such as MP3s, cameras and TV remotes are the example of standalone embedded devices. For the example of integrated embedded devices car and nuclear power plant are some good examples. GPS, fuel injection controller, anti-locking brake system, transmission controller, cruise control, active suspension, air- bag system, air-conditioner, display monitor-all the devices are integrated in a modern car system. The term 'firmware' is used to refer the program instructions written for embedded systems. It is stored in ROM (Read Only Memory) or in a flash memory chip. Resources like computer hardware do not need much to run. Another important characteristic of embedded systems is the dedicated user interface. It may range from no user interface to complex graphical user interface. For simple button and LED system, no user interface is needed. User interface means the task of button can change with the on-screen display and the selection depends on the user.

The specialization of embedded system often comes with one or more drawbacks of the following type:

- **Limited processing power** implies that an embedded system typically cannot run applicationsthat are used for defenses against attacks in conventional computer systems (e.g.,virus scanner, intrusion detection system).
- **Limited available power** is one of the key constraints in embedded systems. Many such systems operate on batteries and increased power consumption reduces system lifetime(or increases maintenance frequency). Therefore embedded system can dedicate only limited power resources to providing system security.
- **Physical exposure** is typical of embedded systems that are deployed outside the immediate control of the owner or operator (e.g., public location, customer premise). Thus, embedded systems are inherently vulnerable to attacks that exploit physical proximity of the attacker.
- **Remoteness and unmanned operation** is necessary for embedded system that are deployed in inaccessible locations (e.g., harsh environment, remote field location). This limitation implies that deploying updates and patches as done with conventional workstations is difficult and has to be automated. Such automated mechanisms provide potential targets for attacks.
- **Network connectivity** via wireless or wired access is increasingly common for embedded systems. Such access is necessary for remote control, data collection, updates. In cases where the embedded system is connected to the Internet, vulnerabilities can be exploited remotely from anywhere.

These characteristics lead to a unique set of vulnerabilities that need to be considered in embedded systems.

Vulnerabilities

Embedded system are vulnerable to a range of abuses that can aim at stealing private information, draining the power supply, destroying the system, or hijacking the system for other than its intended purpose. Examples of vulnerabilities in embedded systems are:

- **Energy drainage (exhaustion attack):** Limited battery power in embedded systems makes them vulnerable to attacks that drain this resource. Energy drainage can be achieved by increasing the computational load, reducing sleep cycles, or increasing the use of sensors or other peripherals.
- **Physical intrusion (tampering):** The proximity of embedded systems to a potential attacker create vulnerabilities to attacks where physical access to the system is necessary. Examples are power analysis attacks or snooping attacks on the system bus.

Applications Of Embedded Systems:

As we describes earlier, embedded systems have become parts and parcels of our daily life in term of use. From the following table we can easily understand our daily use of embedded systems.

Home Applications	Dishwasher, Washing Machine, Microwave Oven, Top-set Box, Home Security Systems, HVAC system, DVD player, Answering Machine, Garden Sprinkler Systems, Lighting Systems, Remote Controls, Air Conditioners, Sprinklers.
Consumer Electronic Products	Cell phones, Cordless Phones, Digital Cameras, Video recorders, DVD players, TV set, Calculators, MP3 Players, Stereo Systems, Cable TV tuners, Digital watches, Personal PDA, iPhone.
Industrial applications	Personal Smart Phone, Fax Machines, Photo Copy Machines, Printers, Scanners, Assembly Line, Data Collection System, Monitoring Systems on Pressure, Voltage, Current, Temperature, Hazard Detecting System, Industrial Robot.
Business Equipment	ATM, Cash Registers, Alarm Systems, Card Readers, Finger Print Detectors, Automatic Toll Systems, Voice recognizers, Smart Vendor Machine, Cash Register, Bar Code Reader.
Automobile	GPS, Fuel Injection Controller, Anti-locking Brake System, Transmission Controller, Cruise Control, Active Suspension, Air- bag System, Air-Conditioner.
Communication Systems	Router, Hub, Cell Phone, Web Camera, Modem, Network Cards, Tele-conferencing System.
Aerospace	GPS system, Automatic Landing System, Flight Attitude Controller Inertial Guidance System, Space Robotics, RADAR.
Medical Technology	CT scanner, ECG, EEG, EMG, MRI, Glucose Monitor, Blood Pressure Monitor, Diagnostic Device, X-ray machines, Digital Pulse Monitor.
Security Systems	Face Recognition System, Finger Recognition, Irish Recognition, Building Security System, Airport Security System, Alarm System, Digital Access Card, Fingerprint based Smart Card.

Classroom applications	Smart Board, Smart Room, OCR, Calculator, Smart Cord, Stereo Systems, Projector.
Game and Entertainment	Video games

Causes Of Security Threats Of Embedded Systems

In this age of advanced technology, almost all of the embedded systems are connected to different network systems such as internet. At one side, these embedded devices are being more connected to our life day by day whereas on the other hand its security threats are also increasing as a proportional rate. Security threats in the embedded systems are not a new concept at all.. Some major causes of embedded system security threats are explained below: One of the major limitations of embedded systems are they are very cost sensitive. A little change in cost can make a big difference in the case of heavy manufacture devices. This cost sensitivity leads manufactures to use4-bit processor or 8-bit processor. Bigger cryptographic key cannot be stored by many of these 8-bit microcontrollers. Embedded devices have to perform same task again and again usually by using loop. Here, speed can easily reach to 100 loops in every 5 seconds with strong real-time constraints. Therefore, a single delay of even 0.01 second can cause a loss of control loop stability which means the system can be vulnerable to attack that is designed to destroy the system timing. In the most of the time, embedded systems have no real administrator by which an internet connected device can be easily launched by distributed denial-of-service (DoS) attacks by the hackers. Many embedded systems are designed and developed by the small development teams even by the single engineer sometime. Organizations that write few kilobytes of code per year usually cannot afford any embedded system security specialist even they do not understand the importance the necessity of the security specialists as well. There are many embedded systems that have significant battery constraints and powered by battery as well such as PDAs or cell phones. Some embedded systems can get fresh battery charge daily but other must last months or years depending on a single battery only. An attacker can create system failure by seeking to drain the battery especially when the security of the system is very high or almost impossible to break the security system of that particular device. This vulnerability is very much critical and worsens the security of the device. As an example, ensuring enough security in the battery-powered device is not easy at all that uses the power-hungry wireless communication system. Firmware is being completed day by day and will be more completed in near future. This will increase more bugs and other security problems. One reason may be the use of more popular programming languages such as C and C++ as they are very efficient for embedded systems. However they cannot protect against the simple kinds of attacks such as buffer overflows. Although small programs can be theoretically prove as safe but it is about impossible against complex programs.

Solutions Of Security Threats In Embedded Systems

Security requirements of embedded devices can vary from different aspects. As an example of a cell phone system, end user may be concerned about his private data protection while content provider may be concerned about copy protection of the multimedia contents delivered to the cell phone and manufacturers may be concerned about the proprietary firmware that has been used in that cell phone. Here the system of attack may also vary for users, content providers, manufacturers etc. We have already described different challenges of embedded

systems in term of security and in this section we will describe some probable solutions also to get rid of those problems also. Modern cryptography techniques provide strong defiance against the conventional attacks. However, much more effort and care is still required in the software design to make the system more protected from bugs and design flaws. Designers should be emphasizing more on Software Development Life Cycle (SDLC). Different secure level practices should be applied which can be classified into three. They are the design level, the implementation level and the testing level. Tamper-resistance techniques should be strengthening more to protect the system against different software and hardware attacks. These techniques can be used for attack detection, recovery and prevention as well. To prevent side-channel attacks, different hardware and software level approaches have been proposed to identify symptoms that allow the leak of the system's side-channel information like power dissipation, timing and electromagnetic radiations. Software based countermeasures include randomization instruction sequence, introducing dummy instructions, bit splitting and balancing hamming weights of internal data. Randomization can also be applied on the clock signal or the power consumption. It has been experimented that software based countermeasures are most efficient although they slightly

Conclusions

Embedded devices have made our life more easy and comfortable by meeting almost all the real-time constraints. Although it is very popular among the mass people but they are quite unconscious about the probable security threats till now even the manufactures and the engineers associated with embedded devices. Expert hackers from the different parts of the world have already found many security pitfalls of the embedded devices and they are further working on it. So, it is very clear that it could create a huge blow in near future for the technological industry if the engineers and the manufactures do not take the necessary security solutions as proposed in this paper to protect the unauthorized access from the unsecured third party. We heartily believe that more concentration on cryptography, tamper-resistance techniques, advanced microcontroller and algorithms can mostly make the embedded devices secure enough. At the same time, it is also important for the manufacturer companies to design and implement the whole embedded system with much more security concern.

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Study of Advances in Artificial Intelligence and Deep Learning

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Abstract –

Artificial Intelligence (AI) is a multidisciplinary field whose goal is to automate activities that presently require human intelligence. Reasoning is concerned with higher level cognitive functions such as planning, drawing inferential conclusions from a world model, diagnosing, designing, etc. In this paper we have observed the extended goals of Artificial Intelligence including logical reasoning, knowledge representation, planning and navigation, natural language processing, perception and emergent intelligence.

Machine learning is an integral part of artificial intelligence, which is used to design algorithms based on the data trends and historical relationships between data. Also, Deep learning is an emerging area of machine learning (ML) research. It comprises multiple hidden layers of artificial neural networks.

This paper elaborates some basic machine learning tasks adopted by researchers in their common applications of AI. The recent machine learning techniques accomplished by the researchers has also been presented in this paper. It has been noted that, in recent years, machine learning has achieved great success in many fields, such as computer vision and natural language processing. Compared to traditional computer based learning methods, machine learning has a strong learning ability and can make better use of datasets for feature extraction. The study concludes that, we need to provide a machine learning framework to construct and implement models for general purpose tasks useful for common people for successful delivery of AI-based systems.

Keywords – Artificial Intelligence, Machine Learning, AI Assistants, Supervised Learning, Unsupervised Learning, Chatbots

Introduction

Artificial Intelligence is a method of making a computer, a computer-controlled robot or a software think intelligently in a manner similar to the human mind. AI is accomplished by studying the patterns of the human brain and by analyzing the cognitive process. The outcome of these studies develops intelligent software's and systems. Researchers extend the goals of AI to the following:

Logical Reasoning: AI programs enable computers to perform sophisticated tasks. On February 10, 1996, a computer called Deep Blue, designed by IBM, won a game of chess against the former world champion, Garry Kasparov.

Knowledge Representation: Smalltalk is an object-oriented, dynamically typed, reflective programming language that was created as the language to underpin the "new world" of computing demonstrated by "human-computer symbiosis."

Planning and Navigation: The process enabling a computer to get from point A to point B. A prime example of this is Google's self-driving Toyota Prius.

Natural Language Processing: Set up computers that can understand and process language.

Perception: Use computers to interact with the world through sight, hearing, touch, and smell.

Emergent Intelligence: An intelligence that is not explicitly programmed, but emerges from the rest of the explicit AI features. The vision for this goal is to have machines exhibit emotional intelligence, moral reasoning and more.

Some of the Artificial Intelligence based applications used today are given below: Top companies are constantly rolling out revolutionary changes to how there should be an interaction with machine-learning technology. For Example, DeepMind Technologies, a British artificial intelligence company created a Neural Turing Machine, allowing computers to mimic the short-term memory of the human brain. Google's driverless cars and Tesla's Autopilot features are the introductions of AI into the automotive sector. It uses vast amounts of data from image and audio recognition systems, along with new ML called Deep Learning and Deep Nets, to build systems that can drive autonomously. The technology teaches the cars about the nature of objects on the road and understand how they would react, the audio recognition technology using audio sensors based ML systems to teach the vehicle to diagnose cars problem themselves whereas, the Deep nets are used for everything from prediction to planning to mapping and simulation.

Common applications of AI utilized by most of the people is virtual personal assistants in the smartphones. These applications collect information, interpret what is being asked and then supply the answer via fetched data and each one gradually improves based on user preferences.

Machine Learning –

Machine Learning is a form of artificial intelligence that automate data analysis to enable computers to learn and adopt through experience to do specific tasks without explicit programming.

Machine learning, as a key subset of artificial intelligence (AI), Machine Learning has come a long way and with its numerous algorithms, can accomplish a great deal of impressive tasks. Machine Learning concepts and techniques includes supervised and unsupervised learning, mathematical and heuristic aspects to develop algorithms.

Netflix recommendations and virtual personal or AI assistants like Siri, Cortana, Alexa and Google Assistant are some of AI's best-known applications which uses machine learning techniques and are found in iOS, Windows and Android phones. AI assistants emulates human interaction using the voice enabled technology to perform particular tasks like personal assistance. It has the capacity for learning, reasoning and understanding which the three key elements are required to emulate the ability to solve the problems. The trouble is that collecting, analyzing and utilizing all this data has grown beyond what is humanly possible, even using traditional data analytics.

The solution to process this ore of data into material that's suitable for construction lies in using machine learning to automate the creation of data analysis models. Humans can typically create one or two good models a week; machine learning can create thousands of models a week. Machine learning not only handles vast amount of raw, unlabeled data, it craves it. The more you feed it, the smarter it gets. Machine learning algorithms can determine clusters, patterns and

relations among data and then predict outcomes and even recommend actions. With the power of machine learning and other applications of AI, the users can make the data useful for the growth to business and the customers.

Armed with this huge volume and wide variety of data, machine learning algorithms can be "trained" based on past experience, then exposed to new data and unleashed to hunt for patterns, learn from what they find and even build predictive models on their own.Machine learning is now useful to organizations of any type andany size, for processes ranging from theroutine to the revolutionary.

The two most widely adopted machine learning methods involved supervised learning andunsupervised learning.

1. Supervised learning uses structured data, stored in relational databases, this is the type of data that's most familiar to businesses, but it was noted that, only comprises about 20 percent of all data. Structured data comes in from human input, mechanical sensors, website or other automated logs, point of sale devices and similar sources. Supervised learning algorithms are useful when the desired output is known, or if you have a specific question you want to ask such as finding new data points that match a specific target value. This is useful for functions like inventory control, recommendation engines and predictive maintenance.

2. Unsupervised learning uses data that is unstructured, contains no historical labelsand doesn't fit neatly into a database. Such data includes customer transactions, social media, document text, graphics, video and other content. It was observed that, approximately 80 to 90 percent of the data in most organizations is unstructured. With unsupervised learning, the algorithm must draw its own inferences to figureout what it's looking at. It does this by finding clusters and hidden patterns, such as similarities between behaviors and customers. This type of learning is especially useful for market segmentation (marketing campaigns), fraud detection and hardware fault diagnostics.

Some of the top roles of AI and ML includes

AI/machine learning researcher make its use to Research and identify improvements to machine learning algorithms. AI software development, program management, and testing: Develop systems and infrastructure that can apply machine learning to an input data set.

Data mining and analysis: Investigate large data sources, often creating and training systems to recognize patterns.

Basic Machine Learning Tasks

ML techniques provides a set of tools that can automatically detect patterns in data which can be utilized for predictions and for developing models. Developments in ML algorithms and computational capabilities have now made it possible to scale engineering analysis, decision making and design rapidly. Following ML tasks are prominently done,

- Performance Measures
- Classification
- Regression
- Clustering

Some of the live projects on which researcher are working recently that can be found on the internet are

Project 1: Build a Predictive Model for Housing Prices

Project 2: Build a Phishing Website Detector Using LR Algorithms
Project 3: Build a Phishing Website Detector Using KNN Algorithms
Project 4: Build an MNIST Classifier

Machine learning applications:

Apply machine learning or AI framework to a specific problem in a different domain. For example, applying machine learning to gesture recognition, ad analysis or fraud detection.

The researchers used supervised or unsupervised machine learning, or a combination of the two (known as semi-supervised learning), these are the three ways for any business, regardless of industry, can utilize such algorithms to help build a competitive advantage.

1. Automating Business Processes
2. Marketing - AI and machine learning are commonplace tools for digital marketers.
3. Improving Customer Experience–Some of the ways of utilizing machine learning used today to optimize the marketing and advertising, both online and offline are:

- Demand forecasting and sales projection
- Determining customer lifetime value
- Streamlining lead sourcing
- Customer churn risk modeling
- Product pricing and dynamic pricing (based on real-time demand)
- Dynamic and personalized product ranking (website)
- Visual merchandising placement (retail)
- Augmented reality (AR) integration (retail)
- Purchase recommendations
- Micro-segmentation
- Personalized headline and ad/email copy
- Optimized message targeting
- Automated and real-time media buying/ ad insertion
- Customer qualifying/lead scoring using web data
- Content research and creation
- Automatic translations
- Plagiarism detection
- Social monitoring (for issues, affinity and competition)
- Social media posting and advertising
- Text-to-video creation

To get the most out of machine learning, all this diverse data is usually stored in a type of repository known as a "data lake". A term coined in 2010 by James Dixon, the founder and CTO of Pentaho, data lakes differ from traditional data warehouses in that they store all their data in its raw, natural state, regardless of whether it is structured, semi-structured, or unstructured. A data warehouse only keeps data in a very structured format.

While this makes data easier to find specific things, its inflexibility makes it difficult to perform innovative analyses. "Structured data enables us to answer certain questions, but the structure may not accommodate questions that arise at some point in the future," explains Jared

Crapo, Senior Vice-President at Health Catalyst. "The data lake concept allows for unstructured data—and more flexibility to answer new questions.

Machine learning not only automates this intelligence gathering from familiar sources and internal databases; the algorithms actually go into the outside world to collect, analyze, learn and predict.

A form of artificial intelligence, machine learning is revolutionizing the world of computing as well as all people's digital interactions. By making it possible to quickly, cheaply and automatically process and analyze huge volumes of complex data, machine learning is critical to countless new and future applications. Machine learning powers such innovative automated technologies as recommendation engines, facial recognition, fraud protection and even self-driving cars.

The Machine Learning techniques are used to accomplish the following:

- Master the concepts of supervised, unsupervised and reinforcement learning concepts and modeling.
- Gain practical mastery over principles, algorithms, and applications of machine learning through a hands-on approach which includes working on various projects.
- Acquire thorough knowledge of the mathematical and heuristic aspects of machine learning.
- Understand the concepts and operation of support vector machines, kernel SVM, naive Bayes, decision tree classifier, random forest classifier, logistic regression, K-nearest neighbours, K-means clustering and more.
- Comprehend the theoretical concepts and how they relate to the practical aspects of machine learning.
- Be able to model a wide variety of robust machine learning algorithms including deep learning, clustering, and recommendation systems

Chatbots and other applications of machine learning can handle a number of routine, repetitive HR tasks, including:

- Screening and shortlisting job applicants from hundreds of résumés
- Scheduling interviews, performance reviews and other group meetings
- Measuring and managing employee engagement
- Streamlining office workflows
- Tracking and enhancing employee rewards and recognition programs
- Identifying knowledge gaps or opportunities for employee development
- Answering questions about company policies, benefits, office procedures and even basic conflict resolution
- Attracting and reaching out to top talent (through such sites as Glassdoor, LinkedIn or Indeed)

Machine learning is also excellent at examining vast amounts of historical sensor, logistics and failure data from appliances, machinery or vehicles. The models' predictions could then recommend preventive maintenance, mitigate transportation or supply chain risks or even detect anomalies in real time that would indicate a failure is imminent.

Future Scope

Machine learning is set to redefine the world of software and IT in the near future. Machine Learning supports the technologies such as Data Science, Big Data and Data Analytics which are increasingly shaping future of work and jobs.

Data Science:

Dealing with unstructured and structured data, Data Science is a field that comprises of everything that related to data cleansing, preparation, and analysis. Data Science is the combination of statistics, mathematics, programming, problem-solving, capturing data in ingenious ways, the ability to look at things differently, and the activity of cleansing, preparing and aligning the data.

Applications of Data Science

Internet search: Search engines make use of data science algorithms to deliver best results for search queries in a fraction of seconds.

Digital Advertisements: The entire digital marketing spectrum uses the data science algorithms - from display banners to digital billboards. This is the mean reason for digital ads getting higher Click Through Rate (CTR) than traditional advertisements.

Recommender systems: The recommender systems not only make it easy to find relevant products from billions of products available but also adds a lot to user-experience. A lot of companies use this system to promote their products and suggestions in accordance with the user's demands and relevance of information. The recommendations are based on the user's previous search results.

Big Data:

Big Data refers to humongous volumes of data that cannot be processed effectively with the traditional applications that exist. The processing of Big Data begins with the raw data that isn't aggregated and is most often impossible to store in the memory of a single computer. A buzzword that is used to describe immense volumes of data, both unstructured and structured, Big Data inundates a business on a day-to-day basis. Big Data is something that can be used to analyze insights which can lead to better decisions and strategic business moves.

The definition of Big Data, given by Gartner is, "Big data is high-volume, and high-velocity and/or high-variety information assets that demand cost-effective, innovative forms of information processing that enable enhanced insight, decision making, and process automation".

Applications of Big Data

Big Data for financial services: Credit card companies, retail banks, private wealth management advisories, insurance firms, venture funds, and institutional investment banks use big data for their financial services. The common problem among them all is the massive amounts of multi-structured data living in multiple disparate systems which can be solved by big data. Thus big data is used in a number of ways like:

- Customer analytics
- Compliance analytics
- Fraud analytics
- Operational analytics

Big Data in communications: Gaining new subscribers, retaining customers, and expanding within current subscriber bases are top priorities for telecommunication service providers. The solutions to these challenges lie in the ability to combine and analyze the masses of customer-generated data and machine-generated data that is being created every day.

Big Data for Retail: Brick and Mortar or an online e-tailer, the answer to staying the game and being competitive is understanding the customer better to serve them. This requires the ability to analyze all the disparate data sources that companies deal with every day, including the weblogs, customer transaction data, social media, store-branded credit card data, and loyalty program data.

Data Analytics:

Data Analytics the science of examining raw data with the purpose of drawing conclusions about that information. Data Analytics involves applying an algorithmic or mechanical process to derive insights. For example, running through a number of data sets to look for meaningful correlations between each other.

It is used in a number of industries to allow the organizations and companies to make better decisions as well as verify and disprove existing theories or models. The focus of Data Analytics lies in inference, which is the process of deriving conclusions that are solely based on what the researcher already knows.

Applications of Data Analysis

Healthcare: The main challenge for hospitals with cost pressures tightens is to treat as many patients as they can efficiently, keeping in mind the improvement of the quality of care. Instrument and machine data is being used increasingly to track as well as optimize patient flow, treatment, and equipment used in the hospitals. It is estimated that there will be a 1% efficiency gain that could yield more than $63 billion in the global healthcare savings.

Travel: Data analytics is able to optimize the buying experience through the mobile/ weblog and the social media data analysis. Travel sights can gain insights into the customer's desires and preferences. Products can be up-sold by correlating the current sales to the subsequent browsing increase browse-to-buy conversions via customized packages and offers. Personalized travel recommendations can also be delivered by data analytics based on social media data.

Gaming: Data Analytics helps in collecting data to optimize and spend within as well as across games. Game companies gain insight into the dislikes, the relationships, and the likes of the users.

Energy Management: Most firms are using data analytics for energy management, including smart-grid management, energy optimization, energy distribution, and building automation in utility companies. The application here is centered on the controlling and monitoring of network devices, dispatch crews, and manage service outages. Utilities are given the ability to integrate millions of data points in the network performance and lets the engineers use the analytics to monitor the network.

Conclusions

This is the early stages of AI world in which machine learning is morphing from a lab curiosity to a rich, pervasive technology value-add.

ML is at the centre of a new enterprise to build computational models of intelligence. The main assumption is that intelligence (human or otherwise) can be trained by using voluminous data available on the Internet to solve the above mentioned problems where ML can be rigorously used with the help of a digital computer. Aspects of intelligent behaviour, such as

solving problems, making inferences, learning, and understanding language, have already been done using ML, and within very limited domains. ML can outperform human experts. Now the great challenge of AI and ML is to find ways of representing the commonsense knowledge and experience that enable people to carry out everyday activities such as holding a wide-ranging conversation, or finding their way along a busy street. Conventional digital computers may be capable of running such programs, or there is a need to develop new machines that can support the complexity of human thought.

Machine Learning Architects have defined, evaluated and recommended machine learning architectures and frameworks that support ML and AI initiatives.The need is to develop a ML prototype utilizing ML frameworks. There is an availability of pre-trained models and machine learning services — also called machine learning APIs which can be utilized for the designated problems. There is a need to provide a machine learning framework to construct and implement models for general purpose tasks useful for common people for successful delivery of AI-based systems.

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An Overview of "Cloud Computing"

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Abstract:

In the last few years there has been a rapid exponential increase in computer processing power, communication and data storage. But still many complex and computation intensive problems, which cannot be solved by supercomputers. In the field of computing, a lot of changes have been observed due to the increased use and popularity of the Internet and the availability of high-speed networks.

Resource sharing in a pure plug and play model that dramatically simplifies infrastructure planning is the promise of "Cloud computing".

The paper aims to provide a means of understanding the model and exploring options available for complementing your technology and infrastructure needs. Also explore some of the basics of cloud computing with the aim of introducing aspects such as:

1. Realities and risks of the model
2. Components in the model
3. Characteristics and Usage of the model

Keywords: Cloud computing, SLA, SaaS, Paas, Iaas, Daas, Cloud Service Provider, Cloud computing metaphor

Introduction:-

Cloud Computing

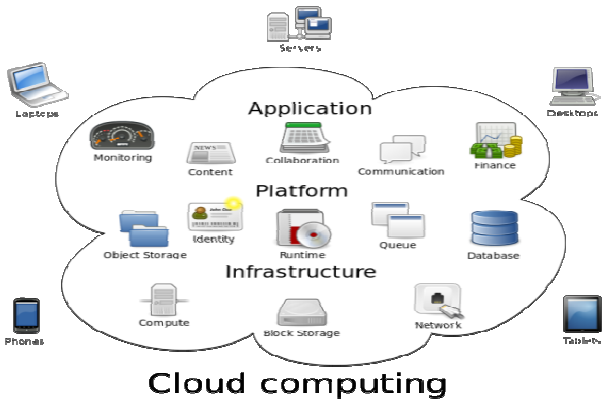
Cloud computing is an on demand service model for IT provision. Cloud Computing is a technology which depends on sharing of computing resources.

In Cloud Computing, the word "Cloud" means "The Internet", so Cloud Computing means a type of computing in which services are delivered through the Internet.

In the past, people would run application or programs from software downloaded on a physical computer or server in their building. Cloud computing allows access tom the same kinds of applications through the internet on a virtual server.

Cloud computing is a complete new technology. It is the development of parallel computing, distributed omputinggrid computing, and is the combination and evolution of Virtualization, Utility computing, software as a service,(SaaS), Platform as a Service (PaaS), Infrastructure as a Service (IaaS), Desktop as a Service(DaaS) or as a utility. cloud computing provides shared

resources, software and information through Internet as a PAYGO (Pay-as-you-go) basis. We just by using the need internet.



Cloud computing metaphor: the group of networked elements providing services need not be individually addressed or managed by users; instead, the entire provider-managed suite of hardware and software can be thought of as an amorphous cloud.

"Cloud is a parallel and distributed computing system consisting of a collection of inter-connected and virtualized computers based on service-level agreements (SLA) which established through cooperation between the service provider and consumers."

Cloud computing is a computing example, where a large pool of systems are connected in private or public networks which provide dynamically scalable infrastructure for application, data and file storage.

Cloud computing is a practical approach for to experience direct cost benefits and it has the potential to transform a data center from a capital-intensive set up.

The idea is based on a very fundamental principal of „reusability of IT capabilities'. The difference is that to bring compared to traditional concepts of "grid computing", "distributed computing", "utility computing", or "autonomic computing".

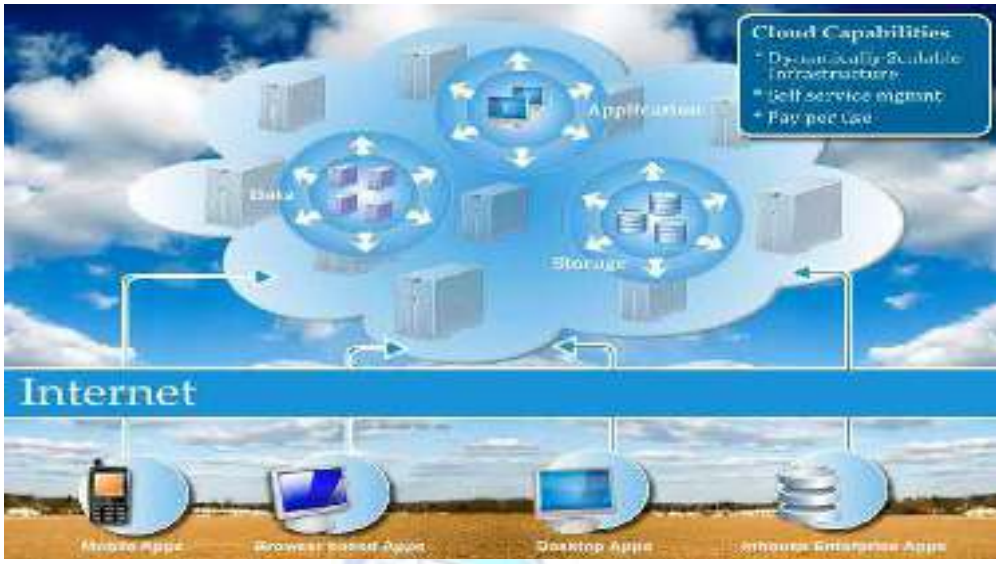
. "Cloud is a parallel and distributed computing system consisting of a collection of inter-connected and virtualized computers that are dynamically provisioned and presented as one or more unified computing resources based on service-level agreements (SLA) established through negotiation between the service provider and consumers."

Fig. 1: Cloud computing concept

Fig. 1 shows that how users can connect to the cloud services which is provided by cloud service provider by using any device over the internet. It includes scalable resources in storage, network, and compute & also contain virtualized infrastructure and provide that services to the users.

Forrester defines cloud computing as:

"A pool of abstracted, highly scalable, and managed compute infrastructure capable of hosting end-customer applications and billed by consumption."



It cuts the operational and capital costs and permits the IT departments to focus on strategic projects instead of keeping the datacenter running. It provides the services on Infrastructure level, Platform level, and Software level, many features such as speed, scalability of resources, parallel processing, to choose another technology at any time to further work like 24/7 availability of services, device and location independent and security etc. Cloud computing has five essential features such as rapid elasticity, measured services, on-demand self-service, resource pooling, and board network access. as shown in Fig. 2.

Fig. 2: Five features of cloud computing

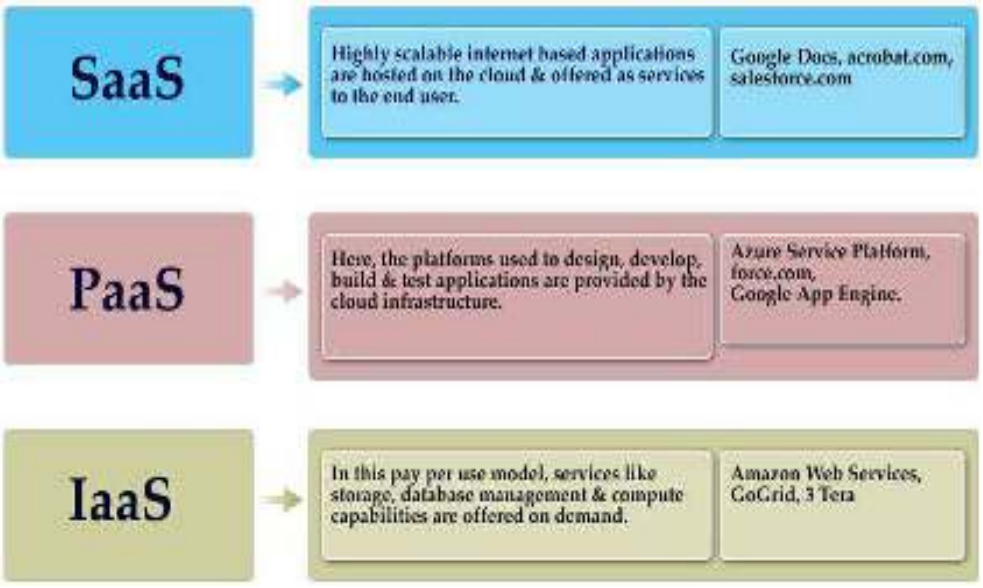
Cloud Computing Models:

Cloud service Providers following 3 types of Models:-

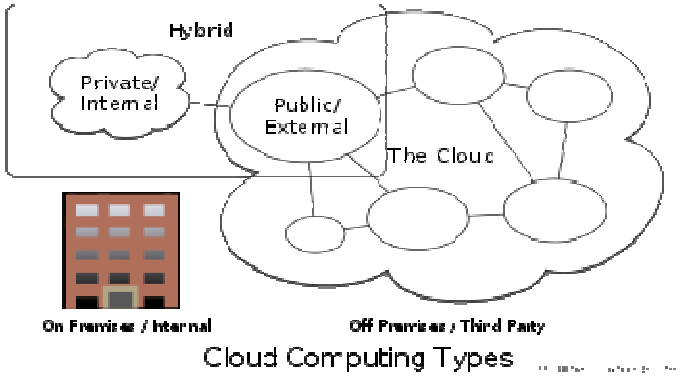
1. Software as a Service (SaaS): In this model, a complete application is offered to the customer, as a service on demand. A single instance of the service runs on the cloud & multiple end users are serviced. Today SaaS is offered by companies such as Google, Salesforce, Microsoft, Zoho, etc.

2. Platform as a Service (Paas): a layer of software, or development environment is encapsulate & offered as a service, upon which other higher levels of service can be built. In this model The customer has the freedom to build his own applications, which run on the provider‟s infrastructure. PaaS providers offer a predefined combination of OS and application servers, such as LAMP platform (Linux, Apache, MySql and PHP), classified J2EE, Ruby etc. Google‟s App Engine, Force.com, etc

3. Infrastructure as a Service (Iaas): IaaS provides basic storage and computing capabilities as standardized services over the network. Servers, storage systems, networking equipment, data centre space etc. The customer would typically deploy his own software on the infrastructure. Some common examples are Amazon, GoGrid, 3 Tera, etc.



Public, Private, Hybrid & Community Cloud:-



Cloud Computing Types

Fig. 3: cloud computing Types

Public Cloud

Public clouds are owned and operated by third parties; they deliver better economies of scale to customers, as the infrastructure costs are spread among a mix of users, giving each individual client an attractive low-cost, "Pay-as-you-go" model. One of the advantages of a Public cloud is that they may be larger than an enterprises cloud, thus providing the ability to scale seamlessly, on demand.

For example the Internet and Public

Switched Telephone Network (PSTN) etc

Private Cloud

Private clouds are built exclusively for a single enterprise. They aim of Private Cloud is to address concerns on data security

There are two variations to a private cloud:-

- On-premise Private Cloud: also known as internal clouds are hosted within one own data center.
- Externally hosted Private Cloud: This type of private cloud is hosted externally with a cloud provider.

Hybrid Cloud

Hybrid Clouds combine both public and private cloud models.. The Hybrid cloud environment is capable of providing on-demand, externally provisioned scale.

Community cloud

Community cloud implies an infrastructure shared between organizations, usually with the shared data and data management concerns. For example, a community cloud can belong to a government of a single country. Community clouds can be located both on and off the premises.

Cloud Computing Characteristic:-

1: Dynamic computing infrastructure
2: IT service-centric approach
3: Self-service based usage model
4: Minimally or self-managed platform
5: Consumption-based billing
6. Reduced Cost
7. Increased Storage
8. Flexibility
9. Data Protection
10 Data Recovery and Availability
11. Management Capabilities
12. Disaster Recovery
13. Automatic Software updates
14. Free Capital- expenditure
15. Work from anywhere
16. Document control
17. Security

Advantages of Cloud Computing

Shared Resources:

it shares resources to provide the services to multiple users.

Pay-As-You-Go:

Users only need to pay those resources which are used by them. They can demand for more resources if they required

Better Hardware Management:

It is easy for cloud service provider (CSP) to manage the hardware easily because all computers run the same hardware.

Area of Cloud Computing:

1. Banking
2. Insurance
3. Weather Forecasting
4. Space Exploration
5. Software as a service
6. Platform as a Service
7. Infrastructure- as -a-Service

Scope:-

Cloud computing is a tremendous innovation in the digital landscape that has changed the way IT solution are delivered and how end-users put them tom use. The cloud computing aspect is growing and will continue to do so.

Conclusion:-

Cloud computing is a new technology of computer network, providing the web services at lower cost comparing to normal technique. It contribute to improve the service in other related technologies like,Grid Computing, Cluster Computing, Utility Computing / Automatic Computing Distributed Computing with cloud computing, to the interface between service suppliers and multiple groups of service consumers. Cloud services will demand expertise in distributed services, procurement, risk assessment and service negotiation — these are the areas that many enterprises are only modestly equipped to handle, has changed the way IT solution are delivered and how end-users put them tom use. The cloud computing aspect is growing and will continue to do so.

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Universal Knowledge Discovery From Big Data

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Abstract-

Big data is a set of techniques and technologies that require new forms of integration to uncover large hidden values from large datasets that are diverse, complex, and of a massive scale. The one aspect that differs now (if compared with the past) would be the sheer scale and accessibility of Data, which is the direct result of the super efficient speeds in which data can now be computed. Big Data is therefore an all-encompassing term for any collection of large data sets that were once difficult to process. organizations are capturing data at deeper levels of detail and keeping more history than ever before. As a result, managing these increasing volumes of data is emerging as a key challenge for companies. The challenges include analysis, capture, curation, search, sharing, storage, transfer, visualization, and privacy violations.

Introduction:

Knowledge Discovery from Data (KDD) [1] refers to a set of activities designed to extract new knowledge from complex datasets. The KDD process is often interdisciplinary and spans computer science, statistics, visualization, and domain. Due to Increase in the amount of data in the field of genomics, meteorology, biology, environmental research and many others, it has become difficult to find, analyze patterns, associations within such large data . Interesting association is to be found in the large data sets to draw the pattern and for knowledge purpose. Big Data are the large amount of data being processed by the Data Mining environment. In other words, it is the collection of data sets large and complex that it becomes difficult to process using on hand database management tools or traditional data processing applications, so data mining tools were used. Big Data are about turning unstructured, invaluable, imperfect, complex data into usable information. [2]

The benefit of analyzing the pattern and association in the data is to set the trend in the market, to understand customers, analyze demands, predict future possibilities in Big Data typically differ from data warehouse in architecture; it follows a distributed approach whereas a data warehouse follows a centralized one. One of the architecture laid describes about adding new 6 rules were in the original 12 rules defined in the OLAP system defined the methods of data mining required for the analysis of data and defined SDA (standard data analysis) that helped analysis of data that is in aggregated form and these were much well timed in comparison with the decision taken in traditional methods. [3].Specifically, knowledge discovery processes are comprised of:

- Collection of data, storing the data, organizing the data in proper format.
- To understand the application of modern data analysis tools and methods.
- To understand the problem of structure and meaning of data.

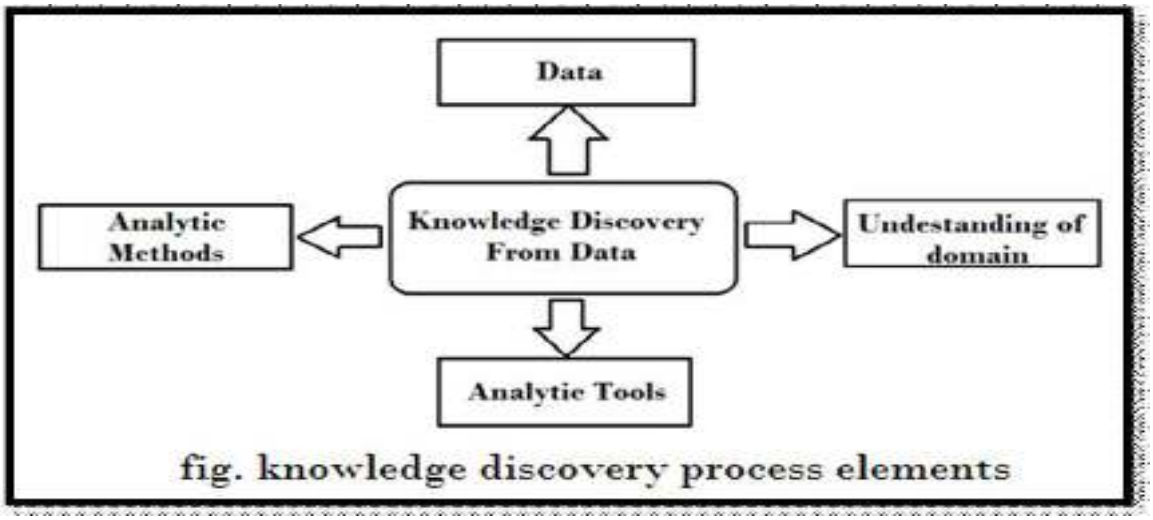

fig. knowledge discovery process elements

We believe that the application of some core principles can yield economical, comprehensive, flexible, and secure solutions for the federal government's big data needs . It helped organization to increase innovation, retain customers, and increase in operational efficiency[4] .According to Gartner definition big data is measured in 3 V's: variety, volume, velocity and value. [4][5]

Volume:

Big data uses massive datasets, including for example meta-data from internet searches, credit and debit card purchases, social media postings, mobile phone location data, or data from sensors in cars and other devices. The volume of data being produced in the world continues to increase rapidly. The Boston Consulting Group estimates total growth of 2.5 exabytes, which equals 2.5 billion gigabytes, per day[6].

Variety:

Big data often involves bringing together data from different sources. Currently it appears that big data analytics mainly uses structured data[7], e. g in tables with defined fields, but it can also include unstructured data. For example, it is possible to obtain a feed of all the data coming from a social media source such as Twitter. This is often used for 'sentiment analysis', i. e to analyse what people are saying about products
or organisations.

Velocity:

In some contexts, it is important to analyse data as quickly as possible, even in real time. Big data analytics can be used to analyse data 'in motion', as it is produced or recorded, as well as data 'at rest' in data stores. A potential application of 'in motion' analysis is in credit card payments. For example, Visa[8] is looking at using big data analytics to develop a new ways of authorising credit card payments.

Assumption I

Design principles are largely concerned with maximizing the controllable factors and thereby enabling researchers to explore, analyze, and interact with data in as easy manner as possible.

Assumption Ii:

It support variety of analytical tools: Knowledge discovery from big data science employs methods from distributed programming, data mining, statistical analysis, machine learning, visualization. These methods often employ vastly different tools and techniques. For example, programmers may use Java to write distributed computation while statisticians may feel more comfortable using R, SAS, etc.

Statistical Analysis:

1. It is concerned with summarising large datasets.
2. Most statistical tools (i.e., R, SAS) prefer to compute data over numerical data organized in tabular format.
3. It require organization step specially for unstructured data.
4. Currently in our system various statistical tools are available like SQL,R and Python.

Data Mining:

1. Data mining (the analysis step of the "Knowledge Discovery in Databases" process, or KDD) [10] an interdisciplinary subfield of computer science.
2. Each and every day the human beings are using the vast data and these data are in the different fields .It may be in the form of documents, may be graphical formats ,may be the video may be records (varying array) .
3. As the data are available in the different formats so that the proper action to be taken. Not only to analyze these data but also take a good decision and maintain the data .As and when the customer will required the data should be retrieved from the database and make the better decision .This technique is actually we called as a data mining or Knowledge Hub or simply KDD(Knowledge Discovery Process).
4. It is the computational process of discovering patterns in large data sets involving methods at the intersection of artificial intelligence, machine learning, statistics, and database systems.[11]

Data visualization and visual analysis:

1. Data visualization or data visualisation is viewed by many disciplines as a modern equivalent of visual communication.
2. A primary goal of data visualization is to communicate information clearly and efficiently to users via the information graphics selected, such as tables and charts.
3. Effective visualization helps users in analyzing and reasoning about data and evidence. It makes complex data more accessible, understandable and usable.
4. Users may have particular analytical tasks, such as making comparisons or understanding causality, and the design principle of the graphic (i.e., showing comparisons or showing causality) follows the task. Tables are generally used where users will look-up a specific measure of a variable, while charts of various types are used to show patterns or relationships in the data for one or more variables.

Assumption Ii:

Comprehensive KDD architecture provide a variety of data analysis method , it must also supply a mean of storing and processing of data. Single storage mechanism is for small data volumes like local file.system. But it is more problematic for large-scale data analysis. B, we

argu that different types of analysis and the intermediate data. structures required by these (e.g. graphs for social network analysis) call for specialized data management systems . Others have also recognized that the time of the single style database that fits all needs is gone [12].

Data Preparation and Batch Analytics :

Data preparation is the first step in the analytics pipeline. At this stage, the data may contain errors, missing values, and is often in an unusable format (i.e., a compressed binary format). In our experience, Hadoop is an ideal tool for this stage. Hadoop is a collection of open source software based on Google's BigTable [13] and Google File System [14]. It includes Map Reduce [15] component (for distributed computation) and a scalable storage component that can often replace costly SAN devices. Hadoop sub-project such as Hive and HBase offer additional data management solution for storing structured and semi-structured data sets. In oursystems we rely on HDFS as a data landing platform and use Hive as our batch-oriented data warehouse.

Processing Structured Data :

Often the product of the data preparation stage is a set of highly structured, relational data. Although Hadoop can process such data (via Hive), we have found distributed analytic databases [16] to be useful for storing and analyzing such data.

Processing Semi-structured Data

Not all data can be easily modeled using relational techniques. For example hierarchical documents, graphs, and geospatial data. Such data is extremely useful for social network analysis, natural language processing, and semantic web analysis. We provide HBase [17] and Cassandra [18] for hierarchical, key-value data organization. For graph analysis, we employ both open-source (e.g., Cray's uRiKa platform). Finally, for geospatial data we employ open-source tools (e.g., PostGIS, GeoTools) and proprietary tools (e.g., ESRI software).

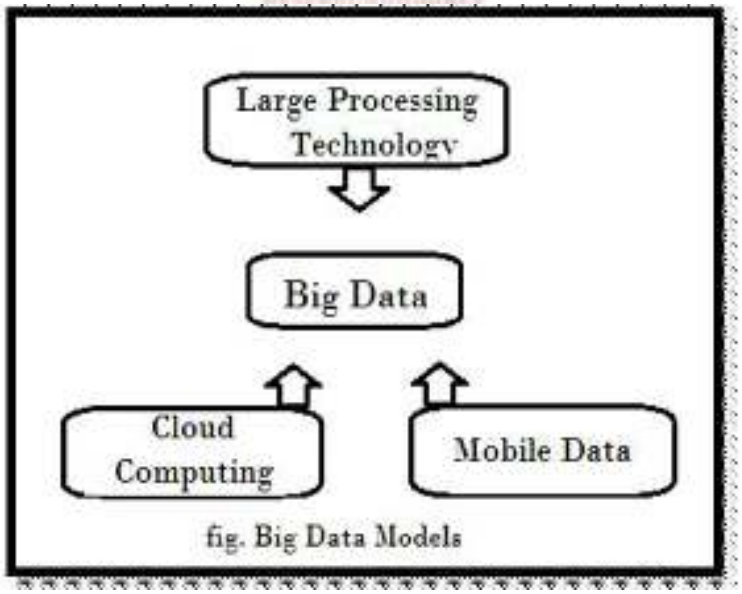

fig. Big Data Models

The semi-structured and unstructured data may not fit well in traditional data warehouses on relational databases Furthermore, data warehouses may not be able to handle the processing demands posed by sets of big data that need to be updated frequently or even continually -- for example, real-time data on the performance of mobile applications or of oil and gas pipelines. As a result, many organizations looking to collect, process and analyze big data have turned to a

newer class of technologies that includes Hadoop and related tools such as MapReduce and NoSQL databases. Those technologies form the core of an open source software framework that supports the processing of large and diverse data sets across clustered systems.

Hadoop

Hadoop is a free, Java-based programming framework that supports the processing of large data sets in a distributed computing environment. It is part of the Apache project sponsored by the Apache Software Foundation.Hadoop makes it possible to run applications on systems with thousands of nodes involving thousands of terabytes. Its distributed file system facilitates rapid data transfer rates among nodes and allows the system to continue operating uninterrupted in case of a node failure. This approach lowers the risk of catastrophic system failure, even if a significant number of nodes become inoperative.

MapReduce

MapReduce is a software framework that allows developers to write programs that process massive amounts of unstructured data in parallel across a distributed cluster of processor or stand-alone computers. It was developed at Google for indexing Web pages and replaced their original indexing algorithims and heuristics in 2004.The framework is divided into two parts:

1. Map, a function that parcels out work to different nodes in the distributed cluster.
2. Reduce , another function that collates the work and resolves the results into a single value.
3. The MapReduce framework is fault tolarent because each node in the cluster is expected to report back periodically with completed work and status updates. If a node remains silent for longer than the expected interval, a master node makes note and re-assigns the work to other nodes.

Application :

Understanding and Targeting Customers

This is one of the biggest and most publicized areas of big data use today. Here, big data is used to better understand customers and their behaviours and preferences. Companies are keen to expand their traditional data sets with social media data, browser logs as well as text analytics and sensor data to get a more complete picture of their customers. The big objective, in many cases, is to create predictive models.

Understanding and Optimizing Business Processes

Big data is also increasingly used to optimize business process. Retailers are able to optimize their stock based on predictions generated from social media data, web search trends and weather forecasts. One particular business process that is seeing a lot of big data analytics is supply chain or delivery route optimization. Here, geographic positioning and radio frequency identification sensors are used to track goods or delivery vehicles and optimize routes by integrating live traffic data.

Improving Science and Research

Science and research is currently being transformed by the new possibilities big data brings. Take, for example, CERN, the Swiss nuclear physics lab with its Large Hadron Collider, the world's largest and most powerful particle accelerator. Experiments to unlock the secrets of our universe – how it started and works - generate huge amounts of data. The CERN data center

has 65,000 processors to analyze its 30 petabytes of data. However, it uses the computing powers of thousands of computers distributed across 150 data centers worldwide to analyze the data. Such computing powers can be leveraged to transform so many other areas of science and research.

Optimizing Machine and Device Performance

Big data analytics help machines and devices become smarter and more autonomous. For example, big data tools are used to operate Google's self driving car. The Toyota Prius is fitted with cameras, GPS as well as powerful computers and sensors to safely drive on the road without the intervention of human beings. Big data tools are also used to optimize energy grids using data from smart meters. We can even use big data tools to optimize the performance of computers and data warehouses.

Future Work

Although our infrastructure is used for real-world applications, we treat these systems as a research platform and expect it to continuously evolve as the state-of-the-art advances. We have developed our knowledge discovery principles during the course of implementing these applications and standing up our own systems.

Conclusions

The big data movement has energized the software architecture world, and it has introduced complex, interesting questions for the community. As organizations continue to collect more data at this scale, formalizing the process of big data analysis will become paramount. In this paper, we introduced principle that we believe can guide organizations into developing a sound, useful, and flexible data analysis pipeline.We have instantiated these principles in our own infrastructure and havefound the principle to be useful guides.

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The Role of Cloud Computing in Education

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Abstract:

Cloud computing as an exciting development in a educational Institute and online marketing perspective. Students and administrative personnel have the opportunity to quickly and economically access various application platforms and resources through the web pages on-demand. Application of storage technology can significantly reduce the amount of cloud storage servers, thereby reducing system development costs; reduce the system caused by the server a single point of failure.

Cloud storage services meet this demand by providing transparent and reliable storage solutions In this paper shows that the cloud computing plays an important role in the fields of Educational and online Marketing and it is helpful to provide the data to the Students and online customer respectively. The results show the beneficial of the cloud computing in Educational and online marketing for customers.

Keywords: virtualization, security, cloud computing, web based storage, distributed data base.

Introduction

The nature of the Internet was constantly changing from a place used to read web pages to an environment that allows end-users to run software applications. The need for education is increasing constantly and the development and the improvement of the e-learning solutions is necessary. Also, the E- learning systems need to keep the pace with the technology, so the new direction is to use cloud computing. Cloud computing is becoming an attractive technology because of its dynamic scalability and effective usage of the resources; it can be utilized under circumstances where the availability of resources is limited.

The need for education is increasing constantly and the development and the improvement of the e-learning solutions is necessary. cloudbased applications reduce infrastructure and IT costs, increase accessibility, enable collaboration, and allow organizations more flexibility in customizing their products both for their brand and for their audience.The benefits of cloud computing are being recognized in almost all kinds of institutions across the board, with 90 percent of organizations currently using some kind of cloud-based application. First, let us understand what exactly cloud computing is and what services it provides.

Cloud Computing Challenges:

The reason for the success of Cloud computing lies in its easy-to-use computing model and the benefits it brings to the users. Cloud computing has emerged as an important solution offering enterprises a potentially cost effective model to ease their computing needs and accomplish business objectives. Some features of cloud computing are:

1. Optimized Server Utilization

As most enterprises typically underutilize their server computing resources, cloud computing will manage the server utilization to the optimum level.

2. On-Demand

Cloud computing provides users with customized environments that are tailed to individual requirement. This feature is more user friendly than Grid computing where the application has usually to be adapted to the target architecture.

3. Dynamic Scalability

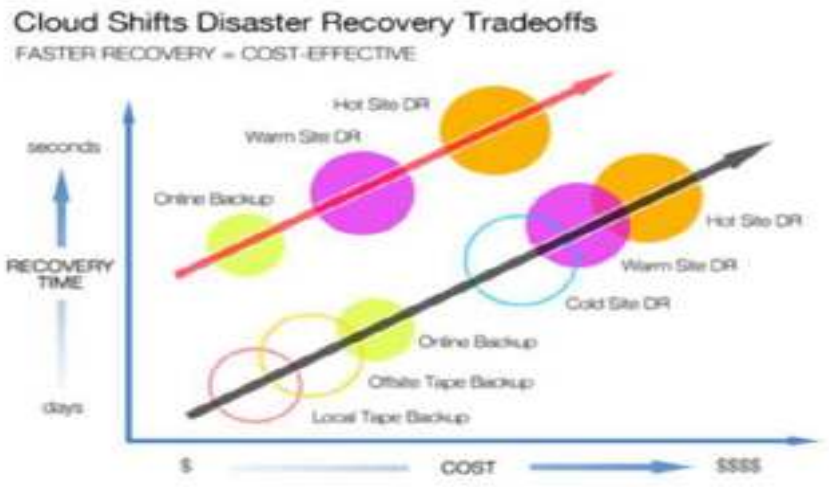
Many enterprises include a reasonably large buffer from their average computing requirement, just to ensure that capacity is in place to satisfy peak demand. Cloud computing provides an extra processing buffer as needed at a low cost and without the capital investment or contingency fees to users.

4. Disaster Recovery

It is a concern of enterprises about the resiliency of cloud computing, since data may be commingled and scattered around multiple servers and geographical areas. It may be possible that the data for a specific point of time cannot be identified. Unlike traditional hosting, the enterprise knows exactly where the location is of their data, to be rapidly retrieved in the event of disaster recovery. In the cloud computing model, the primary CSP may outsource capabilities to third parties, who may also outsource the recovery process. This will become more complex when the primary CSP does not ultimately hold the data. The Cloud technology is currently still in the development phase. As the sensitive applications and data are moved into the cloud data centers, run on virtual computing resources in the form of virtual machine. One of the most significant advantages to cloud computing is how it changes disaster recovery, making it more cost-effective and lowering the bar for enterprises to deploy comprehensive DR plans for their entire IT infrastructure.

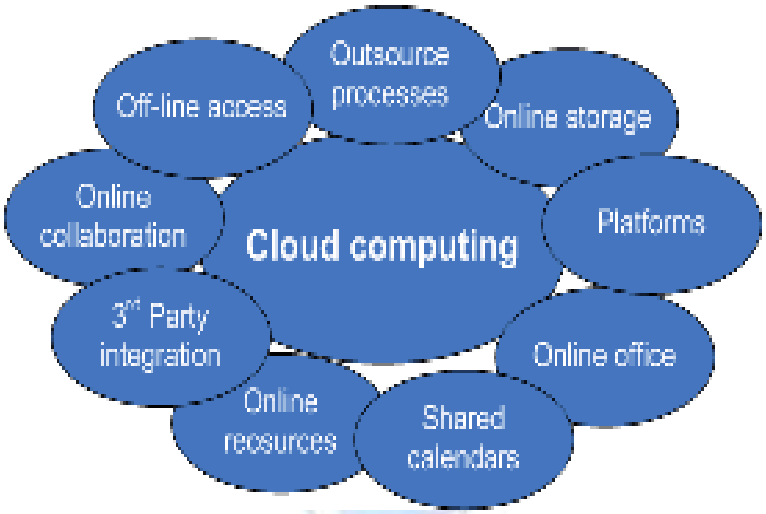
Cloud Computing delivers faster recovery times and multi-site availability at a fraction of the cost of conventional disaster recovery. With cloud computing, warm site disaster recovery becomes a very cost-effective option where backups of critical servers can be spun up in minutes on a shared or private cloud host platform. Applications and servers that are deemed less critical in a disaster can be tuned down with less resources, while assuring that the most critical applications get the resources they need to keep the business running through the disaster.

And many more application of cloud computing work but the above applications and the challenges in it.



Educational Usage Of Cloud Computing.

There was a time when, to use files (word processing files, spreadsheets, etc.) on different computers. Cloud computing is a new business model wrapped around new technologies like virtualization, SaaS and broadband internet. The safety, stability, and ease-of-use of cloud computing in education is resulting in widespread adoption in educational institutions of all sizes and types. loud computing entails using a network of remote servers hosted on the internet as opposed to a local server. This helps cut IT costs as well as simplifies content management processes for schools and educational systems. The results of a survey that have been completed in 2009 by Gartner analysts (Figure 1) about the IT trends (especially cloud computing) show that it is being used more in the areas of finance and business when compared to other sectors.



1. Back Up

An important function of the Cloud is that it automatically saves content, making it impossible to lose or delete any valuable material. This means that even if a computer crashes, all documents and content will remain safe, saved, and accessible in the cloud.

2. Storage

The Cloud allows its users to store almost all types of content and data including music, documents, eBooks, applications, photos, and much more. We share the information of Attendance and Assignment in our Institute of students in Google doc and share all the information of students on doc via using an ERP Software and utilize the cloud resources.

3. Accessibility

Any data stored in the Cloud can easily be accessed from almost any device including mobile devices such as phones or tablets. In our institute an URL provide to the students for accessing the data inside the campus or outside the campus.

4. Collaboration

The Cloud allows multiple users to work on and edit documents at the same time, it enables effortless sharing and transmission of ideas. It also provides the security to edit only those people who gain the right from admin. With this feature, group projects and or collaborative lesson plans can be optimized for both teachers and students.

5. Resource and Time Conscious

With the availability of content online, it is no longer necessary for teachers to spend time and resources printing or copying lengthy documents or lesson plans. Now, students are able to access homework assignments, lesson notes, and other materials online like ERP Systems of education institute and parents also see the details of the students. Cloud can be used in underdeveloped or emerging countries creating a way of being able to teach children who would not ordinarily have access to education. Students and teachers can share their work without having to use paper. Using paper is costly both to the environment and in monetary terms and is therefore no longer a viable way to educate.

Adavantages cloud computing in E-Commerce

For describing the different aspects of an online commerce systems, digitally enabled commercial transactions between and among organizations and individuals. Cloud computing is now evolving like never before, with companies of all shapes and sizes adapting to this new technology. The Figure 4 shows a high-level view on an E-commerce system's architecture. If used properly and to the extent necessary, working with data in the cloud can vastly benefit all types of businesses. Industry experts believe that this trend will only continue to grow and develop even further in the coming few years. While cloud computing is undoubtedly beneficial for mid-size to large companies, it is not without its downsides, especially for smaller businesses.

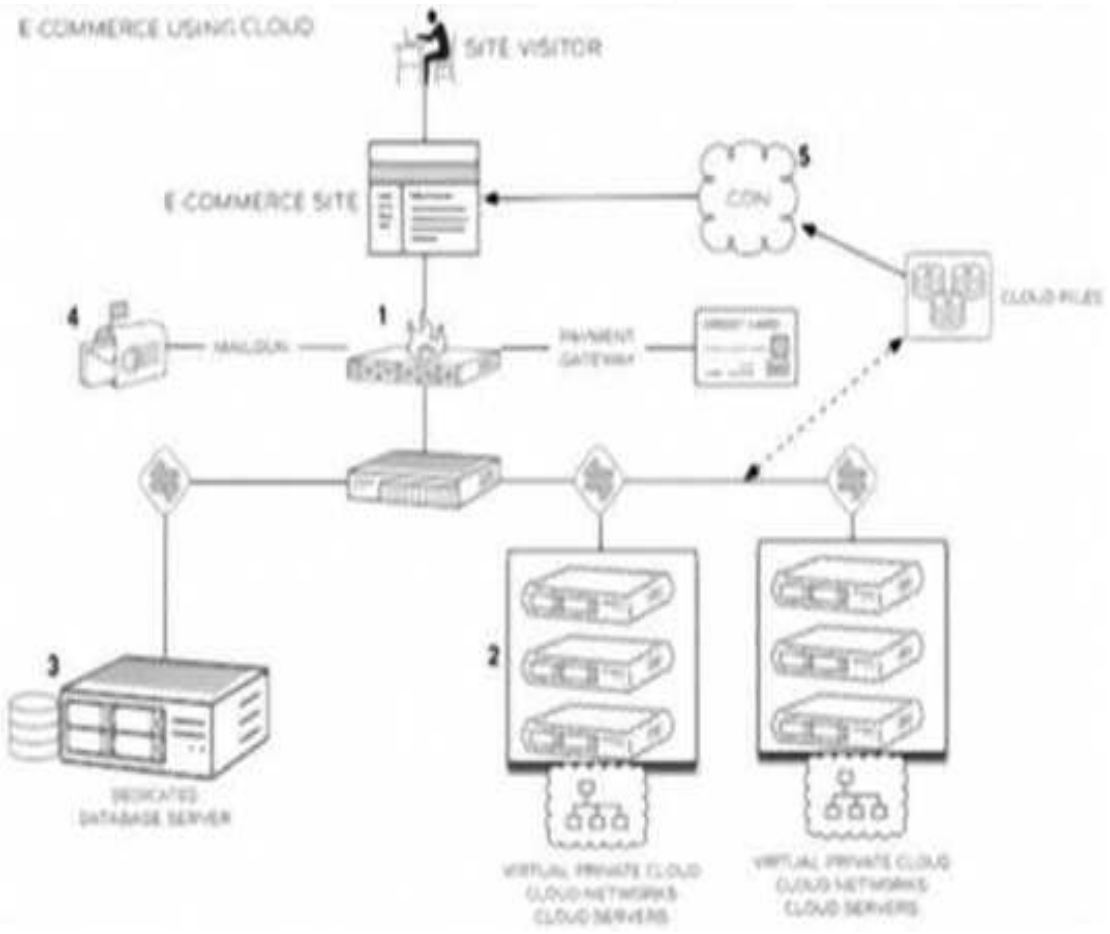


Fig:-E-commerce System

1. Unlimited Accessibility

Developing a business means being constantly connected With Cloud, you can manage your online shop from anywhere and at any time. A browser and an Internet connection are all it takes to process orders, interact with customers, schedule deliveries or generate invoices.

2. Security and Stability

Security is one of the most important advantages of the Cloud technology. In the Cloud system, the data of each client is completely partitioned, so that none of the areas interferes with the others. The connection to the servers is secured according to the highest standards, making sure that you are the only one with access to your data. It's like having your own server, without paying considerable amounts of money.

3. Full Scalability

Your business grows, so will your technical requirements. Unlike open source ecommerce solutions, which would normally require new investments for extending the technical infrastructure, a Cloud ecommerce system will always be ready to efficiently sustain your new volume of clients, orders, traffic and continuously growing product catalog.

4. Minimal Costs or No Costs

Cloud solution for E-Commerce, you don't need to worry about the initial investments. You don't need to buy your own server or pay for a separate hosting service. Depending on your business needs, you can always increase or limit the amount of resources you use and also optimize your costs thanks to the scalability of the system.

Cloud computing is probably the most cost efficient method to use, maintain and upgrade. Traditional desktop software costs companies a lot in terms of finance. Adding up the licensing fees for multiple users can prove to be very expensive for the establishment concerned.

5. Quick Deployment

Lastly and most importantly, cloud computing gives you the advantage of quick deployment. Once you opt for this method of functioning, your entire system can be fully functional in a matter of a few minutes. Of course, the amount of time taken here will depend on the exact kind of technology that you need for your business.

Various Types Of Services Provided By Cloud

A. SaaS (Anytime Anywhere apps)

It stands for Software as a Service. It describes any cloud service where consumers are able to access software applications over the internet. The applications are hosted in ―the cloud and can be used for a wide range of tasks for both individuals and organizations. Google, Twitter, Facebook and Flickr are all examples of SaaS, with users able to access the services via any internet enabled device. SaaS is beneficial to organizations in many ways like no additional hardware costs, no initial setup costs, usage is scalable, updates are automated, accessible from any location etc. This cloud service allows educational institutions to subscribe to online software hosted by a cloud provider. If proprietary software is used, educational institutions need to pay for the usage of the software. SaaS removes the need for organizations to install and run applications on their own computers or in their own data centers. This eliminates the expense of hardware acquisition, provisioning and maintenance, as well as software licensing, installation and support

B. PaaS (the operating environment in which applications run)

It stands for Platform as a Service. It is a category of cloud computing that provides a platform and environment to allow developers to build applications and services over the internet. PaaS services are hosted in the cloud and accessed by users simply via their web browser (ex: Google App Engines etc.).Platform as a Service allows users to create software applications using tools supplied by the provider. Services are constantly updated, with existing features upgraded and additional features added. It supplies an operating environment for developing applications. Some of the benefits of PaaS are: they don't have to invest in physical infrastructure, flexibility, adaptability, teams in various locations can work together, security etc. IT courses that require hands-on practice on a client-server structure, such as database systems or application development courses, PaaS is the one to use. PaaS does not typically replace a business' entire infrastructure. Instead, a business relies on PaaS providers for key services, such as Java development or application hosting. C. IaaS (the on-demand data centres) It Stands for Infrastructure as a Service. It provides access to computing resource in a virtualized environment, ―the Cloud, across a public connection, usually the internet. In the case of IaaS the computing resource provided is specifically that of virtualized hardware, in other words, computing infrastructure. The definition includes such offerings as virtual server space, network connections, bandwidth, IP addresses and load balancers. Some benefits of IaaS are: scalability, no investment in hardware, utility style costing, location independence, physical security of data centre locations etc. Microsoft Windows Azure and Amazon Web Service (AWS) provide IaaS. This service can mainly be used to satisfy the infrastructure needs of the students, faculties or researcher globally or locally with some specific hardware configuration for a specific task. IaaS platforms offer highly scalable resources that can be adjusted on-demand. This makes IaaS well-suited for workloads that are temporary, experimental or change unexpectedly

Implementation Of Cloud Technology In Education System

Cloud computing technology can provide solutions for the above mentioned problems in education system. Cloud computing enables users to control and access data via the Internet.The main users of a typical higher education cloud include students, Faculty, administrative staff, Examination Branch and Admission Branch as shown in Figure 1. All the main users of the institution are connected to the cloud .Separate login is provided for all the users for their respective work. Teachers can upload their class Tutorials, assignments, and tests on the cloud server which students will be able to access all the teaching material provided by the teachers via Internet using computers and other electronic devices both at home and college and 24X7. The education system will make it possible for teachers to identify problem areas in which students tend to make mistakes, by analyzing students' study records. In doing so, it will also allow teachers to improve teaching materials and methods. This will not only make it possible for students to use online teaching materials during class but they will also be able to access these materials at home, using them to prepare for and review lessons. Utilization of cloud computing systems will reduce the cost of operation because servers and learning materials are shared with other colleges

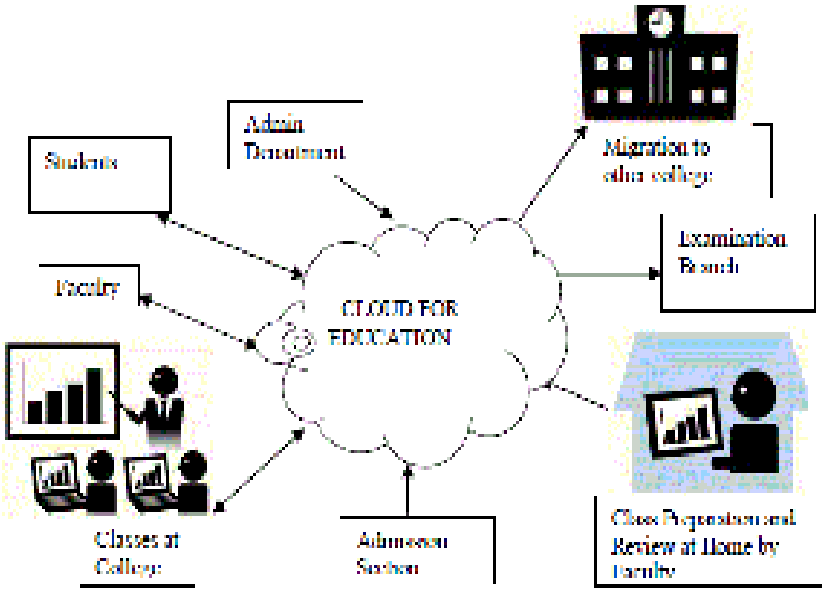


Figure 1: Services attached to Education Cloud

Figure 2: Users of an Education Cloud Computing System

In the traditional deployment model, all Information Technology resources are housed and managed in-house. Many aspects of these services and tools may be migrated to the cloud and consumed directly over the Internet either as fully functional applications (SaaS), development platforms (PaaS) or raw computing resources (IaaS).Figure 2 shows how the different categories of university users may consume cloud services.

Benefits Of Cloud Computing For Institutions And Students

1. Personalized Learning: Cloud computing affords opportunities for greater student choice in learning. Using an Internet-connected device, students can access a wide array of resources and software tools that suit their learning styles and interests.
2. Reduced Costs: Cloud-based services can help institutes reduce costs and accelerate the use of new technologies to meet evolving educational needs. Students can use office applications for free without having to purchase, install and keep these applications up to date on their computers. It also provides the facility of Pay per use for some applications.
3. Accessibility: Availability of the services is the most important and desired by the user using the education cloud.24 X7 is the availability that is needed by this system without failure. From anywhere one can login and access the information.
4. No Extra Infrastructure: Colleges and governments are now free to focus on their goals that is making more research facilities available to the students and making the environment global in spite wasting time on worrying about the buildings, labs, teachers etc.
5. Go Green: Education cloud will surely reduce the carbon footprint. 6. User Friendly: This new facility is user friendly and no need to worry about the complexity. It is easy to understand and easy to operate

Conclusion

Although still quite a vague term for some, cloud computing is definitely one of the major innovations that entered worldwide classrooms in recent years. With the ability to cut IT costs and at the same time create a modern collaborative

The cloud allows us to access our work anywhere, anytime and share it with anyone. It frees us from needing a particular machine to access a file or an application like a word processor or spreadsheet program. In the present paper a cloud education system is introduced and how it is beneficial for students, faculty and the educational institutes for providing quality education

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A Survey on one Time Password: That Provides Protection Against Various Password - Based Attacks.

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Keywords: Network security, Password reuse attack**,** Password cracking system, User authentication.

Abstract:

A password is a sequence of characters used for user authentication to prove identity or access authorization to gain access to the resources which should be kept secret. Passwords are the powerful equipment's that tend to keep all data and information digitally safe. Text based words are most well liked style of user authentication on websites due to its convenience and easiness. The easier the password is for the owner to remember usually means it would be easier for an attacker to guess. And also the security of system can be reduced by passwords that are difficult to remember. However, user's passwords are at risk to be exploited and compromised underneath different threats and vulnerabilities. Security of Password is very important for user authentication on networking system. Passwords are prone to various types of attacks like password stealing attack, password reuse attack, password cracking attack, brute force attack etc. Passwords can be protected by various methods introduced by different researchers. To decrease the harm caused by phishing and other attacks, banks, governments, and other industries are deploying One-Time Password systems.

Introduction:

Internet and user authentication is the most essential component within the field of Security. Computer users are asked to create, preserve and remind an increasing number of passwords for host accounts, email servers, online financial services and e-commerce sites. Password based user authentication can defend against dictionary attacks and brute force attacks if users opt for strong passwords to provide enough entropy. Most users choose easy to remember passwords (i.e., weak passwords) even if they know that these passwords might be unsafe. Another decisive problem is that users tend to reuse same passwords across a variety of websites. Negative influence of human factors is the basic reason behind all the above problems. Thus far, researchers have investigated a variety of technologies to trim down the negative influence of human factors in the authentication procedure. Since humans are more skillful in remembering graphical passwords than text passwords, many graphical password strategies were designed to deal with human's password recall problem. Hence, Password management tools were designed. Strong passwords are automatically generated by these tools, which discourses password reuse and password recall problems. Here, users have to memorize a master password to access the password management tool. Three factor authentication is another attractive strategy. It is a method of computer access control in which user is granted access after successfully presenting several pieces of evidence to an authentication mechanism; of following categories: knowledge (something user know); possession (something user have), and inherence (something users are).For authentication procedure, the user must enter a password and input a

pass code generated by the token, and scan the biometric features. Two factor authentication is more eye-catching and convenient than three-factor authentication. Two factor authentication is a authentication procedure in which user has to provide two means of identification from different categories; first is a personal token, such as a card, and second is the memorized security code. Disadvantage is that users simply forget to carry the token one time password (OTP) systems provide a mechanism for logging on to a network or a service using a unique password which can be used only once, as the name suggest. This prevents some forms of identity theft by making sure that captured username/password cannot be used second time. Typically user logon name stays same, and one time password changes with each login. One time passwords are a form of so-called strong authentication, provides much improved protection to on-line banking accounts, corporate networks and other systems containing sensitive data. Strong authentication systems addresses the limitations of static passwords by incorporating an additional security credential, a one-time password (OTP) strategy, to protect network access and end users digital identities. This adds an extra level of security and it will be extremely challenging for an attacker to access unauthorized data, networks or online accounts.

Working with OTP

Methods of generating OTP:

OTP generation algorithms make use of pseurandomness or randomness, and also hash functions, which can be used to obtain a value but are hard to reverse and therefore hard for an attacker to obtain the records used for hash.

Time Synchronized:

A time synchronized OTP is generally related to a piece of hardware called a security token (one time password is generated by this token).Inside the token, there is an accurate clock which is synchronized with the clock on the authentication server. Time based One Time Password Algorithm (TOTP) is an example of time synchronized OTP of standard .TOTP is an algorithm that calculates one time password from a shared secret key and the synchronized.

Mathematical Algorithm:

A mathematical algorithm generates a new password based on the previous passwords (OTPs are efficiently a chain that must be used in predefined order).Here, new password is based on a challenge (a random number chosen by the authentication server or transaction details) and/or a counter. Each new OTP is created from past used OTP.[6]

Delivering OTP and its methods:

Text Messaging:

A frequent technology used for the delivery of OTPs is text messaging. Because text messaging is an ever-present communication channel, and is directly available in almost all mobile handsets and, through text-to-speech conversion, to any landline telephone or mobile handset, text messaging is likely to reach all customers with a low cost to implement. OTP over text messaging might be encrypted using an A5/x standard, which some hacking groups report can be effectively decrypted within minutes or seconds, or the OTP over SMS might not be encrypted by one's service-provider at all. The mobile phone operator becomes a part of the trust chain. In the case of roaming, more than one mobile phone operator has to be trusted. Using this data may increase a man-in-the-middle attack.[6]

Mobile phones:

Steps to get OTP on Mobile Phone a mobile phone keeps costs low as a very large number of people use mobile phone for various reasons other than generating OTPs. Mobile phones additionally support any number of tokens within one installation of the application, and from one device user will be authenticated to multiple resources. Model-specific applications according to user's mobile phone are also available.

Proprietary tokens:

HID Display Card Token HID Display Card Tokens enable organization to apply strong authentication to their network, system and cloud based applications. The Display Card tokens fit easily into user's wallet, and are highly portable and convenient .When needed, users simply click a button and Display Card Token generally generates a one-time password they can use to authenticate to the resource they need. RSA Secure ID Token RSA SecureID is an alternate type of token which is used for generating one time passwords. More advanced hardware tokens use smart cards that are microprocessor based to calculate one time passwords. Smart cards are used for strong authentication and include data storage capacity, processing power, portability and ease of use. They are fundamentally more secure than other OTP tokens because they store personal data, and do not transmit personal or private data over network.

Web based methods:

Authentication offers various web based methods for delivering one time passwords without the use of hardware tokens. Such techniques depend on user's ability to recognize pre-chosen categories from a randomly generated collection of pictures. When registering on a website, the user chooses several categories of pictures; such as animals, cars, celebrities and flowers. Whenever user would login the website they are presented with a randomly generated grid of picalphanumeric character overlaid on it. The user looks for pictures that fit their pre-chosen categories and enters the associated alphanumeric characters to form one time password.

Hardcopy:

In some countries for online banking, the bank sends user a list of OTPs that are printed on paper. Other banks send plastic cards with actual OTPs covered by a layer that the user has to scratch off to disclose a numbered OTP. To carry out online transaction, the user is required to enter a specific OTP from that list. Some system inquire for numbered OTPs sequentially, others pseurandomly choose an OTP to be entered.

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Iot – Smart Farming Solution

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Abstract:

IoT (Internet of Things) has transformed our lives in many ways. The concept has enhanced our comforts through automation. The IoT has also opened up new opportunities for the agricultural sector through productive ways of monitoring agriculture process. This paper focused on how IoT can be used to improve quality of agro products with minimum overheads. To meet growing demand of food, farmers and agricultural companies are turning to the Internet of Things for analytics and greater production capabilities. Internet of Things (IoT) can play big role in increasing productivity, obtaining huge global market, idea recent trends of crops.

Keywords: Internet of Things, Smart Farming, Productivity, Agriculture.

What is IoT:

The IoT is the internetworking of physical devices, vehicles and other objects which consists of an embedded system with sensors and network to collect and exchange data. It is an integration of physical world into computer based system which results in improved accuracy, efficiency and economic benefit.

Importance of Agriculture

India is agricultural country. Rapid growth in population leading to huge demand in agricultural edible products like grains, vegetables, fruits etc. but rapid changes in climate, constantly diminishing land under cultivation & depleting water sources are major reasons for declining productivity in agriculture sector[2]. With the help of efficient management, optimized use of seeds and fertilizers along with precise and continuous monitoring can improve productivity to compensate the losses due to above mentioned uncontrolled factors. Today, farmers in developing regions with a small-scale land can increase the production if they get the right and real-time information for taking farming decisions.

What is Smart Farming?

The internet-enabled objects and sensors can be deployed anywhere to gather data on moisture level and crop health. The farmers can readily access the stored data through their tablets and mobile phones. They can also select between manual and automated options for taking necessary actions based on this data. For example, if the soil moisture level decreases, the farmer can deploy sensors to start the irrigation. Now, this is what we call a smart farming.

How do Smart Farming solutions work?

Smart farming solutions work through sensors. Farmers can monitor various conditions like soil moisture, water level, light, humidity, obstacles, and motion from anywhere by combining sensors, motion detectors, button camera, and wearable devices. The IoT-based smart farming automates the irrigation system and is highly efficient as compared to the conventional operations. This concept can help farmers to do farming in ultramodern way in era of manpower

scarcity & very busy lifestyle. It is easy to follow the trends in organic farming, family farming, group farming etc.[4]

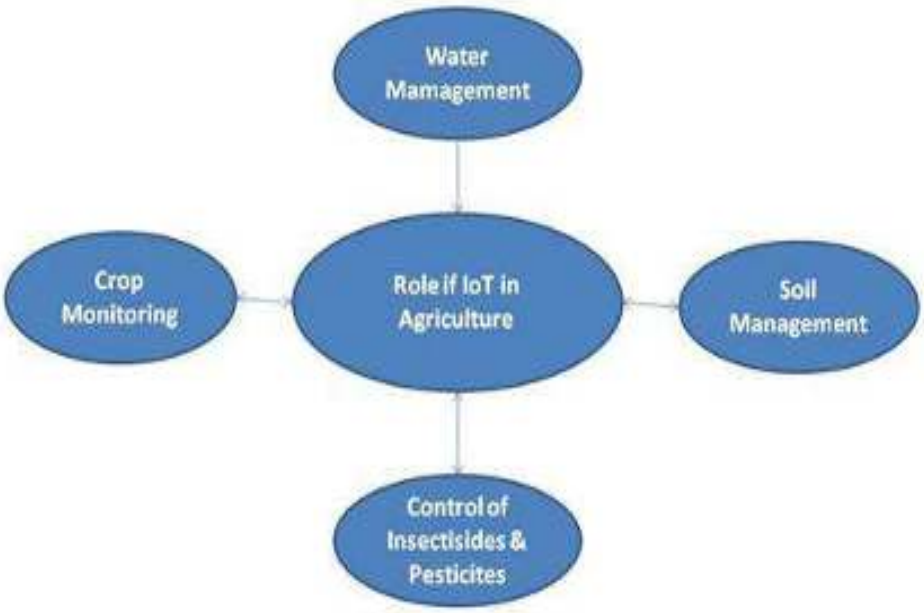

Figure 1. Role of IoT in the agriculture sector:

Plant and Soil Monitoring:

The soil sensors [5], which are at uniform distances across the farmland, can alert farmer to any irregular conditions like high acidity or low moisture. The farmers can get an accurate soil data either by the dashboard or a customized mobile application. Figure 2. sensors are used to sense the moisture content in the soil. It works on the principal of electrical conductivity. Resistance of the sensor is inversely proportional to moisture content in the soil. Moisture content of the soil is a major factor determining plant growth. The present work Comprises of development of a soil moisture sensor.

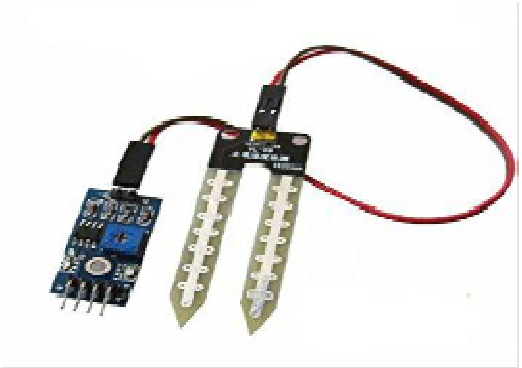

Figure 2. soil sensors

Humidity sensors

Humidity sensors measure the relative humidity in the air. Humidity directly influences the water relations of plant and indirectly affects leaf growth, photo synthesis, pollination and finally economical yield. Leaf growth not only depends on synthetic activities resulting from biochemical process but also upon the physical process of cell enlargement.

Figure 3. Humidity sensors

Smartphone Applications

Smartphone plays key role in Internet of Things (IoT) for data aggregation and speedy processing to bring up-to-date, actionable information to small farmers regarding seeding, weeding, fertilizing, and watering. Smartphone applications gather data from handheld sensors, remote sensors, and weather stations, creating in-depth analyses and valuable recommendations. Several applications have been developed specifically targeting the small-scale farmer

1. Disease Detection and Diagnosis: Photos taken of suspect plants can be forwarded to experts for analysis.
2. Fertilizer Calculator: Soil sensors and leaf color can determine what nutrients are needed.
3. Soil Study: Capturing soil images, as well as pH and chemical data from sensors, allows farmers to monitor and adjust to changing soil conditions.
4. Water Study: Determining Leaf Area Index from photos and brightness logging can help farmers determine water needs.
5. Crop Harvest Readiness: Camera photos with UV and white lights accurately predict ripeness.

Advantages of IoT in Farming:

1. The key advantages of using IoT in farming are as follows[7]:
2. Water management can be efficiently done using IoT with no wastage of water using sensors.
3. IoT helps to continuous monitor the land so that precautions can be taken at early stage.
4. It increases productivity, reduce manual work, reduce time and makes farming more efficient.
5. Crop monitoring can be easily done to observe the growth of crop .
6. Soil management such as PH level, Moisture content etc. can be identified easily so that farmer can sow seeds according to soil level.
7. Farmers can easily connect to the global market without restriction of any geographical area which leads increased crop sale in global market.
8. In person monitoring is not required which is prerequisite for timely decision making for higher production & profitable farming

Conclusion

Farming is very important for India. To improve production in farming , smart farming is essential. Internet of Things will help to enhance smart farming. IoT works in different domains

of farming to improve time efficiency, water management, crop monitoring, soil management, control of insecticides and pesticides etc. It also helps to minimize human efforts. IoT provides simple techniques of farming and helps to gain smart farming. Along with these features smart farming can help to grow the market for farmer with single touch and minimum efforts.

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THE RISKS AND LIMITATIONS OF SECURITY MECHANISMS ON IOT ENVIRONMENTS

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ABSTRACT

Internet of Things is the technique which is provided by the unique identifiers that can automatically transfer the data over the wide network without the help of human being. The devices uses are vulnerable to hack. The purpose of hacking the devices of Internet of Things may not be accessing data only, but it could be harming the users of those devices. In other words, it might affect them economically, endanger their health or put their lives at risk since this technology is directly connected to their daily lives, and this is considered a violation of users'privacy.The devices of Internet of Things are hacked and exploited in order to attack the Internet infrastructure supplied by some major companies. In this paper we have token an overview about the security of Internet of Things, we are trying to cover the possible security measures to put a stop to attacks from the previous research scholars on the topic of security of Internet of Things. We propose a one of a kind concept of three Layered Security to prevent the malicious activities of Cyber-criminals. In these three layers we have ponder the Device Security, Communication Security and Server Security. Risks and Limitations are also discussed here.

Keywords-IoT Security; Three layered Security; Network Security; Risks; Limitations

1. Introduction

Internet of Things (IoT) is considered as an integrated part of Internet, also defined as a global network infrastructure and dynamic composed of a large number of objects, able to communicate and interact with each other, with end users [1, 2, 3].These objects must have unique identities which allow interactivity. Firewalls cannot be being embraced within embedded systems. The appealing targets of hackers and cyber-criminals are embedded computing devices. The very last lessons and hacking occurrences in Internet of Things have challenged the security expert professionals. The PC security ways out could not provide complete solution for the security to be as long as for Internet of Things. The significant functionality of Internet of Things has given much wider scope for the cyber-attacks and leaded to catastrophic punishments. Duplication is widely found in embedded devices for the hacker. If the cyber-criminal could find the methodology or cracking mechanism for one, it can be applied to all replicated devices and leads to great havoc. Many people believe that the cryptographic algorithms enforcements alone provide the security. Some investigators could implement the cryptographic protocols as a 2nd kind of link in Internet of Things. Much the same implementing of technology knows how to minimize the risk of the physical attacks in IoT will be adequate enough to security in Internet of Things. Implementing UVEEPROM or Flash erasure or Laser glitching or Laser Assisted power analysis can be certain of the security for IoT.As the matter of fact, the implementation of any security measures cannot give most appropriate security to the IoT so much further. The cyber criminals have somehow broken the security layers and instigating the attacks [4].This paper is organized as follows. In section 2, we presents the related work, section 3 a proposed security model according to areas of interest to today worked in IoT is presented, section 4 describe risks in IoT respectively, section 5 discuss result and analysis. The final section 6 conclusions and future work is presented. To suggest highly a novel security distinguishing with three layered security for Internet of Things.

2. Related Work

The rapid development of information technology and Internet security information about IoT, a new problems and potential security over information has been rise. Therefore, it becomes a focus aspect to build a safety and reliability system in the IoT context.IoT has knowledgeable the logical attack surface. These attacks have been successfully picked up by the TCB of devices involved architecture with wider perspective has given enough security measures for the attacks.IoT is wealthy with complex software and rich operating systems. The amplified security is essentially gad to have to provide the protection against the surface attacks. This has been effectively encountered by the Logical TCB conducting [4].

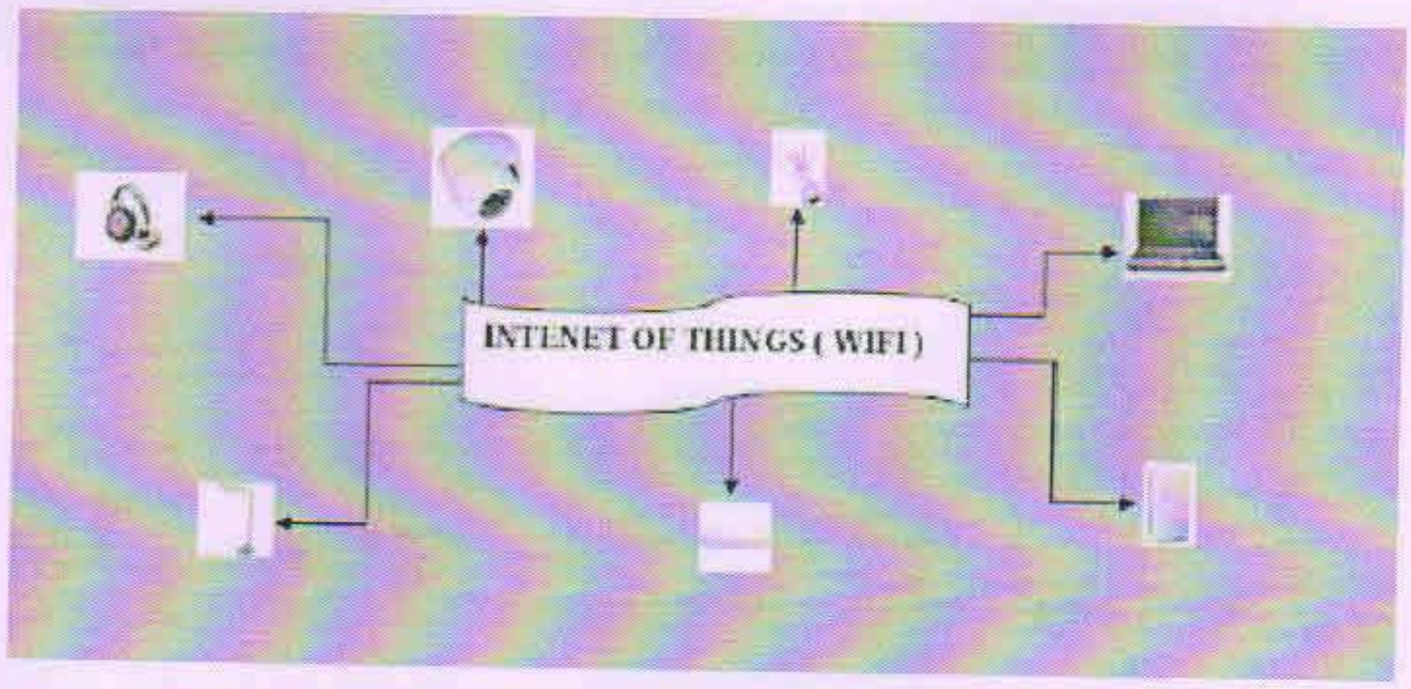

Figure 1: IoT Security Provision.

The Internet of Things is a virtuousness hacking target for all widespread cyber-criminals. The motor vehicles and transportation systems which are working with the Internet of Things are the pinnacle targets for hackers. They have already call attention to their attacks and did prospective damage to the automobile segment. Symantec firm has advised a protecting code embedded in the drives of IoT.This code makes it possible for the devices to work against the hacking technology and will not uncover the way for incursion [2].

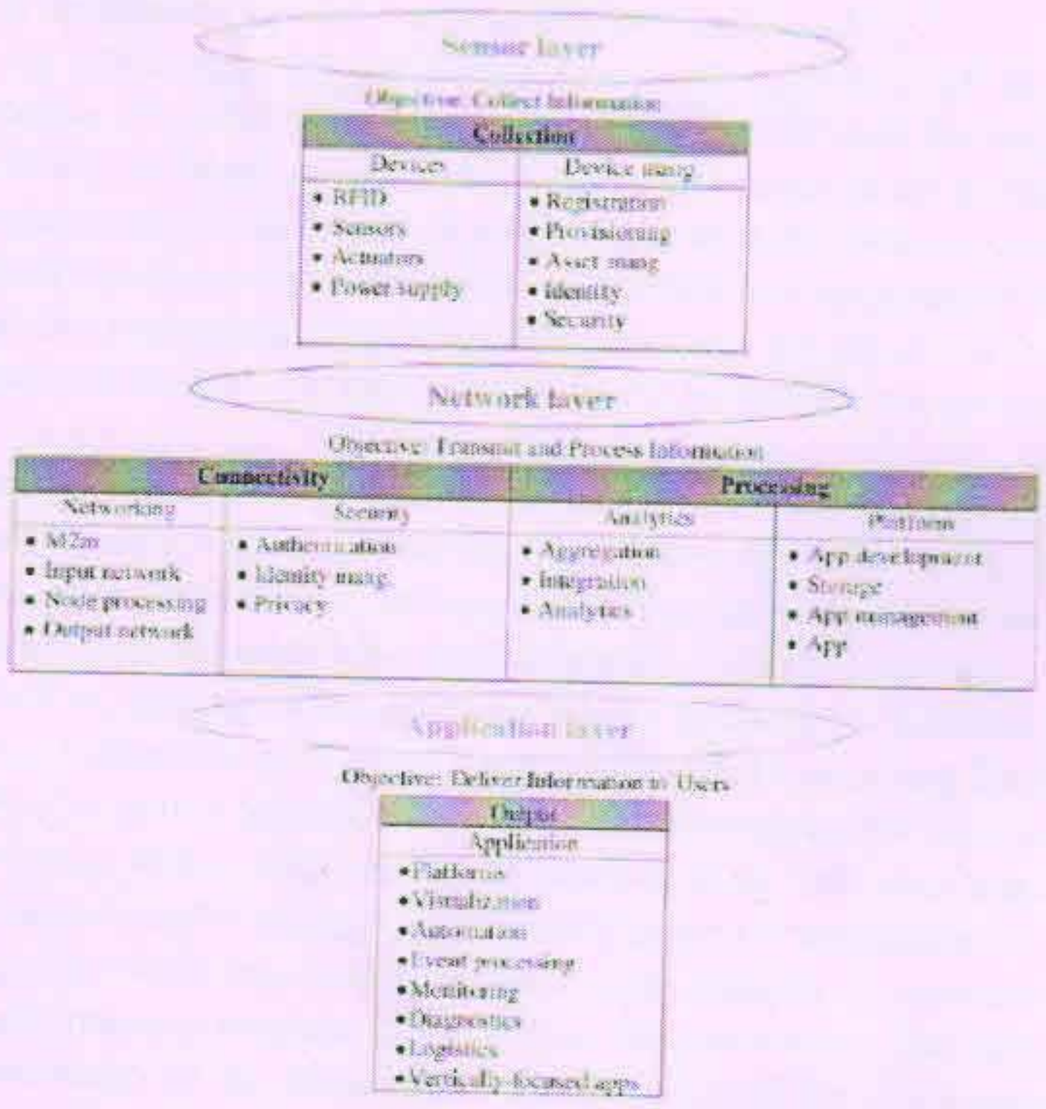

Figure 2: Three layered Security

The three layered security implementations of IoT operations of any kind of system. The security implementation is developed and framed in a three-layer framework for the IoT security to implement the safe and secure operation of remotely performing controlling and monitoring operations of the users for the targeted devices. The proposed security model is describe below.

3. Security Model Proposed

Due to Internet of Things is a large field with various technologies, a categorization of the issues and technologies was made, this categorization is the basis for analysing some detail of security and privacy in the respective fields. Figure 3 shows a categorization of the issues and their respective technologies used in each of the topics that make up the Internet of Things. According with figure 3, it can be identified eight major areas within IoT which must be specified level of security related studies .They are describe below [5].

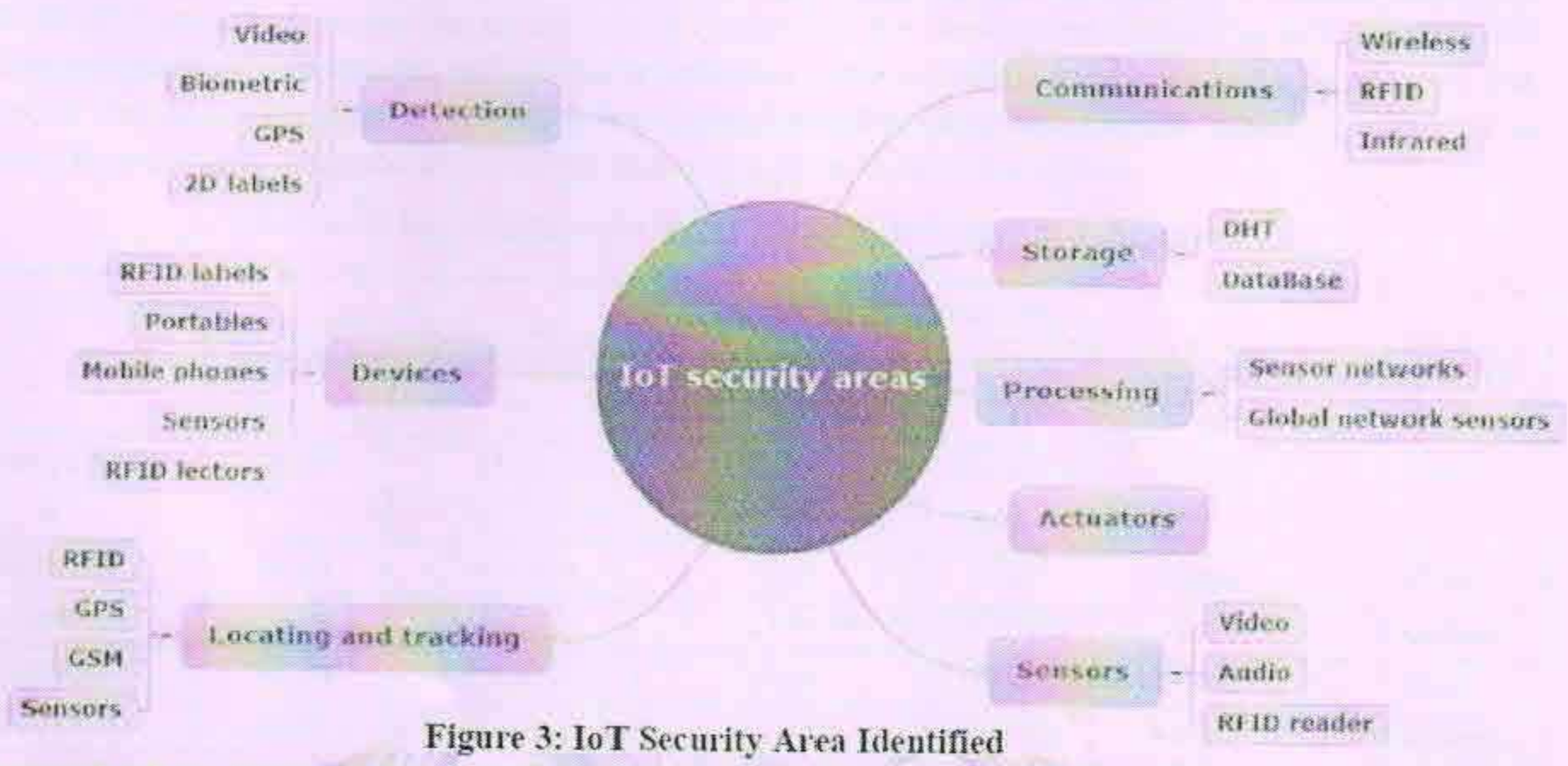

Figure 3: IoT Security Area Identified

1. Communication: Research on communication protocols has come up with solutions that provide the integrity, authenticity and confidentiality. such as TLS or IPsec. Privacy needs have been addressed by different routing schemes as Onion Routing or Free-net, but these are not widely used.

2. Sensors: Integrity and authenticity of the sensor data is an objective of the current research. The confidentiality of data sensors is a very vulnerable condition therefore the need for confidentiality in the sensor is low, so that confidentiality is based on the confidentiality of communication. Mechanisms such as face blurring video data are important to implement in order to preserve the privacy of individuals and objects. Sensors availability depends mainly on the communication infrastructure. Regulations are necessary to preserve the privacy of individuals who are currently most often unconscious on the sensors, such as video cameras.

3. Actuator: Integrity, authenticity and confidentiality of data in an actuator depends primarily on the security of communications.

4. Storage: Security mechanisms for storage devices are well established. Data storage is highly sensitive to privacy and there are many cases of violation of privacy regulations should be widely distributed to provide an adequate response to user privacy protection. Storage availability depends mainly on the availability of the communication infrastructure and well-established mechanisms for redundancy storage.

5. Devices: Within the field of integrity of the devices, a device is free from malware. This property has also been called ''admissibility'' a presently open issue, researched Trusted Computing Platform (TPM) and highly sensitive. The authenticity of a device handles all the communication parts, not seen such as the end point of connection .Confidentiality is a device with integrity to ensure that no third party has access to internal data devices. Devices privacy depends on the physical privacy and privacy of communication.

6. Processing: Integrity in data processing services is based on the integrity of communication devices. Also, it depends on the design and proper execution of algorithms for processing. The authenticity of processing depends solely on the authenticity of the device and the authenticity of the communication. The property of confidentiality in processing depends only on the integrity of the device, and in the case of distributed

processing, depends on the integrity of the communication. The availability of processing depends on the device and the availability of communication exclusively.

7. Location and Tracking: The integrity of Location and Tracking is based on the integrity of Communication and the integrity of the reference signals used in the location, such as GSM or GPS.It also depends on the authenticity of the authenticity and integrity of communication devices. The confidentiality of data tracking and tracing are of great importance to ensure user privacy and therefore is very sensitive. Confidentiality in this context means that an attacker is not able to disclose the location data and therefore is primarily based on the confidentiality of communication. Data privacy location means that there is no way for an attacker to reveal the identity of the person or object and the location and tracking is not possible without the agreement or explicit knowledge.

8. Identification: It uses same sensitivities than Location and Tracking. One difference is the higher sensitivity on the integrity part. It is easier for an attacker to manipulate the identication process as it is handling the localization process. This translates mainly due to technology used (eg RFID or Biometrics) is more likely that an attacker manipulate location technologies (eg GSM).From this basic classification criteria are defined to determine the relevance of the security level on each of the areas identified in table 1.

Table1: Recommendation Criteria in Security Areas

Properties	Security Principles					
	Integrity	Authenticity	Confidentiality	Privacy	Availability	Regulation
Communication	High	High	High	Medium	High	Low
Sensors	High	Medium	Low	High	Low	High
Actuators	Low	Low	Low	Medium	Low	Medium
Storage	High	Medium	High	High	Low	High
Devices	High	Low	Low	Medium	Medium	Medium
Processing	Medium	Low	Low	High	Low	High
Location and Tracking	Low	Low	High	High	High	High
Identification	Medium	High	High	High	High	High

Recommendations

1. It is highly recommended to incorporate the security at the design phase of IoT of a specific device.
2. It is highly recommended to promote security updates and vulnerability management for the proposed IoT.
3. It is highly recommended to apply the TLS and DTLS data encryption for the data transmitted in IoT management.
4. Authentication and key management is a mandatory solution to be followed by IoT users.
5. The strong communication should be established with the system and the devices that are operated in IoT regardless of manufacturer of the devices.

4. Risks in Internet of Things

Any device connected to the Internet like a smart car, a camera surveillance and a smart lamp, which has its own system that performs a specific task. It is apt to hacking more than computers because their security system is extremely weak. The most significant problems are summarized as follows [6]:

1. Privacy problems that might put the user data at risk, however this data is considered too sensitive.
2. Material damage that could be caused by tampering with instruments which can lead to harming the user, such as home appliances.
3. Misusing this technology for purposes like monitoring users and violating their privacy.
4. Possibility of exploiting location data of those devices for example determining the car site.
5. Exploiting those internet devices for hacking electronic governments and major companies that are associated with the Internet.

4.1 Security vulnerabilities of Internet of Things

1. Vulnerabilities in communication interfaces between the user and Internet of Things is insecure, where the user can bypass, access and control the device.
2. Weakness in the authentication process [7].
3. There are not enough methods to identify the authorized users, and this allows unauthorized people to log in to those devices.
4. Insecure software occurs when programmers focus only on the speed of transfer data neglecting the security aspect.
5. Using insecure protocols for data transfer.
6. Easiness of scanning and knowing the devices connected to the Internet.

4.2 Possible solutions to reduce risk

1. Default passwords and ideally default usernames to be changed during initial setup.
2. Ensuring user accounts cannot be enumerated using functionality such as password reset mechanisms.
3. Ensuring account lockout after 3-5 failed login attempts.
4. Ensuring the cloud-based web interface is not susceptible to XSS, SQLi or CSRF.
5. Ensuring credentials are not exposed over the Internet.
6. Implement two factor authentications if possible.
7. Implemented Secure Sockets Layer (SSL) and Transport Layer Security (TLS).
8. Automatic update IoT devices with security patches when packages update become available.
9. Disable Universal Plug and Play (UPNP) protocol for prohibit from discover hacker to know devices in your network.
9. Most devices exploit by mira virus must be updated firmware.

5. Result and Discussion

Implementation of security architecture for every devices connectivity with the internet servers to protect the systems from possible attacks from Cyber-Criminals or hackers. The security architecture should consist of device manufacturing specifications as well as the system specification to have proper integration and transparency over the devices and servers [8, 9].

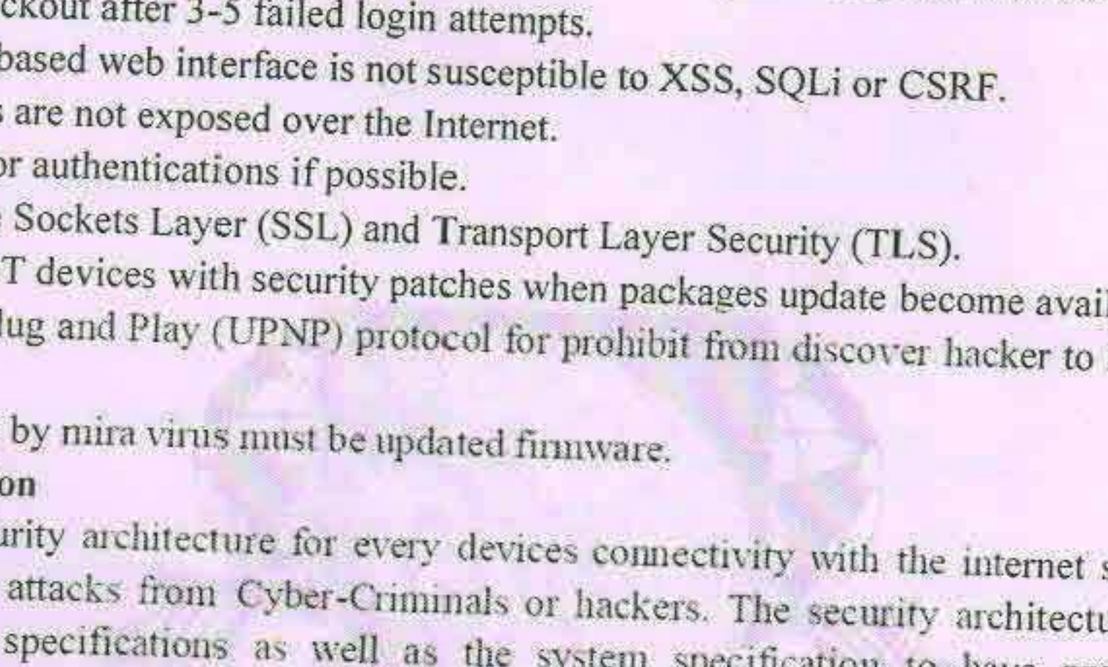

Figure 4: Three layered Security.

The three-layer security should be implemented at Device Level, Communication Level and finally the Server Level. The security updates against the possible attacks and unknown vulnerability should be continuously done. The management should always implement build on proven security practices needed for IoT implementation for specific device management. The transparency should be maintained between the operation of IoT developers, IoT devices manufacturers, communication providers and industrial and business-level consumers [10, 11].

Taking advantage of the security for IoT is the aspiration of the project. The proposed fitting solution is meted

out in three levels. The security implementation is at Server Level is the first juncture. The 2nd level is implementing the vastly level security in Communication layer. Finally, the 3rd level security is ought to be implemented at Device Level. The security level at virtual servers will be conjunct with the Cloud Computing servers. Each of these servers are operated by the remote users to control over the devices and gadgets. Above and beyond the cloud server's security the increased security needs to be implemented in the Server Level with formidable authentication and authorization with digital encryption standards. The second level security must have to be implemented at Communication Level. The communication effectively between the servers and users and the communication between the servers and devices are predominant. The security implementation need to be incorporated at Communication layers of the IoT operations. This implementation can be done with incorporating network security algorithms and strong admeasures for external attacks. The proposed solution is stressing on the third level security at Device Level. The devices embedded with chips to store the software should also implement with the anti-virus and protection against the vulnerabilities and external attacks to compromise the devices. The devices are same and connected in multiple number with the servers. If the attacker compromise one single device can easily compromise other devices. Hence the Device Level security is equally important in IoT operations.

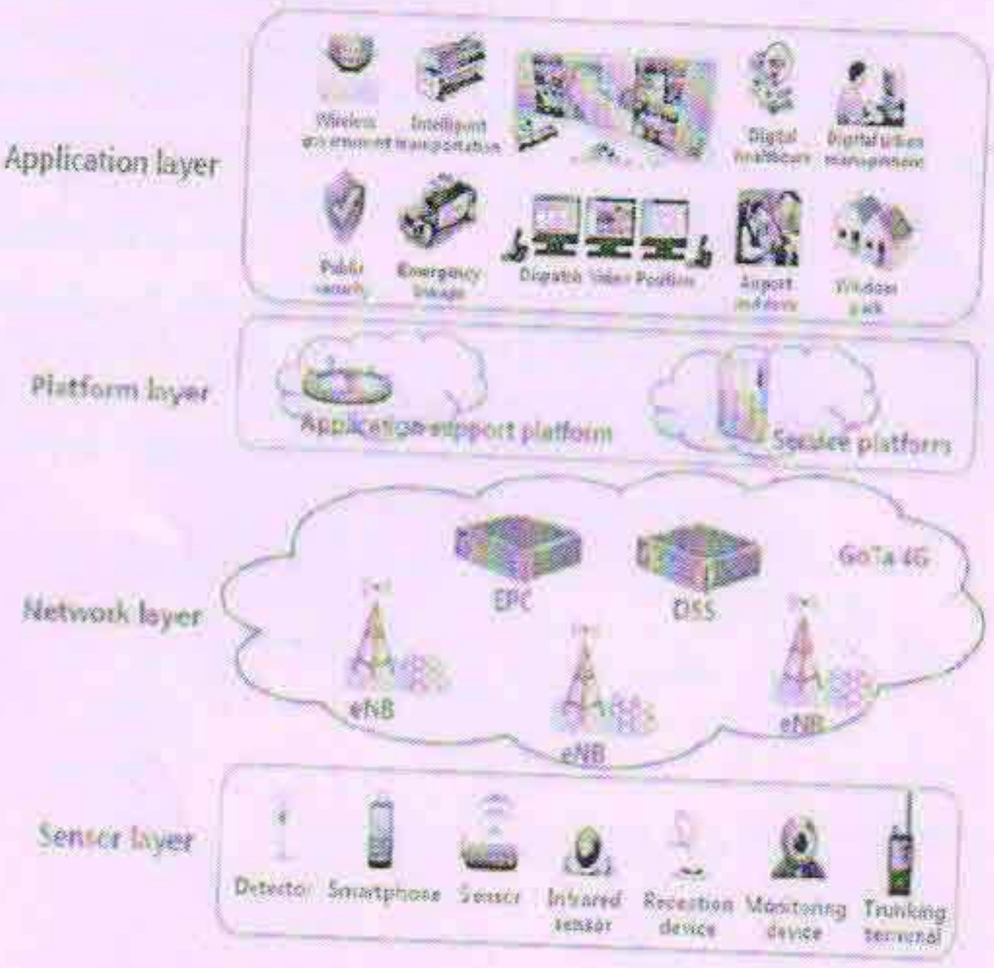

Figure 5: Security Integration Points in IoT.

6. Conclusion

The goal of this paper shows what has happened and maybe happen in the future as well as the work of the crisis precautions to reduce risk. The aim of the paper is to suggest the three-layer security implementation for the IoT working mechanism. In this paper the possible high-level security implementation has been suggested at Device Level, Communication Level and Server Level. In addition to that the mandatory implementation of security monitoring and updating the security implementations time to time to prevent the attacks in IoT.Finally, the paper has recommended the possible precautions to implement strong security in IoT.As future work, is foreseen to carry out a characterization of these problems, so that from an ontological model and intelligent agents it can be carried out the appropriate identification of security mechanisms from most frequent problems in the IoT environments. This would facilitate security alternatives identification, deployment access models IoT devices first.

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STUDY OF VARIOUS IMPLEMENTED APPROACHES FOR RUMOUR DETECTION OVER SOCIAL MEDIA PLATFORM

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Abstract

The rapid growth of World Wide Web has resulted in substantial increase in use of social media.Social interactions can be inferred on the web using the mailing list and home page links. It also represents the social lives of the individuals, collaborations, communities and relationship. Social networking groups are becoming increasingly important due to the volume and activities. The social media data consists of comments, Feedback and reviews.Rumour detection is used for text classification which classifies text into Positive, Negative and Neutral. The increasing use of social media platforms for information and news gathering, its unmediated nature often leads to the emergence and spread of rumours. The aim of the survey is to provide a study on various implemented approaches for rumour detection over social media.

Keywords- Social Media, RumourDetection,SVM,KNN,NB,ME.

1. Introduction

An online social media is a big platform to share thoughts, ideas and knowledge. Now days the day life stress with social platform and end on it as well this will become big media of communication. This media will share the good as well as bad thoughts. People from different geometric locations to talk, share photos, ideas and interests, or make new friends as a virtual community is a website on the internet that serves as an ultimate location for. Online social network increase in security treats and rumors with the rapid increase in popularity. By exploiting user's privacy, identity and confidentiality the intruders and attackers are able to outsmart the security measures by using several techniques [1]. Numerous information is propagating through on-line social network similarly as every positive and negative information. The information posted on social media not always right or not truthful. All people can share information and also give their opinions on that platform is an advantage of social media. The disadvantage of such rapid diffusion of information is that negative information are also spread [2]. Rumour detection is consider as a binary classification task where predefined set of category of binary class as {Rumour, Non-Rumour}.Automatic resolution of rumours is a challenging task that can be broken down into smaller components that make up a pipeline including Rumour detection, Rumour tracking and stance classification leading to the final outcome of determining the veracity of a rumour [3]. A rumour detection system that identifies, in its early stages, postings whose veracity status is uncertain, can be effectively used to warn users that the information in them may turn out to be false.This study include various classification of rumour detection techniques over social media platforms such as machine learning approaches and Lexical based approaches with their comparative analysis.

2. Rumour Detection Approaches:

In Broadly , there exist two types of methods for rumour Detection : Machine Learning methods often rely on supervised Classification approaches, where rumour detection is framed as a binary(i.e. positive or negative).On the other hand ,Lexicon based methods make use of a predefined list of words. Various implemented techniques for rumour detection over social media are discussed with more detail[4].

minimization principle. It is a supervised learning method widely used for classification and regression tasks.SVM is using the concept of train and test dataset [8].The classifier will be trained with target values and features intrain set. The trained classifier will be tested with new features without target value. The algorithm will produce high dimensionofgeneralizationthantheoriginalsetofdata.

2.1.3Artificial Neural Network [ANN]:

The original goal of the ANN approach was to solve problems in the same way that a human brain would. However, over time, attention moved to performing specific tasks, leading to deviations from biology. Artificial neural networks have been used on a variety of tasks, including computervision, speech recognition, machine translation, social network filtering, playing board and video games and medical diagnosis.ANN is a tool to develop machine learning applications [9]. It is also called as multi-layer perceptions. Input, output, and hidden layers are the part of ANN. The hidden layer will perform operations related to the given problem. The user can have multiple hidden layers to get the optimum results. ANN environment provides Feed forward, Recurrent, Convolutional, Botlmann machine, and Hopfield networks to the users.

2.1.4Naïve Bayes:

Naïve Bayes is a simple and easy but effective classification algorithm. It is mostly used for document level classification. The basic idea is to calculate the probabilities of categories given a test document by using the joint probabilities of words and categories. Naïve Bayes is optimal for certain problem classes with highly dependent features. It uses Bayes theorem to predict the probability which migt be offer feature set belongs to a selected label [9].

2.1.5Bayesion Network

In essence, Bayesian means probabilistic. The specific term exists because there are two approaches to probability. Bayesians think of it as a measure of belief, so that probability is subjective and refers to the future.Frequentists have a different view: they use probability to refer to past events - in this way it's objective and doesn't depend on one's beliefs. The name comes from the method - for example: we tossed a coin 100 times; it came up heads 53 times, so the frequency/probability of heads is 0.53.

2.1.6Maximum Entropy:

The Max Entropy classifier is a probabilistic classifier which belongs to the class of exponential models. Unlike the Naive Bayesclassifier that we discussed in the previous article, the Max Entropy does not assume that the features are conditionally independent of each other. The MaxEnt is based on the Principle of Maximum Entropy and from all the models that fit our training data, selects the one which has the largest entropy [10]. The Max Entropy classifier can be used to solve a large variety of text classification problems such as language detection, topic classification, sentiment analysis and more.

2.2Lexicon Based Approach:

In unsupervised technique, classification is done by comparing the features of a given text against sentiment lexicons whose sentiment values are determined prior to their use. Sentiment lexicon contains lists of words and expressions used to express people's subjective feelings and opinions. For example, start with positive and negative word lexicons, analyze the document for which sentiment need to find. Then if the document has more positive word lexicons, it is positive, otherwise it is negative. The lexicon based techniques to Sentiment analysis is unsupervised learning because it does not require prior training in order to classify the data.

The basic steps of the lexicon based techniques are outlined below [2]:

1. Preprocess each text.
2. Initialize the total text sentiment score: $s \leftarrow 0$.
3. Tokenize text. For each token, check if it is present in a sentiment dictionary.

(a)If token is present in dictionary,

i. If token is positive, then $s \leftarrow s + w$.

ii. If token is negative, then $s \leftarrow s - w$.

4. Look at total text sentiment score s,

(a) If $s >$ threshold, then classify the text as positive.

(b) If $s <$ threshold, then classify the text as negative.

2.2.1 Dictionary-based Approaches:

In dictionary based techniques the idea is to first collect a small set of opinion words manually with known orientations, and then to grow this set by searching in the WorldNet dictionary for their synonyms and antonyms. The newly found words are added to the seed list. The dictionary based approach have a limitation is that it can't find opinion words with domain specific orientations [11].

2.2.2 Corpus-based Approaches:

Corpus based techniques rely on syntactic patterns in large corpora. Corpus-based methods can produce opinion words with relatively high accuracy. Most of these corpus based methods need very large labeled training data. This approach has a major advantage that the dictionary-based approach does not have. It can help find domain specific opinion words and their orientations. The final weight of each individual sentence is calculated after considering the whole sentence structure, contextual information and word sense disambiguation [11].

3. Comparative study

Provide comparative studyof existingtechniques for rumourdetection includingmachine learningapproaches and lexicon-basedapproaches, together with evaluation factors[12, 13]. Comparative analysis of Rumour detection classification techniques on variant parameters i.e Techniques, Classification used, Advantages, Disadvantages.From this comparative study It is also observed that different techniques can be combined to overcome each others limitation and provide a better classification all around. Given Table shows the comparative study of existing techniques for rumourdetection[14,15].

Table 1: Comparative Analysis of Rumour Detection Approaches

Techniques	Learning Methodology	Advantages	Disadvantages
Decision Tree	Supervised	*This is very fast in Learning data. *Easyfor understanding purpose.	* It has problem that it is difficult to handle data with noisy data. * over fitting of data.
SVM	Supervised and unsupervised	*High dimensional input space. *Few irrelevant features. *document vectors are sparse.	* a large amount of training set is required. * Data collection is tedious.
KNN	Supervised	*Based on the fact that the classification of an instance will be somewhat similar to those nearby it in vector space. *it is considered computationally efficient.	*Large storage is required. *Computationally intensive recall.
Naïve Bayes	Supervised	*Simple and intuitive method *It combines efficiency with reasonable accuracy.	*Mainly used when the size of the training set is less. *It assumes conditional independence among the linguistic features.
Maximum Entropy	supervised	*This method do not assume the independent features like NB method. *can handle large amount of data.	*Simplicity is hard.
Dictonary Based	Unsupervised	*In this the newly found words are added to the seed list.	*it can't find opinion words with domain specific orientations.
Corpus-Based	Unsupervised	*It helps to find domain specific opinion words and their orientations.	*This method can produce opinion words with relatively high accuracy

4. Analysis & Discussion

Supervised machine learning techniques have shown relatively better performance than the unsupervised lexicon based methods. However, the unsupervised methods is important too because supervised methods demand large amounts of labeled training data that are very expensive whereas acquisition of unlabelled data is easy. Most domains except movie reviews lack labeled training data in this case unsupervised methods are very useful for developing applications. Most of the researchers reported that Support Vector Machines (SVM) has high accuracy than other algorithms.Supervised text categorization requires the extra effort to predefine the categories and to assign category labels to the documents in the training set. This can be very tedious in a huge

and dynamic text databases. Also, for a supervised categorization, different human experts may disagree when deciding under which category to categorize a given document. This leads us to believe that by nature the ideal multilingual text categorization should be an unsupervised task ratherthan a supervised one. both supervised and unsupervised learning methods have the potentials for multilingual text categorization.

5. Conclusion

Machine learning methods like SVM, NB, Maximum Entropy methods were discussed here in brief, along with some other interesting methods that can improve the analysis process in one or the other way. Rumour detection using syntatic analysis of the text is of great consideration. In the world of Internet majority of people depend on social networking sites to get their valued information, analyzing the reviews from these blogs will yield a better understanding and help in their decision-making. It is also observed that different techniques can be combined to overcome each other's limitation and provide a better classification all around. More work is needed in order to further improve the classification techniques.

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Formulation and Evaluation of Moisturizing Skin Serum With Hyaluronic Acid By Using Nano Technology

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Keywords: Nanotechnology Hyaluronic Acid Skin Serum Stability Testing.

Abstract:

Nanotechnology is widely used in skin care products,this technique is specially designed for target drug delivery.Nanoparticulate delivery system is more reliable and effective. Basically, nanoparticles are colloidal drug delivery system. Nanotechnology can be used in the product like lipstick, soap, antiwrinkle cream, perfume, toothpaste etc. serum are light weight moisturisers that penetrate deeper to deliver active ingredients into your skin. This study presents methods, characterization of hyaluronic acid nanoparticles, further formulation of skin serum and its evaluation at different parameters.

Introduction:

Nanotechnology is fastest growing area for the maintenance of skin health as well as for the diagnosis and management of cutaneous disease. It enriches the study of particles smaller than 100 nm in size. The prefix "nano" from nanotechnology it is a Greek word, in which "nano" means small or little [1]. Nanoparticle is type of colloidal drug delivery system where the particle size ranges from 10—1000 nm in diameter. The sub particles are prepared from a variety of material and synthetic polymers that include gelatine, poly methacarylate some biopolymers etc. Drugs can be dissolved, entrapped, or encapsulated into the nanoparticl es, on simply absorbed on their surface. Nano sphere consists of a dense polymeric matrix in which the drug can be dispersed, whereas, Nanocapsules are constituted of a liquid core surrounded by a polymeric shell. Nanoparticles are formed by single layered shell and are filled with oil which tends themselves ideally as carriers for lipophilic agents [2]. Nanoparticles in cosmetic preparations are found to improve stability of various cosmetic ingredients such as unsaturated fatty acids, vitamins or antioxidants by encapsulating them, increase the efficacy and tolerance of UV filters on skin surface, make the product more aesthetically pleasing and enhance the penetration of certain active ingredients to the epidermis [3].

1.1 Nanoparticles under the skin in cosmetics:

The important route is through dermal exposure. The dermis has a rich supply of blood and tissue macrophages, lymph vessels, dendritic cells, and five different types of sensory nerve endings. An increased inflammatory activity and epithelial translocation of manmade 20 and 30 nm solid particles was observed already 20 years ago. Broken skin represents a readily available entry even for larger (0.5-7 micro meter) particles, as evidenced by reports about accumulation of large amounts of soil particles in inguinal lymph nodes from people who runs or walks bare feet. However report shows that broken skin is not necessary for uptake of nanoparticles. Tinkle et al hypothesized that skin when flexed- as in wrist movements- can make the epidermis more

permeable to nanoparticles and then favour uptake into lymphatic system and regional lymph nodes [4].

Advantages

1. Large scale production is possible.
2. Long term stability
3. Controlled and sustained release of active drug can be achieved.
4. Organic solvents can be avoided.
5. It can be lyophilized.
6. It can be freeze dried to form powder formulation.
7. By autoclaving and gamma radiation sterilization is possible.
8. It improves skin protection with organic compound.

Disadvantages

1. Poor drug loading capacity.
2. High water content dispersion.
3. The low capacity to load hydrophilic drugs.

Objective:

The aim of my work was to prepare and investigate hyaluronic acid in skin serum by using nanotechnology.

In the first part of the investigation, nanoparticles were prepared with a method described below and further synthesizing its size.

The main steps are as follows:

- Reactions under the same conditions and with concentration of Hyaluronic acid, oxalic acid, sodium monostearate, 1-(3- dimethylaminoproyl)-3-ethylcarbodiimide hydrochloride. The standard solutions were prepared with appropriate concentrations, pH was adjusted, the preparation of hyaluronic acid, oxalic acid, sodium monostearate, 1-(3- dimethylaminoproyl)-3-ethylcarbodiimide hydrochloride solutions respectively , the mixing and stirring time the temperatures applied, maintain storage conditions.
- Confirmation of nanoparticles by LM 20 nanosight. In the second part of the investigation, the formulation and evaluation of skin serum was studies as follows:
- Formula was set for the formulation of skin serum.
- Physical appearance and Stability testing of the batches
  was studied with different concentrations of active. Serum was checked at different parameters and also microbial growth studies were done.

Experimental

2.1 Method Of Preparation

1. High pressure homogenization.
2. Hot homogenization.
3. Cold homogenization.
4. Micro emulsion technique.
5. Ultra sonication or high speed homogenization.
6. Double emulsion method.

7. Spray drying method.

High pressure homogenization:

In high pressure homogenization liquid is pushed at high pressure 100-2000 bar through a narrow gap. The fluid accelerates at very high velocity (1000 km/h). In this typical lipid contents in the range of 5-10% which represents no problem to the homogenizer. Higher lipid concentrations up to 40% have been also homogenized to lipid nano dispersions. It is widely used than any other method, because it is advantageous than other method. Following are some of the advantages of this method are that it is easy scale up and powerful techniques, short production times and more feasible [1].

Hot Homogenization:

This method is similar to homogenization of an emulsion, because this is also carried out at temperature above the melting point of lipid. In the hot homogenization method the drug is dissolved or dispersed in melted solid lipid for SLN or in a mixture of liquid lipid (oil) and melted solid lipid for nano structured lipid carrier. This lipid melt containing drug is then mixed by high speed stirring in a solution of the hot surfactant at same temperature (5– 10 °C) above the melting point of the solid lipid or lipid blend). This pre-emulsion is then passed through a high pressure. Homogenizer adjusted to the same temperature, generally applying three cycles at 500 bar or two cycles at 800 bars. This technique can be used for lipophilic and insoluble drugs as well as for the heat sensitive drugs because the exposure time to high temperature is comparatively short. The technique is not suitable for inclusion of hydrophilic drugs into solid lipid nanoparticle because of larger portion of drugs is in water during homogenization which leads to low entrapment capacity [5].

Cold homogenization:

This technique is developed to overcome the problems which are associated with hot homogenization like temperature induced drug degradation and drug distribution into the aqueous phase during homogenization [1]. In the cold homogenization method, the lipid micro particles are obtained by melting and subsequent cooling of drug containing lipid melt followed by crushing, grounding and diffusing in cold surfactant to obtain a cold pre-suspension of micronized lipid particles. This suspension is then forced to pass through a high pressure homogenizer at room temperature applying typically 5–10 cycles at 1500 bar. This method is the first choice for hydrophilic drugs with good as well as low solubility (surfactants are added to improve solubility). This technique avoids and shortens melting process of lipid and hence it is appropriate for thermo sensitive and thermo labile drugs [5].

Micro emulsion technique:

This method is based on the dilution of micro emulsions. As micro-emulsions are two-phase systems composed of an inner and outer phase. Micro emulsions are clear, thermodynamically stable system composed of a lipophilic phase, water, surfactant and co-surfactant. Micro emulsions are produced at a temperature above the melting point of the lipids, so the lipid should have melting point above room temperature [1]. Solid lipid nanoparticles can also be prepared by micro emulsification of inner molten lipids phase (oil) which is preloaded with drug (at 65-70 °C), followed by dispersion in cold aqueous phase with mechanical stirring (at 2-3 °C). The dispersion is washed two times with distilled water by ultra filtration. After

washing, the suspension is freeze dried. The diameter of the disperse phase droplet should be always below 100nm. There is no need of energy for this preparation [5].

Ultra sonication or High speed homogenization:

Solid lipid nanoparticles were also developed by high speed stirring or sonication. The most advantage of this method is that, the Equipments that are used here are very common in every lab [1]. Solid lipid nanoparticles can also be prepared by sonication or high speed stirring. This is very general and simple technique and can be beneficial over other methods like hot and cold homogenization but with drawback of distribution of larger particle size ranging between micrometer range leading to physical instability such as particle growth upon storage and also metal contamination due to ultra sonication [5].

Double emulsion method:

It is a novel method of preparation of solid lipid nanoparticles loaded hydrophilic drug moiety and is based on solvent emulsification evaporation by drug encapsulation in the outer water phase of w/o/w double emulsion along with a stabilizer to avoid partitioning of the drug to outer water phase during solvent evaporation [5]. For the preparation of hydrophilic loaded SLNs, a novel method based on solvent Emulsification-evaporation has been used. In double emulsion technique hydrophilic drugs was dissolved in aqueous solution, and then was emulsified in melted lipid. In this method the drug is encapsulated with a stabilizer to prevent drug partitioning to external water phase during solvent evaporation in the external water phase of w/o/w double emulsion. Stabilized primary emulsion was dispersed in aqueous phase which contains hydrophilic emulsifier after that the double emulsion was stirred and was isolated by filtration [1].

Spray drying method:

It is an alternative procedure to lyophilisation in order to transform an aqueous SLN dispersion into a drug product. This method is cheaper than lyophilisation. This method cause particle aggregation due to high temperature, shear forces and partial melting of the particle. In this method short drying time and consequently fast stabilization of feed material at moderate temperatures make spray drying method suitable for producing nanoparticles of drugs that are thermo labile. The 20% trehalose in ethanol-water mixtures (10/90 v/v). Due to high temperature and shear force it may cause aggregation of particle [1].

Materials and Method:

Hyaluronic acid Hyaluronic acid (HA) is a high molecular weight biopolysacharide, discovered in 1934, by Karl Meyer and his assistant, John Palmer in the vitreous of bovine eyes. Hyaluronic acid is a naturally occurring biopolymer, which has important biological functions in bacteria and higher animals including humans. It is found in most connective tissues and is particularly concentrated in synovial fluid, the vitreous fluid of the eye, umbilical cords and chicken combs. It is naturally synthesized by a class of integral membrane proteins called hyaluronan synthases, and degraded by a family of enzymes called hyaluronidases [6]. Following are important points about hyaluronic acid. Hyaluronic acid derives from the Greek "hyalos", glossy vitreous and uronic acid. The molecule binds water and functions as lubricant between the collagen and the elastic fibre networks in dermis during skin movement. Effect on skin is that it hydrates viscoelastic film on the skin. The polymer may also be injected to obtain a smoother surface and reduce the depth of wrinkles. Properties: Most powerful moisturiser and humectants known so far provide smoothness and softening to the skin, reduce appearance of wrinkles. Ideal ingredient after skin peels. Usage typically used at 0.1-2%. Hyaluronic acid is not readily soluble in water as it binds water very quickly forming a gel [7].

Method of preparation of hyaluronic acid nanoparticles :

The present study relates to the development of a hyaluronic acid nanoparticles for the administration of active molecules. These nanoparticles are made up of hyaluronic acid in salt form, preferentially the sodium salt of the polymers. In a typical experiment, the procedure comprises the following stages:

Flow chart 1: Method of hyaluronic acid nanoparticles

Preparation of aqueous solution of salt of HA (6 mg/ml)

↓

Preparation of an aqueous solution of hydrazide (3 mg/ml oxalic hydrazide)

↓

Preparation of sorbitan monostearate (1-2 % w/v)

↓

Addition of the hydrazide solution (3 mg/ml) to the solution of Hyaluronic acid, followed by injection of 1-(3-dimethylaminoproyl)-3- ethylcarbodiimide hydrochloride (EDC1) solution (2.7 mg/ml)

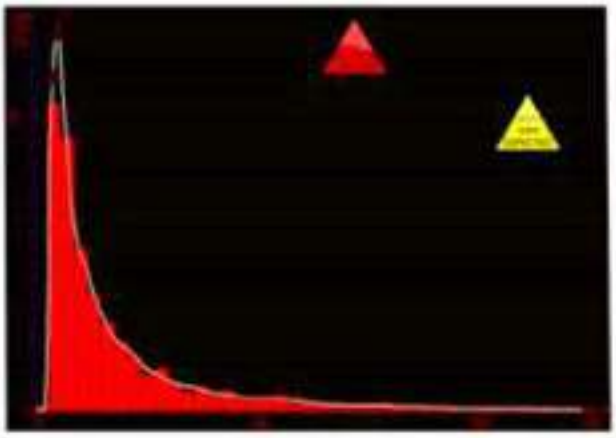
↓

Addition of the surfactant solution and mixing under magnetic stirring, lowering the pH and maintaining the stirring overnight, which will produce the Nanoparticles.

The work-up of the Nanoparticles was as follows: pH was increased to the range of 8-9, followed by the addition of alcohol to precipitate the Nanoparticles. The precipitated Nanoparticles were kept in drying oven at 25°C for six hours to dry. The resulting Nanoparticles can be kept in the refrigerator for storage [8].

Characterization of Nanoparticles

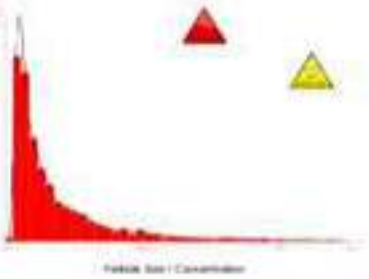
Estimation of particle size by LM 20 Nano Sight Nanoparticle tracking analysis divulges size of nanoparticles by tracking the Brownian motion of particles freely suspended in colloidal solution. Mean size of nanoparticles was calculated by tracking minimum of 1000 nanoparticles active in Brownian motion. The size histograms of hyaluronic acid are evident from Fig. 1 (a, b and c) respectively [9].



(a)

Particle Size / Concentration

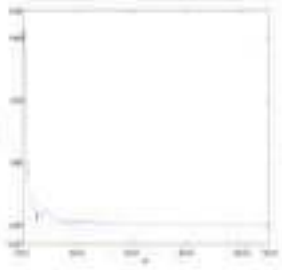
(b)



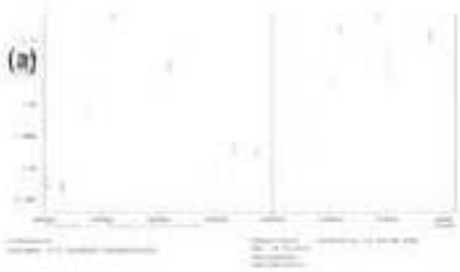
(c)

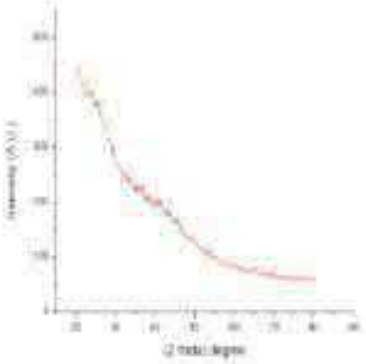
2.4 U.V. Spectrophotometry

Ultraviolet (UV) and visible radiation comprise only a small part of the electromagnetic spectrum, which includes such other forms of radiation as radio, infrared (IR), cosmic, and X rays. Figure 2 (a), (b), (c) respectively [9].



(a)





Fourier Transform Electron Microscopy:

A mathematical operation known as Fourier transform (FT) can separate the individual absorption frequencies from the interferogram, producing a spectrum virtually identical to that obtained with a dispersive spectrometer. This type of instrument is known as Fourier transforms infrared spectrometer [10].

X-ray Diffraction:

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θangles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacing allows identification of the mineral because each mineral has a set of unique d-spacing. Typically, this is achieved by comparison of d-spacing with standard reference patterns. All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this [11].

Results And Discussion:

The particle size mean of hyaluronic acid found to be 44nm whereas the mode is 11nm and standard deviation is 57nm. While the U.V. visible spectrophotometry shows that figure 2(a) absorbance is shown at peak of 257 nm. The XRD (X-ray Diffraction) result in figure 2(c) shows that the sample is of amorphous nature.

Skin Serum

A serum is a product typified by its rapid absorption and ability to penetrate into the deeper layers of the skin, together with its non-greasy finish and intensive formula with a very high concentration of active substances. Like many other skin products, serums are designed to focus on different actions – anti-ageing, brightening, acne prevention, etc. Because of the high concentrations of the active elements, it is common for cosmetic serums to contain only a few

active ingredients which provide intensive nutrition for the deeper layers of your skin. The oil-free finish doesn't leave your skin feeling tight after use: instead it should feel velvety smooth because of the serum's intensive and deep-layer action. Since the active ingredients are so highly concentrated, a serum will produce more visible results in less time than a simple moisturiser or other skin product. Sometime the high concentration of active ingredients can irritate sensitive skin [12].

Material and Methods

Table no. 1 formulation of serum

Sr. No.	Ingredients	Quantity for 100 gm			Uses
		F1	F2	F3	
1	Carbopol 940	0.5 gm	0.5 gm	0.5 gm	Gelling agent
2	Olive oil	1 ml	1ml	1ml	Emollient
3	Almond oil	1 ml	1 ml	1 ml	Emollient
4	Tween 80	1 ml	1.2 ml	1.3 ml	Emulsifier
5	Propylene glycol	2 ml	2.5 ml	2.8 ml	Humectant
6	Poly sorbate 60	1 ml	1.5 ml	1.8 ml	Solubuliser
7	Ethylenediaminetetraacetic Acid	0.1 gm	0.1 gm	0.1 gm	Chellating agent
8	Triethanaloamine	0.3 ml	0.5 ml	0.6 ml	Stabiliser
9	Iso propyl alcohol	q.s	q.s	q.s	Solubuliser
10	Glycerine	0.7 ml	0.8 ml	0.9 ml	Humectant
11	Perfume	q.s	q.s	q.s	Perfume
12	DM DM Hyadantoin	q.s	q.s	q.s	Preservative

13	Hyaluronic acid	0.8 gm	0.5 gm	1 gm	Active
14	DM water	To make 100 ml	To make 100 ml	To make 100 ml	Aqueous phase

Observation:

From the above observation formula F2 was selected as it was stable and it shows consistency, spreadability and feel and active was added with different concentration and evaluated for in vitro study as per IS and in vivo study with human volunteers.

Procedure for base formula: Take clean apparatus. Weigh Carbopol 940 disperses in distilled water containing EDTA, DM DM Hyadantoin and glycerine. After proper mixing add TEA drop by drop to form a gel, then take another beaker to this add almond oil, olive oil, rose oil, Polysorbate 60, Tween 80, propylene glycol, stir it well and then pour it into gel under stirring slowly, allow it to stir for some more time and then fill it into suitable container.

Table 2: Optimization of serum base

Sr. No.	PARAMETER	F1	F2	F3
1	Appearance	**	***	***
2	Colour	**	***	**
3	Odour	*	**	**
4	Consistency	**	**	*
5	Feel	*	***	**
6	Spread ability	**	***	**

Good= * Better = ** Best = ***

Evaluation of skin serum

Determination of physical parameters

In physical parameters, appearance, consistency, colour, odour, and spreadability was taken into consideration. The Physical Parameters are determined by visual observation by taking small amounts of sample. The Serum and lotion samples were kept at various temperatures such as room temp, at 45°C and at the elevated temp (freeze temp.).The

formulations were checked after every 10 days for parameters such as colour, odour, consistency, spreadability and appearance [13].

Determination of pH (IS: 6608 - 1978)

For oil-in-water emulsion Serum Accurately 5±0.01 g of the Serum was weighted in a 100ml beaker. 45ml of water was added and the Serum was dispersed in it. The pH of the suspension at 270 C was determined using the pH meter [13].

Determination of total fatty substance content: (Indian Standard skin creams — specification, 2004)

For this the emulsion is broken up with dilute mineral acid and the fatty matter is extracted with petroleum ether. It is weighed after removal of the solvent. Accurately about 2g of sample was weighted into a conical flask, about 25ml of dilute HCl was added, reflux condenser was fitted into the flask and the content of the flask was boiled until the oil and water phases have separated. The content of the flask was poured into 300 ml separating funnel and it was allowed to cool to 20°C. The conical flask was rinsed with 50ml of ethyl ether in portions of 10ml. The ether rinsing was poured into separating funnel. The separating funnel was shaking well and leave until layers separate. Separate out with 50ml portions of ether twice. All the ether extracts was combined and washed them with water until free of acid. The ether extracts was filtered through a filter paper containing sodium sulphate into a conical flask which had been previously dried at temperature of 6°C ±2°C and then weighed. The sodium sulphate was washed on the filter paper with ether and the material remaining in the flask was dried at a temperature of 6°C ±2°C to constant mass [13].

Total fatty substance % by mass =100x M1/M2.

Where, M1 is Mass in g of residue and M2 is Mass in g of material taken for the test.

Determination of Thermal Stability:

A 20 mm broad and 5 mm thick strip was spreaded from the material to be tested on the internal wall of a beaker of 100ml capacity in its total height. The beaker was kept for 8 hrs. in the humidity chamber at 60 to 70% relative humidity and temperature 37± 1°C.

Microbial examination of Serum: T.

The test consist of pleating a known dilution of the sample on soya bean casein digest agar medium suitable for the total count of aerobic bacteria and fungi after incubating them for a specified period to permit the development of visual colonies for counting Pre-treatment of sample: To 10 ml of sodium chloride solution pH 7 or any other suitable medium add 1gm or 1ml of sample Total bacterial count: Pipette out in duplicate 1ml of pre-treated sample aseptically into 5 sterile Petri dishes. Pour 15 to 20 ml of molten soya bean casein digest agar maintained at about 45°C. Mix the content of the plate by swirling. Allowing the incubate the plates at 37°C +1°C in inverted position for three days Count the number of colonies in each plate. Determine the average number of colonies on plates and multiply by dilution factor. This will be the number of microorganisms per gm of the sample. If no colony was recovered from any of the plate it can be stated as less than 50 microorganisms per gm.

Total fungal count:

Pipette out in duplicate 1ml of pre treated sample aseptically into 5 sterile petridishes. Pour 15 to 20 ml of molten sabouraud's chloranphenicol agar (SCA) maintained at about 45°C mixes the content of the plate by swirling. Allowing the plates to solidify, invert and incubated at 23+2°C for three days. Count the number of colonies in each plate.

Stability studies of Serum:

Stability studies for Serums were carried out according to ICH guidelines. The Serum samples were kept on the 5°C, room temperature, and 40°C. The changes in the physical appearance, colour, odour etc and chemical changes such as change in pH, viscosity, pH separation were checked and thus. The formulation of Serum was optimized.

Table3: Evaluation Of Physical Parameters

Sr. No.	PARAMETERS	F1	F2	F3
	(A) Physical appearance			
1	Appearance	serum like	serum like	serum like
2	Colour	white opaque	white opaque	white opaque
3	Odour	pleasant	pleasant	pleasant
4	Consistency	semi liquid	semi liquid	semi liquid
5	Spread ability	good	good	very good
6	Oily/tacky feel	No	No	No

Accelerated stability studies:

To ensure that a cosmetic remain stable till the consumers has used the entire cosmetic or has stopped using it, a number of special accelerated test procedures have been developed. The evaluation employs a combination of tests. This method of evaluation not only indicates stability of Base formulation but also indicates the stability of functional ingredient [13].

Freeze thaw cycle:

These tests are not carried out at fixed temperature and humidity. In these tests, temperature was changed cyclically every day e.g. Low-high-low-high-low-high, to simulate changes in temperature daily [13].

Table 4: Freeze Thaw Cycle

Sr. No.	PARAMETERS	F1	F2	F3
1	Freeze thaw cycle	Stable	Stable	Stable

Result and Discussion
In Vitro-Study

Table No. 5: Determination of physical parameter of a Skin Serum containing hyaluronic acid as active. (Stability study after 10 days).

Sr. No.	PARAMETERS	F1	F2	F3
	Physical appearance	**	**	**
1	Appearance	**	**	**
2	Colour	**	**	**
3	Odour	**	**	**
4	Consistency	**	**	**
5	Spread ability	**	**	**
6	Oily/tacky feel	**	**	**

Change = * No change = **

Table No. 6: Stability study after 20 days

Sr. No.	PARAMETERS	F1	F2	F3
	Physical appearance	**	**	**
1	Appearance	**	**	**
2	Colour	**	**	**
3	Odour	**	**	**
4	Consistency	**	**	**
5	Spread ability	**	**	**
6	Oily/tacky feel	**	**	**

Table No. 7: Stability study after 30 days

Sr. No.	PARAMETERS	F1	F2	F3
	Physical appearance	**	**	**
1	Appearance	**	**	**
2	Colour	**	**	**
3	Odour	**	**	**
4	Consistency	**	**	**
5	Spread ability	**	**	**
6	Oily/tacky feel	**	**	**

Table No. 8: Determination of pH of serum containing hyaluronic acid as active. Standard value 5 to 9

Sr. No.	Time Interval	F1	F2	F3
1	0 Day	6.23	6.21	6.19
2	8th Day	6.21	6.2	6.18
3	16th Day	6.23	6.19	6.15

4	24th Day	6.22	6.17	6.11
5	30th day	6.23	6.16	6.12

Graphical Representation of data:

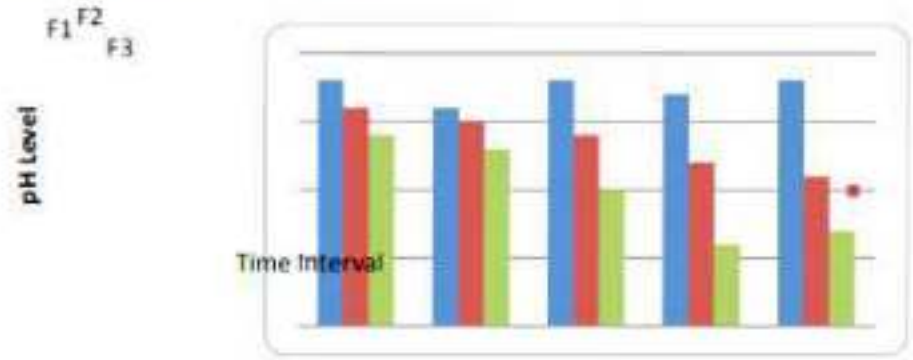


Table 9: Determination of Total fatty matter of serum containing hyaluronic acid as active (Standard value 5.0%)

Sr. No	Parameter	F1	F2	F3
1	TFM % by Mass	4.55%	4.65 %	4.60 %

Graphical Representation of data:

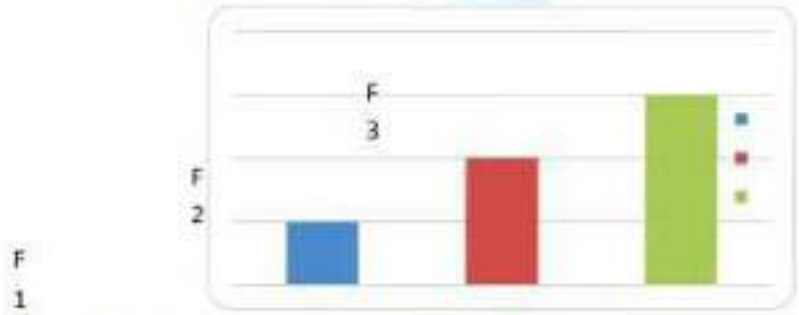


Table 10: Determination of Thermal Stability serum containing hyluoronic acid as active.

Sr. No	Parameter	F1	F2	F3
1	Thermal Stability	passed	passed	passed

4.2 Microbial examination of a Serum

Table No. 11: Microbial examination of a serum containing hyaluronic acid as active

Sr. N	Name of the test	Result	Specification	Unit

o				
1	Total bacterial count	10 CFU/gm	NMT100 CFU/gm	CFU /gm
2	Fungal count	Nil	NMT10CFU/gm	CFU /gm

Conclusion:

Nanoparticles are one of the promising drug delivery systems, which can be of potential use in controlling and targeting drug delivery. They possess better stability when compared with liposomes. They have various applications such as ophthalmic drug delivery, intravenous delivery as carriers for radio nucleotides in nuclear medicine, as cosmetics for the skin and hair care, sustained release formulations and many more. Nanoparticles formulated as amorphous spheres offer higher solubility than standard crystalline formulations, thus improving the poor aqueous solubility of the drug and hence its bioavailability. While serum on the other side, is a concentrated product widely used in cosmetology. The term itself comes from professional cosmetology. Cosmetic skin serum is a highly concentrated product based on water or all as any other cream. Serums are concentrates containing approximately 10 times more of biologically active substances than creams, therefore quicker and more effectively coping with cosmetic problems. The effect of serum when concentrates are that it immediately gets the necessary amount of active substances such form which assimilates easier. The active substances in high concentration act in the same way as cream they moisturise, rejuvenate, lift up, etc. The only difference is that in case concentrates are used correctly the noticeable result will be reached quickly.

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Encapsulation of Moisturizer in Bath Preparation To Improve Skin Conditioning

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Abstract :-

Microcapsules are small particle that contain an active agent or core material surrounded by a coating layer of shell. Sometimes each microcapsules may contain several cores, either of the some component or various components. At present, there is no universal accepted size of microcapsules & their diameter may vary from 1 to 1000 m, capsules smaller than 1 m are often called nanocapsules, and capsules larger than 1000 m are called microcapsules or beads. Commercial microcapsules typically have a diameter between 3 and 800 m.

The wall thickness of microcapsule ranges from 0.5 – 150 m, and the content of active ingredient [encapsulated component] may vary from 25-90% of the total weight. [Microcapsules technology is non-irritating, nontoxic & non allergenic, has been explored for application like Bath Preparation.].

Keywords : Jojoba oil, coconut oil, and apricot oil, Bath Preparation, Encapsulation technology.

Introduction :

Microcapsules may have a variety of structures. Ranging from spherical and irregular shape with one core to multicore & even multilayer coating, obviously the structure of the microcapsules depends on many parameters, such as the rigidity of the coating layer, the type of core material.

Moisturizers are the substances which moisturize the horney layer. The mechanism can be broadly considered in terms of the boney layer & the dermis. In the horney layer, the natural moisturizing factor (NMF) which consist of amino acids etc. sebum and skin surface lipids derived from epidermal oil components, are very important. But in the dermis, it is hydrophobic substances. Such as phospholipids and macroemolecular hydrophilic substances like hyaluronic acid, collages and elastin that are considered to be important. If something goes wrong with the moisturizing mechanism at the horney layer level, it is essential to lighten the burdess of the skin in order to make it healthy & beautiful again and this can be alone by giving it a good balance of high quality oils & hydrophilic substances with great moisturizing this must be corrected through the use of skin care cosmetics which are designed to redness the moisture balance.

Body washes have a lower P^H level than bar soap and therefore are milder than bar soap. Also body wash is proven to retain 30% more of skin natural moisture versus ordinary bar soap. Many consumer find body wash to be more convenient since there is no messy bar to deal. with and some consider it more sanitary because more than one person are use it. Much attention has

recently towards cleansing of the skin especially body skin in order to remove serum and environmental dirt thoroughly while not drying the skin to accentuate wrinkle, cleansing is now a part of daily skin treatment routine incorporating a variety of products Eg. Body wash for all types of skin and application method, depending upon current marketing trend. Body cleanser means body wash, which act upon the skin surface by dispersing by emulsifying and removing all types of surface oil.

Body wash is 100% soap free body wash specially formulated with jojoba oil, coconut oil and apricot oil, which act as natural moisturizer. Body wash used for treatment of and it also remove dust, bacteria & skin impurities with in the pores while maintaining the required moisture balance.

Material And Mehods

Physical methods of manufacturing microcapsule:-

1) Air Suspension coating:- It is known as fluid be coating. The particles with better control & flexibility are produced by this method. The particles to be coated are suspended in an upward moving air stream. They are supported by a perforated plate with different types of holes from inside & a cylindrical insert from outside just sufficient air is allowed to rise though the outer annual space to fluidize the setting particles. Most of the air flows inside the cylinder, causing to particles to rise rapidly. At the top, as the air stream diverges & slow, they being to settle bace on to the outer bed & moves downward to repeat the cycle. The particles pass through the inner cylinder many times in a few minutes.

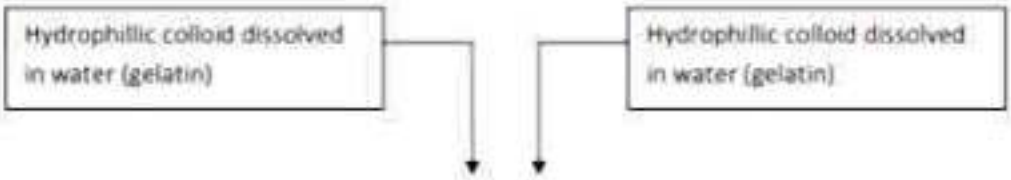
2) Centrifugal extrusion :- In this process, liquids are encapsulated using a rotating extrusion head containing concentric nozzles. A jet of core liquid is surrounded by a sheath of wall solution or melt. As the jet moves through the air, it breaks into droplets of core, each coated with the wall solution. Since most of the droplets are within 10% of the mean diameter, they land in a narrow ring around the spray nozzle. Hence, if needed, the capsules can be hardening bath. This process is excellent for forming particles 400-2000 micrometer in diameter. This process is suitable for liquids and slurry.

3) Spray drying :- This method serves as a micro-encapsulation technique when an active material is dissolved or suspended in a melt or polymer solution and becomes trapped in the dried powder. The main advantage of this method is the ability to handle liable material because of the short contact time in the dryer, in addition the operation is economical.

Chemical Methods For Microencapsulation:

1) Complex Coacervation :- This method of micro-capsulation is based on the ability of water soluble oppositely charged polymers to interact while forming a new liquid polymer- rich phase, which is called a "Complex coacervation".

Process Chart



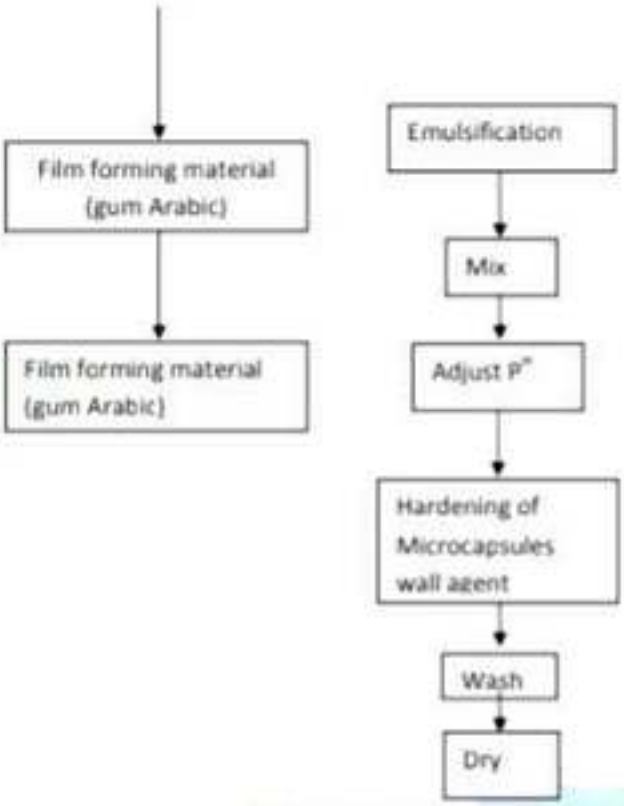


Fig. : Microencapsulation by complex coacervation.

In Situ Polymerization :

The Shell material is directly polymerized onto the core. Microcapsule are prepared by Urea-formaldehyde on melamine-formaldehyde resin. Polymerization occurs in continuous phase. This method is suitable for water miscible liquid. This method does not require special equipment. Examples of wall material : polyurea, polyamicle, polyurethane, epoxy resin. This method gives a uniform shall deposition. The shell thickness ranges from 0.2 to 75 Micrometer. Microcapsule of 3 to 6 micrometer in diameter are by this method.

Interfacial polymerization :

In this method, the two reactants in poly condensation meet at an interface and react rapidly. Basis of this method is the reaction between an acid chloride & a compound containing an active hydrogen atom.

Polymers Used for Microencapsulation :

Acacia, Agar, Albumin, Acrylic polymers, Alginate, carboxy vinyl polymer, cellulose derivatives, Dextran, Gelatine, Hydrogenated castor oil, polycimide, polymide, polyester, polyglycolic acid, polyvinyl alcohol, polyvinyl pyrolidone, shellac, starch, stearic acid, waxes [beeswax carnauba wax, paruffinwax].

Application of Microencapsulation :

A) Skin care products :

- UV Protective Creams
- Depilatory Creams

- Skin tanning
- Cleansing Creams
- Skin depigmentation
- Emollients
- Deodrants
- Bath Powders containing microcapsulated oils

B) Hair care products:

- Hair Cream and ointments
- Shampoos
- UV Scrunning lotions

C) Nail varnish and makeup removes :

- Nail varnish removes
- Make up removes

D) Cosmetic colorant composition

- Lipstick
- Blushes and eye shadows
- Face powders

Advantages of Micro-encapsulation:

- In some cases, the care must be isolated from its surrounding as in isolating vitamins from the deteriorating effect of oxygen.
- Likewise, retarding evaporation of a volatile care.
- Improving the handling properties of a sticky material or isolating a reactive case from chemical attack.
- In other cases, the objective is not isolate the case completely but to control the rate of which it leaves the microcapsule, as in the controlled release of always.
- The hygroscopic properties of may core material may be reduced by micro-encapsulation.
- The flow properties could be improved by micro-encapsulation.
- To Provide protection to the core material against atmospheric effects.
- To reduce the volatility of several substances (Such as peppermint oil)
- In compabilities between drugs can be prevented by micro-encapsulation.

Components: Active & formulation aids.

Active :

Examples of micro-encapsulation based delivery systems includes incorporating of active such as Jojoba oil, Coconut oil, and apricot oil.

Formulation Aids :

Ethyl cellulose, methanol, chloroform, sodium Lavryl ether, sulphate cocoamidopropyl betaine, Glycerin, carbomer, triethanolamine, methyl paraben, propyl paraben, Disodium EDTA, Water.

Methods :

a) Preparation of Microsphere: (Unloaded)

Preparation of Ethylcellulose Microsphere:

2 gm of ethylcellulose was dissolved in 100ml mixture of chloroforms & methanol in proportion 1:1 this was emulsified in fine dropiets into 150ml of ice cold water under high speed stiring for 2hr. The stirring was continued for 1 hour at room temperature to produce microcapsule. It is filtered 4 washed with water and finally it is air dried on the Petri-dish.

Flow chart of Ethylcellulose microsphere.

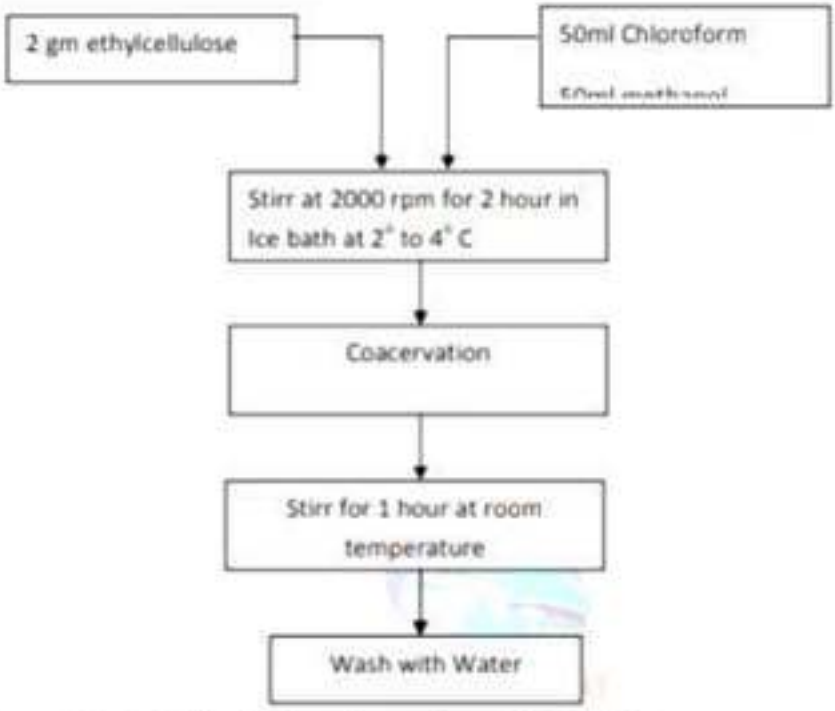
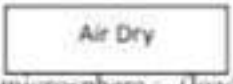


Fig: Flow chart of ethylcellulose microsphere. (Unloaded)



b) Preparation of Ethylcellulose microsphere :- (loaded with moisturizer oil)

2gm of ethyl cellulose was dissolved in 100ml mixture of chloroform and methanol in proportion 1:1. This mixture was stirred for 10 minute. Afterward moisturizer oil of active was added and above whole mixture was then emulsified in fine droplets into 150ml of ice cold water under high speed stirring for 2 hour.

The stirring was then continued for 1 hour at room temperature to produce microcapsules. The above method is same for Jojoba, coconut and apricot oil.

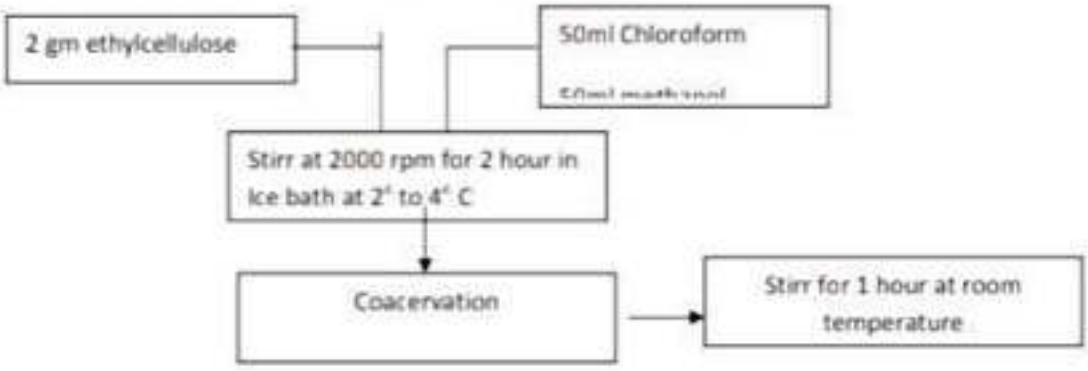


Fig: Flow chart of ethylcellulose microsphere loaded with moisturizer oil.

Formulation Of Bodywash And Inoculation Microsphere In Preparation :

Bodywash :

Soak carbopol 940 in half quantity of water for 24 hour containing preservative, colour, triethand amine, and Glycerin. Then add sodium lavrylether sulphate, coco amidopropyl betaine, in the carbopol 940 and remaining water to above mixture.

Table No. 1 shows the composition of various body wash formulation No.F_2 was found to be stable. So further only this formulation was taken for inoculation of microsphere.

Innoculation of Microcapsules in the body wash:

After the preparation of body wash, the required amounts of moisturizer oil loaded microcapsules were incorporated directly into the body wash with slow stirring for few minutes. The moisturizer oil loaded microspheres were inoculated in each which contains approximately 70% to 80% of oil.

Evaluation of Microcapsules:

Micrcapsules was evaluated by using different methods such as determination of particle size, photo micrographic valuation and assay for loading efficiency of moisturizer oil in microcapsules.

Evaluation of Body wash :

Body wash was evaluated by using different methods such as accelerated stability studies, determination of PH determination of viscosity, determination of foaming power & determination of thermal stability.

TABLE NO. 1 Formulation of Body wash.

Sr.No.	Ingredients	Quantity taken for 100%		
		F_1	F_2	F_3
1.	Carbopol 940	0.75%	0.8%	0.85%
2.	Sodium Lavryl ether Sulphate	30 %	35%	40%
3.	Cocoamidopropyl Betaine	5%	8%	10%
4.	Glycerin	2%	3%	4%
5.	Triethanolamine	0.1%	0.2%	0.3%
6.	Methyl Paraben	0.05%	0.05%	0.05%
7.	Propyl Paraben	0.5%	0.5%	0.5%
8.	Disodium EDTA	0.01%	0.01%	0.01%
9.	Water	Up to 100	Up to 100	Up to 100

Result And Discussion :

Preparation and optimization :

The batches of cross linked microsphere prepared by using 2% ethylcellulose polymer which coacervated with methanol had large particle with wide range of size distribution (h mean = 10.20 m). Hence batches were prepared using different moisturizer oil i.e. Jojoba oil, coconut oil and apricot oil (5%, 6%, 7%).

The Concentration of 5% reduce microsphere size (6 to 10 m) but had large size distribution also, as concentration of mostureizer oil increased batch yield as compared to other batches.

TABLE NO. 2 Particle size analysis of Jojoba oil microsphere.

Sr.No.	Microsphere	Techniques	Conc.of Jojoba oil	Solvent (1:1)	Particle size
1.	Ethylcellulose	Coacervation	5	Methanol and	7.21

		Phase separation		Chloroform	
2	Ethylcellulose	Coacervation phase separation	6	Methanol and Chloroform	8.43
3	Ethylcellulose	Coacervation phase separation	7	Methanol and Chloroform	9.25

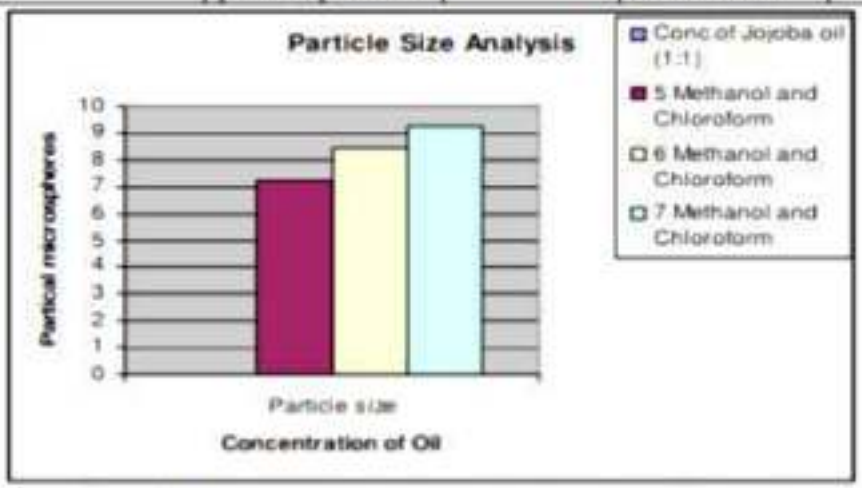


TABLE NO. 3 Particle size analysis of Coconut oil microsphere.

Sr.No.	Microsphere	Techniques	Conc. of Coconut oil	Solvent (1:1)	Particle size
1	Ethylcellulose	Coacervation Phase separation	5	Methanol and Chloroform	7.41
2	Ethylcellulose	Coacervation phase separation	6	Methanol and Chloroform	8.63
3	Ethylcellulose	Coacervation phase separation	7	Methanol and Chloroform	9.57

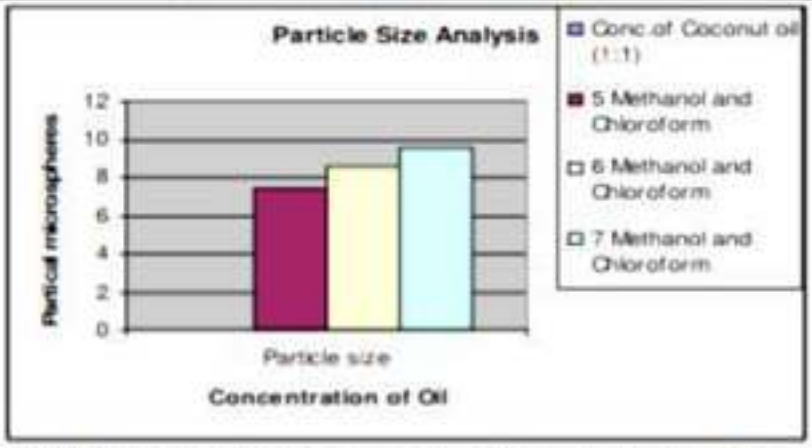


TABLE NO. 4 Particle size analysis of Apricot oil microsphere.

Sr.No.	Microsphere	Techniques	Conc. of Coconut oil	Solvent (1:1)	Particle size
1	Ethylcellulose	Coacervation Phase separation	5	Methanol and Chloroform	7.17
2	Ethylcellulose	Coacervation phase separation	6	Methanol and Chloroform	8.29
3	Ethylcellulose	Coacervation	7	Methanol and	9.31

		phase separation		Chloroform	

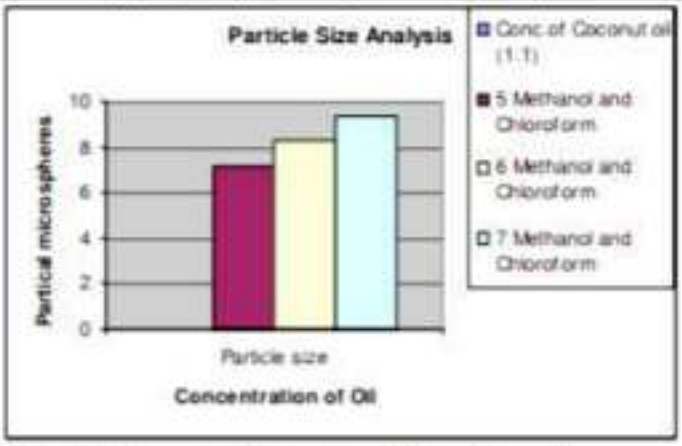
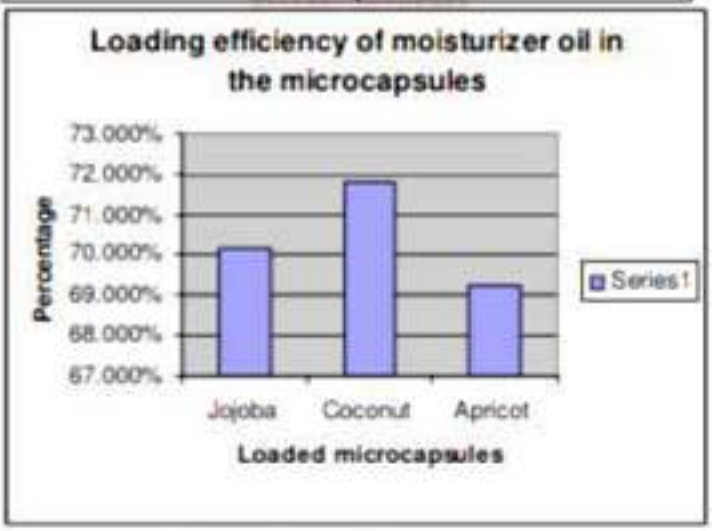


TABLE NO. 5 Loading efficiency of Moisturizer oil in microsphere.

Sr. No.	7% of oil used	Wt. of Ethylcellulose used (a)	Total wt of oil used (b)	Wt of Ethylcellulose microsphere loaded oil	Wt of unloaded a+b=d
1	Jojoba oil	2.0 g	6.3 gm	6.7	1.6
2	Coconut oil	2.0 g	6.4 gm	7.1	1.3
3	Apricot oil	2.0 g	6.3 gm	6.5	1.8

Actual loading (b-d)	Entrapment % of entra
4.7	70.147
5.1	71.83
4.5	69.23



Accelerated stability studies:

TABLE NO. 6 Effect of P^{H} on body wash at Room temperature.

Physical parameters	F-2 A micricapsules loaded with 7ml Jojoba oil.	F-2 B microcapsule loaded with 7ml Coconut oil	F-2 C microcapsule loaded with 7ml apricoted

P^H	6.34	6.35	6.34

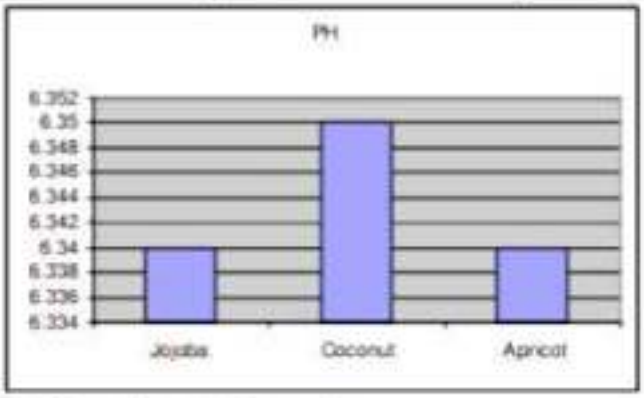


TABLE NO. 7 Effect of Viscosity on body wash.

Physical parameters	F-2 A micricapsules loaded with 7ml Jojoba oil.	F-2 B microcapsule loaded with 7ml Coconut oil	F-2 C microcapsule loaded with 7ml apricoted
Viscosity	8740	8742	8748

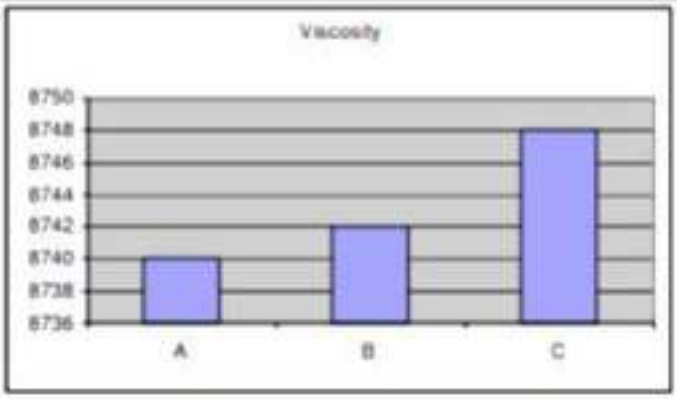
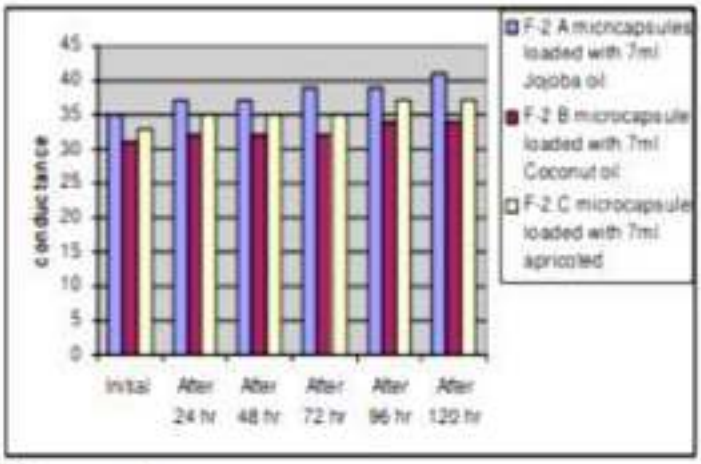


TABLE NO. 8 Testing of Moisturizing activity of body wash formulation of mechanical method.

Days	F-2 A micricapsules loaded with 7ml Jojoba oil.	F-2 B microcapsule loaded with 7ml Coconut oil	F-2 C microcapsule loaded with 7ml apricoted
Initial	35	31	33
After 24 hr	37	32	35
	37	32	35
After 48 hr	39	32	35
	39	34	37
After 72 hr	41	34	37
After 96 hr			
After 120 hr			



Stability study of Microcapsules :

The present stability is carried out according to guidelines given by International council of Harmonization. In view of the potential utility of ethylcellulose microcapsule formulation, stability studies were carried out. The formulation was tested for stability at 5+2°C, 25+2°C, 40+2°C temperature. Formulation were stored in glassed bottles/ vials and then they were evaluated after 15, 30, 45 days for change.

Formulation and Evaluation :

Three different batches of Body wash with different ingredients were formulated & formulation 2 (F_2) as given in Table 1 respectively was selected on the basis of optimization.

In Vivo-Studies :

For Body Wash.

Patch test / Photographic Evaluation :

1) Material : Product containing active.
2) Preparation of sample : Sample of product containing active was prepared with known concentration.
3) Selection of volunteers : The healthy subjects were selected.
4) Mode of execution.

Photographic evaluation of microcapsule

Microscopic photograph of microcapsules

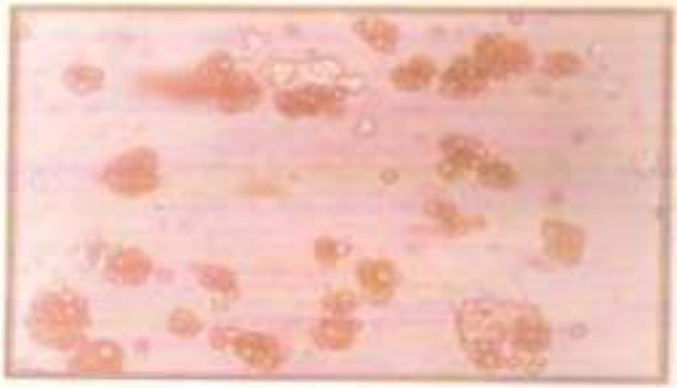


Fig No. 9 : Photograph of microcapsule

In-vivo testing for moisturizing property.

In Vivo Case Study of Body Wash Containing Apricot Oil Microcapsule

Before Application

After Application

In Vivo Case Study of Body Wash Containing Jojoba Oil Microcapsule

Before Application

After Application

In Vivo Case Study of Body Wash Containing Coconut Oil Microcapsule

Before Application

After Application

Conclusion:

Over the past few years, several methods are developed to formulate novel cosmetic products with profound effects on the various application. Present day skin cleanser often are formulated with highly effective soaps and synthetic surfactants, particularly anionic surfactant that effectively cleanse the skin. However after washing the skin can left in cosmetically. Unsatisfactory state because soap and anionic surfactant based skin cleansers not only remove the dirt and soil from the skin, but also removes oils that are naturally present on the surface of the skin. Thus the main cause of the dry feeling after the bath. The purpose of encapsulated moisturizer bath product is to restore and maintain the skin in a good looking, fully moisturized condition. The stratum corneum must be in a fully hydrated condition that allow flexibility and elasticity. A moisturizer find its maximum use in serving as an occlusive agent i.e. hydrophobic material which reduces or prevents passage of water into or though a film of these substances.

The effect of moisturizer oil reduces as it stickyness while applying. To minimize this drawback, attempts were made in the present study to microcapsulate the moisturizer oil and inoculate them into the base of body wash. Differently jojoba, Coconut and apricot oil, microcapsule, were prepared and incorporated into the body wash.

The subjective studies were carried out on clients having different microcapsule. On the basis of subjective study it was concluded that the moisturizing effect of Jojoba oil was more than apricot and coconut oil respectively.

Thus the result obtained in the present study shows that the encapsulation of moisturizer oils by ethylcellulose more stable and give more effect.

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The Dead Sea Mud and Salt: Its Characterization, Contaminants, and Beneficial Effects

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Abstract:

The Dead Sea has been known for its therapeutic and cosmetic properties. The unique climatic conditions in the Dead Sea area make it a renowned site worldwide for the field of climatotherapy, which is a natural approach for the provision of medications for many human diseases including unusual exclusive salt composition of the water, a special natural mud, thermal mineral springs, solar irradiation, oxygen-rich and bromine-rich haze. This research focuses on the physical, chemical, and biological characteristics of the Dead Sea mud and salts, in addition to their contaminants, allowing this research to serve as a guide to interested researchers to their risks and the importance of treatment. Beneficial effects of Dead Sea mud and salts are discussed in terms of therapy and cosmetics. Additional benefits of both Dead Sea mud and salts are also discussed, such as antimicrobial action of the mud in relation to its therapeutic properties, and the potency of mud and salts to be a good medium for the growth of a halophilic unicellular algae, used for the commercial production of β-carotene: Dunaliella.

Keywords: Dead Sea mud, Dead Sea salts, Therapeutic properties, Cosmetic properties.

Introduction:

The Dead Sea (DS), the lowest geographical location on earth, is considered to be the biggestnatural saline reserve in the world. The sea's salt content, approximated to be (348 g/L), makes its salinity 10 times the typical salinity of oceans [1]. The Dead Sea is located in the Syrian – East African rift valley and surrounded by the Moab Mountains to the east and the Judean Mountains to the West [2,3].

The atmosphere of the DS is rich in oxygen by 10% more than any other typical sea, which might be attributed to its exceptionally low altitude [4], approximated to be 396 meter below sea level[5]. However, the unparalleled salinity is not the only extraordinary characteristic of the DS, as it contains natural thermo-mineral waters, mineral muds, higher bromine content in the air, as well as high selenium content of local drinking water[6].

Due to the rarity of its atmospheric and climatic features, the DS is considered to be an attractive for patients who seek a medication for diseases such as psoriasis[3,7], rheumatic disorders [6, 8], and atopic dermatitis[6]. Treatments are mainly based on: (a) bathing in the DS water while exposing the skin to filtered UV radiation, and (b) mud packs prepared from highly saline black mineral mud that is rich in sulfide, which is found abundantly in the area [8,9].

Furthermore, the distinctive combination of photobiologic characteristics and elemental properties of the DS gives this area the uniqueness that cannot be found elsewhere. The sunburn spectrum of ultraviolet light (UV) is very weak at the DS[10], because of a continuous mist that is established above water level. This mist results from remarkably high rates of water evaporation estimated at 2*109 m3/year. Consequently, most UVB sun-burning rays (290-320nm) are filtered out, which allows a better exposure to the longer wavelength UVB and penetrating

natural UVA rays (320–400nm) [11]. The sun and the sea are two factors that have played a main role in the management of many different medical illnesses, especially dermatological diseases [12,13].

Besides the essential health purposes that the DS can serve, cosmetics is a field that has not been overlooked. Over the past years, many units of DS related cosmetic products have been marketed. These natural beauty products are made from natural pure components and extracts in addition to the DS mud, salts and minerals which are extracted directly from the DS area. Despite the great benefits associated with the dead sea products, it is important to note that risks or side effects may be associated with these products dues to the possibility of the presence of contaminants such as heavy metals, microorganisms, or radioactive elements. We believe that treatment is required to avoid risks of such contaminants, and it is considered a challenge to find a suitable technique to detect the presence of those contaminants and to remove them without affecting the benefit of DS products. Yet, barely any research is found in the literature concerning the treatment of the DS products. Only lately one study was published by our group, [14],in which we assessed some heavy metals in the DS mud and optimized a treatment methodology using chelating agent.

On these basis, this review aims to provide details regarding the characteristic of the DS natural mud and salts, as well as their contaminants. Additionally, it aims to give an overview of their beneficial effects.

Dead Sea Mud:

The DS mud is derived from older sediments or the red-brown soils that are usually swept back into the sea during the winter time[15]. It is well known for its therapeutic properties for skin diseases, as it contains a unique composition of minerals. Khlaifat et al., 2010 focused on studying the chemical and physical properties of DS mud samples collected from three different locations (north, middle, and south collection points). The results indicated that the chemical analysis of mud samples has revealed high CaO concentrations (20.61 - 27.86 wt.%), high CO2 concentrations (15.47 - 25.01 wt.%) and high SiO2 concentrations (23.74 - 33.66 wt.%) while the total soluble salts (T.S.S), chlorides and sulfates were 10.19, 4.48 and 0.056 wt.% respectively. Regarding physical properties, it was found that in individual grain size characteristic, most the samples are classified as fine grained, the liquid limit values range from 7 to 23, plasticity index range from 5 to 18, and the specific gravity ranges from 2.257 to 2.386. The variation in DS mud samples prosperities depends on the collection locations and this due to the different processes taking place at the different location[16]. Physical properties of DS mud were also studied by Arab and Alshikh, 2012 who found that the liquid limit value was about 44, plasticity index was about 15 and Plastic limit value was about 29[17].

Dead Sea Salts:

The dead Sea is the most hypersaline waterbody on earth. Its water has pH value of about 6 and contains about 348 g/L mineral salts [1]. When compared with other oceans and seas, the DS is more abundant in many elements, including chloride (212.4 g/l), magnesium (40.65 g/l), sodium (39.15 g/l), calcium (16.86 g/l), potassium (7.26 g/l), and bromide (5.12 g/l). Conversely, it has a lower concentration of sulfate (0.47 g/l), and bicarbonate (0.22 g/l) [2,18-20]. In the period between 1959 and 1960, the DS had approximately 290 g in total of dissolved salts per liter. However, with time and due to high evaporation rates, water level decreased dramatically. This

led to an increase in the salinity to become approximately 340 g/L in 1979[21]. Since, that time, the overall concentration of salts in DS has not changed significantly, with a value of 348 g/L in 2010 [1]. Despite the continuing decrease in water level and the supersaturation of DS with salts, especially sodium chloride (NaCl), the actual concentration of sodium (Na) has decreased due to the huge quantities of halite (rock salt) that precipitated in the bottom of the DS[22-24]. However, the concentrations of other soluble ions increased significantly, such as magnesium; the most prevalent divalent cation, leading to a belief that the DS is principally a magnesium chloride lake[25].

Furthermore, the DS minerals consist of specific elements that participate in regulatory activities of skin metabolism. Magnesium, potassium, and calcium are the most substantial elements present. It was proved that magnesium (Mg+2) is a co-factor for phosphate transferring enzymes, and participates in balancing the regulation between cyclic adenosine monophosphate (c-AMP) and cyclic guanosine monophosphate (c-GMP). Potassium (K+) promotes CO2 transport, and calcium is the inducer of lamellar secretion and the regulator of cell membrane permeability[26,27].

It is also important to note that minerals have the capability in restoring moisture and enhancing intracellular water capacity due to their hygroscopic characteristics. Therefore, if absorbed into skin, they can contribute to the skin's natural moisturizing factor (NMF)[28]

Contaminants of Dead Sea mud and salts:

Contamination in the DS mud and salts represents a potential risk to the local population and for cosmetics producers who usually use the black sea mud which they claim to impart a relaxed feeling, nourishing the skin, activating the circulatory system and ease rheumatic discomfort [8,29,30].This section will provide an overview of the most important contamination sources and how they can influence the current uses of the DS mud and salts.

Heavy metals:

Heavy metals comprise a well-known group of inorganic chemical hazards. Furthermore, it was proved that chromium (Cr), cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), mercury (Hg), nickel (Ni), and arsenic (As) are usually found at contaminated areas[31]. The abnormal accumulation of heavy metals in soils of both urban and rural environments comes because of a slow occurring geochemical cycle of heavy metals, therefore causing risks to human, animals, plants, and other ecosystems[32].

Comparing the DS water and mud for the presence of heavy metals, DS water is found to be rich in heavy metals while the mud is found to contain very low levels of trace elements. Studies in literature show that it is more appropriate for heavy metals is to join to soluble salts in the acidic water rather than precipitating in mud[33]. These studies also revealed that the black mud usually has low content of heavy metals, thus low toxicity. Moreover, the results of sequential extraction showed that Ni and Co were found in the carbonate fraction. Mn was joined up with iron oxide, and the residual phase contained Cr, Cu, Fe and Pb.Abdel-Fattah and Pingitore, 2009, investigated the composition of the DS mud samples (from 3 spots in the Jordanian side of the DS) and found that toxic heavy metals present in concentrations below standard levels. In the same investigation, 16 commercial DS mud-based and mudenhanced cosmetic products, which were marketed in Jordan and in the USA, were analyzed.

levels exceeding those in the plain DS mud samples in several of the commercial muds and in one facial mask. It was concluded that there is risk regarding mineral toxicity from DS mud or DS mud-based products[34]. Similarly, Khlaifat et al., 2010, determined physical and chemical properties of 24 different DS mud samples collected from three different locations on the eastern seaside of the DS. Their results showed that the mud samples were rich in some elements (Barium, Vanadium, Strontium, lead, cadmium and zinc), although there were significant differences between mud samples collected from different locations, there was no strong correlation between the location and the elements content. The most abundant element was strontium followed by barium, vanadium and lead, with the concentration ranges of 410–810, 155–380 , 209–264 , 108–114 part per million (ppm) respectively [16].Arab and Alshikh, 2012, conducted another investigation to measure the concentrations of trace elements in DS mud using Atomic Absorption Spectra and Polargraph instrument. The results of atomic absorption spectra approved that iron has the highest concentration 964.036 ppm, followed by Selenium 6.4 ppm, zinc 5.72 ppm, and lead 3.64 ppm. On other hand, Copper concentration were very low, with a value of 0.58 ppm, while Cadmium concentration was as low as 0 ppm. Similar results were obtained by using polagraph instrumental, confirming their validity[17].

Such studies that reveal the presence of heavy metals caused the development of numerous processes that were developed to remove high concentrations of dissolved heavy metals. These include, but not limited to, ion exchange, oxidation-reduction, precipitation-filtration, membrane separation, solvent extraction, as well as reverse osmosis[35,36].

Moreover, much attention has been paid to applying biotechnological methods for controlling and removing heavy metal pollution in recent years. Despite this, alternative processes are available, including biosorption (metals sequestering), which utilizes various natural materials derived from bacteria, fungi, yeast, and algae. These biosorbents can decrease the concentration of dissolved heavy metal from part per million (ppm) to part per billion (ppb) level. This technique is considered to be a natural and an applicable technique to treat waste water with both low and high levels of metals due to the potency of biosorbents to sequester metal ions from diluted solutions[37].

Microorganisms:

The domestic microbial flora of DS mainly involves a limited number of microorganisms which can be divided into two main groups, obligate halophilic bacterial strains (such as Sarcina-like coccus Halobacterium sp.) and facultative halophytic algae (such as Dunaliella). The recorded number of microorganisms' species at DS is reported to be very low, whereas the total biomass is relatively high (about 105 bacteria/ml and 104 algal cells/ml). Two different antagonistic mechanisms are reported at DS, which are developed by both bacteria and algae. The bacteria adjust their internal inorganic ionic strength to that of the medium. On the other hand, the algae developing a mechanism for salts exclusion from the intracellular fluid using osmotic regulation and glycerol[38].

In addition to bacteria and algae, six different genera of fungi were isolated from DS water, suggesting that the DS water may have health hazard. This was concluded from a study conducted by showed fungi contamination. The recovered fungi genera included Aspergillus versicolor (44.1%), Chactomium globosum (20.6%), Hortaea werneckii (13.2%), Aureobasidium pullulans (11.8%), Eurotium spp (8.8%) and Gymnascella spp (1.5%). It was concluded that

Aspergillus versicolor and Chactomium globosum are the most prevalent genera[39]. During the twentieth century, biological monitoring for the microorganisms in the DS revealed the presence of pathogenic non-halophilic Sporohalobacter lortetii[40], Haloferax volcanii, Haloarcula marismortui, Halorubrum sodomense, Halobaculum gomorrense [1]. These are present alongside the different types of cyanobacteria, and several Dunaliella species which could grow in DS water such as Dunaliella viridis and Dunaliella parva [41, 42]. On the other hand, protozoa were not found at all due to the extreme salinity of the water[1]. Throughout the years, there was a negative balance between DS water level and salinity. On one hand, this created an environment for salt-tolerant algal genus. On the other hand, Dunaliella cells cannot survive in DS water due to this negative balance[43].

Recent studies in the literature directed their focus towards the metabolic potentials of halophilic archaea and bacteria, as well as the possibilities to use them in bioremediation applications [44] Other studies focused on the potential of halophilic bacteria in biotechnological applications such as PHA production, extracellular protease production, halocin production and bioemulsifier production[45].

Beneficial effects of Dead Sea products:

Therapy

Since ancient times, DS mud has been used for treatment of various skin disorders, as it contains high concentration of minerals, allowing it to retain heat for hours and be highly absorbent [6,46-48]. Thus, DS mud can stimulate blood circulation, enhance lymphatic flow, cleanse the skin from dead cells, and help in wounds healing and soothing irritation[47, 49]. DS salt solution, which is rich in magnesium, has many therapeutic uses. It was proved that bathing in this salt solution improves skin hydration, enhances functions of skin barriers, and reduces dry skin inflammation[50]. In addition to magnesium, other elements are present. This ncludes zinc, which plays a role in wound healing and epidermal regeneration[51]. Wound healing potential of natural and compounded facial masks prepared from DS black mud was tested on wounds created on the dorsum region of BALB/c mice by Abu-Al-Basal, 2012. Test mice were treated once a day for two consecutive days with 0.1% natural or compounded DS black mud or 0.2% nitrofurazone, in addition to untreated mice group used as a control. Wound healing was evaluated at day 3, 7, 14 and 21 from wounding day, by measuring weight and percentage of tissue granulation. The results showed that wound healing process (which includes wound contraction, granulation, epithelialization, angiogenesis, and collagen deposition) were accelerated when DS black mud was used compared with nitrofurazone, with note that compounded facial masks have healing property greater than that of natural black mud[52].

In addition, other medicinal properties of DS have been known for thousands of years. The major diseases, such as rheumatoid arthritis, osteoarthritis, ankylosing spondylitis, low back pain, psoriasis, atopic dermatitis, and other joint diseases[2, 53-54]. This success in treatment comes due to the high mineral content in the D [1, 10], and to the UVB radiation which is an attenuated radiation that leads to elevate the concentration of atmospheric oxygen and other relaxation factor[29].

Furthermore, Psoriasis is considered to be one of the most important diseases that are often treated by DS spa therapy. Several studies have proved that DS mud is efficient in Psoriasis

treatment [2,12,29,55-66], in addition to DS salt which also help in Psoriasis treatment due to the effects of magnesium bromide or magnesium chloride[19,67,68].

Psoriasis is highly affected by exposure to the sun, which acts as the main factor in the treatment process. However, the effect of solar radiation could be enhanced by bathing in DS water. This was concluded from a study conducted by Even-Paz et al., 1996, when eighty-one patients with Psoriasis (plaque type) underwent treatment at the DS for four weeks. They were divided into three groups: DS water bathing only; sun exposure only; and sun exposure combined with DS water bathing. Psoriasis area and severity index (PASI) was used to measure the reduction percentage in the psoriasis area, which was scored 28.4% for the first group (when patients only bathed in DS water), 72.8% for the second group (when patients exposed only to sunbathing), and 83.4% for the third group (for patients who bathed in DS water and exposed to sunbathing). This study was also found that there were no significant seasonal differences in the results related to the sun-exposure groups[69].

Similarly, Elkayam et al., 2000 used balenotherapy (treatment of diseases by bathing) and phototherapy (treatment of diseases by radiation) to treat forty-two psoriatic arthritis patients at DS area. From these forty-two, twenty-three patients were receiving additional treatment with mud packs and sulfur baths, while nineteen patients did not receive any type of additional treatment. The results revealed that both groups showed significant improvement in right and left grip, patient self assessment, morning stiffness and axial skeleton movements. Over the time, better results were observed in the group that received mud packs and sulfur baths[70]. Furthermore, Fibromyalgia (musculoskeletal disorder) is another disease that can be treated with balneotherapy at the DS. This has been extensively studied by Sukenik et al., 2001 when twenty eight patients with fibromyalgia and psoriatic arthritis were treated with balneotherapy at the DS area, and were followed-up by assessment of several clinical indices such as number of active joints, duration of morning stiffness, a point count of eighteen fibrositic tender points, and determination of tenderness threshold in nine fibrositic and in four control points using a dolorimeter. The results revealed a reduction in both number of active joints and number of tender points which was reduced from 18.4 to 9 for active joints, and from 12.6 to 7.1 for tender points in men, while there was also a decrease from 13.1 to 7.5 for tender points in women[71].

A clinical trial optimized the use of combined mud bath treatment to treat fibromyalgia patients who have a poor response to drugs. This study was performed by Fioravanti et al., 2007. Forty patients were submitted to a cycle of twelve mud packs and thermal baths, while forty other patients were employed as a control group. Then, patients were evaluated by FIQ (fibromyalgia impact questionnaire), tender points count, VAS (visual analogue scale) for minor symptoms, HAQ (health assessment questionnaire), and AIMSI (arthritis impact measurement scales). After sixteen weeks of treatment, the results proved the efficiency of mud bath treatment of all evaluation parameter[72]. DS spa has a therapeutic potential in atopic dermatitis, which was evidenced by Shani et al., 1997 and Giryes et al., 1997 when they reported 90% clearance of lesions in a study sample (n=1408) after 4-6 weeks of therapy at the DS area[65-66].

Mud packs and sulfur baths (each separate or in combination) can be used as an effective treatment for rheumatoid arthritis patients, which was evidenced through randomized controlled trials for two weeks therapy at the DS area[5]. On the other hand, employment of mud compresses on the hands of patients suffered from swollen and tender joints could relives pain[73].

Osteoarthritis is a joint disease that affects the articular cartilage. This may cause bone to grow at the margins of joints, and leads to changes in the synovial membrane. Over the time, joints loss its normal motion which later causes swollen and pain[69]. Osteoarthritis is one of arthritis and occurs equally in men and women, and could be treated by pharmacological mediations, physiotherapy treatments or balneotherapy.

Flusser et al., 2002 reported a comparison between compresses prepared from unaltered DS mud and mineral-poor DS mud. Fifty-eight knee osteoarthritis patients were selected randomly and treated as follow: forty patients were treated with compresses prepared from unaltered DS mud, and eighteen patients were treated with compresses prepared from mineral-poor DS mud. Using Lequesne index, the results indicated that knee pain can be reduced. Data suggested a better outcome for patients treated with unaltered DS mud packs compared to those treated with mineral-poor mud packs[74].

Ma'or et. al., 2003 prepared compresses, bandages, warps, and dressings from small magnetic particles added to Nano-powders of DS salts. Magnetic particles were absorbed to epidermalm, layer of skin and provided a magnetic field that helps in pain relief when those compresses, bandages, warps, or dressings placed in a direct contact with the patient's skin, above painful region[75]. Additionally, it is important to finally note that one of the main therapeutic uses of the DS is the role of DS minerals in anti-aging. The effect of minerals on keratinocytes cultures and human skin were investigated by Soroka et al., 2008. The obtained results revealed that DS minerals can decrease the expression of some aging markers, enhance proliferation, stimulate mitochondrial activity and limit apoptotic damage after UVB irradiation[76].

Cosmetics

Cosmetics products that contain either DS mud or salts have been used for long years and many companies offer product lines that feature DS minerals. Such products include bath salts, mineral mud soaps, mineral peeling soaps, hand and body lotions, eye cream, cleansing mud masks, body butter, body exfoliates, acne lotions, sunscreens, lightening cream with sun protection factor (SPF), collagen firming creams with SPF, firming night creams, scalp masks, antidandruff and numerous other shampoos, and products that have an 'anti-wrinkle effect'. DS water is widely used in cosmetics, because of its moisturizing and smoothing properties. This is ultimately due to the high magnesium content that enhances water retaining in the skin[77,78], and CaCl2 which provides the DS water its oily feel [12, 18-20]. To prove the efficiency of DS water in skin smoothing, Ma'or et al., 1997 tested three liquid gels prepared from DS products. Those gels were applied on twenty women twice daily over four weeks. Computer-aided laser profilometry, in accordance with standard testDIN 4768 ff (German Institute of Standardisation (Deutsches Institut für Normung)) were used to determine skin roughness parameter for women at the beginning and at the end of the study. By the end of this study, it was found that skin roughness parameter could be reduced by 40.7% when using liquid gel containing 1% of a DS mineral solution, 27.8% when using liquid gel without mineral additives, and 10.4% when using control gel without anti-wrinkle agents or the additives[77].

Zeng et. al., 2004 prepared a skin caring product that contained DS mud and salts, hydrolyzing collagen, Ginseng Radix, and optionally one or more materials selected from soybean isoflavone, sea snake bile and bamboo charcoal. The resulting product has proven

improvement in skin cleansing, supplying skin with necessary nutritional ingredients and removing dead skin[79].

Fleischmann, 2004 prepared bathing solutions that contained DS salt, silica, and bicarbonate; whose preparations showed effectiveness in dehydration, weight loss, improving bowel movement[80]. Another bathing product contains DS salts prepared by Hasunuma et. al., 2000, this product has the property to form bubbles when components were mixed and have an influence on skin moisturizing and conditioning[81].

Moreover, an invention was recorded in 2005 by Braun et. al. This invention concerned the preparation of skin formulations containing urea and DS mud or salts that helps in reducing skin irritation and skin damage[82].

A cosmetic preparation (formulated as cream, paste, milk or face mask) comprises mainly of DS salt, coenzyme Q10 and natural active ingredients was prepared by Beckermann 2001 as anti-wrinkling products that reduce skin wrinkles without causing irritation. The composition also comprised colloid former(s), with high molecular weight organic thickener, and was present as a stable colloidal formulation. The preparation contained also other additives such as organic solvent, inorganic thickener, surface active agent, antioxidant, antibacterial agent, gelling agent, fat, polysaccharide, oil, colorant and/or odorant[83].

Beckermann 2004 prepared face and body oil that composed of two phases; phase A (water, allantoin, DS salt, pentylene glycol) and phase B (soy oil, octyl decanol, perfume, jojoba oil), in addition to other cosmetic and dermatological formulations prepared from aqueous phase and oily phase (vicinal diol with 3-6 carbon atoms) without using of surfactants or emulsifiers[84]. Furthermore, and with regards to hair cosmetics, Robert et. al., 1997 focuses on alopecia patients and used the DS mud to prepare formulation that helps in retardation of hair loss and restoration of hair growth[85].

For aesthetic characteristics, Hwang et. al.,1998 prepared formulation containing DS mud which have an excellent impact on the prevention of dandruff, excluding itching, increase hair gloss and conditioning[86].

Additional benefits:

In addition to previously mentioned therapeutic properties of DS mud, antimicrobiocidal action is another property which is probably attributed to the combination of high salt and sulfide concentrations in plus low pH. This anitimicrobiocidal efficiency may explain the antiacne effect of facial DS mud masks because of the inhibitory effect on skin (Ma'or, unpublished observations, 1998). This was proved by Ma'or. et al., 2006 when suspensions of P. acnes, E. coli, and C. albicans were mixed with DS mud, then it found that the number of colonies that could be recovered declined rapidly[87].

There are also beneficial eukaryotic algae exist in the DS area, such as Dunaliella, which was reported for the first time at DS in 1940 by Elzari-Volcani. Dunaliella, is a unicellular biflagellate alga, and considered as the richest natural source of the β-carotene, the most widely used and commercially important carotenoid. β-carotene is generally used as an antioxidant, food coloring agent and source of pro-vitamin A. Thus, there is a global trend to develop anticancer medicine from β-carotene based on its antioxidation feature. The halophilic species of Dunaliella could be also used as a source of glycerol, since it can accumulate high concentrations of glycerol [88].

In 2013 Emeish S. performed a study in Jordan aimed to investigate the probability of β-carotene production from Dunaliella isolated from the at the laboratory scale cultures, followed by subjecting the produced β-carotene to enzymatic oxidation to produce tretinoin (vitamin A). The amount of β-carotene produced during this study was 3-6% of the dry weight of cultured Dunaliella[39].

Conclusion:

The Dead Sea is the biggest natural saline reserve in the world. Characterization of DS mud and salts showed high concentrations of sulfates and mineral salts, which cause low pH value (approximately 6.0) of its water. DS mud and salts have been used for a long time for treatment of various disorders such as wound healing, rheumatoid arthritis, joint diseases, skin disorders and aging effects. In addition, it has been used as a constituent of several cosmetic products. Despite the wide uses of DS mud and salts, it was found that they contain some contaminants which adversely affect the efficiency of their use such as heavy metals and microorganisms. Literature revealed that heavy metals are concentrated more in DS water, whereas microorganisms are found both mud and salts. Thus, for safety purposes we recommended that care must be taken for the treatment of DS mud and salts before use in any therapeutic or cosmetic product.

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Activated Charcoal in Cosmetics

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Abstract-

The cosmetics industry is known for its innovative and "thinking outside the box" products. Latest in the cosmetics industry world has been the use of activated charcoal for whiter teeth and clearer skin, but what are the regulations on these products. What makes activated charcoal the new miracle for skin and dental health, is presented in this study. The idea behind this new trend of adding charcoal to just about everything is based on the same idea of how activated charcoal works in filters. It removes contaminants and toxins from whatever it is in contact with due to its large surface area on a microscopic level causing it to have important absorption properties. Therefore the idea is that it traps impurities before or while they are in the body before causing unwanted damage such as acne or other skin health issues.As this is becoming more and more popular amongst cosmetics products, it is important to ask what impacts it will have on your body in the long run. As with all new ingredients, very little is said as to what it will do over time. However, several studies have concluded that it is safe for external use- inhaling it is not safe and digesting it is fine in small quantities- and the FDA has also deemed it harmless due to its mineral like qualities. Activated charcoal is produced from carbonaceous source materials- nut shells, wood, coal and by either having it go through physical activation with hot gases or through chemical activation using an acid, strong base or salt introduced into the carbon and then carbonized at temperatures between 450 and 900 degrees celsius. This is where regulation is important because if carbonized with dangerous chemicals that remain in the final product it could then be detrimental to the user's health. Regulations also allow for the Activated Charcoal to in fact be "activated" like the consumer expects. No one wants plain coal in their beauty products just like they don't want it in their stockings at Christmas.

Introduction-

The skin is the biggest organ of our body and it acts as protective layers against bacteria and other harmful germs. Everyday our body is assaulted by harmful chemicals, dirt and grime. It needs special attention.Before considering skin cleansing one needs to have a clear understanding of the main kinds of impurities on the skin. These include residues of cosmetic products, pharmaceuticals products and secretion from the skin glands as well as desquamating cornified cells and environmental pollutants such as dust and soot and micro-organisms. An adsorbent skin cleansers should use for facial cleansing.

Activated charcoal means the carbon is infused with oxygen and is prepared for human ingestion (in the case of poisoning or detox) and skincare products. This oxygenation creates a super porous surface, increasing its ability to absorb matter and toxins. Possibly the most absorbent cosmetic ingredient out there, activated charcoal is said to have the ability to absorb thousands of times its own weight. Activated charcoal powder has been used for years in the East as a teeth whitener and has repeatedly proven its effectiveness. Incorporating this charcoal

powder into your routine will grant you a brighter smile, detoxify your mouth all without the use of nasty chemicals. Activated charcoal is blessed to have a unique carbon chemical structure. Because of this, it is highly capable of absorbing toxins on a microscopic level.

Activated charcoal draws bacteria, poisons, chemicals, dirt and other micro-particles to the surface of skin, helping you to achieve a flawless complexion and fight acne. Charcoal is not metabolized, adsorbed or absorbed by the body, but it can be used to treat some poisonous bites and disinfect some wounds. Activated charcoal powder is proven to adsorb thousands of times its own mass in harmful substances, which makes it a popular ingredient in facial mask.

The History of Activated Charcoal

The first recorded use of charcoal for medicinal purposes was found in Egyptian papyri around 1500 BC as a method of staving off infection from open wounds. Since then, healers have used activated charcoal to soak up poisons and improve intestinal health through a process called "**ad**sorption." No, that's not a misspelling. It's important to understand the difference between **ab**sorption and **ad**sorption. When something is **ab**sorptive, that means it soaks up other substances, but when something is **ad**sorptive, that means it binds to substances. Activated charcoal actually uses a thin film on its outside surface to bind toxins and poisons. Ancient physicians used regular charcoal for a variety of medical purposes, including treating epilepsy and anthrax. In the early 20thcentury, the development of activated charcoal sparked many medical journals to publish research revealing its effectiveness as an antidote for poisons. Today, beyond use in hospitals as an antidote for drugs and poisons, activated charcoal is a global remedy for general detoxification and intestinal disorders.

Other than the usual charcoal that we use to light up the barbecue activated charcoal for cosmetic use is often made from made from coconut shells, bamboo, peat or olive pits.

Activated Charcoal for Skin

- **Smaller pores**

Throughout the day, toxins from the world around us clog pores of the skin. When skin pores aren't clear, neither is complexion. Activated charcoal when **used in a face mask** it binds to dirt and helps pull it out of pores of the skin, making them less visible. It's the oil and dirt that makes them appear bigger. This leaves face feeling fresh. When an activated charcoal is used with an exfoliating scrub, the dead skin gets off and the skin experienced an even deeper clean.

- **Balances oily skin**

When used in a cleanser or mask, activated charcoal can pull the unwanted excess oils from skin, leaving it smooth.

- **Treat acne**

Depending on the specifics of acne how severe it is, what's causing it and what else is going on, activated charcoal may be able to help. In soap form, it's slightly gritty, which might provide the gentle exfoliating. It will also absorb oils and toxins on and below the skin.

- **Deep cleanse your skin**

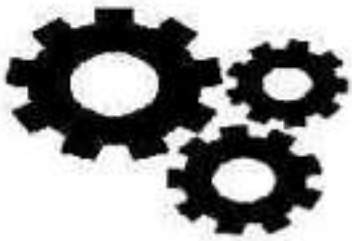
Because toxins stick to the activated charcoal, it makes a good deep cleanser and detoxifier. It's all-natural and won't add new chemicals to skin when you use it.

- **Soothe and heal bites, cuts and skin irritations**

Whether there were stung by a bee or had a cut from the kitchen that's become infected, activated charcoal can help speed the healing and relieve the symptoms. For minor skin ailments including insect bites, stings, cuts, scrapes and minor infections, activated charcoal can be applied topically. The activated charcoal, when applied as a paste, helps absorb venom and infection. It will also bring down swelling and lessen pain.

Activated Charcoal for Acne

The idea behind activated charcoal for acne is that it will bind acne-causing bacteria, excess oil, dirt, chemicals or other microparticles and thus help to heal and prevent acne. The recent trend has led to a whole spectrum of skin products that contain charcoal, for e.g. charcoal scrubs, charcoal masks or charcoal soaps for acne.



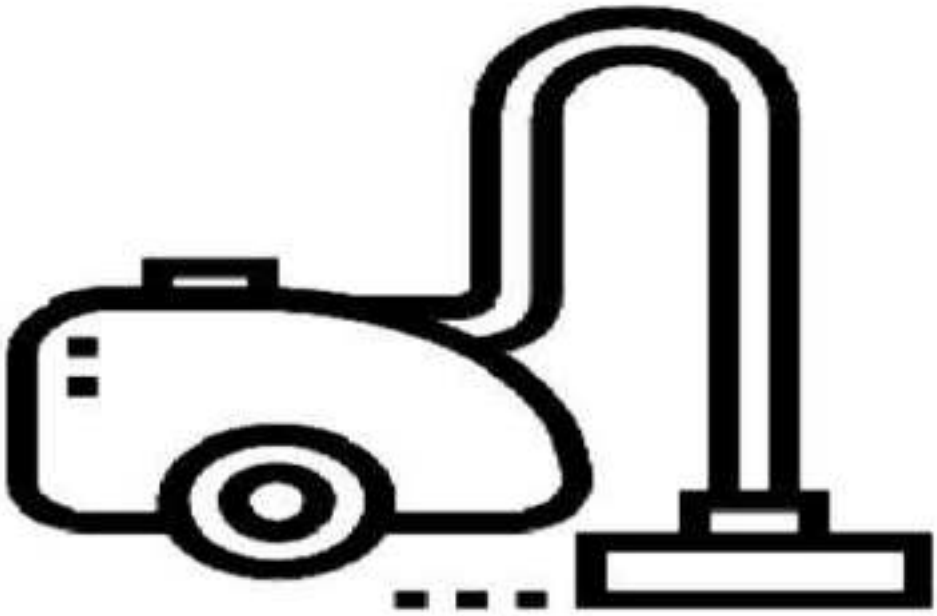
Its millions of tiny-little pores increase the surface area of charcoal immensely and enable it to carry other microparticles up to 1000 times of its own mass. However, the structure alone is not enough. Additionally, it is negatively charged which attracts positively charged particles like toxins, bacteria or chemicals and traps them inside the pores.

The fact that charcoal is not absorbed by the body ensures that the toxins are carried out of the body when taken orally or if applied on the skin, draws them out.

The Benefits of Activated Charcoal for Acne

- **Sucks up excess sebum**

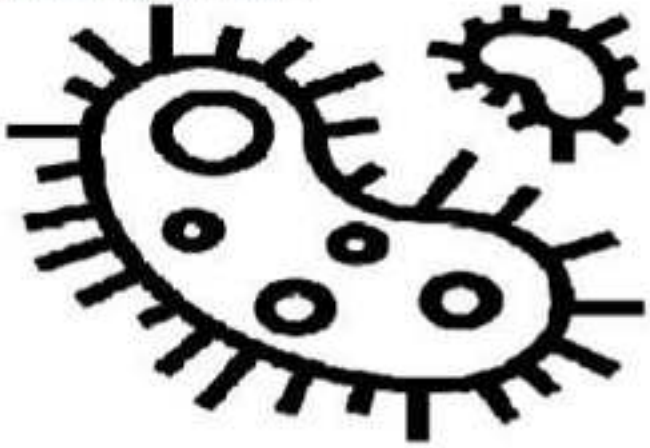
Activated charcoal really is a sponge, that's why it is so effective against overdoses and poisonings. Thus, it will also suck up and control excess sebum (The skins Oil) and prevent pores from clogging.



- **Draws out acne-causing bacteria**

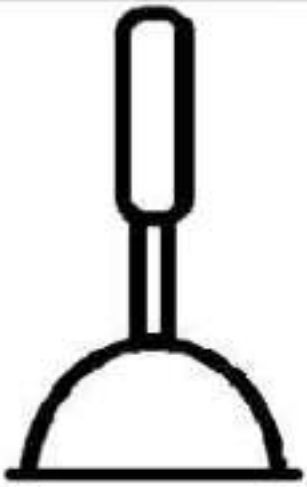
Bacteria are naturally present on the surface of the skin. For people that are prone to acne and oily skin, the bacteria can flourish in the anaerobic environment of the oily skin. Charcoal will bind bacteria that are present on the skin and thus, positively affect acne.

For bacteria that are deeper inside the skin, it is not clear and scientific studies must tell. However, due to its negatively charged structure, it is likely that charcoal will draw out bacteria and toxins that lie underneath the skin's surface.



- **Unclogs pores**

Besides, preventing pores from clogging because of its cleaning and oil-diminishing capabilities, activated charcoal can also help to unclog pores as it removes the sebum, dirt and dead skin from the pores. It will smoothen the skin's appearance.



- **Frees the skin of other toxins, dirt, and chemicals**

Just as in the stomach, it will bind any positively charged toxins, dirt, chemicals or heavy metals that are present on the skin which will be removed when the skin is rinse off.

Additionally, it is 100 % sure that activated charcoal is inert and doesn't cause any allergic reactions, irritation or inflammation and won't make acne worse.

To sum up, there are some **very convincing benefits** that activated charcoal could have for acne. The environment on the surface of our skin might look very different from our stomachs at first sight but when we take a closer look at the mechanisms – drawing out chemicals, toxins or other microparticles – things become more coherent. In addition to the fact that activated charcoal won't harm or make your skin worse, it is worth a try in fighting acne.

Activated Charcoal for Hair

- **Rid your hair of toxins**

A shampoo with activated charcoal can gently detox by attracting dirt and oil which is then washed away. And because it's gentle, it won't disrupt hair's natural moisture levels. White charcoal is derived from Binocotan Oak Trees, known for its soothing properties.

- **Add volume to your hair**

If there is enough dirt and oil around, hair will start to sag and regular shampooing may not be getting it all out. In fact, hair can gain roughly 4 percent of its own weight in build-up from scalp oils, pollution and dry shampoo. Regular shampoos remove surface dirt, but activated charcoal will pull out even more. The other difference, and this is big, is that activated charcoal isn't going to leave the residue some shampoos do, so hair will feel lighter and have more volume.

- **Remedy scalp conditions**

Dandruff, redness, oily and itchy scalps may be relieved with activated charcoal. One can use it as a scalp treatment before shampoo or can be mixed in with shampoo. The activated charcoal will work on scalp the way it does on skin and hair, pulling out toxins and purifying. It's unclear how deep into the hair follicle is being cleaned, but the results should be noticeable.

Activated Charcoal for Teeth

Teeth are highly sensitive and thus the activated charcoal should be from food/ supplements from coconut and wood and not from petroleum which is highly corrosive. Coconut and wood-based carbon have greater microporosity, therefore, best suited to remove organisms that have a low concentration. Activated charcoal is tasteless and odorless so it might not be very irritating on the mouth.

Its microporosity nature allows it to bind to organic compounds such as tartar, plaques, stains, viruses and bacteria found in the mouth which have high molecular mass and are neutral in chemical nature. But it does not bind to minerals such as calcium so it's safe to use on teeth. The existence of charcoal protects it from being swallowed by the stomach.

Its adsorption properties allow it to bind to the toxins and restrain them. Due to the high heating temperatures the activated charcoal contains negative ionic charges which when in contact with toxins or chemicals which are positively charged it binds to them and moves them out of the body. It is not absorbed by the body, therefore, it is able to pass through the digestive tract through to the intestines and finally be eliminated from the body.

Benefits of Brushing Teeth with Charcoal

- **Activated Charcoal for Tooth Infection and Prevent Cavities**

Cavities cause teeth discoloration. It occurs in the presence of excess phytic acid from foods such as nuts, seeds, soybeans and other grains. Activated charcoal which is an alkaline, neutralizes the acids and are able to treat the cavities and prevent tooth discoloration.

- **Change the PH of the mouth**

Diet, stress, and hormones can make the saliva too acidic such that is affects the teeth resulting to cavities that cause tooth discoloration. This also happens when food particles combine with bad bacteria in the mouth. It causes gingivitis and tooth decay which is associated with discoloration of teeth. Activated charcoal alkaline in nature helps to get rid of these toxins and provide a PH balance in the mouth thus whitening the teeth.

- **Prevent Tannin**

Tea, coffee, wine contain tannin which when taken in excess accumulate in areas around the teeth and causes them to have a brown, yellow color. Activated carbon attaches to the tannin and absorbs it through their pores and bring color to the teeth.

- **Clears nicotine stains**

When nicotine gets sticks to the tooth enamels causes brown or yellowish staining.Activated charcoal binds itself to the nicotine or tobacco stains and absorbs then into its pores and eliminates the stain whitening teeth in the process.

- **Aging**

As we age the tooth enamel starts to wear off and it exposes the dentin layer which has a yellower tone. A thin enamel exposes a yellower dentin. Current products in the markets leak through the enamel into the dentin which affects tooth color. Activated charcoal slows down the cell changes that are associated with aging. It slows down the brain's release of toxins that hasten wearing off of the enamel. This brightens teeth.

- **Removes Plaque**

Plaque results from the build up of tartar and creates a yellow sticky substance on the teeth. Through its adsorption properties which bind to the tartar and plaque formed and eliminating them leading to cleaner teeth.

Discussion and Conclusion

Activated charcoal, which is carbon that's been treated to increase its absorbency, isn't new. It's been used in hospital emergency rooms for years to treat alcohol poisoning and drug overdoses. It works by attaching to toxins in the stomach and absorbing them before the bloodstream can. The theory behind including activated charcoal in beauty products is similar. It'll act like a magnet to attract and absorb dirt and oil. And the experts say that theory holds water. "When dirt and oil in your pores come in contact with the carbon, they stick to it and then get washed away when you rinse,"The secret to an effective "whole body detox" might just be activated carbon.Ancient physicians used regular charcoal for a variety of medical purposes, including treating epilepsy and anthrax. Today, beyond use in hospitals as an antidote for drugs and poisons, activated charcoal is a global remedy for general detoxification and intestinal disorders.The porous surface of activated charcoal has a negative electric charge that attracts positively charged toxins and poisons. It binds them, and escorts them out of your body through the elimination process of your intestines.Activated charcoal is completely odorless, tasteless, and safe.

Putting charcoal in your hair and on your face might not seem glamorous, but it's proven to have many health and beauty benefits when used safely and properly.

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Formulation and Development of Clerodendrum Sulphate free face Wash

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Abstract:

The present research has been undertaken with the aim to formulate and evaluate the clerodendrum sulphate free facewash.Clerodendrum phlomidisLinnhas been used as anti-bacterial, anti-fungal,anti-inflammatory, anti-oxidant and wound healing activity. The face wash formulation was design by using extract of clerodendrum phlomidis leaves. Face washwas prepared by using polymer that is carbopolultrez 20, sodium lauryl sarcosinate, lauryl glycoside, coco amido propyl betain, glycerin, sodium benzoate, clerodendrum extract, disodium EDTA, triethanolamine, perfume, color and require amount of distilled water. The skin pH is 4-5.5 was maintained by drop wise addition of triethanolamine. The physicochemical parameters of formulations (pH, viscosity, foaming power etc.) were determined. Stability study have carried out as per ICH guideline for 30 days at different temperature and humidity. The result shows that the formulation containing 1% clerodendrum extract have better stability and good results than any other formulation.

Keyword: Clerodendrum phlomidis,sulphate free face wash, antibacterial activity, anti-fungal activity, antioxidant.

Introduction:

According to World Health Organization (WHO), medicinal plants would be best source to obtain a variety of drugs. Plants produce diverse range of bioactive molecules, making them a rich source of different type of medicinal compound. Over 50% of all modern clinical drugs are of natural product origin. Clerodendrum phlomidis Linn. Belonging to family Lamiaceae, have an antioxidant, antifungal, antibacterial, anti-inflammatory and wound healing activity. So the aim of the present study was to formulate and evaluate the clerodendrum sulphate free face wash.

Materials And Methods:

Plant material:

The clerodendrumphlomidisLinn was collected from vardha district, Maharashtra India. The plant leaves were collected, and washed with running water to remove dust, shade dried, crushed by a mechanical grinder and passed through a 40 mesh sieve.

Preparation of extract:

The 5g powered material of clerodendrum were successively extracted with ethanol and water (50-50), by hot continuous method in soxhlet apparatus for 24 hrs. The concentrated extract was obtained.

Chemicals:

Carbopol ultrez-20 (Lubrizol Pvt ltd, Mumbai), glycerin (Gangwal Chemicals Pvt ltd), sodium lauryl sarcosinate (Galaxy Surfactant Pvt ltd, Mumbai), coco-amido propyl betain (Galaxy Surfactant Pvt ltd, Mumbai), lauryl glycosides (Gangwal ChemicalPvt ltd, Mumbai),

sodium benzoate (Vaibhav ChemicalsPvt ltd, Mumbai), Di sodium ethylene diamine tetra acetic acid (Omkar Traders, Mumbai), perfume (Gangwal Chemicals Pvt ltdMumbai), colour (Nilikon Pvt ltd Mumbai.)

Sulphate Free Face Wash:

Sulphate refers to a family of cheap detergent used in soaps and other personal products as a grease cutting or lather agent. Sulfates are commonly found in shampoo, toothpaste, face wash. Sodium lauryl sulphate cuts though grease, which is great for some, but not so great for certain skin or hair type. In addition to being a potential skin irritant, it produces acne and perioral dermatitis. Sodium laureth sulphate removes the natural oil from skin that actually needed for protection and your skin end up producing more oil leaving your face more oiler. So here is sulphate free face wash which removes skin dirt and impurities within the pores also maintain the required moisture balance.

Different combinations of clerodendrum phlomidis leaves extract (0.5%, 1%) were tried with different combination of ultrez 20 using various formulae. The following formulation is selected.

Formulation 1

Sr. no	Ingredients	Quantity
1	Distilled water	70.84
2	Carbopol Ultrez 20	0.9
3	Sodium lauryl sarcosinate	4
4	Lauryl glucoside	10
5	Coco amido propyl betain	7
6	Glycerin	5
7	Sodium benzoate	0.2
8	Clerodendrum extract	1
9	Disodium EDTA	0.1
10	Triethanolamine	0.45
11	Perfume	0.5
12	Color	0.01

Method of preparation of face wash

All the apparatus were cleaned and weigh all the ingredient as per the formulation of face wash. Take the water in beaker and sprinkle Carbopol ultrez 20 and allow to swell for 20 minutes with continuous stirring. Then add sodium lauryl sarcosinate with slow agitation. Neutralize the polymer by adding TEA. Add CAPB, lauryl glucoside, glycerin, sodium benzoate with continuous stirring. Add clerodendrum extract. And perfume and colour.

Evaluation Of Face Wash.

a) Determination of physical parameters

1) Appearance- Visually appearance of the formulation was observed.

2) Color- Color of the formulations also checked visually.

3) Consistency- Consistency was also checked whether it is satisfactory or poor or viscous.

4) Tacky feel- When face wash taken on palm for application then checked whether it feels tacky or not.

b) Determination of pH

Face wash are used for topical applications, so their pH should be similar to the skin.The skin has acidic mantel and the pH of the face wash as per the standards should be in the range of 5.0-9.0

Apparatus- pH meter equipped with glass electrode.

1- Procedure- Determine the pH at a temperature of 27 +2°C. Read the pH directly by dipping electrode of pH meter in sample.

c) Determination of Viscosity

2- Viscosity is a measure of a fluid's resistance to flow. It is measured and expressed in term of centipoise (cP).

3- Apparatus- Brookfield Viscometer

4- Procedure-The viscosity of the prepared formulations was determined using Brookfield viscometer RV series model. The selected formulations were poured into the sample adaptor of the viscometer and viscosity was measured at 25°C. The measurements were carried out using spindle number 6 at the speed of 20 rpm.

d)Determination of foaming power

In order to check the ability of a face wash to produce lather.the volume of foam obtained under specific experimental condition is determined.

Apparatus- Beaker, Measuring cylinder

Procedure- Firstly 5ml of face wash taken in a beaker and then 45ml of water was added in it. Stir it well before solubilizing the face wash in water, then this solution was transferred in 250 ml measuring cylinder and inverted for 2 sec and again reverted to its normal position to get one shake. Such 12 shakes were given to the face wash solution. After 12 shakes, the cylinder was kept aside for 60 sec. and reading were taken, by measuring the volume of foam and water together and volume of water alone.

Formula

Foaming power = $F_1 - F_2$

Where,

F_1 Foam + water

F2- water (in ml)

e) Determination of Microbial Examination

Microbial growth may occur in cosmetics and Personal care product like face wash, lotion, and gel many more are intended to be used as skin care preparation, hence they come in contact with skin directly. Hence it is very important that the cosmetics product, must to free from microbial contamination, so that it will ensure safety product to the client. The cosmetics product must be safe and adequate preserved.

Apparatus: Test tube, Petri dish, colony counter, autoclaves.

Media and Buffer:

1. Soybean casein digest agar medium –

Dissolved in 40 gm of soybean casein digest Agar in 1000 ml of distilled water. Boil if necessary in order to have a uniform. Close the flask with the metal cap and autoclave at 122°C for 20 minute. After autoclaving store it in a cool place can be use with 3 weeks.

2. Stock solution pH 7.2 phosphate buffer –

Dissolve 34 gm of potassium phosphate in about 500 ml of water content in a 1000 ml volumetric flask. Adjust the pH to 7.2 by addition of NaOH (4%) add water to make up volume and mix. Sterilize at 122°C for 20 minute, store under refrigeration.

3. Dilute phosphate buffer solution pH 7.2 –

Dilute 1 ml of flask solution with distilled water in the ratio of 1:800 fill 50 ml each in conical flask with cotton and sterilize at 122°C for 20 minute.

Procedure- Melt sufficient number of soybean casein digest agar medium in test tubes in a hot water bath and transfer while hot into constant temperature water bath maintained at 48 ± 2°C. Weigh hand transfer aseptically 1 gm of the sample to conical flask containing sterile 50 ml of dilute phosphate buffer pH 7.2 shake well pipette out 1 ml portion into three sterile dishes. Pour melted and cooled soybean casein digest agar medium over it and rotate the plates to mix thoroughly. Include the plate at 32°C for 72 hours in an inverted position.

Determine the average no. of colonies on soybean casein digest agar medium plates and multiply by 30, the dilution factor. This will be the no. of micro-organisms per gram of the sample.

f) Determination of Thermal stability

In any rational design and evaluation of dosage form for drug, product the stability of the active component must be major criterion in determining their acceptance or rejection. Stability of a drug can be defined as the ability of particular formulation, in a specific container, to remain within its physical, chemical, therapeutic and toxicological specifications. Optimized formulation was selected and kept for stability studies. Formulation were packed in a suitable container and sealed tightly and studies were carried out for 30days. The international conference on Harmonization (ICH) guidelines titled "stability testing of new drug substances and products" describes the stability test requirements for drug registration application in the European Union, Japan and the United States of America.

B) In- Vivo Evaluation of face wash.

a) Photographic Evaluation

Photographic evaluation is carried to see the effect of the product visually .In case of determination of cleansing activity. Photographic evaluation was adopted. In this method the photograph of the skin before and after rinsing of skin were taken out and effect of product was determined.

b) Determination of exfoliation

In that volunteer was selected. Photograph of nose was taken before application of product, and then product was applied on nose, rinse with water. After rinsing photograph difference was observed.

Result And Disscussion

1) Determination of physical parameter

5- Table No 1: Determination of physical parameter

Sr.No	Physical parameters	Result
1.	Color	Light green
2.	Viscosity	Spreadable
3.	Spread ability	Good

3.	2nd week	6.31
4.	3rd week	6.32
5.	4th week	6.33

It shows slight changes in pH but remains stable.

4) Determination of viscosity

Table no 6: Determination of viscosity

Sr. No	Days	Viscosity
1.	Initial	1750
2.	1st week	1750
3.	2nd week	1749
4.	3rd week	1748
5.	4th week	1748

It shows slight changes in viscosity but remains stable.

5) Determination of foaming power

Table no 7: determination of foaming power

Sr. No	Days	Foaming power
1.	Initial	92mm
2.	1st week	92mm
3.	2nd week	91mm
4.	3rd week	91mm
5.	4th week	90mm

The foaming power of face wash was not drastically change so the foaming power was acceptable with good range of pH stability.

6) Determination of microbial count.

Table no 8: Determination of microbial count.

Sr. No	Parameter	Result	Specification	Unit
1	Total microbial count	1cfu/gm	NMT/100cfu/gm	Cfu/gm

The microbial count of face wash was not more than 100cfu/gm as per ideal specification so it passes the microbial count test.

7) Determination of thermal stability.

Table no9: Determination of thermal stability

Sr. No	Parameter	Days	Result
1	Thermal stability	30 days	Passed

As it is stable for 30 days the face wash passes the test.

Conclusion

Water acts as a good cleanser for skin surface however it has limited ability to dissolve andremove oil sebum and dirt, hence a surfactant is a unique structure which has a good cleansing effect. Present study that is sulphated free face wash containing clerodendrum extract satisfied all the desired characteristics and provide better antibacterial activity, skin tonicity on long term usage, exfoliating along with efficient cleansing property without causing any damage to skin.

The sulphate free face wash are most stable form and resulting in healthy, smooth, won't clog pores, with oil free skin after application without causing irritation.

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Metallic Nano-Particle – As A Novel Drug Carrier in Cosmetics

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Abstract:

Nanotechnology, from the Greek "nano" for dwarf, can be defined as research for the designing, synthesis and manipulation of the structure of particles with a dimension smaller than 100 nm. Nanotechnology can be defined as research for the designing, synthesis and manipulation of the structure of particles with a dimension smaller than 100 nm. The nanoparticles are of great scientific interest as they bridge the gap between bulk materials and atomic or molecular structures. Metallic nanoparticles have received particular attention for their positive impact on improving many sectors of the economy, including consumer products, pharmaceuticals, cosmetics, energy and agriculture, etc., and are produced for a wide range of industrial applications. Widely used metallic nanoparicles in cosmetics are Gold nanoparticles, Silver nanoparticles, Iron nanoparticles, Palladium nanoparticles, Platinum nanoparticles etc.

Keywords: Nanotechnology, Nanoparticles, Metallic Nanoparticles, Silver Nanoparticles etc.

Introduction:

Nanotechnology, from the Greek "nano" for dwarf, consists of manipulating materials at the atomic and molecular levels to create new molecular structures known as "Nanomaterials" having unique and new characteristics that differ from those of the original materials they are derived from. A Nanomaterial is defined as a "material with one or more external dimensions, or an internal structure, on the nanoscale, which could exhibit novel characteristics compared to the same material without nano scale features". Nanoparticles (NP) are a subset of NM and were defined as single particles with a diameter below 100 nm, although their agglomerates may be larger. Nanoparticles are nanosized structures in which at least one of its phases has one or more dimensions (length, width or thickness) in the nanometer size range (1 to 100 nm).

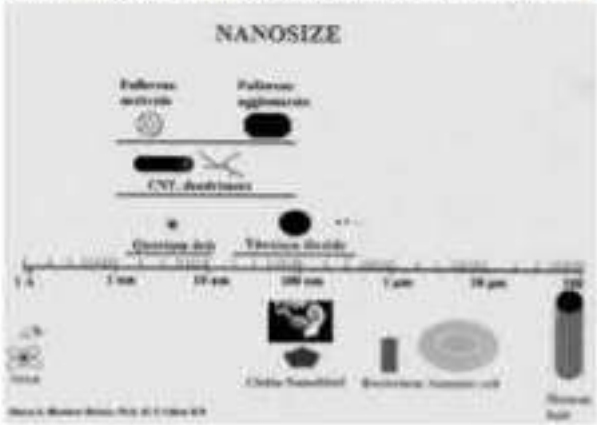

Figure 1: Nano size / Nanoparticles

Nature depends fundamentally on structures and processes operating at the nanoscale, from simple colloids such as milk to highly sophisticated proteins. Free Nanoparticles also occur naturally as by-products of combustion and cooking. In some sense, nanoscience and nanotechnologies are not new: size-dependent properties have been exploited for centuries. For

example, Silver (Ag) and Gold (Au) nanoparticles (particles of diameter less than 100 nm) have been used as colored pigments in stained glass and ceramics since the 10th century AD. Nanotechnologies have been used to create the features on computer chips for the past 20 years. However, through the invention of imaging techniques like the Scanning Tunneling Microscope and the Atomic Force Microscope, our understanding of the nano world has improved dramatically. The Working Party on Manufactured Nanomaterial (WPMN) of the Organization for Economic Cooperation and Development (OECD) has selected a list of representative manufactured Nanomaterial considering those materials which are:

- Single-Walled Carbon Nanotubes (SWCNTs)
- Multi-Walled Carbon Nanotubes (MWCNTs)
- Silver Nanoparticles
- Nan clays
- Iron Nanoparticles
- Carbon Black
- Titanium Dioxide
- Aluminum Oxide
- Cerium Oxide
- Silicon Dioxide
- Polystyrene
- Dendrimers

Metallic Nanoparticle:

The term metallic nanoparticle is used to describe nanosized metals with dimensions (length, width or thickness) within the size range 1-100 nm. The existence of metallic nanoparticles in solution was first recognized by Faraday in 1857 and a quantitative explanation of their color was given by Mie in 1908. Metallic nanoparticles have received particular attention for their positive impact on improving many sectors of the economy, including consumer products, pharmaceuticals, cosmetics, energy and agriculture, etc., and are produced for a wide range of industrial applications. Some widely used metallic nanoparticles in cosmetics are;

- Gold nanoparticles
- Silver nanoparticles
- Iron nanoparticles
- Palladium nanoparticles
- Platinum nanoparticles etc.

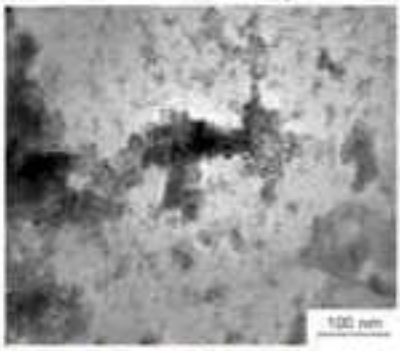

Figure 2: TiO2 Nanoparticles

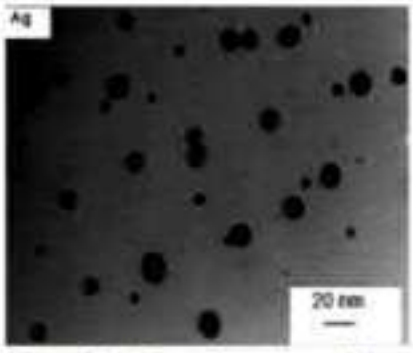

Figure 3: silver Nanoparticles

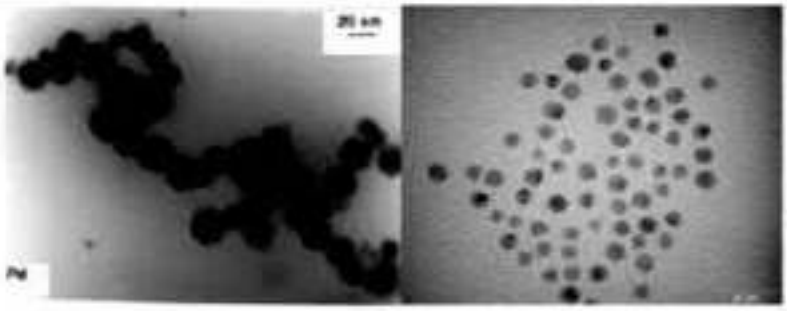

Figure 4: Palladium Nanoparticles **Figure 5: Gold Nanoparticles**

The Main Characteristics Of Metallic Nanoparticles (Mnps):

Metallic Nano-Particles has following characteristics;

- large surface-area-to-volume ratio as compared to the bulk equivalents;
- large surface energies;
- the transition between molecular and metallic states providing specific electronic structure (local density of states LDOS);
- Plasmon excitation;
- quantum confinement;
- short range ordering;
- increased number of kinks;
- a large number of low-coordination sites such as corners and edges, having a large number of "dangling bonds" and consequently specific and chemical properties and the ability to store excess electrons.

Synthesis Methods:

Ideally metallic nanoparticles should be prepared by a method which is reproducible and may control the shape of the particles. Also, yields monodisperse metallic nanoparticles. The method should be easy and cheap. In the synthesis method should use less toxic precursors like in water or more environmentally benign solvents (e.g. ethanol), also use least number of reagents. Reaction temperature should be close to room temperature. Process should have few synthetic steps as possible (one-pot reaction). Lastly minimize the quantities of generated by-products and waste. There are two main types of synthesis methods which are chemical and physical methods which are listed bellow;

A.Chemical Methods

1. Chemical reduction of metal salts
   1.1. The alcohol reduction process
   1.2. The polyol process
2. Microemulsions
3. Thermal decomposition of metal salts
4. Electrochemical synthesis

B. Physical Methods

1. Exploding wire technique
2. Plasma
3. Chemical vapor deposition

4. Microwave irradiation
5. Pulsed laser ablation
6. Supercritical fluids
7. Sonochemical reduction
8. Gamma radiation

Characterization:

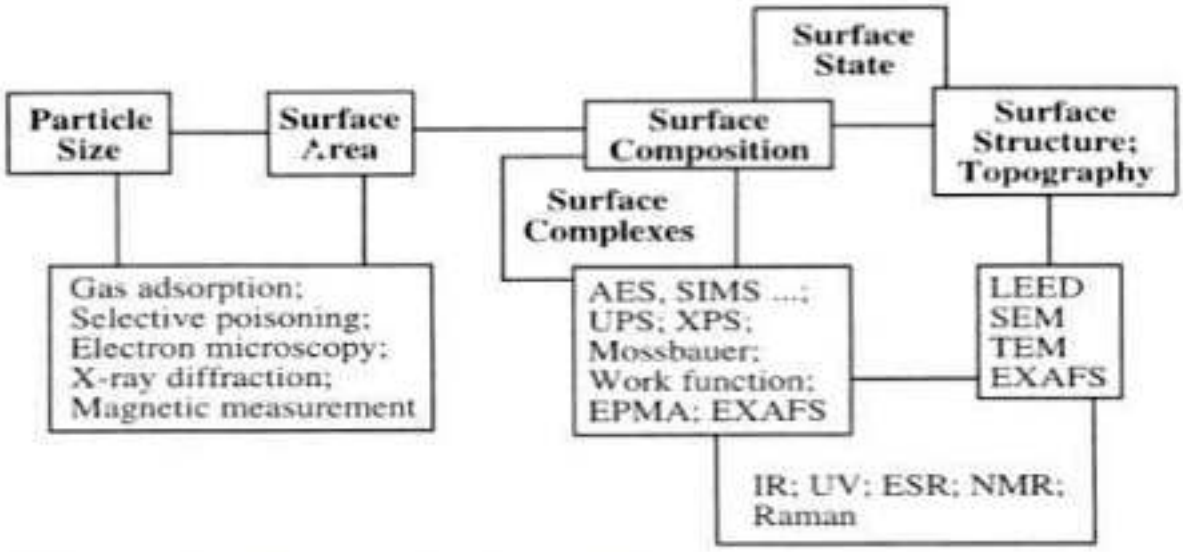

Figure6: Common methods available for the characterization of metallic nanoparticles.
[J.D. Aiken III, Journal of Molecular Catalysis A: Chemical 145 (1999)]

Advantages:-

1. In cosmetics it is aimed to make fragrances last longer, sunscreens more effective and anti-ageing creams.
2. To optimize manufacturing conditions for skin care formulation, a multicomponent system.
3. To prevent hair from turning grey and also for prevention of in treatment of hair loss & used to preserve active ingredients, such as vitamins and anti-oxidants, and their lightness and transparency.
4. To improve the UV protection in combination with organic sunscreens such as 2-hydroxy-4-methoxy benzophenone this allows a reduction of the concentration of the UV absorber.

Disadvantages:-

1. Smaller particles have a greater reactivity, are more chemically reactive and produce greater numbers of reactive oxygen species.
2. It may result in oxidative stress, inflammation, and consequent damage to proteins, membranes and DNA.
3. Nanomaterial has proved toxic to human tissue and cell cultures, resulting in increased oxidative stress and cell death.

4. Inhaled ultrafine particles induce pulmonary inflammation when the particles are quartz, minerals, dust, coal, silicate, and asbestos. These can induce pulmonary fibrosis, cytotoxicity, and even malignancy.

Properties Of Nanoparticles:-

• They are effectively a bridge between bulk materials and atomic or molecular structures.

• A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed.

• For bulk materials larger than one micrometer (or micron), the percentage of atoms at the surface is insignificant in relation to the number of atoms in the bulk of the material.

• The high surface area to volume ratio of nanoparticles provides a tremendous driving force for diffusion, especially at elevated temperatures. Sintering can take place at lower temperatures, over shorter time scales than for larger particles.

• Suspensions of nanoparticles are possible since the interaction of the particle surface with the solvent is strong enough to overcome density differences, which otherwise usually result in a material either sinking or floating in a liquid.

• Nanoparticles also often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects. For example gold nanoparticles appear deep red to black in solution.

• Nanoparticles with one half hydrophilic and the other half hydrophobic are termed Janus particles and are particularly effective for stabilizing emulsions. They can self-assemble at water/oil interfaces and act as solid surfactants.

• The photo catalytic activity of the nanoparticles must not lead to a self destruction of the composite system, and it is essential to check this point before fixing a combination of polymer matrix and nanoparticles.

• A higher concentration of ferrite particles clearly increases optical absorption. Furthermore, the strong increase in absorption for shorter wavelengths is shifted significantly to shorter wavelengths when the concentration is reduced. This blue shift may be attributed to a smaller particle size or surface phenomena on the band gap.

methods for the preparation of nanoparticles:-

A. The sol–gel method
B. Vacuum deposition method
C. Ball milling method
D. Pyrolysis
E. Other methods like Arc (DC) plasma, Laser Processes, Wire electrical explosion, Sputtering, Droplet-to-Particle Conversion, Flame synthesis

A. The sol–gel method:-

Silver nanoparticles are prepared by mixing the AgNO3 solution with tetraethylorthosilicate, ethanol and water then with a few drops of HNO3 as a catalyst. The mixed solution was dispersed and dried. The dried gels were reduced at a temperature of 400 co for 30 min in hydrogen gas. The Ag particles have a size of about 5-10 nm with a profile distribution in the form of lognormal distribution. The nanoparticles are embedded in silica glass in well separated and protected matrix. The preparation of iron nanoparticles embedded in glass

can be prepared with the same method by substituting FeCl3 for the silver salt. The sol–gel method has advantages of yielding high purity, isotropic, and low temperature annealing while with shortage of cracking after dried by heavy doping. The free water absorbed in the porous gel and the H-O bonds desorbed on the porous surface.

B. Vacuum deposition method:-

The presence of inert gas in vacuum chamber and lowering down the substrate temperature to liquid nitrogen temperature during thermal evaporation can reduce the momentum of the evaporated metallic atoms or clusters by collision with gas to obviate their further aggregation on the substrate. The evaporated metal atoms condensed just at where they reached without migration to the potential minimum thereby lose Vander wall attraction between particles. The resulting smokes can be collected from the substrate or walls of the evaporation chamber with the particle sizes can be easily controlled between 30-1000 Å depending on the gas pressure, the evaporation speed, the type of gas used, and the substrate temperature. Direct (DC) or radio frequency (RF) sputtering with the structure of deposited films mostly to be amorphous without substrate heating can successfully deposit refractory metals and alloys.

C. Ball milling method:-

Hard and brittle ceramic materials can be ball-milled into nanoparticles to produce nanocrytals, noncrystals, and pseudo crystals. Powders of 500 nm sizes can be milled into several nm by strong vibrations when mixed with tungsten-carbide spheres. The shortages of ball milling are the surface contamination of the products and non uniformity of the structure but are a simple method.

D. Pyrolysis:-

In pyrolysis, a vaporous precursor (liquid or gas) is forced through an orifice at high pressure and burned. The resulting solid (a version of soot) is air classified to recover oxide particles from by-product gases. Pyrolysis often results in aggregates and agglomerates rather than single primary particles. The thermal plasma temperatures are in the order of 10,000 K, so that solid powder easily evaporates. Nanoparticles are formed upon cooling while exiting the plasma region. The main types of the thermal plasma torches used to produce nanoparticles are dc plasma jet, dc arc plasma and radio frequency (RF) induction plasmas.

methods for preparation of solid lipid nanoparticles:-

a) High shear homogenization and ultrasound
b) High pressure homogenization
c) Solvent emulsification /evaporation
d) Micro emulsion based SLN preparations

a) High shear homogenization and ultrasound

High shear homogenization and ultrasound are dispersing techniques which were initially used for the production of solid lipid nano dispersions. Both methods are wide spread and easy to handle. However, dispersion quality is often compromised by the presence of micro particles. Furthermore, metal contamination has to be considered if ultrasound is used. A Lak Tek rotor–stator homogenizer (Omni International, Gainesville, USA) to produce SLN by melt–emulsification.

They investigated the influence of different process Para meters, including emulsification time, stirring rate and cooling conditions on the particle size and the zeta potential. Lipids used in this study include trimyristin, tripalmitin, tristearin, a mixture of mono-, di- and triglycerides and glycerol behenate , poloxamer 188 was used as steric stabilizer (0.5 w%). ForWitepsoleW35 dispersions the following parameters were found to produce the best SLN quality: stirring for 8 min at 20 000 rpm, the optimum cooling conditions: 10 min at 5000 rpm at room temperature. In most cases, average particle sizes in the range of 100–200 nm were obtained in this study.

b) High pressure homogenization

High pressure homogenization (HPH) has emerged as a reliable and powerful technique for the preparation of SLN. Homogenizers of different sizes are commercially available. HPH has been used for years for the production of Nanoemulsions for parenteral nutrition. High pressure homogenizers push a liquid with high pressure (100–2000 bar) through a narrow gap (in the range of a few microns). The fluid accelerates on a very short distance to very high velocity (over 1000 km/h). Very high shear stress and cavitation forces disrupt the particles down to the submicron range. Typical lipid contents are in the range 5–10% and represent no problem to the homogenizer. Even higher lipid concentrations (up to 40 %!) have been homogenized to lipid Nano dispersions.

There are generally two methods

1. Hot Homogenization

2. Cold Homogenization

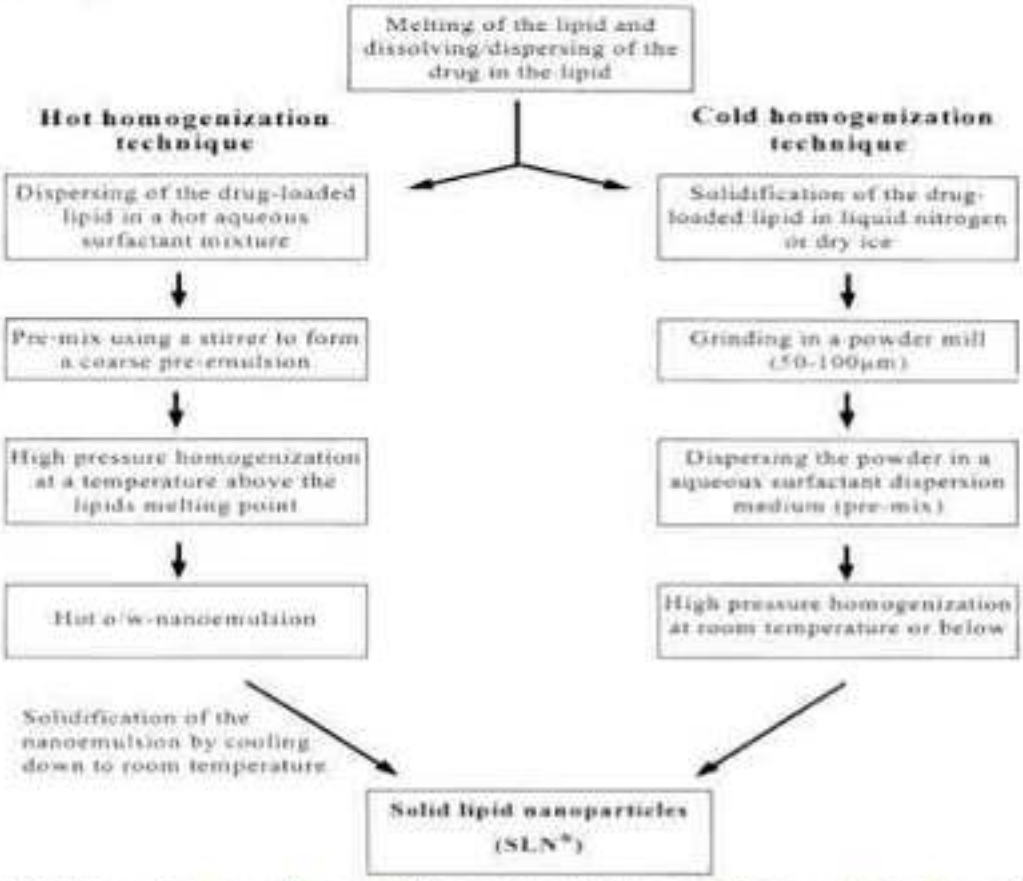

Figure: 7 Schematic procedures of hot and cold homogenization techniques for SLN production.

c) Solvent emulsification /evaporation

In this method lipophilic material is dissolved in a water-immiscible organic solvent (e.g. cyclohexane) that is emulsified in an aqueous phase. Upon evaporation of the solvent Nanoparticles dispersion is formed by precipitation of the lipid in the aqueous medium. The mean diameter of the obtained particles was 25 nm with cholesterol acetate as model drug and by using a lecithin /sodium glycocholate blend as emulsifier. The cholesterol acetate nanoparticles prepared by such method has particles size of 29 nm.The nanoparticles of tripalmitin prepared by dissolving the triglyceride in chloroform. This solution was emulsified in an aqueous phase by High Pressure Homogenization. The organic solvent was removed from the emulsion by evaporation under reduced pressure (40–60 mbar). The mean particle size ranges from approximately 30 to 100 nm depending on the lecithin/co-surfactant blend. Particles with average diameters as small as 30 nm were obtained by using bile salts as co-surfactants. Very small particles could only be obtained with low fat loads (5 w %) related to the organic solvent. With increasing lipid content the efficiency of the homogenization declines due to the higher viscosity of the dispersed phase. The advantage of this procedure over the cold homogenization process described before is the avoidance of any thermal stress.

d) Micro emulsion based SLN preparations

Micro emulsions are two-phase systems composed of an inner and outer phase (e.g. o/w-micro emulsions). They are made by stirring an optically transparent mixture at 65–70oc which is typically composed of a low melting fatty acid (e.g. stearic acid), an emulsifier (e.g. polysorbate 20, polysorbate 60, soy phosphatidylcholine, and taurodeoxycholic acid sodium salt), coemulsifiers (e.g. butanol, sodium monooctylphosphate) and water. The hot micro emulsion is dispersed in cold water (2–38C) under stirring. Typical volume ratios of the hot micro emulsion to cold water are in the range of 1:25 to 1:50. The dilution process is critically determined by the composition of the micro emulsion. The droplet structure is already contained in the micro emulsion and therefore, no energy is required to achieve submicron particle sizes.

Applications Of Metallic Nanoparticles In Cosmetics:

- **Gold nanoparticles :** Used in:
- Nano-gold face mask.
- Anti-aging or anti-wrinkle preparations.
- Also in colored make-up cosmetics.
- **Silver nanoparticles :** Used in:
- Toothpastes, soaps and face creams etc.
- Silver nanoparticles have a potent ability to kill bacteria.
- Silver nanoparticles act as a good preservative.

Conclusions

- The 21st century has brought a great interest and expansion of the nanomaterials due to unique properties that exist at the nanometric scales.
- Nanotechnology is a rapidly expanding and potentially beneficial field with tremendous implications for Society, Industry, Medicine, and Cosmeceuticals.
- Nanomaterial has been incorporated into a number of skin care products to take advantage of the unique properties of matter on a nanoscale.

- Recent advances in the design and preparation of metallic NPs have proved that a numerous variety of MNPs can nowadays be synthesized through different preparation routes.
- Synthesis of MNPs is important because of their novel electrical, optical, magnetic and chemical properties.
- Silver NPs are of strong research focus because of their unique functional properties which lead to varied applications.
- It is critical for dermatologists intimately involved with the health of the skin to be aware of this new technology, to educate our own colleagues about it, and to play an active role in evaluating this technology and setting policies and guidelines for its safe and fruitful use.

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Formulation and Development of Hydrating Gel By Using Liposome Technology

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Abstract:

In this article we are going to clarify the importance and practical role of liposome in cosmetics. Liposomes are simple microscopic vesicles in which lipid bilayer structures are present with an aqueous volume entirely enclosed by a membrane, composed of lipid molecule. There are a number of components present in liposomes, with phospholipid and cholesterol being the main ingredients. The ratio of phosphatidyl choline, cholesterol and span 80 is important for preparation of fine liposome. The size of liposome was controlled by sonication and vacuum filtration. Classification of liposomes is based on lamellae and composition and on the basis of size and number of lamellae. Rotary evaporator, well known method of preparation was used. Cosmetic technology is constantly developing raw material with active ingredients. The new surfactant molecules, the search for original active substances and effective combination and the design of liposome or carrier has led to the implementation of new cosmetic systems in contrast to the classic forms such as cream, gels and, lotion. The development and delivery systems in cosmetic industry has blurred the line between what is considered to be materials that affect the upper layers of skin and those "active compounds" that affect skin biochemistry. Thus one of the objectives of the present study was to increase the drag stability of the active. Controlled release reduced toxicity and increased stability (for certain active) and increased bio availability are just a few benefits of liposomal formulations. Thus the active was protected from environmental degradation and thus improved its handling and usage life.

Keywords: Liposomes, sonication, Lamellae, phospholipid, carrier, Penetration.

Introduction:

Liposomes are microscopic vesicles composed of one or more lipid bilayers arranged in concentric fashion enclosing an equal number of aqueous compartments. Liposome's are kinetically stabilized systems and are usually not affected by active. Liposomes are hollow colloidal particles dispersed in aqueous medium with a lipid bilayer membrane capable of encapsulating both lipophyllic materials within the bilayers and hydrophillic material into their interior. The bilayer membrane is most frequently composed of lipid bilayers made from natural or synthetic polar found in vesicles include phospholipids (egg of Soyalecithin), glycolipids sphingoliopids.(Ceramides), and even skin lipids (cholesterol, fatty acids, cholesterol sulfate) [1]

Advantages of liposome as drug carrier systems:

Similar to biological membranes they can store water-soluble and lipophilic substances in their different phases i.e. it readily incorporate a wide variety of hydrophilic and hydrophobic

drugs. liposomes are biodegradable and non-toxic which is important to avoid side effects. to act as "drug localizers" - not only as "drug transporters". i.e. to enhance significantly the accumulation of drug at the site of administration as a result of the high substantivity of liposomes with biological membranes [2]. The uptake of intact liposomes by the reconstructed epidermis, these vesicles do not penetrate through healthy skin. Yet, this is to be expected in diseased skin without intact epidermal barrier.

Profile of selected active:

Introduction to Guava tree:

In the recent year, the use of herbal products has been increasing. In developing countries, Psidium guajava L (Guava), Family Myrtaceae, is an important dietary plant used traditionally for medicinal and cosmetic purpose in the world. The fruit part of guava is used because of its food and nutritional value but other parts of Guava plant are used in rational system due to their medicinal and cosmetic properties. Since each part of guava tree possess the economic value. [3] The recent studies on the Pharmacological and Cosmeceutical properties of bark, fruit and leaves depicts antibacterial, hypoglycaemic, anti-inflammatory, anti-pyretic, spasmolytic and central nervous syatem depressant activities. Thus, review depicts the Pharmacological, Cosmeceutical, medicinal and nutritional value of Guava in the management of various disorders.

Biological Source: Guava (Psidium guajava L), Family-Myrtaceae, is a traditionally used plant because of its food and nutritional value.

Geographical Source:

Guava is widely grown in tropical and many areas like Bangladesh, Florida, and West Indies. Deferent parts of guava are reported to be used in folk medicine.

Psidium guajava is the large evergreen shrub or small tree that grows upto 15 m in height. It is the native to and widely distributed in Mexico and Central America and is common throughout all warm area of tropical America and West indies [4]

FIG 1: Psidium guajava L

Phytochemical Constituents:

Guava is rich source of diatery fibres, vitamin A, C, Folic acid, and various dietary minerals like potassium, copper, and manganese. Guava fruit contains about 4 times the amount of vitamin C as an Orange. Leaf extract of the guava has been reported for the anti-bacterial

activities because of the presence of Flavonoids Glycosides, guava carotenoids which is responsible for anti-oxidant activity. Guava is Rich in tannis, Phenol, flavonoids, essential oils , lecithins, Vitamins, fibres and fatty acids especially quercetin, which is mainly responsible for the anti bacterial activities.

Uses:

Guava (Psidium Guajava) is the well known plant. Traditionally it is used to treat the various conditions. Fruit is the rich source of dietary fibres Vitamin A and C, folic acid,and Vitamin B3. The various part of the plant like root bark leaves and fruit and found to possess many pharmacological and cosmecutical properties used in different treatment [5]

Method of Preparation of Liposome:

Thin film Hydration method:

In these methods, the lipids are casted as stacks of films from their organic solution using flash rotary evaporators. Under reduce pressure (or by hand shaking) and then casted film is dispersed in an aqueous medium. Upon hydration the lipids swell and peel from the wall of round bottom flask and vesicles forming multilamellar vesicles (MLVS). The mechanical energy required for the swelling of lipid film is imparted by manual agitation or by exposing the film to a stream of water saturated nitrogen for 15 minutes followed by swelling in aqueous medium. Multilamellar vesicles formed on hydration of dried film could be further engineered for their size and characteristic.

Membrane Extrusion Liposome:

In this method the size is reduced by passing them through a membrane filter of defind pore size. There are two types of membrane filter. The tortuous path type and the nucleation track type. The former is used for sterile filtration. In this random path arise between the criss cross fibres. The average diameter of these fibers is controlled by the density of fibres in the matrix. Liposomes that are larger than the channel diameter get struck when one tries to pass them through such membrane. The nucleation track type is composed of thin continuous sheet of polycarbonate. They will offer less resistance to passage of liposomes as these consist of straight sided pore holes of exact diameter bored from one side to another. This method can be used to process both LUVs and MLVs.

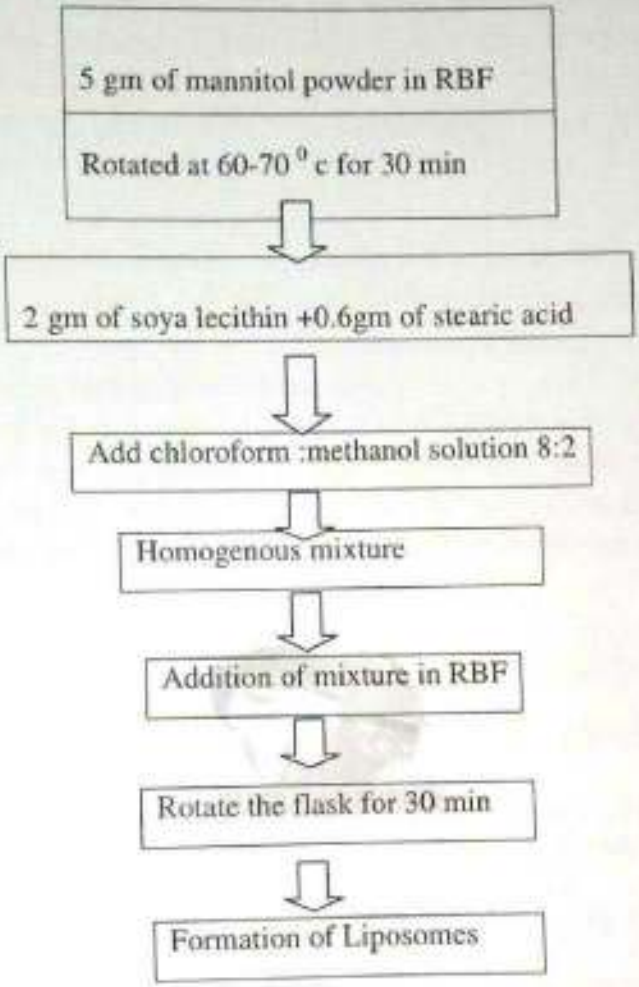
Preparation of Liposome of soya Lecithin and Stearic acid

FORMULA	B	B1	B2	B3
SOYA LECITHIN	0.5%	1%	1.5%	2%
STEARIC ACID	0.2	0.4	0.6	0.8

The formulation was prepared by taking 5 mg of mannitol powder (sieved with 120 mesh) was placed in 100ml around bottom flask which was held at 60-70°C temperature and the flask was rotated at 90 -100rpm. The rotating flask was kept into the water bath at 70-80 rpm and mannitol was dried under vacuum for 30 min. After drying the temperature of the water was adjusted to 40-50^{0} C then in beaker soya lecithin 2gm and 0.8gm stearic acid is taken. In that add a mixture of organic solvent i.e. chloroform: methanol, 8:2 v/v; After the formation of one phase solution with the help of syringe of 0.5ml add the solution into the flask containing mannitol powder, 0.5ml solution was added at the interval of 10 min up to

the solution get finished After the last loading flask containing the proliposome. That should be kept in desiccators for overnight or in sunlight. After it get complete dry pass from the sieve. The collected powder was transfer into the glass bottle and get stored.

flowchart of procedure of unlodaded liposome



Final formulation for Hydrating Liposomal Gel:

Sr.no	Phase	F2
1	Carbopol	0.8%
2	Glycerin	5%
3	Triethanol amine	0.2%
4	EDTA	1%
5	Distill water	upto 100%
6	Active loaded liposome	2 %

Liposome in Cosmetics:

Recently, a great deal of interest in the use of liposomes in skin gels or skin creams has been generated in the field of cosmetics. Vegetable phospholipids are widely used for topical applications in cosmetics and dermatology, since they have a high content of esterified essential

fatty acids, especially linoleic acid which is believed to increase the barrier function of the skin and decrease water loss within a short period of time after application. Soya

phospholipids or other vegetable phospholipids, due to their surface activity and their ability to form liposomes, are also an ideal source for possible transport of linoleic acid into the skin [6]. They predicted that liposome technology offers great opportunities for several new cosmetic products and that cosmetic developer would now have to deal very intensively with questions of raw material selection, characterization of raw and finished formulations, and clinical safety of these unique formulations. They suggested that Soya phospholipids in the form of liposomes satisfy many of this requirements [7]

Summary:

Cosmetic technology is constantly developing raw material with active ingredients. The new surfactant molecule, the search for original active substance and effective combination and the design of liposome or carrier has led to the implementation of new cosmetic system in contrast to the classic forms such as gels, creams lotion.

Objective of selection of guava extract was that, it is a transparent liposome dispersion which nourishes skin cell, heals skin inflammation, it is facial cleanser, protects the skin damage caused by free radicals. Guava extract itself use to reduce skin inflammations. It is also applied directly to the skin for nerve pain. Some people also use it topically as an astringent to tighten skin.

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Formulation and Evaluation Multiple Use Hair Lotion With Herbal Actives

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Abstract:

Hair cosmetics are an important tool that helps to decrease the hair disorder like alopecia and scalp treatments. The aim behind this work is to provide a single product which performs several activities such as prevent hair loss, inhibit dandruff, increase hair growth, prevent premature graying of hairs, prevent damaged hairs, etc.This hair lotion is a mixture of several herbs in a base which contains emollients ,humectants, etc. It contains herbs like rosemary oil, soya bean extract, licorice extract, amla extract and neem extract.

Keywords: Hair lotion, rosemary oil, soya bean extract, liquorice extract, amla extract, neem extract.

Introduction:

Although dermatologists are experts in managing scalp and hair diseases, the esthetic of some cosmetic therapies still remain elusive. Knowledge of hair cosmetics and esthetic procedures as well as of the hair shaft structure and physical behavior is indeed relevant in today's medical practice.[1] The aim of this work is to provide a single product which not only improve the hair condition, but also treat hair and scalp disorders such as dandruff, brittle hairs, etc. This hair lotion contains multiple herbal extracts and essential oil which play an active role in overcoming the hair disorders. The herbal extracts and essential oil used in this hair lotion are rosemary oil, soya bean extract, liquorice extract, amla extract and neem extract. This lotion is formulated using ingredients such as oil, humectants, emulsifier, antimicrobial agent and moisturizing agent. This lotion specifically work on hair disorders such as hair fall(loss of hair), premature graying of hairs, defected hair shaft(split ends), inhibition of hair growth(thining of hairs) and dandruff. The hair disorder occur due to several reasons such as inproper nourishment, over exposure to chemical treatments such as hair colouring, straightening, curling and etc.

The introduction to hair disorders is as follows:

1.1.Hair loss (alopecia) is a disorder in which the hair falls out from skin areas where it is usually present, such as the scalp and body. This loss interferes with the many useful biological functions of the hair, including sun protection (mainly to the scalp) and dispersion of sweat gland products. Because hair has psychological importance in our society, patients with hair loss suffer tremendously.

1.2.Greying of hair involves a loss of pigment from the hair shafts and a progressive loss of tyrosinase activity from the hair bulbs[2] Premature graying is an important cause of low self-esteem, often interfering with socio-cultural adjustment. The onset and progression of graying or canities correlate very closely with chronological aging, and occur in varying degrees in all individuals eventually, regardless of gender or race. Premature canities may occur alone as an autosomal dominant condition or in association with various autoimmune or premature aging syndromes. It needs to be differentiated from various genetic hypomelanotic hair disorders. Reduction in melanogenically active melanocytes in the hair bulb of gray anagen hair follicles

with resultant pigment loss is central to the pathogenesis of graying. Defective melanosomal transfers to cortical keratinocytes and melanin incontinence due to melanocyte degeneration are also believed to contribute to this. The white color of canities is an optical effect; the reflection of incident light masks the intrinsic pale yellow color of hair keratin.[8,9]

1.3. Dandruff is a common scalp disorder affecting almost half of the post pubertal population of any ethnicity and both genders. The exact nature and etiology of dandruff have always been controversial since the time of Greeks. Dandruff represents 25% of all scalp disorders and is present in an estimated 15-20% of the total population and more than 50% of adult population .[6,7]

1.4.Defected hair shaft(split ends, Trichorrhexis nodosa), a response to physical or chemical injury in which an apparently normal hair becomes swollen and split to form a node at which the hair subsequently fractures.[2]

To overcome all this problems was the main intention of our project. So we developed a marvel hair lotion a polyherbal product, which is a multipurpose product for hair treatment.

2. Description of herbal extract and essential oil:

2.1. Neem Extract:

Neem; Azadirachta indica (A.indica), is one of the most promising medicinal plant, having a wide spectrum of biological activity and well known for its insecticidal properties. Every part of neem tree have been known to possess a wide range of pharmacological properties, specially as antibacterial, antifungal, repellent, pesticide, inhibitor, sterilant, etc and thus commercially exploitable, hence traditionally used to treat large number of diseases. It is native to India water soluble extract of A.indica leaves was found to possess significant hypoglycemic, hypolipidemic, hypertensive and etc activities.

Active constituents: It contains diterpenes (sugiol, nimbiol) , triterpenes (β-Sitosterol, stigmasterol) , limonoids- maliantriol, nimbidinine, nimbendiol and azadiractin, it also contains glycosides such as quercetin, myrecetin, kaempferol.

Uses: Deals with Frizzy Hair, lice remover, removes split-ends, treats dandruff, maintains healthy hairs by balancing the pH, improves blood circulation in scalp,Provides sheen and gloss to hairs.

2.2.Liquorice:[24-29, 38]

It is a plant of ancient origin in history. Liquorice extract and its principle component, glycyrrhizin have extensive use in both cosmetics as well as pharmacy, and is traditionally used as herbal medicine. As a result it is used for treatment of several disorders. It performs several activity such as anti ulcer, anti inflammatory, antifungal, antibacterial, antioxidant. Glycyrrhiza glabra, also known as liquorice and sweet wood, belonging to family Leguminaceae is native to the Mediterranean and certain areas of Asia.

Bioactive constituents: A large number of components have been isolated from the liquorice roots. 40-50 percent of total dry material weight of Glycyrrhiza glabra is accounted by water-soluble, biologically active complex. Starches (30%), pectins, polysaccharides, simple sugars, gums, mucilage (Rhizome), amino acids, triterpene saponin, flavonoids, mineral salts, bitters, essential oil, fat, asparagines, female hormone estrogen, tannins, glycosides, protein, resins, sterols, volatile oils and various other substances are components of this complex. The primary active ingredient, Glycyrrhizin (glycyrrhizic acid; glycyrrhizinate) constitutes 10–25%

of liquorice root extract. It is a saponin compound (60 times sweeter than cane sugar) comprised of a triterpenoid aglycone, glycyrrhetic acid (glycyrrhetinic acid; enoxolone) conjugated to a disaccharide of glucuronic acid.

Reported Pharmacological activities:

1. Anti-tussive & expectorant activity, 2.Antioxidant activity, 3.Skin lightening and skin tightening activity, 4.Anti-inflammatory activity, 5.Anti-viral effects, 6.Anti-fungal activity, 7.Anyi-bacterial activity, 8.Anti-malarial activity, 9.Anti-hyperglycemic activity, 10.Immunostimulatory effect, 11.Memory enhancing activity, 12. Anticoagulant, 13. Hair growth stimulatory activity.

The explanation of hair growth stimulatory activity:

The hydro-alcoholic extract of liquorice showed good hair growth promoting activity. Comparison between liquorice extract and the standard drug used (Minoxidil 2%) showed that, 2% concentration of liquorice extract showed better hair growth stimulatory activity than 2% Minoxidil. Thus, after efficacy and safety analysis, it has been be concluded that, liquorice has a significant hair growth activity and it can be safely used in herbal formulations in treatment of various types of Alopecia.

Dandruff can be controlled by keeping oil production down. Glycyrrhizin present in Licorice can minimize the scalp's secretion of oils. Licorice also contains salicylic acid which helps to lower the secretion of oil.

2.3. Rosemary:[36-37, 39]

Rosemary (Rosmarinus officinalis L.) is an aromatic, evergreen plant which grows in the wilderness on the coasts of Mediterranean Sea and in the southern part of Crimea. Its name derives from Latin from words rosa- rose and marinus- nautical.

Fundamental substances which rosemary contains

Rosemary is rich in compounds which show biological effect. Apart from etherical oil the raw material contains flavonoids (luteolin, genkwanin, diosmetin and their cardiac glycosides), tannin (8%) and di and triterpenes, phenol acids, and among them it has a rosemary acid .

Chemical composition of R. officinalis L. essential oil:

Tricyclene 0.5%, α- pinene -1.5%, Camphene- 6.3%, β- pinene- 3.5%, 3-octanone - 0.8%, β- myrcene -1.6%, p-cymene -3.0%, 1,8-cineole-15.2%, l-limonene -2.8%, Linalool- 2.6%, Chrysanthenone- 1.0%, Camphor -6.8%, Borneol- 8.6%, 4-terpineol-1.5%, Verbenone- 8.6%, (+)-2,2,3-trimethylcyclopent- 3-ene-1-ethanol- 1.0%, Geraniol-1.8%, Borneol acetate- 6.1%, Trans caryophyllene-1.7%, Caryphyllene oxide-1.7% .

2.4.Soya bean :[38-42]

The soybean (Glycine max) is an annual legume of the Fabaceae family. The soybean [Glycine max(L.) Merrill] a native of China, have been extensively used as important source of dietary protein and oil throughout the world. Dry soybean contain 36% protein, 19% oil, 35% carbohydrate (17% of which dietary fiber), 5% minerals and several other components including vitamins. Soybean is a better source of B-vitamins compared to cereals, although it lacks B12 and vitamin C. Soybean oil also contains tocopherols, which are excellent natural antioxidants. Soybean oil contains α-tocopherol, β-tocopherol, γ-tocopherol, and δ-tocopherol in trace amount (mg/kg). Soybean also contains ~5% minerals. It is relatively rich in K, P, Ca, Mg, and Fe. Soy

ferritin can supplement reasonable quantities of iron. It is a package of several constituents which are helpful for human health as well as appearance. It contains fats like omega-3, omega-6,etc. It contains proteins like arginine, glycine, lysine, etc.

Uses of soya bean: It prevents premature graying of hair by supplying proteins and minerals, acts as 5α-reductase inhibitor which is key factor for hair loss, maintains hair healthy, nourishes the hairs, supplies essential vitamins such as B-complex vitamins.

2.5.Amla :[43-44]

Medicinal plants are natural gift to human lives to promote disease free healthy life. Emblica officinalis, commonly known as amla is widely distributed in tropical and subtropical areas and has therapeutic potential against deleterious diseases. Earlier it becomes a notable fruit for its rich amount of vitamin C, polyphenols such as tannins, gallic acid, ellagic acid, flavonoids like quercetin and rutin. It contains the highest vitamin C (478.56 mg/100 mL). It also contains gallic acid, ellagic acid, 1-O-galloyl-beta-Dglucose, 3, 6-di-O-galloyl-Dglucose, chebulinic acid, quercetin, chebulagic acid, corilagin, 1, 6-di-O - galloyl beta D glucose, 3 Ethylgallic acid (3 ethoxy 4, 5 dihydroxy benzoic acid) and isostrictiniin21. Phyllanthus emblica also contains flavonoids, kaempferol 3 O alpha L (6" methyl) rhamnopyranoside and kaempferol 3 O alpha L (6"ethyl) rhamnopyranoside.

Pharmacological activity:

Antitumor, hepatoprotective, antioxidant, anti-inflammatory, helps in hair growth(by stimulating hair follicle).

3. Material and Method:

The material used for preparation of hair lotion are as follows

Sr no.	Common name	Biological name	Uses
1.	Neem (extract)	Azadirachta indica	Anti- dandruff
2.	Licorice (ethanolic extract)	Glycyrrhiza glabra	Hair growth promoter, anti-dandruff
3.	Rosemary(oil)	Rosmarinus officinalis	Hair growth promoter, anti-dandruff
4.	Soyabean (ethanolic extract)	Glycine max	Hair growth promoter, anti-dandruff
5.	Amla (ethanolic extract)	Emblica officinalis	Hair growth promoter, anti-dandruff, premature hair graying preventer.

The lotion is an emulsion (oil in water type) which contains ingredients like emulsifiers, moisturizing agent, humectants, preservatives, antioxidant, solvent, and some synthetic agents.

3.1 Collection of herbs:

Different parts of plant were selected to study the hair care property. The plants are neem leaves (Azadirachta indica) , licorice root (Glycyrrhiza glabra), rosemary oil of fresh flowering tops and leaves (Rosmarinus officinalis)], soyabean dried beans(seeds) (Glycine max), amla dried fruit(Emblica officinalis). All the mentioned herbs were collected from the local market and were proceed for extraction.

3.2 Extraction Process:

3.2.1. Neem :[45]

Neem leaves were collected and were washed to remove the traces of dust. After this they were crushed mechanically(in morter-pestal). It was then macerated using water and alcohol. About 100 g of coarsely grounded(crushed) leaves were steeped in hydroalcohol (1:1) for one week at ambient temperature and then filtered. This extraction was repeated with another fresh portion of hydroalcohol (1:1) for about one week. The hydro alcohol macerate extracts were combined and evaporated up to dryness, dark brown coloured product was obtained. The was stored into container.

3.2.2.Licorice:[46]

Licorice roots were collected from local market and were powdered evenly to achieve a proper extract. It was extracted using maceration process. The powder of roots was socked into alcohol of 70% proof for about 7 days with little stirring. Licorice extract was prepared by macerating 50 g of dry powder with 100 ml of 70% (w/v) ethyl alcohol for a week in a round bottom flask with occasional shaking. The extract was then filtered through a muslin cloth for coarse residue and finally through Whatman No. 1 filters paper and was stored at 4°C for further use. As alcohol itself is an antibacterial and antifungal agent hence no additional preservatives were added. The filtrate was stored into container and on it identification test were performed.

3.2.3.Rosemary oil:

It was directly collected from the local market.

3.2.4.Soyabean:[47]

Totally dried soyabean seeds were collected from the local market. The seeds were subjected to powder formation with the help of grinder. The powder obtained was not too fine and coarse so as to achieve proper extract. The powder was further subjected to maceration(extraction) using alcohol as an solvent for about 7-8 days so as to bring up complete saturation of the solvent with active constituents such as vitamin, protein, etc. After completion of time period the saturated solvent was filtered using vacuum pump. The marc was also pressed to obtain an concentrated extract. The extract was stored into container and was further proceed for identification test of active constituents.

3.2.5.Amla :[48]

Sr no.	Ingredients	Quantity (for 100%)
1.	Stearic Acid	3%
2.	Cetyl Alcohol	1.5%
3.	Bees Wax	1.5%
4.	GlycerylMonoStearate	4.5%
5.	Butylated Hydeoxy Toluene and Propyl Paraben	0.05% each
6.	Isopropyl Mysistate	25%
7.	Triethanolamine	0.5%
8.	Borax	0.5%
9.	Xanthane Gum	1%
10.	Propylene Glycol	10%
11.	Methyl Paraben	0.05%
12.	Distilled Water(Aqua)	Upto 100ml

13.	Extracts and Oil	5%

Amla fruits were collected from local market and it was subjected for shade drying and was further subjected for powder formation. It was extracted using soxhlet extraction method. About 25 gm of shade dried powder of plant materials were filled separately in the thimble and was extracted successively with 150 ml each of methanol. The extract was filled into container and was further proceed for identification test of active constituents.

3.3.Preparation of marvel hair lotion:

The marvel hair lotion is an emulsion base with herbal extract and some synthetic constituents.

3,4.Formulation table of marvel hair lotion is as follows(formulation of 5% batch):

The hair lotion was formulated in 3 batches in different concentrations of herbal extract and that of the egg albumin. The chart showing concentration of herbal extract and egg albumin is as follows:

Sr no.	Common name	2% concentration	5% concentration	7% concentration
1.	Neem (extract)	0.5%	1.25%	1.75%
2.	Licorice (extract)	2%	5%	7%
3.	Rosemary oil	2%	5%	7%
4.	Soyabean (extract)	2%	5%	7%
5.	Amla (extract)	1.5%	3.75%	5.25%
6.	Egg albumin	1%	2.5%	3.5%

4.Evaluation:

Post-formulation Evaluation Parameters:[53]

A. **Organoleptic evaluation:**

Organoleptic evaluation parameters include colour, odour, and texture. these all parameters were carried out. Colour and texture was evaluated by vision and touch sensation respectively. Odour was evaluated by olfaction(by smelling the sample). Organoleptic evaluation is based on personal observation. The aim behind this evaluation is to confirm whether the sample can be accepted by consumer or not.

B. **Thermal stability:**

With the help of spatula, insert the cream/lotion into glass bottle and tap it to settle to the bottom. Fill up to two third capacity of bottle and insert plug and tighten the cap.

Keep the filled bottle erect inside the incubator at 45 ^{0}C for 48 h. The sample shall be taken to have passed the test, if on removal from the incubator shows no oil separation or any other phase separation. It indicates that the sample is thermally stable.

C. **Determination of pH:**

APPARATUS

A pH meter, preferably equipped with a glass electrode.

PROCEDURE

For Oil-in-Water Emulsion Creams/Lotions

Weigh accurately 5±0.01 g of the cream in a 100 ml beaker. Add 45 ml of water and disperse the cream/lotion in it. Determine the pH of the suspension at 27°C using the pH meter. The pH must be as per the standard.

D. Determination of total fatty content:

Principle Of The Method

The emulsion is broken with dilute mineral acid and the fatty matter is extracted with petroleum ether. It is weighed after removal of the solvent.

Reagents:

1. Dilute Hydrochloric Acid — 1:1 (v/v).
2. Petroleum Ether (60-80°C)
3. Methyl Orange Indicator Solution — Dissolve 0.1 g of methyl orange in 100 ml of water.
4. Sodium Sulphate — Desiccated.

Procedure:

Weigh accurately about 2 g of the material into a conical flask, add 25 ml of dilute hydrochloric acid, fit a reflux condenser into the flask, and boil the contents until the solution is perfectly clear. Pour the contents of the flask into a 300 ml separating funnel and allow it to cool to room temperature. Rinse the conical flask with 50 ml of petroleum ether in portions of 10 ml. Pour the petroleum ether rinsings into the separating funnel, shake the separating funnel well and leave until the layers separate. Separate out the aqueous phase and shake it out with 50 ml portions of petroleum ether twice. Combine all the ether extracts and wash them with water until free of acid (when tested with methyl orange indicator solution). Filter the petroleum ether extracts through a filter paper containing sodium sulphate into a conical flask which has been previously dried at a temperature of 90 ± 2°C and then weighed. Wash the sodium sulphate on the filter with petroleum ether and combine the wash ings with filtrate. Distil off the petroleum ether and dry the material remaining in the flask at a temperature 90±2°C of to constant mass.

Calculation:

Total fatty substance, percent by mass $= 100 \frac{M_1}{M_2}$

Where,

M_1 = mass in g of the residue, and

M_2 = mass in g of the material taken for the test.

E. DETERMINATION OF RESIDUE:

PROCEDURE

Weigh accurately about 5 g/ml of the material in a weighed, clean and dry squat form weighing bottle and dry to constant mass at 105 ±1 ^{0}c. Cool in a desiccators and weigh.

CALCULATION

Residue percent by mass $= 100 \frac{M_1}{M_2}$

Where,

M_1 = mass in g of the residue, and

M_2 = mass in g of the material taken for test.

F. Accelerated stability study:[52]

Accelerated tests, developed because of the relatively short development cycle for cosmetic products, enable the prediction of stability. A commonly accepted practice is to support the

forecasts obtained from accelerated stability testing by carrying out periodic post-launch monitoring of retained samples stored at ambient temperatures. The resultant information can also be useful in further improving the product and in refining the methodology used for accelerated stability testing.

Tests are often performed at 37°C, 40°C or 45°C during 1, 2, 3 months but the temperature used and the duration will depend on the product type. For instance, for certain product categories other temperatures may prove to be more useful.

5. Result and Discussion:

The evaluation includes several parameters like organoleptic evaluation, thermal stability, pH, TFM/TFC, total residue, etc. The results of these tests are as follows:

A. Organoleptic Evaluation:

Organoleptic evaluation parameters were carried out successfully. The test results are listed in the table below:

Sr no.	Organoleptic Evaluation	2% concentration	5% concentration	7% concentration
1.	Colour	Light cream	Cream	Dark cream
2.	Odour	Slight pleasant	Pleasant	Pleasant
3.	Texture	Smooth and easy to spread	Smooth and easy to spread	Smooth and easy to spread

Thermal stability:

Thermal stability test concluded that all the three concentrations of marvel hair lotion were stable as per the procedure.

B. Determination of pH:

The pH of all the three concentration of the marvel hair lotion was determined with the help of pH meter.

C. Determination of Total Fatty Content (TFM/TFC):

The TFC was carried out to determine the concentration of fatty substance in the finished product. The TFC was carried out as per the standard process and was calculated by following formula.

Formula:

Total fatty substance, percent by mass $= 100 \frac{M_1}{M_2}$

Where,

M_1 = mass in g of the residue, and

M_2 = mass in g of the material taken for the test.

The results of all the concentration are given below in table no: 8.

D. Determination of Residue:

The determination of residue test was carried out as per the standard process and the results were calculated by following formula:

Formula:

Residue percent by mass $= 100 \frac{M_1}{M_2}$

Where,

M_1= mass in g of the residue, and

M_2= mass in g of the material taken for test.

E. Determination of Accelerated Stability:

The accelerated stability study was carried out by placing all the three concentration of lotion at different temperature and humidity.

The tables of above test are as follows:

Sr no.	Test Performed	Standard Requirement	2% concentration results	5% concentration results	7% concentration results
1.	Thermal Stability	To Pass The Test	Pass(thermally stable)	Pass(thermally stable	Pass(thermally stable
2.	pH	4.0 – 9.0	5.5	6.0	6.5
3.	Total Fatty Content	5.0 Minimum	5	5.1	5.1
4.	Total Residue	10	10	10	10

Results of Thermal Stability, pH, TFM/TFC, Total Residue.

Sr no.	Temperature	Standard	2% concentration	5% concentration	7% concentration
1.	Freeze Temperature (below 0^0c)	Sample must be stable	Sample was stable.	Sample was stable.	Sample was stable.
2.	Room Temperature	Sample must be stable	Sample was stable	Sample was stable.	Sample was stable.
3.	Hot temperature (above 45^0c)	Sample must be stable	Sample was unstable	Sample was stable.	Sample was unstable

Results of Accelerated Stability

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Formulation & Development of Antibacterial & Antifungal Sanitizer

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Abstract:

The Present work is to formulate effective hand sanitizer by selecting broad sprectum antibacterial and antifungal agents. Increased need of easy to use hand sanitizer in pharmaceutical,food processing industry,hospitals and in clinical laborateries.necessited development of the best possible product.formulations were prepared using Benzethoniumchloride,ketaconazole,and zinc pyritione as a potent antibacterial ant antifungal agent along with 65 % alcohol. In low concentration they were highly effective without leaving any toxic effect on the users skin. Asynergistic effect was observed when ethyl alcohol was used in combination suitable emollient and skin conditioning agents were used to avoide possible dehydrating effect on the user skin.volatility of the preparation was observed after use leaving a thin antimicrobial film on the users hand the use of suitable excipients brought effective removal of after the use leaving asoothing effect on skin.

The aim of present work is to develop hand sanitizer formulation which evaporates quickly after application leaving no trace on hands as in case of hand wash gel. The present formulation was found to be effective when compaired with marketed hand sanitizer.The aim for the preparation of a hand sanitizer is for "hand hygiene".It is a vital principle in the prevention, control, reduction and of any acquired infection.Mainly hand sanitizer can stop the chain of transmission of micro organisms and other bacteria from hand to different parts of our body.So,maintaining hand hygiene as the prime criteria-instead of some synthetic formulation,an attempt has been made to formulate an hand sanitizer It is sure that these ingredients on combination behave as an effective hand sanitizer.Hand sanitizer is formulated and used to reduce bacterial load on the skin.Benzethoniumchloride,ketaconazole,and zinc pyritioneinhibited all the microorganisms tested with highest and least zones of inhibition against Staphylococcus aureus and Enterococcus faecalis, Pseudomonas aeruginosarespectively.

Keywords :Sanitizers, Microorganisms, hygiene, Antibacterial,Antifungal

Introduction

Hand sanitizer of the alcohol-based type is preferred to hand washing with soap and water in situations in the healthcare setting.It is generally more effective at killing microorganisms and better tolerated than soap and water.Hand washing should still be carried out if contamination can be seen or following the use of the toilet.The general use of non-alcohol based versions has no recommendations. Outside the health care setting evidence to support the use of hand sanitizer over hand washing is poor.

Microorganism:

Escherichia coli,Pseudomonasspp.and Staphylococcus aureus are commonly involved opportunistic microorganisms that primarily cause nosocomial infections.Generallytract,and central nervous system.These pathogens also tend to become incorporated infectious sites are urinary tract,surgicalwounds,respiratorytract,skin,blood gastrointestinal into the normal flora of

health care workers.Pseudomonasaeruginosa is the most commonly detected microorganism in hospitalized patients and Immune suppressed people

Antibacterial:

Antibacterials,are a type of antimicrobial drug used in the treatment and prevention of bacterial infections.They may either kill or inhibit the growth of bacteria.A limited number of antibiotics also possess antiprotozoal activity.Antibiotics are not effective against viruses such as the common cold or influenza,and their inappropriate use allows the emergence of resistant organisms.Drugs which inhibit viruses are termed antiviral drugs or antivirals rather than antibiotics.

Antifungle:

Antifungle are arebiocidal chemical compounds or biological organisms used to kill fungi or fungal spores.fungistatic inhibits their growth. Fungi can cause serious damage in agriculture, resulting in critical losses of yield, quality, and profit.Fungicides are used both in agriculture and to fight fungal infections in animals.Chemicals used to control oomycetes, which are not fungi, are also referred to as fungicides,asoomycetes use the same mechanisms as fungi to infect plants.

1] Benzethonium Chloride

Benzethonium Chloride is asynthetic quaternary ammonium salt.This compound is an odourless white solid,soluble in water .these are effective in low concentrations against a wide variety of micro organisms.

2] Ketaconazole :

Ketoconazole is an imidazolincontaining fungistaticcompound.azole is main compound.it is used as a broad spectrum antifungal agent for the treatment of prevention of fungal infection especially against thrush.gastrointestinalinfection,and infections of skin nails and scalp.

3) Zinc Pyrithione :

Zinc pyrithione has abroad antimicrobial spectrum of efficacy against various microorganism such as bacteria,fungi,algae,and indirectly against dust mites.The outstanding properties with regards to effectiveness and compactibility.

Experimental:

Sr.no.	Ingredients		Qty for 100 ml		
		F1	F2	F3	F4
1.	Carbopol 940	0.4%	0.4%	0.4%	0.4%
2.	TEA	0.5%	0.5%	0.5%	0.5%
3.	Glycerine	0.5%	0.5%	0.5%	0.5%
4.	Vitamin E	0.5%	0.5%	0.5%	0.5%
5.	Water	25.5%	25.5%	25.5%	25.5%
6.	Isopropyl alcohol	20%	20%	20%	20%
7.	Ethyl alcohol	52%	52%	52%	52%
8.	Benzethonium chloride	0.1%	0.1%	0.1 %	0.5%
9.	Ketaconazole	_	0.5 %	0.5 %	0.5 %
10.	Zinc pyrithione	_	0.10%	0.20 %	0.15%
	Total	**100%**	**100%**	**100%**	**100%**

Procedure:-

Clean all the apparatus and weigh all the ingredient as per formulation. Carbopol 940 was added to deionized water with constant stirring. After uniform mixing, triethanolamine (TEA) was added with slow stirring to avoid formation of possible air bubbles in the product and the blend was kept aside for 24 hour.Then all the active that is Benzethoniumchloride,Ketaconazole,Zincpyrithion was added in ethyl alcohol,Isopropyl alcohol along with glycerin and vitamin E mixed with slow stirring to obtain uniform formulation Prepared product was stored in air tight containers.

Result:

The prepared formulation of hand sanitizer showed significant results against bacterial and fungus species. The significance was found to be more in comparison to the commercially available hand sanitizer or hand disinfectant. The composition Benzethoniumchloride,Ketaconazole,ZincPyrithione has been attributing with properties like antimicrobial and Antiviral.The alcohols have excellent, rapid (within few seconds) germicidal activity against vegetative bacteria, fungi, and many viruses and antimicrobial activity is based on protein denaturation of microorganisms. Alcohol based hand sanitizers are highly effective against mycobacteria (the bacteria most resistant to the disinfection process) and multidrug-resistant pathogens. Alcohol based hand sanitizer are approximately 100 times more effective against microorganism than commercially available hand sanitizer. hand sanitizer offer numerous advantage sover commercially available hand sanitizer onto both hands usually requires only 15 to 30 seconds. Whereas vigorous friction, rinsing with water, and drying with a towel are not needed like hand disinfectants or soaps.

It was found that the formulation F3 were slightly white in colour,formulation F1,F2 and F4 were clear with ethanolic odour and smooth feel.the PH and viscocity of the different formulation were studied amongst the four different formulation F1 and F2 were not effective against micro organism ,while F3 and F4 were most effective against the micro organism with killing,but F3 suffered from some miscibility problem,thus it can be shown formulation F4 that had the best activity amongst the formulated products was observed to be better than all the formulation.

Discussion:-

As the skin protects the internal organs and tissues, it also harbours microorganisms ranging from normal flora to pathogenic species .Human skin provides nutrients and suitable growth conditions for most pathogens as well as opportunistic bacterial pathogens and these bacteria evidently have the ability to be resistant to most of the cleaning regimen, thus contributing to their persistence in an ecosystem .The use of sanitizer is one of the means of reducing the bacterial load on the surface of the skin; hence reducing the pathogen load especially on the skin. Comparatively, the sanitizer reduced the bacterial load on the hands of the subjects than the controls. From the results obtained in this study, there is an indication that the reduction in the bacterial load may not just be ascribed to the mechanical action of the sanitizer onsurface of the skin but could probably be due more to the action of the biocides (active ingredients) present in the sanitizer products examined. The skin is the largest organ in the human body with its structure and physiology varying from person to person due essentially to genetic, physiological and environmental factors The results of this study further confirm the antibacterial activity that are commonly used in the study area evidently had the highest zones of inhibition and hence was the most effective on the test

pathogens.Compliance to hand hygiene is recognized to break the cycle of transmission both in the hospital and at home .Application could therefore, be very useful and accepted to play a significant role in the health care facilities and households, as it reduces the bioburden on the hand and as well as prevents irritation due to constant hand washing. The in situ assessment using the spread method, showed a complete inhibition of the test bacteria .The usage of the could prevent infection especially tested inhibited the growth of the organism, which is the causative agent of typhoid fever. The high activity of and its superiority over the other brands observed in this study may most probably be ascribed to the chemical components present, especially antimicrobial which was absent in the others. It has been reported to have strong antibacterial activity against pathogens such as methicillin-resistant and other pathogenic bacteria Some of the product examined did not inhibit the growth of the test bacteria probably as a result of low concentrations or lack of biocides in them and or noncompliance to stringent condition (good manufacturing practices) during production among other reasons. Gross contamination of hand sanitizer during manufacturing may also compromise their effectiveness and or quality and possibly lead to infection of the users eventually . Conclusively, it could be used for cleaning of hands and/or any other part of the skin/body surface as they characteristically reduce microbial load. The use could also aid compliance to hand hygiene both at home and in the health care facility since they do not easily cause skin irritation and or dryness. From this study, are shown to be relevant for cosmetic purposes (complementary) and not alternatives to hand washing with soap and water. Manufacturers should therefore, maintain the quality of their products in order to avoid or prevent false safety assurance.

Conclusion:-

Hands are the most common mode of transmission of pathogens to patients and proper hand hygiene can prevent health care associated infections and the spread of antimicrobial resistance. Scientific evidence and ease of use support of alcohol-based hand sanitizers during patient care. It may be concluded that Hand Sanitizer has a significant anti-microbial effect on the specified microorganisms. Thus, there is immense potential in establishing the use of antimicrobial products as a measure to control the multidrug resistant microbes as well as to check their spread through hands from one geographical region to another.

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Characterists of Electronic Transducer in Biomedical Instruments

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Abstract:

I instruments various transducers are used for measurements of various physiological parameters. The biomedical system cannot be designed until and unless proper transducer is selected for measuring physiological parameters. The present scenario of transducers in biomedical instruments is discussed in this paper. The various researchers had used different methods of measurements of body temperature. Some of these methods are discussed in this paper. The researcher has designed body temperature measuring transducer using UJT time base circuit, thermister and LDR. The designing technique of the transducer is discussed in this paper. The F-T characteristic of this transducer is' plotted and the performance of transducer is compared with existing transducers used in the instruments for the purpose.

Introduction:

Biomedical instruments have been developed in various stages. Old biomedical instruments, constructed by transducer/sensor worked on the principle of analog type (resistive, capacitive, and inductive). The ac or dc amplifiers constructed by the transistors was used to manipulate the output of the sensors/transducers. The analog meter (D'Arsonal movement), graph plotter, indicator were used to display or record of physical signal.

Research in the electronics field has developed biomedical instruments, stage-wise. The ac or dc amplifier has been replaced by operational amplifier, which is found suitable to detect even weak signals from the body. The advanced display system like Cathode Ray Oscilloscope (CRO), digital display, LED, LCD etc. have been used to display or record.

data either in form of waveform or digital display. The microprocessor, microcontroller and personal computer provide intelligence to biomedical instruments. Advanced biomedical instruments with their functional blocks are shown in Fig. 1.

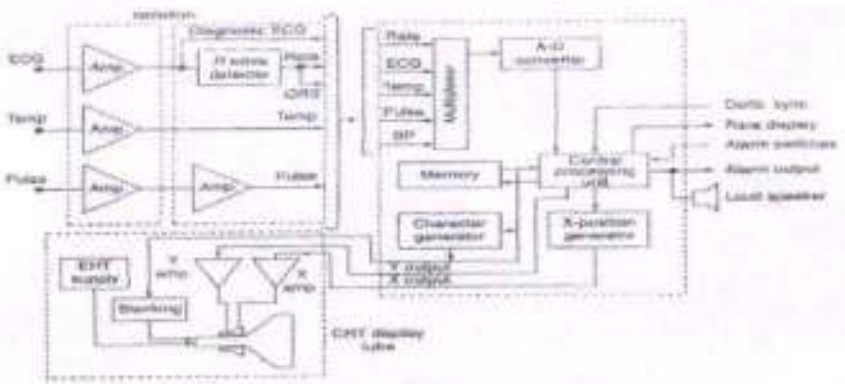

Fig. 1: Block diagram of advanced biomedical system.

Sensors/Transducers In Biomedical Instruments-Present Scenario;

Advanced biomedical instruments function better than old ones only when new technology has been employed in the sensing part of biomedical instruments. This requirement has been fulfilled by reviewing the various technologies of sensors/transducers used in biomedical instruments for sensing physical activities of the body. Various physiological parameters have to be measured as such as body temperature, blood pressure by direct and indirect method, blood flow, cardiac output, heart rate, phonocardiogram, impedance cardiogram, respiration rate, tidal volume, and gases in expired air, diffusion of inspired gases during the treatment of patient in clinics or hospitals. The researcher has attempted to develop the biomedical instruments for body temperature measurement. Therefore, it was important to know the various methods for body temperature measurement. The biomedical system cannot be developed until and unless the proper sensors/transducers cannot be selected to measure the physiological parameter in biomedical system, which has been developed by the researcher.

Methods of Measurement for Body Temperature in Biomedical Instruments;

Temperature of human body:-

Thermal behavior of biological material, particularly living tissue depends on passive or intrinsic property and active response of the biological system to thermal stimuli. The intrinsic thermal physical properties influencing heat transfer in biological material are the same as those in any other material, thermal conductivity, diffusivity, and specific heat. The magnitude of these properties tends to be quite variable not only in the body but also within the same tissue. These properties are directly dependent upon the inherent inaccuracies in the thermal calculation of living tissue. The physical parameters observed from tissue of human body are temperature, heat, fat and movement. Temperature of living tissue is a measure of tendency of the body to transfer heat from one body part to other. The average normal body temperature is in the range of 37°C to 41 °C and it remains almost constant with ±0.6°C for healthy person. In normal condition, it is generally considered to be 37°C.

Existing temperature measuring system for human body:-!.

The body temperature is measured by expansion of mercury (Hg) in a glass capillary. Calibration and conversion was required for measurement of temperature, which is a difficult task.

Thermocouple is a junction of two different material wires, which is formed by two or more junctions. One junction is cold or reference junction (kept at 0°C) and other junction is hot or measuring junction. Thermo electromotive force (emf) generated across wire is developed current in the circuit. The emf generation range is in mill volt with resrjeet to temperature Copper-constant. A combination of thermocouples is preferred for medical application. In this construction, a one junction is kept at 0°C while other is kept at 37°C. An ice bath is used to maintain constant temperature, which is a major drawback in measuring system.

The temperature dependence of resistance of certain metals (platinum or nickel) makes it convenient to construct temperature transducer for biomedical instruments. Most of the metal resistance depends on temperature. Thermometer constructed from coil of the metals is used for skin, rectal and oesophageal temperature measurement. The coefficient of receptivity of platinum is 0.004 ohm/°C. Practically the measurement of resistance with respect to temperature is quite

difficult because circuit resistance and electrochemical changes affect the resistance of metal during measurement. The temperature coefficient is very small.

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4. Thermistors: -

Thermistors are the oxides of certain metals like manganese, cobalt, nickel which have large negative temperature coefficient (NTC) of resistance. The sensitivity is about 4% change In resistance per degree. This device Is a better solution for the measurement of temperature in medical applications. However a major disadvantage observed here is that, the resistance of thermistor are exponentially changes with respect to temperature. In a temperature-measuring instrument, resistance should change linearly with respect to temperature. The thermistor is a better solution for sensing of temperature, but its characteristic has to linearized by some technique. The researcher has proposed the technique for linearization of characteristic of thermistor.

Study orrime-based oscillating circuit in quick recoverv sensors^

The pulses are developed across capacitor CE, RBI and Rg2- The voltage-time signals across RBI, RBI and CE during the continued time interval, are shown in (Fig. 2) during charging and discharging action of CE.

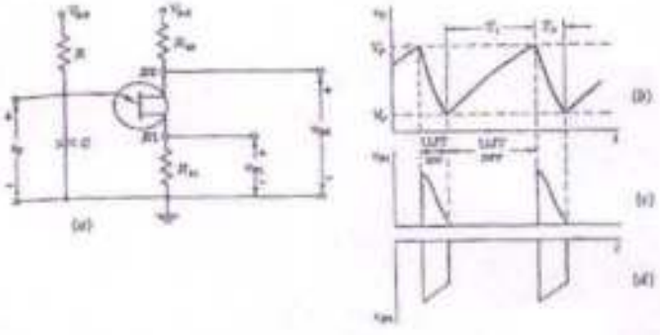

Fig. 2: Time- based oscillating circuit and its waveform.

The pulses at the base BI is an abrupt leading edge, but the anticipated drop at the trailing edge may not be easily apparent charging the holding current, which is small in comparison with the current at the moment of breakdown. The Ie2 current is smaller because the Base current IBI is equals the emitter current. Iea is nearly constant during the capacitor discharge. The linearity of the waveform may be obtained by feedback methods.

Studies of Thermistor Characteristics:

Another type of thermal resistor (the thermistor) is made of evaporated films, carbon or carbon compositions, or eeramic-like semiconductors formed of oxides of copper, cobalt, manganese, magnesium, nickel, titanium or uranium. Unlike the basic RTD device, thermistors can be molded or compressed into a variety of clever shapes to fit a wide range of applications. These devices have a resistance change characteristic of 4 to 6%/°C with generally a negative temperature coefficient. Special classes of thermistor, called posistors, which are made of barium

titanate or strontium titanate ceramics, have a positive temperature coefficient. Positive temperature coefficients are also found in silicon thermistors in which the Si semiconductor is doped to a density of about $10^{16}/cm^3$. The resistance vs. temperature characteristic of thermister is non linear in certain part of its range.

Studies of Light Dependent Resistor (LDR) Characteristics:

Optoelectronic devices generate electric current when they are subjected by light energy. The optoelectronic devices include photoconductive device, photodiodes, phototransistors, LEDs and injection laser diodes etc. These devices operate when they are subjected to optical irradiation. The semiconductor material such as silicon and germanium cannot be used to construct a photoconductive cell. The most commonly used compounds are cadmium sulphide (CdS), cadmium selenide and cadmium telluride. CdS is mostly used photoconductive material. Photoconductive cell is bulk device rather than junction device and it does not have any semiconductor junction. Photoconductor is commercially known as light dependent resistor (LDR). The photoconductive material CdS is deposited on a cylindrical ceramic base in a zigzag fashion. This construction adopted to increase the area of the CdS so that its resistance value can be controlled with light exposed on the surface. Metal contacts are formed at the end points of the zigzag structure from, which external leads are taken out. L-R characteristics of photoconductive cell show exponential decay in the resistance with respect to light intensity (light flux in lumens).

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Design Techniques Of Quick Recovery Temperature **Transducers**

Time based oscillating circuit; thermister, LED, and LDR may be used in designing the quick recovery temperature sensors. In the present study QRTS is designed by time based oscillating circuit and temperature sensing components as thermister. The thermister has been selected in a probe shape to measure surface temperature of the body easily. In time base oscillating circuit, the emitter resistance RE is replaced by thermister resistance RT. Before replacing emitter resistance by thermister resistance, it has been observed that output of sweep signals of the time base oscillating circuit depends on RE. The capacitor Cehas been chosen with fixed value to produce constant frequency of sweep signal. The resistor RE has been chosen to get the frequency of output signal in the frequency range of 200Hz to 300 Hz. It has been observed that the R-T (resistance-temperature) curve of thermister is mostly nonlinear in the range of medical temperature measurements. The graphs have been plotted between temperature sensed by thermister and the frequency of output sweep signal. F-T characteristics of QRTS are shown in figure-3. This characteristic has been plotted with rise (24 to 48 degree centigrade) and decay (48 to 24 degree centigrade) of temperatures. Accuracy has been achieved in the measurement of temperature with rise and decay of temperature and by repeating the experiment for four times.

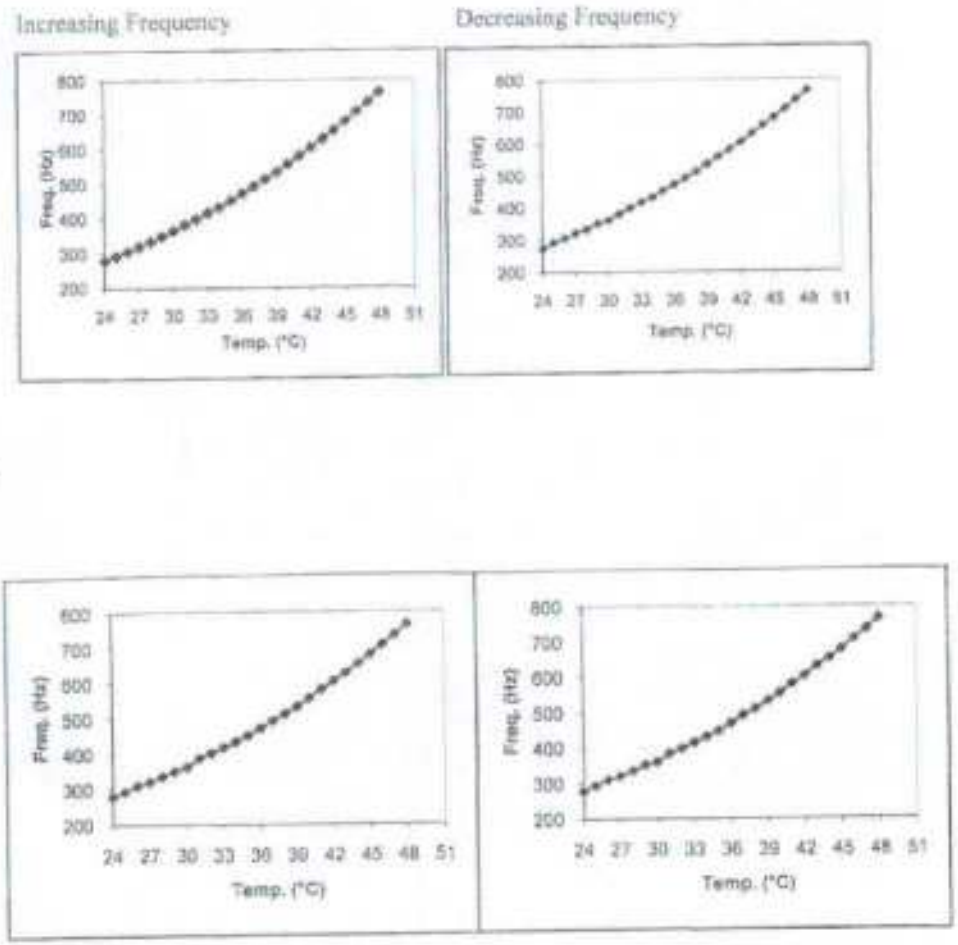

Fig. 3: F-T characteristics of QRTS

Analysis & Results:

The QRTS transducer is designed by researcher for body temperature measurements by producing frequency output in the range of 200 Hz to 800 Hz which changes linearly with respect to change in temperature. The frequency output of QRTS is easily digitalized as compared to existing senor output.

The variation of output sweep signal frequency is linear in the body temperature range and QRTS is most useful for body temperature measurements in comparison to existing sensors studied by researcher.

The sensitivity is measured about 12 Hz per degree centigrade. The sensitivity is very good as compared to existing sensors studied by researcher.

QRTS is constructed by semiconductor components. It could be fabricated as a compact sensor by integrated technology. The smart sensor technique is popular now a day in designing of sensors/transducers to measure physiological parameters in biomedical instruments. QRTS could also constructed by SST for embedded biomedical instruments to measure body temperature.

QRTS is low cost, simple in construction and easy to operate with low power.

Researcher has found the response of QRTS is similar when compared with existing sensors used in body temperature measurements.

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Use of AINN Filters for Reduction of Noise from ECG Signals

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Abstract—

The leading cause of death in the world is the heart attack. Therefore it is very important to know the facts about heart. ECG is the collection of electrical signal acquired from the heart of human body. But these signals are affected due to noise and artifacts. The noise included inherent noise in Electronic equipments, ambient noise, motion artifacts, power line interference, base line drift, electrosurgical noise and inherent instability of signal. By using conventional methods, it is very difficult to reduce the noise from biomedical signal. Therefore different methodologies are used to remove noise and artifacts. This paper describes the AI filters which are used to reduce noise from ECG signals.

Keywords- Adaptive filter, Ainn, Ecg, Lms, Nlms, Nslms

Introduction:

ECG is an instrument which is used to observe and analyze the electrical activity of heart. This signal is normally a function of time and is described in terms of its amplitude, frequency, and phase. The analysis of ECG signal is very important for researchers as well as medical practitioners for careful and proper treatment of the patient. If the signals are not properly diagnosed and analyzed, it will lead to wrong diagnosis and can be dangerous for human beings.

While recording of ECG signal, the original signal is corrupted due to noise. The noise included inherent noise in Electronic equipments, ambient noise, motion artifacts, power line interference, base line drift, electrosurgical noise and inherent instability of signal and this reduces the performance of desired signal. Therefore for the proper treatment of a patient, it should be removed from the desired signal. Using an amplifier with high gain, high input impedance and differential input with good common mode rejection and various filter circuits could reduce the noise from ECG signal. But conventional methods are not sufficient to reduce noise from ECG signal. Therefore intelligent solutions are required.

Most recent years, various mathematical techniques and Artificial Intelligence approaches are being used for noise reduction. Literature reviews shows that mathematical models such as Wavelet Transform, Time Frequency Approaches, Fourier Transforms, Wegner-Villie Distribution, Statistical Measures and Higher Order Statistics are used in nonlinear system identification. Artificial Intelligence (AI) includes artificial neural network, dynamic recurrent neural network, Fuzzy logic system and genetic algorithm are used.

The researchers are especially interested to design the techniques which provide noiseless biomedical signals. R. Sehamby and Buta Singh (2016) [11] have designed the adaptive

electrocardiogram filter to reduce noise caused by external systems & body artifacts. R. J. George (2015) [9] reveals in his study that the pipelined DLMS adaptive FIR filter is faster than non-pipelined LMS adaptive FIR filter. H. K. Gupta, R. Vijay and N. Gupta (2013) [5] have observed that the accuracy has been increased by increasing filter order as well as with increased in step size, convergence rate took place fast. B. Chandrakar, O. P. Yadav and V. K. Chandra (2013) [8] have studied Finite Impulse Response (FIR) filter based on various windows and Infinite Impulse Response (IIR) filters for noise removal of ECG signal. The researcher D. C. Dhubkarya and A. Katara [10] have studied the comparison of MATLAB Simulation and DSP Processor implementation of an adaptive filter on Least Mean Squared (LMS) and Normalized Least Mean Squared (NLMS) Algorithms. They suggested NLMS algorithm is superior in hardware implementation.

Software Specification Requirement And Implementation Details;

In real time situations, the accuracy of the measurement is required. As we know that ECG signal is error prone due to complicated situations. AI can be used to obtain reasonably good accuracy and intelligently reduce the noise. In this section, we have simulated the MATLAB codes for the data conversion, adaptive filter algorithm, artificial intelligent training and its testing.

Database collection:

To design AINN Model, a sufficiently large amount of data is required for training and testing. We have collected standard data bases for biomedical signal from the following websites.

https://physionet.org

http://www.emglab.net

https://drive.google.com/file/d/0B3NaVR72FYQcaHAybXVCZ0ViVVk/view.

We have used 500 samples for the training and testing of Adaptive filters and AINN based filters.

Software specification:

matlab (matrix laboratory), 2014b is used for simulation. it is a numerical computing environment and fourth-generation programming language developed by math-works. matlab allows matrix manipulations, plotting of functions and data, implementation of algorithms, creation of user interfaces, and interfacing with programs written in other languages, including c, c++, java, and fortran.

implementation details:

the gui is constructed by using matlab codes. other set of codes have been used to run the various algorithms for noise removal in matlab simulator.

the main gui contains four parts-

1] file input and its conversion

2] adaptive filter algorithm and its input parameter section

3] output parameters section

4] artificial intelligent noise removal section.

file input and its conversion:

Most of the data bases are available in .dat or .xls format. To read this in Matlab, we have designed a code which will convert and save the .dat file or .xls file in .mat file format.

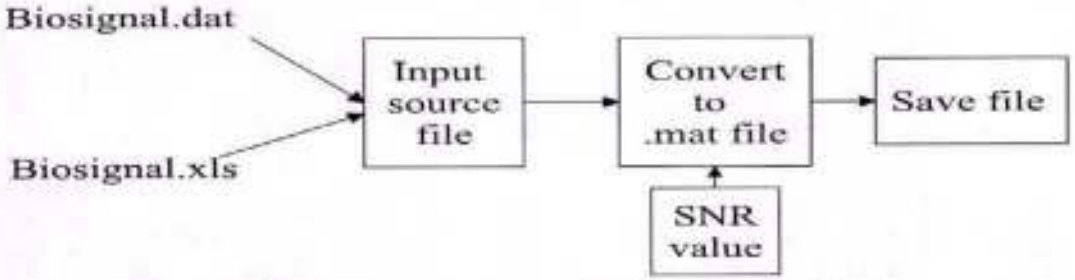

Figure 1: Block diagram of conversion of .dat and .xls files into .m files.

Adaptive filter section and its Input parameter section:

There are numerous Adaptive filter algorithms [22], out of which 3 algorithms were used. These are

1] Adaptive Least Mean Square (LMS) Algorithm:

If w (n) is the filter coefficient vector at step n (time), then its' updated value w (n +1) is given by

$$w(n+1) = w(n) + 2\mu\, e(n)\, x(n)$$

Where, Filter output $y(n) = w^T(n)\, x(n)$

Error $e(n) = d(n) - x(n)$

Filter taps at time n, $w(n) = [w_0(n)\ w_1(n) \ldots\ldots\ldots w_{M-1}(n)]$ and

Input data, $x(n) = [x(n)\ x(n-1) \ldots\ldots\ldots\ x(n-(M+1))]^T$

2] Adaptive Normalized LMS Algorithm:

The updated value w (n +1) is given by

$$w(n+1) = w(n) + \frac{1}{x^T(n)\, x(n)}\, e(n)\, x(n)$$

with

$$\mu(n) = \frac{1}{2\, x^T(n)\, x(n)}$$

3] Adaptive Normalized Sign LMS Algorithm:

The updated value w (n +1) is given by

$$w(n+1) = w(n) + 2\mu\, \frac{Sign(e(n)\, x(n))}{\left\| x(n) \right\|^2}$$

Output parameter section:

The performance of ANN is assessed on the basis of performance parameters Signal to Noise Ratio (SNR_out).

The output SNR (SNR_out), is calculated from the power of input signal x (n) and noise signal e (n) and is given by,

$$SNR\_out = 10\ Log_{10}\left(\frac{\text{Signal Power}}{\text{Noise Power}}\right)$$

Or $SNR\_out = P_{signal}/P_{noise}$

Where the power is expressed in decibel.

Artificial intelligent noise removal algorithm:

We have designed an artificial intelligent model for removal of noise from ECG signal by using Matlab coding. The fig. 2 shows the block diagram of proposed artificial intelligent neural network model.

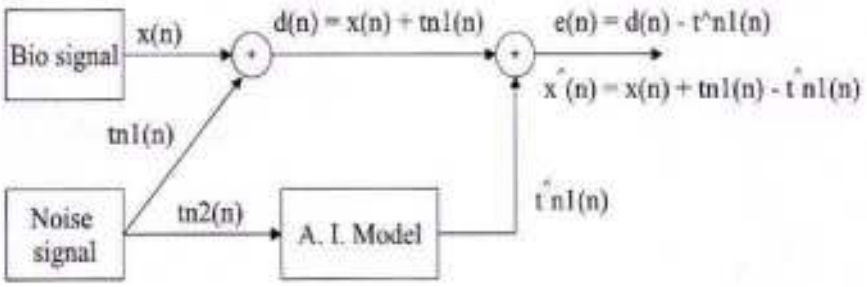

Figure 2: Block diagram of proposed AINN Model

For the design of model, we used layer recurrent neural network (Figure 3). The values of parameters selected to design of LRN are given below.

a) Number of neurons: 15
b) Training method: Layer recurrent neural networks
c) Epoch number: 30

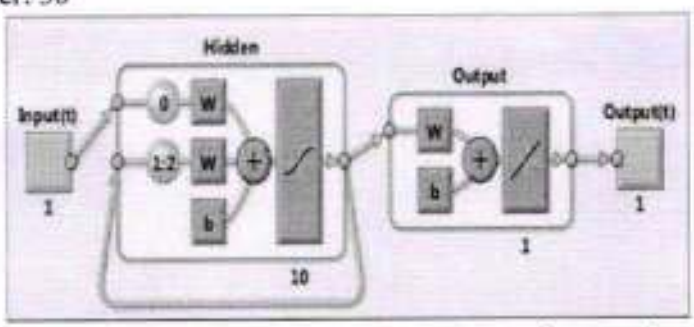

Figure 3: Layer recurrent neural network

Simulation Results

The major objective of this study was to investigate a noise removal filters. For this, simulations are carried out on ECG signals. The results are obtained on output parameter section of Matlab based GUI for removal of noise from biomedical signal. The Table 1 shows the signal to noise ratio of adaptive Filter using algorithms LMS, NLMS and NSLMS, for various step sizes on ECG signal 1.

Table 1: SNR_out Vs Step size for adaptive filter using various algorithms
No. of taps= 2 and SNR_in= 0

Step Size	SNR_out		
	LMS	NLMS	NSLMS
1e-7	-0.19906	26.7339	26.7339
1e-8	0.21109	26.7339	26.7339
1e-9	1.23573	26.7339	26.7339
1e-10	10.2783	26.7339	26.7339
1e-11	24.5255	26.7339	26.7339
1e-12	26.7039	26.7339	26.7339

1e-13	26.7336	26.7339	26.7339
1e-14	26.7339	26.7339	26.7339
1e-15	26.7339	26.7339	26.7339

Table 1 shows that Normalized LMS and Normalized Sign LMS algorithm performed better at a small step size also. But overall, all algorithms have good performance on step size 1e-10, which governs the rate of convergence, speed of tracking ability.

For this study, the AINN based filters are examined on various ECG Signals. The SNR_out of AINN based filters are compared with the adaptive filters for the selected parameters; No. of Taps= 02, SNR_in= 0 and Step size= 1e-10. The Table 2 shows the comparison of SNR_out of Adaptive and AINN based filters.

Table 2 (i) and (ii): Comparison of SNR_out of Adaptive and AINN based filters for various ECG Signals.**(i)**

Algorithm	AINN based Filter SNR_out	Adaptive Filter SNR_out
	ECG Signal 1	
LMS	36.7437	10.2783
NLMS	36.7437	26.7339
NSLMS	36.7567	26.7339

(ii) Algorithm	AINN based Filter SNR_out	Adaptive Filter SNR_out
	ECG Signal 2	
LMS	27.0429	10.2783
NLMS	27.0429	26.7339
NSLMS	27.0424	26.7339

From the Table 2, it is inferred that SNR_out for all selected algorithms show excellent signal to noise ratio as compared to Adaptive filters. Thus all algorithms are excellently filtered out noise signal from ECG signals.

Discussion:

The typical amplitude of ECG signal is obtained in mV. Thus the signals are easily affected by various noise sources resulting degradation of the signal. The researchers are doing hard work in designing filters for noise removal. We are designed AINN based filtering algorithms. This has only two processes- training and testing. Training process based on subset outcomes of adaptive filtering algorithm in initial stages, which may not require in later time even on change of source input as well, called trained filter / smart filter. Such intelligent filters give the freedom of selection of signal with different SNR values; also not bother about number of parameter settings which lead one more step towards the auto filter concept.

We have used different ECG signals for the simulation. The simulation results are carried out by measuring the performance parameters SNR_out and these results are summarized in

tabular form in the Tables 1 and 2. The comparison of these two filters reveals that the AINN based algorithms give better results than the adaptive filter algorithms.

Conclusion:

Artificial Intelligent Neural Network filters are designed to reduce the noise from the ECG signals. The implementations of ECG signals on various adaptive algorithms (LMS, NLMS, NSLMS, SLMS and SSLMS) are successfully performed. The result shows that the AINN gives better results than the adaptive filter algorithms. Thus AINN is an excellent system to filter out the noise signal from the ECG signal.

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Necessity of Internationalization of the Curriculum for Indian Universities

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ABSTRACT

This paper discusses the need and changing wants associated with internationalization of the curriculum in the context of Indian universities. The demand for international curriculum is growing day by day. To cater these needs institutions of higher education have started to take initiatives in this direction. Besides, traditional providers of higher education and new knowledge providers from corporate houses have started developing innovative curriculum modules for delivery to hone the urgently required skills among the learners as per the demand of the global market. Our courses designed in the past used to be centrally focused on imparting information and upgrading the depth of knowledge, lacking in honing various skills of the learners. But in the changed circumstances it has been observed that the curriculum designed today in the similar fashion that of the past has lost its relevance, practicability and applicability. We are shaping human resources on large scale but have forgotten the qualitative requirement of the global society. We have to think and rethink again and again as to why our degrees have not been proving self-sufficient to quench the quality requirement of the society at large.

1. Introduction

Internationalization of the curriculum is a broad term. It involves plethora of activities such as study abroad programs (short and long term), foreign language courses, interdisciplinary or area programs, or the provision of programs or courses with an international, intercultural, or comparative focus. But, in the present work, an internationalized curriculum will refer to course content, teaching and learning approaches with higher emphasis on an intercultural and international association. Thus, the attention is given on the subject matter of the curriculum and the educational institutions of teaching and learning approaches that will enccurage the involvement of international students.

2. Importance of Internationalization of the curriculum

It is believed that curriculum is generally reflective of the values, attitudes, and beliefs of a particular culture and an institution. In Western countries, the emphasis of education is on a didactic lecture format involving group discussions, tutorials and seminars that edify discussion, critical thinking, and active learning. This approach many a times leads to alienation of international students who are familiar to different styles of teaching and learning. Hence, internationalization of the curriculum is an essential component to develop an academic environment that supports the diverse cultural learning requirements of international students and valuing their contribution.

Internationalization of the curriculum is an effective tool for creation of optimal learning environment as it concurs with diverse cultures, perspectives and experiences of students. Hence, many researchers have outlined the importance of internationalization of the curriculum and associated teaching and learning processes as vital elements of internationalization. Curriculum is considered as the backbone of the internationalization process. Other researchers have agreed on the importance of an internationalized curriculum in providing a better student-centered learning experience for all students and in preparing students to be successful in today's progressively interdependent global society. It opens new avenues and opportunities for securing a better job in multinational companies and institutions of high repute on a better and larger level.

3. Challenges associated with Internationalization of curriculum

The internationalization of the curriculum is an unending, multidimensional process that involves the cooperation and support of faculty members, students, academic departments and the institutional administration. It needs visionary leadership, dedication and commitment to the process, high intercultural sensitivity, full financial support, willingness, personal interest, open lines of communication, and interdisciplinary cooperation. A lack of these necessities either individually or in harmony can result in a number of challenges to internationalizing the curriculum including the following:

- In India, senior administrators from UGC and state governments and members of different bodies of a university try to use 'one size fits all' method. This results in homogeneity of curriculum, thereby, diminishing internationalizing the curriculum.
- Faculty, who are the important to curricular reform essential to become engaged in the internationalization process,
- Senior administrators who traditionally make decisions regarding the curricular reform process often don't have the required interdisciplinary, intercultural, and pedagogical competencies required to engage in this process.
- Faculty often neglects to draw upon the experiences of international students and domestic students who have international or intercultural experiences as potential resources for internationalizing their curricula and pedagogical practices.

- Support for the curricular reform process must be recognized within written policy statements and strategic plans of the university and colleges and must be effectuated at the departmental and institutional levels.
- The lack of a continuous curricular review and assessment process at the majority of Indian universities is a major barrier to the curricular reform process
- Insufficient funding and resources to support the internationalization of the curriculum can also be serious.
- Faculty must believe that the academic and humanistic rationales for internationalizing the curriculum will enrich the learning environment for the benefit of everyone on campus rather than simply being an avenue of revenue generation which will increase the institution's potential of recruiting international fee-paying students
- Institutions that neglect to consider faculty's international experience and competence in their recruitment and hiring processes and fail to introduce reward and promotion strategies for faculty based on their involvement in international activities such as internationalizing the curricula impede the curricular reform process
- Lack of funding to support faculty development and to aid faculty in increasing their levels of international awareness and expertise through international research, study, and teaching activities can also negatively impact on the process of internationalizing of the curriculum.
- Lack of personal knowledge, skills, or interest in internationalization, and a lack of intercultural knowledge and sensitivity are other reasons for the lack of faculty involvement in international curricular reform initiatives.
- Ethnocentricity, a disbelief that knowledge is socially constructed, a belief that their discipline is already international, and a neglect to engage in self-reflection regarding the impact of their personal cultural beliefs on their choice of course content and pedagogical practices are all issues in faculty reluctance to engage in curricular internationalization and reform.
- Faculty may be reluctant to internationalize the curriculum at the expense of the basic knowledge required within the discipline and may question whether they should be creating a distinction between the international and traditional content within their courses or integrating the two.
- Student diversity is a crucial factor. It is essential to know that international students cannot be considered a homogeneous group. Their personal and cultural background, level of adjustment and ability to face problems vary significantly in a foreign educational environment. Students from families and cultures that differ widely from that of the host environment may have the greatest difficulty adjusting to the new culture.
- Linguistic and communication difficulties present one of the extreme academic challenges for international students whose first language differs from that of the host country.
- Pedagogical styles and expectations for learning approaches that differ from those to which the international students are accustomed in their own cultures may also be a source of difficulty

4. Approaches to Internationalizing the Curriculum

The internationalization of the curriculum requires an ongoing, collaborative, interdisciplinary approach combining the support, knowledge, efforts, and skills of inter-culturally sensitive and internationally experienced faculty, students, and administrators. Such a curricular reform process must be institution-wide in order to best meet the needs of all students in all departments and faculties. The three approaches to internationalizing the curriculum are:

- ✓ **The add-on approach**: It is the simplest and widely used strategy in many universities. It is highly useful for traditional courses. The add-on approach is the earliest used approach to internationalizing the curriculum and is characterized by adding international or intercultural content or themes to existing curricula and courses without modifying the original structure or pedagogical approaches.

- ✓ **The infusion approach:** The infusion approach to internationalizing the curriculum is the one most normally employed in western countries today. Within this approach, the curriculum is infused with content that enhances students' cross-cultural understanding and knowledge of diverse cultures. The infusion approach focuses on the interdisciplinary nature of the internationalization of the curriculum and exposes students in all fields of study to international and multicultural perspectives.

- ✓ **The transformation approach:** The transformation approach is probably the most difficult to adopt and the least utilized approach to modify the curriculum. This approach, which is based upon the tenets of critical pedagogy, "encourages new ways of thinking, incorporates new methodologies, so that different epistemological questions are raised, old assumptions are quested, subjective data sources are considered, and prior theories either revised or invalidated".

5. Practical Suggestions for Internationalizing the Curriculum

An internationalized curriculum stresses to move from the traditional lecture and discussion style of teaching to a more inclusive, student-centered, interactive, and centered at teacher as well as learner experiential learning environment. Such a learning environment should encourage diverse learning styles.

6. Examples of Potential Learner-Centered Instructional Strategies

- Peer learning
- Small and large group discussions and projects that incorporate diverse groups of students and examine particular issues from various cultural perspectives
- Reaction papers and reflective writing assignments focusing on intercultural issues
- Analyses of international case studies
- Problem solving exercises focusing on international or intercultural contexts
- The use of multimedia and technology within the classroom
- The incorporation of international students and international guest speakers in the class

7. Suggestions for Faculty Members

- Faculty should explicitly outline the academic expectations and teaching and learning style requirements of the new educational environment
- Faculty should guide and support students in understanding their reasons and goals for utilizing particular teaching strategies within the classroom environment
- Faculty members must provide sufficient time to enable international students to modify and add to their existing repertoire of learning styles to more successfully engage in their new learning environment.
- Faculty should incorporate wherever possible sources representing local, national, and international perspectives.
- Knowledge should be examined not from the perspective of a single discipline, but from multidisciplinary contexts.
- Internationalized course content should be carefully chosen to ensure it accurately reflects different countries and cultures and should encourage students to critically reflect on their own socially determined cultural identity.
- Faculty should employ a diverse range of assessment strategies to better meet the learning needs of international students.

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5. Dr. Ambedkar's Contribution to the Emancipation of Women

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Introduction

"I measure the progress of a community by the degree of progress which women have achieved."- Dr. B.R. Ambedkar

Dr. B.R. Ambedkar played many roles such as a noted scholar, teacher, lawyer, parliamentarian, administrator, journalist, political leader, and economist and so on. Dr. B.R. Ambedkar acquired deep knowledge in every field of human activity to become a founder of his own independent ideology. Dr. B.R. Ambedkar was a saviour of the suppressed classes, the chief architect of Indian constitution a profound scholar, overall a multifaceted personality, and intellectual revolutionary leader of the downtrodden and underprivileged section of Indian society. He worked tirelessly throughout his life to challenge the legitimacy of orthodox Hindu social order that upheld unequal gender relations.

Dr. Ambedkar started his movements in 1920. He raised his voice against the Hindu social order and social system through renowned journal Mook Nayak in1920 and Bahishkrit Bharat in 1927. The content of all issues used to be on gender equality, women education and exposed the problems related to women and other depressed class. He strongly advocates for family planning measures for women and equal opportunity and equal share with their male counterpart in Indian Society in Bombay Legislative Assembly. Dr. Babasaheb Ambedkar fought for woman's economic liberation and for securing woman's social rights. He stressed the need to safeguard the dignity and to respect the modesty of the women. He studied extensively the Hindu Shastras and Smritis to find out the root cause of degraded status of women in India. (Godbole 2015)

His Struggle for women's rights

Dr. B.R. Ambedkar's perception on Women's problem emphasized on women's right to education, right to property, involvement in the political process, gender equality. He believed in the strength of women and their role in the process of social reform and progress of the society

which can be achieved by accelerating male educations persuaded side b
education. To strengthen his movement and to raise the voice for liberation o
promoting the need for women's education he started his owned newspaper MookNayak and Bahishkrit Bharat. His emphasis was to upgrade the social status and to motivate women to participate in social reform movements against social evils. Dr Babasaheb was a great believer of women's organization.

In 1927 after getting nominated as a member of Bombay Legislative Council Dr. Babasaheb urged the need to recognize the dignity of women and supported maternity benefit bill for women labourers. His stand and argument was that it was in the interest of the nation that the mother ought to get certain amount of rest during the pre-natal period. In January 1928, a women's association was founded in Bombay with Ramabai, Dr. Ambedkar's wife, as its president. In the Kalaram Temple Entry Satyagraha at Nasik in 1930, five hundred women participated and many of them were arrested along with men and ill treated in jails. The encouragement of Dr. Ambedkar to empower women to speak boldly was seen when Radhabai Vadale addressed a press conference in 1931. She said "It is better to die a hundred times than live a life full of humiliation. We will sacrifice our lives but we will win our rights." The credit for this self-respect and firm determination of women goes to Ambedkar. Dr Ambedkar believed in the strength of women and their role in the process of social reform. The historic Mahad Satyagraha witnessed participation of three hundred women along with their male counterparts. Addressing another meeting of about 3000 women, he said, "I measure the progress of community by the degree of progress which women had achieved. Let every girl who marries stand by her husband, claim to be her husband's friend and equal, and refuse to be his slave. I am sure if you follow this advice, you will bring honour and glory to yourselves." (M.R. Singariya 2)

The Hindu Code Bill and Women Rights

The Hindu Code Bill was the most debated legislative measure of modern India. This bill was to put an end to a variety of marriage systems prevailing in India and legalise only monogamous marriages. The Code also sought to confer on women the right of property and adoption which had been denied by traditional laws. This bill was put men and women on an equal level in all legal matters. Dr. Ambedkar said, "I should like draw attention of the house to one important fact. The great political philosopher Burke who wrote his great book against the

French Revolution said that those who want to conserve must be ready to repair. And all I am asking this House is: If you want to maintain the Hindu system, Hindu culture and Hindu society, do not hesitate to repair where repair is necessary. This Bill asks for nothing more than to repair those parts of the Hindu system which have become dilapidated." (Ambedkar and Social Justice 119) Unfortunately his dream bill could not pass in the parliament hence he offered resignation.

The Indian Parliament had seen equally stormy scenes on the issue of women's rights, when on February 5, 1951, Dr. Ambedkar, India's first Law Minister, moved the Hindu Code Bill in the Constituent Assembly. The process of reform and codification had been opposed strongly by the self-proclaimed defenders of Hindu culture and tradition including the predecessors of the present rulers organised then in the Hindu Mahasabha. After months of prevarication, Nehru withdrew the Bill. Ambedkar disgusted with Government capitulation handed in his resignation letter on September 27, 1951 in which he wrote "For a long time I had been thinking of resigning my seat from Cabinet. The only thing that held me back from giving effect to my intention was the hope that it would be possible to give effect to the Hindu Code Bill before the life of the present Parliament came to an end. I even agreed to break up the Bill and restricted it to Marriage and Divorce in the fond hope that at least much of this labour may bear fruit. But even that part of the Bill has been killed. I see no purpose in continuing to be a member of your Cabinet." (Brinda Karat)

The Hindu Code Bill was later split in to four Bills, and the same were put on the Statue Book by Parliament. The Hindu Marriage Act, 1955; The Hindu Succession Act, 1956; The Hindu Minority and Guardianship Act, 1956 and The Hindu Adoption and Maintenance Act, 1956 are the four enactments which incorporate the ideas and principles of Hindu Code Bill formulated by Dr Ambedkar. They give independent status to women and endow them with the right of adoption, succession and property, so completely denied by Manu. Therefore, it is truism to say that it is due to Dr. Ambedkar that a large part of the Hindu social law is now on par with the legal system prevailing in advanced western countries (Ahir 1990).

Constitutional Provisions

In Indian Constitution, there are few articles exist that help the women of Indian society to improve their position and to compete with their male counterparts. For example:

- Article14 – All are equal in the eyes of law and equally protected by the law. It means equal rights and opportunities in political, economic and social spheres.

- Article 15 prohibits discrimination on the ground of sex.
- Article 15(3) enables positive discrimination in favour of women.
- Article 16 mentions there shall be equality of opportunity for all citizens in matters relating to employment or appointment to any office without any discrimination on the basis of religion, caste, creed and sex.
- Article 24 prohibits the employment of children below the age of 14 years in factories, mines or in any other hazardous employment.
- Article 39 and 39(d) state Equal means of livelihood and equal pay for equal work.
- As per article 41 the state shall guarantee within its economic limits to all the citizens, the right to work, to education and public assistance in certain cases.
- Article 42 the state makes provision for Human conditions of work and maternity relief.
- Under article 44, the state provides a uniform Civil Code to all the citizens throughout the territory of India.
- Article 46 – The state to promote with special care, the educational and economic interests of weaker section of people and to protect them from social injustice and all forms of exploitation.
- Article 47 – The state to raise the level of nutrition and standard of living of its people and the improvement of public health and so on.
- Article 51 (A) (C) – Fundamental duties to renounce practices, derogatory to the dignity of women.
- Article 243D (3), 243T (3) & 243R (4) provides for allocation of seats in the Panchayati Raj System.

Ambedkar not only ascertain constitutional guarantees to women but also introduced and got passed four Acts which strengthened the position of women in the society. (Milind Ubale 2)

Dr.Ambedkar and The Hindu Succession Act, 1956

This Act contains the following provisions for women:

1. A widow has a right to adopt a son or a daughter which was not there in the Hindu Law.
2. It also provided an opportunity to be independent and dispose of her property by will as she wishes and desires (Sec. 14).

3. Auniform scheme of succession to the property of a Hindu female, who dies, intestate after commencement of the Act, was made in Section 15. (Milind Ubale 3)

Conclusion

He is true celebrated champion of the underprivileged. Dr. Babasaheb spent his life for the betterment of women even involved in bad practices and professionals like prostitutions. Ambedkar created awareness among poor, illiterate women and inspired them to fight against the unjust and social practices like child marriages and devdasi system. Dr. Ambedkar tried an adequate inclusion of women's right in the political vocabulary and constitution of India. He insisted on Hindu Code bill suggesting the basic improvements and amendments in assembly. He also insisted and evoked all the parliamentary members to help to pass the bill in parliament. Thus his deep concern and feelings for all round development of women is expressed from his each sentence and word.

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Resource Sharing and Knowledge Management System in Acadamic Libraries

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Abstracts:

This paper gives a basic concept about knowledge management and resource sharing by using the ICT. Knowledge management provides right information to right users by using ICT. Information creates by human mind and for sharing the information need proper process or planning to convert information into knowledge.

Key word: Knowledge management, Resource Sharing, Information Communication Technology

Introduction:

In the present information and knowledge era, knowledge has become a key resource. In these days modern academic libraries are very attractive than traditional libraries. The traditional library is in agreement with the industrialized society and the modern library with, what we originally call the information and media society. The conventional function of academic libraries is to collect, process, disseminate, store and utilize information to provide service to the academic community. Knowledge Management (KM) is a concept that emerged explosively in the business community over the last few years. It is a relatively recent phenomenon and as a key component of the strategic planning process which developed in the mid-1990s. Day by day all types of libraries are undergoing to drastic changes, they are becoming as a knowledge resource center. Today for teaching, learning and research, it is expected to provide standard information resources. Today, academic libraries are struggling to keep their place as the major source of investigation in the face of rising digital technology. The new role of academic libraries in the 21st century needs to be as a learning and knowledge center for their users. In the present age of information and communication technology (ICT) information, communication technology and knowledge have become essential ingredients due to multi-dimensional use and application in the society. They have also been playing an important role to change and improve the current society for future vision. Knowledge Management is an emerging field and complex process, which deals with creations, acquisitions, storage, packaging and application of knowledge. It is the systematic, explicit and deliberate building renewal and application of knowledge related effectiveness and returns from its knowledge assets. Library & Information Science professional have realized the importance of knowledge management.

Types of Knowledge:

In 1991 Ikujiro Nonaka raised the conception of "tacit" knowledge and "explicit" knowledge as well as the theory of "spiral of knowledge". Knowledge is a product of human experience and it can be defined as the management of creating, sustaining, applying, and renewing knowledge resources of an organization including its relationship with seeker and service provider. Knowledge can be broadly divided into two types:

Tacit Knowledge: Tacit knowledge remains in the minds of people. The acquisition of tacit knowledge is usually improved through a process of trial and error during practical experience.

Explicit Knowledge: Explicit knowledge easy to communicate to others and it is the knowledge of unity.

Research Objectives:

The main objectives of this research paper are

*To identify knowledge base of captured tacit and explicit knowledge of staff and students/ Institute •

*To study the application of ICT and web technology for creating knowledge

*To identify and analyze the development of knowledge management processes.

Information Management:

Information management tries to make the right information available to the right person at the right time though a variety of database driven information applications. Before we discuss about knowledge management it is essential to clear the concept of information management. According to Wikipedia, Information

Knowledge Management (KM):

Knowledge Management (KM) means management of knowledge. KM deals with creating, securing, capturing coordinating, and combining, retrieving and disseminating knowledge. Knowledge management is essentially about getting the right knowledge to the right person at the right time. Knowledge management (KM) is the process of capturing, developing, sharing, and effectively using organizational knowledge. Knowledge management may also include new knowledge creation, or it may solely focus on knowledge sharing, storage, and refinement. KM is the systematic management of an organization's knowledge assets for the purpose of creating value and meeting tactical & strategic requirements management is the collection and management of information

Knowledge Communication

Knowledge communication is the (deliberate) activity of interactively conveying and co-constructing insights, assessments, experiences, or skills through verbal and non-verbal means. Knowledge communication has taken place when an insight, experience or skill has been successfully reconstructed by an individual because of the communicative actions of another. The process of knowledge communication hence requires more reciprocal interaction between decision makers and experts because both sides only have a fragmented understanding of an issue and consequently can only gain a complete comprehension by interactively aligning their mental models. All of this means that when we communicate knowledge, we are still communicating information and emotions, but we also create a specific type of context so that this information can be used to re-construct insights, create new perspectives, or acquire new skills. By examining the communication problems which often impede knowledge transfer in detail, we can look into this black box and propose pragmatic ways of improving knowledge communication, especially among experts and managers from one or more sources and the distribution of that information to one or more users.

Benefits Of Knowledge Management In Modern Academic Libraries

Today's library holds a wealth of knowledge. Often the most valuable knowledge is the expertise of senior employees or information professionals and is often dispersed around the organization. Here are some advantages of KM are given below

1. Knowledge management has help for libraries to respond to challenges to faces in an frequently changing environment.
2. KM provides Current awareness and automated information digests.
3. KM provide day night through internet access to the library's resources, for users every time.
4. Improve performance and users focus solutions.

Knowledge Resources Management

Modern library is also like a digital library, here use Library Automation, (acquisitions, cataloguing, circulation and OPAC), CDs, DVDs, Microfilm, E-Books, E-Journals, Databases, Library Co-Operation and Resource Sharing, (Inter-Library loan) Networked digital information resource sharing, (web OPAC, SDI, CAS, Article alert service),etc. The librarians today distinguish their role more as a custodian of knowledge. Modern libraries need to develop their resources access and sharing strategies from printed to electronic and digital resources in concert with their mission and charges. Restricted by limited technology, staff, and space libraries must carefully analyze the needs of their users and seek to develop cooperative acquisition plans to meet these needs.

Importance Of Km To Resources Sharing In Acadamic Library:

As a learning organization, libraries should provide a strong leadership in knowledge management. Libraries should improve their knowledge management in all of the key areas of library services. To cope with the exponential growth in human knowledge, libraries need to develop their resources access and sharing strategies from printed to electronic and digital resources. Limited by funding, technology, staff and space, libraries must carefully analyze the need of their users and seek to develop cooperative acquisition plans to meet the needs of users. Libraries had a long tradition of resources sharing and networking. These have been greatly expanded by the rapid development of computers ,telecommunication, networking and digital technologies in modern library various type of collection made available through digital library via networking tools like E-book, E-newspaper, E-Journals, E- databases like N-List, E-thesis, dissertations and projects, library network, web OPAC, mobile OPAC like.

To facilitate the implementation of knowledge management, a well-defined and operational knowledge management system should be in place. Latest information technology should be used in the libraries. In this regard, the library director / librarian should consider himself as the chief knowledge officer of the entire organization and should work together with the chief information officer, heads of the planning department, the computer and information technology center, the human resource management department, the finance department etc., to design and develop such a system. Such knowledge management system should be built on the existing computer and information technology infrastructure including upgraded intranet, Extranet, internet and available software programs to facilitate the capture, analysis, organization, storage and sharing of internal and external information resources for effective knowledge exchange among users.

Knowledge Management Tools for Academic Libraries The continuing education through professional training courses or workshops plays a significant role in the implementation of knowledge management in all contemporary organizations. Members within the community of practice freely exchange knowledge which creates an even greater resource base of knowledge. Information Technology (IT) serves as a powerful enabler and provides effective and efficient tools for all facets of knowledge management including capturing, sharing, and applying knowledge. New technologies have dramatically transformed the library world too. It can also support knowledge sharing by facilitating people to locate as well as communicate each other Knowledge Management in an academic library therefore is to ensure an all-round improvement of library staff's capacity; promotion of relationships between libraries and library users; it promotes knowledge innovation, strengthening knowledge internetworking and quickens knowledge flow. Other objectives are highlighted below. Implementations of Knowledge Management in Academic Libraries A knowledge management initiative in libraries becomes imperative in order to harness the wealth, wisdom, expertise, and experiences embedded in the heads of such employees before they leave the library. This can be achieved through brainstorming, open discussions, and provision of fertile ground for creativity, sharing of ideas, organizing workshops, conferences, mentoring, web archiving, digitization, and identification and collectively addressing problems and finding solution. Therefore there are a number of approaches that academic librarians

Conclusion :

At the concluding that the major trust of KM in librarianship is to enhance accessibility of information, and customize to the professional needs. But there is a need to reshape the structure of academic libraries for them to be able to improve the services they provide to library users. Libraries have a long and well-off experience in the management of information. They should be in a position to map internal and external knowledge that would assist them in increasing their efficiency. In the present scenario knowledge management is a powerful tool for promoting innovation, realizing g the various aspects of day to-day activities of an organization. Knowledge is growing very fast in every aspect of life and it is becoming very difficult for knowledge professionals to capture and disseminate the available information to the deserving person without using the emerging technologies. Librarians should work together with IT professionals and others to develop the proper knowledge management system. The new role of modern libraries in the present day needs to be as a learning and knowledge centre for their users. These include acquisition of modern tools, updating skills and standardization, knowledge creation, knowledge capturing, knowledge sharing, and skills in ICT.

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Bianchi Type –VI Model With Anisotropic Dark Energy in A Scalar Tensor Theory of Gravitation

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Abstract:

Exact solution of Einstein's field equations are obtained for cosmological mode of Bianchi type –VI space time using the technique given by Letelier [1]in the presence of dark energy . To get the deterministic solution of the field, assuming a special law of variation for the mean Hubble parameter, which yield a constant value of the deceleration. Some physical and geometric properties of the model are discussed

Keywords: Scalar Tensor Theory , Dark Energy

Introduction

Saez and Ballester [2] proposed a scalar-tensor theory of gravitation in which the metric is coupled with a dimensionless scalar –field in a simple manner. This coupling gives a satisfactory description of the weak fields. Inspite of the dimensionless character of the scalar field an antigravity regime appears in this theory. Also, this theory, suggests a possible way to solve missing matter problems in non-flat FRW cosmologies. Letelier has obtained the solution of Einstein's field equations of a cloud of strings with spherical, plave and cylindrical symmetry. The in 1983, he solved Einstein's field equation cloud of massive strings and obtained cosmological models in Bianchi type-I and Kantowski- Sachs space-times.

Nordtvedt [3] proposed a general class of scalar tensor gravitational theories in which the parameter ω of the Brans- Dicke theory is allowed to be an arbitrary (positive definite) function of the scalar field $(\omega \to \omega(\phi))$.. Considering the static spherically symmetric solution for a point mass sourse, Nordtvedt [3] found a variety of experimental consequences of $\omega' \neq 0$, including a contribution to the rate of precession of Mercury's perihelion.

Dark energy has conventionally been characterized by the EoS parameter given by $\omega(t) = \frac{p}{\rho}$ which is not necessarily constant, where p is energy density

([4],[5],[6],[7],[8],[9],[10],[11],[12]) are some of the authors who have investigated dark energy models with variable EoS parameter.

Rao et al.[13] Have obtained Bianchi type-I dark energy model in scalar tensor theory of Saez and Ballester [2]. Recently Pradhan and Amirhashchi [10] obtained a new class of dark energy models in LRS Bianchi type- II.

Spatially homogeneous and anisotropic cosmological models play a significant role in the description of large scale behaviour of universe and such models have been widely studied in framework of General Relativity in search of a realistic picture of the universe in its early stages.

Dark Energy has been conventionally characterized by the equation of state (EoS) parameter mentioned which is not necessarily constant. Recently, the parameter $\omega(t)$ is calculated with some reasoning which reduced to some simple parameterizations of the dependences by some authors Huterer and Turner [14]. The simplest dark energy candidate is the vacuum energy $\omega = -1$, which is mathematically equivalent to the cosmological constant $(\wedge)$. The other conventional alternatives, which can be described by minimally coupled scalar fields, are quintessence $(\omega > -1)$, phantom energy $(\omega < -1)$,and quintom and have time dependent EoS parameter. Astrophysical observations indicate that this expansion of the universe is driven by an exotic energy with large negative pressure which is known as dark energy (DE). Inspite of all the observational evidence dark energy is still a challenging problem in theoretical physics. The data indicates that the universe is spatially flat and is dominated by 76% dark energy 24% by other matter (20% dark matter and 4% other cosmic matter).

In this paper, we investigate Bianchi type- VI model dark energy in Saez and Ballester [2] scalar tensor theory . The out line of the paper is as follows: In section 2 , the metric and field equations are described. Section 3 deals with the solutions of the field equations. Section 4 deals with physical and geometric behaviour of the model. Lastly ,conclusions are summarized.

Metric and Field Equations:

We consider the totally anisotropic Bianchi type-VI line element, given by

$$ds^2 = -dt^2 + a^2 dx^2 + b^2 e^{2x} dy^2 + c^2 e^{-2x} dz^2) \qquad (1)$$

where the scale factors a , b and c are functions of cosmic time only. By preserving the diagonal form of the energy momentum tensor in a consistent way with the above metric, the simplest generalization of EoS parameter of perfect fluid may be to determine it separately on each spatial axis. Therefore the energy momentum tensor of perfect fluid is taken as

$$T_i^j = diag[T_0^0, T_1^1, T_2^2, T_3^3]$$

Thus, one may parameterize it as follows

$$\begin{aligned} T_i^j &= dia[\rho, -p_x, -p_y - p_z] \\ &= dia[1, -\omega_x, -\omega_y, -\omega_z]\rho \\ &= dia[1, -\omega, -(\omega+\delta), -(\omega+\gamma)]\rho \end{aligned} \qquad (2)$$

where ρ is the energy density of the fluid p_x, p_y, p_z are the pressures and $\omega_x, \omega_y, \omega_z$ are the directional EoS parameters along the x, y, z respectively, $\omega(t) = p/\rho$ is the deviation free EoS parameter of the fluid. We have parameterized the deviation from isotropy by setting $\omega_x = \omega$ and then introducing skewness parameter δ *and* γ which is the deviation from ω along both y and z-axes respectively. Also we obtain $\delta = \gamma$ because of the that in Bianchi type-VI space – time $T_2^2 = T_3^3$

The field equations given by Saez and Ballester [2] for the combined scalar and tensor fields are

$$R_{ij} - \frac{1}{2} R g_{ij} - \varpi \phi^n (\phi_{,i}\, \phi_{,j} - \frac{1}{2} g_{ij} \phi_{,k}\, \phi^{,k}) = -T_{ij} \qquad (3)$$

And the scalar field ϕ satisfies the equation

$$2\phi^n\phi^i_{,i} + n\phi^{n-1}\phi_{,k}\phi^{,k} = 0 \qquad (4)$$

where ϖ and n are constants, T_{ij} is the energy momentum tensor of the matter and comma and semicolon denote partial and covariant differentiation respectively.

By adopting commoving coordinates the field equations (3), for the Bianchi type-VI space-time, the field equations take the form

$$\frac{b_{44}}{b} + \frac{c_{44}}{c} + \frac{b_4c_4}{ac} + \frac{1}{a^2} + \varpi\phi^n\frac{\phi_4^{\,2}}{2} = -\omega\rho \qquad (5)$$

$$\frac{a_{44}}{a} + \frac{c_{44}}{c} + \frac{a_4c_4}{ac} - \frac{1}{a^2} - \varpi\phi^n\frac{\phi_4^{\,2}}{2} = -(\omega+\delta)\rho \qquad (6)$$

$$\frac{a_{44}}{a} + \frac{b_{44}}{b} + \frac{a_4b_4}{ab} - \frac{1}{a^2} - \varpi\phi^n\frac{\phi_4^{\,2}}{2} = -(\omega+\delta)\rho \qquad (7)$$

$$\frac{a_4b_4}{ab} + \frac{b_4c_4}{bc} + \frac{c_4a_4}{ca} - \frac{1}{a^2} + \varpi\phi^n\frac{\phi_4^{\,2}}{2} = \rho \qquad (8)$$

$$\frac{c_4}{c} - \frac{b_4}{b} = 0 \qquad (9)$$

Using equation (4), we get

$$\frac{\phi_{44}}{\phi} + \frac{a_4}{a} + \frac{b_4}{b} + \frac{c_4}{c} + \frac{n}{2}\frac{\phi_4}{\phi} = 0 \qquad (10)$$

where a subscript 4 indicates differentiation with respect to t.

Solutions of the field equations

Equation (9) leads to

$$b = lc \qquad (11)$$

where l is an integrating constant.

Using (11), Equations (5) to (10) reduce to

$$2\frac{a_4b_4}{ab} + \frac{b_4^{\,2}}{b^2} - \frac{1}{a^2} + \varpi\phi^n\frac{\phi_4^{\,2}}{2} = \rho \qquad (12)$$

$$\frac{a_{44}}{a} + \frac{b_{44}}{b} + \frac{a_4b_4}{ab} - \frac{1}{a^2} - \varpi\phi^n\frac{\phi_4^{\,2}}{2} = -(\omega+\delta)\rho \qquad (13)$$

$$2\frac{b_{44}}{b} + \frac{b_4^{\,2}}{b^2} + \frac{1}{a^2} - \varpi\phi^n\frac{\phi_4^{\,2}}{2} = -\omega\rho \qquad (14)$$

$$\frac{\phi_{44}}{\phi} + \frac{a_4}{a} + 2\frac{b_4}{b} + \frac{n}{2}\frac{\phi_4}{\phi} = 0 \qquad (15)$$

According to the proposed law, the variation of the mean Hubble parameter for the Bianchi type -VI metric may be given by

$$H = k(ab^2)^{-\frac{n}{3}} \qquad (16)$$

where $k > 0$ *and* $n \geq 0$ are constants. The spatial volume is given by

$$V = R^3 = ab^2 \qquad (17)$$

where R is the mean scale factor. The mean Hubble parameter H is given as

$$H = \frac{R_4}{R} = \frac{1}{3}\frac{V_4}{V} = \frac{1}{3}\left(\frac{a_4}{a} + 2\frac{b_4}{b}\right) \qquad (18)$$

The directional Hubble parameters in the directions of x,y and z respectively may be defined as

$$H_x = \frac{a_4}{a} \qquad and \quad H_y = H_z = \frac{b_4}{b} \qquad (19)$$

The volumetric deceleration parameter is

$$q = -RR_{44} \Big/ R_4^{\,2} \qquad (20)$$

On integrating, after equating (16) and (18), we obtain

$$ab^2 = c_1 e^{3kt} \qquad for \quad n = 0 \qquad (21)$$

$$ab^2 = (nkt + c_2)^{\frac{3}{n}} \qquad for \quad n \neq 0 \qquad (22)$$

here c_1 *and* c_2 are positive constants of integration. Using (16) with (21) for $n = 0$, and with (22) for $n \neq 0$ mean Hubble parameters are

$$H = k \quad for \quad n = 0 \qquad (23)$$

and

$$H = k(nkt + c_2)^{-1} \quad for \quad n \neq 0 \qquad (24)$$

Using (21), (22) and (17) in (20), we get constant values for the deceleration parameter for the mean scale factor as:

$$q = n - 1 \quad for \quad n \neq 0 \qquad (25)$$

and

$$q = -1 \quad for \quad n = 0 \qquad (26)$$

The sign of q indicates whether the model accelerate or not. The positive sign of q $(i.e.n > 1)$ corresponds to decelerating models whereas the negative sign $-1 \le q < 0$ *for* $0 \le n < 1$ indicates acceleration .

Integration , after subtracting equation (8) from (7) , we get

$$\left(\frac{a_4}{a} - \frac{b_4}{b}\right)\left(\frac{V}{\lambda}\right) = \exp\left\{\int\left(-\delta\rho + \frac{2}{a^2}\right)\left(\frac{a_4}{a} - \frac{b_4}{b}\right)^{-1} dt\right\} \qquad (27)$$

where λ is an integration constant. The integral term in above equation vanishes for

$$\delta = \frac{2}{\rho a^2} \qquad (28)$$

Using equation (28) in equation (27) it follows that

$$\frac{a_4}{a} - \frac{b_4}{b} = \frac{\lambda}{V} \qquad (29)$$

by considering (23) and (24) we obtain

$$\frac{a_4}{a} - \frac{b_4}{b} = \frac{\lambda}{c_1 \exp(3kt)} \qquad for \quad n = 0 \qquad (30)$$

$$\frac{a_4}{a} - \frac{b_4}{b} = \frac{\lambda}{(nkt + c_2)^{3/n}} \qquad for \quad n \neq 0 \qquad (31)$$

Model for $n = 0 \quad (q = -1)$

On integration of (30) and using (21) we get the following exact expression for the scale factors:

$$a = \left(\frac{c_1}{k_1^{\,2}}\right)^{\frac{1}{3}} \exp\left\{kt - \frac{2\lambda}{9c_1 k} e^{-3kt}\right\} \tag{32}$$

$$b = c = \left(\frac{c_1}{k_1}\right)^{\frac{1}{3}} \exp\left\{kt + \frac{\lambda}{9c_1 k} e^{-3kt}\right\} \tag{33}$$

where k_1 is positive constant of integration.. The spatial volume of the universe is found as

$$V = c_1 e^{3kt} \tag{34}$$

The directional Hubble parameters are

$$H_x = k + \frac{2\lambda}{3c_1} e^{-3kt} \tag{35}$$

$$H_y = H_z = k - \frac{\lambda}{3c_1} e^{-3kt} \tag{36}$$

The anisotropy parameter of the (Δ) is defined as

$$\Delta = \frac{1}{3}\sum_{i=1}^{3}\left(\frac{H_i - H}{H}\right)^2 \tag{37}$$

where $H_i\,(i = 1,2,3)$ represents the directional Hubble parameters in the direction $x, y, and\ z$ respectively.

By using (23) ,(35) , (36) in (37) , we get

$$\Delta = \frac{2}{9}\left[\frac{\lambda^2}{c_1^{\,2}k^2} e^{-6kt}\right] \tag{38}$$

The expansion scalar θ is found as

$$\theta = 3k = 3H \tag{39}$$

The shear scalar σ^2 is found as

$$\sigma^2 = \frac{3}{2}\Delta H^2 = \frac{\lambda^2}{3c_1^{\,2}} e^{-6kt} \tag{40}$$

Using equation (15), the scalar field is found as

$$\phi = \left[\frac{n+2}{2}\left(\frac{-\alpha}{3k} e^{-3kt} + \beta\right)\right]^{\frac{2}{n+2}} \tag{41}$$

Using equations (41) ,(19), (35), (36) in (12), we obtain the energy density for the model as

$$\rho = 3k^2 - \frac{\lambda^2}{3c_1^{\,2}} e^{-6kt} - \left(\frac{k_1}{c_1}\right)^{\frac{2}{3}} \exp\left\{-2kt + \frac{4\lambda}{9c_1 k} e^{-3kt}\right\} + \frac{1}{2}\varpi\alpha^2 e^{-6kt} \tag{42}$$

Using equations (42) in (28), we obtain the deviation parameter as

$$\delta = \gamma = \frac{2\left(\frac{k_1}{c_1}\right)^{2/3} \exp\left\{-2kt + \frac{4\lambda}{9c_1 k} e^{-3kt}\right\}}{3k^2 - \frac{\lambda^2}{3c_1^{\,2}} e^{-6kt} - \left(\frac{k_1}{c_1}\right)^{\frac{2}{3}} \exp\left\{-2kt + \frac{4\lambda}{9c_1 k} e^{-3kt}\right\} + \frac{1}{2}\varpi\alpha^2 e^{-6kt}} \tag{43}$$

Using equation (35) (36),(42) and (43) in equation (14), we obtain the deviation –free parameter as

$$\omega = -\frac{3k^2 + \frac{\lambda^2}{3c_1^{\,2}} e^{-6kt} + \left(\frac{k_1}{c_1}\right)^{\frac{2}{3}} \exp\left\{-2kt + \frac{4\lambda}{9c_1 k} e^{-3kt}\right\} - \frac{1}{2}\varpi\alpha^2 e^{-6kt}}{3k^2 - \frac{\lambda^2}{3c_1^{\,2}} e^{-3kt} - \left(\frac{k_1}{c_1}\right)^{\frac{2}{3}} \exp\left\{-2kt + \frac{4\lambda}{9c_1 k} e^{-3kt}\right\} + \frac{1}{2}\varpi\alpha^2 e^{-6kt}} \tag{44}$$

Physical behaviour of the model for $n = 0$ $(q = -1)$:

For this model $q = -1$ *and* $\frac{dH}{dt} = 0$, which implies the greatest value of the Hubble parameter and the fastest rate expansion of the universe. Thus, this model may represent the inflationary era in the early universe and the very late times of the universe.

The spatial volume V is finite at $t = 0$, expands exponentially as t increases and becomes infinitely large at $t = \infty$. The directional Hubble parameters H_x *and* $H_{y,z}$ are finite at $t = 0$.

The expansion scalar is constant throughout the evolution of the universe. The scalar is also finite at $t = 0$ .The anisotropy of the expansion decreases monotonically as t increases .

The ratio $\frac{\sigma^2}{\theta^2} \to 0$ *as* $t \to \infty$. Hence the model isotropizes for large value of the t.

The EoS parameter of the DE ω may begin in phantom $(\omega < -1)$ or quintessence $(\omega > -1)$ region and tends to -1 (cosmological constant $\omega = -1$) by exhibiting various patter as t increases.

Model for $n \neq 0$ *and* $q \neq -1$:

On integration (30) and using (22) we obtain the following exact expressions for the scale factors:

$$a = c_3^{2/3}(nkt + c_2)^{\frac{1}{n}} \left\{\exp\left(\frac{2\lambda}{3k(n-3)}\right)(nkt + c_2)^{\frac{n-3}{n}}\right\} \tag{45}$$

$$b = c = c_3^{-1/3}(nkt + c_2)^{\frac{1}{n}} \left\{\exp\left(\frac{-\lambda}{3k(n-3)}\right)(nkt + c_2)^{\frac{n-3}{n}}\right\} \tag{46}$$

where c_3 is the positive constant of integration. The spatial volume of the universe is found as

$$V = (nkt + c_2)^{\frac{3}{n}} \tag{47}$$

The directional Hubble parameters are found as

$$H_x = (nkt + c_2)^{-1} k + \frac{2\lambda}{3}(nkt + c_2)^{-3/n} \tag{48}$$

$$H_y = H_z = (nkt + c_2)^{-1} k - \frac{\lambda}{3}(nkt + c_2)^{-3/n} \quad (49)$$

Using (48), (49) in (37) we get

$$\Delta = \frac{2}{9}\frac{\lambda^2}{k^2}(nkt + c_2)^{2\left(1-\frac{3}{n}\right)} \quad (50)$$

for the anisotropy parameter of the expansion. The expansion and shear scalars are, respectively, found as

$$\theta = 3H = 3k(nkt + c_2)^{-1} \quad (51)$$

$$\sigma^2 = \frac{\lambda^2}{3}(nkt + c_2)^{-\frac{6}{n}} \quad (52)$$

Using equation (15), the scalar field is found as

$$\phi = \left[\left(\frac{n+2}{2}\right)\left(\frac{P}{n-3}\right)(nkt + c_2)^{n-3/n}\right]^{\frac{2}{n+2}} \quad (53)$$

Using (48), (49), (52) in (12) we get the energy density for the model as

$$\rho = 3k^2(nkt + c_2)^{-2} - \frac{1}{3}\lambda^2(nkt + c_2)^{-\frac{6}{n}} - c_3^{-4/3}(nkt + c_2)^{-2/n} \exp\left\{\frac{-4\lambda}{3(n-3)k}(nkt + c_2)^{\frac{n-3}{n}}\right\} + \frac{1}{2}\varpi P^2 k^2 (nkt + c_2)^{-\frac{6}{n}} \quad (54)$$

Using (54) in (28), we get the deviation parameter as

$$\delta = \gamma = \frac{c_3^{-4/3}(nkt + c_2)^{\frac{-2}{n}}\left\{\exp\left(\frac{-4\lambda}{3k(n-3)}\right)(nkt + c_2)^{\frac{n-3}{n}}\right\}}{3k^2(nkt + c_2)^{-2} - \frac{1}{3}\lambda^2(nkt + c_2)^{-\frac{6}{n}} - c_3^{-4/3}(nkt + c_2)^{-2/n} \exp\left\{\frac{-4\lambda}{3(n-3)k}(nkt + c_2)^{\frac{n-3}{n}}\right\} + \frac{1}{2}\varpi P^2 k^2 (nkt + c_2)^{-\frac{6}{n}}} \quad (55)$$

Using (54),(49), (52) and (54) in (13) we get the deviation- free parameter as

$$\omega = -\frac{(3-2n)k^2(nkt + c_2)^{-2} + \frac{\lambda^2}{3}(nkt + c_2)^{-6/n} + c_3^{-4/3}\left[(nkt + c_2)^{-2/3}\exp\left\{\frac{-4\lambda}{3(n-3)k}(nkt + c_2)^{\frac{n-3}{n}}\right\}\right] - \frac{1}{2}\varpi P^2 k^2 (nkt + c_2)^{-\frac{6}{n}}}{3k^2(nkt + c_2)^{-2} - \frac{1}{3}\lambda^2(nkt + c_2)^{-\frac{6}{n}} - c_3^{-4/3}(nkt + c_2)^{-2/n} \exp\left\{\frac{-4\lambda}{3(n-3)k}(nkt + c_2)^{\frac{n-3}{n}}\right\} + \frac{1}{2}\varpi P^2 k^2 (nkt + c_2)^{-\frac{6}{n}}} \quad (56)$$

Physical behaviour of the model for The spatial volume V is finite at $t = 0$ and becomes infinitely large as $t \to \infty$. In this model , the average scale factor $R = (nkt + c_2)^{\frac{1}{n}}$. It has point

singularity at $t = -\frac{c_2}{nk}$. The Hubble parameters H_x, H_y, H_z *and* H are infinite at this point but here the spatial volume vanishes.

The anisotropy of the expansion $\Delta \to null$ as $t \to \infty$ for $m > 3$ while $\Delta \to \infty$ as $t \to \infty$.

The EoS parameter of the DE ω may begin in phantom $(\omega < -1)$ or quintessence $(\omega > -1)$ region and tends to -1 (cosmological constant $\omega = -1$) by exhibiting various patter according to the choice of the parameter.

The ratio $\frac{\sigma^2}{\theta^2} \to 0$ *as* $t \to \infty$. Hence the model isotropizes for large value of the t (*for* $0 < n < 3$).

Conclusion

Inspite of the that there are several dark energy models in the literature, the problem of cosmic acceleration is still a challenge for modern cosmology. With the advent of scalar tensor theories, this problem gained importance. Here we have investigated Bianchi type-VI dark energy model in the scalar theory of gravitation formulated by Saez and Ballesters [2].Since scalar fields plays a significant role in the early stage of evolution of the universe.

Exact solutions of Einstein's field equations have been obtained by assuming a special law of variation for the mean Hubble parameter, which yields a constant value of the deceleration parameter and is not inconsistent with observations. Some basic geometrical and kinematical features of the models and the dynamics of the anisotropic DE in these models have been examined.

The space approaches to isotropy in the models for large value of the t.

The energy density of the fluid and the deviation free EoS parameter ω and the deviation parameter δ are dynamical.

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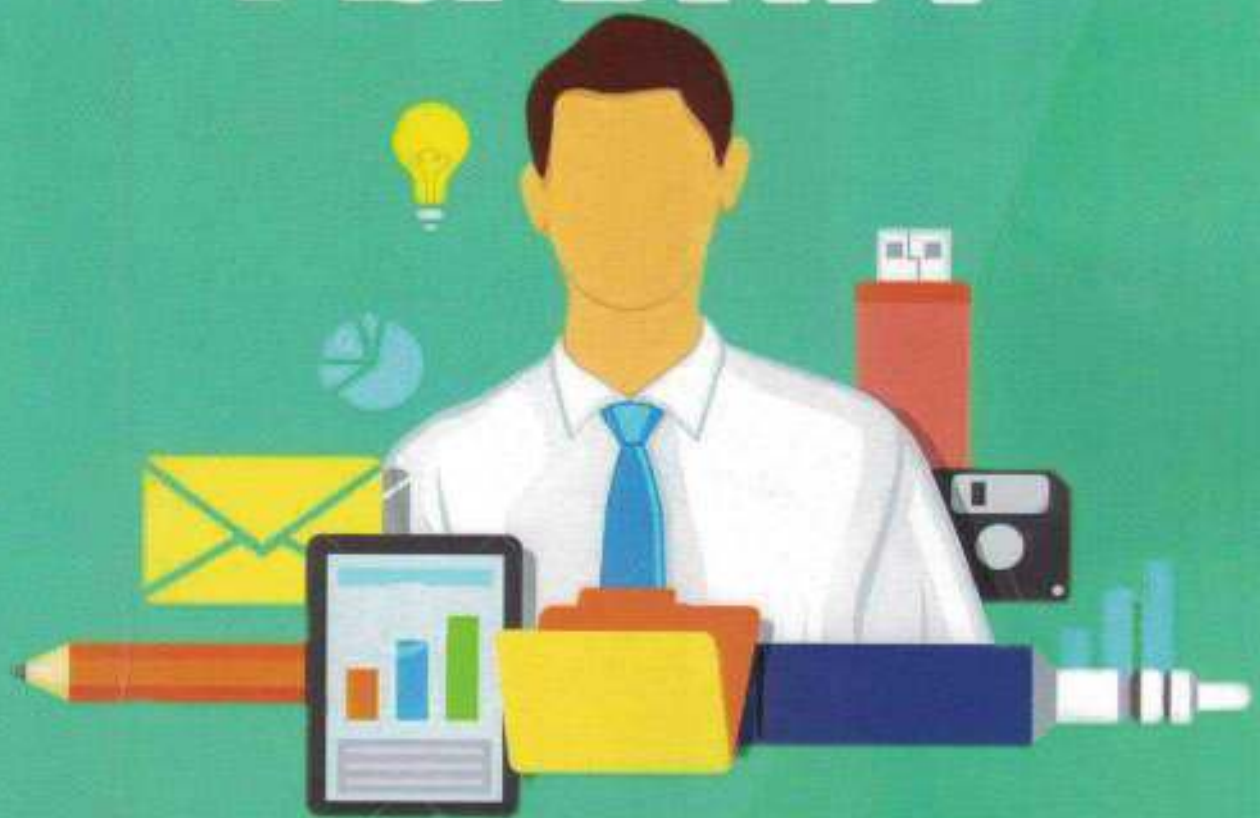

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11. Sports Nutrition

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Abstract

This article highlights the Nutrition Role in Sports performance and Fitness. Games Nutrition applies nourishment standards to brandish with the goal of expanding exhibition. Diets have been endorsed for diverse classifications of games relaying on the form weight and vigor needs. This article outlines the current energy, nutrient, and fluid recommendations for sports person. The performance of athletes and sports person can be enhanced by well-chosen nutrition strategies. It outlines the stance on nutrition factors that have been determined to influence sporting performance and emerging trends in the field of sports nutrition.

Introduction

Games nourishment gathers basic vitality in light of the fact that long before inadequacy manifestations begin seeming, physical exhibition decays. It might not be reasonable to think regarding least ought to keep the blood levels or chemical levels at ordinary points of confinement. Rather endeavours ought to be made to figure out the level beneath which physical exhibition begins appearing. The level, which allows the jok to attain the greatest conceivable physical exhibition, ought to be the base level pointed in the games nourishment.

An optimal eating methodology may be described as one in which the supply of needed supplements is satisfactory to blanket vigor use, for tissue support, repair and development. The wholesome needs vary from single to single dependent upon age, sex, form measure and arrangement, occupation, physiological condition and so forth. Numerous mentors make dietary suggestions dependent upon their particular "sentiments" and past encounters as opposed to depend on accessible experimental confirmation the way that players frequently have either lacking or erroneous informative content concerning judicious dietary rehearses and the part of particular supplements in the eating regimen.

Meaning of Energy Requirement

It is a created certainty that sustenance plays an imperative part in physical exhibition, separated from preparing and other identified segments. In India, games sustenance is yet to be distinguished as a paramount part of preparing project, and seems to be expansively dismissed.

drink supplements, energy bars, and energy gels currently represent the largest segment of the dietary supplement. They are typically fortified with vitamins and minerals and differ on the amount of carbohydrate, protein, fat they contain. Use of these types of products can be particularly helpful improving carbohydrate, protein, and other nutrients prior to exercise. Care should also be taken to make sure they do not contain any banned or prohibited nutrients.

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regulators of metabolic and neural control. Some minerals have been found to be deficient in athletes or become deficient in response to training and / or prolonged exercise. When mineral status is inadequate, exercise capacity may be reduced. Dietary supplementation of minerals in deficient athletes has generally been found to improve exercise capacity. Additionally, supplementation of specific minerals in non-deficient athletes has also been reported to affect exercise capacity. Iron supplementation in athletes prone to iron deficiencies and anemia has been reported to improve exercise capacity. Sodium phosphate loading has been reported to increase maximal oxygen uptake, anaerobic threshold, and improve endurance exercise capacity by 8 to 19%. Increasing dietary availability of salt (sodium chloride) during the initial days of exercise training in the heat has been reported to help maintain fluid balance and prevent dehydration. There is no benefit of mineral supplementation for athletes and it is unethical for a sports nutrition specialist to recommend that their clients take minerals for health and / or performance benefit is not consistent with current available literature.

Water

Most important nutritional ergogenic aid for athletes is water. Exercise performance can be significantly impaired when 2% or more of body weight is lost through sweat. Weight loss of more than 4% of body weight during exercise may lead to heat illness, heat exhaustion, heat stroke, ad possibly death, for this reason, it is critical that athletes consume a sufficient amount of water/sports drinks during exercise in order to maintain hydration status. Athletes should not depend on thirst to prompt them to drink because people do not typically get thirsty until they have lost a significant amount of fluid through sweat, they should weight themselves prior to and during exercise training to ensure that they maintain proper hydration and make sure that they consume more fluid in hotter/humid environments. Sports nutrition specialists can play an important role in educating athletes and coaches about proper hydration methods and supervising fluid intake during training and competition.

Dietary Supplements

Dietary supplements can help athletes to consume proper amount of calories carbohydrate, and protein in their diet. However, they should be viewed as supplements to the diet, not replacements for a good diet. Most dietary supplements available for athletes have little scientific date supporting their potential role to enhance training and performance. As, number of nutrients and dietary supplements have shown to help in improving performance and recovery. Supplementation with these nutrients can help to augment normal diets which help to optimize performance. Also, convenience supplements which are meal replacement powders, ready to

have revealed that many are susceptible to maintaining negative energy intakes during training. Female athletes have been reported to have a high incidence of eating disorders. Some athletes do not like to exercise within several hours after eating because of sensations of fullness and predisposition to cause gastrointestinal distress. Care should be taken to plan meal times in concert with training, as well as to make sure athletes have sufficient availability of nutrient dense foods throughout the day for snacking between meals.

Carbohydrate

Athletes must consume proper amounts of carbohydrate, protein and fat in their diet. However, athletes involved in moderate and high volume training need greater amounts of carbohydrate and protein in their diet to meet macronutrient needs. Many sports nutrition specialist recommend that athletes consume concentrated carbohydrate juices/drinks and consume high carbohydrate supplements to meet carbohydrate needs. Care should be taken to consider the type of carbohydrate to ingest prior to, during, and following intense exercise in order to optimize carbohydrate availability.

Protein

If insufficient amount of protein is obtained from the diet, an athlete will maintain a negative nitrogen balance, which can increase protein catabolism and slow recovery which way lead to muscle wasting and training intolerance. Care should be taken to ensure that athletes consume a sufficient amount of quality protein in their diet to maintain nitrogen balance. Proteins differ based on the source that the protein was obtained, the amino acid profile of the protein, and the methods of processing or isolating the protein and anabolism.

Vitamins

Vitamins are essential organic compounds that serve to regulate metabolic processes, energy synthesis, neurological processes, and prevent destruction of cells. 2 primary classifications of vitamins are fat and water soluble. Some vitamins may help athletes tolerate training to a greater degree by reducing oxidative damage (Vitamin E, C) and help to maintain a healthy immune system during heavy training (Vitamin C). Since dietary analyses of athletes have found deficiencies in caloric and vitamin intake, many sports nutritionists' recommend that athletes consume a low dose daily multivitamin and / or a vitamin enriched post workout carbohydrate / protein supplement during periods of heavy training.

Minerals

Minerals are essential inorganic elements necessary for a host of metabolic processes. Minerals serve as structure for tissue, important components of enzymes and hormones, and

Sports Authority concerning India (SAI) stresses every now and then on games nourishment and readiness of menus for the diverse games disciplines. As Nutrition goals and requirements are not static. Athletes undertake a periodized program in which preparation for peak performance in targeted events is achieved by integrating different types of workouts in the various cycles of the training calendar. Nutrition plans need to be personalized to the individual athlete to take into account specificity & uniqueness of the event, performance goals, practical challenges, food preferences, responses to various strategies. Energy availability, which considers energy intake in relation to the energy cost of exercise, sets an important foundation for health and the success of sports nutrition strategies. The achievement of the body composition associated with optimal strategies. The achievement of the body composition associated with optimal performance is now recognized as an important but challenging goal that needs to be individualized and periodized. Training and Sports nutrition guidelines should also consider the importance of the timing of nutrient intake and nutritional support over the day and in relation to sport rather than general daily targets. Competition nutrition should target specific strategies that reduce or delay factors that would otherwise cause fatigue in an event; these are specific to the event, environment / scenario in which it is undertake and the individual athlete. A pragmatic approach to advice regarding the use of supplements and sports foods is needed for high prevalence of interest and use by athletes and the evidence that some products can usefully contribute to a sports nutrition plan and / or directly enhance performance.

General Dietary Guidelines

A well-designed diet that meets energy intake needs and incorporates proper timing of nutrients is the foundation upon which a good training program can be developed. Maximum research has clearly shown that not ingesting a sufficient amount of calories and/or enough of the right type of macronutrients may impede an athlete's training adaptations while athletes who consume a balanced diet that meets energy needs can augment physiological training adaptations. Incorporating good dietary practices as part of a training program is one way to help optimize training adaptations and prevent overtraining.

Energy Intake

To optimize training and performance through nutrition is to ensure the athlete is consuming enough calories to offset energy expenditure. For elite athletes, energy expenditure during heavy training or competition may be enormous. Maintaining energy deficient diet during training often leads to significant weight loss, illness, onset of physical and psychological symptoms of over training, and reductions is performance. Nutritional analyses of athletes' diets

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Synthesis and Humidity Sensing Investigations of Nanostructured ZnO Doped SnO_2 Thick Films

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Abstract:

In present study, ZnO and SnO_2 nanoparticles was synthesized by a chemical precipitation method. Structural and compositional characterizations have been studied from X-ray powder diffraction (XRD). Surface morphologies of the samples were analyzed using Field Emission Scanning electron microscopy (FE-SEM) for thick flim of different molecular weight ratio. Further, humidity sensing investigations of these nanocomposites sensing materials were done. Our result indicates that ZnO doped SnO_2 in form of thick film for different molecular weight ratio was most sensitive for humidity in comparison to pristine materials under same conditions. The hysteresis plot between increasing and decreasing the RH range of 30–90% and vice versa. The samples resistance of sample ZS-3 decreases from 1011 Ω to 105 Ω in comparison with the pristine materials. The similar change was also observed in sensitivity. Activation energy measured from Arrhenius plot of conductivity at different RH and found to be 1.7010-3 eV respectively. The results were re- producible up to ± 77% after 2 months of observations.

Key words: ZnO, SnO_2 nanocomposites, Humidity sensor.

Introduction

Recently, the development in humidity sensor has receives much more attention due to the necessity of controlling and monitoring environment in many varrious fields like industrial and domestic part [1-3]. Semiconducting oxides based humidity sensors has many advantages when compared to other types of humidity sensors, such as low cost, simple construction, small size etc in operating the environment. The metal oxide such as SnO_2 , ZnO, WO_3, TiO_2, $BaTiO_3$ etc the change in electrical conductivity depends upon the composition of the gas/humidity surrounding them. Therefore, they are used as popular and useful sensing materials for making inexpensive gas sensing devices [4]. The nanocomposites of ZnO and SnO_2 seem to be one of the most promising metal oxide semiconductor for gas/ vapours/ humidity sensing. It has been observed that these nanostructure materials are more perceptive due to their high surface volume ratio, large band gap energy and have more chemically active [5-7].

In present study, nanocomposites of ZnO and SnO_2 thick films were prepared by screen printing method and the humidity sensitive properties of the nanocomposites films were investigated and compared with those of the pure films. The variation of resistance was studied as a function of relative humidity.

Experimental

Synthesis of zinc oxide (ZnO):

ZnO Nanoparticle were synthesized by solid state reaction method, using Zinc acetate dehydrate $Zn(O_2CCH_3)_2(H_2O)_2$, sodium hydroxide as starting materials . In preparation Zinc Oxide (ZnO) 0.2M Zinc Acetate dehydrates was dissolved in 100 ml deionised water was ground for 15 min and then mixed with 0.02 M solution of NaOH with the help of glass rod. The mixed and the solution were kept under constant magnetic stirring for 15 min. and then again it was ground for 30 min. The white precipitate product was formed at the bottom. Then abundant liquid was removed and the product was washed several times with the deionized water and methanol to remove by products. The final products was then filtered and it was kept in a vacuum oven at 80 ^oC for 4 hrs. so the moisture will removed from the final product. Then this dry product was calcinated at temperature 800 ^oC for 6 hrs. in the auto controlled muffle furnace (Gayatri Scientific, Mumbai, India.) so that the impurities from product will be completely removed and get a final product of ZnO nanoparticles.

Synthesis of tin oxide (SnO_2) :

In preparation of SnO_2 nanoparticle the Stannous chloride dehydrates ($SnCl_2.2H_2O$), Ammonia solution and deionized water were used as starting materials. Initially, 2 g (0.1 M) of stannous chloride dehydrate ($SnCl_2.2H_2O$) is dissolved in 100 ml water. After complete dissolution, about 4 ml ammonia solution is added to above aqueous solution with magnetic stirring. Stirring is continued for 20 minutes. White gel precipitate is immediately formed. It is allowed to settle for 12 hrs. Then it is filtered and washed with water 2-3 times by using deionized water. The obtain precipitate were mixed with 0.27 g carbon black powder (charcoal activated). The obtained mixer is kept in vacuum oven at 70 ºC for 24 hours so that the mixer gets completely in to dried powder. Then this dry product was crushed into a find powder by grinder. Now obtained product of fine nanopowder of SnO_2 was calcinated at 700^oC up to 6 hours in the auto controlled muffle furnace (Gayatri Scientific, Mumbai, India.) so that the impurities from product will be completely removed.

Preparation of thick films :

The thick film were prepared by screen printing technique on a glass substrate. Initially, for the screen printing the thixotropic paste was formulated by mixing the sintered fine powder of pure and composite nano powder of ZnO and SnO_2 in different molecular weight ratios, a with a solution of ethyl cellulose as (10% temporary binder) in a mixture of organic solvent such as butyl cellulose, butyl carbitol acetate and turpineol. The ratio of inorganic to organic part was kept as 75:25 in formulating the paste. The paste of pure and composite materials of ZnO and SnO_2 and it was screen printed on a glass substrate in the form of thick films and it was dried at 80-110^oC in oven for 1hrs. The dried films is fired at 500^oC for 25 min in muffle furnace (Kumar make Mumbai), to remove organic impurities form the sensor material. For the surface conductance measurement the electrodes of silver paint were formed on adjacent sides of the films.

Characterization Technique

X-Ray Diffraction (XRD)

The XRD pattern pure zinc oxide (ZnO) synthesized nanostructure in figure (1). The crystalline nature with 2θ peak lying at (100), (002), (101), (102), (110) and (103) planes. All the peaks match are perfectly with the standard hexagonal wurtize structure of zinc oxide (ZnO) with lattice constants a = b = 0.3249 nm and c = 0.5206 nm [JCPDS card no. 36-1451] and indicates the high purity of the obtained ZnO nanoparticle. The average crystalline size was found to be 37.32 nm calculated by Deye-Scherrer formula [8].

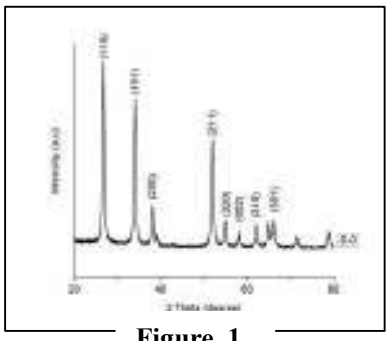

Figure. 1

The XRD pattern pure SnO_2 nanostructure is as shown in figure (2). It is clearly observed that the highest intensity peak is obtained at (110) crystal planes and other peaks lying at (101), (200), (211), (220) and (002) of SnO_2. All the peaks match well with the standard tetragonal structure of SnO_2 with lattice constant a = 4.723 nm and c = 3.238 nm and its unit cell volume (V=72.24A^{o3}) with JCPDS card no. 71-0652. The average crystalline size was found to be 23.19 nm [9].

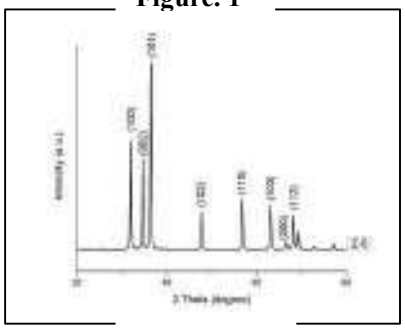

Figure. 2

The observes peaks are the mixed combination of ZnO and SnO_2 semiconducting metal oxides as shown in figure (3). In these case from crystal quantization plot mostly the peaks about (90%) corresponds to ZnO nanomaterial and very few about (10%) corresponds to SnO_2 nanomaterials. The XRD pattern of the sample such as ZS-1, ZS-3,and ZS-5shows crystalline nature and crystalline planes are obtained due to ZnO and SnO_2 both. The average crystalline size is obtained by using scherrer formula and has been found to be 36.42 nm, 28.33 nm, 42.5 nm respectively.

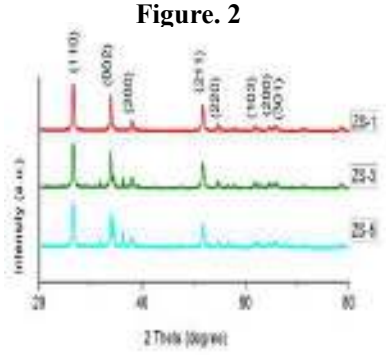

Figure. 3

Field emission Scanning Electron Microscopy (FE-SEM)

Figure (4a, 4b and 4c) decipts the FE-SEM micrograph of pristine SnO_2 and ZnO nano composites thick films. The FE-SEM morphology shows the particles are small sized, almost spherical, rod like structure. The micrograph of ZS-3 reveals that they possess the grain size of nanometre order and shows nonporous structure. It means that the structure is likely to facilitate the adsorption and condensation processes of water molecules because of the capillary pore and having large surface area. This porosity leads to an effective response and recovery towards humidity [10].

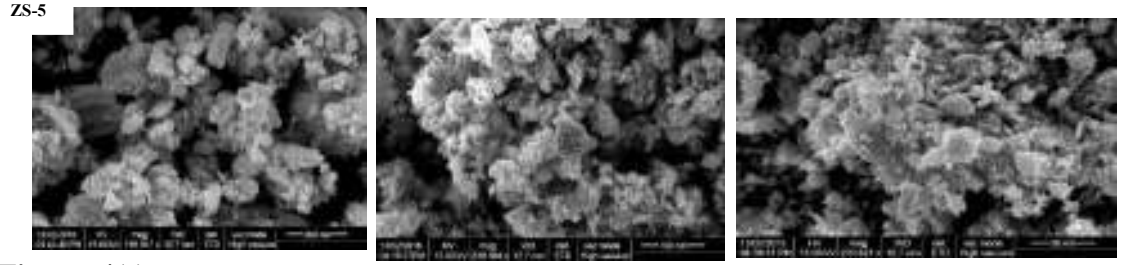

Figure. 4 (a) **Figure. 4 (b)** **Figure. 4(c)**

4. Results and Discussion

Hysteresis plot.

Hysteresis plot shows the variation between resistances of sample with respect to the relative humidity in increasing and decreasing order from 30 to 90 % RH at constant temperature as shown in the figure (5). A very small hysteresis present during forward and reverse cycle of relative humidity, where as a very significant average change observed in the value of resistance of sample, in the sample ZS-3 (30ZnO - 70SnO_2) the change in value of resistance is from 10^{11} ohm to 10^5 ohm, these is a remarkable change in the value of resistance.

In all the samples hysteresis is present which shows processes of regeneration is slower as compare to the samples. On the other hand a sample shows comparable decrease in resistance with an increase in % RH which indicates that the conduction occurred at the grain surface by release of electron from the water molecule. However, the sample ZS-3 shows the remarkable change in the resistance values in between the humidity range 30-90 % RH and possessed a high sensitivity factor due to large surface area and porosity in the form of thick films.

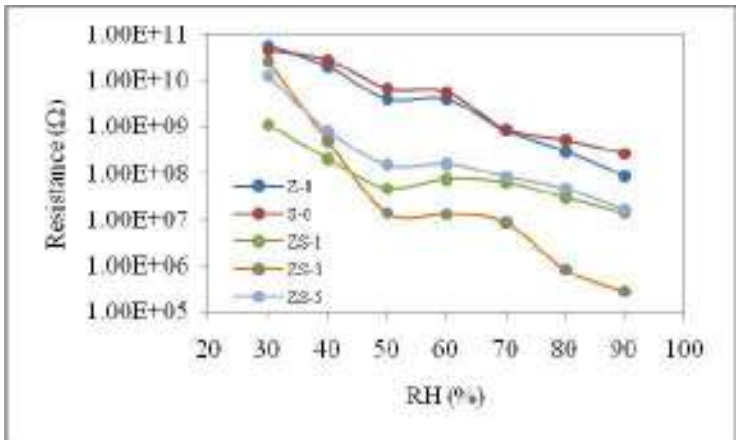

Figure 5: Hysteresis plot.

Sensitivity

In the above samples the sensitivity is found to be increasing with the RH for all the samples of thick films and it is increasing up to some particular RH and then afterward it remains constant as shown in figure (6). For higher RH the sensitivity is found to be higher in case of all samples of thick films. The sensitivity of ZS-3 (30ZnO-70SnO_2) is more than ZS-1(10ZnO-90SnO_2) and ZS-5 (50ZnO-50SnO_2) samples and also from the pristine samples S-0 and Z-0. The ZnO-SnO_2 composite sensors exhibits significantly higher sensitivity than sensor constructed specially from ZnO and SnO_2 nanoparticles itself due to the formation of heterogeneous interface between them and more adsorption site was created to absorbed more water vapuors [11]. The fall in resistance is mainly due to the increased amount of conduction electron or charge carrier upon adsorption of water vapours by the surface layer of the thick films. Initially, at low humidity levels the adsorbed water molecules get ionized on the surface and the hydronium ions are produced by the assistance of high electric charge density in the neighbourhood of the hydroxyl (OH-) sites resulting in the protonic conduction to the adjacent sites [12]. The change in conductivity is more in ZS-3 nano-composite the similar change is observed in sensitivity also and hence ZnO-SnO_2 based nano-composites sensors exhibit significantly higher sensitivity than other samples.

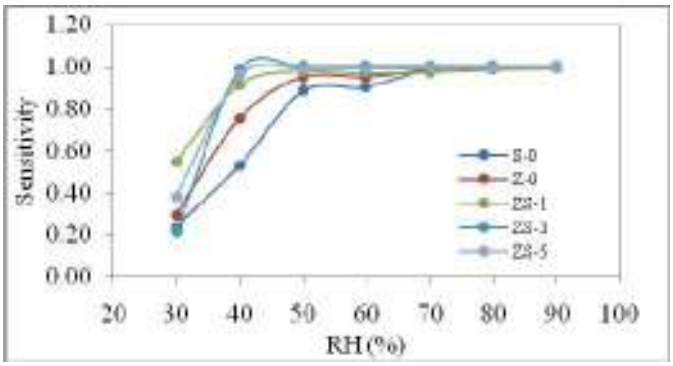

Figure 6: Variation of Relative Humidity with Sensitivity.

Activation Energy

The Arrhenius plot for all the samples found to be linear and by using Arrhenius equation;

$$\sigma = \sigma 0\ (-\Delta E/KT) \quad \text{..... (1)}$$

The activation energy ΔE For all the samples the activation is found to be quite reasonable for the electrical conduction the values of activation energy for the pristine SnO_2 and ZnO which is much more smaller at constant different RH. This shows that the smaller amount of energy is required for the conduction of electrons due to absorption of water molecules there by increasing the number of donor electron [13]. The activation energy of sample ZS-3 was found to be 1.70x 10^{-3} eV.

Conclusion

Nanostructured ZnO and SnO_2 was successfully prepared via chemical precipitation method. Minimum crystallite size was found to be for ZnO is 37.32 nm and for SnO_2 it is found to be 23.19 nm . Surface morphology of ZS-3 shows that most particles are spherical in shape leaving more space as pores and hence it was most sensitive among all the prepared samples. The Hysteresis plot shows very significant average change in the value of the resistance from 10^{11} ohm to 10^5 ohm during forward and reversed cycles of sample ZS-3(30ZnO-70SnO_2). The sensitivity is found to be increasing with the RH for all the samples of thick films and it is increasing up to some particular RH and then afterward it remains constant. Amongst all the prepared samples ZS-3 is more sensitivity than other prepared samples. Activation energy measured and found to be 1.7010^{-3}eV respectively. This nanocomposites carries a good scope for the development of moisture sensor in the range of relative humidity 30% to 90% RH.

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Effect of Uv Radiation on The Dielectric Properties of Salicylic Acid Doped Polymer Thin Film of PMMA

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Abstract: -

The thin films of PMMA, pure and doped with 1%, 3%, 5%, 7%, 9% salicylic acid (SA) were prepared by using isothermal evaporation technique .The measurement of dielectric constant (ε_r) for all above samples have been carried out within the temperature range 323k-363k and at frequencies in the range 1KHz-1MHz.The results reveal that the dielectric constant decreases with the increase in the exposure time of UV radiations. The samples were characterized by XRD, SEM and FTIR.

Key words: - PMMA-Polymethylmethacrylate, SA-Salicylic acid, UV- Ultraviolet Radiation.

Introduction:

Low dielectric materials have been intensively researched by ceramic and polymer scientists (Shen et al., 2007) (Jousseaume et al., 2007) (Singh et al., 2006). However, these materials posses a vast myriad of electrical, thermal, chemical and mechanical properties. Therefore, in many cases, the application of low dielectric constant materials are dictated by these other properties and the choice of low dielectric material may have a tremendous effect on a device's performance and lifetime.

Modern ultra-large scale integration (UWI) devices contain 10^8-10^9 transistors in an area smaller than 1 cm^2 and operate at a clock frequency approaching several GHz (Baklanov et al., 2000). As device dimensions shrink, the switching speed of its basic element increases as a consequence of the decrease in carrier's transit time across the length of a transitory channel, Of course, these basic elements must be interconnected to make the ULSI device functional.

As the functional complexity of devices increases, the number of interconnections levels and metal length continue to increase to the extent that an advanced ULSI device may consist of 8-10 levels of metal lines. For this reason, the effective speed of the device is becoming ever more dominated by the signal propagation through the horizontal and vertical metal interconnects of components with various functions. It is here that the resistance (R) and capacity (C) characteristics of the interconnect materials become important. In fact, the rapid increase in RC delay time is one of the main bottlenecks in deep submicron devices. The RC delay is given by

$$\mathbf{RC = 2\rho k\varepsilon_0 = (4L^2/P^2 + L^2/T^2)} \ldots\ldots\ldots\ldots \mathbf{(1)}$$

ρ – is the metal resistivity, ε_0 is the vacuum permittivity, k is the relative dielectric constant of interlayer dielectric (ILD), P is the metal line pitch (Sum of the line width and line spacing), T is the metal thickness and L is the metal line length. This equation demonstrates that RC delay can be reduced using metals with low resistivity and dielectric materials with a low dielectric constant. The introduction of copper and low dielectric const materials has improved

the situation as compared with the conventional Al/SiO_2 technology by reducing both the resistivity and capacitance between wires.

Copper is becoming the common metallization material. Further lowering of the signal delay by introducing low-k dielectrics is one of the main challenges today (Maex et al, 2003). A description of all the problems related to the introduction of copper and low-k dielectrics is beyond the scope of this paper and hence we have limited our discussion to approaches to decreasing the dielectric constant of polymer thin film of PMMA, So that it will act as interlayer dielectric (ILD) .

Classically, the dielectric constant of materials is described by Clausius- Mossoti Equation

$$(k-1)/(k+2) = 4\pi N\alpha \ldots\ldots\ldots\ldots\ldots (2)$$

Where, $k = \varepsilon/\varepsilon_0$

ε And ε_0 are the dielectric constants of material and vacuum, N is the number of molecules per unit volume (Molecular density) and α is total polarizability, including electronic (α_0), distortion (α_d) and orientation (α_0) polarizabilities. According to equation (2), the dielectric constant of materials can be reduced by decreasing the total polarizability and density. Early generations of low-k dielectrics were obtained by doping the traditional SiO_2 with fluorine and carbon during the chemical vapor deposition (CVD) of the dielectrics which typically have a k value in the range of 3-3.5. Other types of low-k dielectrics are based on organic polymers. Saturated hydrocarbons have a lower polarizability than unsaturated conjugated and aromatic hydrocarbons. Most of the organic low-k films with sufficient thermal stability have dielectric constant close to or in the range of 2.6-3.0. Decreasing the density produces a further reduction in the dielectric constant. Therefore, ultra low k dielectrics with k less than 2.6 must be porous (Mikhail R B et al 2006).

In this paper, we have discussed the effect of UV radiation on dielectric constant of salicylic acid doped polymer thin films of PMMA. Especially we have focused on lowering dielectric constant of thin films for the development of microelectronic devices based on low dielectric constant polymer films. For this purpose weight of PMMA in all sample remains fixed and salicylic acid doped at different weight percentage, so that we can find the optimum percentage ratio of SA that exhibits lowest dielectric constant value.

Experimental Procedure:

Materials:

In this study, PMMA (Sigma Aldrich), dopant salicylic acid (SA), and solvent THF (J.T. Baker) were used without further purification. Isothermal evaporation technique (Narayan et al., 1991) (Bahri et al., 1997) (Sangawar et al., 1995) (Belsare et al., 1998) was used to prepare the thin films of polymer.

Preparation of thin films:

1gm. PMMA was dissolved in THF (Tetrahydrofuran), and doped with salicylic acid in different weight percentage (1%, 3%, 6%, 7%, and 9%). The solution was cast on a glass plate and was allowed to evaporate slowly. This process has produced a mechanically stable and a free standing thin film.

UV Irradiation

A low pressure mercury vapor lamp (TUV 30W, Philips, Holland), which emits radiation at 254 nm, was used. The intensity of the incident light was 24 W m^{-2}. Films of the same thickness and surface area were placed at 15 cm distance from the light source. Irradiation times were for 0, 5, and 10 minutes. All irradiations were performed at room temperature in air.

Thickness Measurement:

The thickness of the film was measured by digital micrometer (Mitutago Corporation, Japan)

Dielectric constant measurement:

The AC conductivity of the samples was determined by 4284 A precision LCR meter over the frequency range 20 H_z to 1MH_z supplied by Agilent Technology, Singapore and corresponding dielectric constant (ε_r) was measured in the temperature range 323 K- 363K.

Characterization

X-ray diffraction (XRD)

The amorphousity of polymer thin films was investigated using XRD. The XRD pattern were recorded on Siemens D 5000 diffractometer with Cu-K α radiation (λ=1.54060A) over the range of $2\theta=10^{o}$-60^{o} at ambient temperature.

Scanning Electron Microscopy (SEM)

The morphology of polymer thin films at room temperature was studied by SEM.

FTIR Study:

To study the structural changes including the alteration in position and intensity of the characteristic bands Fourier Transform Infrared (FTIR) spectroscopy using Shimazu FTIR spectrophotometer 8300) over the range 400- 4000 cm-1 was used.

Prominent findings

Dielectric constant

i) decreases with increase in frequency at different constant temperatures.

ii) increases with increase in temperature at different constant frequencies
iii) decreases with increase in dopant percentage at constant temperature and constant frequency
iv) decreases with increase in time of exposure to UV radiation at constant temperature, frequency and dopant percentage.

Results and Discussion

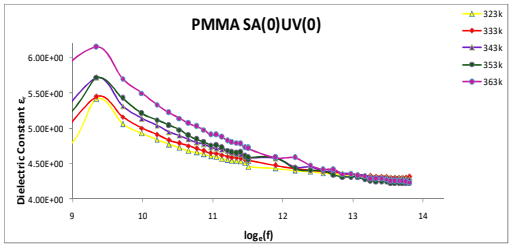

Fig 1: Variation of dielectric constant with log f at different constant temperatures

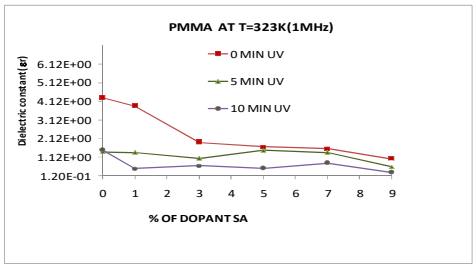

Fig 2: Variation of dielectric constant with percentage of dopant at increasing time of exposure to UV radiation

From fig.1 it is clear that dielectric constant decreases with the increase in frequency and increases with the increase in temperature. This can be explained as PMMA is weakly polar polymer (Tager et al., 1972) under alternating electric field, polar polymers require some time to align the dipoles. At very low frequencies the dipoles have sufficient time to align with the field before it changes direction. At very high frequencies the dipoles do not have time to align before the field changes direction. At intermediate frequencies the dipoles move but have not completed their movement before the field changes direction and they must realign with the changed field. The electronic polarization and to some extent atomic polarization, is instantaneous, at high or low frequency for both polar and non polar polymers. Therefore, polar polymers at low frequencies (e.g. 60 Hz) generally have dielectric constants of between 3 and 9, and at high frequencies (eg 1MHz) generally have dielectric constants of between 3 and 5. So as frequency increases, the orientational polarization decreases since it takes more time than electronic and atomic polarization .This decreases the value of dielectric constant with frequency reaching a nearly constant value at high frequency. The motion possibly occurring in amorphous material in the order of increasing temperature are: side chain motion, motion of two four moieties in the main chain (The Schatzki Cruck shaft effect), motion of moieties containing hetero atoms in polymer chain, motion of segments containing 50-100 backbone atoms (corresponding to Tg) and motion of the entire chain as a unit (Seanor1982). These motions are responsible for the freeing of change carriers and assisting the orientation of polar species as per the variation in the direction of applied AC electric field of constant frequency. The total polarization of the sample arises from the electronic polarization, atomic or ionic polarization and orientation polarization. Among these three contributions; orientation polarization is greatly assisted by the increase of

temperature. This result is in agreement with those reported in the literature (Muhd. Akram et al., 2005; Reda 2006; Rao et al. 2000). The dielectric polarization results from molecular dipoles (Goel et al.,2000,Srivastava et al.,1977) ,which remain frozen at lower temperature and attains rotational freedom at higher temperature ,when the effect of molecular interaction energy becomes weaker than that of the thermal energy (Goel et al.,2000) .Therefore dielectric constant increases with temperature.

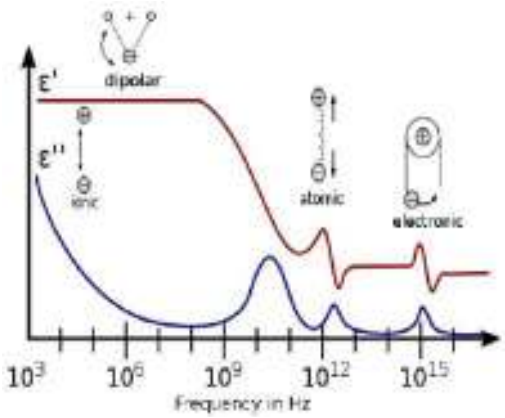

Fig 3 Dielectric constant and loss dispersion of dielectric materials against frequency.

The dielectric constant gets decreased with the increase in dopant percentage (Fig 2). As the dopant salicylic acid has –OH and –COOH groups ortho to each other, both these groups have tendency to release their hydrogen atoms as H^+ ions and the –COO group is electron hungry segment of PMMA that attracts the electrons present in C-CH and O-CH_3 bonds towards itself. As a result of this, a drift of electrons from nearby bonds starts flowing towards the COO group that imparts polarity in the parent molecule. But due to proximity and availability of electron rich centers within the molecule, the H^+ ions of Salicylic acid tend to form intramolecular hydrogen bonding. As a consequence of this, dopant salicylic acid remains unmoved. Under vigorous conditions, these H^+ ions may get departed partially but it is difficult to break their association completely from parent molecule. In this situation if we go on increasing the percentage of doping that may enhance the complexity due to which the dielectric constant gets decreased with the increase in dopant percentage.

From fig 2 it is clear that, before irradiation value of dielectric constant is in the range of 4.3-1.03. After irradiation the value of dielectric constant is in range 1.5-0.64 for 5 min irradiation and for 10 min irradiation value is in the range of 1.5- 0.30.This means the dielectric constant gets decreased with the increase in time of exposure and the rate at which the dielectric constant decreases also becomes higher with the increase in time of exposure. This can be explained as; the bonds between the atoms in many polymers have dissociation energies that are very similar to the quantum energy present in UV radiation which is capable of breaking the bonds in the polymer chain to generate a cascade of reaction, oxygen radicals, hydro peroxide unit's carbonyl group formation, chain cleavage. As a result, the polarization group may get reduced and dielectric constant gets decreased as shown in fig (2) (Scierka et al, 2003).Also the evaporation of THF solvent during the preparation of thin film may have led to the formation of pores in the thin film (Stephan A. M. et al., 2000). It should be emphasized that the formation of porous film follows the principle of phase separation. In this principle one phase is induced to create the matrix and the other (i.e. solvent) to create convex surface shapes, which can be

removed to leave free space by evaporation. Decreasing the density produces a further reduction in the dielectric constant. Therefore, ultra low k dielectrics with k less than 2.6 must be porous (Mikhail R B et al 2006). So from above explanation, we can say that after exposure the porosity in film gets increased (Khol et al., 2006) .But lowest value of dielectric constant observed for PMMA SA (9) at 5 and 10 min exposure is 0.60 and 0.30 which is very less than dielectric constant of air .As reported by Mikaail Ballanov et al, the material with dielectric constant less than 2.6 must be porous and materials with dielectric constant less than one is called metamaterials (Dixon 2012). These materials are made with high dielectric inclusions with specific shapes and sizes in a lower dielectric matrix.

So here we conclude that, the dielectric constant of material can be reduced by doping with salicylic acid and increasing time of exposure to UV radiation and with increase in time of irradiation the porous material becomes to metamaterials.

The FTIR spectra of PMMA shows the presence of C=O stretching at 1064cm^{-1}confirms the presence of ester moiety. The bend for CH_2 is observed at 1442cm $^{-1}$ also for CH^3 at 1367cm^{-1}.The sp^3 C-H stretching has been observed at 2854cm $^{-1}$ .The IR spectrum of PMMA SA (3) and PMMA SA (9) shows the C=O stretching at 1612.49 cm^{-1}.The SEM photographs (Fig 5) shows the amorphous nature of PMMA SA (0), PMMA SA (3), PMMASA (9) which is in agreement with XRD results (Fig 6)

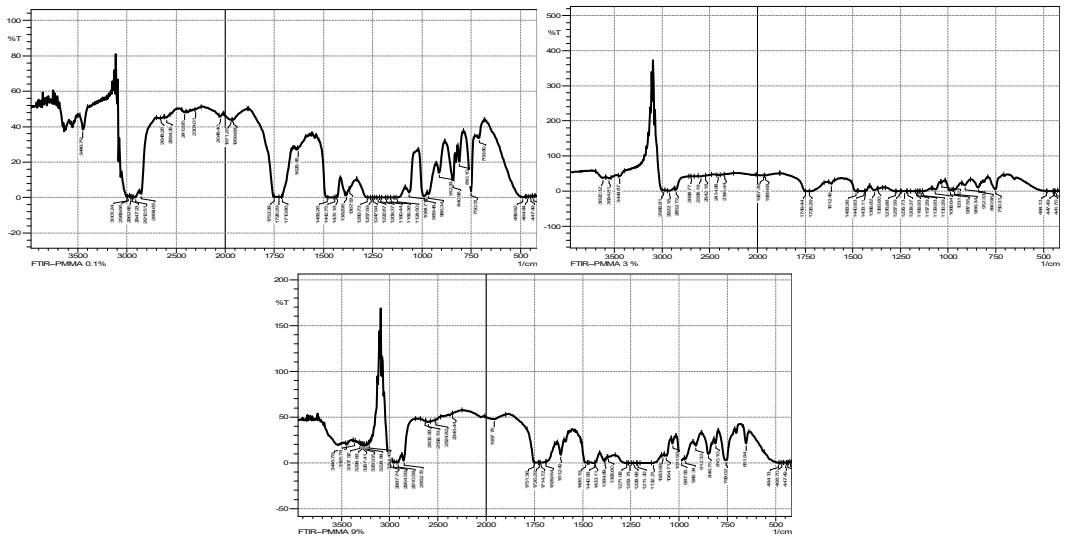

Fig 4: FTIR spectra of a) PMMA SA (0) b) PMMA SA (3) c) PMMA SA (9)

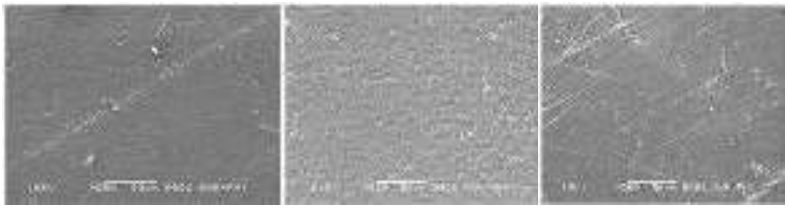

Fig 5: SEM images for a) PMMA SA (0) b) PMMA SA (3) c) PMMA SA (9)

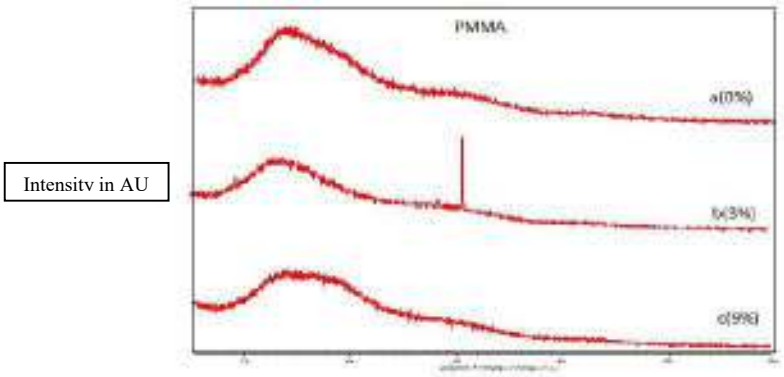

Fig 6: XRD spectra of a) PMMA SA (0) b) PMMA SA (3) c) PMMA SA (9)

Conclusion:

The dielectric constant of thin films of PMMA, pure and doped with salicylic acid at different weight percentage, can be reduced by doping with salicylic acid and by exposure to UV radiation so that it can be used as interlayer dielectrics in microelectronic devices.

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Surface Activated Cr_2O_3 Based Thick Film for Ammonia Gas Sensing

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Abstract:

Pure chromium oxide (Cr_2O_3) nanoparticles powder was prepared by chemical co-precipitation method. The structural behaviour of Cr_2O_3 nanoparticles was examined by X-ray diffraction. Thick films of pure chromium oxide were prepared by the screen printing technique. The Fe_2O_3-modified films obtained by dipping pure Cr_2O_3 thick films into an aqueous solution of ferric chloride ($FeCl_3$) for 3min. and fired at 500^0C for 30 min. Pure and Fe_2O_3 modified Cr_2O_3 thick films were examined by FE-SEM and EDX. Thick film of pure chromium oxide was almost insensitive to ammonia gas. Thick film of Fe_2O_3-modified Cr_2O_3 (3 min dipped) was observed to be highly sensitive to ammonia at100^0C. The instant response and fast recovery are the main features of this sensor. The effects of surface modification on the gas response, selectivity, response time and recovery time of Cr_2O_3 based thick film gas sensor in the presence of NH_3, Cl_2, LPG, CO_2, H_2S and C_2H_5OH gases ware studied and discussed.

Keywords: Chromium oxide, X-ray diffraction, Ammonia gas, Gas response.

Introduction

The metal oxides based semiconductor gas sensors are playing an important role in the detection of toxic pollutants in air and to control the industrial processes. It is observed that when the sensors are exposed to the atmosphere, the chemical species to be detected in the atmosphere can enter in to the interface of the p-n junction. So there are changes in electrical properties at the junction [1-3]. Therefore, the gas sensors were synthesised by using, ZnO, SnO_2, TiO_2, WO_3, Cr_2O_3**,** etc**.** materials in pure and modified forms to detect toxic, harmful, flammable and explosive gases [4,5] in the environment. Cr_2O_3 has a Hexagonal-Rhombic corundum crystal structure showing p-type semi- conductivity and has a high melting temperature (~ 2300^0C). In the recent years, p-type Cr_2O_3 is useful for sensor applications as it has an energy band gap of ~3.4 eV and widely been used in variety of applications, such as, catalytic reactions, optical coating and infrared sensors [6–9]. It has been studied that Cr_2O_3 [10-13] is used as a gas-sensing materials. Cr_2O_3 is the transition-metal oxide and the transition-metal oxides are more sensitive to the change of outside ambient and these types of oxides could be more preferable for the use in gas sensors [14]. It has been found that a pure Cr_2O_3 thick film has poor gas sensitivity to reducing gases but Fe_2O_3 modified Cr_2O_3 thick film is the most sensitive to LPG, C_2H_5OH, NH_3 and Cl_2 gases [12].

The particle size plays an important role in gas sensing. The reduction in grain-size is one of the prominent factors for enhancing the gas sensing properties of semiconducting oxides. Many preparation techniques for synthesis of Cr_2O_3 nanoparticles are described, such as hydrothermal reduction [15], solid thermal decomposition [16], urea method [17], and mechanochemical reaction [18], etc. In present work, co-precipitation methods (chemical route methods) were adopted, as they are easy, suitable and economically low coast to synthesize Cr_2O_3 nanostructures.

The aim of the present work is to fabricate the ammonia sensor by modifying pure Cr_2O_3 thick films, which is able to detect ammonia at trace levels. Among the various metal oxide additives tested, Fe_2O_3 is outstanding in promoting the sensing properties of the Cr_2O_3 sensor for ammonia. The present paper reports the structural, morphological and gas sensing properties of pure and Fe_2O_3 modified Cr_2O_3 based thick films.

Experimental Details

Preparation of Nanocrystalline Cr_2O_3 Powders

All chemicals were of analytical grade and used directly without further purification. Nanocrystalline Cr_2O_3 powders were synthesized by chemical precipitation method. The details regarding preparation of nanocrystalline Cr_2O_3 was already published in our earlier publication [19]. The synthesized Cr_2O_3 nanostructure product was used for further study.

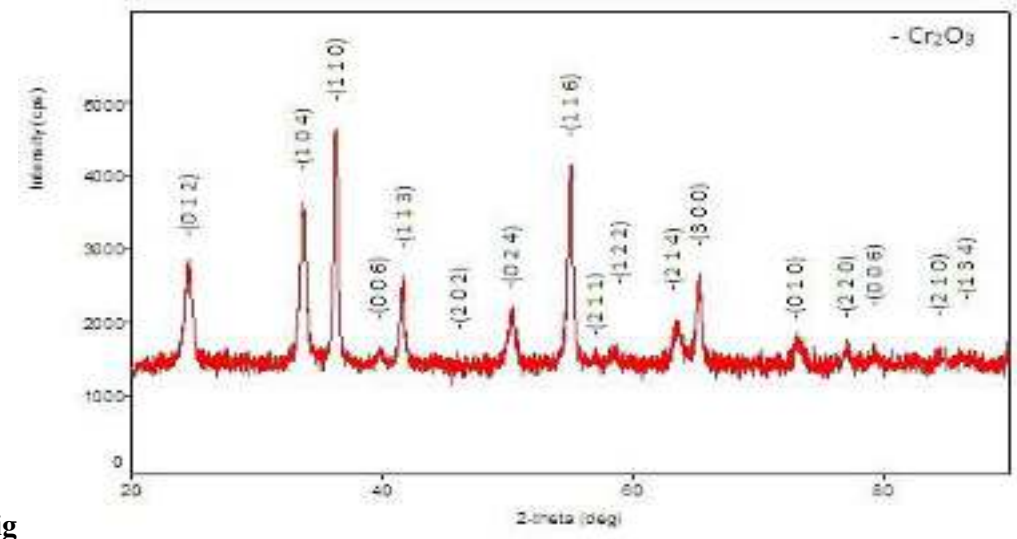
Fabrication of thick films and Fe_2O_3 modified Cr_2O_3 thick films

Thick films of pure chromium oxide were prepared by the screen printing technique. In this process thixotropic paste was formulated by proper method and then the thixotropic pastes were screen printed on a glass substrate in desired patterns. The films prepared were fired at 500^0C for 12 h. Prepared thick films termed as pure Cr_2O_3 thick films. The surfaces of pure Cr_2O_3 thick films were modified by dipping them into 0.01M aqueous solution of $FeCl_3$ for 3 min. The $FeCl_3$ dispersed on the film surface was oxidised to Fe_2O_3 in firing process and sensor elements with Fe_2O_3 on the surface of Cr_2O_3 thick films were obtained. These surface modified thick films are termed as Fe_2O_3 modified Cr_2O_3 thick films.

Results and discussion

X-ray diffraction

Fig. 1 shows X-ray diffraction (XRD) pattern of synthesized pure Cr_2O_3 powder sample. The observed peaks are matching well with JCPDS reported data of pure Cr_2O_3 with hexagonal in structure (JCPDS card no.70-3766). The characteristic peaks observed in the spectrum are higher in intensity which indicates that the as-synthesized samples are of good crystalline in nature. The domain size of the crystal can be estimated from the full width at half maximum (FWHM) of the peaks by means of the Scherrer formula [20]. The average crystallite size (D) was estimated from the Debye–Scherrer's equation: $D = 0.9\ \lambda / \beta \cos\theta$; where λ is the wavelength of X-rays (1.54056 Å), β is the FWHM of the peak in radians, θ is the diffraction angle at which the full width at half maximum (FWHM) measured and k =0.9, is Scherrer constant. The average crystallite size of the synthesized Cr_2O_3 nanoparticles calculated from (110) peak was approximately 26 nm.

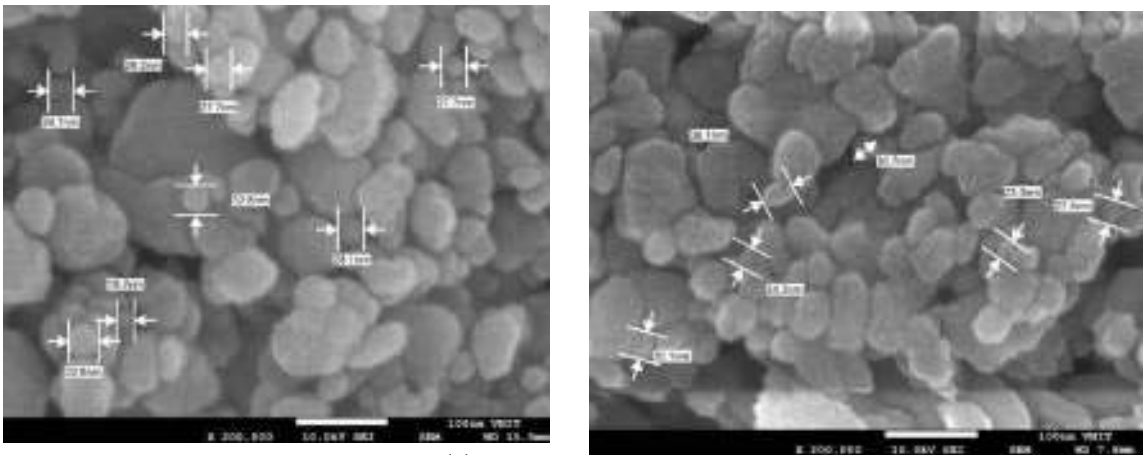


Fig

Scanning electron microscopy

Fig. 2 (a-b) depicts the FE-SEM images of the pure Cr_2O_3 film and Fe_2O_3 modified Cr_2O_3 thick film (3 min dipped). Fig. 2 (a) shows the FE-SEM image of the pure Cr_2O_3 film, which consists of randomly distributed grains with larger size and shape distribution. The average size of Cr_2O_3 grains are approximately 37 nm. The appearance of the film looks porous, which supports the adsorption and desorption type of gas sensing mechanism. The nano scaled grains exhibit high surface to volume ratio.

Fig. 2 (b) depicts the microstructure of Fe_2O_3 modified Cr_2O_3 thick film for 3 min dipped consists of large number of almost similar sized grains of Fe_2O_3 associated with the comparable sized grains of Cr_2O_3.The film consists of grains with sizes ranging from 19 nm to 33 nm distributed non-uniformly. The appearance of the film looks porous in nature (not looks masked). Thus increase in surface to volume ratio, which enhances the large number of gas adsorption upon exposure giving larger gas response. This film is observed to be the most sensitive to 100 ppm NH_3 gas at 100 ^{0}C due to its porous nature.



(a)

(b)

Fig. 2: FE-SEM microstructures for (a) Pure Cr_2O_3 thick film (b) Fe_2O_3 modified Cr_2O_3 thick film (3 min dipped)

Quantitative Elemental Analysis (EDX)

The quantitative elemental composition of the pure and Fe_2O_3 modified Cr_2O_3 thick films were analyzed using an Energy Dispersive Spectrometer (EDS). Fig.3 (a-b) represents the EDS patterns of pure and Fe_2O_3 modified Cr_2O_3thick films (3min dipped). In chromium oxide, stoichiometric mass percentage of chromium and oxygen are 68.420 and 31.580 respectively.

The prepared powder of pure Cr_2O_3 is excess in oxygen, which increases its p-typeness characteristic. It leads to semiconducting nature of the synthesized pure Cr_2O_3. Excess or deficiency of the constituent element leads to the semiconducting nature of the material. Also, the mass % of Cr and O in each activated samples are not as per the stoichiometric proportion and all samples are observed to be oxygen deficient or excess in chromium. Thus, the maximum numbers of electrons are free to conduct the current and electrons behave as the majority current carriers. This enhances n-typeness of activated Cr_2O_3. Thus, dipping process is the simple and low cost technique to activate the surface of the film. This forms heterojunctions on the surface of the film which increases the resistivity.

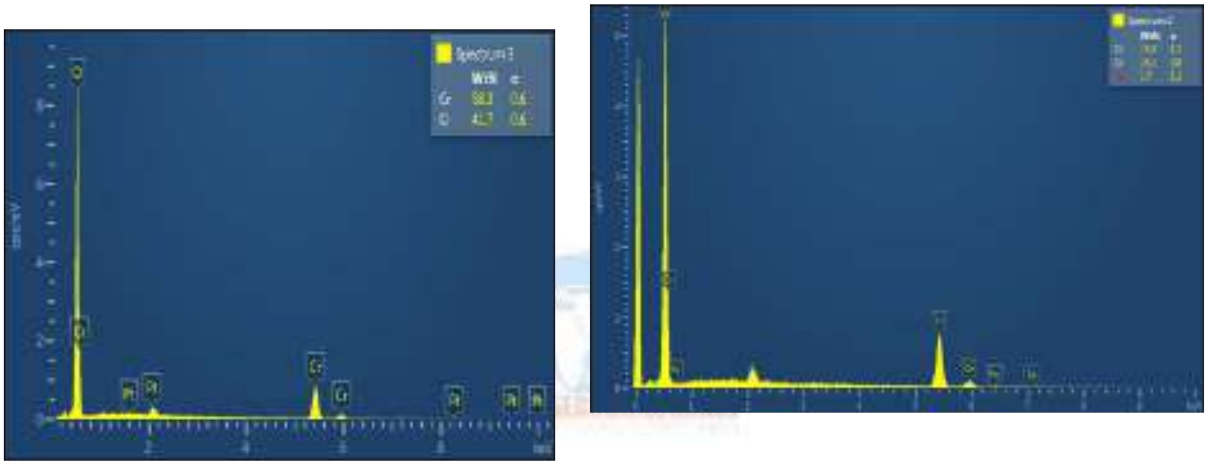


Fig.3: EDS patterns for a) pure Cr_2O_3 thick film b) Fe_2O_3 modified Cr_2O_3 thick film (3 min dipped)

I-V characteristics pure and Fe_2O_3 modified Cr_2O_3 thick films

Fig.4 depicts the I-V characteristics of pure and Fe_2O_3 modified Cr_2O_3 thick films. It is clear from the symmetrical I-V characteristics that the silver contacts on the film were ohmic in nature. Fig. 4 also shows that the conductivity of pure Cr_2O_3 film is larger than Fe_2O_3 modified Cr_2O_3 thick films.

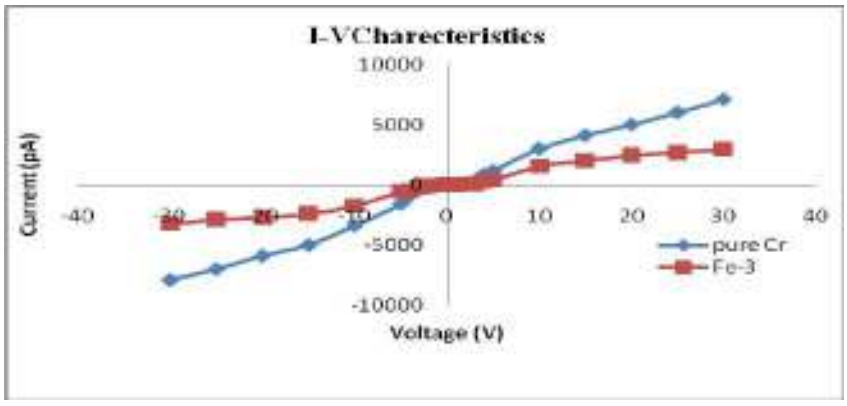


Fig.4: I-V characteristics of pure and Fe_2O_3 modified Cr_2O_3 thick films at room temperature.

Gas Sensing Performance of Pure and Fe_2O_3 modified Cr_2O_3 thick films

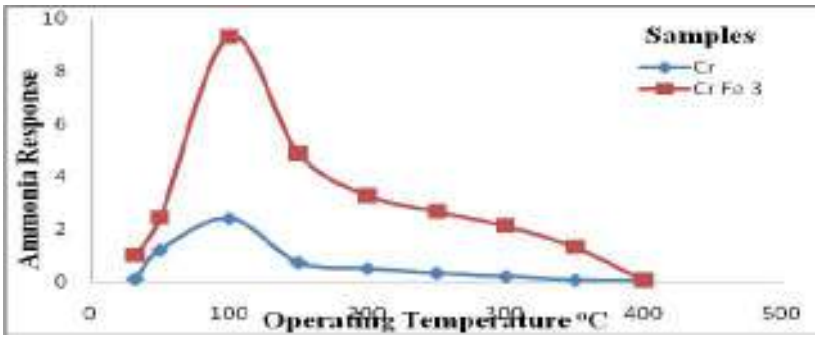


Fig 5: Variation of gas response of pure and Fe_2O_3 modified Cr_2O_3 thick films with operating temperature

Fig. 5 depicts the gas response of pure and Fe_2O_3 modified Cr_2O_3 thick films versus operating temperature. The gas response of pure and Fe_2O_3 modified Cr_2O_3 thick films to 100 ppm NH_3 were investigated at various operating temperatures ranging from room temperature to 400^0C. Fig. 5 also shows that the gas response to NH_3 gas goes on increasing with operating temperature, reaches to a maximum at 100^0C and then decreases with the further increase of operating temperature. As we know that, response to a NH_3 gas is generally depends on the number of oxygen ions adsorbed on the surface of the film with a target gas. If the film surface chemistry was favourable for adsorption, response and selectivity would be enhanced. In the case of pure Cr_2O_3 thick film, oxygen adsorption seems to be poor and hence it shows poor response to NH_3. So, to improve and enhance the sensing performance of pure Cr_2O_3, it is essential to modify pure Cr_2O_3. It is also clear from figure that Fe_2O_3 modified Cr_2O_3 thick film at 3 min dipping time gives highest response to 100 ppm NH_3 at 100^0C. When the optimum amount of Fe_2O_3 (3 min dipping) is dispersed on the surface of Cr_2O_3 thick film, the Fe_2O_3 grains would be distributed uniformly throughout the surface film. These Fe_2O_3 grains form potential barrier (p-n heterojunctions) with Cr_2O_3. Due this potential barrier, sensor element offers high resistance. So such amount of high resistance would be sufficient to promote the catalytic reaction effectively. These overall changes lead to high gas response when this type of sensor element expose to NH_3 gas.

Fig. 6 depicts the selectivity of all, pure and Fe_2O_3 modified Cr_2O_3 thick films towards LPG, C_2H_5OH, CO_2, NH_3, H_2S and Cl_2 for 100 ppm concentration at100^0C. It is observed from figure that the 3 min. dipped Fe_2O_3 modified Cr_2O_3 thick film is most sensitive to NH_3 gas at100^0C among all other tested gas.

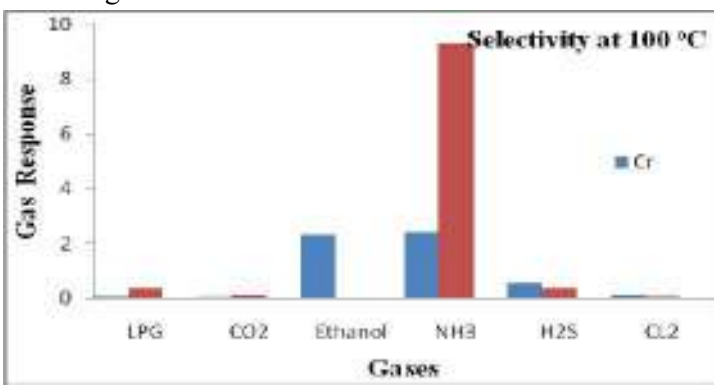


Fig. 6: Selectivity of pure and Fe_2O_3 modified Cr_2O_3 thick films.

Fig. 7 exhibits the relation between gas response of pure and Fe_2O_3 modified Cr_2O_3 thick films and concentration of NH_3 gas at 100^0C. It is clear from the figure that the gas response of Fe_2O_3 modified Cr_2O_3 thick film (3 min dipping) increases linearly with gas concentration up to 100 ppm. The rate of increase in response was relatively larger up to 100 ppm and saturated beyond 100 ppm. The active region for the ammonia sensor is up to 100 ppm. At low gas concentration, the monolayer of NH_3 gas molecules formed on the surface of film. So, the NH_3 response increases in proportion up to active region. At high gas concentration, the multilayer of NH_3 gas molecules on the sensor surface would result into saturation in response beyond 100 ppm gas. So, for proper functioning, the sensor should work in the active region only.

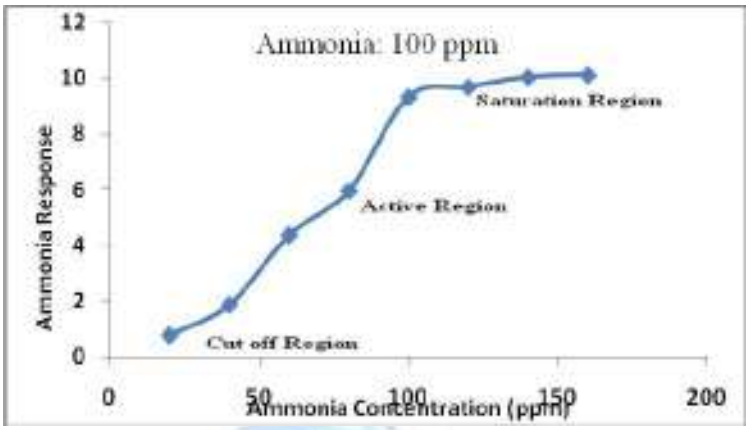


Fig 7: Variation of NH_3 response with NH_3 concentration (ppm)

The response and recovery of the Fe_2O_3 modified Cr_2O_3 thick film (3 min. dipped) to 100 ppm of NH_3 are 7 s and 10 s respectively. Thus the sensor showed very rapid response and recovery time to NH_3 gas. For better performance of the sensor the recovery should be very fast. When the gas exposure was switched off, the sensor returned back to its original chemical status, within very short time (10 s). This is the main feature of this sensor.

The response of this sensor towards 100 ppm of NH_3 gas at 100^0C was measured for two month in the interval of 10 days and found almost constant. The good stability could be attributed to calcinations at high temperature and aging of sample for a few days. Thus the sensor showed a very stable response confirming the stability and hence reproducibility of the material.

Gas sensing mechanism

In sensor, the surface is the region where periodicity of the crystal can be interrupted. Due to this, localized energy levels are formed in the forbidden gap, which can either capture electrons or give up electrons. In case of pure or Fe_2O_3 modified Cr_2O_3, the surface oxygen ions donate electrons. The response could be attributed to the adsorption-desorption type sensing mechanism. Gas Oxidation depends upon the amount of oxygen species ($O_2^- \rightarrow 2O^- \rightarrow O^{2-}$) adsorbed on the surface. Gas sensing mechanism is mostly explained in terms of conductance, by adsorption of atmospheric oxygen on the surface or by direct reaction of lattice oxygen or interstitial oxygen with the test gases. The working principle of thick film semiconducting gas sensors is based on the change of the electronic conductivity of the semiconducting material on exposure of target gas. In such mechanism, the atmospheric oxygen molecules O_2 (air) are adsorbed on the surface of the thick film. They capture the electrons from the conduction band of the thick film material as:

$$O_{2\,(air)} + 4\,e^-_{(cond.band)} \rightarrow 2\,O^{2-}_{(film\ surface)}$$

It would result in decreasing conductivity of the film. As we know that, the lone pair of electrons of NH_3 provides strong electron acceptor behaviour. But it acts as an electron donor to the metal oxide, when reacted with the adsorbed oxygen ions on the surface by returning the trapped electrons to conduction band. The reactions that generates free electrons when the number of oxygen ions reacted with NH_3 molecules, given in the following equations [21].

$$4NH_3 + 3O_{2\,(adsorbed)} \rightarrow 6H_2O + 2N_2 + 6e-$$

Or

$$2NH_3 + 3O^-_{(adsorbed)} \rightarrow 3H_2O + N_2 + 3e-$$

Upon exposure, ammonia molecules react with adsorbed oxygen on the surface of the film got oxidized to nitrogen oxide gas and water vapors as the products liberating free electrons in the conduction band. The following possible reaction would take place.

$$2\,NH_3 + 7\,O^{2-}_{(film\ surface)} \longrightarrow 2\,NO_2\uparrow + 3\,H_2O\uparrow + 14\,e^-$$

Conclusions

The results of pure and Fe_2O_3 modified Cr_2O_3 thick films can be summarized as follows

1. The pure Cr_2O_3 film was more conductive than Fe_2O_3 modified Cr_2O_3 thick film (3min dipped).
2. Fe_2O_3 was found to be outstanding in enhancing the gas sensing performance of Cr_2O_3 based gas sensors.
3. Surface modification by dipping process was one of the most useful methods of modifying the thick film surface for the gas sensing performance of metal oxide based gas sensors.
4. A pure Cr_2O_3 thick film was almost insensitive to all tested reducing gases.
5. Fe_2O_3 modified Cr_2O_3 thick film (3 min dip) showed higher gas response to 100 ppm at 100^0C.
6. The sensor showed good selectivity to NH_3 gas against Cl_2, LPG, CO_2, H_2S and C_2H_5OH gases at 100^0C.
7. The sensor showed very rapid response and recovery time to NH_3 gas.

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Study of Variation of Ac Electrical Conductivity of 4:1 PMMA+PS Polyblends With Constant Temperature and Varying Frequency

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Abstract :

It is intended to use the polymers such as PMMA:PS. The polyblends are prepared by using these polymers in different proportions. The polyblends formed by using these component polymers with the addition of some dopent (malonic acid) or THF tried to modify their electrical and dialectical properties.

Introduction :

The term "polymer" is derived from the Greek "poly", meaning "many" and "mer", meaning "parts"- thus POLYMERS are substances made of "many parts".In most cases the parts are small molecules which react together hundreds, or thousands, or millions of times. A molecule used in producing a polymer is a "monomer"- mono means single.

The resulting molecules may be long, straight chains, or they may be branched, with small chain extending out from the molecular backbone. The size of polymer molecule is important. A polymer is analogous to a necklace made from many small monomers (beads).

The process by which the monomer molecules are linked to form a big polymer molecule is called "polymerization". Polymers range from families synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. The term was coined in 1883 by Jones Jacob Berzelius, through with a definition distinct from the modern IUPAC definition. Unmatched in the diversity of their properties, polymers such as cotton, wool, rubber, Teflon and all plastic are use in nearly every industry. Natural and synthetic polymers can be produced with a wide range of stiffness strength, heat resistance, density and even price. With continue research into the science and applications of polymers, they are playing an ever increasing role society.

When two or more polymers are mixed together, polyblends or polymer alloys are obtained. This physical mixing or blending of two polymers produces alloys with quite different properties, which can be potentially useful (Bahadur, 2003). Two polymers are generally incompatible as they have very low combinatorial entropy of mixing for the components. This is insufficient to overcome the positive heat of mixing of polymers to make the Gibb's free energy of mixing negative. Only in the presence of specific interaction between two polymers (e.g. Hydrogen bonding, acid-base type interaction etc.), heat of mixing is negative that makes the free energy of mixing a negative quantity and then the mixing is spontaneous.Two polymers may form the compatible blend, which exists as single phase. The incompatible blends on the other hand exist as two- phase system. Since most blends combine immiscible components and so the material that results contains tiny particles of one polymer in a matrix of the other. Controlled mixing and cooling of the blend makes it possible to form the particles in the optimum concentration and range of sizes. Blending makes it possible to combine the good properties of several polymers. The most direct method to obtain a polyblend is to mix two component polymers in the molten state (melt mixing). In this case the extent of mixing depends on the rate

of diffusion of the molecules. Since such a mixing requires high temperature, the polymer may decompose and undergo chemical transformation. It is, therefore, that mixing process is restricted to thermally stable polymers.Another process involves the mixing of two polymers lattices performed by emulsion polymerization technique. The polyblend can be obtained by coagulating the mixed latex system. A polyblend can also be obtained by mixing the polymers in a mutual solvents followed by the removal of solvent e.g. by drying.

Method and Preperation:

It is intended to use the polymers such as PMMA: PS. The polyblends will be prepared by using these polymers in different proportions. The polyblends formed by using these component polymers with the addition of some doping will be tried to modify their electrical and dialectical properties. The methodology to be use in progress of the work can be broadly classified into following stages.

1) Selection of polymer materials, their solvent which are useful in the field of insulating, electrical, dielectrical application in the blended forms.

2) Selection of power measuring instrument, electrical and electronic
circuits. Designing of essential circuits and sample holders suitable for system.

3) Preparation of homogeneous solution of the base polymers to form polyblends, which will be further converted in the form of thin film
samples to measure their electrical and dialectical properties.

4) Arrangement of experimental setup to carry out the measurement.

5) Tabulations, calculations and study of the results obtained.

6) Comparison of the results obtained with the standard properties. Analysis
and new finding in the blend systems.

Measurement of AC Electrical Conductivity and Dielectric Constant:

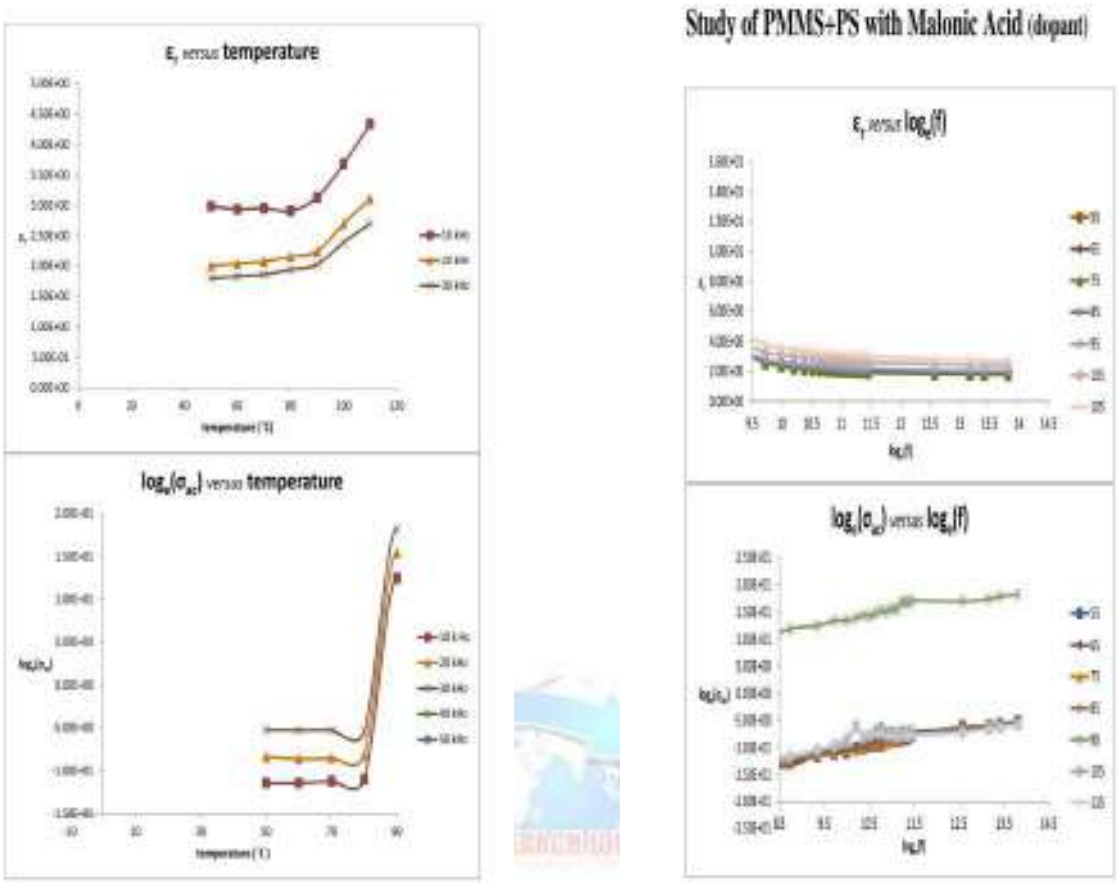
The film sample was loaded into the sample holder in an oven (as shown in above figure). The AC frequencies were applied (in the range 1 KHz –1 MHz) across the sample by using the 4284 A precision LCR meter (20 Hz –1 MHz) supplied by Agilent Technologies, Singapore. The corresponding dielectric constants were measured by using LCR meter. From the dielectric data, the AC conductivity of the samples was calculated by using the relation [Rao, 2000].

Measurement of film thickness:

The thickness of each sample film was measured at four different places by using a digital micrometer. The average of the four readings (which were nearly same) was takes as the sample thickness.

Measurement of AC Electrical Conductivity and Dielectric

Study of PMMA+PS without Malonic Acid **Study of PMMA+PS with Malonic Acid**



Study of PMMA+PS without Malonic Acid

Constant:

The film sample was loaded into the sample holder in an oven (as shown in above figure). The AC frequencies were applied (in the range 1 KHz –1 MHz) across the sample by using the 4284 A precision LCR meter (20 Hz –1 MHz) suppliedy Agilent Technologies, Singapore. The corresponding dielectric constants were measured by sing the relation [Rao, 2000].

Results and Discussion:

From the graph it is conclude that as we increase the frequency, ac conductivity increases linearly at constant temperature i.e it obeys ohms law. It is conclude that , conductivity of all samples shows the increase with respect to the rise in temperature.

Conclusion:

In 4:1 PMMA PS polyblend , conductivity increases with increase of temperature.
Rise in electrical conductivity from undoped melonic acid.In 4:1 PMMA + PS polyblend, conductivity increases with

1) Increase in temperature.
2) Increase of electric field.

Rise in electrical conductivity from undoped of malonic acid is less marked while electrical conductivity increases very remarkably as the dopent percentage is increases.

* Range of variation of electrical conductivity suggests that the doped polyblends are predominantly insulators.

* They demonstrate semiconducting properties in a sense that the electrical conductivity icreases with temperature.

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AC Conductivity and Dielectric Study of PVA Based Solid Polymer Electrolyte

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Abstract :

The solid polymer electrolytes based on polyvinyl alcohol doped with ammonium bromide was prepared using solution cast technique. The ionic conductivity has been found to increase with increasing salt concentration upto 25mol% and increase with increasing temperature. Dielectric constant and dielectric loss decreases exponentially with increases of frequency for ammonium bromide doped PVA polymer electrolyte.

Keyword- Electrical properties, Ammonium bromide, polyvinyl alcohol,

Introduction :

In recent year, researcher fascinated toward solid proton conductor due to their ease of handling, low cost, high environment stability. Studies on electrical properties has been driven special attention due to their potential application in electronic devices such as rechargeable batteries, supper capacitor, fuel cells, gas sensors and electrochromic display devices [1-4]. The role of polymer electrolyte in these application are provide good electrode –electrolyte interface, provide good electrolyte insulation and allow a fast and selective transport of the ions. It is extremely important to understand the charge transport mechanism of polymer electrolyte for practical application. Electrical properties of polymer can be suitability modified by adding of salt. In present study, PVA has been chosen as polymer host due to their mechanical strength, excellent film-forming ability, dopant-depenent electrical and optical properties, low cost and high tensile strength (5-6). PVA is semicrystalline material and it contain hydroxyl group attach to methane carbon which can be source of hydrogen bounding. As per literature survey ammonium salt are very good proton donor (7-8).

Experimental details;

In the present study, polyvinyl alcohol, ammonium bromide, and double distilled water were used to prepare solid polymer electrolyte. The film of pure and different composition of PVA-NH_4Br has been prepared by solution cast technique. In this technique, appropriate amount of PVA and NH_4Br have been dissolved individually in double distilled water .These solution have been mixed together in different molar ratio (95:05) (90:10) (85:15) (80:20) (75:25) and stirred well by using magnetic stirred for 10-12 hr to obtained homogenous mixture. The obtained mixture is casted in petri dish. The whole assembly was placed in dust free chamber. The solvent was allowed to evaporate slowly at room temperature for 3-4 days. The thicknesses of the film were in the range of 0.032-0.021 mm.

Result and Discussion

The frequency dependent conductivity

Fig (1a) shows the variation of AC conductivity with frequency for pure PVA and doped with different concentration of ammonium bromide and Fig (1b) shows the Variation of AC conductivity with frequency at different temperature for 25 mol % NH_4Br.

It is observed that the frequency dependent conductivity spectra consist of three different regions, low-frequency region, a frequency-independent plateau region in the mid frequency and final high frequency region.

The low frequency region is observed to the space charge polarization at the blocking electrode [9]. The plateau region observed at intermediate frequency corresponds to the frequency-independent conductivity. This conductivity value was assigned to the bulk conductivity of the (σ_{dc}). The high frequency region, corresponding to bulk relaxation phenomena [10]. The total conductivity of polymer electrolytes may be expressed using Jonscher's universal power law equation [11].

$$\sigma(\omega) = \sigma_{dc} + A\omega^{s} = \sigma_{dc} + \sigma_{ac} \quad \text{----------(1)}$$

where σ_{dc} is the frequency-dependent conductivity of the prepared polymer electrolyte. A is the temperature dependent parameter and s is the power law exponent.

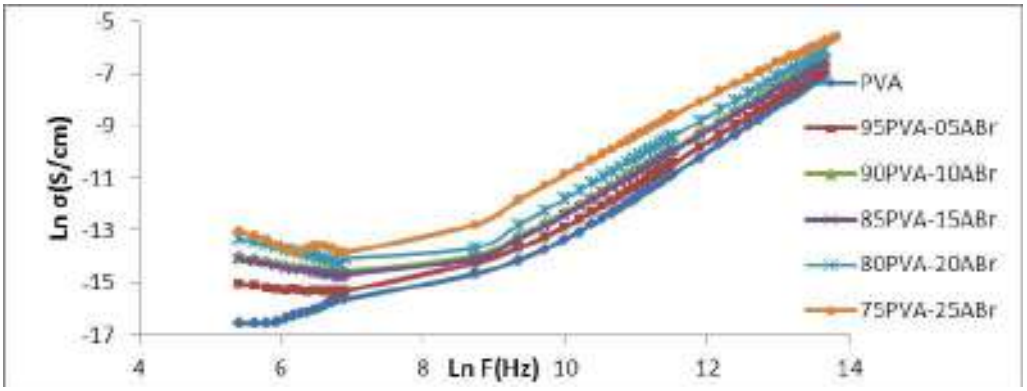

Fig 1a. Variation of AC conductivity with frequency for pure PVA and doped with different concentration of ammonium bromide

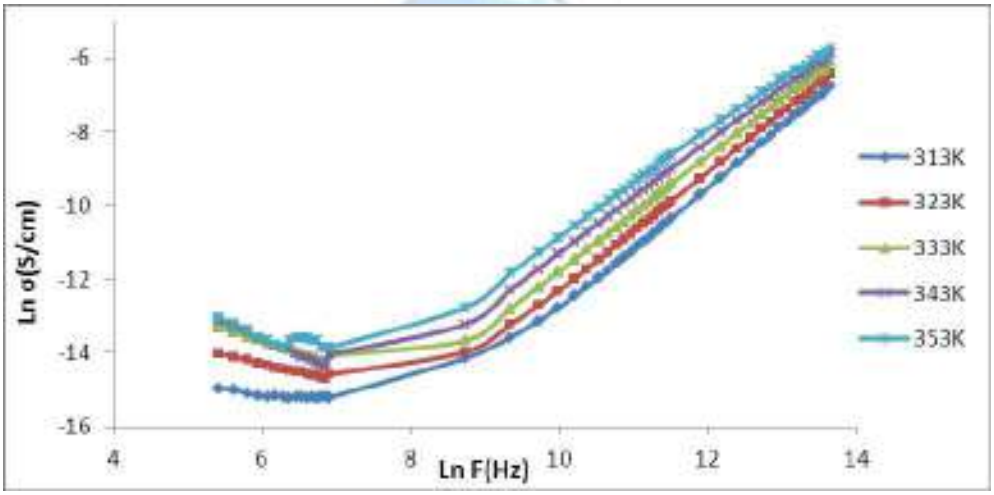

Fig. 1b. Variation of AC conductivity with frequency at different temperature for 25 mol % NH_4-Br.

From fig 1a. It is found that conductivity of PVA increases with increase in salt concentration upto 25mol% due to the enhancement of ionic mobility and the large number of carrier ions being introduced into the complex [12]

From fig 1b.It is found that conductivity increases with increase in temperature which suggests that the free volume around the polymer chain causes the increases in mobility of ions and polymer segments, and hence the conductivity increases [13].

Dielectric studies

Fig 2a shows the variation of dielectric constant as function of frequency for different concentration of ammonium bromide and Fig 2b shows the variation of dielectric loss as function of frequency for different concentration of ammonium bromide

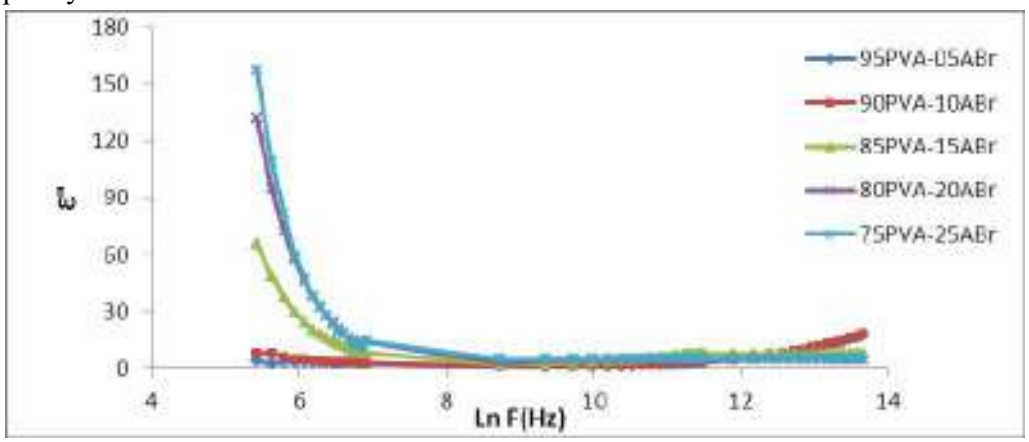

Fig 2a shows the variation of dielectric constant as function of frequency for different concentration of ammonium bromide

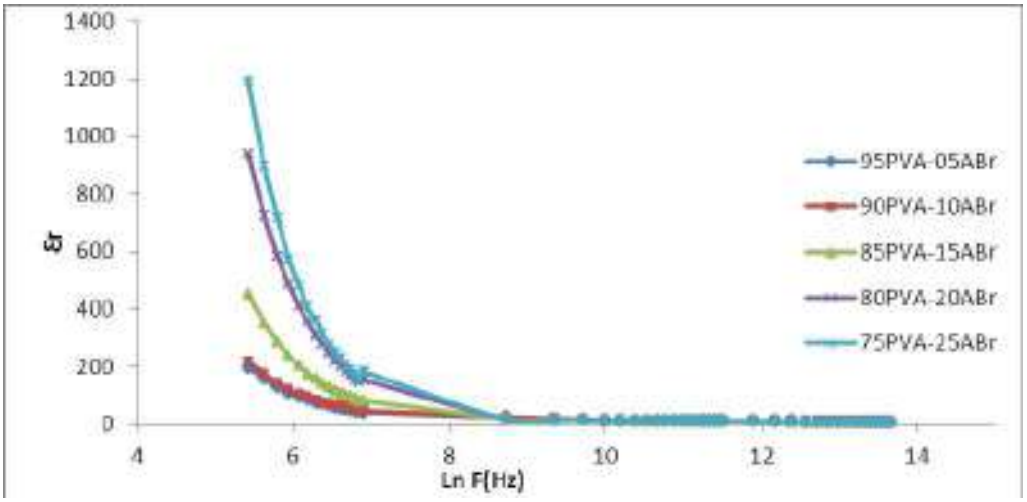

Fig 2b shows the variation of dielectric loss as function of frequency for different concentration of ammonium bromide

It is clearly indicated that dielectric constant and dielectric loss for composition of PVA doped with ammonium bromide polymer electrolyte system decreases with increase in the frequency and approaches to constant value. The higher values of dielectric constant at lower frequencies are due to the accumulation of charge at the interface lead to electrode polarization effects [14-15]. At higher frequency periodic reversal of the field takes place so rapidly that the charge carriers will hardly be able to orient themselves in the field direction resulting in the observed decrease of dielectric constant and dielectric loss

Also it is observed that dielectric constant and dielectric loss increases with increase in salt concentration, due to the increase in the number of dipole contributing to the material [16].

Conclusion

In the present studies the solid polymer electrolytes based on polyvinyl alcohol doped with ammonium bromide was prepared using solution cast technique. The maximun conductivity has been obtained for the dopant concentration of 25 mol %. Conductivity increase due to the

enhancement of ionic mobility and the large number of carrier ions being introduced into the complex Dielectric constant and dielectric loss decreases exponentially with increases of frequency for ammonium bromide doped PVA polymer electrolyte.

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The DC Electrical Properties of Composites Polymer Electrolytes

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Abstract:

The D.C electrical conductivity of (PVA-NH_4NO_3-ZrO_2) composite has been investigated. The composite polymer electrolyte prepared with different mole percentages of nanofiller ZrO_2. The experimental results showed that the D.C electrical conductivity increased with increasing the nanofiller concentrations and temperature. The increase in amorphous nature of the composite polymer electrolytes has been confirmed by SEM analysis.

Keywords: Composites, polyvinyl alcohol, SEM, DC Electrical Properties.

Introduction:

Composite which are made up of polymer with nanofiller have been used in electrical and electronic industries. Nanofiller can improve mechanical thermal and electrical (conductivity and permittivity) properties [1]. The conductivity of proton conducting polymer increases due to addition of nanofiller [2]. Polyvinyl alcohol has been particular chemical and physical properties as well as industrial applications [3-4]. Its good film forming nature, high dielectric strength, good charge storage capacity, and dopant dependent electrical and optical properties. It has carbon chain backbone with hydroxyl group attach to methane carbon [5].

Ammonium salts are very good proton donor. Hemaetal studied that the AC electrical conductivity of proton conducting solid polymer electrolyte based on PVA with ammonium salts (NH_4Cl, NH_4Br, NH_4I). It has been found that PVA doped with ammonium iodide have high ionic conductivity and its activation energy is low [6]. G. Hirankumaretal reported that the conductivity of pure PVA is of the order 10^{-10} S/cm at ambient temperature and its value increases 10^4 times when complex with 20% ammonium acetate [7]. So in the present work to study, DC electrical conductivity of proton conducting composite polymer electrolyte PVA:NH_4NO_3 doped with nanofiller ZrO_2 of different molar ratio.

Materials and experimental technique

Polyvinyl alcohol with molecular weight 125,000 (AR grade Sd fine), ammonium nitrate (AR grade merck), nanofiller ZrO_2 and deionized distilled water as a solvent have been used to prepare composite polymer electrolyte by solution cast technique. In this method PVA and ammonium nitrate have been dissolved separately in deionized distilled water by mole percent. And this solution are mixed together. Then different mole percent of nanofiller ZrO_2 (0, 0.5, 1.0, 1.5, 2) in PVA:NH_4NO_3 (80:20) and the solution is stirred well using magnetic stirred, until homogenous solution was formed. These homogeneous solution was casted in petri dish and evaporated slowly at room temperature. The film has been formed with uniformed thickness. DC electrical conductivity has been measured at different temperatures (313K- 353K) at the different voltages.

Results and discussion

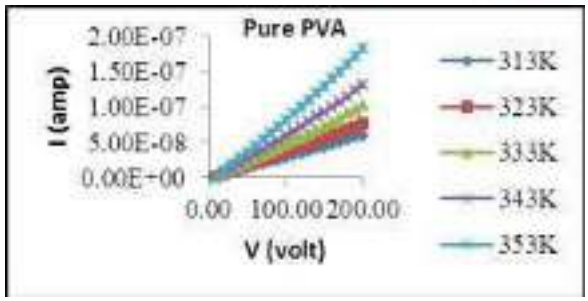
Scanning Electron Microscope (SEM)

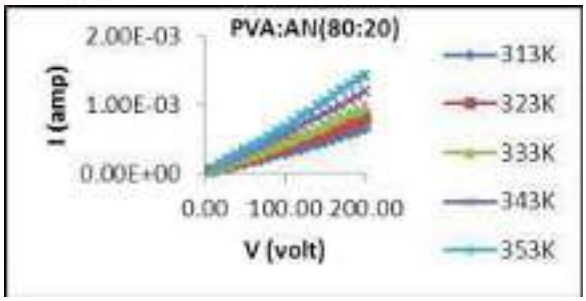
Fig: 3.1a **Fig: 3.1b** **Fig: 3.1c**

Scanning Electron Microscope of Pure PVA Scanning Electron Microscope of 80PVA:20AN Scanning Electron Microscope of 80PVA:20AN:2.0(ZrO_2)

It has been observed that the ammonium nitrate salts has been broken in to small pieces and is mixed with PVA as shown in fig 3.1b. The mobile ions H^+ from (NH^{4+}) are responsible for conductivity when an electric field is applied across the polymer electrolytes.The number of charge carrier increases with increase in salt content up to 20 mole% and decreases from 25 mole%. It is due to aggregation of salts as observed from SEM image of 80PVA:20 NH_4NO_3[8]. After the addition of nanofiller ZrO_2as shown in fig3.1c, it can be seen that the added fillers were homogeneous distributed in the polymer matrix, the surface morphology becomes smoother with the addition of micron-sized fillers, which represents a more amorphous phase. The conductivity will increase as a consequence of the increase of amorphous phases in a polymer electrolyte. These results have been proved with the better ionic conductivity. A smoother surface with more amorphous phase will cause the electrolyte becomes more flexible, the conducting ions will move more freely in the electrolyte with smoother surface morphology and thus the conductivity enhancement is detected [9-12].

3.2 Variation of current (I) with Voltage (V)





3.2a Variation of current (I) with Voltage (V) of Pure PVA **3.2b Variation of current (I) with Voltage (V) of PVA:AN(80:20)**

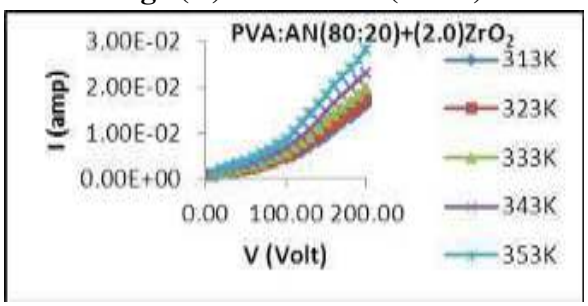


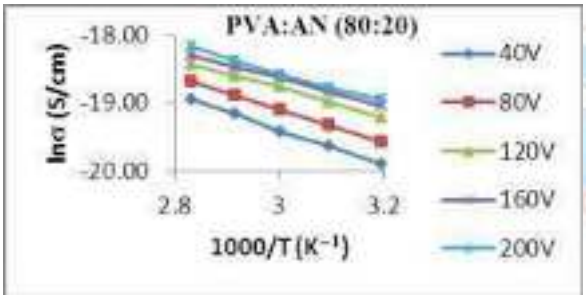
Fig: 3.2c Variation of current (I) with Voltage (V) of 80PVA:20AN:2.0 (ZrO_2)

Fig. 3.2a shows the pure PVA and 3.2b shows PVA with ammonium nitrate (80:20) of I-V relation on five different temperatures 313 K to 353 K. The result shows ohmic behavior.

Again, it is observed that the current increases with increasing temperature in ohmic region for all samples [13-14].

But when addition of nanofiller (ZrO_2) in PVA with ammonium nitrate (80:20) as shown in fig 3.2c at 2.0 mole % the current increase nonlinearly with increase in voltage and behavior is different from intrinsic semiconductor [15-16]. This nonlinearly increase in current can be explained by conduction mechanisms of composite polymer electrolyte. In doping process, the insertion of ions in to the polymer electrolyte take place over a bulk volume of the material rather than just at surface and as a result, a very large amount of charge carriers are produce per unit volume. Here the negative and positive charges initially added to the polymer chain upon doping do not simply begin to fill the rigid conduction or valence bands. Therefore there are no permanent dipoles. However there exist random charge (polarons) trapping in the sample. Under the influence of applied external field, a strong coupling between electron and phonons cause lattice distortions around the doped charge and hence charge (polarons) trapping result in to strong one and their localized motion (short range) serves as an effective electric dipole [17]. This leads to the formation of new quasi particles such as solitons, polarons and bipolarons [18-19]. Here the charge transport through these polarons and bipolarons. As the applied the increase the formation of polarons and bipolarons increases which contributes to the rapid increase in current to applied voltage and we get non-linear I-V curved.

Variation of conductivity ln ( ) with temperature at different voltages (Arrhenius plots).



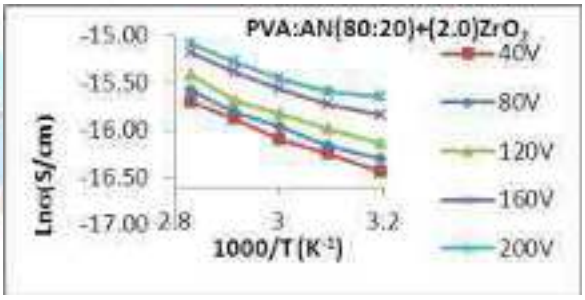


Fig: 3.3a Arrhenius plots for PVA:AN (80:20) **Fig:3.3b Arrhenius plots for PVA:AN(80:20)+(2.0)ZrO_2**

The temperature-dependent ionic conductivity of proton conducting polymer electrolytes has been evaluated to analyze the mechanism of ionic conduction in polymer electrolyte. Fig 3.3a PVA:AN (80:20) and fig 3.3b PVA:AN(80:20):(2.0)ZrO_2 shows the variation of ionic conductivity with the reciprocal of temperature for the polymer electrolytes. The linear variation of log versus 1000/T plot suggests an Arrhenius type thermally activated process. The conductivity can be express as [20]

$$= {}_0\exp(-E_a/K_T)$$

Where $_0$ is the pre exponential factor, E_a is the activation energy

As temperature increases, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion [21]. This in turn favors inter-chain hopping and intra-chain ion movements, and accordingly, the conductivity of the polymer electrolytes become high.

Conclusions:

The composite polymer electrolyte PVA-NH_4NO_3-ZrO_2 with different mole % have been prepared by solution cast methods. The increase in amorphous nature of the composite polymer electrolytes has been confirmed by SEM analysis. The Temperature dependence of ionic conductivity of these electrolytes exhibited Arrhenius behavior. The D.C electrical conductivity of the poly-vinyl alcohol increases by increasing the nanofiller ZrO_2 concentrations and the temperature.

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Study of Effect of ZnO on Changing Electrical Properties of Polyprrole Composites

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Abstract:

PPy/ZnO composites with different weight percentage of ZnO (10%, 20%, 30, 40% and 50%) were obtained by in situ emulsion polymerization of pyrrole in an aqueous solution. The characterizations of different composites were done with the help of X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier Infrared Spectroscopy (FTIR). The dc conductivity of the composites was measured as a function of temperature in the range 30^0C to 240^0C and was found maximum for PPy/ZnO-30% composition (98.88 x 10^{-4} S/cm, at 240^0C). The prepared samples also studied to check the ac conductivity as a function of frequency and its maximum value was found to be 107.55 x 10^{-3} S/cm for PPy/ZnO-30% at room temperature 30^0C.

Keywords: PPy/ZnO Composites, dc and ac Electrical properties, SEM, XRD, FTIR.

Introduction:

Conducting polymers recently emerged as a new class of potentially useful materials in the era of electrical conductivity and other many applications as successful agents. More works on conducting polymers have been done by many groups all over the world to understand their exceptional electrical, optical and chemical properties. Recently, the nanocomposite materials have become one of the most extensively studied material all over the world as they have shown to possesses several technological application such as magnetic recording materials sensors, effective quantum electronic devices, etc. [1]. Nanocomposite material composed of conducting polymers & oxides have open more field of application such as conductive paints, drug delivery, rechargeable batteries, smart windows, toners in photocopying, etc [2]. Applications of polymers have begun to emerge a new era. These include coating and blends for electrostatic dissipation and electromagnetic interface (EMI) shielding. Electromagnetic radiation absorbs for welding of plastics, conductive layers for light emitting polymer devices and anti corrosion for iron and steel [3]. Semiconductor nonmaterial has been received great attentions. Among these various semiconductors oxide nonmaterial zinc oxide is a versatile material because of its physic-chemical properties such as mechanical, electrical, optical, magnetic and chemical sensing properties. It has a wide band gap of 3.3 eV and it is used in various applications of electronic devices, biomedical field, variety of sensors, etc [4-5]. In the present paper, the author has reported PPy/ZnO composites, which were synthesized by in-situ polymerization method. These composites were characterized by using Fourier transform infrared spectroscopy (FTIR), X-Ray diffraction (XRD) analysis, Scanning Electron Microscopy (SEM) and studied the electrical properties of prepared composites.

Experimental:Materials

Pyrrole monomer (C_4H_5N) was previously distilled under vacuum and subsequently stored in a dark refrigerated environment (0°C), since it is a very sensitive to light and moisture. All

chemical reagents, such as zinc oxide (ZnO), ferric chloride hexahydrate ($FeCl_3$.$6H_2O$) and sodium dodecyl sulfate ($C_{12}H_{25}NaO_4S$), were of analytical grade.

Preparation of PPy/ZnO composites

PPy/ZnO composites were obtained by in situ emulsion polymerization of pyrrole in an aqueous solution containing sodium dodecyl sulphate (SDS) and ZnO. Initially, an aqueous solution of deionized water (40 mL) containing the surfactant (SDS, 2.4 mMoles) was prepared. The solution was stirred vigorously for 10 minutes and 0.5 mMoles of pyrrole monomer were then added to the mixture. After 20 minutes of vigorous stirring, 42.1 µMoles of ZnO were added. Subsequently, the solution was maintained under vigorous stirring for 20 minutes and 400.0 µL of $FeCl_3$ (1M) was added drop by drop. Finally, the solution was kept under vigorous stirring for 24 hours to ensure complete polymerization. To obtain a powder composite material, 70 mL of methanol was added to the colloidal dispersion, forming a black precipitate, which was then dried at 40°C and thoroughly dried in a vacuum desiccator at room temperature [6]. In present work, PPy/ZnO nanocomposites containing various weight percentages of ZnO (10 %, 20 %, 30 %, 40 %, and 50 %) in PPy were synthesized.

Characterization

X-ray diffraction (XRD) studies were performed using Philips X-ray diffractometer with CuKα as the radiation source. The morphology of the Zinc oxide and composites in the form of powder was investigated using SEM, Fourier transformed infrared spectra of these composite were recorded in the range 4000-400cm^{-1}. dc conductivity of these composites are also studied by using Keithley electrometer, Frequency-dependent ac conductivity were measured by employing LCR meter.

Results and discussion

X-Ray diffraction

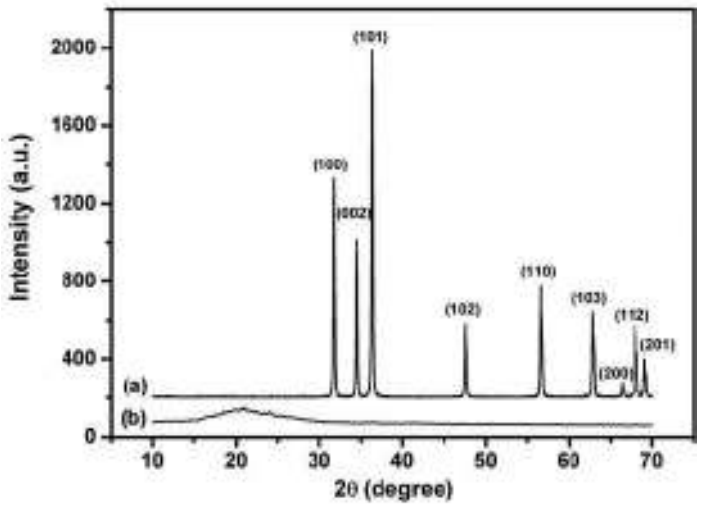


Figure 1. X-ray diffraction patterns obtained for: (a) ZnO (b) PPy/ZnO

Figure 1 (a) shows the XRD pattern of ZnO. The XRD diffraction peaks of ZnO powder are shown in a good agreement with hexagonal structure reported in JCPDS File Card (No.05-0664). The intensity of diffraction peaks for PPy/ZnO composite is lower than that for ZnO. The

presence of amorphous PPy reduces the percentage ratio of ZnO and sequentially weakens diffraction peaks of ZnO. Figure 1 (b) shows X-ray diffraction pattern of PPy/ZnO. A broad peak centered at 2θ at 22.17^0 may be assigned to the scattering from the polypyrrole chains at interplanar spacing which clearly implies the amorphous nature of polypyrrole.

Fourier Infrared Spectroscopy

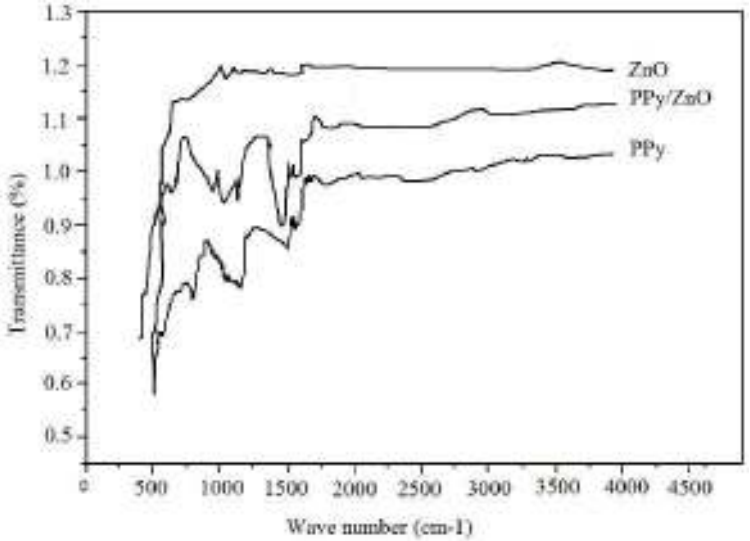
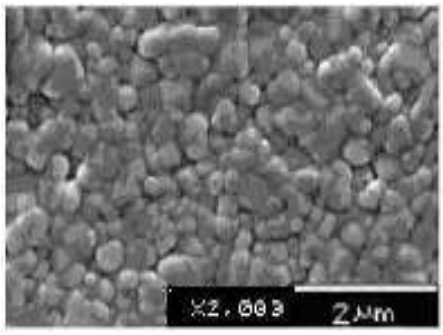
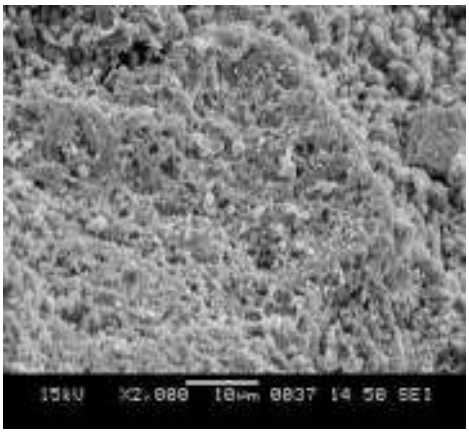


Figure 2. FTIR spectrum of: (a) ZnO (b) PPy and (c) PPy /ZnO composite

The FTIR spectra measurement was carried out to study the molecular bonding of the PPy and PPy/ZnO composites (ZnO 50 wt % in PPy). For the pure PPy, the characteristic peaks appear at 1546 cm^{-1} due to C=C stretching, FTIR spectra of pure Zinc oxide has predominant peaks at 987 cm^{-1} and 1534 cm^{-1} conforms the formation of ZnO compounds. FTIR of PPy/ZnO composite shows peaks at 768 cm^{-1}, 1465 cm^{-1} and 1755 cm^{-1} suggested the absorption at these wavelengths.

Scanning Electron Microscopy





(a)

(b)

Figure 3. SEM image of: (a) ZnO and (b) PPy/ZnO-30% composite

SEM pictures show the porosity of ZnO and PPy/ZnO composite (50 wt % of ZnO in PPy). From figure 3 (b), more porosity is observed with doping of ZnO in PPy thereby decreases

the granular size. The SEM image also reveals the presence of ZnO in PPy which is homogeneously distributed throughout the polymer sample.

dc conductivity

The dc conductivity of PPy/ZnO composites having different weight percentage was carried out in the temperature range 30^0C to 240^0C. The variations are shown in following figure 4.

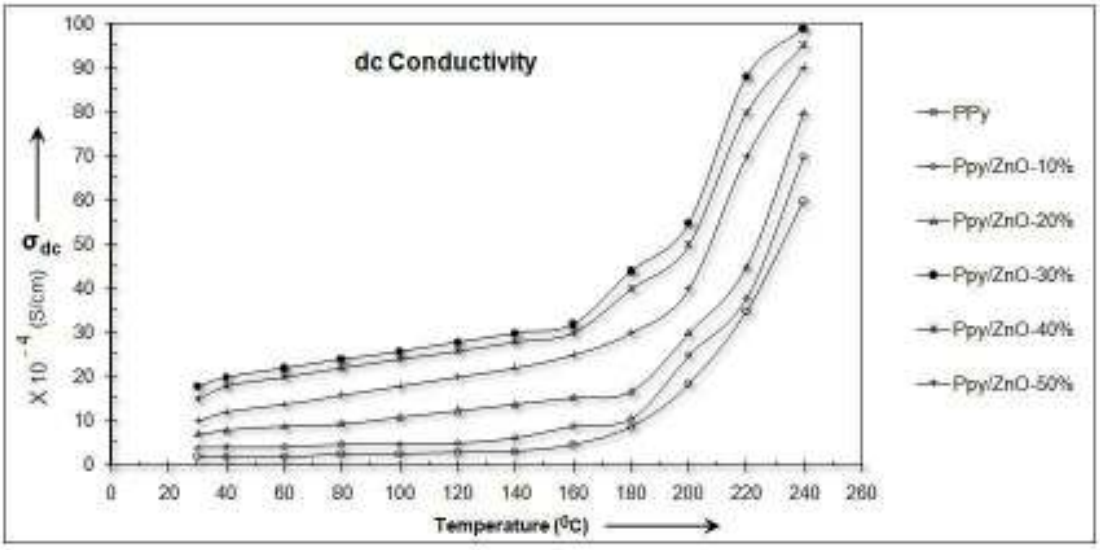


Figure 4. Variation of dc electrical conductivity with temperature

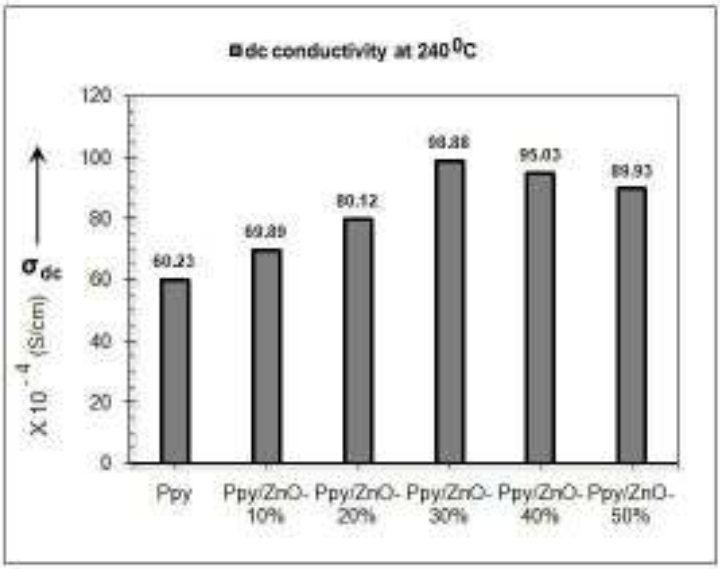


Figure 5. Bar Graph of variation of dc conductivity with PPy/ZnO composites at 240^0C

The dc conductivity varies directly with temperature by the equation $\sigma = \sigma_o \exp\left(-T_o/T\right)^{1/4}$ where, σ is the conductivity at temperature T and σ_o is the conductivity at characteristics temperature T_o. From figure 4, it is manifested that with increase in temperature, conductivity initially increases slowly and then rapidly. Also, dc conductivity increases with increase in ZnO percentage in PPy and becomes maximum for PPy/ZnO-30% composition (98.88 x 10^{-4} S/cm, from figure 5 at 240^0C). With further increase in weight percentage of ZnO, conductivity

decreases. This increased in conductivity could be due to charge exchanging between ZnO and PPy chain with increase in temperature.

ac conductivity

The variation of ac conductivity with frequency at room temperature (30^0C) is shown in figure 6.

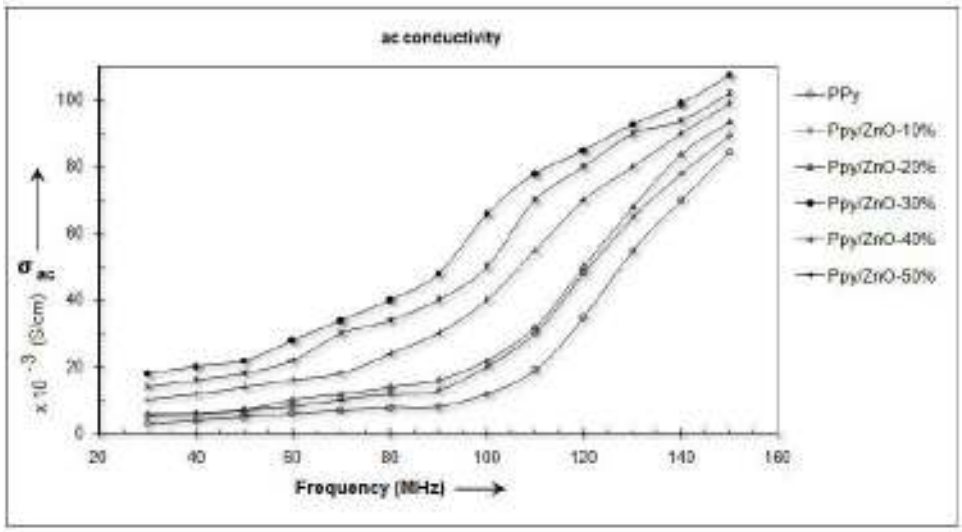


Figure 6. Variation of ac electrical conductivity with frequency

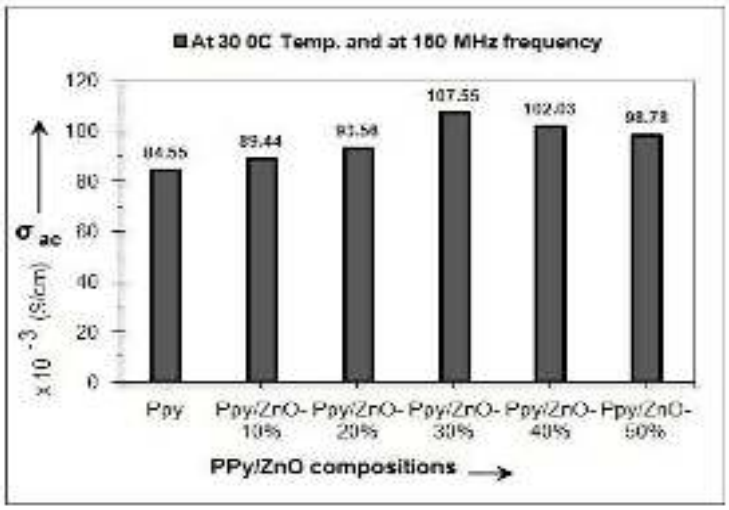


Figure 7. Bar Graph of variation of ac conductivity with PPy/ZnO composites

The ac conductivity was carried out at room temperature (30^0C) using LCR meter. From figure 6, it is manifested that ac conductivity increases with increase in frequency and it has enhanced value for PPy/ZnO-30% composition, also it is shown in figure 7. This maximum value is 107.55 x 10^{-3} S/cm. Increased value of ac conductivity for PPy/ZnO-30% composition may be due to electric polarization of the dipoles.

Conclusion

PPy/ZnO composition with different percentage ratio was prepared by in situ emulsion polymerization of pyrrole in an aqueous solution. Electrical conductivity (dc and ac) were studied and found that dc conductivity increases with increase in temperature and ac conductivity increases with increase in frequency. Both the conductivities become maximum for PPy/ZnO-30% composition. This showed that PPy/ZnO nano-composites are best materials in voltage-current applications.

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Effect of Oxalic Acid on DC Electrical Conductivity of Doped Polyvinylchloride and Poly(Methyl Methacrylate) Polyblends

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Abstract:

The present work devoted to measurement of the electrical conductivity of doped and undoped Oxalic acid Polyvinyl Chloride (PVC) - Polymethyl Methacryalate (PMMA) blends at temperatures (313K - 373K). The conductivity of PVC-PMMA polyblends found to be decreases after adding oxalic acid.

Key words: PVC, PMMA, Polyblends, Oxalic Acid.

Introduction

High molecular weight compounds constitute one of the major fields of modern technology. Thus high polymers either natural or synthetic participate in a wide range of industrial applications [1]. Composite systems consisting of an insulating matrix and randomly dispersed fine conductive particles have generated significant research interest, mostly, due to their electrical and electromagnetic performance [2] .The blending of two polymers is found to be new polymeric material which new materials may be promising candidate than indivisible polymer [3]. There are many investigations on polymer blending [4]. The conductivity study gives the origin of the charge carrying species, their number, and the way in which they move through the bulk of the material. These parameters are interlinked with the chemical composition of the microstructure and the morphology of the particular material.

PVC is a polar molecule and one of the most important commercially available polymer due to its light, electrical & chemical resistant and it has the ability to get mixed with other to produce verity of compounds which has a wide range of physical & chemical properties.

PMMA is strongly polar and it is a hard, rigid and transparent polymer which has good outdoor weatherability and it has more impact resistance than glass. PMMA is a versatile polymer showing plenty of application. Blends of these two polymers are expected to yield strong and long lived electrets useful for industrial application. Both PVC- PMMA are rigid polymers but by blending PVC with PMMA make the resultant blend soft & open to make useful applications. Many researchers reported the electrical conductivity and experimental observations in PS-PMMA [5], PVC-PMMA blends [6], [7], [8]. The conductivity studies on PVC-PMMA polymer blends electrolytes shows stability [6].

Poly methyl methacrylate (PMMA) is one of the well known brittle materials. In order to enhance the physical and mechanical properties of PMMA, numerical studies on the improvement methods have been extensively carried out in the past decades. The most common method for promoting the toughness of PMMA is blending with the PVC. A large number of studies indicate that the tacticity of PMMA affects strongly the miscibility of PVC-PMMA

blends. The present investigation is concerned with detailed studies on the DC electrical conductivity of PVC-PMMA blends doped with Oxalic acid.

Experimental

The polymers, PVC (Aldrich) and PMMA (Otto kemi, Mumbai) in 4:1 weight proportions were dissolved in 20 ml solvent cyclohexanone (SD Fine Chemicals, Mumbai) respectively. Oxalic acid used as a dopant in these selected polymers. The dopant & polymer mixture were mixed together and this mixed solution was kept in a stand for three days so as to get the complete homogenous dissolution of blends. After three days, the solution mixture was poured on perfectly plane and chemically clean glass plate, which is kept floating freely in a pool of mercury for perfect horizontal leveling. It was, thereafter, allowed to evaporate in air at room temperature. Further, it was dried for 48 hrs. to remove any traces of solvent.

The dried film was removed from the plate and cut into small pieces (samples) of desired size, which were then coated on both sides with silver paste (Eltecks Corporation, Bangalore) so that electrical contact hold very well. These polyblends films of PVC-PMMA doped with 0%, 5%, 10%, 15% Oxalic acid (wt. percentage) were kept between the electrodes of a specially designed sample holder having gold plating. The variation between current and voltage measured by using Keithley 6487 Picoammeter / Voltage source meter instruments at various constant temperature by using Digital Micrometer screw gauge (Mitutoyo Corporation, Japan, Least Count 0.001mm).

XRD Measurements

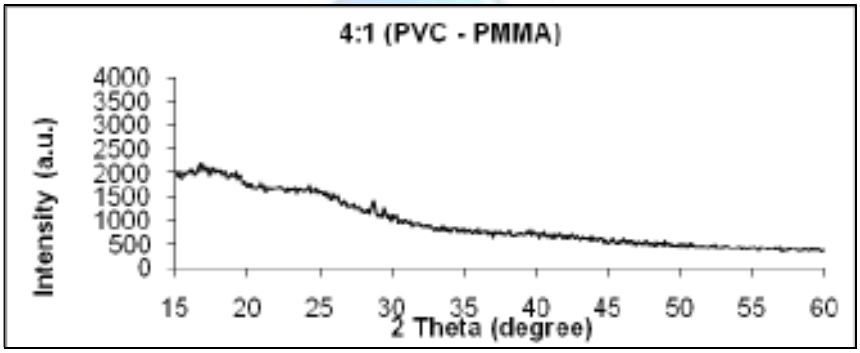

Fig. (2.1) XRD Spectrum of 4:1 PVC-PMMA

Generally, polymer consists of both crystalline and amorphous region. Their conductivity properties are influenced by the presence of amorphous nature. From above Fig.(2.1) we observe that the sample shows noisy spectra. The peak was observed at the position near about 25^{o}, which is attributed to the amorphous nature. Thus the x-ray diffractograms of all the samples ensures the amorphous nature with large diffraction maxima that decreases at large diffraction angles. The shape of the first main maximum indicates the ordered packing of the polymer chains. The intensity and shape of second maxima are related to the effect of ordering inside the main chains. The observed broad hymps in the XRD spectrum indicate the presence of crystallities of very low dimensions. The absence of any prominent peaks in the films indicates the predominantly amorphous nature of the films. This is in agreement with the result reported by Na and Rhee (2006)

Results & Discussion

Ln(I) vs ln(V) plots

Ln(I) vs ln(V) plots of oxalic acid doped PVC–PMMA thin films at various temperatures 323 K, 333 K, 343 K, 353 K and 363 K are shown in figure 3.1 (a),(b),(c),(d).

Fig. 3.1 Variation of Current (I) with Voltage (V) for 4:1 PVC PMMA doped with different wt% of OA.

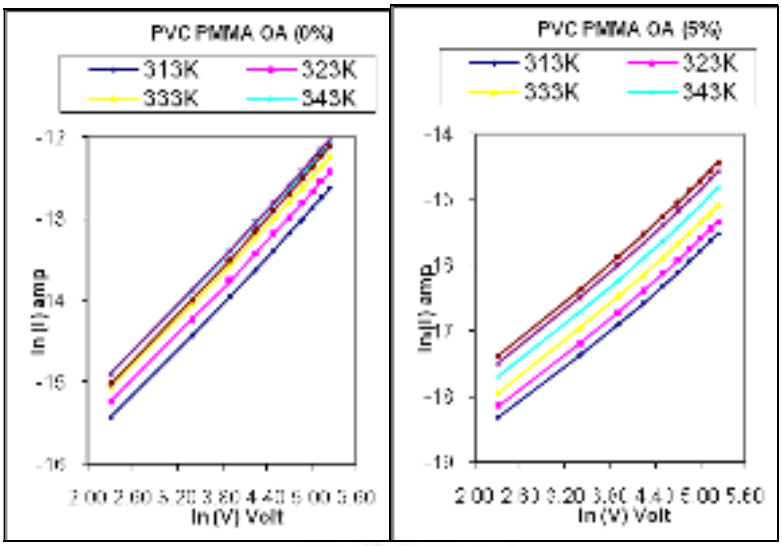

Fig. (a)

Fig. (b)

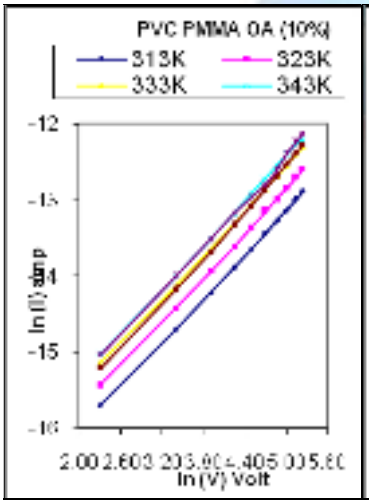

Fig. (c)

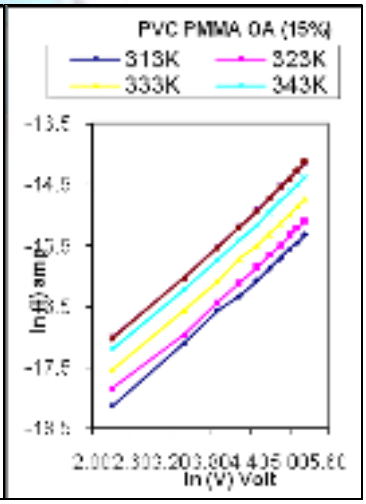

Fig. (d)

From the graph, current increases non-linearly with applied voltage and does not follow a power law, $I = kV^m$, where k and m are constants. The possibility of ohmic conductions as well as space charge limited conduction is ruled out from the observed behavior of I–V characteristics. This is also evident from the fact that Ohm's law follows from the free electron model of a metal. In the present case the constituents of blends are itself insulators and blends almost amorphous, giving wide scope for irregularities in the structure and so ruling out ohmic conduction.

3.2 Effect of Dopant on DC Conductivity

In the blend of (PVC - PMMA), the PVC has chloro side group which is proton donor while PMMA has on ester side group ($–COOCH_3$) containing oxygen as a hetero atom having large electron affinity. The incorporation of more conducting PVC than PMMA (Belsare and Devgaonkar, 1998) imparts a polar character to the blend sample. According to Liang–Tse Yu (1963) and Van Taut Yu (1962), the resistance of the polymer decreases (conductivity increases) when polar substances are introduced into non- polar ones. Hence in case of blended systems the value of conductivity is greater and on making the blends of PVC and PMMA in ratio 4:1 doped with different weight percentage of oxalic acid, the value of DC conductivity decreases with increasing dopant percentage. The Fig. 3.2 (e) to (h) agrees with the theory.

Fig. 3.2 (e) to (h) Variation of conductivity ln (σ) with temperature at different voltages (Arrhenius plots) for 4:1 PVC- PMMA doped with different wt% of OA.

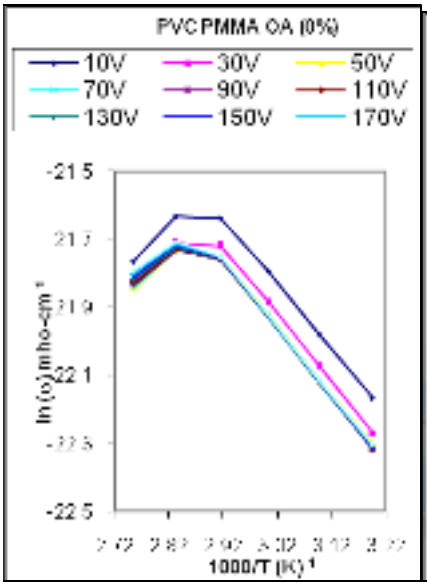

Fig. (e)

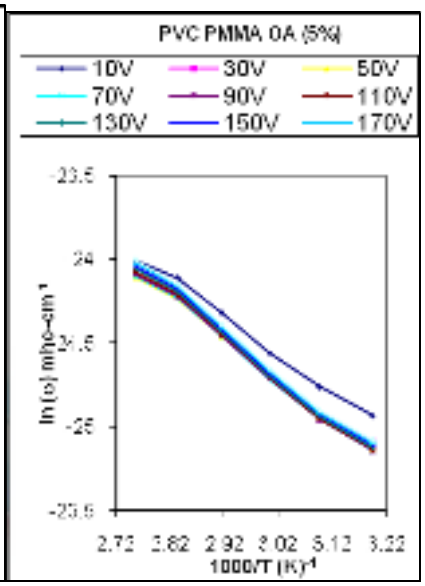

Fig. (f)

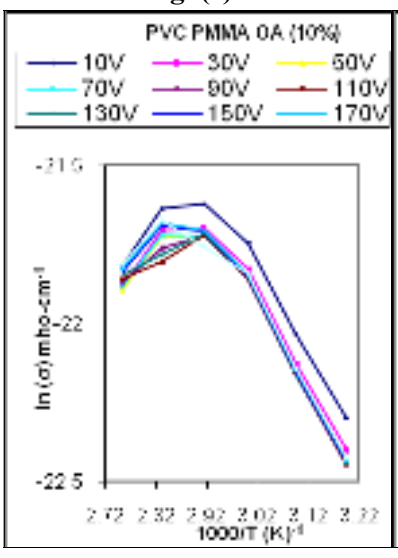

Fig. (g)

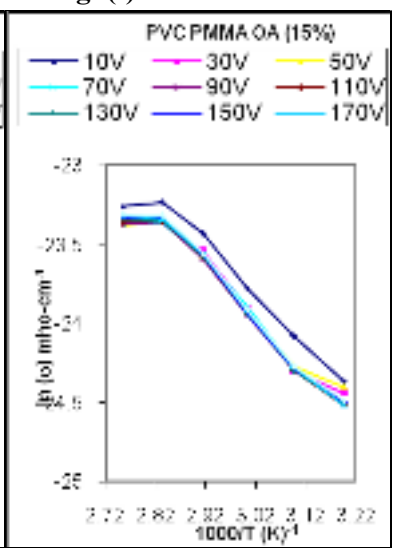

Fig. (h)

Conclusions

DC electrical conductivity have been measured at different temperatures and at the different % of Oxalic acid.

i. DC electrical conductivity of thin film increases with increase in temperature.
ii. DC electrical conductivity of thin film decreases with increasing doping percentage .

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Synthesis of Nanocrystalline Tin Oxide Doped With Copper Oxide And Study of Their Electrical Conductivity Under The Influence of CO_2 Gas

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Abstract :

In this present work sol-gel method used for the synthesis of pristine nanoparticles of SnO_2 , CuO and nanocrystalline tin oxide (SnO_2) doped with copper oxide (CuO) has been successfully demonstrated for CO_2 detection. Thermal treatment of samples is done in the temperature range 50°C to 350°C. The current–voltage (I–V) characteristics of the samples and its temperature dependence have been investigated in air at temperature range 50°C to 350°C. The linear nature of plots shows the semiconducting behavior and obeys Ohms law. The plots Ln (σ) vs.CO_2 gas concentration revealed that conductivity of samples decreases partially linearly with respect to the CO_2 gas concentration but with respect to the temperature the conductivity of samples increases.

Key words: SnO_2 , CuO, CO_2 gas sensors

Introduction:

Carbon dioxide (CO_2) gas concentration is an important parameter for many fields, such as in environmental protection, industrial processing control, medical diagnosis and chemical analysis [1–3]. Carbon dioxide is one of the main gas species causing a global warming of the earth, As such, a gas sensor that is compact, robust, with versatile applications and a low cost, could be an equally effective alternative. The main classes of gas-sensing materials include metal-oxide semiconductors, intrinsically conducting polymer, conducting polymer composite, metal-oxide/polymer composite and other novel materials. These materials can be applied on different transduction units including chemiresistive, surface acoustic wave (SAW), quartz crystal microbalance (QCM), optical transducers and metal-oxide-semiconductor field-effect transistor (MOSFET) [4].Among these, chemiresistive semiconducting metal oxides are among the most potential candidates due to their very low cost,high sensitivity, fast response/recovery time, simple electronic interface, ease of use, low maintenance and ability to detect large number of gases [5].

Semiconducting Oxide gas sensors operate on the principle of conversion of gas concentration into a measurable signal. It was discovered in 1950, that the electrical properties of some metal oxides are changed when they are exposed to gases [6]. Seiyama et al [7] in 1962, proposed the idea of gas sensing using metal oxide thin films. In the same year Taguchi built the first SnO_2 sensor which is most widely used sensing material for the gas sensing applications [8]. SnO2 particles are widely applied for gas sensing application due to their high mobility of conduction electrons, good chemical and thermal stability under the operating conditions of sensors [9]. In the present work nanocrystalline tin oxide (SnO_2) doped with copper oxide (CuO) has been successfully demonstrated for CO_2 detection.

Experimental:

In this present work sol-gel method used for the synthesis of pristine nanoparticles of SnO_2 , CuO [10]. After the synthesis, obtained fine nanopowder of SnO_2 , CuO was calcinated at 800 ^oC up-to 5 hours in the auto controlled muffle furnace (Gayatri Scientific, Mumbai, India.) so that the impurities from product will be completely removed. The obtained product of fine nanopowder is further used for the preparations of samples. The SnO_2 powder was mixed thoroughly with different X mole% of CuO(X = 10, 20, 30, 40, 50, 60, 70, 80, 90) with the aid of acetone by using the mortar and pestle. The mixed powder of SnO_2 : CuO system was further calcinated at temperature 800°C for 5hrs. in the auto controlled muffle furnace (Gayatri Scientific, Mumbai, India.) After, the calcinations again uniformly mixed the powder using the grinder. The sample codes, mole% of powder, and thickness are listed in the Table 2.1.

Table 2.1: Sample Code of (SnO_2 : CuO) System

Sr. No.	Sample Code	mole%SnO_2 : mole%CuO	Thickness (μm)
1	SC-1	90SnO_2-10CuO	20
2	SC-2	80 SnO_2-20CuO	23
3	SC-3	70 SnO_2-30CuO	26
4	SC-4	60 SnO_2-40CuO	26
5	SC-5	50 SnO_2-50CuO	28
6	SC-6	40 SnO_2-60CuO	20
7	SC-7	30 SnO_2-70CuO	35
8	SC-8	20 SnO_2-80CuO	34
9	SC-9	10 SnO_2-90CuO	30

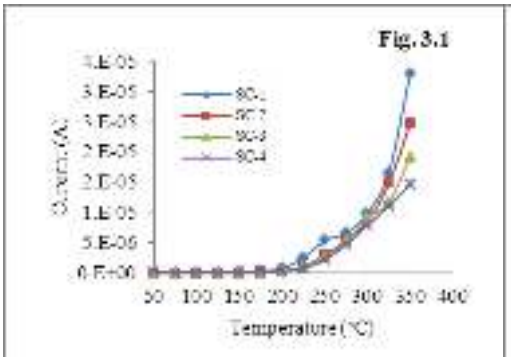
Sensor fabrication:

The sensor was fabricated by employing thick film technology . screen –printing technique is used to prepare thick film.The prepared active powder was used to formulate the paste for screen-printing. EC (Ethyl Cellulose), BCA (Butyl Carbutol Acetate) were used as binders for the screen-printing process [12,13]. The active powder and binder were mixed to form a paste. During this mixing process, the binder was added drop by drop to obtain the proper viscosity of the paste. The glass substrates used for the screen-printing of the paste of sensor material were cleaned initially by distilled water several times. The screen-printing of the paste of active powder mixture was done on glass substrates

Results & Discussion

Thermal Stability of Sensors

Figure (3.1 to 3.2) shows the variation of current Vs. temperature from 50^oC to 350^oC at constant source voltage (10 V DC) by using Keithley (6487) voltage source cum picoammeter.



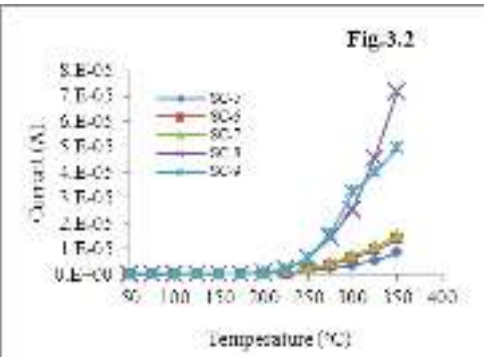
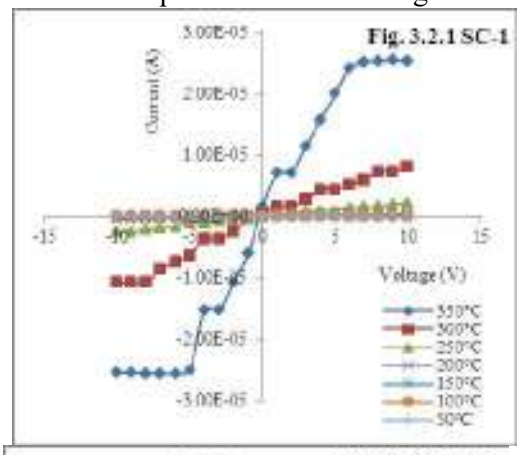


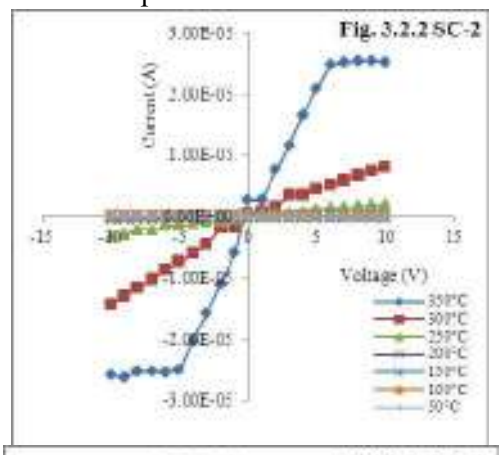
Fig. 3.1 to Fig. 3.2 Thermal Stability Curves of Samples.

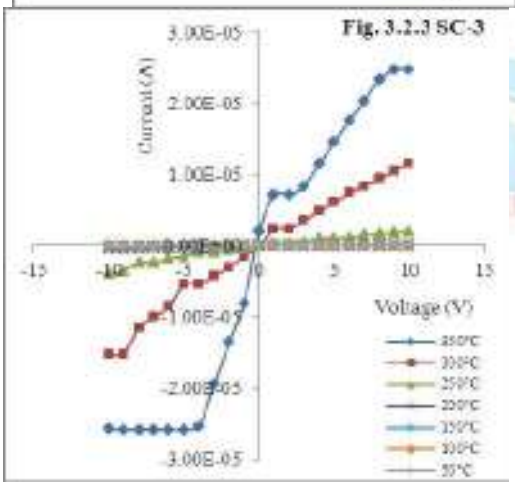
The electrical measurements of compositions samples at constant voltage prior to gas sensing measurement signified that the current increases linearly with the temperature, which is indicating the perfectly ohmic contact of the electrodes to get the correct measurement across the samples for the future reading also.

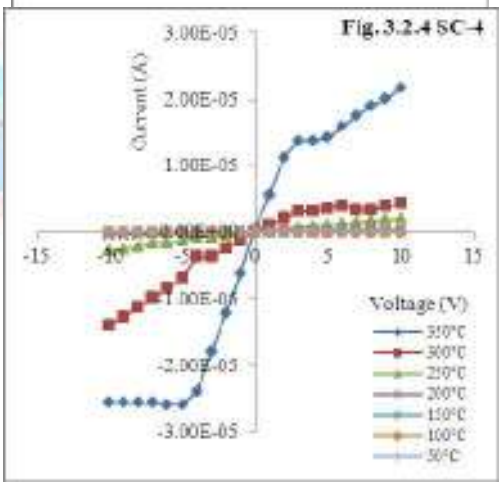
Current–Voltage (I–V) Characteristics of Sensors

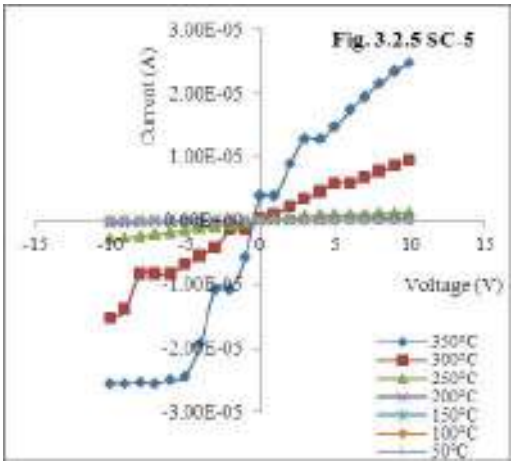
The current–voltage (I–V) characteristics of the samples and its temperature dependence have been investigated in air. Fig. (3.2.1 to 3.2.9) shows the current–voltage (I–V) characteristics samples of Series I having different molar composition

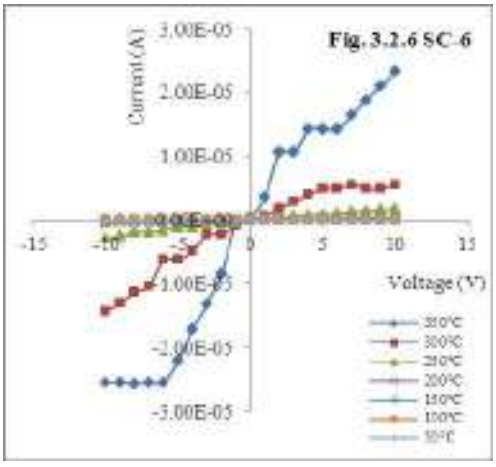












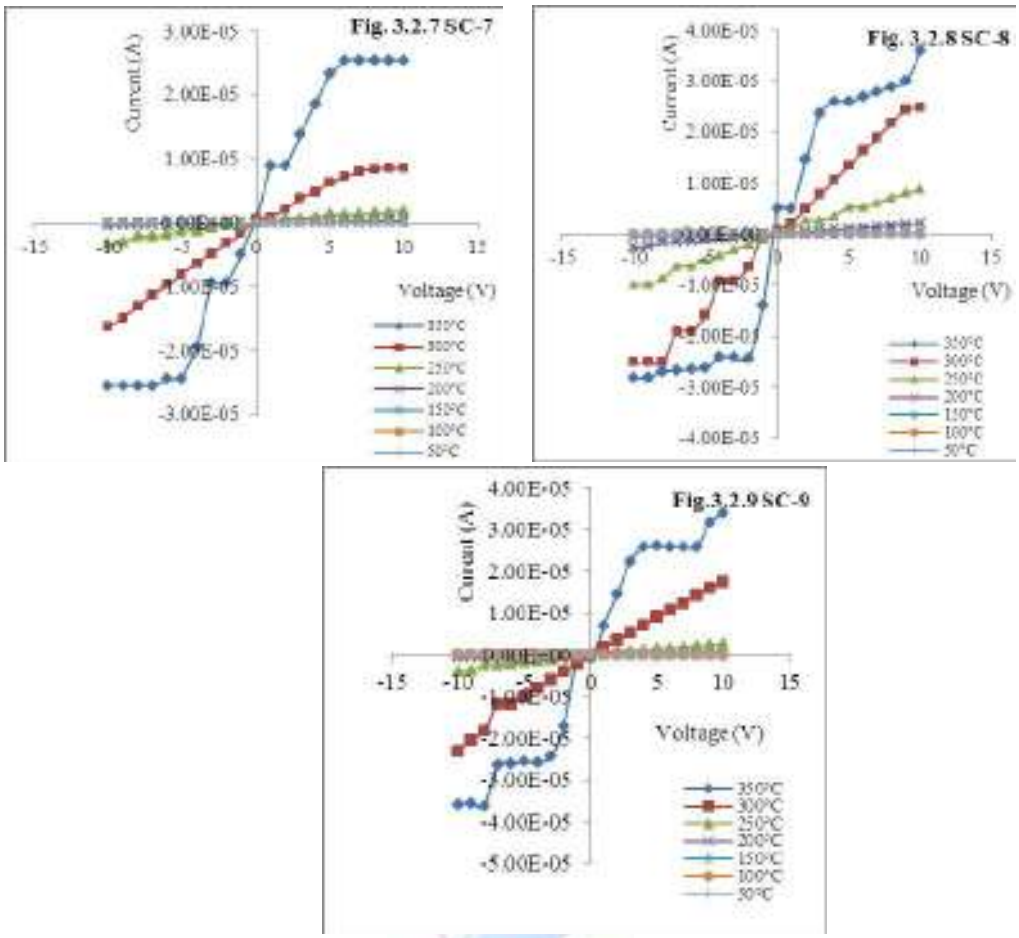


Fig. (3.2.1 to 5.2.9) Current–Voltage (I–V) Characteristic of Sensors

The nature of plot initially linear and then it becomes nonlinear beyond some voltage, said to be exponential nature. The linear nature of plots shows the semiconducting behavior and obeys Ohms law at temperature range 50°C to 350°C. The semiconducting behavior of SnO_2 and CuO composite plays very important role in the CO_2 gas sensing characteristics [15, 16].

DC Electrical Conductivity of Sensors

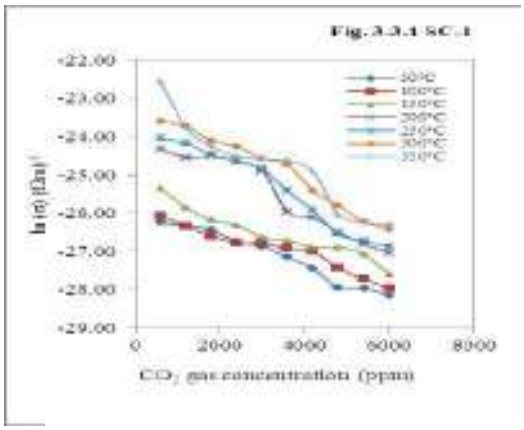


Fig. 3.3.1 Variation of Lnσ with CO_2 gas concentration at constant temperature of sample SC-1

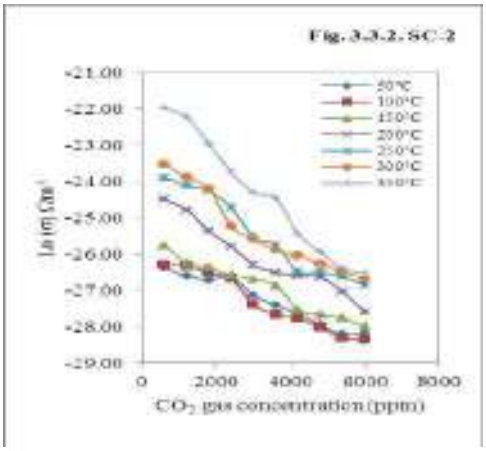
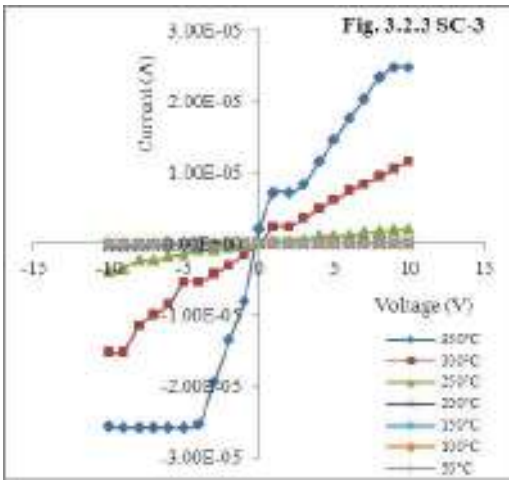
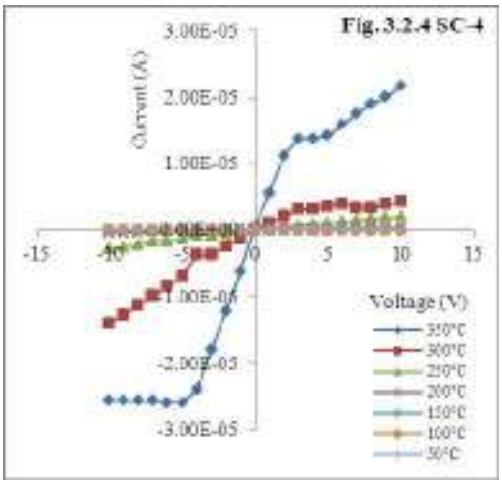
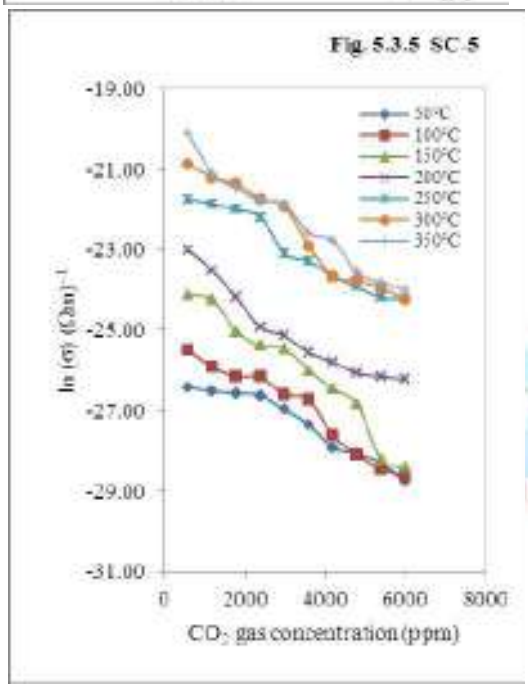


Fig. 3.3.2 Variation of Lnσ with CO_2 gas concentration at constant temperature of sample SC-2







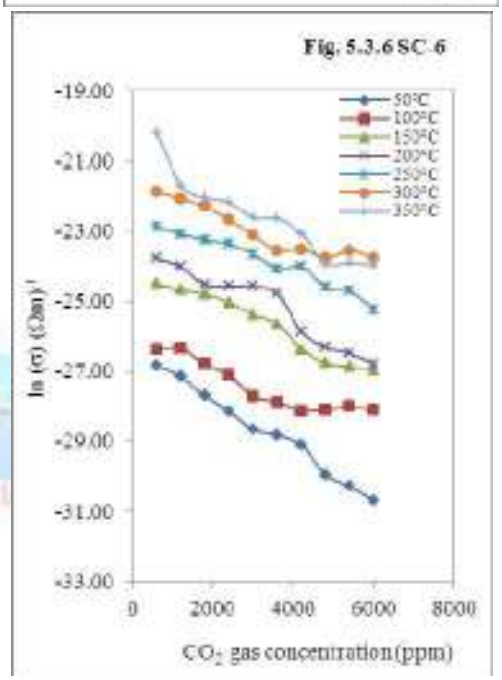
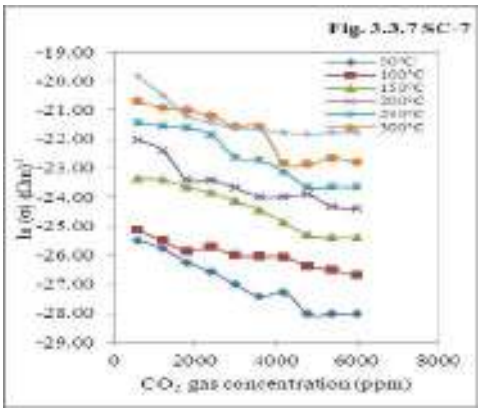
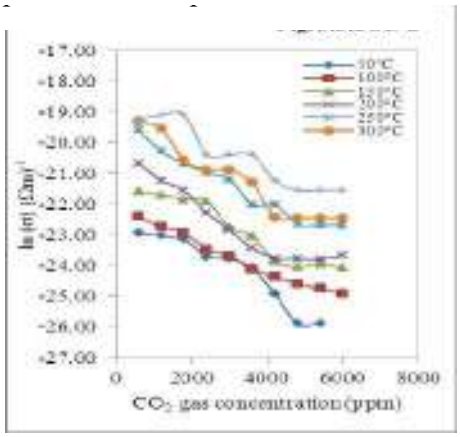


Fig. 3.3.3 Variation of Lnσ with CO_2 gas concentration at constant temperature of sample SC-3

Fig. 3.3.4 Variation of Lnσ with CO_2 gas concentration at constant temperature of sample SC-4





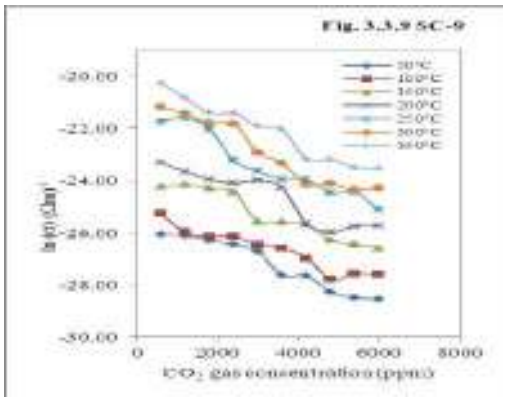


Fig. 3.3.9 Variation of Lnσ with CO_2 gas concentration at constant temperature of sample SC-9

If the absorbing gas is a reducing agent, it injects electrons into the semiconductor and causes the conductivity to increase and if it is oxidizing agent, it extracts electrons from the semiconductor and the corresponding conductivity decreases [17].In all the groups of samples, the conductivity increases with increase in temperature of sensors i.e., the electrical conductivity of all samples increases with increasing the temperature and this represents also a semiconductor behaviour [18].It is observed that the conductivity decreases partially linearly with respect to the CO_2 gas concentration. But with respect to the temperature the conductivity of samples increases.

Conclusions

Due to thermal treatment films show better and excellent sensitivity and stability results without any further mechanical deformations obtained or seen in the films. The linear nature of current–voltage (I–V) plots shows the semiconducting behavior and obeys Ohms law.

The plots Ln (σ) vs.CO_2 gas concentration revealed that conductivity of samples decreases partially linearly with respect to the CO_2 gas concentration but with respect to the temperature the conductivity of samples increases. The CO_2 gas has oxidizing properties which leads to an oxidation of material, thereby reducing its conductivity.

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Physical Properties of Nanostructured WO_3 Thin Films Grown by SILAR Method

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Abstract.

Nanostructured WO_3 thin films have been deposited by Successive Ionic Layer Adsorption and Reaction (SILAR) method onto glass substrate using H_2O_4W and NaOH as cationic and anionic precursors respectively. This Flim characterized by means of FTIR and UV. The electrical resistivity (10^5 Ω cm) and it behave semiconductor with 2.2 eV optical band gap.

Keywords: Thin films; Nanocrystalline materials; Electrical properties; Optical properties.

Introduction:

Since last few decades, thin films of Tungsten oxide have attracted great attention due to its applications in variety of fields such as electro chromic devices [1], gas sensor [2], Solar energy photo thermal conversion [3], Photo catalysis [4], high density memory devices, smart windows [5], Tungsten oxide is one of the most stable rare earth metal oxide having high dielectric constant and high refractive index. Depending on the different oxidation states tungsten, it has different phases such as W_3O, WO_2, $W_{18}O_{49}$, $W_{20}O_{58}$, $WO_{2.9}$ and WO_3 with monoclinic, tetragonal, orthorhombic and hexagonal crystal structure have attracted great attention due to the applications in variety of fields such as elecrtochromic devices respectively. [6, 7]. Amongst them, WO_3 has attracted the great attention of several researchers due to its novel physical, chemical and functional properties. It is one of the promising materials for biomedical and industrial applications owing to its non-toxicity, high chemical stability and high electron transfer capability.

Recently, several researchers have deposited WO_3 thin films by various physical and chemical deposition techniques such as thermal evaporation [8], spray pyrolysis [9], r. f. sputtering [10], pulsed laser deposition [11], sol gel method [12], chemical vapor deposition [13], dip coating[14], electron beam [15],vacuum evaporation[16], chemical bath deposition method [17] etc. However very few reported chemical method for the deposition of WO_3 thin films. Since chemical deposition methods are advantageous over physical deposition methods, first time an attempt has been made to deposit WO_3 thin film by simple, low cost, non-toxic and ecofriendly successive ionic layer adsorption and reaction method. The FTIR, electrical and optical properties of the WO_3 thin films are discussed.

Experimental:

Nanostructured tungsten oxide thin films have been deposited by successive ionic layer adsorption and reaction (SILAR) method onto glass substrates by using 0.1M tungstic acid (H_2O_4W) and 1M NaOH as the cationic and anionic precursors respectively. To deposit WO_3 thin film substrate was immersed in separately placed cationic and anionic precursors alternately. [18, 19]. Before the deposition, all the glassware and substrates were thoroughly cleaned by usual method so as to achieve uniform deposition of the film. Initially, glass substrate was

immersed into the 0.1 M tungstic acid (H_2O_4W) cationic precursor solution for 20s, where substrate surface adsorbs W $(OH)_6^+$ species on the substrate surface then rinsed in de-ionized water for 20s to remove loosely bound species of $W(OH)_6^+$ ions. Further the substrate was immersed in 1 M NaOH anionic precursor solution for 20 s, where OH^- ions react with $W(OH)_6^+$ ions on the substrate surface and form a single layer of tungsten hydroxide $W(OH)_3$. Finally it was rinsed in rinsing water to remove weakly bound species for 20s. This completes one SILAR deposition cycle. To grow the 279 nm thick film, such SILAR cycles were repeated in severals times. The as deposited films were further annealed in air at 473 K temperature for 3 h to obtain pure phase WO_3 thin film.

FTIR unit. The optical absorption studies were carried out within the wavelength range 400 – 800 nm using ELICO ® Double Beam SL 210 UV-Visible Spectrophotometer. The variation of electrical resistivity of WO_3 with temperature was studied by using two probe methods.

Results and Discussion

A typical FTIR spectrum of the WO_3 thin film of thickness 279 nm in the mid-infrared frequency range from 630 to 4000 cm^{-1} is shown in **FIGURE. 1.** It is observed that, the peaks appearing in the spectra are characteristic of the material structure. It is observed that the peaks observed in the spectra at 738.672 cm^{-1} and 870.447 cm^{-1} corresponds to prominent symmetric stretching vibration of low frequency W-O band in WO_3. The bearing free OH groups can further condense leading to high polymers. The W-O-W bridges formed during the poly-condensation process will have one or two water molecules coordinated to the tungsten atom. [20-21]. However, peaks observed at 1365.09, 1414.84, and 1641.01 cm^{-1} more sharp band corresponds to intercalated water molecules (W-OH…H_2O) are characterized by a prominent peak at 2946.80 cm^{-1}[22-23].

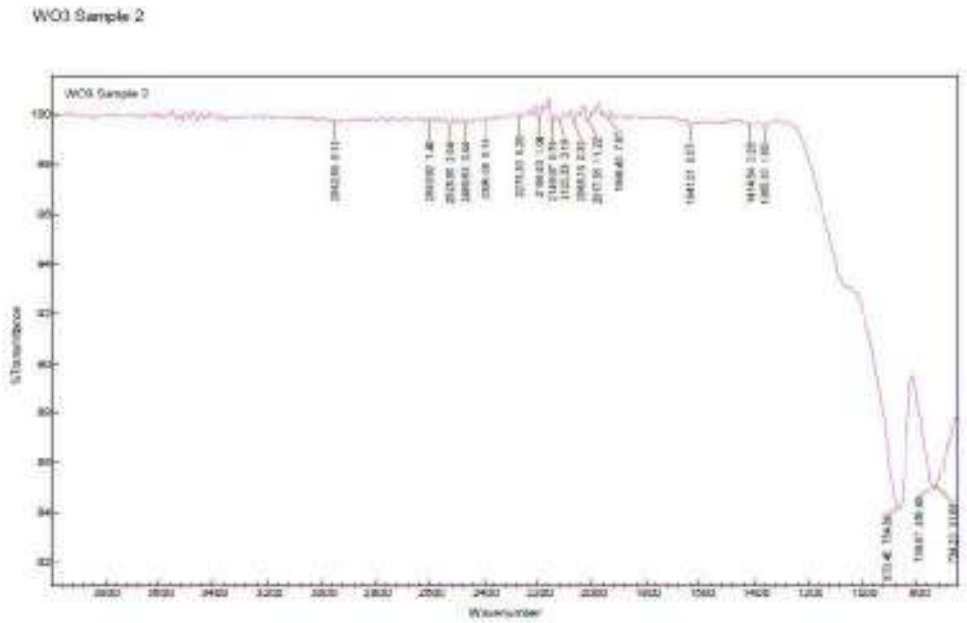

Figure.1. A typical FTIR spectrum of WO_3 thin film of thickness 279 nm.

The optical absorption spectrum of WO_3 thin film was studied in the range of wavelength 400-800 nm at room temperature (**FIGURE.2.)** Shows the variation of the absorbance and of WO_3 thin film Wavelength. The spectrum revels that WO_3 thin film has high absorbance of light in the visible region indicating as an absorbing materials. The optical band gap (Eg) of WO_3 film was calculated using the equation, $\alpha h\upsilon = (Eg - h\upsilon)$; where, 'α' is absorption coefficient, 'Eg' is band gap, 'A' is constant and n is equal to 1/2 for indirect and 2 for direct transition. The plot of $(\alpha h\upsilon)^2$ versus hυ of WO_3film is shown **FIGURE.2.**The direct band gap energy was estimated by extrapolating the linear portion of the plot to the energy axis at $(\alpha\ h\upsilon)^2 = 0$. The optical band gap energy of WO_3 thin film deposited by SILAR method was found to be 2.2 eV which is very close to the results reported (2.5eV) by Lokhande etal. [24, 25]. But quite low as compared with the results reported (2.95 eV) Changa etal. [26]. This decrease in optical band gap energy may be due to quantum confinements of the WO_3 nano particles.

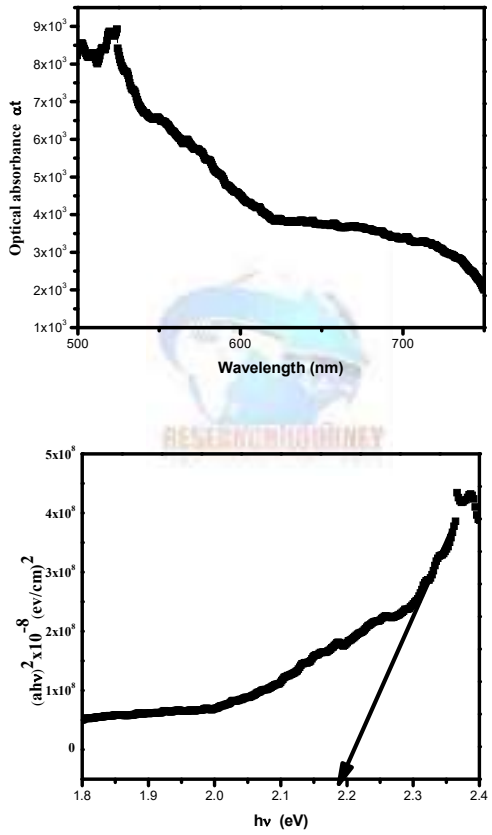

Figure.2. The plot of $(\alpha h\nu)^2$ versus hν (Inset shows optical absorption spectra) of WO_3 thin film.

The D.C two point probe method was employed to understand the variation of electrical resistivity of WO_3thin films with temperature **(FIGURE. 3)**. The decrease in electrical resistivity with increase in temperature indicates semiconducting behavior of WO_3. The electrical resistivity of the WO_3 thin film deposited by SILAR method onto glass substrate is found to be of the order of $10^5\Omega$ cm and it is in agreement with earlier report [27, 28]. The activation energy was calculated by using relation, $\rho = (Ea/KT)$; where 'ρ' is the resistivity at temperature T, 'ρ0' is constant; 'K' is Boltzmann constant and 'E_a' is activation energy. The activation energy of WO_3thin film deposited onto glass substrate was found to be 0.48 eV

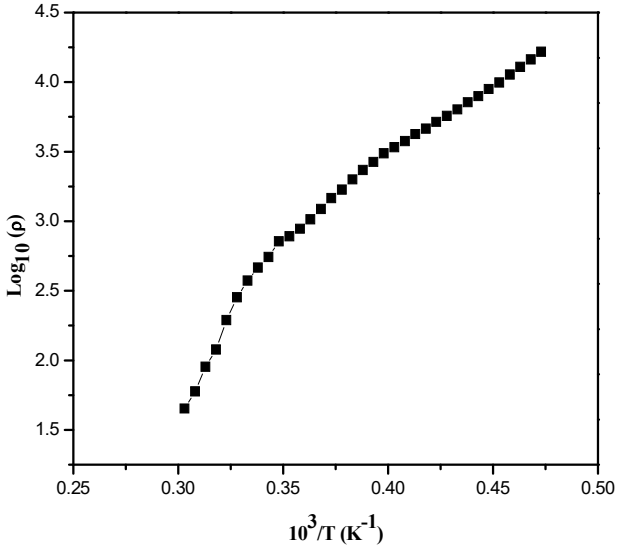

Figure. 3 The plot of log ρ versus 10^3/ T of WO_3 thin film

Conclusions

In present work, nanostructured thin films of tungsten oxide were successfully synthesized by Successive Ionic Layer Adsorption and Reaction method onto glass substrate. The FTIR, characterizations confirms nanocrystalline nature and symmetric stretching vibration of low frequency W-O band of WO_3. The direct optical band gap energy and activation energy of the WO_3 thin film is found to be 2.2 eV and 0.48 eV respectively.

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Study of AC Electrical Conductivity of Polypyrrole Based Composites

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Abstract :

Conducting polymer composites of polypyrrole / Tin oxide (ppy /SnO_2)were synthesized by in polymerization of pyrrole with SnO_2 using $FeCl_3$ as an oxidant. Thermal properties of polypyrrole polymethylmethacrylate (PPY-PMMA)Composites are analyzed by differential scanning calorimetry.The AC conductivity of these composites is studied in frequency range of 600 HZ to 1MHZ and temperature interval 23^0C to 110^0C. The study depending on the frequency has highlighted three domain at 10w frequencies the conductivity is independent of frequency at intermediate frequencies, the ac conductivity follow a power law in frequency and at high frequency the ac conductivity can be explained in term of hopping process. The SnO_2 is varied in five different weight percentage of PPY in PPY/SnO_2 composites. Electrical conductivity of the concentration of SnO_2 in PPY. The frequency dependent AC conductivity reveals that the SnO_2 concentration in PPY is responsible for the variation of conductivity of the composites.

Introduction:

A polymer is large molecule composed of many repeated subunits, known as monomers. Because of their broad range of -properties, both synthetic and natural polymers play an essential and ubiquitous role in everyday life. Polymers range from families synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created polymerization of many monomers. their consequently large molecular mass relative to small molecule compounds produces unique physical properties , including toughness , viscoelasticity , and a tendency to form glasses and semi crystalline structures rather than crystals. Humans have taken advantade of the versatility of polymers for centuries in the frm of oils, tars gums. However, it was not until the industry began to develop. In the late 1830s, Charles Goodyear succeeded in producing a useul form of natural rubber through a process known as "vulcanization". Some 40 years later, celluloid (a hard plastic formed from nitrocellulose) was successfully commercialized. Despite these advances, progress in polymer science was slow until the 1930s, when materials such as vinyl, neoprene, polystyrene and nylon were developed. The introduction of these revolutionary materials began an explosion in polymer research that is still going on today. The term "polymer" derives from the ancient Greek word polus, meaning "many much" and meros, mening "parts", and refers to a molecule whose structure is composed of multiple repeating unites, from which originates a composing polymers derive, actually or conceptually, from molecules of low relative molecular mass. The term was coined in 1883 by Jones Jacob Berzelius, through with a definition distinct from the modern IUPAC definition. Unmatched in the diversity of their properties, polymers such as cotton, wool, rubber, Teflon and all plastic are use in nearly every industry. Natural and synthetic polymers can be produced with a wide range of stiffness strength, heat resistance, density and even price. With continue research into the science and applications of polymers, they are playing an ever increasing role society.

"The term polymer derives from the ancient Greek word polus, meaning many, much and meros, meaning part and refers to a molecule whose structure is compose of multiple repeating units".

1) Polypyrrole is a type of organic polymer formed by polymerization of pyrrole are conducting polymers.

2) Polypyrrole was firstly synthesized by conventional chemical method in insoluble.

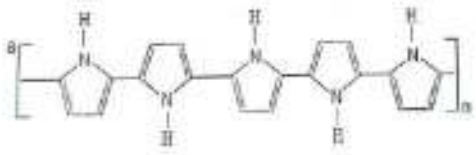


Fig . :- Polypyrrole Structure

Experimental:

Preparation of polypyrrole:

Powder poypyrrole was prepared from 4.290 (high) high weight ratio of pyrrole monomer and oxidant ($FeCl_3$). During the synthesis, concentration of ($FeCl_3$) was kept constant and methanol was used as a solvent. The py- monomer, anhydrous iron chloride ($FeCl_3$) and methanol were used for synthesis of polypyrrole. The solution of 7ml methanol and 1.892g $FeCl_3$ was first prepared in round- bottom flask, and 8.4ml pyrrole monomer was added to ($Fecl_3$+ methanol) solution with constant stirring in absence of light. The amount of pyrrole monomer was dropwise added to the solution in such a way to get maximum yield.In the polymerization reaction of pyrrole, it was observed that as soon as the pyrrole monomer was added to the solution, the colour change to dark green/black. There was an increase in temperature of the solution during the start of reaction, which shows that it was an exothermic reaction. And it was out room temperature for 4 hr. The final precipitated polymer was filtered by a conventional method. The polyrrole was washed with distilled water several times till the filtrate obtain was colorless. To remove last traces of un-reacted pyrrole and remaining ferric and ferrous chloride formed due polymerization, it was then wased with methanol. The polymer obtain in powder form, was dried first at room temperature for a few hours and then finally dried in an oven at 80^0 C for 4 hr.

Preparation of polypyrrole pallet:

.No.	Sample code	Composition	Thickness (mm)
1	PS 1	Pure PPY	2.686
2	PS 2	Pure SnO_2	1.926
3	PS 3	0.2SnO_2-0.8 PPY	1.499
4	PS 4	0.5SnO_2-0.5PPY	1.880
5	PS 5	0.8 SnO_2-0.2 PPY	1.870

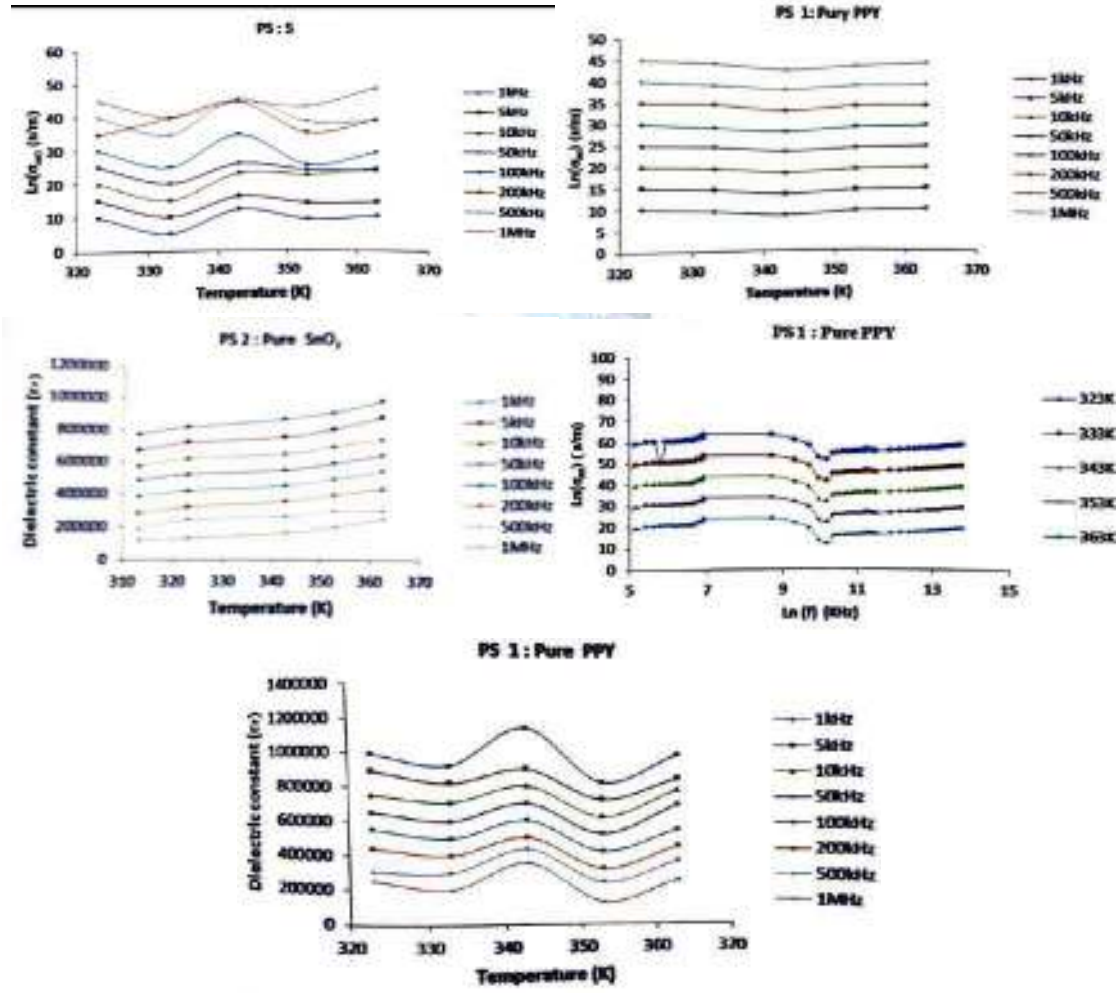
The sample is prepared in pallet formed. In this stannic oxide is used and they are ethyl cellulose (0.05%) used as a dopant in the base material i.e; ppy.The SnO_2 and ppy powdered were crushed by using motor pester to form a fine powder . The two material SnO_2 and PPY are mixed by using molecular weight in different ratio. Now , assemble bottom to top portion of KBr press assembly and place one of the small die up inside the press. Transfer the sample mixture to

KBr press assembly and place second die inside the KBr press assembly down so that sample mixture is now sandwiched between the surface of the each die. Transfer KBr press assembly to press and slowly compress die in KBr press assembly until a pressure 5-8 tones is achieved on gauge. Make sure that pressure release valve is closed. After reached on 8 tones , slowly open the pressure release valve to release the pressure. Remove the bottom portion of KBr assembly and remove the pallet from the die. Check that the pallet is ready. After making the pallet heat in an oven at 70^0 c for 45 min.for the good conductivity of pallet apply silver paint on it. Again heat in oven at 70^0 c for 45 min. finally, pallet is ready for the measurement of dielectric properties and AC conductivity.

Thickness Measurement:

Direct measurement (screw gauge) in present research, the thickness of each sample pallet will measurement by using the digital micrometer.

Structural Characterization:



Results and Discussion :

The conductivity of the material increases with increases in frequency at constant temperature. The conductivity of the material increases with increases in temperature at constant

frequency. From the conductivity of the ppy-SnO_2 composite is greater than that of the conductivity of the pure ppy with frequency at constant temperature. The dielectric constant increases with increase in temperature at constant frequency. The AC conductivity increases with increases in temperature at constant frequency.

Conclusion:

The variation of AC conductivity with frequency at constant temperature, AC conductivity very marginally increases with frequency at temperature it shows that from the graph 1 and 2 in figure can be produce fairly good AC conductivity than graph pure PPY.

Variation of dielectric constant with temperature at constant frequency, dielectric constant decreases with increases of temperature at constant frequency, from a structural point of view the dielectric relaxation involves the orientation polarization, in which turns depends upon the molecular arrangement into the dielectric. It shows that from the graph 3 ,the dielectric decreases with frequency and increasing with temperature . the figure 3 ,the dielectric decreases with frequency and increasing with temperature . the figure 4 and 5 shows AC conductivity with temperature for pure PPY, and their composites with SnO_2 respectively at constant frequency. It is observed that initially, the conductivity is increases for the above sample and as compares to the pristine material and then it remain almost constant all the temperature.

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Synthesis and Characterization of Magnesium Oxide Nanoparticles By Co-Precipitation Method

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Abstract:

The present study illustrates that the characterization and co-precipitation method for synthesis of Magnesium oxide nanoparticles. The magnesium oxide nanoparticles were synthesized by using liquid phase method with large surface area in short reaction time at room temperature and this method is the simplest, cost effective, ecofriendly method. It is also probed for its effect on nanocrystalline size structure via XRD studies of MgO nanoparticles, The crystallite size determined by the Debye-Scherrer formula is 35.62nm. Then application for humidity sensors is studied.

Key words: Co-precipitation, Magnesium Oxide, nanoparticles, electrical measurements.

Introduction:

Metal oxides such as magnesium oxide (MgO) nanoparticles [1] are extremely important technological materials for use in catalyst, catalyst support, electronic, sensors and photonic devices semiconductors, capacitors and batteries [2]. The magnesium nanoparticles were synthesized by Physical methods as well as Chemical methods. But the Chemical methods have advantage over physical methods due to inexpensive and easy to perform.The co-precipitation method is cheaper technique for synthesis of magnesium oxide [3] nanoparticles. The thick films of nanoparticles were prepared by the Screen Printing Method. The three films were prepared by different dipping time with Al2O3 for 1, 2, 3 minutes respectively. In electrical measurements, it has been studied that humidity affects on electrical properties of various metal oxides. The various properties such as electrical conductivity of metal oxide nanomaterial were studied in the presence of humidity.

Experimental Procedure :

Materials:

Magnesium Nitrate Hexahydrade [Mg(NO2)(H2O)6] and Sodium Hydroxide (NaOH) powder of AR grade of high purity (LOBA Chemicals) used as starting materials and . The distilled water and Ethanol (AR grade 99.9% purity) used as a solvent and washing reagent in the chemical reaction respectively.

Preparation of Magnesium oxide nanoparticles:

Initially the Magnesium Nitrate Hexahydrade [3] of wt. 10.256 gm (0.2 M) and dissolved in 200 ml of distilled water. The 1.599 gm (0.2 M) of NaOH in 200 ml distilled water. Then 200 ml of NaOH solution is added in solution of [Mg(NO2)(H2O)6] drop-wise by using glass rod.

After that, solution kept under magnetic stirring for 2 hours after stirring the solution was kept on table at rest for 2 hours so that, the precipitation is formed at the bottom of beaker. This precipitation was filtered and washed several times by using distilled water and Ethanol so as to get the final products. The final product is kept in vacuum oven (Quality Make, India) at 80 °C for 4 hours for drying product and removing the moisture. This dried powder is then crush and make it very fine powder by using mortar pestle. Finally the fine powder of MgO is calcinated at 400°C for 3 hours for the removal of impurities present in the powder. So that we will get synthesized MgO possessed high crystallinity with the particle size in nanosized range.

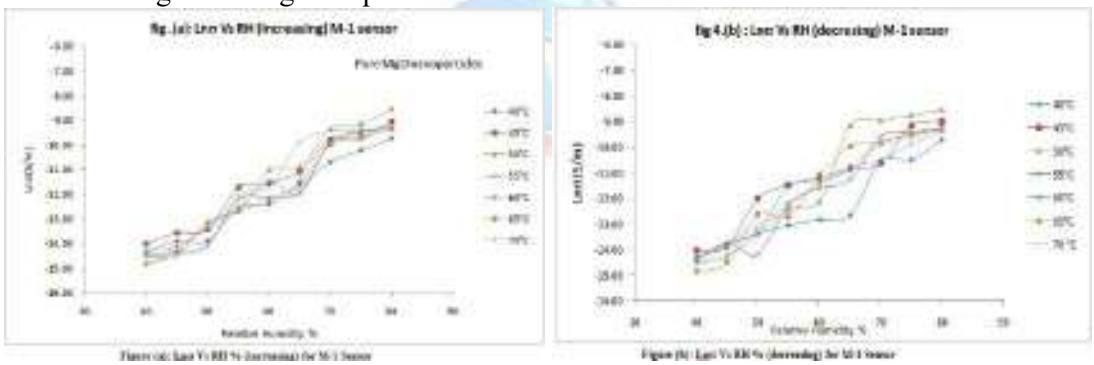
Electrical Measurements:

Characterization of Hysteresis:

In present work it is observed that from hysteresis plot series of a sample which is MgO dipped with Aluminium Chloride for different dipping time i.e for 1,2,3 minutes respectively at respective constant temperature. From hysteresis plot it is clearly seen that there is very small hysteresis [4] is present during forward (increasing) and reverse (decreasing) cycle of RH. It is observed that there is very significant average change was observed in value of resistance of sample in the range of 1010 to 108 ohms.meter. From 40 to 80 % RH except in the sample M-2 (2 minutes) change in value of resistance from 10^9 to 10^7 ohm.meter .There is noticeable change in the value of resistance of sample M-2 at constant temperature 40^0C to 70 ^{0}C

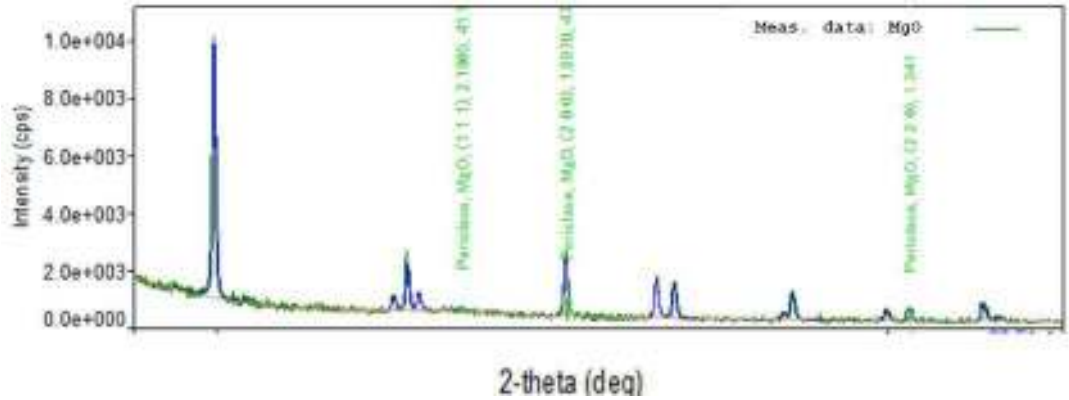
Conductivity Measurements:

It is observed that the conductivity increases partially linearly with relative humidity from 40 to 80 % RH and vice-versa. When the temperature of sample increases, the conductivity also increases. In all the series of sample the conductivity found to be lowest at temperature 40 ^{0}C, while it is highest at high temperatures.



Characterization:

The Fig. shows the X-RD pattern of periclase magnesium oxide nanparticles synthesized . It is clearly observed that the highest intensity peak lying at (111) crystal plane and other peaks at (200),(220) of MgO. An average Nanoparticles size is found to be 35.62 nm calculated by Debye Scherrer formula[5].



Conclusion:

All the peaks are perfectly match with periclase MgO particles. No other peaks were detected in spectrum within detection limit of X-RD instrument, indicating the pure periclase MgO nanoparticle is synthesized. . Conductivity of Sample films linearly responds to Relative Humidity. The Sample films shows the appreciable results regarded with Humidity Sensing.

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Detection of Carbon Dioxide Using Conducting Polymer Polypyrrole and Polyaniline

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Abstract:

The conducting polymers such as polypyrrole and polyaniline and their derivatives have prime importance due to their diversified applications. Because of their flexibility in composition and ease of preparation the properties like conductivity, stability, selectivity and response time can be tuned. These are the most useful especially the polypyrrole is very important when it is exploited for gas sensing. In the present work polypyrrole and doped polypyrrole are prepared in the form of thick film by conventional method. The thick film gas sensors are fabricated on ultrasonically cleaned glass plate by screen printing technique. To check the surface morphology, the samples are characterized by Scanning Electron Microscopy (SEM). The prepared thick films when exposed to CO_2 gas at room temperature, the sensitivity of the sensors increases with the gas concentration. The other properties such as stability, static and dynamic response of the samples are studied.

Introduction:

A Conducting polymer polypyrrole (PPy) has been a subject of many studies because it exhibits relatively high electrical conductivity, good environmental stability and versatility of synthesis. Adhikari et al [1] reported that the majority of sensor devices utilize many polymers with definite roles, either in the sensing mechanism or through immobilizing the species responsible for sensing of the analyte component. While some polymers are intrinsically responsible for a sensor function, other polymers are made to augment the sensing operation through modification of the polymer by functionalization. Polymeric thin film deposition technology and the design of more active sensor, specific polymers will lead to successful miniature, multiple sensor arrays. Bhadra et al [2] reviewed that the synthesis, processing and applications of polyaniline (PANI).The advantages of the intrinsically conducting polymers (ICPs) over the other conducting polymers and the superiority of PANI among other ICPs are reported by them. A detailed discussion on the mechanism of electrical conduction in PANI and the factors those influence the conductivity of PANI is also included. Absorption and desorption of CO_2 molecules interacting with functional groups of polymer molecules will induce an appropriate change in an electrical properties, such as dc/ac conductivity and dielectric constant of the polymer.

Experimental:

Preparation of Polypyrrole (PPy) and Polyaniline (PANI):

The preparation of polypyrrole is chemical polymerization. Powder polypyrrole was prepared with 4.290 (high) weight ratio of pyrrole (Py) monomer and oxidant ($FeCl_3$). During the synthesis, concentration of $FeCl_3$ was kept constant and methanol was used as a solvent. The Py monomer, anhydrous iron (III) chloride ($FeCl_3$) and methanol were used for synthesis of PPy. The solution of 7 ml methanol and 1.892 g $FeCl_3$ was first prepared in round bottom flask and 8.4 ml Py-monomer was added to ($FeCl_3$ + methanol) solution with constant stirring in absence of light. The amount of Py-monomer was added to the solution in such a way to get maximum yield. The polymerization of Py, which was suppressed in a solution, progressed rapidly due to an increase of oxidation potential caused by evaporation of solvent. In the polymerization reaction of Py, it was observed that as soon as the Py-monomer was added to the solution, the colour changed to dark green/black. There was an increase in temperature of the solution during the start of reaction, which showed that it is an exothermic reaction and it was carried out at room temperature for 4 hr. The final precipitated polymer was filtered by a conventional method. The polymer was washed with distilled water several times till the filtrate obtained was colourless. To remove last traces of un-reacted pyrrole and remaining ferric and ferrous chloride formed due to polymerization, it was then washed with methanol. The polymer, obtained in powder form was dried first at room temperature for a few hours and then finally dried in an oven kept at 80^0C for 5-6 hr [6-9]. This polypyrrole is then used for active layers of Semiconductor Gas Sensors.

The polyaniline is prepared by usual method. In 100 ml solution of aniline (0.4 M) and 1M sulfuric acid; 100 ml solution of ammonium persulphate (0.5 M) was added drop wise with constant stirring at room temperature at normal condition. After completion of the oxidant addition, stirring was continued for further 2 h to insure completion of the reaction. During polymerization, the sequence of coloration of the reaction mixture was light blue, blue green and finally greenish black precipitate. This color indicates that the product is conducting emeraldine salt. The reaction mixture was kept overnight. Then it was filtered, washed with distilled water until the filtrate become colorless and finally with methanol to remove the impurities and oligomers.

Sensor preparation:

The ink or paste of the sample was prepared by using screen-printing (thick film technique) technique. The binder for screen-printing was prepared by thoroughly mixing 8 wt% butyl carbitol with 92 wt% ethyl cellulose. On chemically cleaned glass plate, paste of Al_2O_3 was screen printed and it was kept for 24 hr to dry it at room temperature and then heated at 140^0C for 2.5 h to remove the binder. The Al_2O_3 layer provides mechanical support as well as high thermal conductivity. Paste of PPy in proper stiochometry was then screen printed on Al_2O_3 layer. Again plate was dried at room temperature for 24 h and binder was removed by heating it at 150^0C for 2.5 h. Finally PPy and PANI thick film design for detection and monitoring of carbon dioxide gas sensor using conducting polymer polypyrrole and polyaniline.

Finally on the top surface of the sensor, interdigited electrodes [6,7] were fabricated using conducting silver paste as shown in the Fig.1 (b). To measure the sensitivity, electrical resistance was measured with the help of voltage drop method.

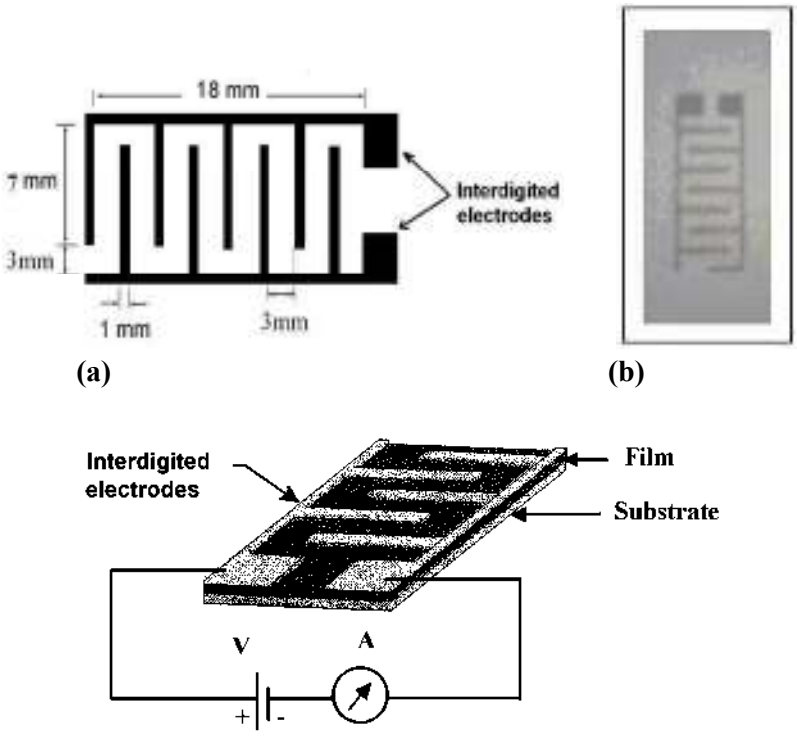

Fig. 1(a): Fabrication of interdigited Electrodes (b) Actual photograph of interdigited electrodes (c) Circuit of resistance measurement using interdigited electrodes.

Results and Discussion:

SEM Analysis:

The SEM pictures of pure PPy and PANI are shown in figs. 2 (a and b) respectively. In fig 2 (a) it is seen that the structure of PPy consists of nano spherical balls connected to each other in a chain. Hence voids and spaces of different size and shapes are created. Whereas in fig 2(b), the spherical balls are not seen but nano size walls are form which are connected randomly to each other, thereby the voids and pores of nano size are formed. Thus the rough surface morphology of both the films favours the adsorption of CO_2 gas.

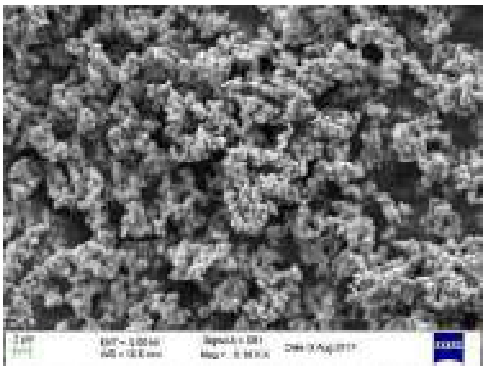

Fig.2(a): SEM of Polypyrrole

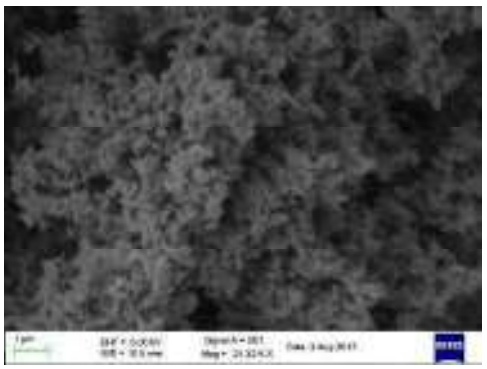

Fig.2(b): SEM of Polyaniline

Table I: Average diameter of pore, number of pores per inch and sensitivity of pure PPy and PANI

Sr. No.	Sample	Average diameter of pore (nm)	Number of pores per inch (in x 2000 magnification)	Sensitivity (s) at 80 ppm at 300K
1	PPy	275	118	0.43
2	PANI	230	70	0.32

From the SEM pictures, it is observed that PPy have maximum pores per inch (calculated for x 2,000 magnification for each composition) than PANI. Thus PPy have more surface area and exhibit more sensing nature (Table I).

Sensitivity of sensor:

The sensitivity of the sensor is given by equation

$$S = \left(\frac{R_{air} - R_{gas}}{R_{air}} \right) = \left(\frac{\Delta R}{R_{air}} \right)$$

Where, R_{air} and R_{gas} are the resistances of sensors in air and gas respectively. Maximum sensitivity was recorded for Polypyrrole gas sensor (Table I).

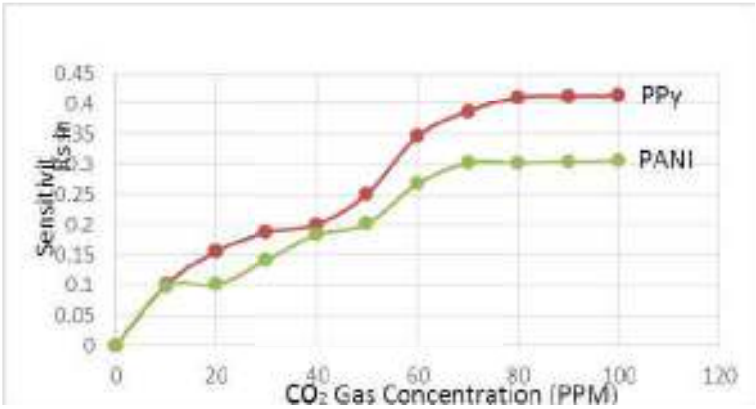

Fig.(3) Variation of sensitivity with of CO_2 gas concentration at room temperature.

From fig.3 it is observed that the sensitivity increases with increase in concentration of CO_2 gas. The increase is linear up to 70 ppm and then it remains almost constant for further increase. The increase in sensitivity is due to change in resistance of the film. This happens because of adsorption of CO_2 gas on the surface of the film. Actually the rough surface morphology of the film is responsible for the adsorption of the gases. This is revealed from the SEM also.

In PANI doped state can be controlled by acid/base reactions which are used to detect acidic and basic gases. When PANI exposed to CO_2 acidic gas , it undergo doping of hydrogen by protonation. The protons on −NH− groups transferred and the ammonium ion decomposed to ammonia gas and proton. When it is reacted with the acidic gases such as CO_2 PANI will get doped and water transfer the protons to PANI. H_2 adsorb on the positive-charged nitrogen atoms of PANI and then dissociate into hydrogen atoms. The formation of new N-H bonds between the hydrogen atoms and nitrogens reduce the resistance of PANI.

Similar type of proton transfer is also present in PPy. It is observed that the decrease in resistance of PPy film when it is exposed to the CO_2 is a reversible process of proton transfer causes the decrease in resistance of the film

Stability of sensor:

Rate of change of resistance of the sensor with respect to time defines the stability of the sensor. A sensor should be more stable for its better response.

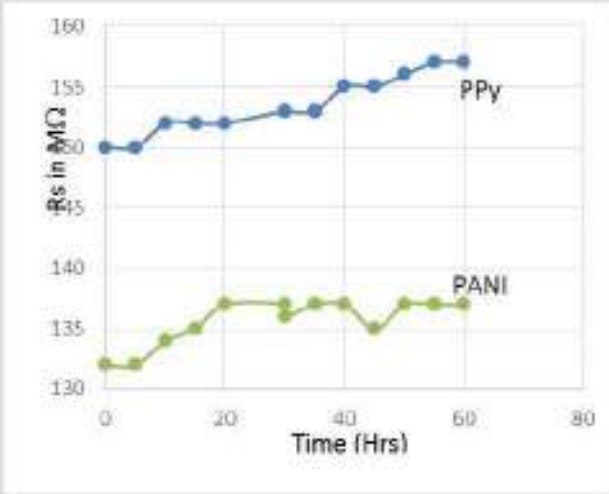

Fig. (4) Stability of the sensor.

From fig. (4), it is observed that resistance of sensor does not change drastically in both PPy and PANI.

Conclusions:

From SEM characterization it is concluded that the surface morphology is rough in both and PANI films. Nano size pores are formed. The spherical balls are attached to each other in chain like structure. It has greater surface area and therefore shows greater response to CO_2 gas. These sensors show good sensitivity and stability.

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Synthesis and Characterization of Proton Conducting Composite Solid Polymer Electrolyte System

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Abstract:

In this work to improve the proton conductivity, the Nano sized TiO_2 was dispersed to obtain (100-x)(80PVA:20AN)(x)(TiO_2) Nano- composite system. X-ray diffraction(XRD) study shows that the addition of filer TiO_2 in polymer not only reduces the intensity of the characteristic (110) peak but also broadens which is an indication of the increase in amorphousness. The Arrhenius plots for different concentrations of TiO_2 in (80PVA:20AN) polymer blend shows the initial increase in ionic conductivity of the composite polymer electrolyte upto 20 wt% filler TiO_2.The proton conductivity increases with increased relative humidity within entire studied range of H_2 partial pressures.

Keywords: Nano Composite solid polymer electrolyte, XRD, polymer blend, relative humidity.

Introduction

Since the inception of polymer electrolytes in the early 1970s, they are adopted in a wide variety of applications. Most attractive applications are secondary batteries, fuel cells, sensors, actuators, supercapacitors, ultracapacitors, electrochromic displays and dye-sensitized solar cells. The primary role of the polymer electrolyte in these applications includes (a) separate two active electrodes, (b) provide good electronic insulation and (c) allow a fast and selective transport of the desired ions. To be suitable for application in a device, a polymer electrolyte must simultaneously satisfy three fundamental requirements: performance, durability and cost.

Compounds containing loosely bound molecules are solid proton conductors. Most of them are hydrates and their conductivity generally strongly depends on their state of hydration. The conduction mechanism is, therefore, similar to that of aqueous solution. Three recognized main transport mechanisms for proton conduction are liquid like transport, H3O+ migration or impurity conduction and H_3O+/H_2O transfer. In general, the term proton conductors is not only referred to materials wherein, the ionic transport is due to H+ motion, but also include materials with complex ions transporting groups like NH_4 +, H_3O+, OH-, etc. However, there are very less number of good protonic conductors.

Composite solid electrolytes are heterogeneous, multiphase, typically two-phase solid systems. The significant enhancement in ionic conductivity in LiI and other ion conducting materials on addition of submicron size particles of inert insulating second phase such as Al_2O_3, or SiO_2 is reported [1-5]. Two main aspects for understanding the conductance of composite materials are (i) the microscopic mechanism, which determines the magnitude of interfacial conductivity and (ii) the percolation theory [6,7]. These complexes are relatively inexpensive and can be easily processed as thin films for applications such as hydrogen sensors [8], electrochromic displays, and PEFC systems. The mechanical and chemical stability of these complexes is relatively poor, and chemical degradation is often observed after

humidification.Most proton conductors show pertinent properties depending on humidity level.Particularly, the conductivity and chemical stability depend strongly on humidity.

As a matter of fact, there is a growing interest in the use of fuel cells (FC) with hydrogen as the main fuel for stationary, mobile and transportation applications. In this context, different types of membranes based on PVA investigation are due to Nikolic et al. [9]. Water-soluble polymer, i.e. PVA used in practical applications because of its ease of preparation, excellent chemical and thermal stability along with good mechanical properties. The PVA/SiO_2 nanocomposites exhibit a significantlyimprovement in thermal resistance in comparison with the pure PVA [10].

During this work an attempt was made to improve further the proton conductivity of highest conductivity giving 80PVA:20AN complex polymer, the nanosized TiO_2 was dispersed to obtain (100- x)(80PVA:20AN):(x)(TiO2) nano-composite systems.

Materials and Method

Poly(vinyl alcohol) (PVA), with a degree of hydrolysis more than 99% and average molecular weight of 146000, was procured from Aldrich, USA. Ammonium nitrate (AN-(NH_4NO_3), titanium oxide (TiO_2) with particle size 182 nm were obtained from Aldrich, USA. Thedouble-distilled-deionized water was obtained using TKA, Germany, water purifier.

It is well known that the preparative rotes and their relevant parameters control the phase formation and properties, govern the performance of electrochemical devices. For synthesis of materials, the solution cast technique is preferred due to straightforward process to produce homogeneous and uniform film. Therefore, the present work was the maiden attempt to synthesize poly(vinyl alcohol) (PVA) based proton conductors by solution cast technique.

The aqueous solutions with desired mole ratios of PVA:AN as (80:20), was prepared by dissolving PVA and AN separately in deionized water and then mixing them together. Later, this aqueous solution was thoroughly stirred for 8–10 h at 60–70 °C using magnetic stirrer so as to obtain the homogeneous single-phase solution. PVA is doped with ammonium nitrate and dispersed with titanium oxidepowder with compositions = (100-x) (80PVA:20AN):x(TiO_2), where x = 5, 10, 15, 20 and 25 wt%. The viscous gel mixture was then casted on the glass plate and dried for one week. The smooth and uniform films were obtained. All the prepared composite polymer electrolytes during present study were then thoroughlycharacterized using various analytical tools.

Results and Discussion

X-ray diffraction

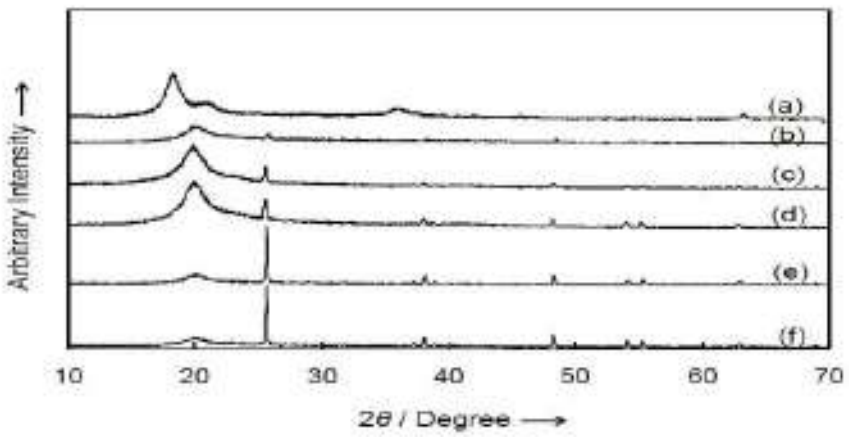

Fig.I:XRD patterns of (a) Pure PVA, (b) 95(80PVA:20AN):5TiO_2, (c)90(80PVA:20AN):10TiO_2,(d)85(80PVA:20AN):15TiO_2,(e)80(80PVA:20AN):20TiO_2 and (f) 75(80PVA:20AN):25TiO_2**.** The XRD patterns of pure PVA and (100-x) (80PVA:20AN):(x) TiO_2 (x = 5, 10,15, 20 and 25 wt%) composite solid polymer electrolytes are shown in Figs.I(a) -(e)and (f), respectively. Addition of filler TiO_2 in polymer not only reduces the intensity ofthe characteristic (110) peak but also broadens, which is an indication of the increase in the degree of amorphousness. Chand et al. [11], also, reported the similarresults. The interaction of the polymer chain with the filler (TiO_2) during the preparationof film usually increases the interlayer spacing of polymer chain and that tends to shift thediffraction peak towards lower angle [11]. But in the present case the peak shifts to higher diffraction angle suggesting decrease in interplaner distance. The characteristic peakscorresponding to TiO_2 are clearly identifiedin 5wt% TiO_2 (Fig.I(b)). The intensitiesof all characteristic peaks of filler TiO_2increases with an increase in its content incomplex polymer, however. The degree ofcrystallinity determined as discussed earlieris presented in the Table I. In this casealso, the amorphousness increases with an increase in filler content.

Samples	X_C (%)
Pure PVA	43
95(80PVA:20AN):5TiO_2	35
90(80PVA:20AN):10TiO_2	30
85(80PVA:20AN):15TiO_2	25
80(80PVA:20AN):20TiO_2	20
75(80PVA:20AN):25TiO_2	12

Table I: Degree of crystallinity obtained from XRD pattern for (100-x) (80PVA:20AN):(x) (TiO_2) composites.

Ionic Conductivity

Arrhenius plots for (100-x)(80PVA:20AN):(x)(TiO_2) complexes at x = 5, 10, 15, 20 and25 (in wt%) are given in Fig.IV.33. All the samples below and above Tg obey theArrhenius law. Furthermore,the ionic conductivity of the Nanocompositepolymer electrolyte initiallyincreases with an increase in the filler TiO_2 concentration up to 20 wt%; beyond thisconcentration conductivity decreases.Furthermore, the magnitude of conductivityenhancement due to TiO_2 addition is higherat low temperature vis-à-vis hightemperature. Further, The activation energy
is found to be minimum for the maximumconductivity giving composition.

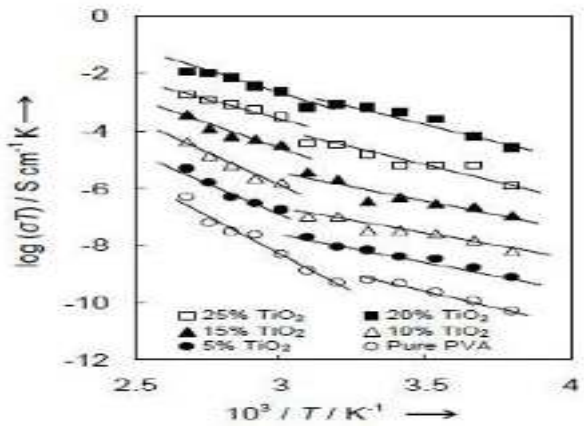

Fig.II: Arrhenius plots for different concentrations of TiO_2 in (80PVA:20AN) polymer blend

The XRD results discussedalready, revealed the dispersion of nano particles of TiO2 in 80PVA:20ANpolymer complex. In other words, the TiO_2 nano particle do not chemically react withpolymer but are disperse uniformly in the polymer matrix. Since TiO_2 is insoluble in PVA polymer it forms heterogeneous composite system and at about 20 wt% gave maximum conductivity (order of magnitude), the possibility of increased conductivity due to dissociation of salt is ruled out. The system under consideration is a heterogeneous i.e., there exists more or less sudden structural changes. Heterogeneities involve distinct interfaces between phases of different chemical compositions. A redistribution of ionic and electronic constituents takes place, so as to attain chemical and electrical equilibria, giving rise to a space-charge region across the interface [12]. The space charge region across the polymer/TiO2 interface is higher conducting compared to bulk polymer complex. The increase in conductivity up to 20 wt% of filler TiO_2 in (PVA:AN) polymer complex is due to the increase in space charge layers in composites. The maximum conductivity at 20 wt% TiO_2 added polymer is attributed to the percolation threshold where ion conducing paths throughout the polymer composites are optimum. Addition of filler in polymer complex beyond 20 wt% leads to aggregation of TiO_2 particles which disrupts the proton percolating paths across the film leading decrease in conductivity. Additionally, such aggregation of filler grains could make the long polymer chains more immobilized, leading to the decrease in the conductivity. Dissanayake et al. [13] have also reported the similar results for 80(80PVA:20AN):20TiO_2. The highest conducting 80(80PVA:20AN):20TiO_2 Nano composite polymer electrolyte film was further studied in detail.

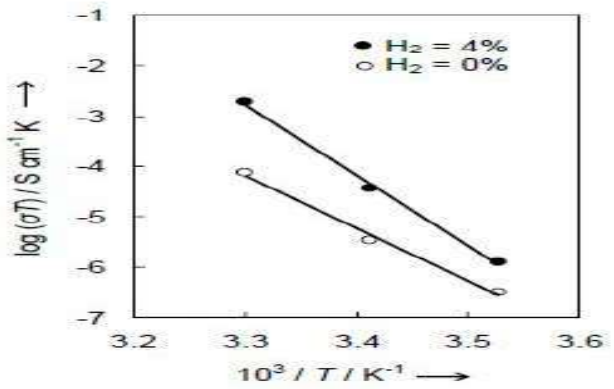

Fig.IIIa: Arrhenius plots of80(80PVA:20AN):20(TiO_2) at fixed hydrogen concentration

The Arrhenius plot for 80(80PVA:20AN):20TiO2 in presence of different hydrogen concentrations are shown in Fig.IIIa. In this system also the conductivity increases with an increase hydrogen concentration. Also, the proton conductivity increases, at fixed H_2 partial pressure, with an increase in relative humidity (Fig.III). The proton conductivity increases with increased relative humidity within entire studied range of H_2 partial pressures as shown in Fig.IIIb. The linear dependence of log(σ) on RH (%) and log(σ) on log(H_2P) are clear from Fig.III(a-c). As already discussed that the increased H_2 partial pressure at porous Pt-electrode increases H+ concentration across Pt-electrolyte interface due to electrochemical reaction. Concurrently, more mobile charge carriers (H+) are available for charge transport through the polymer electrolyte under external electric potential difference leading to an enhancement in conductivity.

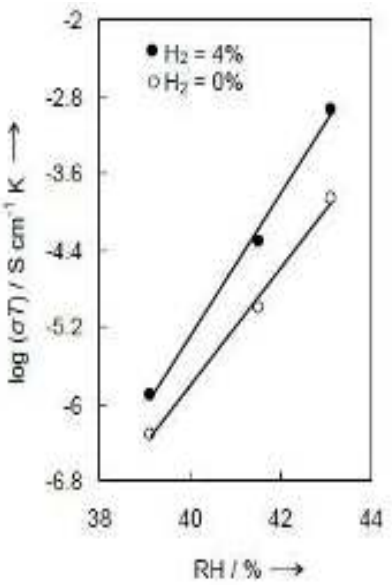

Fig.IIIb: Variation of proton Conductivity with relative humidity at Constant hydrogen concentration

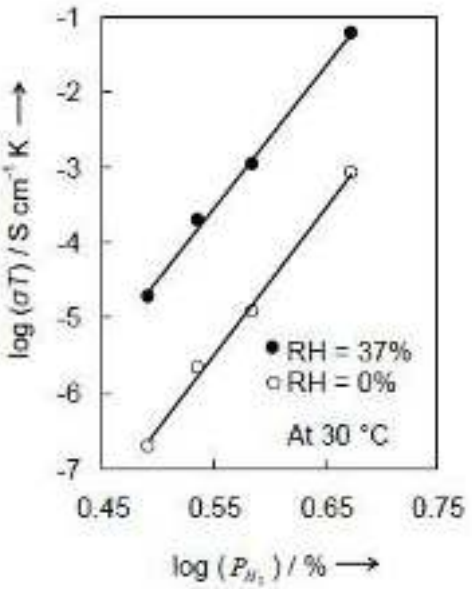

Fig.IIIC: Variation of conductivity of 80(80PVA:20AN):20(TiO2) with H2 partial pressure at fixed (0.0 and 37%) relative humidity

Conclusion

During this work a new type of proton conducting AN doped PVA and fillerTiO2 were studied. PVA is doped with ammonium nitrate and dispersed with titanium oxide powder with compositions = (100-x) (80PVA:20AN):x(TiO_2), where x = 5, 10, 15, 20 and 25 wt%. The XRD results revealed the dispersion of Nano particles of TiO_2 in 80PVA:20AN polymer complex and at about 20 wt% gave maximum conductivityunder normal atmospheric conditions.The ionic conductivity of the Nanocomposite solidpolymer electrolyte initiallyincreases with an increase in the filler TiO_2concentration up to 20 wt%; beyond thisconcentration conductivity decreases.The proton conductivity increases with increasedrelative humidity within entire studied range of H_2partial pressures.Above all, PEFCs based on proton donor and filler hold thelargest potential for developing low temperature PEFCs to be operated at room temperature.

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Investigations of Polymer Blends: Variation of Conductivity and Dielectric Constant Versus Frequency

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Abstract

The objective of this study is to determine the Electrical conductivity and Dielectric constant of the poly (styrene) when blended with poly (vinyl acetate) measured at different temperatures (313K, 323K, 333K and 343K) and at the different frequencies (1KHz to 1MHz) using 4284 LCR meter. It is found that a c conductivity of thin film varies with temperature for all values of frequencies and it varies with increase in frequencies at constant temperature. The dielectric constant also varies with the increasing of the temperature of blends.

Keywords: Polystyrene (PS),Polyvinyl acetate (PVAc), Miscibility, AC Conductivity, Dielectric Constants**.**

Introduction:

Polymer blending is one of the most important contemporary ways for the development of new polymeric materials. Polymeric materials are uniquely recognized by its applications of everyday life as well as in high-technology industries such as electronics, aerospace and medicine. So that polymeric materials has been of great research interest in the past few years because of its importance in applications in many areas. The relationship between their molecular structures and their behavior as materials has been the subject of extensive theoretical and experimental study for many decades. This extensive properties studied by using different solvents during synthesis of polymeric materials. Beth A. Miller-Chou [1] studied effects of different solvents and additives with his co-worker. So conclude that the properties of the solvents used in these processes are critical for surface formation in these polymers. Solvents properties such as polarity, volatility and specific interaction properties with the polymer material are important factors in the process of surface formation. The polymer blends composed of polystyrene (PS) and poly (vinyl acetate) (PVAc) have been widely investigated. The copolymer of PS and PVAc is a typical amphiphilic system in which the PS segment is hydrophobic and the PVAc segment is hydrophilic. Much research has been performed on the graft copolymer of PS and PVAc, including its micelle behavior [2].

Mohammed M. Kummali et-al studied the phase separation process of the polymer blend thin films. In this they made effort to synthesized polystyrene in toluene at a 4% solution concentration. AFM of polystyrene gives the detailed information about the topographical features and the mechanical phase shift imaging of the sample. This phase shift can be correlated with specific mechanical properties which affect sample interaction confirmed by quantitatively measuring the value of the dielectric permittivity [3].

The present paper focused on studies of solvent effects in AC electrical conductivity and dielectric constants at different temperature of polyblends (PS-PVAc). Polymer blends solutions systems are discussed.

Experimental:

Poly (styrene) and Poly(vinyl acetate) were supplied by SIGMA –ALDRICH, Co., 3050 spruce street, St. Louis. MO 63103 USA 314-771-5765. Tetrahydrofuran (THF-E-Merck India Ltd., Mumbai) is being used as a solvent for polyblending process. In the present work, thin films were prepared by isothermal evaporation technique.

Preparation of blends

Poly (styrene) and poly(vinyl acetate) were dissolved in tetrahydrofuran (THF). Stirring was continued for one hour before deposition of film. Total concentration of the polymeric mixture in solvent was kept 5%. Films of polymer blends were prepared by isothermal evaporation technique.

Results And Discussion

3.1. AC Electrical Conductivityand Dielectric Constant Studies

Figure 1 (a) shows the relation between ac conductivity and frequency at different constant temperatures 313K, 323K, 333K and 343K. Plot shows rise in conductivity with increasing frequencies from 1 KHz to 1MHz. The rise of conductivity upon increasing the frequency and temperature is a common respond for polymeric and semiconductor samples. It is due to the tremendous increase of the mobility of charge carriers in the composite film i.e. at higher frequencies blends of molecules starts vibrating with large amplitude within the polymeric chains hence the effect of increase in conductivity of blends [9,10].

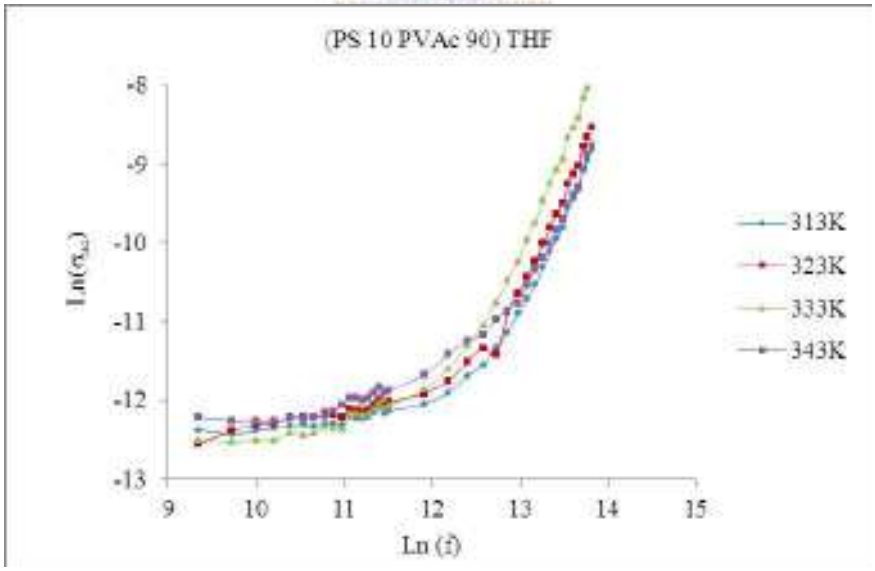

Fig 1 (a): Variation between Ac Conductivity and Frequency at Different Constant Temperatures.

Figure 1 (b) shows the relation between dielectric constant and frequency at different constant temperatures 313K, 323K, 333K and 343K. Plot shows rise in dielectric constant with

increasing frequencies from 1 KHz to 1MHz. The rise of dielectric constant upon increasing the frequency and temperature is a common respond for polymeric and semiconductor samples [11]. It is due to the tremendous increase of the mobility of charge carriers in the composite film i.e. at higher frequencies blends of molecules starts vibrating with large amplitude within the polymeric chains hence the effect of increase in conductivity of blends [12].

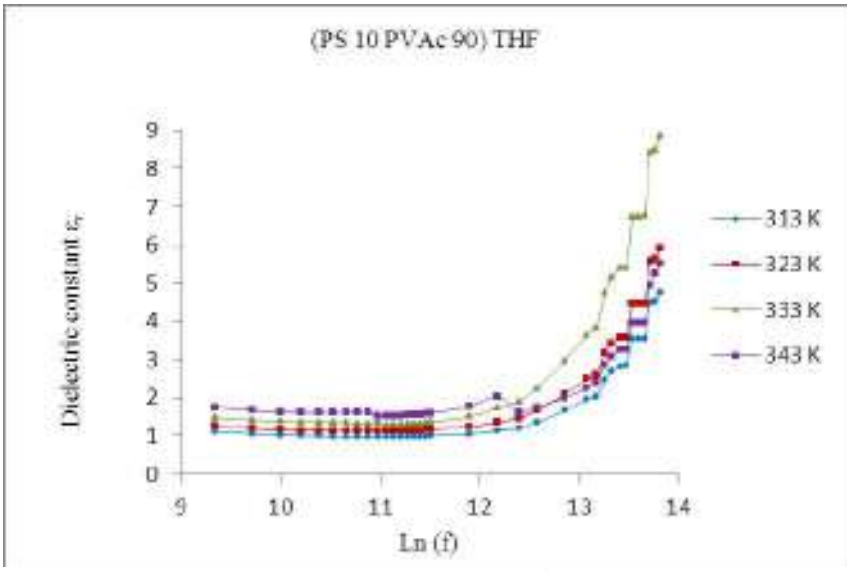

Fig 1 (b): Variation between Dielectric Constant and Frequency at Different Constant Temperatures.

Conclusions

AC electrical conductivity and dielectric constants have been measured at different temperatures and at the different frequencies, it is found that ac conductivity of thin film increases with increase in temperature for all values of frequencies and it increases with increase in frequencies at constant temperature and also the dielectric constant increases with the increasing of the temperature of blends. Hence in this blends the miscibility exists.

Acknowledgement

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Water Vapour Sensing Mechanism of PANI Doped With Zno Nanocomposites

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Abstract:

In this PANI is prepared by situ polymerization method and Zinc Oxide (ZnO) nanopartical prepared by wet chemical method at room temperature. ZnO nanoparticals were combined with PANI via polymerization in acidic aqueous solution to obtain a new type of inorganic – organic composites nanostructured. The samples are prepared in the form of thick film. It is observed that PANI doped ZnO nanocomposites sensor shows a high response and sensitivity with good repeatability as compared to that of pure PANI and ZnO nanoparticle. The effect of hysteresis of the sensors, the effect of pure and composite oxide on sensitivity of the sensors were studied. The crystallinity and the crystallite size were examined by X-Ray Diffraction technique.

Keywords: Polyaniline, ZnO Nanocomposites, Humidity Sensors.

Introduction

The possibility of reliable, reasonably accurate, relatively inexpensive and commercially viable humidity sensors is under investigation using organic-inorganic composites. Humidity sensors are useful for the detection of relative humidity invarious environments [1-3]. Humidity, the concentration of water molecules in air, affects various materials used in daily life and industrial processing of drugs, beverages, food, electronic goods etc. High and low humidity affects human beings adversely. Excessive high humidity causes corrosion in metallic components and failure of electronic as well as optical devices [4, 5]. Therefore, humidity is an important parameter to be controlled. Recently, there have been increased demands for humidity sensing elements for use in automatic humidity control systems. Polymer, polymer composites and modified polymers with hydrophilic properties [6] show excellent humidity sensing properties. Conductivity of polyaniline can be varied over a broad range and hence, it can find wide use in making sensors [7-12]. Capacitive humidity sensors utilize conductive plates formed on a dielectric film. This forms a capacitor that is sensitive to the amount of water vapours in the air. The active portion of the sensor changes its dielectric constant as it absorbs atmospheric humidity, which varies the sensor's capacitance in proportion to variation in relative humidity. Another mode of humidity sensors is resistive sensors which uses a moisture-sensitive material between two metal plates or on an inter digitated electrode substrate [13, 14]. The device's resistance varies with variations in relative humidity. The main advantage of resistive technology

for humidity sensors is that it suits to varying, difficult and condensing environments. It can be synthesized easily and has long stability. In the present work ion conducting metal doped polyaniline pellets have been used as sensing material which is based on variation of the electrical conductivity with variation in humidity.

Experimental : Synthesis of material :

A) Synthesis of Polyaniline (PANI):

In this Polyaniline (PANI) is synthesized by chemical polymerization method in which 0.2 M aniline hydrochloride is used as monomer unit. The synthesis is done by oxidative polymerization with 0.25 M ammonia peroxysulphate in aqeous medium, both solution kept 1 hour at room temperature then mixed in beaker ,briefly stirred. And left at rest to polymerize, next day, the green colour Pani precipitate was collected on a filter and washed with 0.2 M HCL solution and similarly with acetone . The Polyaniline hydrochloride powder was dried in air and then in vaccum at 60°C. Polyaniline prepared under these reaction and processing condition are further referred to as standard sample [15].

B) Synthesis of Zinc oxide:

For the preparation of ZnO nanoparticle, the aqueous solution of 2M of zinc nitrate hexa hydrate in 100 ml of distilled water .To this aquous zinc nitrate solution 0.2 M sodium hydroxide is added and the reaction mixture was heated at 80°C along with stirring and the process is carried out for four 1 hour after which the white precipitate was obtained. Then the precipitate is centrifuged and washed 2 to 3 times with de-ionised water. The obtained material were calcinated at 600°C and finally the pure ZnO nanparticles were obtained.

Characterization :

XRD Pattern of ZnO

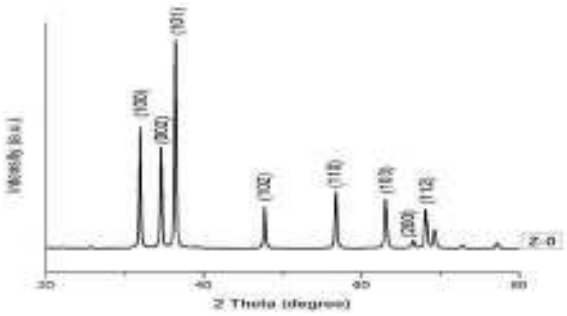

Figure 1: XRD of Pure ZnO

The Figure 1 shows the X-Ray Diffraction pattern of pristine zinc oxide (ZnO) nanostructure synthesized by liquid phase method which is calcinated at 600°C. The crystalline nature with 2θ peak lying at (100), (002), (101), (102), (110) and (103) planes. All the peaks match well the standard hexagonal wurtize structure of zinc oxide (ZnO) with lattice constants , a = b = 0.3249 nm and c = 0.5206 nm [JCPDS card no. 36-1451]. All the peaks are perfectly match with pure ZnO structure, which indicates the high purity of the obtained ZnO nanoparticle. The average crystalline size was found to be 37.32 nm calculated by Deye-Scherrer formula [16].

Result and Discussions:

Hysteresis Plot:

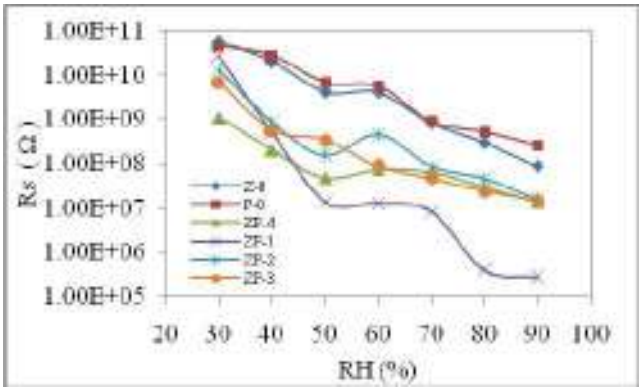

Figure 2: Variation of Resistance with Relative Humidity

Hysteresis plot shows the variation between resistances of sample with respect to the relative humidity in increasing and decreasing order from 30 to 90 % RH as shown in the fig. 2. A very small hysteresis present during forward and reverse cycle of relative humidity, where as a very significant average change observed in the value of resistance of sample, in the sample ZP-1 (10ZnO – 90PANI) the change in value of resistance is from 10^{11} ohm to 10^{5} ohm, these is a remarkable change in the value of resistance.

Sensitivity

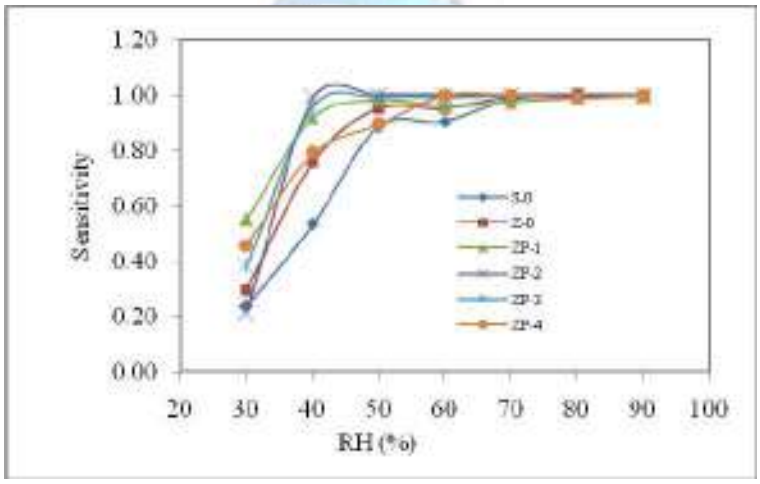

Figure 3: Variation of Sensitivity with Relative humidity

In the above samples the sensitivity is found to be increasing with the RH for all the samples of thick films and it is increasing up to some particular RH and then afterward it remains constant as shown in fig. 3. For higher RH the sensitivity is found to be higher in case of all samples of thick films. The sensitivity of ZP-1 (10ZnO-90PANI) is more than ZP-2, ZP-3, and ZP-4 samples and also from the pristine samples P-0 and Z-0. The (ZnO-PANI) composite sensors exhibits significantly higher sensitivity than sensor constructed specially from ZnO nanoparticles and PANI itself due to the formation of heterogeneous interface between them and more adsorption site was created to absorbed more water vapours.

Conclusion

Nanostructured ZnO was successfully prepared via chemical precipitation method and PANI with IUPAC polimerization technique. Minimum crystallite size was found to be for ZnO is 37.32 nm. The Hysteresis plot shows very significant average change in the value of the resistance from 10^{11} ohm to 10^{5} ohm during forward and reversed cycles of sample ZP-1(10ZnO-90PANI). The sensitivity is found to be increasing with the RH for all the samples of thick films and it is increasing up to some particular RH and then afterward it remains constant. Amongst all the prepared samples ZP-1 is more sensitivity than other prepared composite samples.

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Study of AC Electrical Conductivity and Dielectric Properties of Polypyrrole Based ZnO Nanocomposites

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Abstract:

Polypyrrole based Zinc Oxide (PPy-ZnO) nanocomposites are synthesized by in-situ polymerization in different weight percentages using oxidation method. The surface Morphology and structural properties of prepared sample was studied by using X-ray diffraction and field emission scanning electron micrograph (FE-SEM).The AC electrical conductivity and Dielectric properties of Polymer based nanocomposite of various composites materials were investigated at different temperatures and frequencies from 100Hz to 1MHz. In this the dielectric constant decreased with increase in frequency and temperature. As ZnO concentration increases the AC conductivity increased with frequency. The Activation energy of PZ2 (70%ppy+30%ZnO) was maximum among the samples and it is found to be 0.1106 eV.

Keywords: Polypyrrole, ZnO; Dielectric constant, AC conductivity.

Introduction:

Recently, the conductive polymer like polypyrrole, polythiophene, polyaniline, etc.[1].received a great deal of attention because of its good environmental stability, facile synthesis and significant electrical conducting characteristics [2]. To improve the characteristics of polymer for commercial application, ZnO nanoparticles have also attracted considerable attention in the polymer community as fillers for polymer composites because of wide band gap energy of 3.37 eV and large excitation binding energy of 60 meV at room temperature [3-6]. ZnO nanoparticles into polymers can improve the optical and electrical properties of polymers due to a strong interfacial relations between the organic polymer and the inorganic nanoparticles [7]. In present work, pure PPy and ZnO doped PPy nanocomposites were synthesized by Sit tu polymerization method in a batch process and then characterized by XRD and SEM. The A C conductivities and dielectric properties of polypyrrole and its nanocomposites were measured by using two probe method.

Experimental

Zinc oxide (ZnO):

In preparation ZnO, 0.2M Zinc Acetate dehydrates dissolved in 100 ml de-ionized water was ground for 15 min and then mixed with 0.02 M solution of NaOH with the help of glass rod. After the mixing the solution was kept under constant magnetic stirring for 15 min. and then again it was grinded for 30 min. The white precipitate product was formed at the bottom. The obtained product was washed many times with the deionized water and methanol. The final product was then filtered and precipitate is obtained in the form of white paste. The paste was kept in a vacuum oven at 80^{o}C for 4 hrs. So the moisture will be removed from the final product

and we will get dry product. Then this dry product was crushed into a fine powder by using grinding machine and finally this fine nano-powder of ZnO was calcinated at temperature 800 ^{o}C for 6 hrs. in the auto controlled muffle furnace (Gayatri Scientific, Mumbai, India.) so that the impurities from product will be completely removed and got a final product of ZnO nanoparticles [8].

Synthesis of Polypyrole (PPy):

The Py monomer, anhydrous iron (III) chloride ($FeCl_3$) and methanol were used as received for synthesis of PPy. The solution of 7 ml methanol and 1.892 g $FeCl_3$ was first prepared in round bottom flask. Then 8.4 ml Py monomer was added to ($FeCl_3$ + methanol) solution with constant stirring in absence of light. The amount of Py monomer added to the solution (1/2.33 times of $FeCl_3$) was in such a way to get maximum yield. The ensuing black precipitates are filtered and washed several times with distilled water until clear product is Polypyrole is obtained. The obtained product is dried in oven at 600^{o}C for 4 h. The synthesized materials were characterized by using XRD, SEM.

Preparation of Pellets:

Initially, for the preparation of pellets the synthesized material ZnO and PPy were mixed with different weight percentage in pure and composite form. The pellets of different series of composition of ZnO-PPy nanopowder were prepared by using electrically operated automatic press machine (KBr Press) at load of 5 tons / cm^2 for half an hour. All the pellets were sintered at 150^{o}C for half an hour. The sintered pellets were polished and the electrodes were formed by painting conductive silver paint on the opposite faces. Again pellets were sintered for the drying the silver paint at 100 ^{o}C for half an hour. The different series of composition were listed in the table (1). Table 1

S.No	Nano composites	Sample Code
1	Pure Polypyrrole	P
2	80 % ppy + 20 % ZnO	PZ1
3	70 % ppy + 30 % ZnO	PZ2
4	60 % ppy + 40 % ZnO	PZ3
5	50 % ppy + 50 % ZnO	PZ4
7	40 % ppy + 60 % ZnO	PZ5
8	30 % ppy + 70 % ZnO	PZ6
9	20 % ppy + 80 % ZnO	PZ7
10	Pure ZnO	Z

1. Results and Discussion

1.1. X-ray Diffraction (XRD):

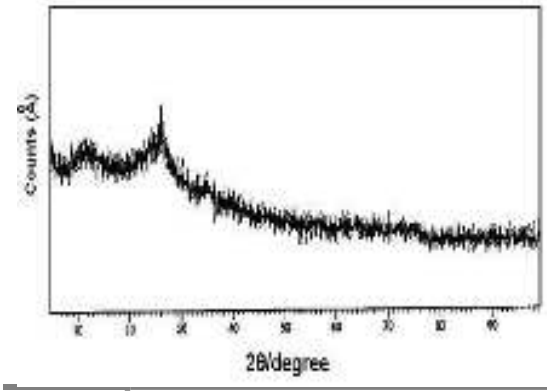

Fig.1. XRD of pure PPy

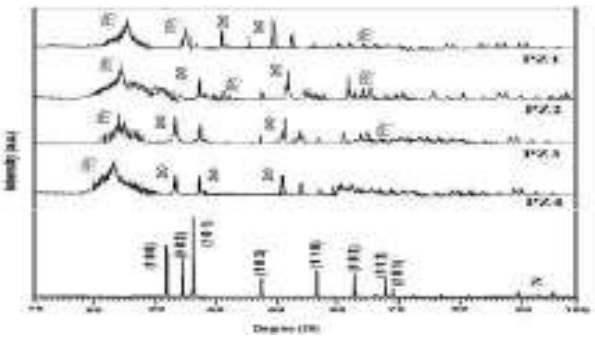

Fig.2. XRD of all composites sample

The X-Ray diffraction pattern of pure polypyrrole (PPy) and there composites are as shown in figure (1 and 2). It is recorded in terms of 2θ in the range 10 to 100°.n The pure Ppy exhibited that, it is amorphous in nature. The broad peak occurred at 24^0 and it is characteristics of amorphous nature of polypyrrole. The broad peak occurs due to the scattering of X-rays from polymer chains at the interplaner spacing. The maximum intensity position of amorphous also depends on monomer to oxidant ratio. The X-ray diffraction patters of composites of PPy, ZnO and pure ZnO, calcinated at 200^0C. All the peaks match well the standard hexagonal wurtize structure of zinc oxide (ZnO) with lattice constants a = b = 0.3249 nm and c = 0.5206 nm [JCPDS card no. 36-1451]. with 100% intensity and the average crystalline size by using Scherer's formula was found to be 99.40nm [9]. All the peaks are for the composites materials. it is observed that average crystallite size of 70PPy:30 ZnO composition is least as compared to other compositions and pure material and hence 70PPy:30 ZnO composition has large active region which tends to increase the conductivity of the composition.

Scanning Electron Microscope (SEM)

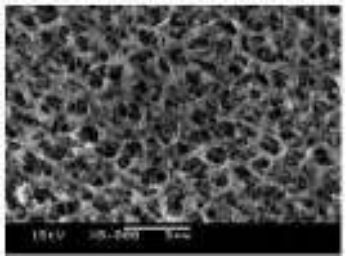

Fig. 3: SEM of Pure PPy

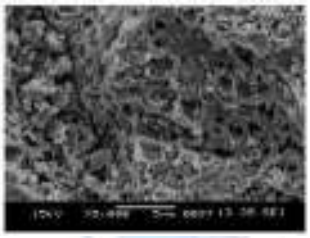

Fig. 4: SEM of PZ2 (70 PPy + 30 ZnO)

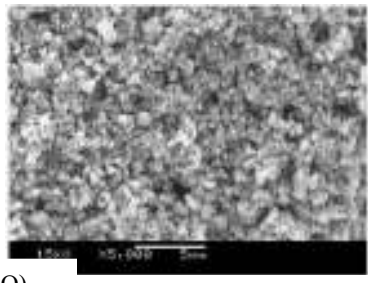

Fig. 5: SEM of Pure ZnO

From the SEM photos, it is observed that in every inch of the region, number of pores was different and an average number of pores was taken for comparative study. From every photo, porosity was calculated for one inch region and listed in the tabular form. From above figures, it is found that number of porosity of 70PPy:30ZnO composition is more and that among the prepared and pure samples. Due to high porosity, available area for the flow of ions and charges is more and conductivity enhances . High porosity reduces the obstacle to the flow of charges and ions as collisions reduce (relaxation time increases) and charges mobility increases. This tends to high electrical conductivity.

Result and Discurssion

AC Conductivity

Figure (6) show the variations of ln(ac σ with ln (frequency) at constant temperature at 300K. From these it is observed that as frequency increases, ac conductivity (ac σ) increases continuously. With increase in frequency, more and more polarization of the sample takes place and it results in increase in conductivity. The Maximum conductivity was found to be for sample PZ2 (70% PPy + 30% ZnO) and its value is ln (ac σ) = - 3.28 i.e. ac σ = 5.248 x 10^{-4} S/cm with increase in temperature, ac conductivity (ac σ) increases continuously. As there is increase in temperature more and more charges become free with increasing mobility and they contribute to the net electrical conductivity enhancement. As doping percentage of ZnO in PPy increases,

conductivity increases and becomes maximum for PZ2 sample and then with further increase in doping percentage of ZnO in PPy, conductivity decreases.

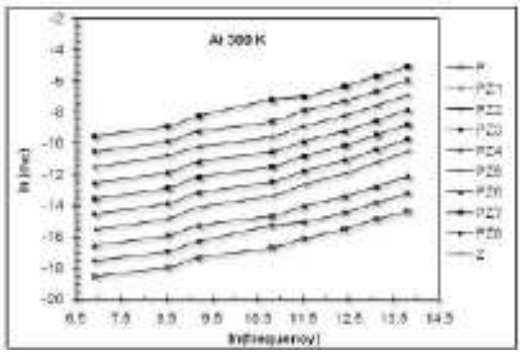

Figure 6 AC conduvtivity of Samples

Dielectric Constant

Figure (7) shows the variation of dielectric constant**(εr)** with temperature at constant frequency, with increase in temperature and increase in doping percentage of ZnO in PPy, in these dielectric constant increases and becomes maximum for 70 % PPy + 30 % ZnO sample (PZ2 sample). With further increase in doping of ZnO in PPy, dielectric constant decreases and becomes minimum for pure ZnO i.e. for Z sample. This is because PZ2 sample may have large number of free charges as compared to other compositions and their more collisions with vibrating atoms results in the increase of refractive index of the PZ2 sample and hence dielectric constant is high among the other compositions.

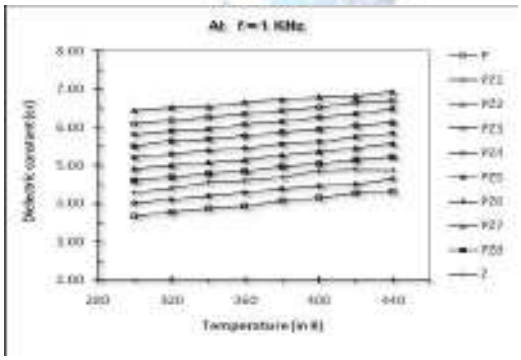

Figure 7: Graph between dielectric constant (εr) and temperature at constant frequency

Ultraviolet (UV) Spectra

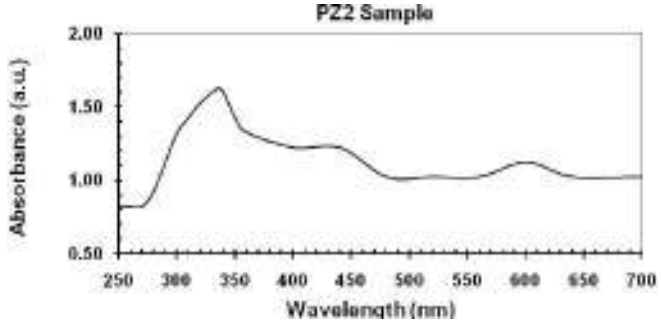

Fig. 8 Variations of absorbance (a.u.) with wavelength (nm)

As percentage of doping of ZnO in PPy increases, band gap energy decreases and becomes minimum (3.7108 eV) for PZ2 sample and with further increase in doping of ZnO, band gap energy increases and becomes maximum for Z sample. It is depicted that band gap energy for above prepared series varies from 3.7108 eV to 3.9215 eV. Minimum value of Eg for PZ2 sample shows that minimum amount of energy required to move the charges to conduction band from lower energy band and hence this sample is best among the remaining samples of the series as it requires lower energy for conduction.

Conclusion

The X-ray diffraction patterns of composites of PPy, ZnO and pure ZnO, and it shows hexagonal wurtize structure and the average crystalline size is found to be 99.40 nm . The series of sample of pure and composite form of PPy and ZnO were prepared in the form of pellet. It was observed that , frequency increases, ac conductivity (ac σ) increases continuously. With increase in frequency, more and more polarization of the sample takes place and the maximum conductivity was found to be for sample PZ2. The dielectric constant increases and becomes maximum for 70 % PPy + 30 % ZnO sample (PZ2) than other prepared sample. The study of UV radiation shows UV radiation minimum band gap energy for sample PZ2 i.e. 3.7108 eV.

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Effect of Deposition Rate on The Structural and optical Properties of Copper Sulphide Thin Films

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Abstract:

We deposited chalcogenidecopper sulphidethin films on different substrates by Chemical Bath Deposition Technique. Structural, Surface Morphology and Optical properties of as deposited CuS films were investigated by XRD, SEM, and UV-VIS Spectrophotometer. The band gap was also calculated from the equation relating absorption co-efficient to wavelength. The band gap indicates the film is transmitting within the visible range and the band gaps changes because of the grain size of the CuS in the films. The physical conditions were kept identical while growing all the samples. Optical properties show that films can find application in optoelectronic devices having a high band gap ranging between minimum of Eg = 2.64 eV to highest of 2.92 eV. We also observed that, the change in preparative parameters affects the deposition rate of thin films. From the observation, it is clear that the growth rate increases as the deposition temperature, deposition time, molarities of the solution increases. It is also clear that the growth rate increases as the film thickness and grain sizes increases while band gap decreases. Depending upon these properties films are used in Optoelectronic devices.

Key words-Chalcogenide, Thin films, Deposition Parameters.

Introduction:

Copper sulfide (CuS) as an important P-type semiconductor material because of itsexcellent optical, electronic, and other physical andchemical properties. [1] Semiconductor chalcogenideshave been of much interest because of their excellentproperties and wide-range potential applications. Inparticular, as a p-type semiconductor with a band gapof 2.37 eV, copper sulfide (CuS) is a promisingmaterial with potential applications in solar energyconversion, catalysis, and sensing. Copper sulfideshave the ability to form various stoichiometries, atleast five phases of which are stable at roomtemperature: i.e., covellite (CuS), anilite (Cu1.75S),digenite (Cu1.8S), djurlite (Cu1.95S), and chalcocite(Cu2S) [1].

In this work we report the preparation of the CuS thin films having a nanometer grain size by using Chemical Bath Deposition (CBD) Technique and study the effect of deposition rate on the properties of thin films. The CBD is one of the most convenient, reliable, simplest, inexpensive method and useful for large area industrial applications as well as preparation of thin film at close to room temperatures. The technique of CBD involves the controlled precipitation from solution of a compound on a suitable substrate. The technique offers many advantages over the more established vapor phase synthetic routes to semiconductor materials, such as CVD, MBE and spray pyrolysis. Factors such as control of film thickness and deposition rate by varying the solution pH, temperature and reagent concentration are allied with the ability of CBD

to coat large areas, in a reproducible and low cost process. Another advantage of CBD method with respect to other methods is that the films can be deposited on different kinds, shapes and sizes of substrates [2-5].

Experimental Details:

Thin films of CuS were deposited from a solution of analytical grade $CuSO_4.5H2O$, a Cu^{++} ion source and Thiourea as an S^{--} ion source in an alkaline solution of Ammonia. Commercial glass slides, used as substrates, were cleaned in acetone and methanol ultrasonically, and finally, again washed with methanol ultrasonically before use. After cleaning the glass slides were kept vertically in a closed beaker with the help of a special holder which is attached to AC Motor having a constant speed of 60 r. p. m. We have double distilled water in a beaker and then added $CuSO_4.5H2O$ of particular molarity as a Cu^{++} ion source slowly under Magnetic stirring. Add liquid Ammonia slowly to the solution for adjusting the pH of solution which is measured on pH meter, providing the temperature to the solution by means of heating coil. Add Thiourea ($SC(NH_2)_2$) of particular molarity as a S^{--} ion source was slowly poured into the solution only when the appropriate temperature i.e. 60°C was reached. Finally the temperature was kept constant with the help of a temperature controller in the range 70°C to 72°C. The time for the deposition was varied from 10 to 60 Min. after achieving constant temperature. After the deposition, the CuS films were washed with methanol ultrasonically to remove the loosely adhered CuS particles on the film and finally dried in air. The same procedure is repeated for different time durations [6].

The crystallographic structure of films was analyzed with a diffractometer (XPERT-PRO) by using Cu-Kα lines (λ= 1.54 Å). The average grain size in the deposited films was obtained from a Debye-Scherrer's formula. Surface morphology was examined by JEOL model JSM - 6400 Scanning Electron Microscope. The absorbance vs the wavelength was recorded with the UV-VIS spectrometer (Perkin Elmer: Lambda 35) in the wavelength range 200–600 nm for a different molarities [6]. Also we were changing the different parameters such as Time, Molarities, pH and Temperature and note the effects of deposition rate on the properties of thin films.

Results And Discussion:

A. XRD Studies:

The X-ray diffractogram of CuS films show broadened diffraction profiles (figure 1). It is observed that XRD patterns show a preferred orientation along (102) plane. The grain size of the nanocrystalline films is estimated using the Scherrer formula [3],

$D = K\lambda/\beta 2\theta \cos\theta$

where K is a constant taken to be 0·94, λ the wavelength of X-ray used (λ = 1·54 Å) and β2θ the full width at half maximum of (102) peak of XRD pattern, Bragg angle, 2θ, is around 26·5°. The grain sizes were found to be within the range 08 to 68nm.

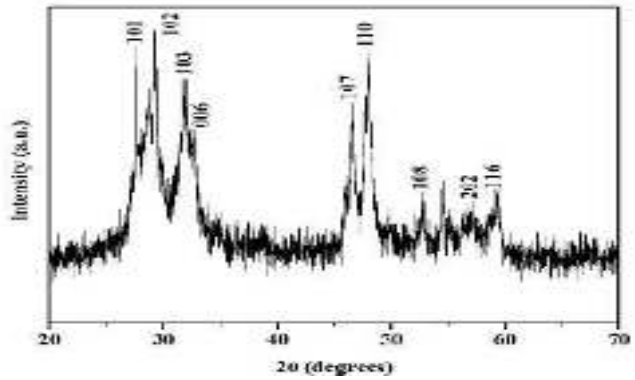

Figure 1. XRD pattern of as-deposited copper sulphide thin films

B. SEM Studies:

Scanning electron microscopy is a convenient technique to study the microstructure of thin films. Figure 2 shows the surface morphology of CuS thin films deposited at different deposition time and substrate observed by SEM. From the micrographs, it is observed that the 'as-deposited' films are not uniform throughout all the regions. But the films are without any void, pinhole or cracks and that they cover the substrates well. From the figure, we clearly observe the small nanosized grains engaged in a fibrous- like structure, which clearly indicates the nanocrystalline nature along with some amorphous phase of CuS thin films. From these images, it can be seen that the grain sizes of the films are not uniform[7-10].

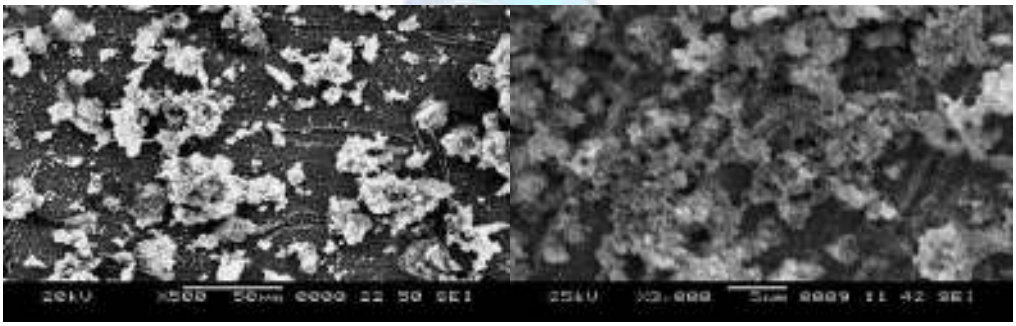

Figure 2. SEM of CuSnanocrystalline films at different deposition time and substrates.

C. Optical Studies:

The UV absorption spectra of CuS thin films taken at room temperature are shown in figure 3. From the spectrograph the absorption edge of the samples are found to occur in the range 350–450 nm for nanocrystalline films. Absorption spectrum shows a clear shift to the lower wavelength side over bulk crystallites at ~ 515 nm. This blue shift of the absorption edge indicates decrease of the crystallite sizes of the samples. CuS is a typical direct band gap semiconductor. According to Tauc relation, the absorption coefficient for direct band material is given by (Tauc 1974; Sharma et al 1992)

$\alpha = c(h\nu - Eg)1/2/ h\nu$

where α is the absorption coefficient, c a constant, hν the photon energy and Eg the band gap. The spectrographs were studied using the standard relation. The band gap increases with the decrease of crystallite size. The increment in band gap is approximately inversely proportional to the square of the crystallite size based on the effective mass approximation[11-13].

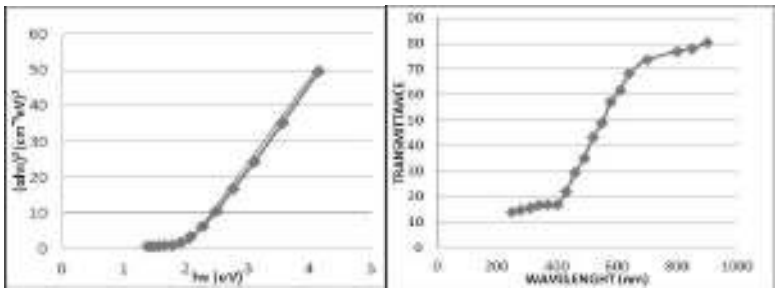

Figure 3. Plot of $(\alpha h\nu)^2$vshv for CuS thin films

D. Study of effect of Deposition Rate:

X-ray diffraction patterns of as-deposited CuS films at substrate temperatures ranging from 313 -345°K are presented in figure 1 and table 1. The films deposited at 313°K were partially amorphous and films deposited at higher temperatures were polycrystalline in nature. Furthermore they showed increasing crystallinity with respect to deposition temperature as shown in figure 4. The diffraction patterns all correspond to the structure of copper sulphide. It was seen from Scherrer width calculation, the crystallite size increased with deposition temperature and deposition rate.

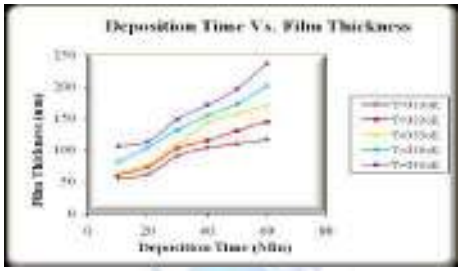

Figure 4. Plot of Film thickness vs. Deposition time at different temperature.

Substrate	Substrate T/°C	Thickness (nm)	Crystallite Diameter/ nm	Deposition Rate (nm/Min)
Cu-1	40	55	8.11	5.5
	50	147	16.24	7.35
	60	225	34.28	7.5
	70	315	40.45	7.87
	72	332	42.43	6.64

Table 1: Variation in film thickness, crystallite diameter size and deposition rate with varying substrate temperature.

Conclusion:

Thin films of CuS prepared by CBD technique are found to be nanocrystalline. The crystallite sizes measured by XRD studies are found to be within 08–43 nm. XRD shows that samples are of single cubic phase, which is important for device performance. SEM studies show presence of long tubes and irregular distributions of particles. The UV absorption studies on films clearly show an increase in band gap with reduction in particle size as compared to bulk materials, and this fact supports the formation of nanocrystallites in these films. The overall

deposition technique clearly observed that higher molarity facilitates the growth of nanocrystallite in CuS films. We concluded that bath parameters and annealing effectively prove to enhance the structure and optical properties of synthesized thin films.From the observation, it is clear that the growth rate increases as the deposition temperature, deposition time increases. It is also clear that the growth rate increases as the film thickness and grain sizes increases while band gap decreases. Depending upon these properties films are used in Optoelectronic devices.

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Gas Sensing Study of SnO_2-ZnO (90-10) Nanocomposite towards H_2S

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SnO_2 and ZnO were synthesized by microwave technique. XRD TEM, SEM, EDAX and SAED of both SnO_2 and ZnO were carried out. Thick films of SnO_2 and SnO_2-ZnO (90-10) composite were fabricated by adopting screen printing technique. For fabricating SnO_2-ZnO (90-10) composite thick film 90 % SnO2 and 10 % ZnO was taken.V-I characteristics and electrical conductivity of SnO_2 and SnO_2-ZnO (90-10) were investigated. Gas sensing response of SnO2 and SnO_2-ZnO (90-10) thick films towards H2S were studied. Highest Response of SnO_2 was 16 at 150 0C and that of SnO_2-ZnO (90-10) composite was 21 at 200 0C.

Key words- microwave technique, SnO_2, ZnO, SnO_2-ZnO (90-10) composite, electrical properties, H_2S sensing.

Introduction:

Tin oxide (SnO_2) is n-type semiconductor having band gap 3.7 eV. It is extensively used in optoelectronic devices and gas sensors for a detection of various toxic or explosive gases in air [1−2]. The sensitivity, selectivity, working temperature and thermal stability of tin oxide sensor can be greatly improved by controllable preparation and surface modification of sensor with different surfactant [3−11].

Field of sensor demands to develop a sensor having various interesting properties, such as, enhanced sensitivity, better adsorption ability, extensive catalytic activity, and high thermodynamic stability. It is difficult to find all these varieties and novelties in a sensor of single metal oxide [12]. Mixtures of metal oxides or composites can however, lead to significant materials that display many of these highly desirable properties [13-19].

Upon burning, toxic hydrogen sulfide gas is oxidized to sulfur dioxide [20]. Combustions of petroleum and coal [21] are the predominant sources of the gases containing sulfur. The gases containing sulfur can result in undesirable disastrous deformations such as infection to respiratory track and lung cancer [21-22]. Infection to respiratory track causes difficult breathing or breathing under pressure. Therefore, monitoring of traces of such gases has become extremely important. In this investigation gas sensing properties of SnO_2 and SnO_2-ZnO (90-10) composite towards H_2S have been studied.

Synthesis of SnO_2 and ZnO nanostructure:

Tin dioxide and zinc oxide was synthesized by using microwave technique [23-24]. For synthesizing SnO_2 and ZnO, the analytical reagent Tin chloride, Zinc chloride and liquid ammonia from Merck India Ltd were used as a basic material without further purification.

Preparation of composite thick films:

For the preparation of SnO_2–ZnO (90-10) nano composite thick films, SnO_2 and ZnO synthesized by microwave assisted technique were used [23-24]. The 90% SnO_2 and 10%, ZnO was taken for fabricating composite thick films. The thick film preparation technique is reported

in other published report [19, 25].The fabricated SnO_2–ZnO (90-10) nanocomposite thick films are named as U90 sensor.

Materials characterization:

Thickness measurement:

The thicknesses of the films were observed in the range from 34 to 38 µm. Rheology and thixotropy of paste was maintained properly for achieving thick films of uniform thickness. Thick films of thickness 36 µm were used for further characterization.

Field emission scanning electron microscope (FE-SEM):

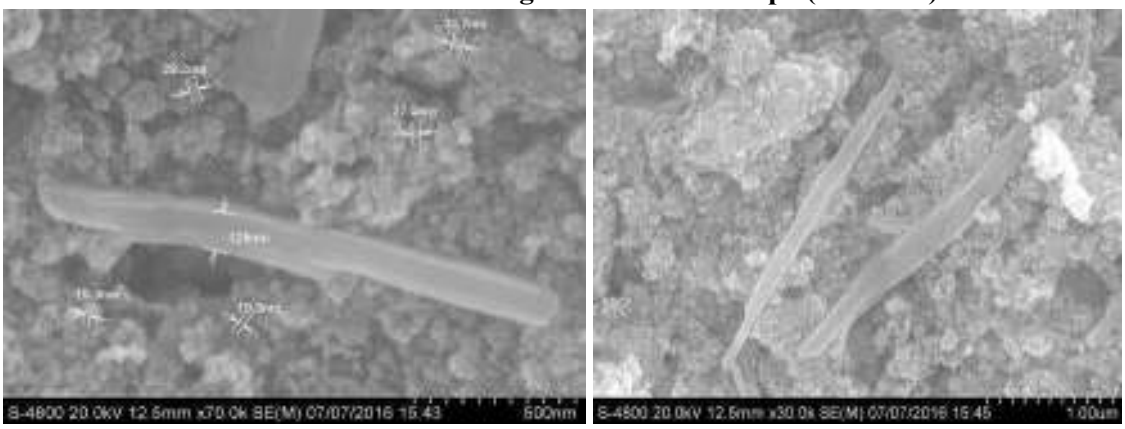

Fig.1-FE- SEM micrograph of U90 nanocomposite thick film

Field emission scanning electron microscope (FE-SEM) was employed to characterize the surface morphology of thick films. FE-SEM micrographs of U90 thick films were taken with the help of field emission scanning electron microscope linked with spectrometer S4800, Hitachi Japan. Fig.1 depicts the FE-SEM micrograph of U90 composite thick films.

In micrograph there are very few larger size distorted ZnO rod (126 nm) in the sea of randomly distributed smaller spherical SnO_2 grains (19.3-37.7 nm).

Energy dispersive analysis by X-ray (EDAX):

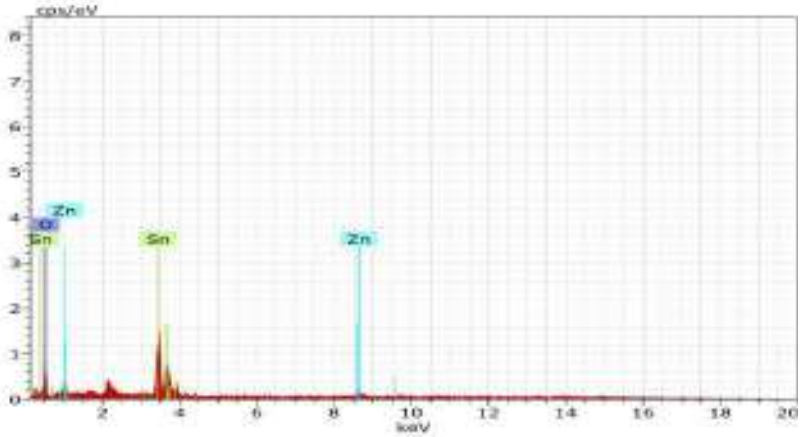

Fig. 2 -EDAX pattern of U90 thick film

Element	Atomic number	Mass %	At. Wt. %
O	8	37.02	79.69
Zn	30	8.64	4.55

Sn	50	54.33	15.76
Total		100	100

Elemental Analysis of U90 composite thick films was carried out by S4800 Hitachi Japan, field emission scanning electron microscope linked with spectrometer. The EDAX pattern of composite thick film is shown in fig.2.The EDAX spectra depicted the presence of Sn, Zn and O in U90 thick films as expected. No other impurity elements were present in the films. From spectra, it is found that the thick films are in non-stoichiometric proportion.

XRD, TEM and SAED analysis of SnO_2 and ZnO are reported in other report [24-25].Particle size calaculated from Scherrer formula and those observed in TEM and FE-SEM matched with each other.

Electrical properties:

-V-I characteristics:

Fig.3. represents the V-I characteristics of U90 nano composite thick films at different temperature.The characteristics was studied with the help of Keithley 6487 picoammeter cum voltage source. Current was measured with forward bias voltage from 0 to 10 V with the step of 2V.The observations are repeated with negative voltage. V-I characteristics of sample showed that, the silver contacts fabricated on the sensor surface are ohmic in nature [26].

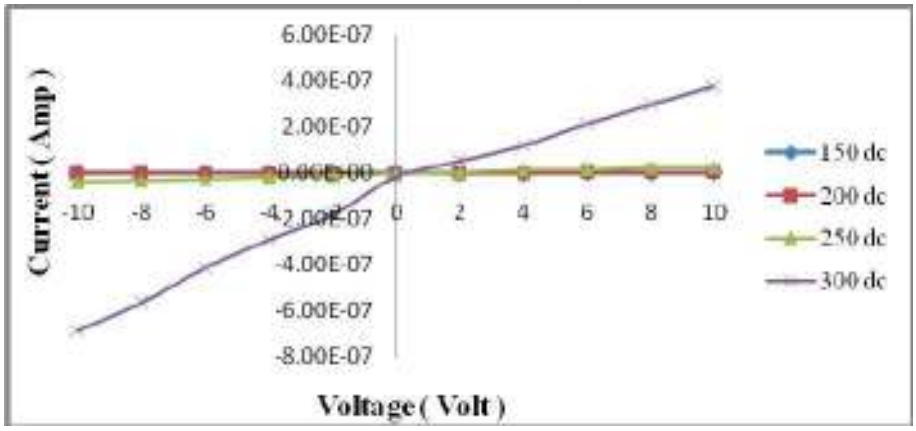

Fig.3-V-I characteristics of various U90 composite thick films (dc means degree celcius)

Electrical conductivity:

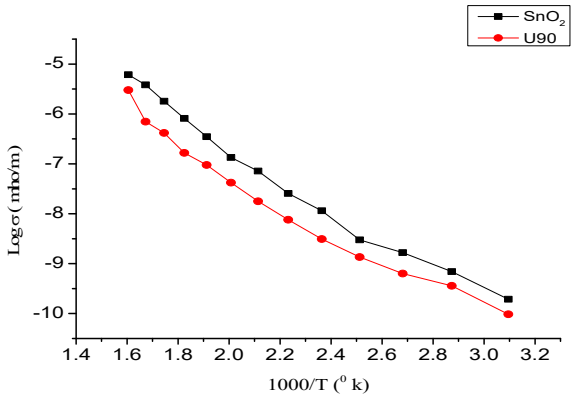

Fig. 4 -Variation of log σ with 1000/T 0k for U90 thick films

The Electrical conductivity was studied with the help of Keithley 6487 picoammeter cum voltage source. The variations of electrical conductivity log (σ) with reciprocal of temperature of U90 thick film is shown in Fig. 4. The conductivity increases with increasing temperature. The nature of conductivity curves shows the negative temperature coefficient of resistance ie semiconducting nature of U90 thick films [27]. From the graph it is observed that, the sample U90 exhibits lower value of log (σ) than SnO_2. This could be attributed to heterojunction present in U90 thick films, hence the higher potential barrier will be developed relative to SnO_2, leading to lower conductivity. Therefore, due to presence of heterocontacts, the resistance of U90 thick film will be high [28-31].

Gas sensing properties:

The gas sensing response can be measures as,

Gas response S =

Where Ia is the current in air ambient and Ig is the current in presence of gas under test. While measuring the current the supply voltage was 10 volt.

5.1-Effect of operating temperature:

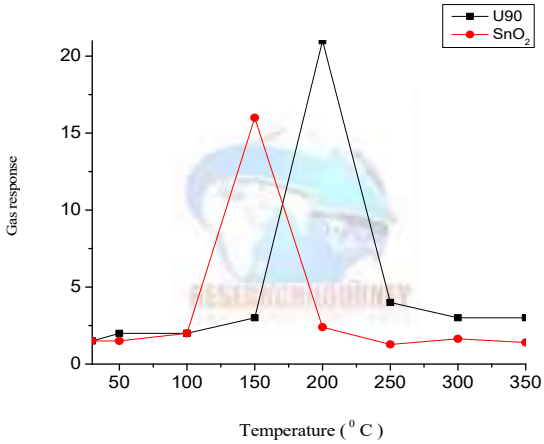

Fig.5 -Variation of gas response with operating temperature

Gas response of fabricated SnO_2 and U90 composite thick films were tested for H_2S, LPG, NH_3 and CO_2 gas at 600 ppm of fixed gas concentration at different operating temperature 30-350 0C in equal step of 50 0C except 300 C reading, by using static gas sensing system. Response of U90 sensor was poor to LPG, NH_3 and CO_2 gas.

Fig.5 depicted the variation of gas response with operating temperature for SnO_2 and U90 composite thick film sensors towards 600 ppm H_2S gas. Highest Response of SnO_2 was 16 at 150 0C and that of U90 was 21 at 200 0C.This can be attributed to lower adsorption of oxygen molecules from air ambient at lower temperature and higher desorption of it from the surface at higher temperature [32-36].

U90 sensor may adsorb more oxygen molecules than SnO_2 and H_2S gas reduced the sensor surface more efficiently at 200^0C. In air ambient, due to formation SnO_2-ZnO heterojunction in U90, oxygen adsorption ability of heterojunction is slightly increased, which trapped more free electrons from conduction band and increased the width of depletion region and height of heterojunction potential barrier. Hence produce less current. This can be verified from the electrical conductivity of the individual SnO_2, and conductivity of U90 sensor. Upon

exposure to H_2S gas, more oxygen ions will be extracted by reacting it with H_2S and release slightly more free electrons to the conduction band for producing more current. Thus the width of depletion region and height of potential barrier decreased and produced high current, which explained the improved response of U90 composite sensor relative to SnO_2. This can be shown by chemical reaction as,

$O_2 + e^- \rightarrow O_{2^-}$

$2H_2S + 3O_{2^-} \rightarrow 2SO_2 + 2H_2O$ + free electrons

Desorption of oxygen molecules might have starts above 200^0C. H_2S molecules may become lighter and fly up in air, hence there will be no reaction between sensor surface and relative gas, which may leads to low response above 200^0C. At relatively low operating temperature, the sensing thick film surface preferentially adsorbs O_{-2} and as a result of that the sensitivity of the material is little. As the operating temperature increases the adsorption of O^- become the dominant process and consequently the sensitivity of the material increases [37-39].
In fact the response of U90 sensor is not improved more relative to SnO_2. Ten percent addition of ZnO made slight effect on sensing performance of U90 sensor.
The observed increased in current in both sensor upon exposure to H_2S is intrinsic nature of n-type SnO_2 and ZnO metal oxides as expected [40].

Variation of gas response with gas concentration:

The variation of response of U90 sensor with H_2S gas concentration at 200^0C is shown in fig. At lower concentration of H_2S, the response of was fast, but as concentration increases, it becomes slow and was saturated at 600 ppm of H_2S. Thus the active region of sensor surface was between 1 to 600 ppm. At lower gas concentration sufficient number of active sites are available for chemical reaction with gas and entire gas molecules contributes in chemical reaction with surface and maximum surface try to get reduce. Hence the response is fast. At 600 ppm concentration of gas, the surface of sensor get reduced completely and above that concentration, multilayer of gas molecules formed on the surface and extra gas molecules remain jobless. Therefore above 600 ppm concentration the response become constant or get saturated [41-43].

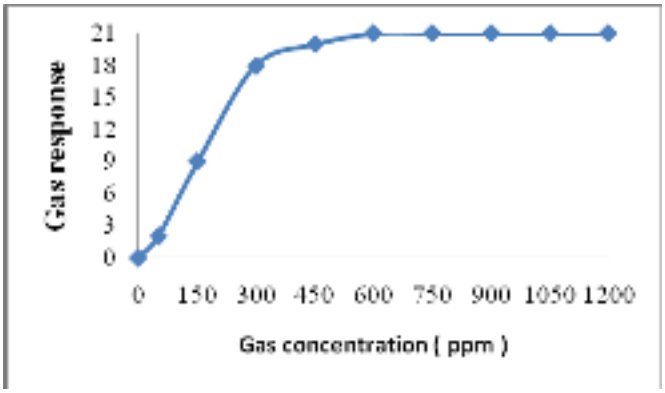

Fig. 6 -Variation of gas response with H_2S concentration for U90 sensor

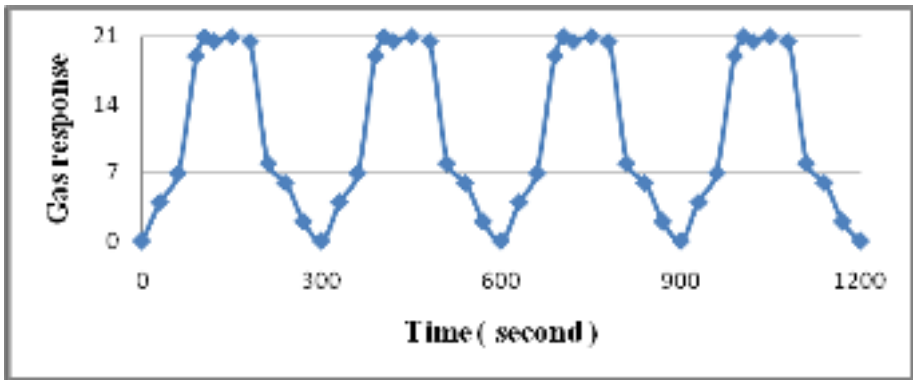

Fig. 7 -Response and recovery time of U90 composite sensor for H_2S gas

The response and recovery time of U90 composite sensor against H_2S at 200 ^{0}C is shown in Fig.7. The response was quick, but it takes 90 second to achieve 90 % response and 90 second for 90 % recovery. When the sensor exposed to H_2S gas, it reacts with adsorbed oxygen and SO_2 is formed. For this it takes 90 second to achieve 90 % reduction of sensor surface. After removal of gas, the oxygen molecules are again adsorbed by sensor surface and trapped the free electrons from conduction band and recover the sensor.

Drability:

Durability of U90 thick film is shown in fig. 8. The gas response of U90 thick film at 200 ^{0}C towards H_2S was tested five times after every seven days and it was found that, the response was almost same. Thus it can be concluded that, U90 thick film sensor has good durability towards H_2S at 200 ^{0}C.

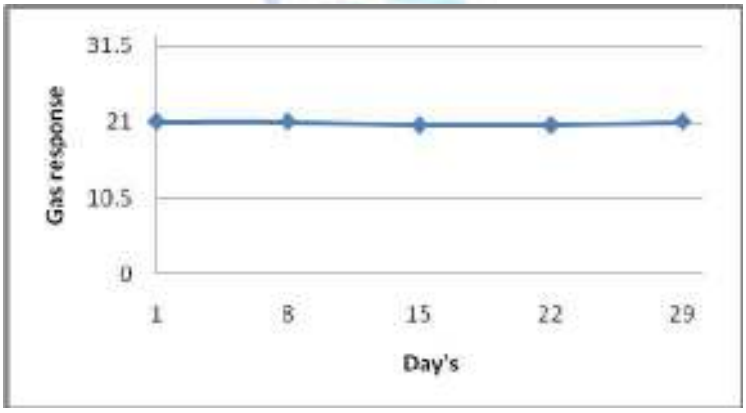

Fig. 8 -Durability of U90 sensor

Selectivity of U0 sensor:

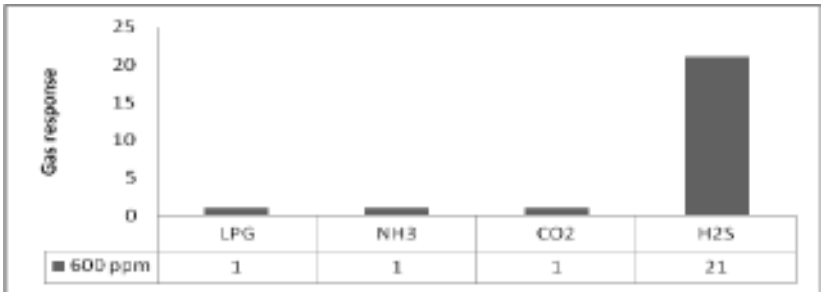

Fig. 9 -Selectivity of U90 sensor at 200 ^{0}C

Selectivity of U90 thick film was tested in presence of 600 ppm of H_2S, LPG, NH_3 and CO_2. U90 sensor is selective only to H2S gas at 200 0C in presence of LPG, NH_3 and CO_2 as shown in fig. 9. It scored response 21 to H_2S in presence of LPG, NH_3 and CO_2. Selectivity of sensor can be attributed to its high response at 200 ^{0}C towards H_2S relative to LPG, NH_3 and CO_2.The U90 sensor were poorly sensitive to LPG, NH3 and CO2 gases at all temperature from 50 to 350 ^{0}C. Therefore the U90 sensor might not be selective to other tested gases.

Summery, Conclusion and future scope:

Thick films of nanocrystalline U90 composite was successfully fabricated by simple mechanical mixing, using pestle and mortar and adopting screen printing technique. The FE-SEM micrograph and EDAX spectrum of sensor was taken. From the FE-SEM micrograph, the spherical structure of SnO_2 having 19.3-37.7 nm particle size and ZnO tube structure with particle size 126 nm were observed. EDAX spectrum and elemental analysis of thick film confirmed that, the thick films are fabricated by using SnO_2 and ZnO. V-I characteristics and electrical conductivity of thick films indicated that, the contacts formed on the sensor surface are ohmic in nature and semiconducting nature of thick film respectively. The gas response of U90 composite thick films towards 600 ppm of H_2S gas was found to be slightly improved relative to SnO_2 thick films. The H_2S response with variation of concentration of H_2S gas was also studied. Active region of U90 sensor was from 1ppm to 600 ppm. Response and recovery time of sensors was found to be improved relative to sole SnO_2. U90 sensor depicted selectivity to H_2S gas in presence of mixture of LPG, NH_3 and CO_2 gas.

SnO_2-ZnO composite sensor can be studied further by varying combination of two components which are not studied here. Attempt can be done by changing synthesis method. Efforts can also be taken with changing one or both the components in the composite.

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CuO Modified ZnO Thick Film Resistors As H_2S Gas Sensors

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Abstract:

Zinc oxide nanostructures were synthesized by chemical route method. The XRD spectrum indicates that the sample is wurtezite (hexagonal) structured ZnO with lattice constants of a = 3.249A0, c = 5.206 A0. Thick films of synthesized ZnO were prepared by screen printing technique. TheCuO modified ZnO were obtained by dipping them into an aqueous solution of copper chloride for different interval of time. Gas sensing properties of pure and modified ZnO thick films were investigated. The CuO modified ZnO thick film dipped for 4 min were observed to be more sensitive as compared to other modified thick films at 1200C. The effect of surface microstructure and CuO concentrations on the sensitivity, selectivity, response and recovery of the sensor in the presence reducing gases ware studied and discussed.

Keywords: Gas sensor, Surface modified gas sensor, Nanostructure ZnO

Introduction

Nanostructured materials such as WO_3, ZnO, SnO_2, and V_2O_5 have shown good sensing properties [1-7]. Among these nanostructure semiconducting materials ZnO has been studied extensively for gas sensing application. It has been proved that ZnO is a good gas sensitive material for detection of both reducing and oxidizing gases [8-16].

Recently, to improve the gas sensing properties of ZnO, various materials have been employed to modify its surface properties [17-20]. Among the many surface doping materials, CuO attract lot of attention, because it is a p-type semiconducting material with energy band gap of
1.2eV. Cupric oxide generally used in solar energy devices, electronics, sensors, magnetic storage media and batteries catalysis [21-28].

In present work, hydrothermally synthesized ZnO nanostructure shows high sensitivity and selectivity to lower concentration of H_2S gas. But its response time is very high and recovery is very slow. To improve response and recovery time efforts are made to prepare CuO activated ZnO nanostructure thick films.

Experimental

All chemicals were of analytical grade and were used as purchased without further purification.

In present work 5.2g of Zinc acetate dehydrate was dissolved in 480 ml of distilled water. Subsequently, 20 ml of 2M NaOH aqueous solution was introduced into the above aqueous solution drop by drop with constant stirring. The obtained mixture was kept at room temperature for 05 min, and then transferred in to 700 ml Teflon-lined stainless steel reactor (autoclave), maintained at temperature 120 ^{0}C for 6hr and then cooled to room temperature naturally. After this process, the resultant white solution was collected in a beaker and sonicated (Ultrasonic

wave treatment) for 90 min, with plus rate 4s and power 0.7 A. The resultant product were collected by centrifugation, washed several times with distilled water and ethanol and dried at temperature 70 ^{0}C for 3 hr. The yield of synthesized ZnO nanostructure was found to be 1.32 g. Thick films of synthesized nanostructure ZnO were prepared by using screen printing technique.

Surface of pure ZnO thick film were modified by dipping them into a 0.01M aqueous solution of copper chloride ($CuCl_2 \cdot 2H_2O$) for different intervals of time (2 min, 4 min, 6 min and 8 min). Dried thick films were calcinated at 500^{0}C for 6 hr in air ambient. The $CuCl_2$ dispersed on the film surface was oxidized in calcination process, and sensor elements with different mass % of CuO on the surface of ZnO thick film were obtained. These surface activated films are termed as CuO modified films.

Materials characterization

X-ray diffraction studies

The crystallographic structure of the synthesized ZnO nanostructure was characterized by powder x-ray diffraction (Philips PW 1710) with Cu-Kα source and 2θ range of 20-80^0. Figure 1 shows the XRD pattern of the ZnO nanostructure. The recorded XRD pattern confirmed that synthesized ZnO are highly crystalline in nature. The corresponding X-ray diffraction peak for (100), (002), (101) and (102) planes confirm the formation of hexagonal wurtzite structure of ZnO (JCPDS card no. 36-1451).

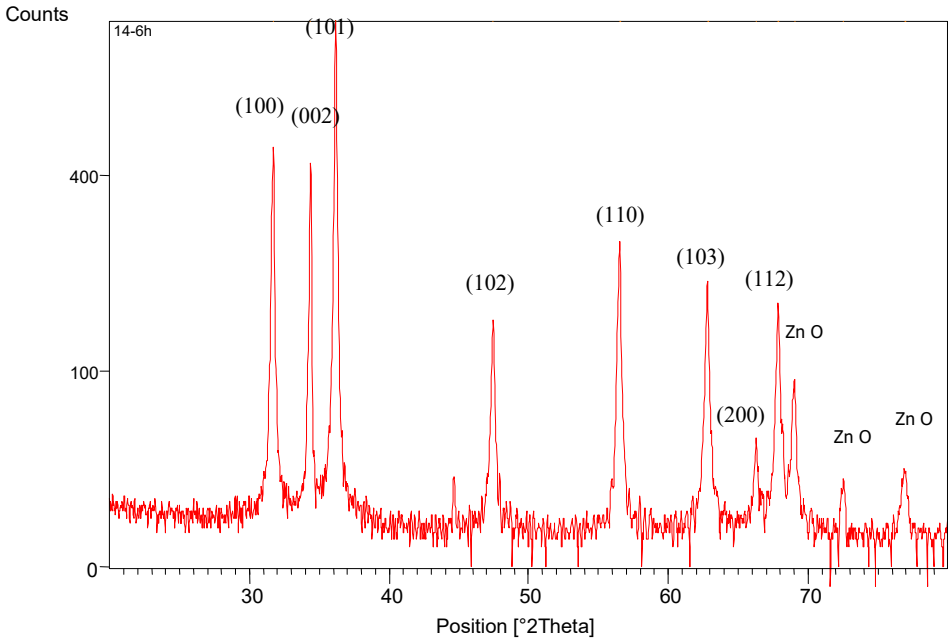

Figure 1 powder XRD pattern of ZnO nanostructure synthesized by hydrothermal route.

Transmission electron microscope

The morphology and structure of the powders were investigated by TEM. For the TEM observation, the as-prepared products were added into an alcohol solution and subjected to violent ultrasonic stirring for hours; subsequently, a drop of solution containing ZnO nanostructure was dipped on a copper grid used for the TEM observation.

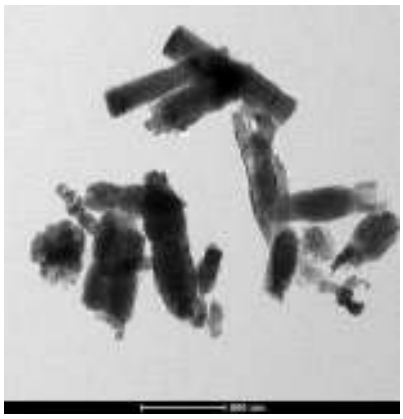

Figure 2 TEM image of ZnO nanostructure synthesized by hydrothermal method

It is clearly seen form the TEM image that the ZnO powders consist of both nanoparticles and nanorods with average crystallite size less than 60nm.

Scanning electron microscope

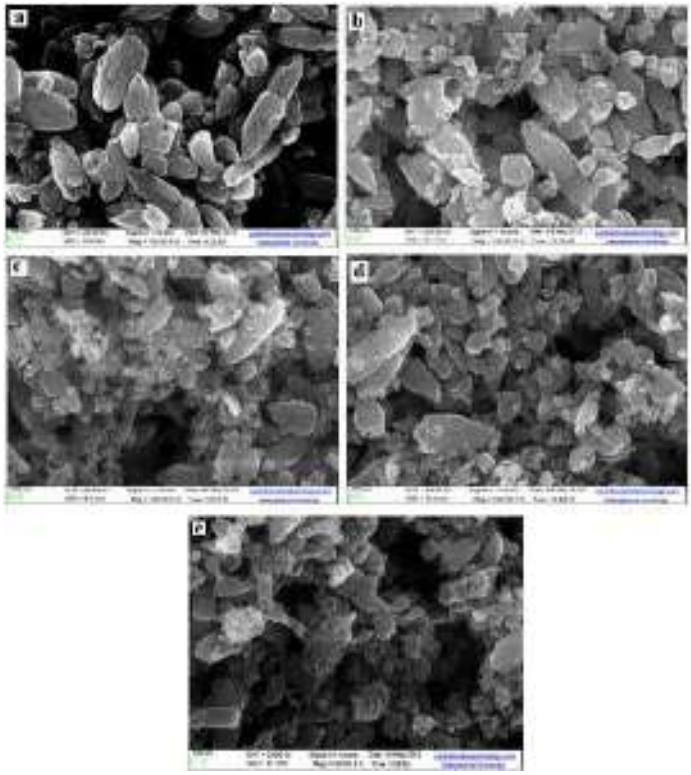

Figure 3 FE-SEM images of **a)** pure ZnO thick film **b)** CuO modified ZnO thick film (2 min dip.) **c)** CuO modified ZnO thick film (4 min dip.) **d)** CuO modified ZnO thick film (6 min dip.) **e)** CuO modified ZnO thick film (8 min dip.).

The FE-SEM images in Figure 3b-3e clearly indicates that after the surface modification by dipping method, the growth of CuO grain began to occur on the surface of ZnO thick film. It is observed that as the dipping time increases, the more and more grain of CuO deposited over ZnO grain.

Results and discussion

Gas response of CuO modified ZnO thick films

The gas response of CuO modified ZnO thick films to 30 ppm H_2S were investigated at various operating temperatures ranging from room temperature to 250^0C. The gas response of CuO modified ZnO thick films as a function of operating temperature is shown in figure 4.

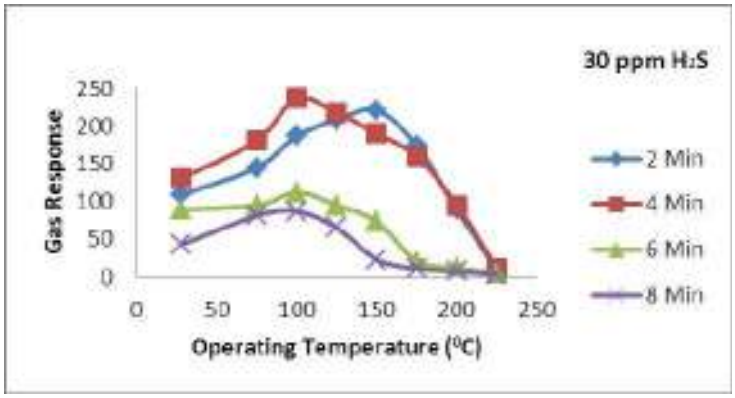

Figure 4 variation of gas response of CuO modified ZnO thick films with operating temperature.

Form figure 10 it can be seen that CuO modified ZnO thick films are very sensitive to low concentration (30 ppm) H_2S at room temperature. When the temperature is about 120^0C, the highest sensitivity of samples is obtained. Higher sensitivity of these thick films can be explained by the following reaction [29]:

$CuO + H_2S \rightarrow CuS + H_2O$

As can be seen CuS is a product of the reaction. CuS being a metallic will destroy the n-p-n junctions as well as the potential barrier, and new type of n-metallic-n heterojunctions will be formed. The destruction of potential barrier results in a sharp increase in the electrical conduction.

When the sensor is brought back in the ambient conditions, the CuS reacts with the oxygen via following reaction.

$$2CuS + 3O_2 \rightarrow 2CuO + 2SO_2$$

Since the CuS converts back to CuO, potential barrier reappears due to formation of n-p-n heterojunctions as well as potential barrier, and hence a low electrical conduction. When temperature increases over 125^0C, the sensitivities of CuO modified ZnO thick films deceases sharply because the lattice structure of CuS changes above temperature 105^0C and decomposes to Cu_2S at temperature 220^0C. The Cu_2S is a high resistivity ionic conductor; due to this CuO modified ZnO thick films show poor sensitivity above 220^0C.

Figure 4 shows that the sensitivity of 4 min CuO modified ZnO thick film is highest among other thick films, it may be attributed to the amount of CuO grains over ZnO grains are suitable. When the optimum amount of CuO (4 min dipping) is dispersed on the surface of ZnO thick film, the CuO grains would be distributed uniformly throughout the surface the film. Due to this, not only the initial resistance of the film is high, but this amount would also be sufficient to promote the catalytic reaction effectively and the overall changes in the resistance on exposure to H_2S gas, leading to high sensitivity. If amount of CuO is too low, the proportion of p-n heterojunctions (CuO-ZnO) in samples also too small, the changes of thick films resistance is a little when the film contact H_2S, so the sensitivities of films to it is low. On the other hand if amount of CuO is too high, formation of p-n heterojunctions is more. When a H_2S reacts with the thick films, the superfluous CuO still forms heterojunctions, so the surface resistances of samples keep high.

Selectivity

Figure 5 depicts the selectivity of all CuO modified ZnO thick films for 30 ppm H_2S gas at room temperature. These modified thick films shows higher selectivity for H_2S among all the gases such as CO_2, NH_3 and LPG.

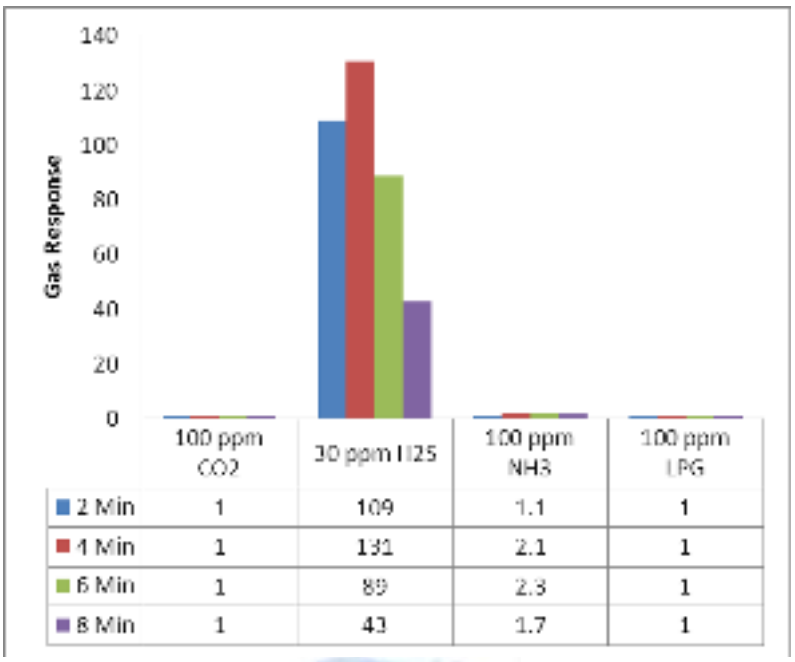

Figure 5 Selectivity of H_2S gas from mixture of gases

Response and recovery

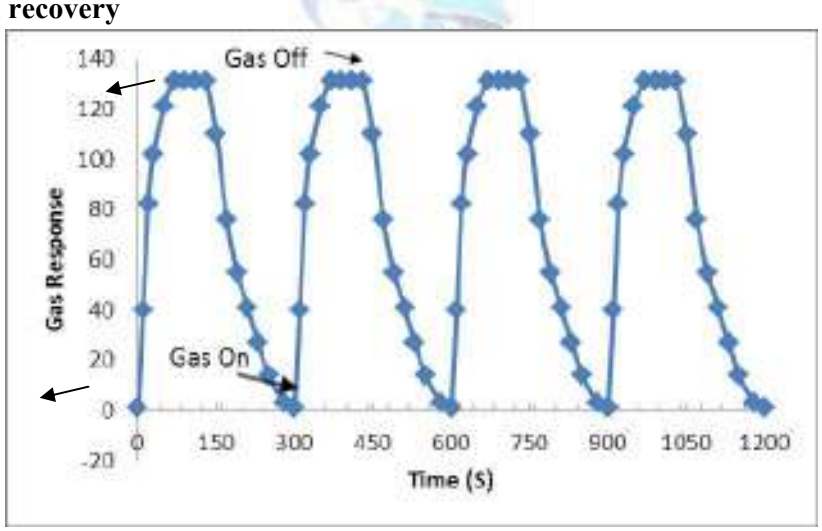

Figure 6 variation of gas response of (4 min dip.) CuO modified ZnO thick film with time

The response and recovery of the 4 min CuO modified ZnO thick are represented in figure 6. The response was quick (54 s) to 30 ppm of H2S, while the recovery is also fast (117 s). The response and recovery time of other thick films were given in the table 1.

Table 1 The response and recovery time of CuO modified ZnO thick films

Sample	Response time (s)	Recovery time (s)

CuO modified ZnO Thick film (2 min dipping)	58	111
CuO modified ZnO Thick film (4 min dipping)	54	117
CuO modified ZnO Thick film (6 min dipping)	65	135
CuO modified ZnO Thick film (8 min dipping)	68	146

The tendency of response and recovery time in figure 6 can be explained by proposed sensing mechanism. The response and recovery time depends on rate of conversion of CuO to CuS and CuS to CuO respectively.

Conclusions

The results of pure and CuO modified ZnO thick films can be summarized as

1. Hydrothermally synthesized ZnO powder consists of nanoparticles and nanorods with average crystallite size 48 nm.
2. All CuO modified ZnO thick films shows sensitive to low concentration of H_2S at room temperature.
3. All CuO modified ZnO thick films shows higher selective to 30 ppm H_2S gas from other test gases of higher concentrations.
4. CuO modified ZnO thick film (4 min dipping) shows higher sensitivity to 30 ppm of H_2S as compared to other CuO modified ZnO thick films.
5. CuO modified ZnO thick films shows very rapid response and fast recovery as compared to pure ZnO thick films.

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Fabrication and Application of Polyprrole (PPy)-ZnO composites to sense NH_3 gas at room temperature

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Abstract:

Nanoparticles of PPy and ZnO are prepared. PPy/ZnO composites with different weight percentage of ZnO (10%, 20%, 30, 40% and 50%) were obtained by in situ emulsion polymerization of pyrrole in an aqueous solution. The characterizations of different composites were done with the help of X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM). Thick film sensor was prepared by screen printing technique. The sensitivity was measured as a function of different concentration of ammonia gas and it was found that PPy-ZnO (20 %) shows more sensitivity (0.94).

Keywords: PPy/ZnO Composites, SEM, XRD, screen printing technique.

1. Introduction:

Conducting polymers recently emerged as a new class of potentially useful materials in the era of electrical conductivity and other many applications as successful agents. More works on conducting polymers have been done by many groups all over the world to understand their exceptional electrical, optical and chemical properties. Recently, the nanocomposite materials have become one of the most extensively studied material all over the world as they have shown to possesses several technological application such as magnetic recording materials sensors, effective quantum electronic devices, etc. [1]. Nanocomposite material composed of conducting polymers & oxides have open more field of application such as conductive paints, drug delivery, rechargeable batteries, smart windows, toners in photocopying, etc [2]. Applications of polymers have begun to emerge a new era. These include coating and blends for electrostatic dissipation and electromagnetic interface (EMI) shielding. Electromagnetic radiation absorbs for welding of plastics, conductive layers for light emitting polymer devices and anti corrosion for iron and steel [3]. Semiconductor nonmaterial has been received great attentions. Among these various semiconductors oxide nonmaterial zinc oxide is a versatile material because of its physic-chemical properties such as mechanical, electrical, optical, magnetic and chemical sensing properties. It has a wide band gap of 3.3 eV and it is used in various applications of electronic devices, biomedical field, variety of sensors, etc [4-5]. In the present paper, the author has reported PPy/ZnO composites, which were synthesized by in-situ polymerization method. These composites were characterized by using X-Ray diffraction (XRD) analysis, Scanning Electron Microscopy (SEM) and studied the sensing nature of prepared sensor to sense NH_3 gas.

2. Experimental

2.1. Materials

Pyrrole monomer (C_4H_5N) was previously distilled under vacuum and subsequently stored in a dark refrigerated environment (0°C), since it is a very sensitive to light and moisture. All chemical reagents, such as zinc oxide (ZnO), ferric chloride hexahydrate ($FeCl_3 .6H_2O$) and sodium dodecyl sulfate ($C_{12}H_{25}NaO_4S$), were of analytical grade.

2.2 Preparation of PPy/ZnO composites

PPy/ZnO composites were obtained by in situ emulsion polymerization of pyrrole in an aqueous solution containing sodium dodecyl sulphate (SDS) and ZnO. Initially, an aqueous solution of deionized water (40 mL) containing the surfactant (SDS, 2.4 mMoles) was prepared. The solution was stirred vigorously for 10 minutes and 0.5 mMoles of pyrrole monomer were then added to the mixture. After 20 minutes of vigorous stirring, 42.1 µMoles of ZnO were added. Subsequently, the solution was maintained under vigorous stirring for 20 minutes and 400.0 µL of $FeCl_3$ (1M) was added drop by drop. Finally, the solution was kept under vigorous stirring for 24 hours to ensure complete polymerization. To obtain a powder composite material, 70 mL of methanol was added to the colloidal dispersion, forming a black precipitate, which was then dried at 40°C and thoroughly dried in a vacuum desiccator at room temperature [6]. In present work, PPy/ZnO nanocomposites containing various weight percentages of ZnO (10 %, 20 %, 30 %, 40 %, and 50 %) in PPy were synthesized and thick film sensor was prepared on clean glass plate to sense NH_3 gas.

2.3 Preparation of Thick film sensor: Screen printing technique

Ethyl cellulose (EC) and Butyl Carbitol acetate (BCA) was kept at the ratio 8:92 and prepared binder. Paste of prepared material was deposited on clean glass plate by screen printing technique.

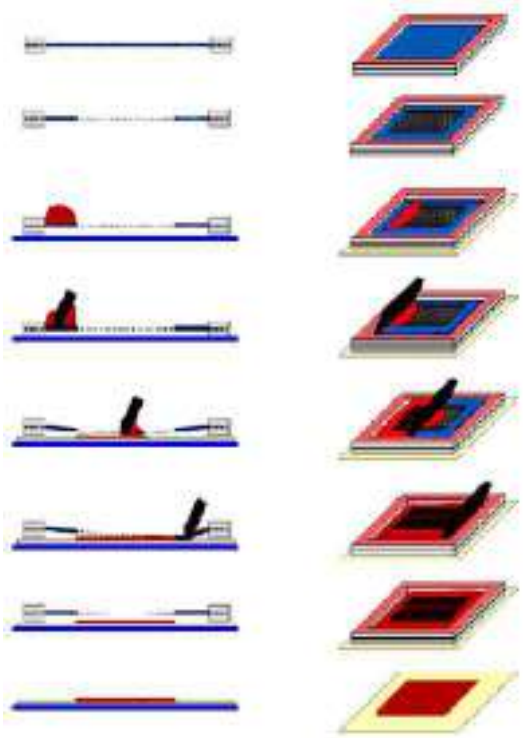
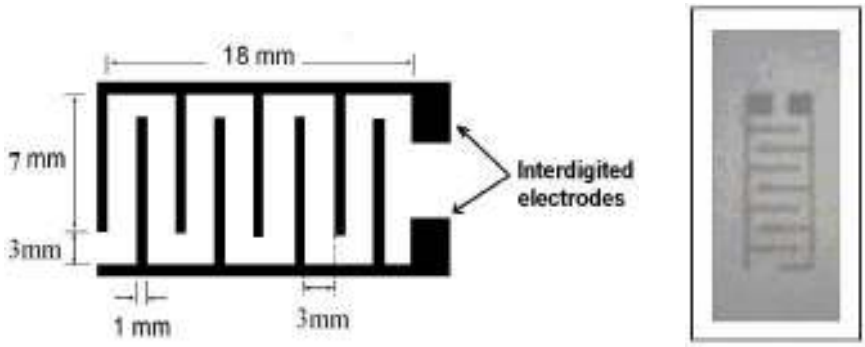


Figure 1. Different steps involved in screen-printing



(a) Integrated electrode (b) Actual sensor film

Figure 2. Prepared sensor and electrode structure

3. Characterization

X-ray diffraction (XRD) studies were performed using Philips X-ray diffractometer with CuKα as the radiation source. The morphology of the Zinc oxide and composites in the form of powder was investigated using scanning electron microscope (SEM).

4. Results and discussion

4.1 X-Ray diffraction

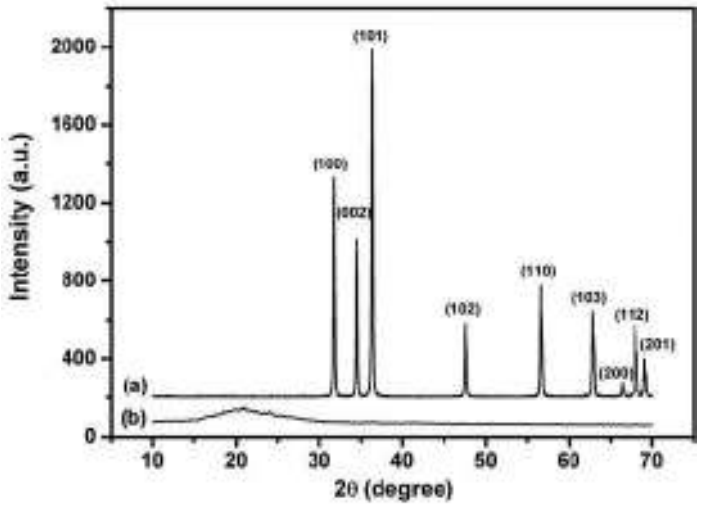
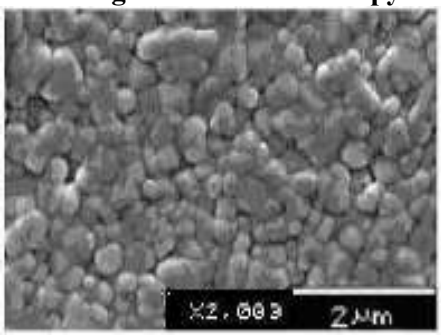


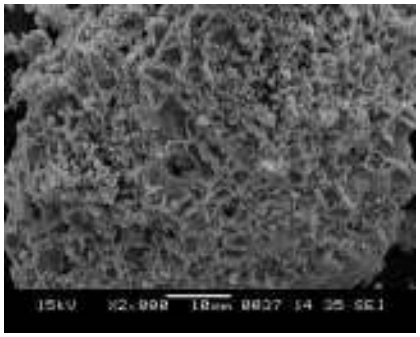
Figure 3. X-ray diffraction patterns obtained for: (a) ZnO (b) PPy/ZnO

Figure 3 (a) shows the XRD pattern of ZnO. The XRD diffraction peaks of ZnO powder are shown in a good agreement with hexagonal structure reported in JCPDS File Card (No.05-0664). The intensity of diffraction peaks for PPy/ZnO composite is lower than that for ZnO. The presence of amorphous PPy reduces the percentage ratio of ZnO and sequentially weakens diffraction peaks of ZnO. Figure 3 (b) shows X-ray diffraction pattern of PPy/ZnO. A broad peak centered at 2θ at 22.17^0 may be assigned to the scattering from the polypyrrole chains at interplanar spacing which clearly implies the amorphous nature of polypyrrole.

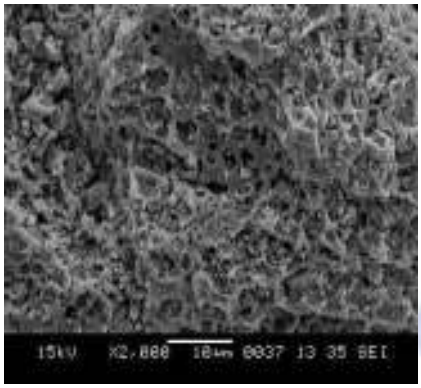
4.2 Scanning Electron Microscopy



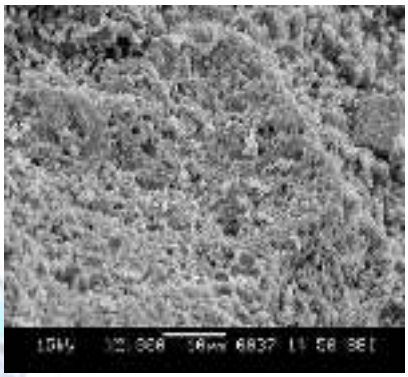
(a) SEM image of ZnO



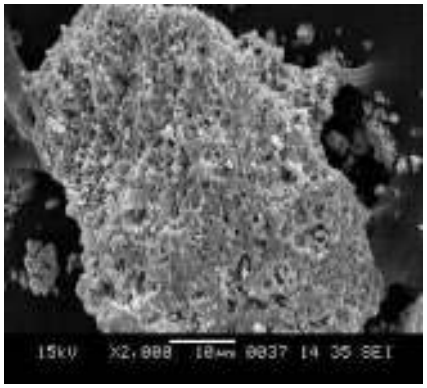
(b) PPy/ZnO-10% composite



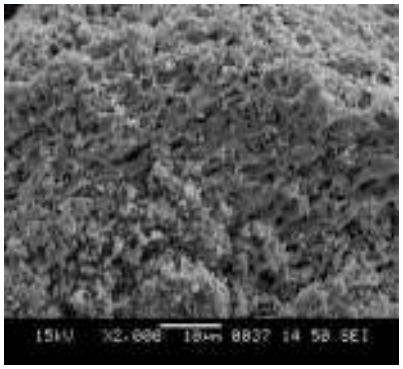
(c) PPy/ZnO-20% composite



(c) PPy/ZnO-30% composite



(d) PPy/ZnO-40% composite



(e) PPy/ZnO-50% composite

Figure 4. SEM image of ZnO and its composites with PPy

In figure 4, SEM pictures show the porosity of ZnO and PPy/ZnO composites having different weight percentage. From figure 4 (c), more porosity is observed with doping of ZnO (20 %) in PPy thereby decreases the granular size. The SEM image also revealed the presence of ZnO in PPy which is homogeneously distributed throughout the polymer sample [5-7].

4.4 Sensitivity measurement

Sensitivity was calculated by using formula [8-10], $S = \left(\frac{R_{air} - R_{gas}}{R_{air}}\right) = \left(\frac{\Delta R}{R_{air}}\right)$

Where, R_{air} is the resistance of the sensor in presence of air, R_{gas} is the resistance of the sensor in presence of gas.

Variation of sensitivity with concentration of NH_3 gas is shown in the following figure.

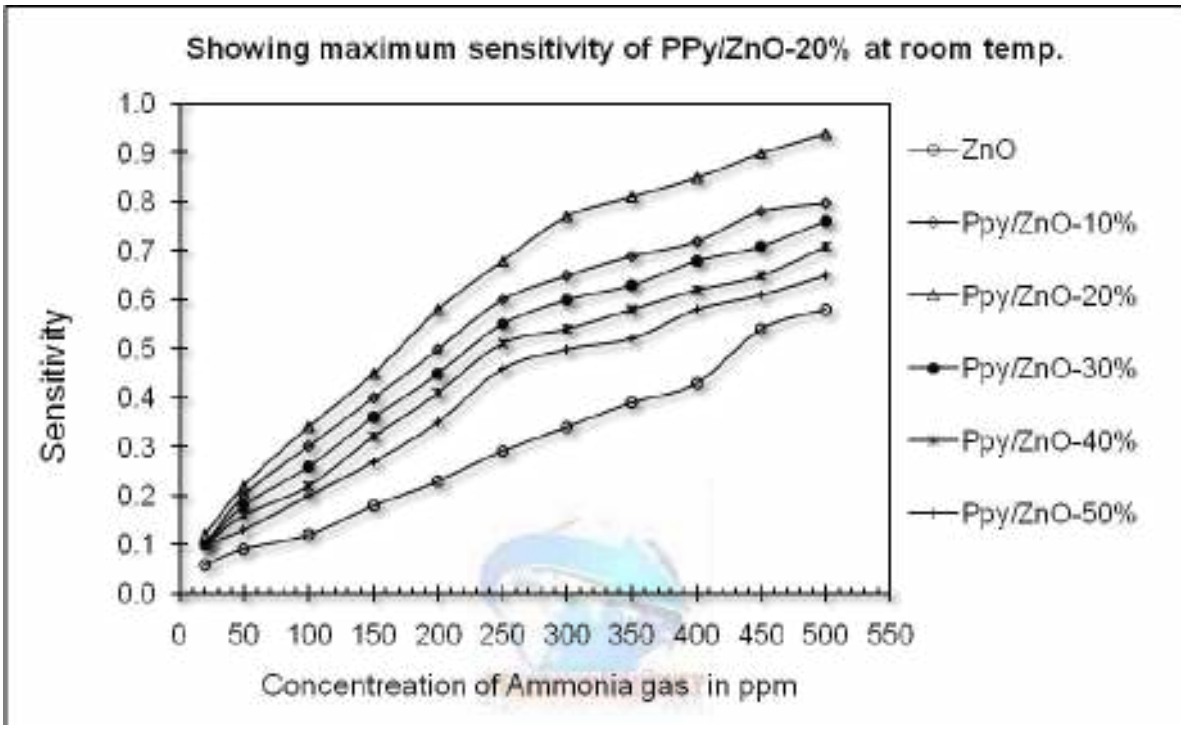


Figure 5. Variation of sensitivity of ZnO and PPy/ZnO composites

This show that the sensitivity of PPy/ZnO 20% composites has found to be maximum at 500 ppm for Ammonia gas at room temperature. It is concluded from the SEM picture that, the porosity of this sensor is maximum among the others. Due to high porosity, it absorbed maximum gas and respond it greatly.

4. Conclusion

PPy/ZnO 20% composite show high sensitivity (0.94). PPy/ZnO composition with different percentage ratio was prepared by in situ emulsion polymerization of pyrrole in an aqueous solution. This showed that PPy/ZnO 20% nano-composite is best materials for the detection of Ammonia gas at room temperature in the concentration range 50 to 500ppm.

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Goldstone Mode fluctuations of ZnO Nanoparticles

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Abstract

The ac electrical conductivity of ZnO nanoparticles is frequency dependent and analyzed through power law relation. The dielectric constant of ZnO nanoparticles increased with increasing temperature but it is decreases with increasing frequency. In case of dielectric loss factor Goldstone Mode (GM) fluctuations are observed near frequency 200Hz.

Key words: *ZnO nanoparticles; liquid-phase synthesis; ac conductivity; dielectric constant; dielectric loss.*

Introduction

Zinc oxide (ZnO) is a piezoelectric, transparent dielectric n-type semiconducting oxides and has a band gap of 3.37ev at 300K [1], it has large excitation binding energy (60 meV). Due to huge industrial application of ZnO such as pigment in paints, flux in ceramic glazes, coating of paper, electro-photography, medicine and cosmetic etc. the zinc oxide is attracting attention in the form of powder as well as thin films.

The electrical conductivity and dielectric constant plays a very important role in several electronic processes of nanostructures and nanocomposites [2,3]. The electrical properties of nanocomposites are found to be drastically different from those of their constituents. The electrical properties of nanophase CdS and ZnS mixed with nanophase silver have been investigated and a drastic change in the ac electrical conductivity and dielectric constant is observed [4]. Dielectric studies of ZnO nanoparticles show frequency dependence dielectric anomaly at low temperature (85–300 K) and results reveal that the capacitance and loss tangent decrease with the frequency of applied signals while these parameters improve with the increasing of temperature [5].

In this paper, the ac electrical conductivity and dielectric properties of ZnO nanoparticles over a wide range of frequencies from 20 Hz to 1 MHz and over a temperature range from 313 to 473 K are reported.

Experimental: *Measurement of AC Electrical Conductivity and Dielectric Constant*

Dielectric and electrical conductivity measurements of pellet (thickness 0.1139 cm) samples placed between a silver electrode sample holder (Pusha Scientific, Hyderabad, India), were measured using an automated 4284A precision LCR meter (20 Hz –1 MHz) (Agilent Technologies, Singapore). The sample holder is kept inside an electric oven and its temperature can be varied by a computerized temperature control. The corresponding effective capacitance (c_p) and effective resistance (R_p) measured at different environment of temperature, finally the dielectric constants and ac electrical conductivity of the samples was calculated using expression [6],

$$\sigma_{ac} = (f \varepsilon' \tan(\delta)) / (1.8 \times 10^{10}) \qquad (1)$$

Where, f is the frequency applied in Hz, (ε') is the dielectric constant or relative permittivity and tan (δ) is the dielectric loss tangent or loss factor.

The values of the real part of the dielectric constant (ε') at different frequencies and temperatures were derived from the measured capacitance (c_p,) and knowing the geometrical dimensions of the pellets using the expression,

$$\varepsilon' = (C_p L) / (\varepsilon_o A) \quad (2)$$

Where, c_p is the measured capacitance, *l* is the thickness of the sample, A is the electrode area and (ε_o) is the permittivity of free space (8.854 X 10^{-12} F/m).

The dielectric loss tangent or dielectric loss factor i.e. tan (δ) can be expressed by relation,

$$\tan(\delta) = \omega . C_p . R_p \quad (3)$$

Where, C_p is the measured capacitance, R_p is the measured resistance and f is the frequency applied field in Hz.

Results and discussion

AC Electrical Conductivity and Dielectric Constant

The ac electrical conductivity of samples is measured by using 4284 A precision LCR meter from applied frequency 20 Hz to 1 MHz at different temperatures (313K, 353K, 393K, 433K and 473K). Figure 2 shows the variation between log of ac conductivity and applied frequency at different temperature of the samples calculated using eq.(1). The ac electrical conductivity of ZnO Nanoparticles shows frequency dependence, increasing with frequency. According to Jonscher's classical equation [7] the real part of ac conductivity has a frequency dependence given by the relation,

$$\sigma_{ac}(\omega) = A\,\omega^s \quad (4)$$

Where, s is close to unity and the parameter A shows little dependence on temperature.

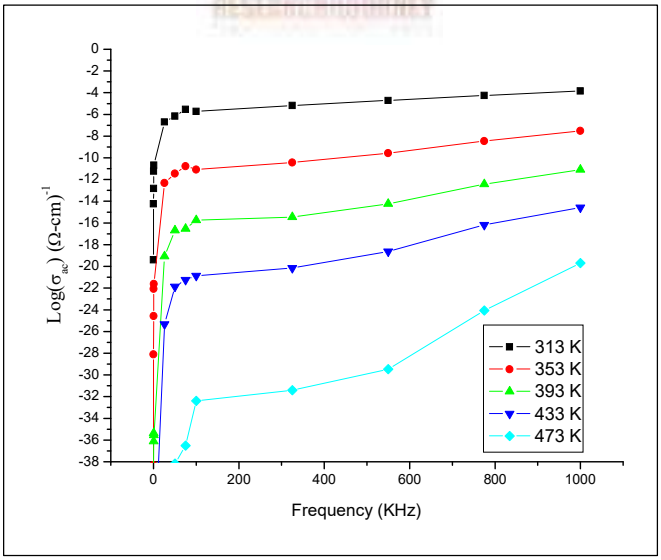

Figure 2 Variation of log (σ_{ac}) with applied frequency at different temperature

Another mechanism of frequency dependence of ac electrical conductivity is explain on the basis of quantum-mechanical tunneling (QMT) through the barrier and classical hopping over the barrier [8].

The values of the real part of the dielectric constant (ε') at different frequencies and temperatures were derived from the eq. (2). The variation of (ε') of ZnO nanoparticles with frequency of the applied field is given in figure 3. The dielectric constant of all the samples is found to decrease very rapidly from 20 Hz frequency to 1 Khz frequency, but after 200 Khz frequency dielectric constant decreases very slowly up to 1Mhz frequency. In a dielectric study, the real part of dielectric constant (ε′) represents the polarizability of the material while the imaginary part (ε′′) represents the energy loss due to polarization and ionic conduction [9]. Generally dielectric materials have electronic, atomic, orientation and interfacial or space charge polarization [10].

Dielectric loss factor (tan δ)

The dielectric loss factor measures a part of polarization, which is out of phase with the applied field. The values of the dielectric loss factor (tan δ) at different frequencies and temperatures were derived from the eq. (3). The variation of dielectric loss factor (tan δ) of ZnO nanoparticles with frequency (from 20 Hz to 1 MHz) of the applied field at different temperature is given in figure 4. Generally two types of rotational fluctuations of molecular dipoles are obtained known as Goldstone Mode (GM) relaxation and Soft Mode (SM) relaxation [11]. In our study, the first type of mode (GM) of fluctuation near frequency 200Hz is seen and another mode of fluctuation is absent.

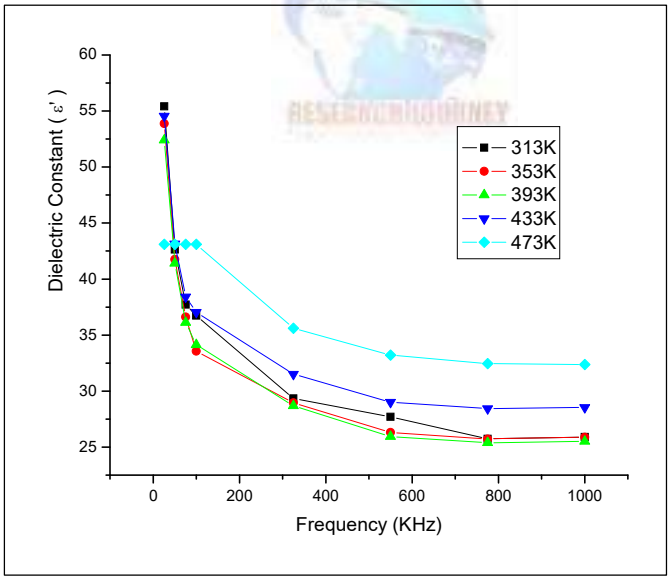

Figure 3 Variation of (ε') with applied frequency at different temperature

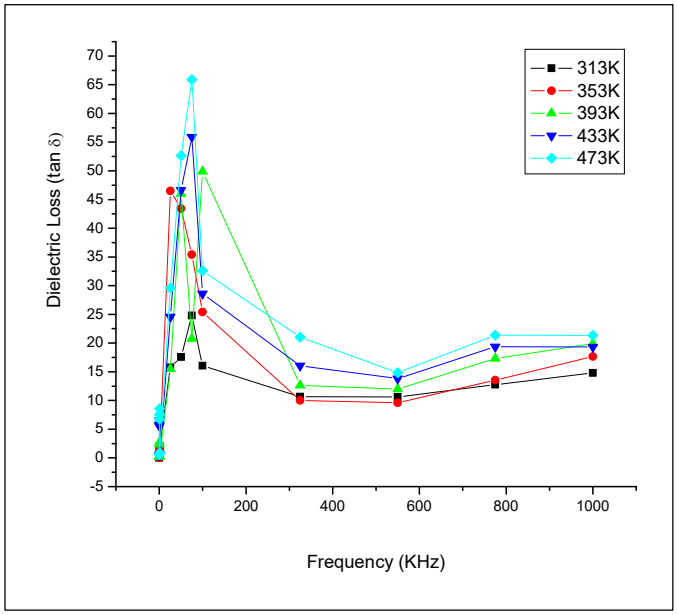

Figure 4 Variation of Dielectric loss tan (δ) with applied frequency at different temperature

Conclusions

The ac electrical conductivity of ZnO nanoparticles is frequency dependent. The dielectric constant of ZnO nanoparticles increased with increasing temperature but it is decreases with frequency and Goldstone Mode (GM) fluctuation are observed.

Acknowledgment

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DC HUMIDITY SENSING PROPERTIES OF NANOSTRUCTURE SnO_2 SYNTHESIS WITH CO-PRECIPITATION METHOD

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ABSTRACT :

In this paper Stanninc oxide (SnO_2) nanoparticles was synthesized by a chemical precipitation method. The synthesized samples were characterized using X-ray powder diffraction (XRD). Sensing material was made as in the form of thick film by using screen printing method. Surface mor- phologies of the samples were analyzed using Field emission Scanning electron microscopy (FE-SEM). The XRD pattern indicates that SnO_2 has a tetragonal phase structure having minimum crystallite size 23.19 nm. Further, humidity sensing investigations of these sensing materials were done. The SnO_2 sample shows good sensitivity towards the relative humidity. Our result indicate that pure SnO_2 resistance decreases from 10^{11} Ω to 10^{8} Ω. in form of thick film was most sensitive. The activation energy measured from Arrhenius plot of conductivity at different RH and found to be 4.6010^{-4} eV respectively. The results were re- producible up to ± 77% after 2 months of observations.

1. INTRODUCTION

Recently, humidity sensors are of great significance in many fields, including environmental monitoring, industrial production, agricultural planting, aviation, and medical and chemical monitoring, etc. [1,2]. There are various kinds of nanostructure materials have been extensively studied. Semiconducting materials, such as SnO_2, WO_3, and ZnO for the humidity sensor are also applied in variety of different areas [3-6]. The band gap SnO2 wide (~3.7 eV) has distinctive electrical properties and high physical/chemical stability [7, 8].The 3D hierarchical SnO_2 dodecahedral nanocrystals based nanosensor, exhibited superior humidity-sensing properties. These nanostructures SnO_2 provides a regular porosity and a large specific surface area, allow high accessibility for the water molecules and providing more active site for the surface physical/chemical interaction between water molecules and the nanostructures SnO_2 materials [9].Thus due to effective approach toward an understanding, and the design, of nanostructure SnO_2 based humidity sensing materials.

2. EXPERIMENTAL

Synthesis of tin oxide (SnO_2) : All the chemicals used in this study were of GR grade purchase from Sd-fine, India (purity 99.99%). The chemicals are used without any further purification. Stannous chloride dehydrates ($SnCl_2.2H_2O$), Ammonia solution and deionized water were used during reaction. The conducting silver paint (Sigma Aldrich Chemical, USA) is used to form electrodes. In preparation of SnO_2 nanoparticle the Stannous chloride dehydrates ($SnCl_2.2H_2O$), Ammonia solution and deionized water were used as starting materials. Initially, 2 g (0.1 M) of stannous chloride dehydrate ($SnCl_2.2H_2O$) is dissolved in 100 ml water. After complete dissolution, about 4 ml ammonia solution is added to above aqueous solution with magnetic stirring. Stirring is continued for 20 minutes. White gel precipitate is immediately formed. It is allowed to settle for 12 hrs. Then it is filtered and washed with water 2-3 times by using deionized water. The obtain

precipitate were mixed with 0.27 g carbon black powder (charcoal activated). The obtained mixer is kept in vacuum oven at 70 ºC for 24 hours so that the mixer gets completely in to dried powder. Then this dry product was crushed into a find powder by grinder. Now obtained product of fine nanopowder of SnO_2 was calcinated at 700°C up to 6 hours in the auto controlled muffle furnace (*Gayatri Scientific, Mumbai, India.*) so that the impurities from product will be completely removed.

glass substrate. Initially, for the screen printing the thixotropic paste was formulated by mixing the sintered fine powder of pure nano powder of SnO_2 in different molecular weight ratios, a with a solution of ethyl cellulose as (10% temporary binder) in a mixture of organic solvent such as butyl cellulose, butyl carbitol acetate and turpineol. The ratio of inorganic to organic part was kept as 75:25 in formulating the paste. The paste of pure materials of SnO_2 was screen printed on a glass substrate in the form of thick films and it was dried at 80-110°C in oven for 1hrs. The dried films is fired at 500°C for 25 min in muffle furnace (Kumar make Mumbai), to remove organic impurities form the sensor material. For the surface conductance measurement the electrodes of silver paint were formed on adjacent sides of the films.

3. CHARACTERIZATION

Figure 1 shows the XRD pattern of pristine stannic oxide (SnO_2) nanostructure synthesized by liquid phase via co-precipitation method calcinated at 400°C it is clearly observed that the highest intensity peak is obtained at (110) crystal planes and other peaks lying at (101), (200), (211), (220) and (002) of SnO_2. All the peaks match well with the standard tetragonal structure of SnO_2 with lattice constant a = 4.723 nm and c = 3.238 nm and its unit cell volume ($V=72.24A^{o3}$) with JCPDS card no. 71-0652. All the peaks are perfectly match with pure SnO_2 nanostructure, which indicates the high purity of obtained SnO_2 nanoparticles. The average crystalline size was found to be 23.19 nm calculated by using Deby

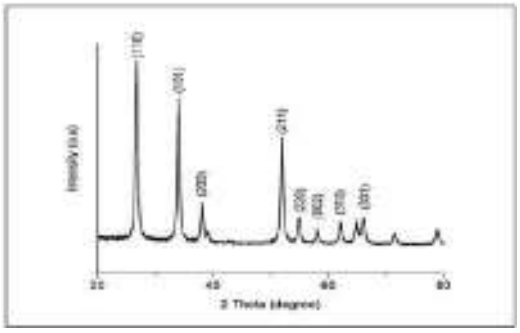

Figure 1: XRD pattern of SnO_2

TEM

Figure 2 shows the TEM image of pristine Stannic oxide (SnO_2) which shows the formation of highly crystalline stannic oxide (SnO_2) nanoparticle by using liquid phase method via co-precipitation method. The shape of SnO_2 nanoparticles are like tetragonal pattern of sports and their average crystalline size is found to be 29.15 nm [11,12].

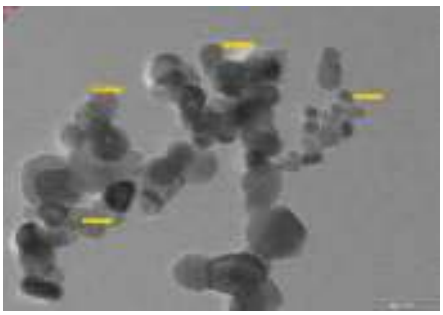

Figure 2: TEM images of SnO_2

FE-SEM

Figure 3 decipts the FE-SEM micrograph of pristine Stannic oxide (SnO_2) nanostructure thick films. In this the particles are found to in the tetragonal shape within the particle size in the range of about 15nm to 31.2 nm. The average particle size observed in both FE-SEM and TEM measurement where found to be nearly equal [13].

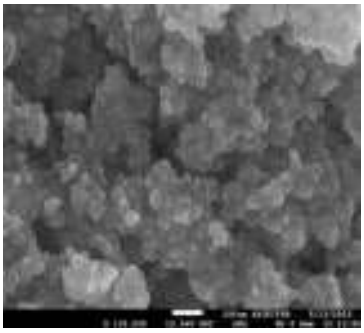

Figure 3: Fe-SEM images of SnO_2

Result and Discursion

Hysterias Plot

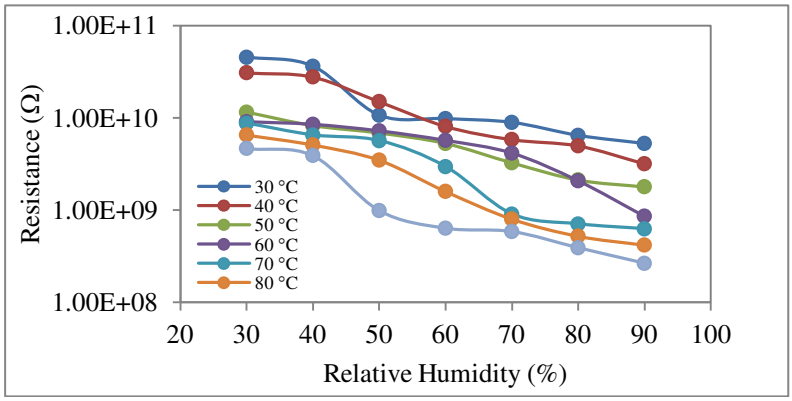

Figure 4: Variation of Relative Humidity with Resistance

Figure 4 shows hysteresis plot of Stannic oxide (SnO_2) at different constant temperature 30° C, 40°C, 50°C and so on. Hysteresis plot shows the variation between resistances of sample with respect to the relative humidity in increasing and decreasing order (30 to 90 % RH and 90 to 30 % RH) in steps of 5 % RH. Particularly, figure 4 is corresponds to resistance measurement by Keithley voltage source meter (2400) at constant temperature 30°C and so on. Overall in all the samples hysteresis plot measurement carried by Keithley voltage source meter (2400) at different constant temperature from 30 °C to 90 °C in steps of 10 °C and relative humidity varies from 30 to 90 % RH in steps of 10 % RH and vice versa also.

In these the resistance of sensors decreases by increasing the relative humidity from 30 to 90% RH and the resistance of sensors increases by decreasing the relative humidity from 90 to 30% RH at respective constant temperature varying from 30 to 90°C and vice versa. The presences of hysteresis shows the processes of adsorption and de-adsorption are not so faster at particular humidity. In this processes the adsorption would not be efficient which cause a small change in the resistance. The physisorbed water molecules is converted into chemisorbed by donating the surface electron at the constant temperature [14] and for the deadsorption it requires large activation energy [15]. On the other hand a sample shows comparable decrease in resistance with an increase in % RH which indicates that the conduction occurred at the grain surface by release of electron from the water molecule. However, the sample pure Stannic oxide (SnO_2) shows the remarkable change in the resistance values in between the humidity range 30-90 % RH and possessed a high sensitivity factor due to large surface area and porosity in the form of thick films.

A very small hysteresis present during forward and reverse cycle of relative humidity, where as a very significant average change observed in the value of resistance of sample, in the range of $10^{11}\Omega$ to $10^{8}\ \Omega$ in all the samples from 30 to 90% RH.

Sensitivity

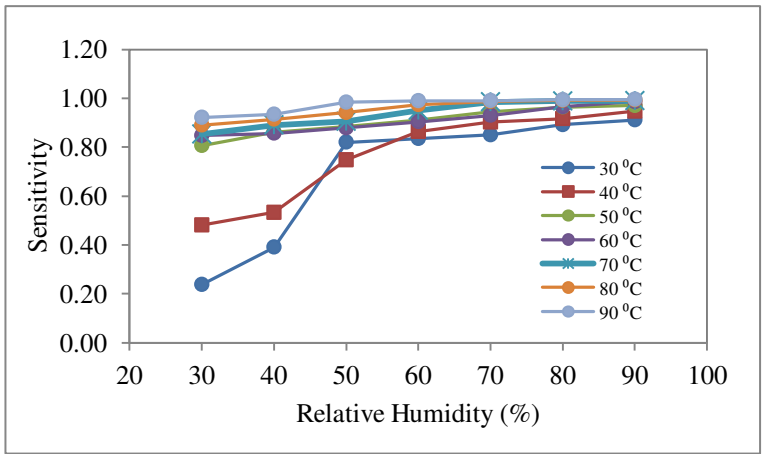

Figure 6: Variation of Relative humidity with Sensitvity of pure SnO_2 nanomaterials

The pure Stannic oxide (SnO_2) nanoparticles thick film exhibits significantly higher sensitivity due to the formation of heterogeneous interface between them and more adsorption site was created to absorbed more water vapuors [16]. The fall in resistance is mainly due to the increased amount of conduction electron or charge carrier upon adsorption of water vapours by the surface layer of the thick films. The fall in resistance is mainly due to the increased amount of conduction electron or charge carrier upon adsorption of water vapours by the surface layer of the thick films. Initially, at low humidity levels the adsorbed water molecules get ionized on the surface and the hydronium ions are produced by the assistance of high electric charge density in the neighbourhood of the hydroxyl (OH-) sites resulting in the protonic conduction to the adjacent sites [17]. For pure Stannic oxide (SnO_2) nanoparticles thick film the sensitivity is found to be increasing with the RH for all the samples of thick films and it is increasing up to some particular RH and then afterward it remains constant as shown in figure 6.

Activation Energy

The Arrhenius plot for all the samples found to be linear and by using Arrhenius equation;

$$\sigma = \sigma 0\ (-\Delta E/KT) \qquad \text{..... (1)}$$

The activation energy ΔE for nanostructured stannic oxide (SnO_2) samples is found to be quite reasonable for the electrical conduction the values of activation energy is much more smaller at constant different RH. This shows that the smaller amount of energy is required for the conduction of electrons due to absorption of water molecules there by increasing the number of donor electron [18]. The activation energy was found to be 4.6010^{-4} eV.

CONCLUSION.

Nanostructured SnO_2 was successfully synthesized by liquid phase via co-precipitation method. Minimum crystallite size was found to be for SnO_2 it is found to be 23.19 nm . Surface morphology of Nanostructured stannic oxide (SnO_2) shows that most particles are spherical in shape leaving more space as pores and hence it was most sensitive. The purity of sample was also conform with Transmission electron microscopy. The Hysteresis plot shows very significant average change in the value of the resistance from 10^{11} Ω to 10^{8} Ω during forward and reversed cycles. The sensitivity is found to be increasing with the RH for all the samples of thick films and it is increasing up to some particular RH and then afterward it remains constant and shows that it more sensitive. This nanocomposites carries a good scope for the development of moisture sensor in the range of relative humidity 30% to 90% RH. Activation energy measured and found to be 4.6010^{-4} eV respectively. This nanocomposites carries a good scope for the development of moisture sensor in the range of relative humidity 30% to 90% RH.

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ICMAM-2018

Study on DC Conductivity of PPy-ZnO Nanocomposites

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Abstract

In the present work, the nanocomposites of PPy-ZnO were prepared by chemical oxidative polymerization technique using an anhydrous ferric chloride ($FeCl_3$) as an oxidizing agent. The prepared samples were characterized via XRD and SEM (Scanning electron microscope) to determine the crystal size and porosity, respectively. Using, screen printing technique, thick films of the samples were fabricated. At room temperature and stepwise increasing temperature, dc conductivity of the samples had been measured and it was found that sample PZ2 has smallest average crystalline size 99.40 nm.

DC conductivity measurement showed nearly linear variation of ln(i) versus ln(V), exhibiting ohm's law being obeyed on logarithmic scale. Maximum value of current density, 1.261 $x10^{-5}$ A/m^2 for PZ2 (70% PPy + 30%ZnO) sample was obtained from schottky plot, at 400 K. Thus PZ2 sample is best among the prepared samples and its activation energy recorded to be 0.1106 eV.

Selection and Peer-review under responsibility of INTERNATIONAL CONFERENCE ON MULTIFUNCTIONAL ADVANCED MATERIALS (**ICMAM-2018**).

Keywords: PPy- ZnO nanocomposites, DC conductivity, activation energy.

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Selection and Peer-review under responsibility of INTERNATIONAL CONFERENCE ON MULTIFUNCTIONAL ADVANCED MATERIALS (**ICMAM-2018**).

1.0 Introduction

Now a day, conducting polymers are class of polymer that possesses high-quality tuneable electrical conductivity. But they are chemically sensitive and have poor mechanical property; on the other hand, nanomaterials exhibit good mechanical properties. Thus, because of good mechanical orientation, oxides nanoparticles showed best utility thereof. Such properties of nanocomposites are strongly dependence of polymer concentration. Separation of nanoparticles in polymer matrix has large effect on the polymers properties [1]. As PPy has good electrical conductivity and good ion-exchange capacity, it is most studied conducting polymer. PPy can be prepared in different forms such as powder, films, colloidal particles and composites in micro and nano sizes [2-5]. Nanoparticles of PPy are prepared by various path such as chemical or electrochemical [6] with organic or inorganic metals. Low conducting polymers have many applications in the fabrication of insulators and dielectrics [7-8].

The present study deals with the synthesis, characterization of Zn/PPy composites and evaluation of dc electrical conductivity for different weight percentages.

2.0 Experimental

2.1 Synthesis of ZnO Nanoparticles

In the present work, chemicals used are of GR grade with purity 99.99%. Zinc acetate dehydrate $Zn(O_2CCH3)2(H_2O)2$, sodium hydroxide, Methanol and de-ionized water was used during reaction. For the preparation, Zinc Oxide (ZnO) 0.2M Zinc Acetate dehydrates dissolved in 100 ml de-ionized water was kept for 15 min and then added with NaOH (0.02 M) solution. After the mixing the solution was kept under constant magnetic stirring for 15 min. and then again it was grinded for 30 min. The white precipitate produced was allowed to wash with de-ionized water and methanol many times so as to remove by-products. Watt-man filter paper was used to filter the product. The obtained white paste was kept in vacuum oven for 4 h at 80^{o}C. Then this dry product was crushed into a fine powder by using grinding machine and finally this fine nano-powder of ZnO was calcinated at temperature 800^{o}C for 6 h.

2.2 Synthesis of Polypyrole (PPy)

Iron (III) chloride ($FeCl_3$), methanol and Py monomer were taken in pure forms for synthesis of PPy sample [10]. 1.892 g $FeCl_3$ was taken in fine power form and it was mixed with 7 ml methanol solution in round bottom flask. Then 8.4 ml Py monomer was introduced to ($FeCl_3$+methanol) solution with constant vigorous stirring in dark. The amount of Py monomer introduced to the solution (1/2.33 times of $FeCl_3$) was in such a way to get peak yield. The resulting black precipitates were filtered and cleaned with copious amount of distilled water until the washings are clean and clear. The obtained PPy was powdered by putting in oven at 600^{o}C for 3 h.

2.3 Preparation of Pellets

Initially, for the preparation of pellets the synthesised material ZnO, and PPy were mixed with different weight percentage in pure and composite forms (Table 1). The pellets of different series of ZnO-PPy nano-powder were prepared by using electrically operated automatic press machine (KBr Press) at load of 5 tons / cm^2 for 0.5 h. All the pellets were heated at 150^{o}C for 0.5 h. These pellets were polished and then electrodes were formed with the help of conductive silver paint on their edges. Again pellets were sintered for the drying the silver paint at 100^{o}C for half an hour.

3.0 Results and Discussion

3.1 X-Ray Diffraction

XRD pattern of polypyrrole (PPy) and its composites are as shown in Fig. 1 and Fig. 2 respectively. XRD pattern of PPy manifested amorphous nature of PPy. At 27^{o} broad peak occurred which is the characteristics of amorphous nature of polypyrrole. Broad peak resulted by scattering of X-Rays from polymer chains at the interplaner spacing. The maximum intensity position of amorphous also depends on monomer to oxidant ratio [9].

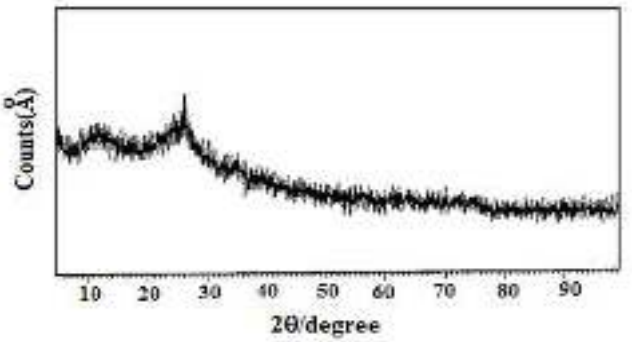

Fig. 1: XRD pattern of PPy

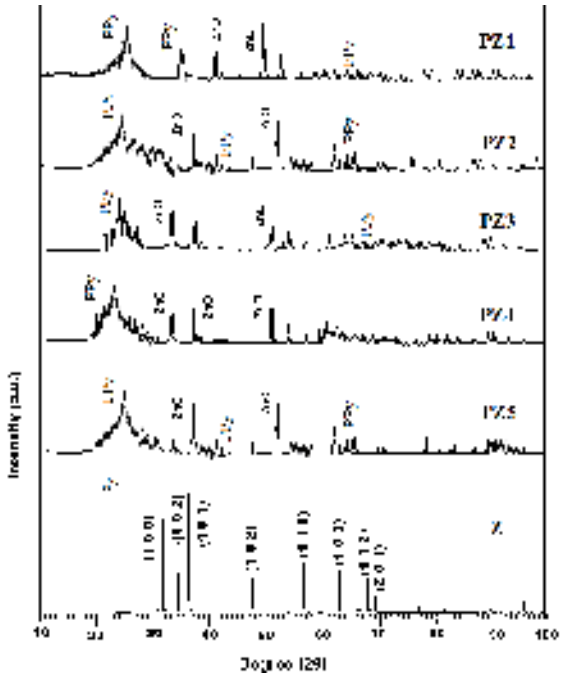

Fig. 2: XRD of PPy and ZnO composites

Table 1: Sample Codes

Sr. No.	Pure Sample and composites	Codes
1	Pure Polypyrrole	P
2	80 % ppy + 20 % ZnO	PZ1
3	70 % ppy + 30 % ZnO	PZ2
4	60 % ppy + 40 % ZnO	PZ3
5	50 % ppy + 50 % ZnO	PZ4
6	40 % ppy + 60 % ZnO	PZ5
7	Pure ZnO	Z

From XRD pattern of composites, it is observed that average crystallite size of 70PPy:30ZnO composition is least (99.40 nm) as compared to other compositions and pure PPy and hence 70PPy:30ZnO composition (PZ2) has large active area which tends to increase the conductivity of PZ2 sample.

3.2 SEM Analysis

The surface morphology of polypyrrole and composites of PPy and ZnO materials were studied by SEM and its pictures are shown in Figs. 3-9.

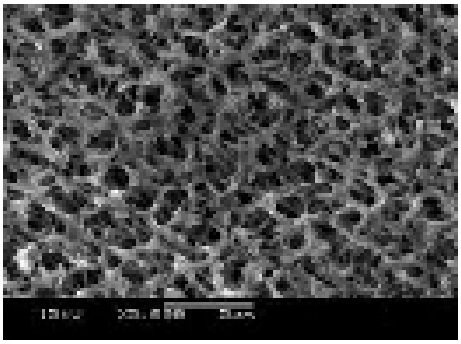

Fig. 3: SEM of P (pure PPy)

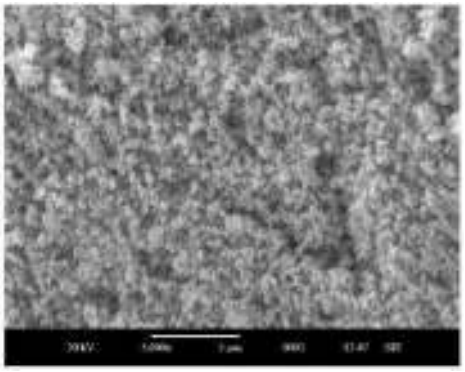

Fig. 4: SEM of PZ1 (80 % PPy + 20 % ZnO)

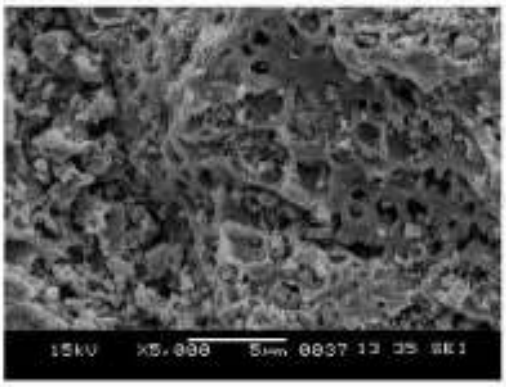

Fig. 5: SEM of PZ2 (70 % PPy + 30 % ZnO)

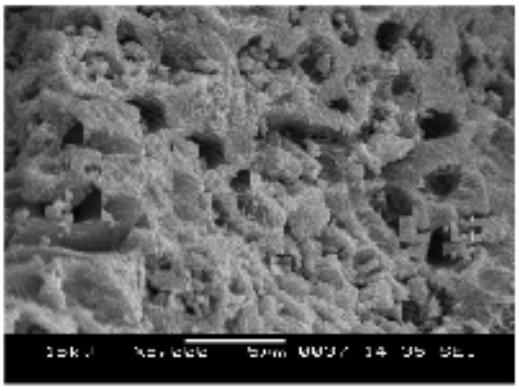

Fig. 6: SEM of PZ3 (60 % PPy + 40 % ZnO)

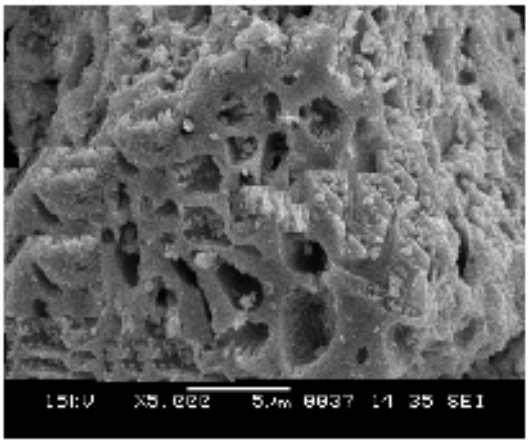

Fig. 7: SEM of PZ4 (50 % PPy + 50 % ZnO)

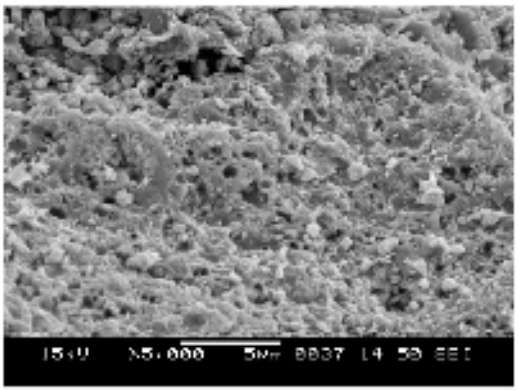

Fig. 8: SEM of PZ5 (40 % PPy + 60 % ZnO)

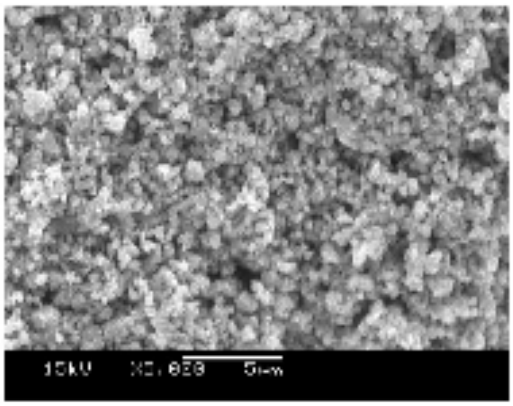

Fig. 9: SEM of Z (pure ZnO)

From the SEM photos, it is observed that in every inch of the region, number of pores was different and an average numbers of pores were taken for comparative study. From every photo, porosity was calculated for one inch square area. From figures, it is found that number of porosity of PZ2 sample is more among samples [10]. Conductivity increases as for the ions and charges surface area is large because of large porosity. Because of the large surface area due to high porosity, collision frequency decreases and obstacle for the flow of ions and charges becomes less. This enhances the charges mobility and tends to increase electrical conductivity.

3.3 DC Conductivity Measurement

Fig. 10 shows the variation of ln(i) versus ln(V) at constant room temperature, 300 K. From this figure, it is manifested that as the doping percentage of ZnO in PPy increases, ln(i) increases current with increase in ln(V). It is maximum for PZ2 sample (70%PPy + 30 % ZnO) amongst the prepared samples. It is also observed that, the nature of all the graphs is nearly straight line with constant slopes, exhibiting that obeys Ohm's law is obeyed on logarithmic scale.

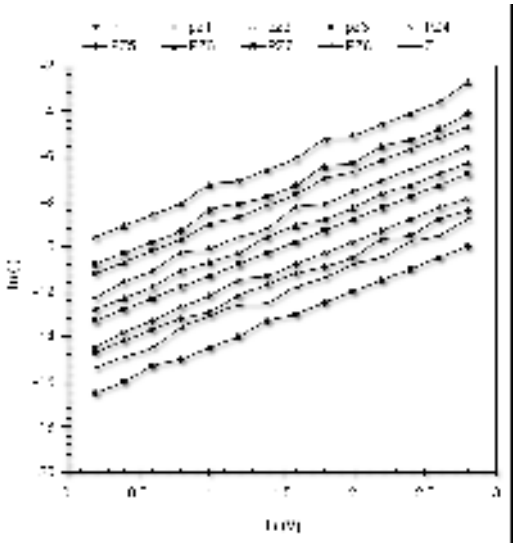

Fig. 10: Variation of ln(i) with ln(V) at room temperature (300K)

3.4 Schottky Plots:

Figure 11 shows the variation of ln(J) with $E^{1/2}$ at room temperature, 300K. The graph is known as Schottky plot and it is observed that as applied electric field E increases, ln(J) increases, speedily in the beginning and then slowly. It is also manifested that, for PZ2 composition, ln(J) is maximum. From Fig. 12, it is observed that, at optimum temperature i.e. 400 K, current density for PZ2 varies from 2.019 x 10^{-6} A/m^2 (minimum) to 1.261 x10^{-5} A/m^2 (maximum). For all remaining samples, current density was low.

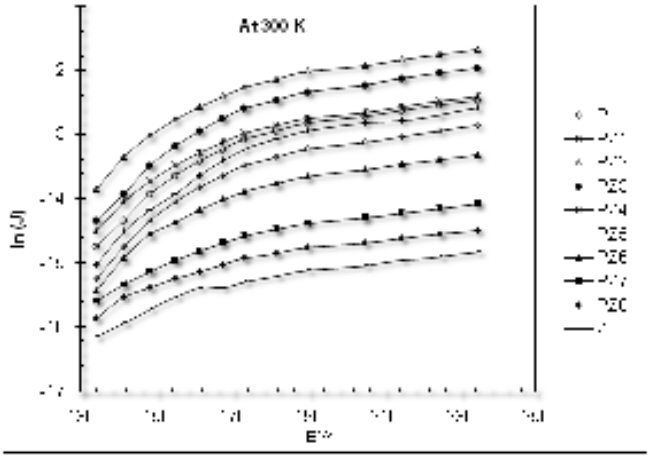

Fig. 11: Variation of ln(J) with $E^{1/2}$ at 300K

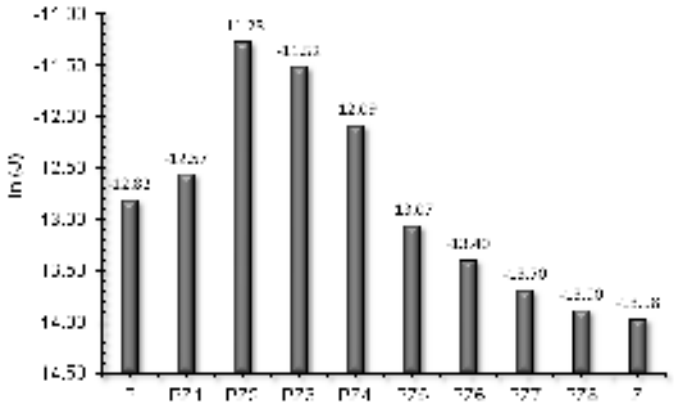

Fig. 12: Variation of ln (J) at 400 K temperature

3.5 Arrhenius Plot

It is seen from figure 13, that as temperature increases, $\ln(\sigma)$ increases. This variation is maximum for PZ2 sample and minimum for P sample. Due to increase of temperature, more and more charges in PZ2 samples become free and contribute to the conductivity and electrical conductivity increases. Slope of the PZ2 sample curve is maximum among the samples. As doping of ZnO in PPy increases, electrical conductivity increases and becomes maximum for 70%PPy + 30% ZnO sample (PZ2 sample) and further increase in doping of ZnO in PPy, conductivity decreases. This decrease may be due to collisions of more free charges with the vibrating local atoms in the sample as collision increases the obstacle to the motion of free charges.

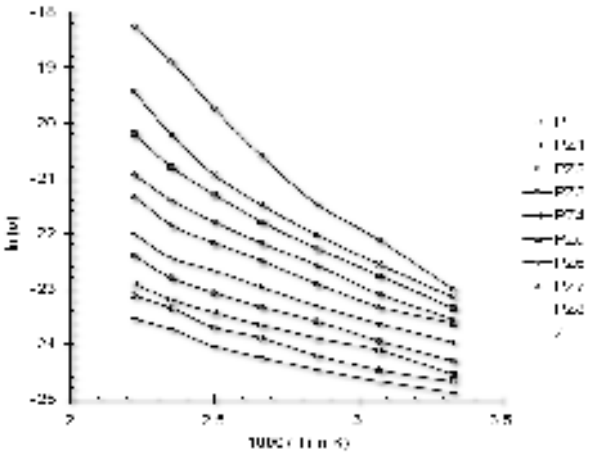

Fig. 13: Variation of ln (σ) with 1000/T(in K)

3.6 Activation Energy

Activation energy is given by, $E_a = -KT \times$ Slope of graph from Arrhenius plot. Figure 14 manifested that activation energy of PZ2 sample is maximum among the samples and it is 0.1106 eV. This value is higher than other prepared samples.

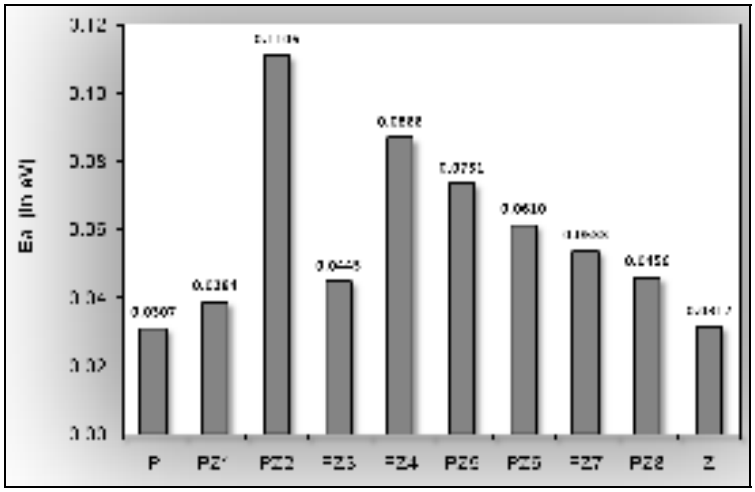

Fig. 14: Variation of ln (σ) with 1000/T(in K)

4.0 Conclusion:

Porosity of PZ2 sample was found to be more and its average crystalline size was found to be 99.40 nm, from XRD pattern. DC conductivity measurement showed nearly linear variation of ln(i) versus ln(V), exhibiting ohm's law being obeyed on logarithmic scale. Maximum value of current density, 1.261 $x10^{-5}$ A/m^2 for PZ2 sample was obtained from schottky plot, at 400 K (shown in bar graph). Thus PZ2 sample is best among the prepared samples and its activation energy recorded to be 0.1106 eV.

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२७. कृषीतज्ञ डॉ. पंजाबराव भाऊसाहेब देशमुख

डॉ. देवेंद्र एस. रंगाचार्य
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स्वातंत्र्य प्राप्तीनंतर देशातील अन्नधान्याची कमतरता दूर करण्यासाठी कृषी क्षेत्राकडे विशेष लक्ष दिले पाहीजे. पंजाबरावांनी पंचवार्षिक योजनाच्या माध्यमातून कृषी उत्पादन आणि उत्पादकता वाढविली. अन्नधान्याच्या संदर्भात आत्मनिर्भरता प्राप्त करण्याचा प्रयत्न केला. देशामध्ये अन्नधान्याचे उत्पादन वाढविण्याच्या दृष्टीने अधिक धान्य पिकवा ही मोहीम सुरु केली आणि देशाला दुष्काळी संकटापासून वाचविले.

भारतीय लोकांना पौष्टीक अन्नधान्य मिळाले पाहीजे. याशिवाय प्रतिव्यक्ती धान्याची उपलब्धता भारतातील सर्व प्रांतात लोकांना मिळाली पाहीजे. भारतातील लोकांच्या आहारामध्ये गहू, तांदुळ, दुध, फळ फळावळे इत्यादींचा अभाव आहे त्याचे कारण म्हणजे भारतीय लोकांचे उत्पन्न कमी आहे म्हणून पंजाबरावांनी देशातील शेतकऱ्यांचे प्रतिव्यक्ती उत्पन्न वाढविण्याचा प्रयत्न केला. कुपोषणाची समस्या निर्माण होवू नये म्हणून त्यांनी प्रयत्न केलेत.

डॉ. पंजाबरावांनी "अधिक धान्य पिकवा" मोहिमेच्या आधारे अन्नधान्याच्या आत्मनिर्भरतेला नवीन जीवन दिले. भारत सरकारच्या वतीने कृषी उत्पादन वाढविण्याला सर्वोच्च स्थान दिले. सधन आणि विविध पिकांचे कार्यक्रम सुरु करण्यावर भर दिला अधिक उत्पादन देणाऱ्या प्रजातीचा विकास केला. चांगल्या बियानाच्या व्यवस्थेसाठी मोठमोठया बीज निर्मिती केंद्राची स्थापना केली, कृषीचे यांत्रिकीकरण केले.

डॉ. पंजाबराव म्हणतात, "भारत तांदुळाचे इतके विक्रमी उत्पादन कसे काय करू शकला? या प्रश्नांच्या उत्तरादाखल म्हणतात हा नियोजनाचा परिणाम आहे. जमीनीची पोत आणि सुपीकता टिकविण्यासाठी तसेच तिचो पिक उत्पादन क्षमता वाढावी म्हणून जपान, चीन सारखे देश शेण खताचा व इतर खतांचा वापर करतात हे विचार कृषी उत्पादन वाढविण्यासाठी पूरक ठरतात असे मत व्यक्त केले.

भारतीय कृषीची उत्पादकता कमी असण्याचो भाऊसाहेबांनी तीन कारणे सांगीतली होती.

१) पाणी पुरवठ्याची अपूर्ण साधने व अपूर्ण पाणी पूरवठा.

२) सेंद्रीय व रासायनिक खते यांचा कमी वापर.

३) पिकांच्या वाढीच्या विविध टप्यांची पुरेशी काळजी न घेणे.

कमी उत्पादकतेची कारणे शोधून शेतीत तंत्रात्मक सुधारणा अंमलात आणायला पाहिजे. संसाधनांचा महत्तम उपयोग करायला हवा तसेच नैसर्गिक संकटाकडे भारतीय शेतकऱ्यांनी दुर्लक्ष करू नये.

केवळ एका वर्गाच्या आर्थिक हिताचा विचार करून कोणतीही योजना देशपातळीवर यशस्वी होणार नाही. भारतीय समाज हा मोठया प्रमाणात समुह रूपाने ग्रामीण भागात राहतो. उदा. शेतकरी, शेतमजूर हा वर्ग प्रामुख्याने उत्पादनातील कार्यप्रवण घटक आहे. त्यांच्या उन्नतीशिवाय देशाचा आर्थिक विकास होवू शकत नाही. असे केल्याने शेतकऱ्यांची व

शेतमजुरांची क्रयशक्ती नाहीशी होईल. त्यांचे वित्तीय जीवन उध्वस्त करण्यास अशा प्रकारच्या नियंत्रणात्मक धोरणांची अंमलबजावणी कारणीभूत ठरेल. आपण शेतकऱ्यांच्या उत्पादित वस्तूंसाठी योग्य व आकर्षक अशा किंमती ठरविणे आवश्यक आहे. त्याशिवाय शेतकरी अन्नधान्याचे उत्पादन शेतीमधून काढण्यास तयार होणार नाही. शेती उत्पादन जर वाढवायचे असेल तर ही योजना शेतकऱ्यांचे आर्थिक हित लक्षात घेवुन जास्तीत जास्त प्रभावीपणे राबवावी लागेल. संपूर्ण देशपातळीवरील कृषकांच्या आर्थिक कल्याणाच्या दृष्टिकोनातून नियोजन करावे व त्या अंतर्गत शेतकऱ्यांना अन्नधान्याचे उत्पादन वाढविण्यासाठी प्रोत्साहित करावे.

भाऊसाहेब म्हणतात जर देशातील शेतकऱ्यांना भरीव मदत दिल्या गेली नाही तर शेकडो एकर जमीन पुढल्या वर्षाला नापीक राहील व त्यामधून काही उत्पादन मिळणार नाही. म्हणून असे विपरीत परिणाम टाळण्याकरीता पडीत जमीन लागवडीखाली आणत असतांना जो खर्च होत आहे तो व्यवस्थित आणि संयुक्तीक व्हायला पाहिजे. केंद्रीय सरकाला व प्रांतीय सरकारला केवळ दोष देणे हा मी प्रतिपादन केलेल्या विचारांचा उद्देश नाही. देशातील लोकांमध्ये मोठया प्रमाणावर असंतोष आहे. या असंतोषाचे निर्मूलन करावयाचे असेल तर त्यांच्या तक्रारी ऐकाव्यात आणि त्यांना तक्रार सादर करण्याची योग्य संधी दयावी ती त्यांना दिल्या जात नाही. देशातील कृषी, कृषक आणि अन्नधान्य ह्या घटकांच्या संदर्भातील विचार प्रतिपादन करणे आवश्यक आहे. प्रत्येकाला भारत हा शेतीप्रधान देशच हवा आहे. परंतु जर लोकांच्या समस्या आणि त्यांच्या गरजांची पुर्तता ह्याकडे जातीने लक्ष दिले नाही तर आपल्यावर पश्चाताप करण्याची पाळी येईल म्हणून शेती प्रधान देशाचे अस्तित्व टिकून ठेवण्यासाठी संभाव्य अर्थव्यवस्थेची आर्थिक घडी सुनियोजितरित्या राबविणे आवश्यक आहे.

भारतासारख्या शेतीप्रधान देशात अन्न धान्याचे उत्पादक शेतकरी कुटूंबे आहेत. शेतकरी कुटूंब आणि शेतीत काम करणाऱ्या शेतमजुरांची संख्या देशात सर्वात जास्त आहे. म्हणून या वर्गाचे हितसंबंध जोपासने काळाची गरज आहे. या वर्गाकडे दुर्लक्ष केल्यास अन्नधान्याचे उत्पादनही होणार नाही आणि देशात प्रचंड प्रमाणावर बेरोजगारी निर्माण होईल. शेती व्यवसायाकडे लोकांचे दुर्लक्ष होईल. परिणामता आर्थिक विकासाच्या प्रक्रियेत अडथळे निर्माण होतील असे त्यांना वाटत होते. देशातील कृषी व्यवसाय व्यापारचक्राला बळी पडू नये अन्नधान्याचे प्रचंड उत्पादन महामंदीत रूपांतरीत होवू नये म्हणून शेतकरी, शेतमजूर यांची क्रयशक्ती वृध्दींगत करावी त्यांनी निर्माण केलेल्या अन्नधान्याला योग्य किंमत ह्यावी असे विचार भाऊसाहेबांनी सांगीतले.

१९१४ पूर्वी म्हणजे पहिल्या महायुध्दापूर्वी हिंदुस्थान हा अन्नधान्याची निर्यात करणारा देश म्हणून ओळखला जात होता. हडप्पा, मोहिंजदडो ह्या शहराच्या उत्खननाच्या शोधातही भारत हा शेतीप्रधान देश होता असे पुरावे मिळतात. प्रत्येक देशाला अन्नधान्याच्या बाबतीत स्वयंपूर्ण व्हायचे होते. म्हणून त्यांनी भविष्यकाळात आपल्या देशात अन्नधान्याचा राखीव साठा राहावा यावर भर दिला होता यावरून डॉ. भाऊसाहेब हे जागतिक स्थितीचा आढावा घेवून वैचारिकतेच्या आधारावर ध्येयधोरण ठरवित होते असे आढळते. त्यामुळे त्यांनी भारताला अन्नधान्याच्या बाबतीत स्वयंपूर्ण करण्याचा प्रयत्न केला. याकरीता त्यांना अन्नधान्याचे स्वावलंबन प्राप्त करून देणारे जागतिक पातळीवरील भारतीय आर्थिक विचारवंत म्हणून संबोधण्यास हरकत नाही.

जर अतिरिक्त अन्नधान्याचा साठा निर्माण होत असेल आणि मंदीची परिस्थिती निर्माण होत असेल तर अतिरिक्त अन्नधान्याचा वापर लाकूड, कागद आणि कागदाचा लगदा तयार करण्यासाठी करण्यात यावा म्हणजे अन्नधान्याच्या किंमती पडणार नाही आणि कृषकांना त्याची हानी पोहोचणार नाही. शिवाय अर्थव्यवस्थेतील सामान्य किंमत पातळी टिकून राहण्यास

उपाय योग्य ठरेल असे त्यांनी सुचविले. शेतकऱ्यांनी पूरक उद्योगही निर्माण करावेत आणि कृषीला उद्योगाचे वैभव व रोजगारी निर्मीतीचे केन्द्र बनावे असे भाऊसाहेबांनी सांगीतले. अन्नधान्याचे उत्पादन, वितरण, विपणन आणि बाजारपेठेतील व्यापार या संबंधातही विविध निर्णय घेण्यात यावेत. अन्नधान्य आणि पोषण, व्यापार, उद्योग आणि वाणिज्य इत्यादी प्रश्नासोबतच मत्स्य व्यवसाय व वनसंवर्धन यांचाही आज कृषी संघटनेने विचार करावा.

आम्हाला जास्तीत जास्त उत्पादन होण्याचा प्रयत्न करावा लागेल. कारण आम्हाला महापूर, अवर्षण, रोगराई, अतिवृष्टी, टाळधोड, उंदीरापासून होणारे नुकसान यासारख्या नैसर्गिक संकटांना तोंड दयावे लागते शिवाय निरंतर वाढत जाणाऱ्या लोकसंख्या समस्येच्या बाबतीत सतर्क राहीले पाहीजे म्हणून माझी अशी इच्छा आहे की, येणाऱ्या काही वर्षापर्यंत आम्ही शेतीमध्ये नवनवीन साधनांचा वापर करण्याचा प्रयत्न करायला पाहीजे त्याचा उपयोग केवळ भातशेतीसाठी नाही तर अन्य पिकांचे उत्पादन वाढविण्यासाठी सुद्धा करायला पाहीजे.

अन्नधान्य उत्पादन, लोकसंख्या विकास

आपल्या देशातील शेतकऱ्यांची, शेत मजूरांची आणि औद्योगिक मजूरांची भूक ही कृषीमधून निर्माण होणाऱ्या अन्नधान्याच्या उत्पादनातून परिपूर्ण होत असते. भारताच्या अर्थव्यवस्थेचा तो एक महत्वाचा घटक आहे. अन्नधान्याच्या प्रक्रिया उद्योगातून जास्तीत जास्त लोकांना रोजगार आणि उत्पन्न मिळते. शेतीमधील अन्नधान्याचा विकास शेतकऱ्यांच्या उत्पन्नावर चांगला परिणाम घडवून आणणारी बाब आहे. कारण त्यामुळे त्यांची क्रयशक्ती वाढते. भारतातील तसेच आंतरराष्ट्रीय उपभोक्ता वर्गाकडून विविध प्रकारचा, उच्च दर्जाच्या आणि सुरक्षित अन्नपदार्थांची मागणी होत असते. त्यामुळे देशातील दर्जेदार अन्नधान्याचे उत्पादन आंतरराष्ट्रीय व्यापारही वाढविते त्यामुळे कृषी क्षेत्राच्या विकासाला महत्व येते. कृषी उत्पादन वाढविण्यासाठी जलसिंचन, पाटबंधारे आणि पडीत जमीन दिकासाकरीता अधिक गुंतवणूक करणे आवश्यक आहे. कृषी क्षेत्राच्या विकासाकरीता विविध पायाभूत सोयींची निर्मिती करणे भाग पडते. भारताला जगातील आघाडीची कृषी व्यवस्था म्हणून नावारुपाला आणण्याची क्षमता भारतीय अन्नधान्य उत्पादन प्रक्रियेत आहे.

ते लोकसंख्येच्या संदर्भात म्हणाले होते, "लोकसंख्या वाढीवर नियंत्रण ठेवण्यासाठी कठोर उपाय योजना करावी लागेल. राष्ट्रीय स्तरावर कृषी तंत्रज्ञान कृषीसाठी जलसिंचनाच्या सोयी कराव्या लागतील सहकारी तत्वांचा अवलंब करून कृषी उत्पादनखर्च व कृषी उत्पादनाची किंमत यात समन्वय साधावा लागेल."

थॉमस माल्थस या अर्थशास्त्रज्ञाच्या मते वाढणारी लोकसंख्या आणि अन्नधान्य यामध्ये असंतुलन निर्माण होते हे सूत्र भारतीय लोकसंख्येच्या संदर्भात डॉ. पंजाबरावांच्या लक्षात आले होते म्हणूनच त्यांनी अन्नधान्य उत्पादन वाढविण्याच्या योजना पंचवार्षिक योजनांच्या माध्यमातून राबविल्या. शिवाय नवनवे पिक प्रयोग उत्पादन वाढविण्यासाठी केले होते. परंपरागत पीक पद्धतीमध्ये बदल करण्यासाठी सुधारित बी-बीयाने शेतकऱ्यांना मिळावेत म्हणून संशोधन केन्द्र निर्माण केले. अन्नधान्याच्या उत्पादनात देश स्वयंपूर्ण झाल्यास आरोग्यात सुधारणा होते. एका गरजेतून दुसरी गरज अशी क्रमवारी निर्माण व्हायला लागते. उदा. अन्न त्यातून वस्त्र आणि नंतर निवारा असे सुष्टचक्र सुरु होते व आर्थिक विकासाची प्रक्रिया कार्यान्वीत होते. सर्व वित्तीय संस्थांची उभारणी आणि रोजगार निर्मितीचा आधारस्तंभ उपभोग्य घटक असतात. उपभोग्य वस्तूतच भांडवली वस्तूंची निर्मिती होते असे त्यांचे विचार होते. म्हणूनच ते म्हणतात "श्रमीक आणि शेतकरी जगाला अन्न पुरवितात."

डॉ. पंजाबरावांचे अन्नधान्य उत्पादन वाढविण्याचे प्रयत्न हे देशाच्या आर्थिक विकासातील एक महत्वपूर्ण कामगिरी होती असे म्हणता येईल. डॉ. पंजाबराव म्हणतात "जनतेला अन्न, वस्त्र, निवारा या गरजांचा पुरवठा करणाऱ्या सेवेसारखी दुसरी सेवा असू शकत नाही. ही सेवा म्हणजेच खरी राष्ट्रीय सेवा होय. भाऊसाहेब म्हणतात भूमी बद्दल प्रेम, वृक्षनिगा, सुधारीत बियाणे, पशूधन विकास, ग्रामगीते, नृत्य, सण इत्यादी माध्यमातून भारतीय भूमी समृद्ध होवू शकते. या बाबीकडे दुर्लक्ष केल्यास ग्रामीण युवकांमध्ये नैराश्य निर्माण होईल आणि ते बेफल्यापोटी शहराकडे स्थलांतरीत होवू लागतील. त्याचे परिणाम आर्थिक विकासावर आणि अन्नधान्याच्या उत्पादनावरही होतील म्हणून उपरोक्त बाबींचे संगोपण करणे काळाची गरज आहे.

निष्कर्ष

१. शेतमालाची सामान्य संतुलित किंमत पातळी टिकवून ठेवली तर आज होणाऱ्या शेतकऱ्यांच्या आत्महत्या टाळता येतील.

२. कृषी क्रांतीच्या माध्यमातून ग्रामीण अर्थव्यवस्थ पयायांने देशाची अर्थव्यवस्था समृद्ध होते.

३. आधुनिकीकरण यातून आर्थिक न्याय मिळवून देणारी अर्थव्यवस्था उभी करता येते.

४. सामाजिक विषमता, आर्थिक गरीबी, लोकसंख्या विषयक समस्या शेतकऱ्यांनी शिक्षणात प्रगती केली तरच दूर होवू शकतात.

५. कृषीविषयक शिक्षण विकासाकरीता मार्गदर्शक ठरेल

संदर्भग्रंथ

१. मोहाडे सुधाकर "जिनिअस - क्रूसेडर डॉ. पंजाबराव देशमुख" श्री दौलतराव गोळे पब्लिशर्स, अमरावती १९९७.

२. कोलते वि.भि. "वैदर्भिय जनतेचे हृदय सम्राट डॉ. पंजाबराव देशमुख, दौलतराव गोळे प्रकाशन, अमरावती १९९६.

३. देशमुख कुसूम "वात्सल्यमूर्ती डॉ. पंजाबराव उपाख्य भाऊसाहेब देशमुख" श्रीमती देशमुख कुसूम दत्तात्रय, रामदासपेठ, नागपूर १९९८.

४. गोळे दौलतराव तु "भारतीय कृषक क्रांतीचे जनक कृषीरत्न डॉ. पंजाबराव देशमुख गोळे दौलतराव तु प्रकाशन, अमरावती १९९६.

५. पवार ना.ग. "महामानव डॉ. पंजाबराव देशमुख" भारती प्रकाशन पूणे १९९३.

६. सावरकर सुदाम "भाऊसाहेब उर्फ डॉ. पंजाराव देशमुख यांचे जीवन व कार्य"श्री. भं. रा. लोंढे, पब्लिशर्स अमरावती १९६७.

७. देशमुख कल्पना "डॉ. पंजाबराव देशमुख यांचे सामाजिक योगदान" प्रदिप मुळे पब्लिशर्स, नागपूर १९९७.

८. देशमुख पी.पी. "शेतकऱ्यांचे कैवारी" कृषीरत्न डॉ. पंजाबराव देशमुख.

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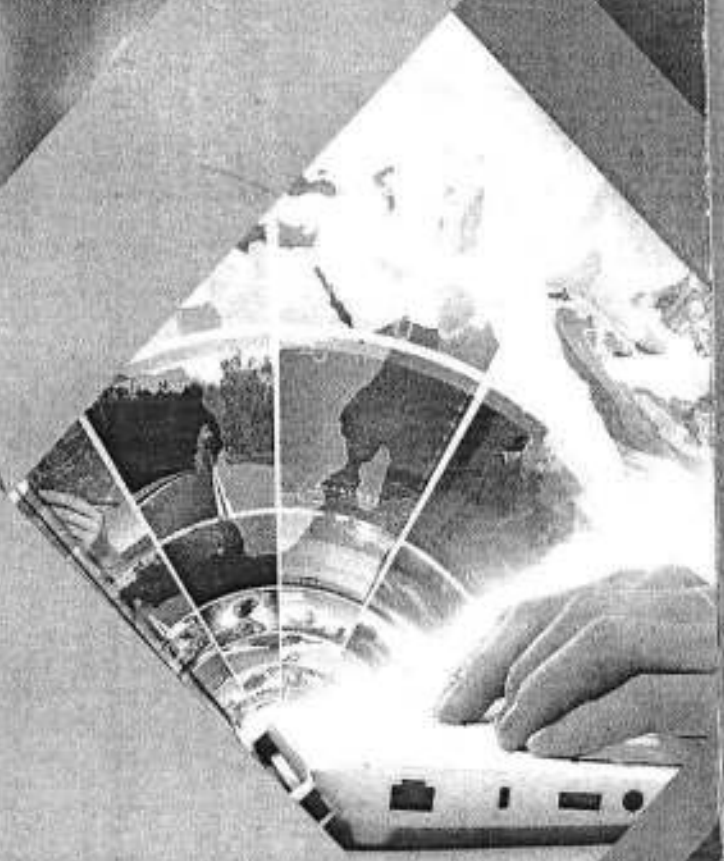

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Ajanta Prakashan

2. A Study of Adolescence Mental Health among Joint Family and Nuclear Family

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Positive psychology is about scientifically informed perspectives on what makes life worth living. It focuses on aspects of the human condition that lead to happiness, fulfillment and flourishing. The aim of positive psychology is to begin to catalyze a change in the focus of psychology from preoccupation only with repairing the worst things in life to also building positive qualities.

According to Abraham Maslow positive psychology that studies the strengths and virtues that enable individuals and communities to thrive. Positive psychology seeks to find and nurture genius, creativity and talent as well as to make normal life more fulfilling not to care mental illness. When we ask what is positive psychology then we receive different answers every time. In this sense, positive psychology is perceived of as a panacea for many modern ills. There are many definitions of positive psychology but all the points in the definitions are same. Some definitions of positive psychology are follows.

Definitio

1) Gable and Haidt (2005):- "Positive psychology is the study of the flourishing or optimal functioning of people, groups and institutions."
2) Martine Seligman (2000):- "Positive psychology is a science of well-being and optimal functioning."

Positive psychology of the subjective level deals with experiences like well-being , contentment satisfaction, hope and optimism, happiness etc. On the contrary at individual level positive psychology deals with positive traits like capacity for love and vocation, courage, inter personal skill, aesthetic sensibility, perseverance forgiveness, originality, future- mindedness, spirituality, high talent and wisdoms. Positive Psychology has common interests with parts of humanistic psychology and its emphasis on fully functioning person (Rogers 1961). We note that

more than 50 years ago, psychology focused on the human's negative aspects like disorder and dysfunction. Maslow (1968) lamented that the science of psychology has been far more successful on the negative than on the positive side. It has revealed to us much about man's short comings, his illness, but little about his potentialities, his virtues, his virtues his full psychological height. Positive psychology promises to get adolescent's internal fires let to help them develop the complex skills and disposition necessary to take their lives, to become socially competent compassionate and psychologically vigorous adults,

Mental Health

In 1955 Erich Fromm explored the 'Sane Society' defining mental health as "The ability to love and to create." (Fromm, P.69). During the same period, social psychologist Marie Jahoda (1958) characterized mental health as the positive condition that is driven by a person's psychological resources for personal growth. She described their six characteristics of the mentally healthy person. Fromm and Jahoda had been rediscovered, contextualized, and incorporated into refined conceptualizations of positive mental health. Family mental health is a group mental health. Family member is an important aspect for mental health of the family. It is seen that sometimes most of the family members have good health but because of one person in the family not having the good health, the whole family gets disturb. At the same time it is also the fact that success of one family member understanding between each other, co-operation etc. improves the mental health of the family.

Generally there are three levels of social class as 1) Higher class 2) Middle class 3) lower class of families. Individuals differ in their personality pattern as values, norms attitudes etc. differ from society to society. As a result there are individual differences in respect personality patterns. Family performs many functions. These certain functions are relevant to health behavior and are important from the mental health point of view.

In this paper we have fluids adolescent mental health among joint family and nuclear family. In this subject development is a important factor, because mental health is depend upon adolescent's development. In this context developmental psychologists focus on the origins and function of behavior. Their scientific efforts shed light on normal developmental processes such as cognitive operations (Piaget 1932), moral judgment (Gillign 1982, Hohlberg 1985) and personality (Allport 1960 Mischel 1979).

Aim of the study

To find out the contribution of positive psychology in mental health of joint and nuclear family adolescence.

Objectives of the study

1) To study the mental health of joint family and nuclear family.
2) To study the effect of sex on mental health

Hypothesis

1) Joint family adolescence has significantly good mental health than nuclear family adolescence.
2) Joint family, nuclear families (boys) have significantly good mental health than Joint family, nuclear family (girls).

Scope of the study

1) This study is useful for the identifying mental health in joint family and nuclear family
2) On the basis of this study we get some suggestion for developing the mental health in joint and nuclear family.

Sample

Sample for present research selected from Amravati city. Age range of sample is 11to 19 years. Sample distribution noted below.

Family type	Joint family	Nuclear family	Total
Sex			
Boys	50	50	100
Girls	50	50	100
Total	100	100	200

Tools to be used

The paper is mainly devoted to the study of mental health among joint and nuclear family. For collecting data "Mental health scale by Dr. (Smt.) Kamlesh Sharma Used.

Statistical treatment of data: - After collecting data the scores obtained from mental health was statistically treated. Descriptive statistics i.e. Mean, SD, calculated and finally two way ANOVA is applied and results are discussed.

Result and Discussion

Effective sample of the study consist of 200 adolescence. Since a 2x2 factorial design was used. In addition to the data analyzed for finding out the role of sex with respect to mental health. By treating obtained data, we calculated separately mean and deviation table no. 1 shows SD and mean.

Table no. 1:- Mean and SD of Joint family and nuclear family for mental health.

	Joint family	Nuclear family	Total
Mean	21.41	19.71	20.56
SD	2.76	4.26	3.68

The value of mean and SD is above table differs from each other mental health of joint family is good than nuclear family because mean of joint family is comparatively higher than mean of nuclear family. But we cannot perfectly conclude anything on the basis of the face values mean and SD only. So we have calculated two way ANOVA. Following table no. 2 shows summary of two way ANOVA.

Table no. 2:- Summary of two way ANOVA for mental health of Joint family and nuclear family.

Source of variance	SS	df	MSS	F
A(family type)	144.50	1	144.50	11.808*
B (sex)	151.38	1	151.38	12.37**
AB	2.88	1	2.88	0.235***
Within group error	2398.52	196	12.237	
Total	2697.28	199		

*Significant at 0.01 level

** Significant at 0.01 level

***Not significant at 0.01 level

The above summary of two way ANOVA shows that F ratio is 11.808 which is significant at 0.01 level for 1 and 196 df because table value of df at 0.01 level is 6.63 and at 0.05 level 3.84. F ratio is greater than both table value of df there for F-ratio is significant at 0.01 and 0.05 level.

On the basis of above discussion we observe that our hypothesis no.1 Joint family adolescence has significantly good mental health than nuclear family adolescence was proved.

In present research second hypothesis is Joint family, nuclear family (boys) have significantly good mental health than Joint family, nuclear family (girls). For testing this we are calculated mean and SD that values shows in table no.3

Table no. 3

	Boys	Girls
Mean	22.40	20.42
SD	2.46	2.71

On the basis of this value we can say that mental health of boys (joint and nuclear family) is good than girls (joint and nuclear family). But it is not sufficient because is there any difference in boys and girls mental health. So we have calculated F-ratio which is shows in table no.4

Table no. 4:

Source of variance	SS	df	MSS	F
Between group	242.51	2	121.25	9.731*
Within group	2454.77	197	12.46	
Total	2697.28	199		

*Significant at 0.01 level

The above summary of ANOVA shows that F-ratio 9.731 at df 2 and 197. Table value of df at 0.01 level is 4.61 and 0.05 level is 3.00. So f-ratio value is greater than this value. On the basis of this we conclude that mental health of boys good than girls. In this way our second hypothesis is proved.

According to positive psychology if family member's thoughts and attitude are negative then mental tiredness and illness is show in family opposite of that if positive thoughts of attitude are present in family, then create happiness and healthy life. According to this we can say that we are stay in joint family we are attaching with lots of members and attach with their positive thoughts. So benefits of this we are develop with positive thoughts and it is useful for our bright future. Also emotional attachment is an important for family mental health. Understanding positive emotions entails the study of contentment with the past, happiness in the present, and hope for the future understanding positive individual tracts for love and work courage compassion, creativity, curiosity integrity, self –knowledge, moderation , self control and wisdom. On the basis of this we can say that joint family is most important for healthy society.

Conclusion

On the basis of above discussion we are conclude that mental health of joint family is good than nuclear family because in joint family are building inner health and happiness, better Understanding of health and functioning of the mind

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Saurian Fauna Inventory of Ladakh Region, Jammu and Kashmir, India.

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Abstract:

The present study gives information about the saurian of Ladakh region of Indian state Jammu and Kashmir. The present study of Saurian fauna has been accumulated primarily from technical report available in scientific journals; personal field observation and personal communiqué with native people and field worker have been taken into interpretation as well. The reviews state the presence of twelve species of lizards belonging to four families. Furthermore in future, there are probabilities of more and more species to be reported of because few habitations in the Ladakh region required to wide-ranging exploration.

Key points: Saurian fauna, India, Jammu and Kashmir, Ladakh.

Introduction

Saurian (Lacertilia = Lizard) is a group of true terrestrial animal belong to the order Squamata in the class Reptilia. They are originated in the Jurassic era of geological time scale and are still in a step of differentiation. They are found almost all part of the world except the polar region. But they are lessening at unparalleled rates due to threat of global climate change, human exploitation, habitat loss, invasive species, pollution and disease (Gibbon et al., 2000).Socioeconomic factor such as rapid population growth, poor education and other cultural aspect that lead to the exploitation of natural resource (Durbin et al.,2003).Continued forest clearance will leads to the eventual fragmentation of the remaining area of forest, which consequence on herpetofauna followed by local and possible complete extinction (Vallen, 2000). The variations in temperature and climatic factors at different season also bring influence on their metabolic activity. Variation in life history attribute such as survival rate, population density are individual growth rate may result from temporal fluctuation in environment variable, such as temperature and ground moisture resulting from the seasonality in rainfall and food availability (Fleming and Hooker, 1975). The diversity and abundance of saurian of an area are now primarily influenced by anthropogenic activities and seasonal variation (Abid and Tantarpale, 2017).

In India, Systematics research was started unwillingly by Sir William Jones (1746-1794). Since then many researcher has been tried to explore the saurian of India. Presently, Lizard is one of the most diversified groups of vertebrates that have over lived on earth over the past 250 million years. Over 5,000 species of lizard have lived on earth, inhabiting a variety of habitats ranging from the highest mountainous peak to the low- lying terrestrial and aquatic habitat (Lalrinchhana et al. 2015).

Methods And Materials

Ladakh is a home to highly adaptable flora and fauna. It represents the westernmost extension of the vast Tibetan Plateau, covering an altitude range from 2700 to 7650 m. Two major mountain chains, the mighty Himalayas and the Karakoram, demarcate its natural borders towards the south and the north respectively, with the Zanskar and Ladakh ranges running through it cut by the flow of the Indus. It constitutes over 80% of the Trans-Himalayan tract in

India and is home to a unique assemblage of flora and fauna. The region is also known as a cold-desert and is characterized by severe, arid conditions. Temperature may drop to – 40oC in the long winter months between December and April and may rise to 35 degree C in the short summer season from July–August. This harsh environment is thus home to only highly adaptable flora and fauna.

Survey method:

1. The present inventory saurian fauna of Ladakh region has been compiled primarily from articles, and technical reports published in scientific journals.
2. However, the personal observation is based on "Visual encounter survey" (Doan 2003), opportunistic finding and indirect sampling such as acquiring information from native people.
3. Specimens were photographed using a canon digital camera.
4. After photography, specimens were identified by using diagnostic keys by smith (1935, 1943). Nomenclature adopted by Das (2000) and Daniel (2002).

Results And Discussion :

The present study is constructed on a review of the earlier checklist published in scientific journal over a past decade and personal field observation. It has been observed

S. No	Family	Species	Common Name
1	AGAMIDAE	Laudakiya himalayana	West-Himalayan Agama
		Laudakiya tuberculata	Tuberculated Agama
		Phyrocephalus theobaldi	Theobalds Toad Agama
		Agama agrorensis	Agor Agama
		Calotes versicolor	Indian Garden Lizard
2	GEKKONIDA	Hemidactylus flaviviridis	Yello-Bellied House Gecko
		Hemidactylus brooki	Spotted House Gecko
		Cyrtodactylus stoliczkai	Kashmir Rock Gecko
3	SCINCIDAE	Scincella himalayana	Himalayan Ground Skink
		Scincella ladacense	Olive Ground Skink
		Eumeces taeniolatus	Yellow-Bellied Mole Skink
4	VARANIDAE	Varanus bengalensis	Common Indian Monitor

presence of twelve species of saurian in Ladakh region. The species list is given in the table.1.

Table.1. Checklist of Saurian fauna in Ladakh region.

From the

Our study Saurian fauna inventory established twelve saurian species within Ladakh. But two species Eumeces taeniolatus and Varanus bengalensis have been mentioned as being present in the area (Sharma et al., 1992). These records are highly questionable from a zoogeographical point of view because during our field we do not observed any of these two species.

Some saurian species like L. himalayana, L. tuberculata, S. ladacense were found abundantly all over the Ladakh region except high altitude, glaciers, vicinity to glacier and water bodies. They are mostly seen in sunny places and appear during morning time.

On the bases of the study it is concluded that there should be developed new strategies to abstain these creatures from the natural calamities such as land slide, floods, avalanche and poaching and myth. Because large number of saurian species and their niches in sloppy areas of Ladakh are always witnessed lying in the range of such natural calamities.

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Checklist of Ophidian Fauna in Amravati City, Maharashtra, India

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Introduction:

Snakes are ectothermic (cold blooded) animals distributed throughout the world, except the very cold regions (Antarctica). Currently there are 3,600 species of snakes in the World belonging to 24 families and 528 genera (Integrated Taxonomic Information System, 2018, Uetz and Hosek, 2018), out of which nearly 278 species of snakes are found in India (Whitaker and Captain 2008). The snakes found in India show great biodiversity and their length varies species to species, for example common worm snake measures 15 cm whereas huge python ranges from 6 mtr to 11 m, while weight also varies and measures between few grams to several kilograms (Khaire, 2010).

Snakes play very vital and important roles in our ecosystem. They are considered as a healthy and effective predator. Snakes are considered as farmers friend and natural pest controllers, they controls rodent populations in particular. Snakes also represent important prey species for other predators. Current development going on threatens the survival of snakes in many ecosystems (Shine and Bonnet, 2000; Bonnet et al., 2002). Zade and Shinde (2017) analyzed the data on the snakes rescued from Amravati region and presented a checklist of rescued snakes. The present study contains a checklist of snakes from Amravati city (M.S.) and its surrounding.

Materials And Methods

The present study contains a checklist of snakes based on opportunistic observations and also snake rescued by snake friends from different localities in Amravati city from Feb 2016 to Jan 2017. Road kills were also examined while driving along roads on various occasions. The Encountered individuals were photographed and identified with the help of keys and methods suggested by Daniel (2002), Whitaker and Captain (2004) and Khaire (2010). The photographs and details of doubtful species were sent to one or more ophiologist for confirmative identification.

Results And Discussion

During the study period, total sixteen species of snakes belonged to six families were identified. From these observed six families, Colubridae family was abundantly observed, while Elapidae was common family of venomous snakes (Table 1).

Sr. No.	Family/ Species	Common Name*	Local Name	Type	WPA
	Family Typhloidae				
1.	Ramphotyphlops braminus	Common worm snake	Waala	NV	IV
	Family Pythonidae				
2.	Python molurus molurus	Indian rock python	Ajgar	NV	I
	Family Boidae				

3.	Gongylophis conicus	Common sand boa	Durkya ghonas	NV	IV
	Family Colubridae				
4.	Ahaetulla nasuta	Common vine snake	Harantol	NV	IV
5.	Amphiesma stolatum	Striped Keelback	Naneti	NV	IV
6.	Argyrogena fasciolata	Banded racer	Dhool Nagin	NV	IV
7.	Coelognathus h. helena	Common trinket snake	Taskar	NV	IV
8.	Lycodon aulicus	Common wolf snake	Kavadya	NV	IV
9.	Macropisthodon plumbicolour	Green Keelback	Gavatya	NV	IV
10.	Oligodon arnesis	Common kukri snake	Kukri saap	NV	IV
11.	Ptyas mucosa	Indian rat snake	Dhaman	NV	II
12.	Xenochrophis piscator	Checkered Keelback	Pan-divad	NV	IV
	Family Elapidae				
13.	Bungarus caeruleus	Common krait	Manyar	V	IV
14.	Calliophis melanurus	Slender coral snake	Powala	V	IV
15.	Naja naja	India spectacled cobra	Naag	V	II
	Family Viperidae				
16.	Daboia russelii	Russell's viper	Ghonas	V	II
	Total species observed	**16**			

Abbreviations: V=Venomous , NV= Non-Venomous, SV-Semi-Venomous,
***According to Captain and Whitaker (2008)**

Table-1. Checklist of ophidian fauna in Amravati City, Maharashtra, India.

Family Typhloidae and Viperidae were observed frequently while family Pythonidae was rarely observed. Among the 16 observed species of snakes, four species were venomous and twelve species were non venomous.

The present study revealed the existence of sixteen species belonging to six families. The maximum number of species were belonged to family Colubridae (09) followed by Elapidae (03), and the remaining family consisting of one species each that is, Typhloidae (01), Viperidae (01) Boidae (01) and Pythonidae (01). Rat snake, checkered keel back, common wolf snake and Indian spectacled cobra were most observed snake and also among the most rescued snakes. During the study period a road kill Indian Rat snake and Checkered Keel Back were also reported.

Recently such types of compositions were reported by Wadatkar (2003) from Amravati University Campus; Nande and Deshmukh (2007) from Melghat region Amravati. Zade and Shinde (2017) documented the snakes rescued from Amravati region, Maharashtra and recorded a total of 1429 snakes comprised of 26 species belonged to 06 families. Out of which 18 species were non-venomous snakes, 3 species were semi-venomous and 5 were venomous species, which was quite similar to our results.

Reptiles, especially snakes are in crisis due to people's poor knowledge of these creatures, influenced by superstitious beliefs. To protect these animals, education of the general public regarding their biology, ecological value and eradication of associated myths must take front stage (Tsetan and Ramanibai, 2011).

Every year large numbers of snakes of various species are translocated from urban habitat to new 'suitable habitats' on the name of 'snake rescues,' being one of the notable translocations of wild animals. Presently, impacts and consequences of such large snake translocations are unknown, giving rise to further debatable questions. A detailed study and monitoring is needed, to find out the impact on the 'recipient' areas. After the release, the fate of these animals is not well known in Indian environment, but few studies abroad indicate that the translocation of reptiles is encouraging their survival and is proven scientifically (Reinert and Rupert, 1999; Vyas, 2013).

In this study, these activities will imply the conservation of ophidian biodiversity in Amravati district (M.S.), as well as neighborhood; because disappearance of snakes will have tremendous social and ecological implications.

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Water Analysis of Wadali Lake in Amravati, Maharashtra

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Abstract

Water is the main constituent of Earth's streams, lakes, oceans and fluid of most living organisms. Water quality is important because it directly affects health of not only human being as well as animals. Water quality monitoring is directly and indirectly related with chemistry, biology, statistics and also economics. This paper describes physico-chemical properties of Wadali Lake in Amravati city. Lakes are beautiful which invokes a natural attraction but there is need to develop these places from water quality point of view. The objective of the study was to monitor the water quality by analyzing the physico-chemical properties of the water of Wadali Lake.

Key Words: Water quality, Wadali Lake, Physico-chemical properties, Amravati.

Introduction

Water is also known as "Blue Diamond". It is one of the most precious gifts to all living creature given by the nature. Man uses water for different purposes like drinking, washing, in agriculture, food processing and in some other applications. People say Earth is "Blue Planet" because when a man in the space looks blue color because of the largest part of the earth is occupied by water. Water covers more than 70% of the earth surface, 97.3% is in ocean and 20% is fresh water there exists a continuous exchange and circulations and water between the earth and atmosphere. The great philosopher, Aristotle has defined together with air fire and earth as constituents of the universe.

The rapid pace of growth of population in India is primarily responsible for the significant increase in the level of pollution of rivers. With the increasing rate of growth of population, the human activities around the bank of rivers also increased, which results in contamination of water. Prabhahar et al., (2012) reported that pollution of water has emerged as one of the most significant environmental problem like one of the seasonal environmental fluctuation in the abiotic factors such as temperature, pH, and alkalinity. Aquatic ecosystems are much too complex and integrated to be simply regulated by a single nutrient productivity and behavior are certainly regulated by many organic compounds in addition to traditional macro factor controls reported by Shinde et al., (2010).

Water resources in India have reached a point of crisis due to unplanned urbanization and industrialization (Pathak and Diwedi, 2007). Urbanization has directly negative impacts on water bodies. Now a day freshwater has become a scare commodity due to over exploitation and contamination (Trivedi and Goel, 1986). Increasing population and its necessities have lead to the deterioration of surface water (Bhadja and Vaghela, 2013).

The important physical and chemical parameters influencing the aquatic environment are temperature, rainfall, pH, salinity, dissolved oxygen and these parameters are the limiting factors for the survival of aquatic organisms observed by Mahesh et al., (2013),

Agarwal and Rajwar (2010) noted physico-chemical and microbial parameters like total solids, total suspended solids, turbidity, total dissolved solids, alkalinity, hardness, pH, dissolved

oxygen, chemical oxygen demand, nitrogen, chloride, nitrate, phosphate, sulphate, calcium, biological oxygen demand of Wadali Lake.

Tinade and Shinde (2012) focused on the seasonal variations in the physico-chemical parameters of the temple pond Prayagtirth at Trimbakeshwar in Nashik of Maharashtra.

The objective of the present study was to document the physico-chemical characteristics of rivers and streams feeding Wadali Reservoir water and suggest appropriate conservation and management strategies. The work is provided future strategies for betterment of nearby villages tribal's because many of the villages are surrounded to the said Reservoir are exclusively from tribal category. Therefore, for the protection of aquatic life bioassay is primary oriented towards developing water quality and then used to develop water quality standards. In future there is a need to preserve and maintain water quality standards. There are some points are considering under the head need of investigation.

material and methods

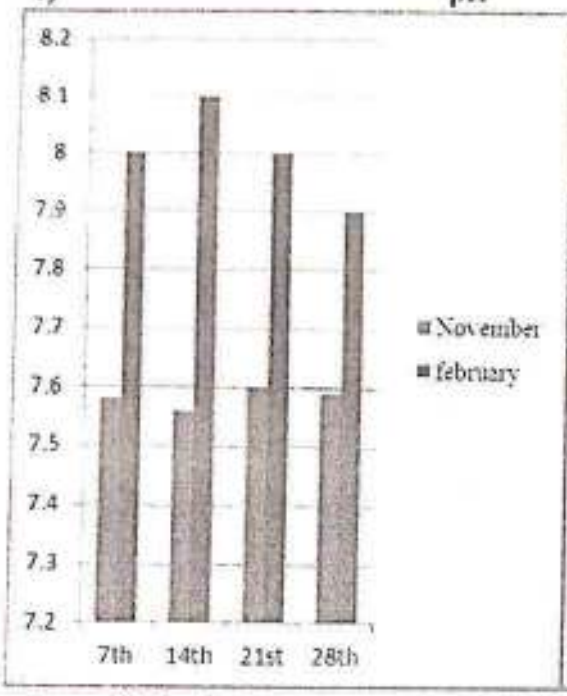
The study was conducted on Wadali Lake situated 4 Km away from Amravati, which lies between 20° 43' 34'' N latitude and 76° 10' 49'' E longitude. The samples were collected during the month of November 2017 and February 2018. Water samples were collected from different station by using glass and polythene bottles. Physiochemical parameters viz. temperature, pH, total hardness, conductivity, total dissolved solid, salinity, alkalinity, dissolved CO2 mg/lit, calcium mg/lit, phosphorous mg/litand nitrate mg/lit, were analyzed following the method of Arora and Pathak,1989; APHA 1992; Raghothaman and Trivedi, (2002).

Result And Disscussion

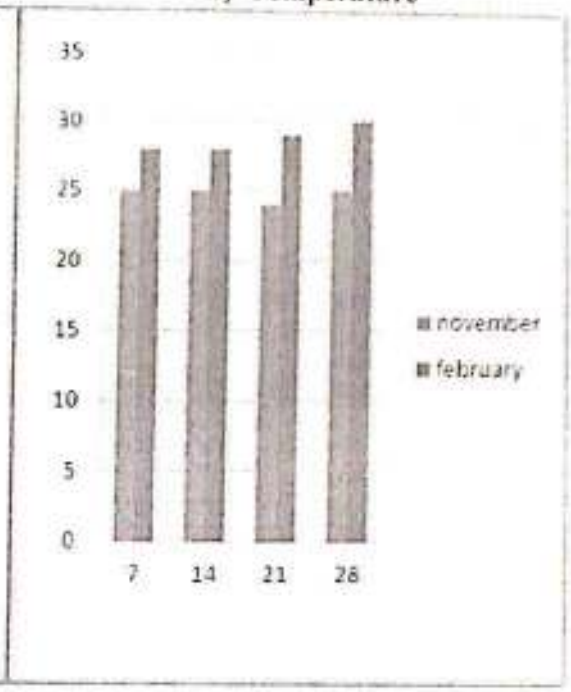
Parameters	Nov 2017	Feb 2018	Nov 2017	Feb 2018	Nov 2017	Feb 2018	Nov 2017	Feb 2018
	7 Days	7 Days	14 Days	14 Days	21 Days	21 Days	28 Days	28 Days
pH	7.58	8.0	7.56	8.1	7.60	8.0	7.59	7.9
Temperature	25°C	28°C	25° C	28°C	24°C	29°C	25°C	30°C
Total hardness	218	219	217	219	218	220	219	219
Conductivity	376	450	376	451	378	449	374	450
Salinity	0.29	0.32	0.27	0.33	0.28	0.31	0.29	0.32
Alkalinity	356	358	354	357	357	359	356	358
Dissolved CO_2	26.4	30.5	26.3	30.4	26.6	30.5	26.5	30.5
Nitrates	3.53	4.17	3.52	4.16	3.55	4.17	3.54	4.18
Phosphorous	0.071	0.061	0.072	0.062	0.069	0.061	0.071	0.063
Calcium	15	17	15	17	17	17	14	18
Note: - All parameters are expressed in mg/ml (except pH & Conductivity)								

Table 1:- Physicochemical parameters and analysis of Wadali Lake (Amravati) during the Month November 2017 and February 2018.

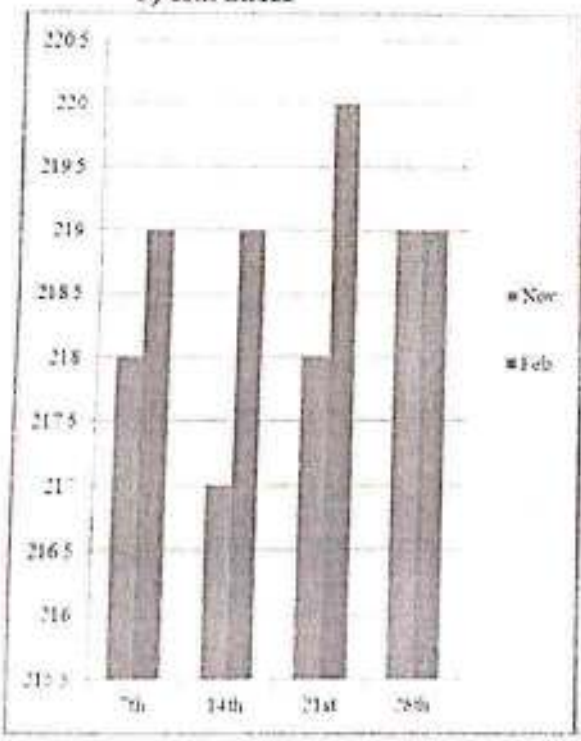
1) pH



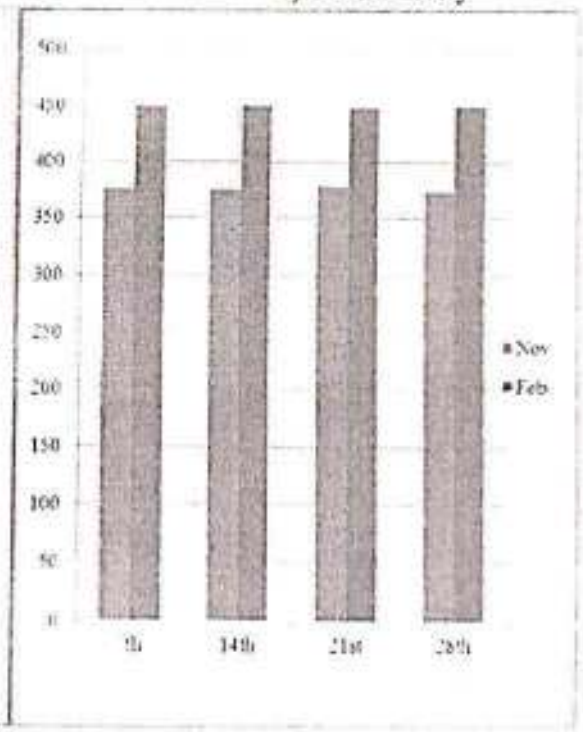
2) Temperature



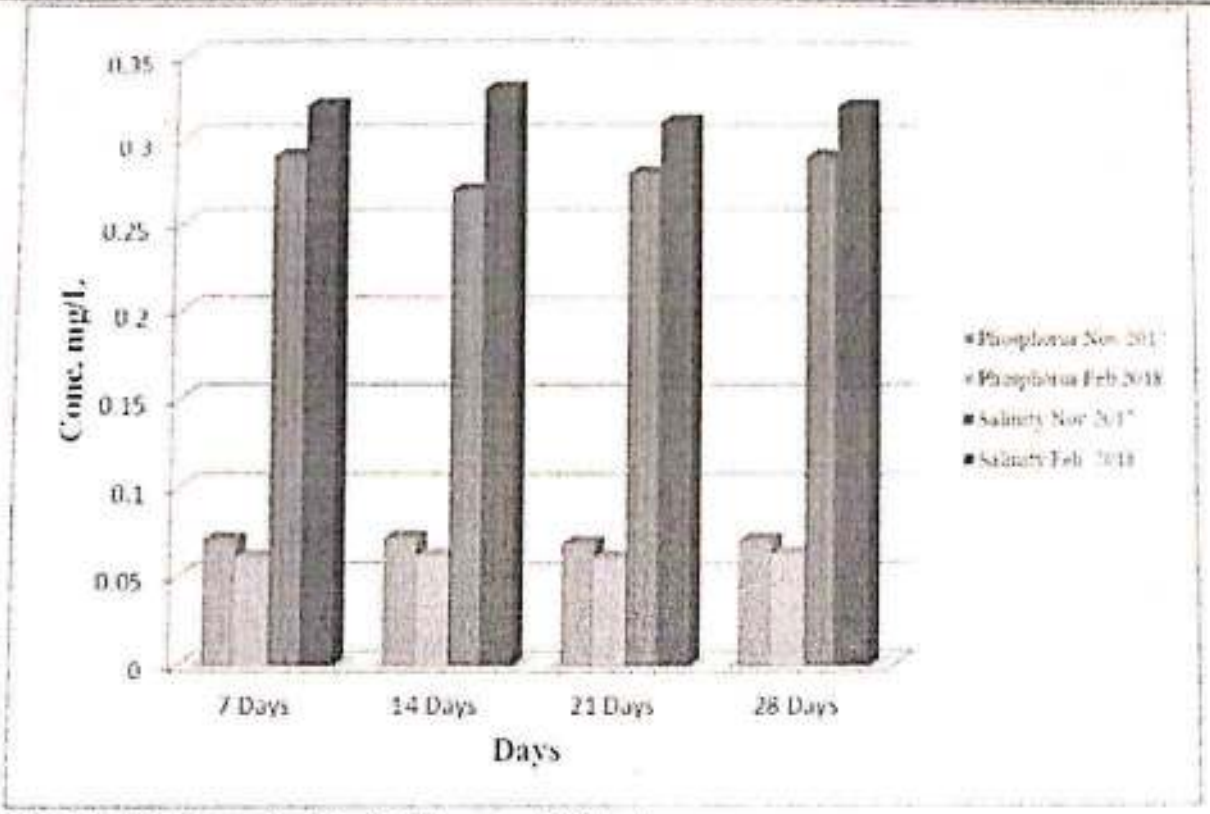
3) Hardness



4) conductivity



5) Phosphorus and salinity



6) Dissolved Carbon dioxide, Calcium and Nitrate

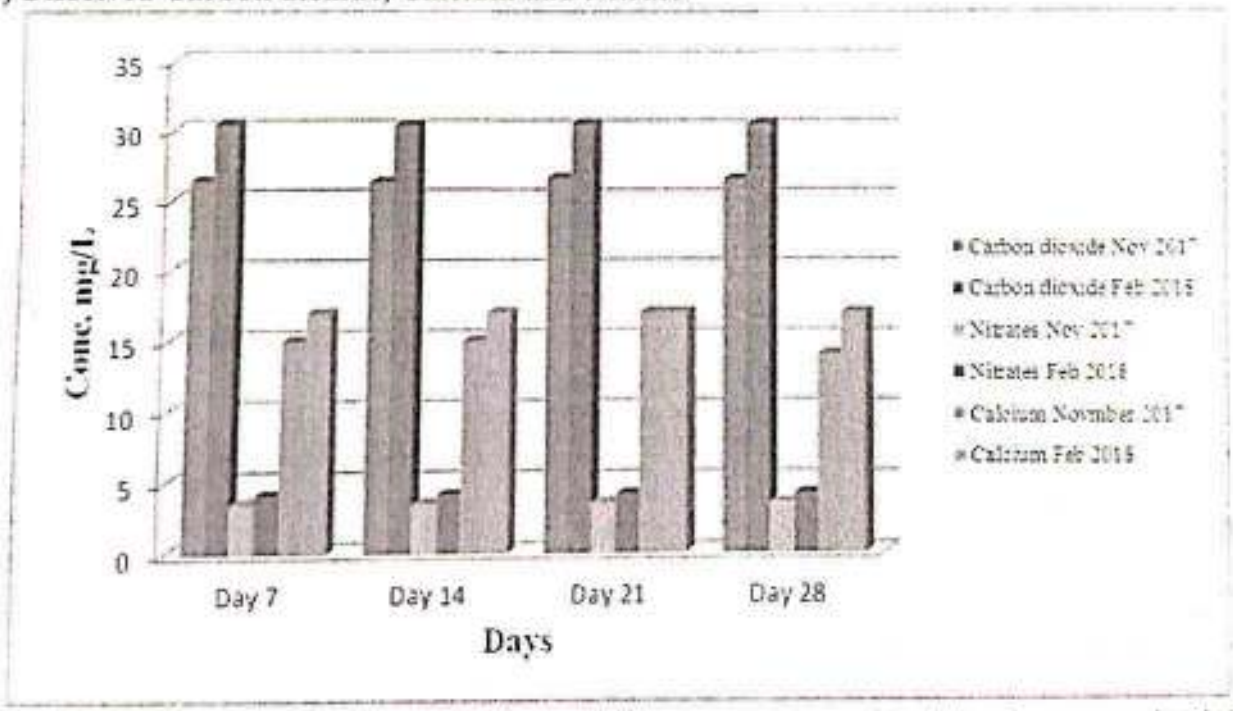


Diagram 1-6:- Graphical representation of Ph, temperature, total hardness, conductivity, salinity, alkalinity, calcium, phosphorous and nitrate.

The result showed a direct relationship between atmospheric temperature and water temperature, pH, total alkalinity, total hardness, calcium and inversed relation between temperature and dissolved oxygen. There is not a single factor but at a time so many factors have direct and indirect influences in the ecological system. It varies at different times of the day and during November 2017 and February 2018.

The total alkalinity of water from the water body was due to bicarbonates. Total alkalinity of the lake was varied from 356 to 358 mg/lit and maximum value was recorded in February and the minimum in November. Katariya et al., (1996) have measured maximum value of alkalinity due to confluence of industrial and domestic waste. Our results are in close agreement with the findings of above authors. Sakare and Joshi (2003) found the alkalinity values from 672 to 1023 mg/lit in Papnas in minor wetland in Tuljapur town, in Maharashtra. The presence of total alkalinity indicated that the Wadali Lake is productive.

The values of calcium were maximum during February 2018 and minimum during November 2018 of Wadali Lake. In November the water temperature were low as compared to February but water becomes clear and calm due to sunlight penetrated in water due to the luxuriant growth of aquatic animals were recorded. Total hardness in water is the sum of concentration of alkaline earth metal cation such as Ca^{**}, Mg^{**}. Total Hardness values were moderate in November month and lower in February month of Wadali Lake. Korai et al., (2008) reported similar observations. Interaction of physiochemical factors influences the diversity of water molds (Paliwal and Sati, 2009).

The study of various physico-chemical parameters such as hydrogen ion concentration (pH), electrical Conductivity, total alkalinity, salinity, dissolved carbon dioxide, total hardness, total phosphorous, total calcium and total nitrate was carried out by using various standard methods reported in the literature. From the study it was clear that the water of Wadali Lake is suitable not suitable for drinking purpose but is suitable for growth of microorganism and fishes.

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Effect of Allium Sativum on RNA,DNA And RNA: DNA Ratio of Freshwater Fish Ophiocephalus Striatus (Bloch, 1793)

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Introduction:

Now a day's ayurvedic medicines have respective position in the developing world and these are mainly based on plants. Safe effective and inexpensive indigenous remedies are gaining popularity among the people of both urban and rural areas especially in India. Information from the ethnic groups or traditional medicines has play vital role in the discovery of the novel products from plants as chemotherapeutic agents **Meena et.al., (2009)**. The use of medicinal plants prevents the illness in aquatic fauna, Over 80,000 species of plants are in use throughout the world. A large number of plants have been used in traditional medicine for the treatment and control of several diseases **Chakraborty et.al., (2011)**. The nutritive value of feed will impact on the growth and development of the organism. Plant products in feed have been reported to promote various activities like anti-stress, growth enhancement, appetite stimulation and immune stimulation in aquaculture practices **Citarasu et.al., (2010); Sivaram et.al., (2004).**

Food quality is complex property for the fishes because of the precise nature of the metabolic changes. It affects the protein quantity, RNA DNA ratio, carbohydrate, lipid and mineral quantity. The RNA:DNA ratio influences the protein quantity of the body of the fish because protein synthesis is complex process in which the basic necessity is DNA and RNA. Thus RNA and DNA ratio provides an index of protein synthesis. In the condition of adequate food availability protein synthesis of fish will be increased by increasing the concentration of RNA ultimately changing the RNA:DNA ratio Bulow (1987) . Nucleic acids play a major role in growth and development. The amount of DNA, the carrier of genetic information, is quasi-constant in somatic tissue and tissue concentration therefore reflects cell numbers. Regnault and Luquet (1974), Dorch et.al., (1983). The amount of RNA in the cell is directly proportional to the amount of protein synthesis occurring. The relationship between RNA and DNA is an index of the cell's metabolic intensity and has been used to measure recent growth in fishes Bulow (1987).

Material and Methods:

The present study were carried out on the freshwater fish Ophiocephalus straitus, the live fishes were collected from the Pedhi river 10 km away from the Amravati city measuring from 13-16 cm in length and 20-24 gm in weight. Fishes were brought to laboratory conditions in glass aquarium and disinfected with the help of 1.0mg/L Kmno4 to remove dermal infection and acclimatized for the time period for 15-15 days.

After acclimatization of 10-15 days fishes has become divided into two groups:

Group I – Control fishes

Group II – Experimental treated fishes

Group I fishes was kept in the Allium sativum free water and served as control and Group II freshwater fishes Ophiocephalus striatus were treated with the prepared dose of Allium

sativum 3.5 mg / kg of fishes. After the interval of 7,14,21 and 28 days from each group fish dissected out and the tissue of liver and muscle of both controlled and treated fishes proceed for the estimation of DNA by Burton (1956) Diphenylamine method (DPA) and RNA by Ashwell (1957) Orcinol method.

Observation and Result:

In the present study it was observed that freshwater fishes Ophiocephalus straitus exposed to 3.5gm/ kg of Allium sativum show gradual increase of RNA in muscle tissue **(Fig. No 1)** 440.62±0.26, 490.36±0.57, 522.90±0.44, 525±0.59 as compared with control group 249.47±0.43, 255.60±1.24, 261.15±0.94, 265.95±0.48. Also increasing trend of RNA were observed in liver of experimental group **(Fig.No.2)** 363.54±1.112, 420.44±0.48, 441.04±0.79, 452.52±0.51 as compared with control group of fishes 242..42±0.25, 252.16±0.33, 258.25±0.39, 265.98±0.22.

Similarly DNA in the muscle tissue of freshwater fish Ophiocephalus striatus exposed to Allium sativum showed increasing trend in experimental group **(Fig.No.3)** 473.28±0.95, 560.93±1.96, 587.31±0.69 and 615.31±0.74 as compared with control 256.92±0.87, 260.45±0.45, 269.164±0.44 and 275.98±1.31. Also increasing trend of DNA were observed in liver of experimental group **(Fig.No.4)** 492.47±0.23, 498.92±0.40, 521.92±0.18, and 532.112±0.43 as compared to control 253.20±0.49, 265.12±0.45 ,273.26±0.43 and 281.45±0.64.

Fig . No. 1 RNA of muscle of freshwater fish *Ophiocephalus striatus* exposed to *Allium sativum*

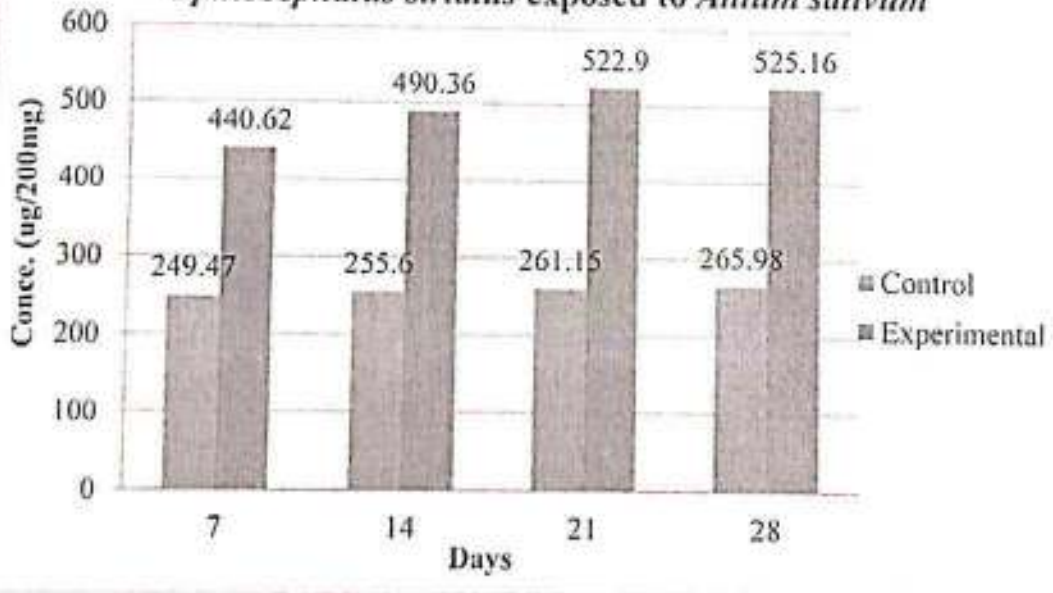

Fig No. 2 RNA of liver of freshwater fish *Ophiocephalus striatus* exposed to *Allium sativum*

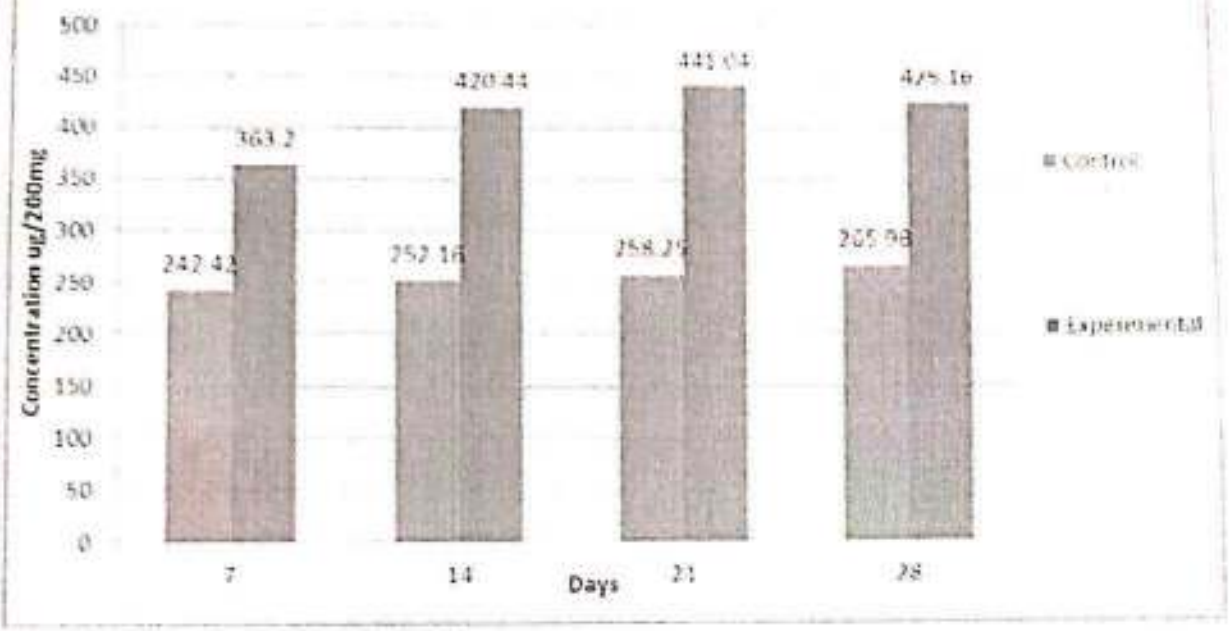

Fig No.3 DNA of muscle of freshwater fish *Ophiocephalus striatus* exposed to *Allium sativum*

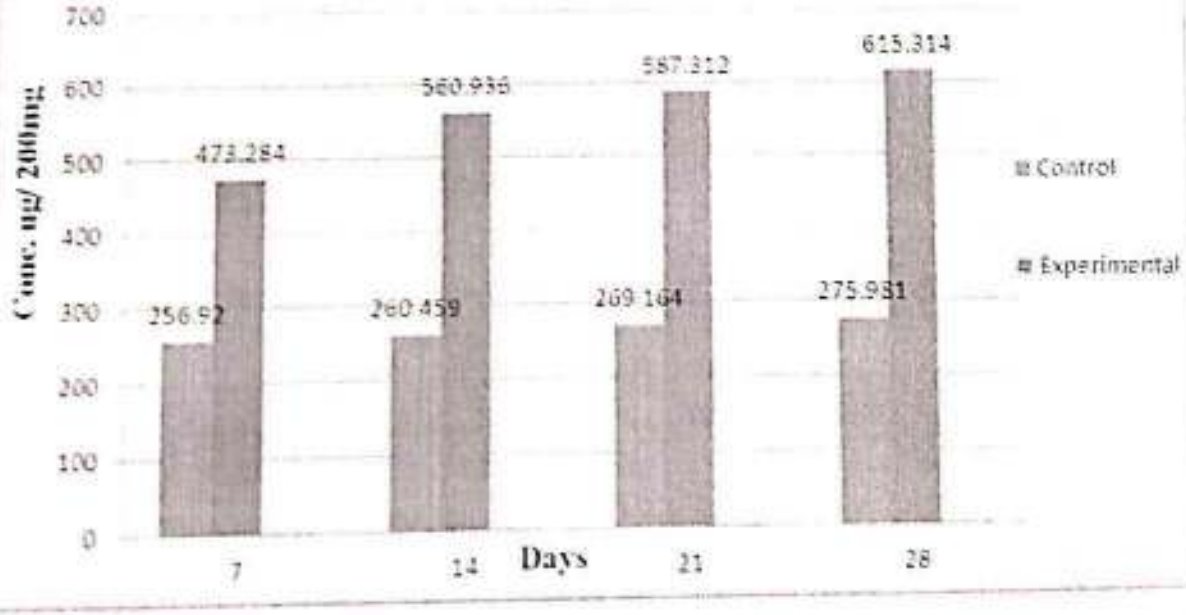

Fig No. 4 DNA of Liver of freshwater fish Ophiocephalus striatus exposed to Allium sativum

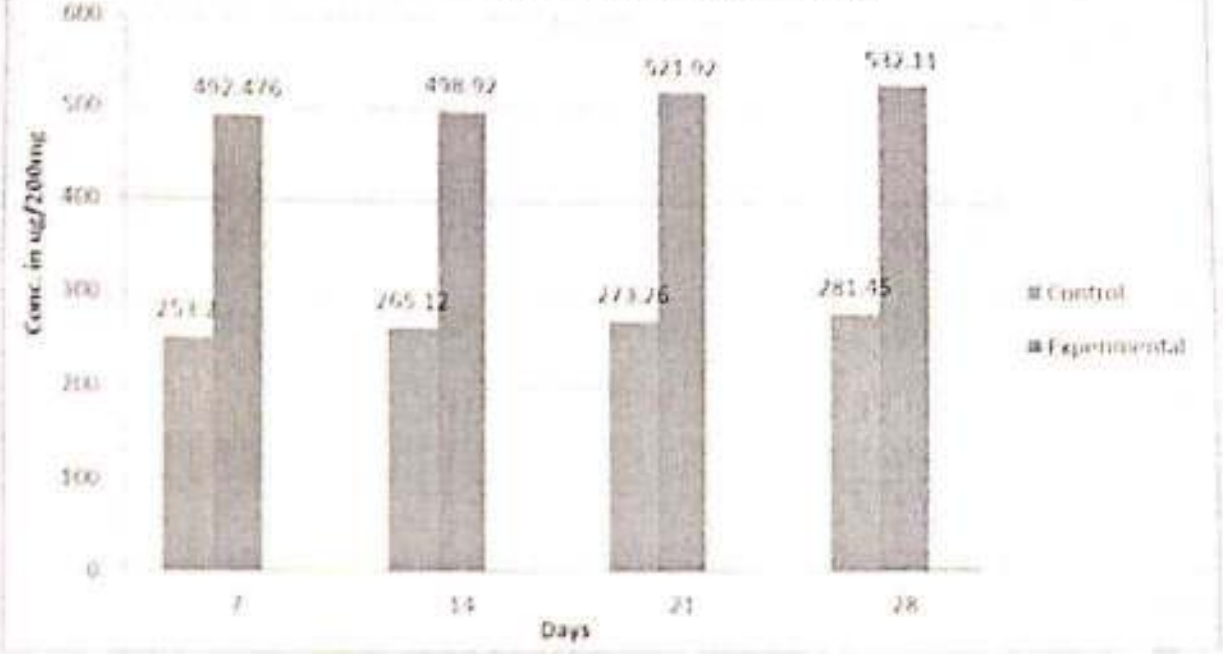

Table No. 1) RNA:DNA Ratio Muscle and Liver tissue of freshwater fish Ophiocephalus striatus exposed to Allium sativum

Sr. No	Days	RNA: DNA Ratio			
		Muscle		Liver	
		Control	Experimental	Control	Experimental
1	7	1.02	1.07	0.95	0.73
2	14	1.01	1.14	0.95	0.84
3	21	1.03	1.12	0.99	0.84
4	28	1.3	1.17	0.93	0.79

Discussion:

In the present investigation the effect of Allium sativum on RNA, DNA of freshwater fish Ophiocephalus striatus showed increased concentration of RNA and DNA in both muscle and liver tissue. Increase in the concentration of RNA and DNA indicates the growth and nutritional status of the fishes. There are several studies in which tissue RNA concentration and RNA/DNA ratios have been used as indicators of recent growth and nutritional status of the fish.

Mitra and Mukhopadhyay (2002)

Similar finding by **Clemmesen (1987)** observed the RNA/ DNA ratio indicates metabolic intensity which is deeply influenced by the nutritional status of the diet. The quality of food has profound effects on cellular growth response in different fishes. So the present studies definitely establish a nutritive effect of Allium sativum on fish growth and RNA/DNA level.

Conclusion:

The study indicates the effect of Allium sativum increased the RNA, DNA concentration in muscle and liver of freshwater fish Ophiocephalus striatus, this indicates significant effects of these medicinal plants for increasing growth and the nutritional status of the fish, therefore

supplementation of Allium sativum in the feeding management of aquaculture is beneficial in aquaculture industry and for small scale fish farmers to increase the nutritional status of the fishes.

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Nutritional Values of Fresh Water Prawns of Amravati Fish Market

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2.

Introduction

In India, millions of people are suffering from malnutrition. Protein deficieney may be minimized to some extent by making available cheaper fish meal items which are available to local communities. Edible Crustaceans, such as Crab, Prawn, Cray fish and Lobster constitute one of the major sources of nutritious food for human beings. The nutritive values of crustaceans depend upon their biochemical composition, such as Protein, Amino acids, Lipids, Fatty acids, Carbohydrates, Vitamins and Minerals. Among the Seafood, Prawns and Shrimps contribute about 20-22% by volume of the world Seafood market (FAO, 2014).

Penaeid shrimps constitute a major capture fisheries component in the Aquaculture practices. Among the Penaeid prawns, Penaeus monodon, P. indicus, P. semisulcatus, Litopenaeus vannamei, Metapenaeus monoceros, M. dobsoni are considered to be important major commercial prawn's species available in India. Among the above prawn species, several are considered to be most prominent promising candidate species for culture activity in India. Prawns and shrimps are highly perishable because of their high moisture content, low connective tissue and their high amino acid content (Shamasunder and Prakash, 1994).

Shellfish contains potent source of nutrients required for the maintenance and growth of human body (Dong, 2001). Due to low price and efficient availability, the prawns and shrimps have good source of animal protein for low income earners (Adeyeye, 1996). Prawn contains good amount of organic and inorganic constituents. The main constituents are proteins, carbohydrates; lipids in addition to that prawn also contain a significant proportion of minerals (Ca, Mg, P, Mn and Cl) and vitamins A, C and D (Abulude et al., 2006).

Reddy et al. (2013), find out the proximate composition of fresh water prawn, Macrobrachium rosenbergii from Andhra Pradesh coast, India. Studies on biochemical composition of haemolymph and muscle of Penaeid prawns, Metapenaeus monoceros (fabricius), Penaeus monodon fabricius; and p. Indicus was also done. Moreno-Reyes et al., (2015) studied that chemical composition like moisture, protein, and lipids of whole animals and main storage tissues such as gonad, hepatopancrease and muscle of C. caementari.

Till date the primary focus of prawn nutrition research has been evaluate diet quality in terms of growth parameters of the cultured prawn species, but knowledge of the biochemical composition of edible organisms, which is extremely important since the nutritive value is reflected in biochemical contents, was not attempted for prawns of Amravati district. Therefore, the present study is aimed to probe into the aspects for the evaluation of proximate composition of basic biochemical constituents including proteins, lipids, and carbohydrates, assess the nutritional significance of Penaeid prawns.

Materials And Methods

Amravati district in the Nagpur Division is situated right in the centre of the northern border of the Maharashtra State. It lies between- 20^0 32' and 21^0 46' north latitude and 76^0 37' and 78^0 27' east longitude.

The prawns for the experiment were collected from Friday fish market Amravati. The average length of the prawn was 68.6 cm and average weight was found to be 350 gm. Since, the prawns were collected in a dead frozen state & directly used for the experiment. No acclimatization process was required. Descriptions of collected specimens are given below:-
Protein was estimated by Lowry's Method (Lowery 1951), total Lipid. Was estimated by Phosphovaniline method and Carbohydrate was estimated by Phenol Sulphate Method.

Results And Discussion:

The biochemical composition of muscle of adult prawn Macrobrachium rosenbergi, Litopenaeus vannamei and Fry (Collected randomly) is presented in the table below.)

Species	Length (cm)	Weight (cm)	Protein (%)	Lipid (%)	Carbohydrate (%)
Macrobrachium rosenbergii	68.6	35.0	54.65 ±0.2400	4.6 ±0.3637	2.45 ±0.4003
Litopenaeus vannamei(Penaeus monodon)	15.2	22.34	46.12 ±0.4691	6.27 ±0.2463	4.3 ±0.2470
Fry(Collected randomly)	4.8	1.75	73.24 ±0.3538	5.53 ±0.43	1.91 ±0.03

Tab 4.1: Biochemical composition in the muscle tissues of Macrobrachium rosenbergii, Litopenaeus vannamei, Fry (Collected randomly).

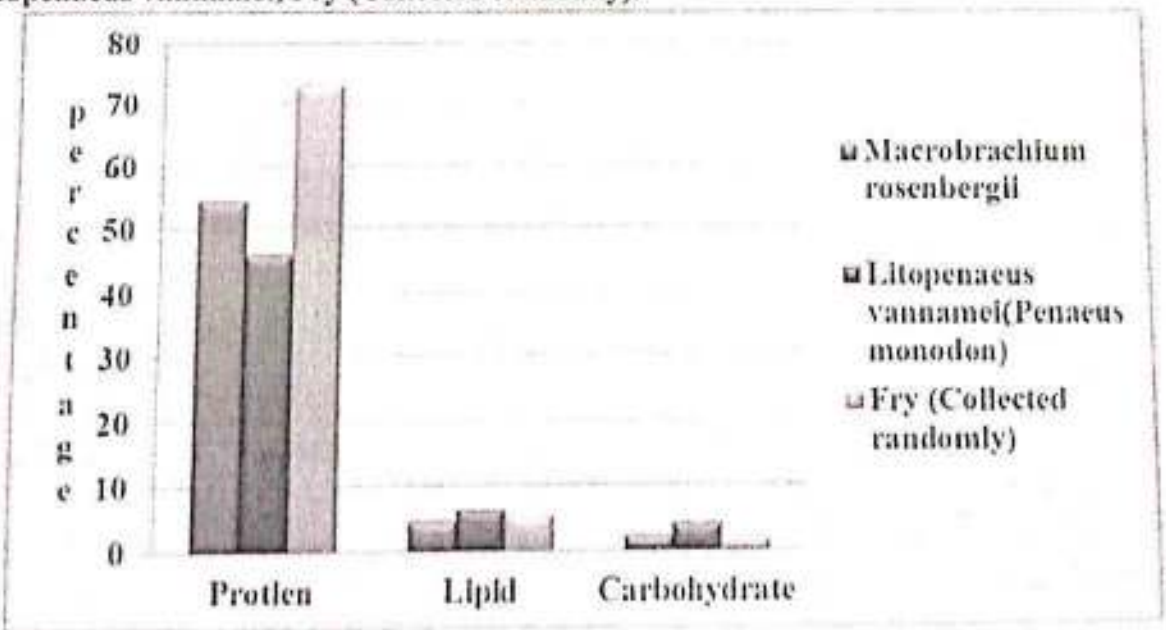

Fig 1: Chemical composition in the muscle tissues of Macrobrachium rosenbergii, Litopenaeus vannamei and Fry (Collected randomly).

The biochemical composition of organisms are known to vary with season, size of animal, stages of maturity and availability of food, temperature etc. Protein is the most prominent biochemical components of crustaceans from eggs to adults and is strikingly dominant in younger phases. The quantity of protein in shrimps is largely influenced by the extent of fat

and water content (Geiger and Bergstrom, 1962). In this study the average protein content in M. rosenbergii was found to be 54.65±0.2400%. Our results were quite similar to the findings of Nair and Prabhu (1990), in which the protein content of M. rosenbergii was found to be 56.26%. Shambhu and Jayaprakash (1994) reported variation in the protein level of M. rosenbergii from 48.62% in adults to 60.89% in younger size groups. Garg et al., (1977) reported that the protein content in Jawla prawn varied from 55.38% to 72.48%. Protein levels in the adults of M. rosenbergii were found to be higher than younger ones of M. rosenbergii.

Carbohydrates constitute a meager percentage of the total biochemical composition in M.rosenbergii muscle when compared to protein and lipid components. Carbohydrates exhibit an inverse relationship with protein content. In the present study the average carbohydrate content in M.rosenbergii was found to be 2.45±0.4003% and the highest carbohydrate content was found in M.rosenbergii with an average length of 68.6 cm having an average weight of 350 gm. Similar findings were also recorded by Nair and Prabhu (1990), Sambhu and Jayaprakash, (1994) and Ravichandran (2000). Kutty and Paruhekar (1984) and Kumar (1990) did not noticed any distinguished trend in carbohydrate fluctuation among the size group of many shrimps including M.rosenbergii. Various factors like gonad development in addition to exercise, starvation and other physiological states.

In general, lipids act as major food reserve along with protein and subjected to periodic fluctuations influenced by environmental variables like temperature (Johnstene, 1971). In the present study the average lipid content in M. rosenbergii was found to be 4.62±0.3637%. The inverse relationship between lipids and protein was earlier reported by George and patel (1956), Pillay and Nair (1973), Radhakrishnan (1979). Gopakumar and Nair (1975) didn't found any variation in the lipid content of muscle of five species of Penaeid shrimps including M.rosenbergii. Our results were also similar to the findings of Dinakaran et al., (2010) who reported the average lipid content in M.rosenbergii to be 4.72%.

Conclusion

From our study it was found that muscle of M. rosenbergii contains more protein that is 54.56% as compared to L .vannamei which have a percentage amount of 46.12%. But Fries, which were collected at randomly has larger protein content 73.54% than both M. rosenbergii and L .vannamei mainly due to the reasons mentioned below.

1. Freshly available in Friday fish Market Amravati, and
2. On a growing stage

The reason for the declined protein amount in adult prawns (M. rosenbergii and L .vannamei) may be considered as they were collected in preserved and frozen state.

So, from our findings we come to the conclusion that fries (shrimps) contains a high amount of protein as compared to the adults ones, as they are easily available in the market and are very fresh. From this study we suggest the common population that consumption of Fries (Shrimp) is recommendable and beneficial than the adult ones (M.rosenbergii and L .vannamei), as prawns are mainly consumed for their proteins and the Fries contains much more protein.

Further it is also recommended that as the adult prawns found in Amravati market are in preserved and frozen form, there may be chance of contamination, hence causing decomposition of the prawns, which will further affect the health of the common population consuming these animals.

Refereences

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Impact of Biopesticide – Azadirachta Indica on Testis of fresh Water Catfish Heteropneustes Fossilis"

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Abstract

The histopathological effects of Azadirachta indica as a biopesticides, on the testis of Heteropneustes fossilis were determined. Fishes were exposed to sub-lethal concentrations of Azadirachta indica for 24 hr., 48 hr., 72 hr. and 96 hrs. respectively. The testis were removed for histological examination. The results showed that in normal normal testis of Heteropneustes fossilis showed the seminiferous tubules were of round or oval shape and contained spermatogonia, spermatocyte, spermatid, spermatozoa, sertoli cells and interstitial cells of leydig but the exposure caused regression and delay in spermatogenesis also flattened seminiferous tubules with scattered spermatozoa, testis interstitial space dilated seminiferous tubules and prominent vacuolation was recorded.

Key Words: Azadirachta indica, Heteropneustes fossilis, sub-lethal concentrations, testis.

Introduction

Water pollution indicates the contamination in water bodies like lakes, rivers, oceans, aquifers and groundwater. Water pollution occurs when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful compounds. Water pollution affects plant and organism living in these bodies of water. In almost all causes the effect is damaging not only to individual species and populations but also the natural biological communities. The fresh water resources are being polluted by indiscriminate disposal of sewage, industrial wastes and a plethora of human activities (Mathew 1999, Arasta et al., 1999).Pesticides are major cause of concern for aquatic environment because of their toxicity, persistency and tendency to concentrate in organisms as they move up the food chain, increase their toxic effects to fauna. These pesticides pose a serious threat to the aquatic organisms bring a change in the cellular functions and affect the vital physiological and biochemical functions of the fishes (Ayotunde et al., 2005). A chemical pesticide is target specific and leaves deleterious impact on the environment (Tilak and Rao 2003).

To overcome the problems of synthetic chemical hazards, one of the best controls measured is the use of plant origin products i.e "Biopesticide". The popularity of the plant products are increasing day by day because of their biodegradability, least persistence and least toxic to non-target organisms with economic and easy availability (Ayuba and Ofojekwu, 2000).

One of the most promising natural compounds is Azadirachtin, an active compound extracted from the neem tree (Azadirachta indica), whose antiviral, antibacterial and antifungal properties have been known for several years (Isman et al., 1990; Harikrishnan et al., 2003; ICAR, 1993). It is generally considered less harmful to the environment than other more commonly used pesticides (Mordue [Luntz] and Blackwell, 1993). Therefore, neem-based insecticides are being investigated as alternatives to synthetic insecticides for the control of agricultural insect pests. However, adverse effects of azadirachtin against beneficial organisms have been reported (Schmutterer and Holst, 1987; Beckage et al., 1988; Hoelmer et al., 1991;

Price and Schuster, 1991). Neem has also been used successfully in aquaculture systems to control fish predators (Dunkel and Ricilards, 1998). Martinez (2002) stated that aqueous extract of neem leaves and other neem-based products have been extensively used in fish-farms as alternative for the control of fish parasites and fish fry predators such as dragon-fly larvae.

Materials And Methods

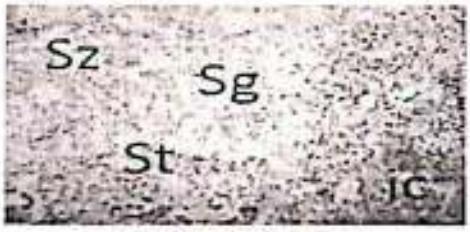
Histo-pathological Studies

Present investigation has been carried out to study the effect of sub-lethal concentration of Azadirachta indica on testis of the freshwater Indian cat fish Heteropneustes fossilis. Healthy and sexually mature specimen of Heteropneustes fossilis measuring about 15-20 cm length and 50-100 gm in weight were selected for the experimental study. These collected fishes were maintained in glass aquaria containing tap water and acclimatized in laboratory conditions at room temperature for one week. The water of the aquarium was changed daily and fishes are fed daily with commercial fish food. Fishes are starved for 24 hours prior to the experiment and are not fed during the period of experiment (Dalela et al., 1979).

In this experiment, the specimens were kept in two experimental groups. Control Group and Experimental Group. Each group was exposed to sublethal concentration of the Azadirachta indica similar set up was also maintained as control. The animals were scarifies for optimal concentration of biopesticides (Azadirachta indica) for different exposure of 24, 48, 72 and 96 Hrs. For histological studies, fishes were scarified during the exposure period of 24, 48, 72 and 96 Hrs respectively. The toxicant was renewed after fixed period. . The technique of Microtomy is being used for the histological study purpose of testis of the fresh water catfish Heteropneustes fossilis.

Observation And Results

Fig :- Effects of Azadirachta indica on Testis of Heteropneustes



Normal Testis

24 Hours Testis

48 Hours Testis

72 Hours Testis

96 Hours Testis

fossilis

Effects of Azadirachta indica on Testis of Heteropneustes fossilis :-

Histologically, the normal testis appeared structurally normal. The seminiferous tubules (ST) were of round or oval shape and contained spermatogonia (Sg), spermatocyte (Sc), spermatid (St), spermatozoa (Sz), sertoli cells (SC) and interstitial cells (IC) of leydig (Fig.Normal testis).

At 24 hours exposure of Azadirachta indica on fish, testis showed regression and delay in spermatogenesis (Ds) as compared to control and flattened seminiferous tubules (FS) with scattered spermatozoa (Ssz) and testis interstitial space (Tis,) (Fig.24 hrs. testis). At 48 hours exposure of Azadirachta indica on fish, testis showed the areas occupied by spermatid (St) and spermatozoa (Sz) in the lobules showed cytolysis and many lobules with empty spaces that leads to vacuole (V) and testis interstitial space (Tis,) (Fig.48hrs. testis). At 72 hours exposure of Azadirachta indica on fish, histological examination testis showed the germinal epithelium was inactive and flattened to single layer, the seminiferous tubules get vacoulated (STv) and dilated (STd). (Fig.72hrs.testis). At 96 hours exposure of Azadirachta indica on fish, histological examination testis showed the extensive damage to germinal epithelium, necrotic cells (N), connective tissues and atrophic and prominent vacuolation (V) was recorded. (Fig.96 hrs. testis).

Discussion

The testis is the male gonad found in pairs as part of the male reproductive system that employs sexual reproduction. The testis produces sperm that is male gamete as well secretes male sex hormones. During experiment the control testis appeared structurally normal. The seminiferous tubules contained spermatogonia, spermatocyte, spermatid, spermatozoa, sertoli cells and interstitial cells of leydig. The exposure caused regression and delay in spermatogenesis also flattened seminiferous tubules with scattered spermatozoa, testis interstitial space dilated seminiferous tubules and prominent vacuolation was recorded. Goktepe et. al. (2004) and Sen et al (2012) have mentioned the contraceptive nature of neem in mammals as well quoted that long term exposure causes the infertility. In our experiment, it has showed the well destructive effect on ovary and testis both. The observations are found compatible with the studies by Omoregie and Okpanachi (1998), Sen et. al. (2012), Thophon et. al. (2003) and, Tantarpale and Rathod (2014)

Conclusion:

The Neem is one of the best Biopesticides which shows very less hazards to environment. But the present study on Heteropneustes fossilis and previous research made on the aquatic organisms especially fresh water fishes proved the hazardous effects of Azadirachta indica on reproductive biology. So, in future there is need of more research to assess the purported benefits of Neem which is a Kalpavriksha for all the mankind. So it suggest that may Azadirachta indica has several medicinal values as well having utility like biopesticides but its exposure showed adverse effect on the testis of fresh water catfish Heteropneustes fossilis.

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Histological Modulation Observed In Intestine of Freshwater fish Channa Striatus Exposed To Deltamethrin

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Introduction

Nowadays, Synthetic pyrethroids are mostly used as a insecticides due to their low environmental persistence and toxicity. In agriculture they are applied to control ectoparasites, especially lice as well as insects in nursery and it is a most popular alternatives for the organophosphates.

Increased use of pesticides not only helped in controlling insects and pests but have created a great environmental pollution specially hazardous influence in aquatic fauna Broadbury and coats (1989) .There are many reports related to toxicity of the chemicals, like organophosphorus and chlorinated hydrocarbons carbamates on the aquatic fauna (Edward and Millburn 1985). Most advantages view of pesticides can also improve the nutritional value of food sometimes its safety (Damalas,2009).Thus from this point of view the pesticides can be considered as an economic labor saving and efficient tool of pest management with grate popularity in most sector of the agricultural production .Despite their extensive use pesticides serious concern about health risks arising from the exposure concern about health risk arising from the exposure of farmers when mixing and applying pesticides or working in treated field and from residues on food and in drinking water for the general population have been raised (Maroni et al.,2006 ;Sodres, 2009).

More recent studies also reported presence of pesticides in surface water and groundwater close to agriculture lands over the world . The organophosphorus compounds are widely used because of their rapid biodegradability and non-persistent nature dimethoate which is used against mites, thrips and aphides on food crops and it persists longer on crops like dicholorvos and other organophosphorus insecticides (Rao, 2006).

The pesticides are frequently used in fish culture water for not only controlling predatory and weed fishes but also killing for other harmful insect Bansal and singh (2006);Mondalet al., (2007). In this paper,the effect of Deltamethrin on intestine of Channa stratiuswere studied and observed.

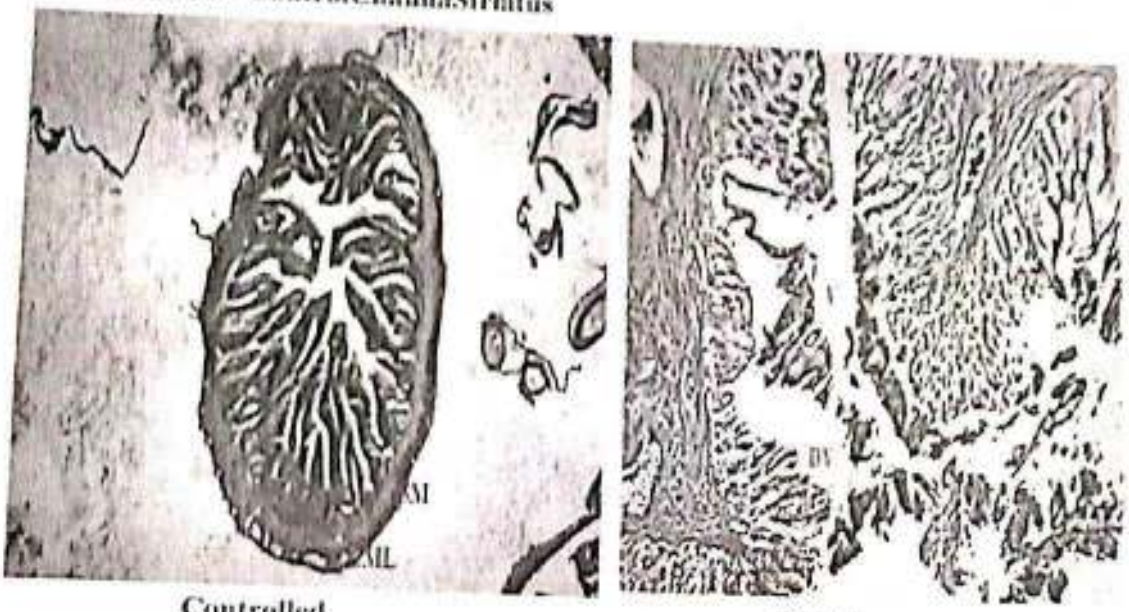
Materials And Methods

Fishes were collected from local Friday market and acclimatized to laboratory condition for at least 10 days. The average weight and length of the fingerlings during stocking was 7.73 + 1.23 g and 13.21 + 0.52 cm.

For toxicity of pesticide treatment, the fishes were divided into two Groups, one for normal or control and another for experimental. The experimental fishes were treated with sub lethalconcentration of Deltamethrin 0 .0002μ/lit at 96 hours. Fishes were sacrificed and tissues of intestines were dissect out and preserved in Bovines solution and proceeded for histological study.

Observations And Results

Plate 1 :Intestine of ControlChannaStriatus



Controlled **96 Hrs**

*S- Serosa V- Vacuolization SM– Sub Mucosa Dv- Disturb Villi LM- lamina propria Rvp- Ruptured Villi Projection LML- Longitudinal Muscle Layer RCC- Ruptured Columnar cell

Fig 1: Effect of Sublethal concentration of Deltamethrin exposed to fresh water fish Channastriutus

The fresh water fish Channa striatus exposed to sub lethal concentration by deltamethrin showed highly disturbed andrestless movements. The fishes moves up and downs, sometimes irregular erratic movements observed, fishes settled down at the bottom of the aquaria, sluggishly. Up to exposure of 96 hours fish lost their equilibrium and response to external stimuli pectoral and pelvic fins affected were spread forward and engulfed air through mouth respiration cases and finally fish died.

The histological investigation of intestine of Channa striatus showed varying degree of degeneration in the longitudinal muscle layer and also disturbed and swelling of lamina propria and dislocation part of serosa. Also necrotization observed in the intestinal villa. Cellular elements disturbed. Histologically the cells were disturbed, also hypertrophy of the epithelial cells, Fusion of villa due to excessive hypertrophy and odemic lamina so the villi of intestine rupture at tip portion.

Discussion

The synthetic pyrethroid deltamethrin is widely used in gardens and agricultural lands to control the pest .But this pesticide adversely affected the human population as well as the water bodies.Exposed to sub lethal concentration of deltamethrin at 96 Hrs. to the fishChannastriatus shows histological modulations in Intestine.The villi of the intestine showed completelyruptured and damage structure. Muscular layer detaches from the sub mucosal layer of intestine epithelial cells, shrunkencolumnar epithelial cells totally damaged.Similar observation were reported by Julin and Sanders (1977), they observed excessive mucous secretion in fixed exposed to phenol.

The intestine play a very important role in body and is connected with several functions.It has directed contact with the pollutant dissolved in water but due to its contact with

blood it is indirectly affected (Thorat, 2001). The intestine of the fish exposed sublethal and lethal concentration of fishChanna gachua by effluent showed hypertrophy of the epithelial cells,swelling oflamina propia (Narnia and Kumar et al., 1990).

Similar epithelial hyperplasia, epithelial necrosis, oedemma, epithelial lifting etc. observed by the histopathology of lambda –cyhaloathrin, a synyhetic pyrethroid pesticide effect on gill ,liver ,kidney and intestine tissue in fishCirrhinusmrigala(Velmurugan et al.,2007).Histologically the intestine of the fish Channa striatus exposed to deltamethrin resulted degeneration of the structural hypertrophy and necrosis and inflammation in the intestinal cell, observed due to stressful condition.

From the present study it is concluded that the fresh water fish Channa striatusexposed to sub lethal concentration of Deltamethrin showedbehavioral alternation which indicates stress situation due to presence of pesticide. The 96 Hrs exposure also leads to alter histology of intestine. So it suggests that Deltamethrin have several adverse effects on the fresh water fish Channa striatus. So it is necessary to monitor the level of pesticides in the aquatic medium to prevent mortality of fishes and its conservation.

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Effect of Norfloxacin on Hatching Rate of Channa Punctatus (Bloch, 1793)

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Abstract

The use of some drugs during pregnancy may causes abnormalities to the embryo. Sometime the drug also effect to the new born if the drug transferred through lactation. The present experiment used the Channa punctatus as model to check the effect of norfloxacin on hatching rate of eggs. The 10, 20, 50, 100 µg/ml concentrations of drug were used. No significant mortality or malformations were observed in fish embryos. Hatching was stared from 36 hr. In control group, 90% hatching rate was observed. Lowest hatching rate was observed in highest concentration (100µg/ml). Present investigation suggests the possibility that high dosage can harm the unborn baby or new born babies, if the mothers use norfloxacin.

Key words: Channa punctatus , fluoroquinolone, hatching rate, norfloxacin.

Introduction

The use of some drug during pregnancy can cause the harm to the fetus. These drugs may be the reason for birth defects, like cleft lip or physiological harms. The improper administration may also leads to miscarriage. If such drug are taken by mother during lactation, it can transfer through the milk and can also affect the new born. These drugs are commonly referred as contraindicated drugs. Norfloxacin, a fluoroquinolone antibiotic, is used to treat certain infections to the woman caused by bacteria, such urinary tract infections; which is frequently prescribed by doctors to pregnant woman (Akerele et al., 2001; McNaughton et al., 2014).
The purpose of the present study was to investigate the effect of norfloxacin on hatching rate of fresh water catfish Channa punctatus embryos.

Material And Experimental

The adult brooder catfish were collected from local water body. After natural fertilization in the aquarium, the fertilized eggs were collected for the experiment through the standard method (Srivastava et al., 2012). The norfloxacin tablets were purchased from the local pharmaceutical stores. The tablets ware grinded and make powder. Then directly used into water. The solutions of the drug were prepared were prepared in distilled water to obtain various dilutions (10, 20, 50, 100 µg/ml).The warmed on a water bath to accelerate the dissolution process as describe previously (Maheshwari et al., 2006). The pH of the solution water was in between 7 to 7.5.

The eggs were collected and rinsed several times with double distilled water. The eggs transferred to various petridishes where the eggs have exposed to the drugs with water. At around 4-6 hr post fertilization, only the fertilized eggs were selected and transferred to the petridishes (20 / plate) containing different concentrations (10, 20, 50, 100 µg/ ml) of norfloxacin of at 320C. The entire experiment was conducted in twice to verify results with a total of 100 eggs for each treatment group (Siu et al., 2002). Treatment effects on the hatching rate was determined by formula of Hajizadeh et al. (2008)

Hatching Rate (HR) = (No.of hatched egg)/(Total no. of egg in batch) × 100

Results And Discussion

Hatching was occurred during 36 to 60 hours. No significant mortality or malformations were observed in fish embryos exposed to the different treatment groups. In control group, 90% hatching rate was observed. Lowest hatching rates were observed in norfloxacin groups treated with in 100 µg/ml concentration which was 30%. Hatching rate was decrease with the increasing amount of concentration.

Present data clearly indicated that low concentration did not cause any detrimental effects on hatching rates. However, higher concentration can effect on hatching rate also. The over-all hatching success rates did not differ significantly among the different exposure groups. Furthermore, no differences were observed in either mortality or incidence of malformations between the treated and control embryos. The concentration threshold did not affect morphologically to the embryo. So, the question of why fish embryos showed concentration threshold that did not affect morphologically to the embryo needed to be satisfied. As stated earlier, the concentrations used in the present investigation were not sufficient to cause morphological or developmental effects. There is a possibility that they can tolerate this amount of concentration. They might develop natural tolerance capacity of toxicity from the natural systems (Luckenbach et al., 2001).

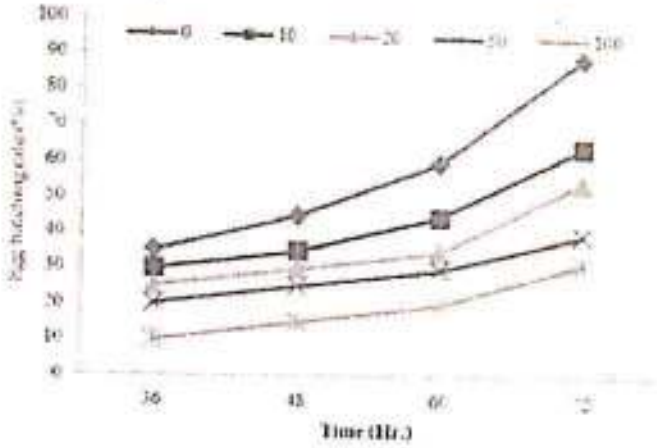

Figure 1: Egg hatching rate of fish treated with norfloxacin

In human, the concentration of drug reaches into the serum level varies which is depending on the types of the drugs and the dosage. In present cases, concentration range of drug varies from 10 to 100 µg. The concentrations like 10, 20, 50, 100 µg/ml were selected for the present investigation because Siu et al. (2002) detected the contraindicated drug from a pregnant woman serum at a concentration of 70 µg/ml. In this point of view, present experiment concentrations are very relevant. The norfloxacin can also alter the expression of Vascular Endothelial Growth Factor (VEGF). It is an important protein which plays a key role for the development of the blood vessels of the heart and also promotes development of endothelial muscle (Chakraborty, 2011; Bally et al., 2017).

Conclusions

To conclude, since the minor concentrations of norfloxacin used in the present study affected the hatching rate in fresh water fish Channa punctatus. It suggests that use norfloxacin drug by a mother can cause harm to the developing baby.

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Effect of Aloe Vera Leaf Extract on The Developmental Stages of Drosophila Melangogaster

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Abstract

Aloe vera is known for its various medicinal properties. In the present study, the effect of Aloe vera leaf extract on the development of different stages of Drosophila melanogaster was observed. The different concentrations of Aloe vera leaf extract were used for calculation of effective dose. The sub lethal dose was calculated by considering the effective dose and available literature. Drosophila flies were fed on media supplemented with sub lethal dose and develop life cycle of next generation on it. Size and growth of different life stages were observed and total protein estimated from it. Polytene chromosome was studied from salivary gland of 3rd instars larva. The reduction in size of different stages and protein concentration were recorded, it may due to the effect of bio-active components present in Aloe vera.

Key words. Aloe vera, Polytene, Drosophila melanogaster.

Introduction

Herbal medicine has long been recognized as one of the oldest forms of remedies used by humans. Many people in developing countries still rely on traditional healing practices and medicinal plants for their daily healthcare needs, in spite of the advancement in modern medicine.

The Aloe vera plant has been known and used for centuries for its health, beauty, medicinal and skin care properties. The name Aloe vera derives from the Arabic word "Alloeh" meaning "shining bitter substance," while "Vera" in Latin means "true." 2000 years ago, the Greek scientists regarded Aloe vera as the universal panacea. The Egyptians called Aloe "the plant of immortality." Today, the Aloe vera plant has been used for various purposes in dermatology (Amar Surjushe et.al, 2008).

Daburkar et.al,(2014) showed that use of Aloe vera gel ethanolic extract attenuated the diabetic foot wound in rats. Another article revealed that Aloe vera could be a treatment of choice for burn injuries. Oryan and coworkers (2016) proved evidences that topical application of Aloe vera would improve the biochemical, morphological, and biomechanical features of the healing cutaneous wounds in rats. A clinical trial investigation reported that Aloe vera and Calendula ointment improve the speed of episiotomy wound healing; therefore it could be considered for quickening the episiotomy healing. By considering above literature we have studied the effect of Aloe vera leaf extract on the development and phenotypic variation in Drosophila melanogaster.

Drosophila melanogaster, also known as the fruit fly, is an excellent model organism widely used in biological research that has made significant contributions to the greater scientific community over the last century. It is because fruit flies are inexpensive to maintain in the laboratory, have simplified genetics, and short generation times allow for quick experiments with high sample numbers.

Sindhu & Lone (2004) observed the effect of diethylstilbestrol (DES) on the development of Drosophila melanogaster by performing special study on nucleic acid and proteins, and they reported that the weights of various developmental stages were drastically affected by the DES content. The macromolecular content were also likely affected e.g. DNA and protein showed negative trends between treatment group. They revealed that DES has an inhibitory effect on the development of Drosophila melenogaster. The present aims to observe the effect of Aloe veraleaf extract on different developmental stages of Drosophila.

Material And Methods

Fruit flies were collected on ripe banana fruits. After that flies were cultured on potato, dextrose & agar culture media. Aloe vera is well known for its marvelous medicinal properties. These plants are oneof the richest sources of health for human beings coming from nature. It has been grown as an ornamental plant widely. Products of various parts of the plant have different effects on the body.

Aloe Vera leaf extraction

Aloe vera leaves were collected and washed in sterile distilled water and evacuated from gel. The leaves were separately shade-dried for 10 day till weight constancy was achieved. The sample was powdered in an electric blender. The extract was prepared with the standard method of percolation. To do this, chopped dried plant leaves in 80% ethanol were percolated for 72 hours. Then, the slurry was filtered with Whattman No. 1 filter paper and centrifuged for 5 min at 5000 rpm. The filtrate obtained from ethanol using a rotary device, the excess solvent was separated from the extract. These crude extract was stored at 4°C until use (Masoud Haghighi, et al, 2014).

Experimental set up

Sr. No.	Control	Experimental
01.	15 gm. Culture media	1 ml extract + 15 gm Culture media
02.	15 gm. Culture media	2 ml extract + 15 gm Culture media
03.	15 gm. Culture media	3 ml extract + 15 gm Culture media
04.	15 gm. Culture media	12µl/ extract + 15 gm Culture media

The measurement of size of the various stages of Drosophila melanogaster was carried out with the help of Oculometer.Thetotal estimation of protein was done by the De" Lowry method. Photographs were taken in the Carl Zeiss trinocular microscope and Stereo microscope. All results are presented as Mean ± SD. Test of significance (t- test) was used to analyze the data collected.

Results And Discussion

There was not a significant effect of Aloe vera leaf extract on the development of Drosophila melanogaster except the less significant effect on the 1st and 2nd instar larvae. At 1 ml, 2ml, and 3 ml Aloe vera leaf concentration, the mortality rate was found to be 100%. At sub lethal concentration i.e. 12 µl of Aloe vera leaf extract, the flies were survived and growth were

occurred. At this concentration, the size of first, third instars, pupa and adult were decreased as compared to control. But the size of second instar larva was slightly increased. The protein concentration found to be decreased in first, third instars larvae, pupa and adult while protein concentration in second instar larva was slightly decreased. Polytene chromosome of salivary gland in 3rd instar larva was observed and it showed some variation. Chromosomal puff was seen.

In the study of Jesikha, M. (2012), evalution of larvicidal efficacy of Aloe vera extract against Musca domestica was carried out. Aloe vera leaves contain a range of biologically active compounds, the best-studied being acetylated mannans, polymannans, anthraquinone, Cglycosides, anthrones and anthraquinones, and various lectins. The extract was found to be quite effective against M. domestica larvae as 100% mortality was observed at 100 ppm in all the three instars.

Larval mortality (I to IV instar) and pupal mortality after the treatment of AVSE. In I instar stage at 20 ppm concentration the larval mortality was 15% whereas at 100 ppm concentration it was increased to 85%. Pupal mortality was 20% at 20 ppm concentration and then it was increased to 79%. Pupae mortality rate was 61.67% and 122.89% respectively. Akapan U.P. et al.,(2012).

The similar results were obtained in the preliminary assays of fifteen extracts from A. turkanensis, A. ngongensis and A. fibrosa against third instar larvae of mosquito A. gambie showed that only nine were active according to their norm ,60% mortality at 2 mg/ml (Matasyoh, et al., 2008).

Aloe Vera with onion extract, alcohol with clove extract and marigold with garlic extract showed good to moderate effect on fourth instar larvae of A. aegypti after 24 hrs of exposure at increasing concentration. The highest mortality rate (100%) was observed in the extract of clove and alcohol followed by aloe vera and onion extract (Susheela, P. et al., 2016).

4.1 Table and Graph representation:

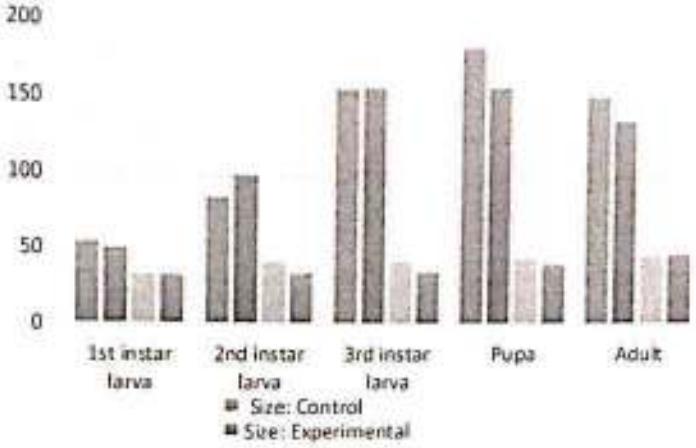
Sr .no.	Developmental Stages	Group	Size (µm)	Protein concentration (µg/g)
1.	1st instars	Control	53.8±3.35	35.25±1.57
		Experimental	50.4±6.65 *** (-6.31)	32.82±1.87)NS (3.794)
2.	2nd instars	Control	84.4±1.44	41.48±0.98
		Experimental	99.8±6.35 NS (18.24)	34.13±2.65*** (1.625)
3.	3rd instars	Control	160.1±2.62	43.216±0.50
		Experimental	160.4±5.64 NS (0.18)	34.79±2.17 NS (6.18)
4.	Pupa	Control	189.5±31.13	45.33±0.26
		Experimental	161.8±1.97 NS (-1.91)	41.38±3.67 NS (5.66)
5.	Adult	Control	156.5±2.15	45.99±0.69
		Experimental	139.7±8.64 NS	47.96±2.90NS

			(-10.09)	(4.28)

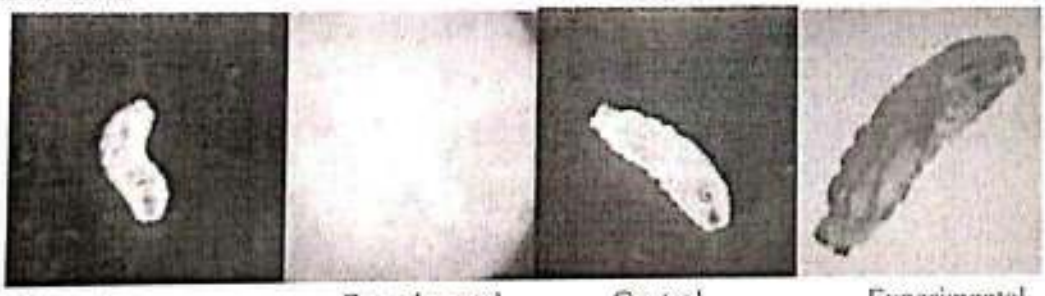
Mean ± of five flies P<0.05(*),P<0.01 and ***P<0.001 and NS= Not significant.**
Figures in parenthesis are indicated the % changes over the control.

Table No.4.1 Size and Protein estimation of control and experimental of larvae, pupae and adults.

Graph No.4.1 Size and Protein estimation of control and experimental of larvae, pupae and adults.

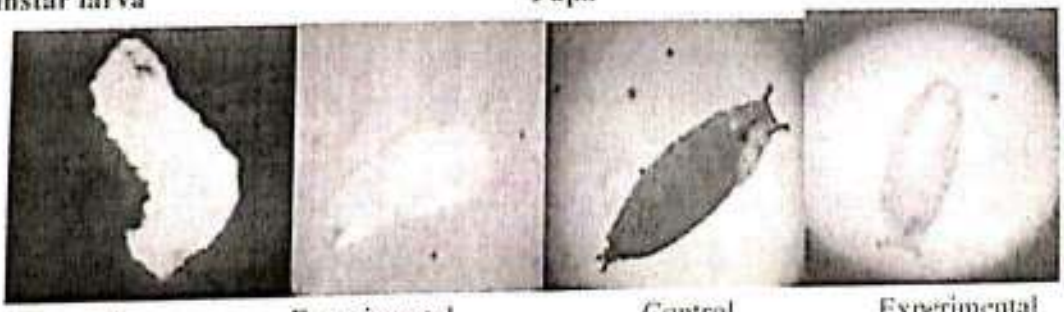


1st instar larva **2nd instar larva**



Control Experimental Control Experimental

3rd instar larva **Pupa**



Control Experimental Control Experimental

Adults Polytene Chromosome of salivary gland of 3rd instars larva

Control Experimental Control Experimental

In the present studywe found that the protein estimation of the different stages were also decreased and it is because of the Aloe Vera has some bio-active components which affect the protein concentration in the fruit flies.The results and observations lead to the conclusion that Aloe Vera contain some chemicals such as Aloin/ Barbaloin and Aloe-emodin which supress the growth and development in the organisms.

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Limnological Studies of Nalganga Reservoir, Nalgangapur, Dist. Buldhana, M. S.

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Abstract

Water samples from Nalganga Reservoir, Buldhana district, Maharashtra were analyzed to find out the suitability of reservoir water for drinking and irrigation purposes. In Egyptian mythology, the Nu was the beginning of everything and represented water. It brought life to their people, but in drought, produced chaos. Loa Tzu quoted "Nothing in the world is more flexible and yielding than water. Yet when it attacks the firm and the strong, none can withstand it, because they have no way to change it. So the flexible overcome the adamant, the yielding overcome the forceful. Every one known this but no one can do it". The quality of drinking water in Indian cities has been deteriorated in the recent years mainly due to the growth of population, unplanned growth of the cities, no proper drainage system and improper disposal of wastewater both from the industrial as well as domestic activities. The finding shows that the contents in majority of sampling locations were below the permissible units and suitable for drinking purpose.

Key words: Water quality, Physico-chemical parameters, Wrinkler method, Nalganga Reservoir.

Introduction

Water is one of the essential requirements of life. In the modern age it also plays a significant role in various economic activities. It is also one of the most exploited natural resources. Most of the fresh water bodies all over the world are getting contaminated due to domestic waste, sewage, industrial waste, agricultural and religious activities lake idol immersion. In India, since ages, there has been a strong interrelationship between religion, customs, rituals and divine rivers. These pious rivers are worshipped right from the time of any person takes birth its death, the entire rituals and ceremonies are associated with these rivers reported by Singh et al., (2009) and Kaur et al., (2013) have reported water quality assessment of river Yamuna in Delhi is stretched by Idol immersion.

In the beginning of 21st century fresh water is going to be scarcest resource and its availability, exploitation and sustainable use will determine standards of life and livelihood in developed, developing and undeveloped nations. The Physical Factors include water movement, light, temperature, turbidity and suspended solids. The Chemical Factors include pH, carbonates, bicarbonates, oxygen, carbon-dioxide, cations, and anions and dissolved organic materials. Gaike et al., (2011) determined the physico-chemical parameters like atmospheric temperature, water temperature, rainfall, Dissolved Oxygen, Calcium, Chloride and CO_2 of Dahiphal Dam.

The earth has a nice combination of water and the land. Much water is not useful for drinking purposes. "The adversity is the opportunity". It means that the scarcity of drinkable water makes us very careful to use it properly. People do not follow the rules of nature. People want to win over the nature. According to the law of Darwin is the "Struggle for existence". We should understand that we are with the nature and not against the nature. The Indian culture guides us to

behave humbly with the nature. It means that, people should use, preserve, and create awareness about the freshwater. Superior quality of water not only enhances the human productivity but also bonus days to the human life in present, past and future also.

Nalganga Reservoir is the second biggest reservoir in Buldhana district of Maharashtra, built on Nalganga River. Buldhana district is situated at westernmost border of Vidarbha which lies between latitude parallel 19° 51' to 21°17' N and longitude parallel 75° 57' to 76° 49' E. District covers 9,640 Sq. km. area. The Buldhana district is transverse by the river Purna and its principal tributaries, viz, the Nalganga, the Vishwaganga and the Gyanganga from the south and the Banganga from the north, and by the river Penganga, constituting together a length of 390 Km of fluvial waters. Nalganga Reservoir is located near Sanglad village 20 Km away from Malkapur, District Buldhana (M.S), India. The River Nalganga rises in the hills at the fact of Buldhana town. The Nalganga reservoir is situated just 16 miles from the origin.

Methods And Materials

The study evolved physico-chemical parameters from the year February 2011 to January 2013. For the study of Nalganga reservoir were selected for analysis. Water samples were collected from different station by using glass and polythene bottles. Before collection of water sample the bottle rinsed and cleaned thoroughly. Water was collected from deep and shallow level of water. Physico-chemical parameters were analyzed by methods suggested by Wrinkler.

Observations And Results

Table no.1: Spot – Nalganga Reservoir

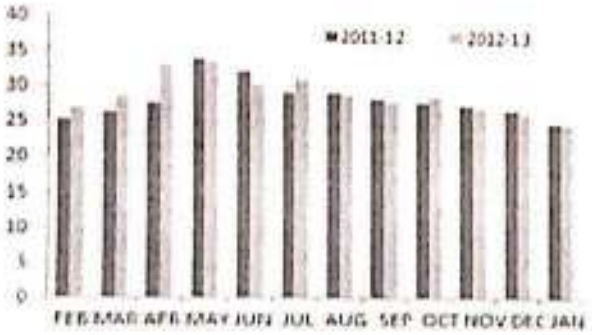
2011-2012													
S.	Parameters	FE	MA	AP	MA	JUN	JU	AU	SEP	OC	NO	DE	JA
1	Atmospheric	25.4	26.4	27.8	34.2	32.4	29.6	29.4	28.6	28.2	27.6	26.8	25.2
2	Water Temp.(^{0}C)	17.2	17.5	18.2	23.4	21.2	19.2	19.0	18.4	18.2	17.5	15.8	14.2
3	Ph	8.36	8.43	8.56	8.85	7.38	7.40	7.32	7.35	7.45	7.54	7.64	7.87
4	Total	437.6	436.6	482.4	572.6	460.4	437.	435.2	430.8	429.4	430.	426.6	425.2
5	Chlorides(mg/L)	144.2	145.8	148.6	156.4	127.2	121.	118.8	115.6	131.6	135.	138.4	140.2
6	Total	480.2	440.4	438.4	436.2	515.4	527.	568.2	602.2	571.2	578.	495.2	432.4
7	Calcium(mg/L)	84.2	86.7	85.9	90.8	86.8	82.2	75.4	74.2	75.6	75.2	76.8	84.2
8	Magnesium(mg/L)	86.4	85.2	91.2	93.4	78.8	76.2	74.4	71.2	75.6	79.4	82.8	84.2
9	Turbidity(mg/L)	7.04	6.72	6.78	6.24	7.12	7.52	7.58	8.18	8.02	7.72	6.58	6.24
10	Total	440.2	410.8	400.2	380.8	565.8	570.	578.4	598.2	490.2	488.	480.8	448.2
11	Dissolved	5.18	5.28	5.76	6.16	6.40	6.78	7.12	7.48	7.82	8.12	8.28	8.58
12	Biological	7.58	8.18	8.52	9.12	9.04	8.52	8.24	8.12	7.56	7.48	7.35	7.12
13	Chemical	32.12	34.56	35.52	36.22	38.56	39.5	39.82	40.54	36.42	35.2	28.62	27.48

2012-2013													
S.	Parameters	FE	M	AP	M	JUN	JU	AU	SE	OC	NO	DE	JA

1	Atmospheric Te	27.	28.	33.	33.	30.6	31.	29.	28.	28.	27.	24.	26.
2	Water	18.	17.	23.	24.	20.8	21.	16.	15.	14.	13.	12.	11.
3	pH	8.5	8.7	9.1	9.4	7.77	7.4	7.3	7.3	7.4	7.5	7.6	7.8
4	Totalalkalinity(	43	44	48	57	459.	43	43	42	42	43	42	42
5	Chlorides(mg/L)	14	14	14	15	130.	12	12	12	13	14	15	15
6	Totall hardness(	48	44	43	43	516.	52	57	61	59	57	48	43
7	Calcium(mg/L)	84.	87.	86.	92.	87.2	83.	77.	76.	75.	75.	77.	82.
8	Magnesium(mg/	82.	87.	93.	94.	82.2	81.	77.	76.	78.	78.	81.	82.
9	Turbidity(mg/L)	7.7	7.7	7.2	7.1	7.71	7.6	8.0	8.2	8.2	8.7	8.1	8.1
1	Total	35	36	44	47	512.	52	53	54	50	48	47	35
1	DissolvedOxyge	4.7	5.3	4.6	4.1	5.72	6.1	5.8	5.9	6.6	7.5	8.2	8.7
1	Biologicaloxyge	7.6	7.7	8.5	9.5	9.52	9.5	9.3	9.1	8.6	7.8	7.0	7.7
1	ChemicalOxyge	56.	49.	47.	46.	44.3	42.	41.	38.	36.	35.	32.	58.

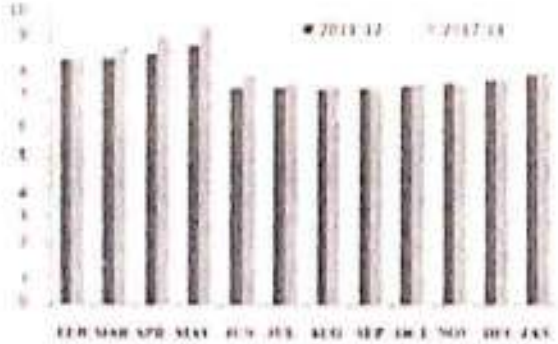
1. Atmospheric Temperature

2. Water Temperature



3. pH

4. Total Alkalinity



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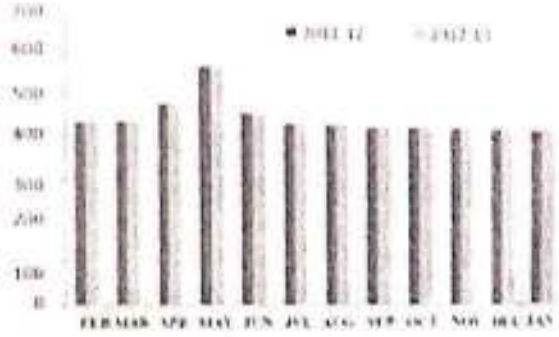
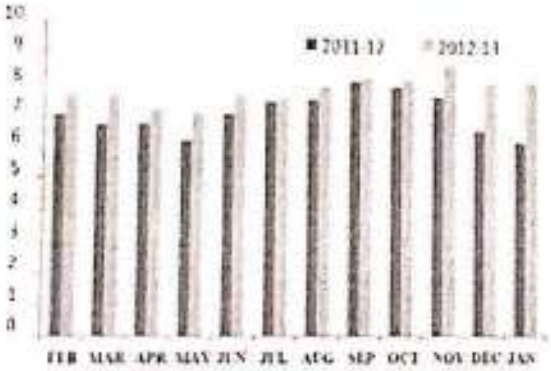


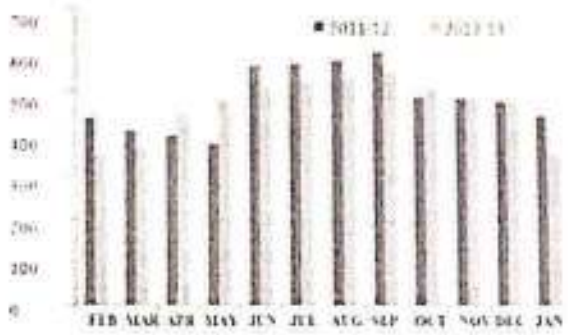
6. Magnesium

7. Turbidity

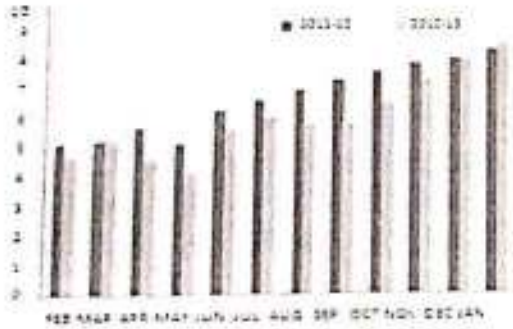
8.TDS

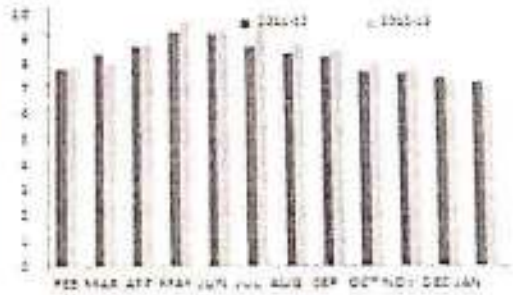


09. Dissolved Oxygen

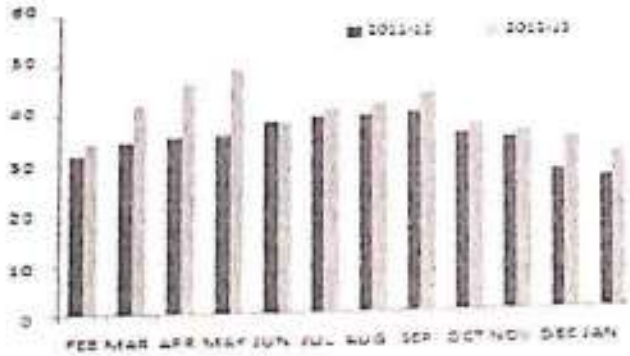


10.BOD





11. COD



Discussion And Conclusion

In April and May temperature of atmosphere were generally higher as compared to other months. Atmospheric temperature was maximum in summer season than other months of both the years and minimum in winter and monsoon season. In winter season the water temperature were low as compared to other seasons in both the years but water becomes clear and calm due to sunlight penetrated in water due to the luxuriant growth of aquatic animals were recorded. In monsoon water temperature were recorded moderated. The pH of rivers and streams feeding Nalganga Reservoir ranged between acidic and less alkaline. It was less alkaline throughout the year and showed minor seasonal variations of rivers and streams also. The present pH ranges showed that the water of the Nalganga reservoir were suitable for aquatic life, irrigation and domestic uses.

The total alkalinity of water from the water body was mainly due to bicarbonates. The total alkalinity values were higher in summer and lower in winter season. The presence of total alkalinity indicated that the reservoir is productive. The chloride values were higher in summer and less in winter of Nalganga reservoir. This indicated that the contamination of water negligible. Total Hardness values were higher in monsoon season, moderate in winter season, and lower in summer season of Nalganga reservoir. The values of calcium were maximum during monsoon and minimum during summer and winter season of Nalganga reservoir. The values of magnesium were maximum during monsoon and minimum during summer and winter season. Magnesium contents were observed relatively lower than calcium in both the years of study period of Nalganga reservoir.

Turbidity: The turbidity of water showed fluctuations. Turbidity values were higher in monsoon, moderated in winter season and lowered in summer season of Nalganga reservoir. Total Dissolved solids means the amount of particles that are dissolved in water. The total dissolved solids were maximum in monsoon and winter season and minimum during summer. The dissolved oxygen values were lower in summer that was created favourable conditions for the development of blue green algae. The dissolved oxygen level rises in winter.

Biological Oxygen Demand: Biological oxygen demand showed variation in dissolved oxygen. The seasonal average concentration of biological oxygen demand showed fluctuations. The maximum value of biological oxygen demand in summer and minimum in monsoon season: The chemical oxygen demand was maximum in summer and winter. It was minimum in monsoon season.

Nalganga Reservoir is a visionary place for the growth of fishes. This reservoir has been extensively utilized for the fish farming. Nalganga Reservoir is the water reservoir specially constructed for irrigation purpose but as the storage capacity of water is more and water remains stagnant throughout the year.

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Multiple quantitative structure-activity relationships (QSARs) analysis for orally active trypanocidal N-myristoyltransferase inhibitors

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ABSTRACT

In the present work, OECD guidelines have been followed for developing QSAR (Quantitative Structure-Activity Relationship) models for anti-HAT (Human African trypanosomiasis) activity of two hundred and seventy pyrazole sulphonamides. The newly developed easily interpretable multiple QSAR models have been successful in identification of many privileged as well as under-privileged molecular descriptors, which could be highly useful for future use of these models by expert and non-experts of QSAR. The multiple QSAR models satisfy threshold values for many statistical parameters such as $R^2 = 0.80–0.83$, $Q^2 = 0.79–0.81$, $CCC_{ext} = 0.82–0.84$, etc. thereby assuring good external predictive ability of the models. The multiple QSAR and pharmacophoric models successfully identified that *N*,4-disubstituted-benzenesulfonamide moiety, frequency of occurrence of H-bond acceptor from Oxygen atom within nine bonds and some other pharmacophoric features that govern the anti-HAT activity of pyrazole sulphonamides. The results could be very useful to synthetic/medicinal chemists for future modifications of pyrazole sulphonamides as drug candidates.

1. Introduction

Human African trypanosomiasis (HAT) or sleeping sickness is a vector-borne disease transmitted by the bite of an infected tsetse fly. The disease is life-threatening, if not treated properly. This disease is caused by two subspecies of the protozoan parasite *Trypanosoma brucei* (*T. b. gambiense* and *T. b. rhodesiense*) [1–6]. Although drugs like Pentamidine, Nifurtimox, Fexinidazole, etc. (see Fig. 1) are available for the treatment of this disease, unfortunately none of them is found to be satisfactory due to toxicity, treatment failures owing to resistance, and the requirement for parenteral administration, which is unsuitable in a rural African setting [2–5,7–11]. Therefore to curb this neglected disease, there is a high need to develop new drugs which target different enzyme or have different mode of action than existing drugs [12–15].

Recently, the enzyme N-myristoyltransferase (NMT) (EC 2.3.1.97), a genetically and chemically validated drug targets in kinetoplastids, has appeared as a promising drug target for the treatment of HAT, due to its essentialness for the parasite [16–18]. In mouse model experiments, it has been found that by blocking NMT in *T. brucei* leads to knockdown of RNAi. This leads to little or no possibility of *T. brucei* survival. Further, it has been pointed out that inhibition of NMT would be expected to have pleiotropic effects through its potential to affect multiple pathways. To add further, NMT has also been identified as a promising target for the treatment of other parasitic diseases including malaria, leishmaniosis, and Chagas disease. Therefore, development of a potential inhibitor of NMT is an attractive area for developing an anti-parasitic drug [16–19].

*Abbreviations: Tb*NMT, *Trypanosoma brucei* N-myristoyltransferase; HAT, Human African Trypanosomiasis; GA, Genetic algorithm; MLR, Multiple linear Regression; QSAR, Quantitative structure-activity analysis; WHO, World health organisation; ADMET, Absorption, Distribution, Metabolism, Excretion and Toxicity; OLS, Ordinary Least Square; QSARINS, QSAR Insubria; OECD, Organisation for Economic Co-operation and Development; OFS, Objective Feature Selection; SFS, Subjective Feature Selection.

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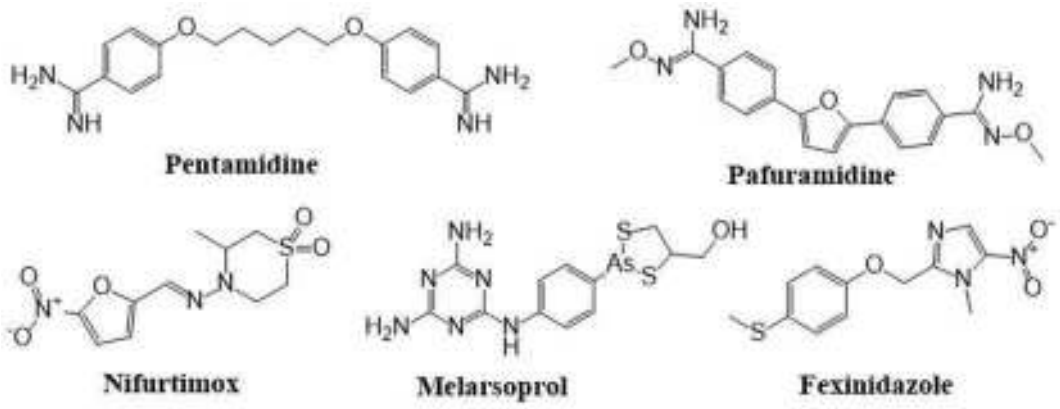

Fig. 1. Some marketed drugs for HAT.

To develop a potent NMT inhibitor, Brand et al. performed high-throughput screening (HTS) against the enzyme NMT using a library of 62,000 compounds, and identified a series of pyrazole sulphonamides as promising inhibitors for developing anti-parasitic therapeutics against *T. brucei* [16,17,19]. In continuation, they synthesized a good number of pyrazole sulphonamides and screened for *in vitro* activity against TbNMT (*T. brucei* NMT), HsNMT (Human NMT) and blood-brain barrier crossing ability, etc. The analysis revealed that many newly synthesized compounds possess activity in μM to nM range with moderate to high blood-brain barrier crossing ability, selectivity for TbNMT, metabolic instability and poor tolerance [16,17,19]. Therefore, effective modifications are necessary to achieve the ADMET (Absorption, Distribution, Metabolism, Excretion and Toxicity) associated goals with retained or improved anti-HAT activity. In such a situation, computer aided drug design (CADD) is an attractive tool for further lead optimization.

In recent time, computer aided techniques have emerged as economical viable alternatives to conventional 'trial and error' methodology of drug design/discovery to understand pharmacophoric requirements for simplification of lead and drug optimization. CADD is a fast and significantly result oriented popular modern technique. It encompasses unification of different scientific fields with main prominence on understanding the interactions of biologically significant molecules, to explore the key steps for disease treatment and to identify the important structural patterns governing with activity/toxicity of a molecule. When popularly used CADD methods viz. QSAR, molecular docking, pharmacophore modeling, molecular dynamics simulations, etc. [20–23] are utilized concurrently then the analysis provides effective information required for lead (and drug) optimization. These methods deliver thorough understanding of pharmacophoric patterns associated with specific activity/toxicity of a drug candidate [24–28].

Even though, Singh et al. [29] developed a 3D-QSAR (CoMFA) model, but the model was developed using small dataset of forty-one molecules only and has poor statistical performance with $r^2 = 0.571$ for the prediction set. A QSAR model is highly useful when it has good external predictive ability and interpretation in terms of structural features [30]. Hence, in the present work, first attempt has been made to develop 2D-QSAR (ligand based drug design technique) using a larger dataset of two hundred and seventy pyrazole sulphonamides using easily understandable molecular descriptors to identify the structural features that have good correlation with the HAT healing activity of pyrazole sulphonamides. Therefore, a better understanding of structural features governing anti-HAT activity of pyrazole sulphonamides would be of high importance to any drug discovery effort.

2. Experimental methodology

2.1. Experimental dataset

In the present work, anti-HAT activity values, reported by Brand et al. [16,17,19], of a diverse dataset of two hundred and seventy pyrazole sulphonamide derivatives covering different cyclic rings and a variety of substituents were subjected to QSAR analysis (See Fig. 2 and Table ST0 in supplementary material). Due to good variation in the type of substituents, the present dataset includes different types of isomers like positional, functional, etc. Consequently, the dataset covers a good chemical space.

The reported IC_{50} (μM) activity values for anti-HAT were converted to pIC_{50} ($pIC_{50} = -\log_{10}IC_{50}$) before QSAR analysis [31]. The IC_{50}, pIC_{50} along with SMILES notations of the molecules have been

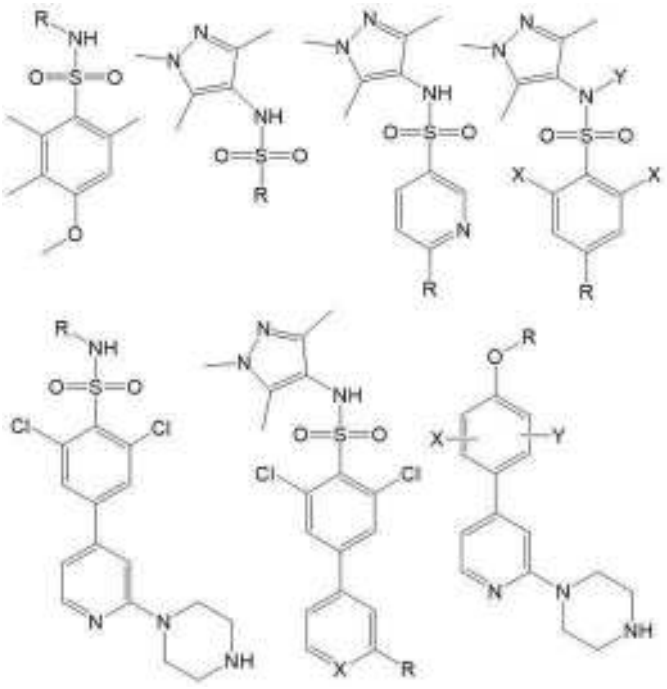

Fig. 2. Variations in pyrazole sulphonamide derivatives used in the present QSAR analysis.

tabulated in table ST0 in supplementary material.

2.2. Modeling and molecular descriptors calculation

In the present work, OECD guidelines and standard protocol suggested and applied by different researchers have been followed for successful QSAR analysis [32–37]. The standard protocol involves (1) Structure drawing: ChemSketch 12 freeware (www.acdlabs.com) was used for structure drawing, (2) Structure Optimization: It was performed using MMFF94 force field available in Avogadro software (v. 1.2) using following settings: ForceField: MMFF94, Algorithm: Steepest Descent, number of steps used for optimization: 1000. (3) Descriptor calculation: The energy minimized 3D-structures were subjected to calculation of myriad number of molecular descriptors (>29,000) using PaDEL 2.21 [38] and *PyDescriptor* [39,40] as a molecular descriptor calculator. (4) Removal of redundant variables: The molecular descriptor pool comprises 1D-to 3D-, electro-topological, finger-prints and other molecular descriptors. As all the calculated descriptors do not encompass important information, hence, objective feature selection (OFS) was accomplished using QSARINS-Chem 2.2.2 [41,42] to exclude all the redundant molecular descriptors. For this, constant, near constant (>98%) and highly correlated ($|R| > 90\%$) descriptors were rejected. OFS resulted in substantial reduction of descriptor pool to a cluster of 1384 molecular descriptors, still covering broad structural and chemical space viz. constitutional (0D-), mono-dimensional (1D-), bi-dimensional (2D-) and three-dimensional (3D-).

2.3. Model development

The QSAR analysis can be used for two types of purposes [43]: (1) Qualitative QSAR: To identify the structural/pharmacophoric features, which are responsible for the activity/toxicity profile of a con-generic series of molecules and (2) Quantitative QSAR: To estimate the activity/toxicity of a molecule before its synthesis and/or biological screening. In the present work, emphasis is on deriving Qualitative as well as Quantitative QSAR models. For this, the strategy reported in our earlier work was employed [44], in which, multiple MLR (Multilinear regression) models were built using undivided dataset, 50% training set and validating them on remaining set (50% prediction set) using random splitting. In next step, the training and the prediction sets were exchanged to develop new multiple models and validating on prediction set (which was initially the training set). This confirms that all significant structural features, which influence the anti-HAT activity of these molecules, are captured during QSAR analysis. In addition, multiple QSAR models were derived using randomly divided (training-85% and prediction-15% set prior to descriptor selection) dataset to verify the capturing of all the relevant structural and activity information (see Fig. 3). The GA (Genetic Algorithm) module of QSARINS-Chem 2.2.2 (Q^2_{loo} as the fitness function) [33,34] was used for selection of optimum number and set of molecular descriptors for each model. For every procedure used for model building, variable selection (descriptor selection) was performed separately every time, that is when using undivided dataset, divided dataset (training: 50, prediction: 50) and divided dataset (training: 85, prediction: 15). The analysis revealed that up to six descriptors there was increase in the value of Q^2_{loo}, but afterwards, it had sharp drop. Hence, the heuristic search was restricted to six descriptors using the defaults settings to avoid over-fitting and have simplicity in understanding the developed QSAR models.

2.4. Model validation

QSAR analysis is unreliable if not validated properly. Appropriate QSAR model validation confirms the external predictive ability of a developed model. Therefore, the statistical qualities and strength of QSAR models were evaluated on the basis of: (a) internal validation: through cross-validation (CV) by leave-one-out (LOO) and leave-many-out (LMO) procedure, (b) external validation: using the prediction set (c) data randomization: by Y-randomization and (d) observing if the following criteria are satisfied: $R^2_{tr} \geq 0.6$, $Q^2_{loo} \geq 0.5$, $Q^2_{LMO} \geq 0.6$, $R^2 > Q^2$, $R^2_{ex} \geq 0.6$, $RMSE_{tr} < RMSE_{cv}$, $\Delta K \geq 0.05$, $CCC \geq 0.80$, $Q^2\text{-}F^n \geq 0.60$, $r^2_m \geq 0.5$, $(1\text{-}r^2/r^2_o) < 0.1$, $0.9 \leq k \leq 1.1$ or $(1\text{-}r^2/r'^2_o) < 0.1$, $0.9 \leq k' \leq 1.1$, $|r^2_o - r'^2_o| < 0.3$ with *RMSE* and *MAE* as low as possible [2,3,11,45–47]. A QSAR model that fulfills the threshold values of above parameters has statistical robustness and good external predictive ability. Consequently, the models that do not fulfil above stated measures were excluded.

3. Results and discussion

QSAR models: Generally, for QSAR model development stepwise regression, GA, etc. algorithms are employed for subjective feature selection (SFS). This results in a good number of MLR

Fig. 3. Strategy adopted in the present work for QSAR analysis.

models having almost equivalent statistical performance, but often involving dissimilar descriptors. Usually, in such a situation, a QSAR modeler selects only one MLR model on the basis of its statistical robustness. This 'first among equals' approach has some serious drawbacks such as [2,3,11,45–47] (1) if the selected QSAR model consist of complex/esoteric descriptors then identification of smooth correlation of descriptors with appropriate structural features is relatively complicated, (2) a single QSAR model may be affected by (i) the method of splitting, composition of training and prediction sets, method implemented for descriptor selection, and (ii) some more influencing molecules in the training/prediction dataset. An easy but highly feasible solution, to overcome above-mentioned shortcomings of 'first among equals' approach, is to create multiple QSAR models based on multiple splitting. Another advantage of this solution lies in its ability to identify under-privileged yet important pharmacophoric/structural features associated with the anti-HAT activity of pyrazole sulphonamides. Consequently, in the present study, multiple QSAR models have been built. Interestingly, univariate statistical analysis for undivided dataset pointed out that anti-HAT activity has good and positive correlation ($R = 0.769$) with the descriptor C_AbSA, which signifies the absolute surface area of carbon atoms. The developed multi-linear GA-MLR QSAR models are as following:

Model-1 (Training: 50%, Prediction: 50%):

$\mathbf{pIC_{50}} = 3.33\ (\pm0.84) + 0.85\ (\pm0.36)$ * **fOacc9B** $+ 0.12\ (\pm0.01)$ * **plus_N_9B** $+ 0.39\ (\pm0.15)$ * **ringC_hy2** $- 0.15\ (\pm0.05)$ * **com_ringC_5A** $- 1.07\ (\pm0.29)$ * **AD2D327** $+ 0.12\ (\pm0.05)$ * **APC2D7_N_X**.

Model-2 (Training: 50%, Prediction: 50%):

$\mathbf{pIC_{50}} = 5.77\ (\pm0.48) - 0.15\ (\pm0.06)$ * **fOringC3A** $- 0.82\ (\pm0.28)$* **fON6B** $+ 0.96\ (\pm0.31)$* **fSacc8B** $- 0.09\ (\pm0.03)$ * **ringC_O_9B** $+ 0.26\ (\pm0.04)$* **SssCH2** $+ 4.68\ (\pm1.36)$* **GGI8**.

Model-3 (Training: 85%, Prediction: 15%):

$\mathbf{pIC_{50}} = 5.45\ (\pm0.23) + 1.74\ (\pm0.32)$ * **fOacc9B** $+ 0.83\ (\pm0.29)$ * **KRFP3542** $+ 0.51\ (\pm0.18)$ * **AD2D636** $+ 0.23\ (\pm0.04)$ * **SssCH2** $- 0.22\ (\pm0.09)$ * **com_ringN_6A** $- 0.21\ (\pm0.10)$ * **fNringC6B**.

Model-4 (Training: 85%, Prediction: 15%):

$\mathbf{pIC_{50}} = 3.49\ (\pm0.49) + 1.55\ (\pm0.32)$ * **fOacc9B** $+ 0.10\ (\pm0.01)$ * **plus_N_9B** $+ 1.06\ (\pm0.29)$ * **KRFP3542** $+ 0.87\ (\pm0.19)$ * **AD2D636** $- 0.13\ (\pm0.05)$ * **com_Cplus_7A**$- 0.19\ (\pm0.09)$ * **SubFPC1**.

Model-5 (Training: 100%):

$\mathbf{pIC_{50}} = 3.47\ (\pm0.47) + 1.35\ (\pm0.30)$ * **fOacc9B** $+ 0.08\ (\pm0.01)$ * **plus_N_9B** $+ 1.02\ (\pm0.26)$ * **KRFP3542** $+ 0.94\ (\pm0.18)$ * **AD2D636** $- 0.13\ (\pm0.04)$ * **com_Cplus_7A** $- 0.45\ (\pm0.20)$ * **ringN_don_2Ac**.

The statistical parameters along with their details for all the derived models have been tabulated in Table 1. Further details of the statistical parameters are available in supplementary material.

Table 1
Statistical parameters for newly derived models 1–5 in the present work.

S.No.	Statistical Parameter	Model-1	Model-2	Model-3	Model-4	Model-5
	N_{tr}	135	135	230	230	270
	N_{ex}	135	135	40	40	–
Fitting Criteria						
	R^2_{tr}	0.83	0.83	0.81	0.81	0.80
	$R^2_{adj.}$	0.83	0.82	0.81	0.80	0.80
	LOF	0.40	0.43	0.44	0.44	0.46
	Kxx	0.25	0.23	0.27	0.27	0.31
	ΔK	0.10	0.11	0.10	0.09	0.08
	$RMSE_{tr}$	0.59	0.60	0.63	0.63	0.65
	MAE_{tr}	0.48	0.48	0.50	0.50	0.52
	RSS_{tr}	47.42	48.00	91.20	91.30	112.86
	CCC_{tr}	0.91	0.91	0.90	0.89	0.89
	s	0.61	0.61	0.64	0.64	0.66
	F	106.90	104.45	160.37	158.16	176.89
Internal Validation Criteria						
	R^2_{cv} (Q^2loo)	0.82	0.81	0.80	0.80	0.79
	$RMSE_{cv}$	0.62	0.63	0.65	0.65	0.66
	MAE_{cv}	0.50	0.50	0.52	0.51	0.53
	$PRESS_{cv}$	52.58	53.59	97.80	97.48	119.54
	CCC_{cv}	0.90	0.90	0.89	0.89	0.88
	Q^2_{LMO}	0.81	0.81	0.79	0.80	–
	R^2_{Yscr}	0.04	0.04	0.03	0.03	–
	Q^2_{Yscr}	−0.06	−0.06	−0.04	−0.04	–
External Validation Criteria						
	θ^*	−6.61	−9.22	−8.38	−10.27	–
	$RMSE_{ex}$	0.85	0.79	0.81	0.78	–
	MAE_{ex}	0.63	0.65	0.69	0.57	–
	$PRESS_{ext}$	97.46	83.33	25.94	24.19	–
	R^2_{ex}	0.68	0.71	0.70	0.74	–
	Q^2-F^1	0.66	0.71	0.69	0.73	–
	Q^2-F^2	0.66	0.71	0.69	0.73	–
	Q^2-F^3	0.66	0.71	0.69	0.71	–
	CCC_{ex}	0.82	0.83	0.83	0.84	–
	r^2m *aver.*	0.56	0.59	0.58	0.57	–
	r^2m *delta*	0.07	0.22	0.14	0.24	–
	R^2-*ExPy*	0.68	0.71	0.70	0.74	–
	R'^2_o	0.63	0.61	0.63	0.58	–
	k'	1.00	1.00	0.97	1.00	–
	1-(R^2/R'^2_o)	0.07	0.15	0.10	0.21	–
	r'^2m	0.53	0.48	0.51	0.45	–
	R^2_o	0.66	0.71	0.69	0.73	–
	k	0.98	1.00	1.01	0.98	–
	1-(R^2-*ExPy*/R^2_o)	0.02	0.00	0.01	0.01	–
	r^2m	0.59	0.70	0.65	0.69	–

The experimental and predicted pIC_{50} by various models along with the status of the molecule are available in the supplementary material.

From Table 1, it is clear that all the developed QSAR models have acceptable statistical performance and satisfy threshold values for many parameters. Consequently, models 1–4 possess good external predictive ability, which is reflected from high value of Q^2-F^n, R^2_{ex}, CCC_{ex}, etc. as well as robust with respect to internal validation ($R^2_{cv} > 0.80$, $CCC_{cv} > 0.87$, etc.). Therefore, the models could be useful for prediction of anti-HAT activity for yet-to-be synthesized pyrazole sulphonamide derivatives. The close value of $R^2_{adj.}$ with R^2_{tr}, for all the models, indicates that the models have been built using appropriate number of molecular descriptors. The statistical significance of all the developed models is reflected from the high value of Fischer ratio (F) [2,3,11,45–47].

The descriptor **fOacc9B**, which stands for frequency of occurrence of H-bond acceptor atom from oxygen atom within nine bonds, has a positive coefficient in model 1, 3, 4 and 5. Hence, any increase in occurrence of H-bond acceptor atom from oxygen atom at nine bonds will be favourable for activity augmentation. Some interesting examples that prove the role of this descriptor are following compared pairs of molecules: **37** ($IC_{50} = 0.29$ μM) with **41** ($IC_{50} = 0.002$ μM) though**37** and **41** are positional isomers, **48** ($IC_{50} = 0.007$ μM) with **41** ($IC_{50} = 0.002$ μM).

The molecular descriptor **plus_N_9B**, which corresponds to the presence of positively charged atoms at a distance of nine bonds from N atoms, has positive coefficient in model 1, 4, and 5. Therefore, such a combination of N and positively charged atoms is beneficial for increasing activity against NMT.

In model 3, 4, and 5, the 2D-molecular descriptor **KRFP3542** (represents *N*,4-disubstituted-benzenesulfonamide moiety) has positive coefficient. Therefore, the presence of *N*,4-disubstituted-benzenesulfonamide moiety is in favour of anti-HAT activity of pyrazole sulphonamides.

In the model 2, the descriptor **fSacc8B** (frequency of occurrence of Sulphur and H-Bond acceptor within eight bonds) has positive coefficient. Hence, in future modifications such a combination of Sulphur and H-bond acceptor must be considered for better anti-HAT activity.

The descriptors **fOacc9B** and **fSacc8B** and **KRFP3542** synchronously highlight the importance of *N*,4-disubstituted-benzenesulfonamide moiety and the presence of Oxygen (as H-bond acceptor) atom. This is confirmed by the difference in the activity of **5** ($IC_{50} = 14$ μM) and **7** ($IC_{50} = 42$ μM).

The negative coefficient of the descriptor **com_Cplus_7A** (number of positively charged Carbon atoms present within 7 Å from center of mass (com)), in the model 4 and 5 indicates that number of positively charged Carbon atoms present within 7 Å from center of mass must be as low as possible. Alike hint is highlighted by the negative coefficient of the descriptor **com_ringC_5A**, which represents number of ring Carbon atoms present within 5 Å from center of mass (com), in model 2. Therefore, the presence of ring Carbon atoms within 5 Å from center of mass has negative effect on anti-HAT of pyrazole sulphonamides. This is established by the difference in activity of following pairs of molecules: **211** ($IC_{50} = 1.1$ μM) with **222** ($IC_{50} = 12$ μM) and **18** ($IC_{50} = 2.8$ μM) with **181** ($IC_{50} = 42$ μM).

In addition, similar insinuation is provided by the negative coefficient of the descriptor **fOringC3A** (frequency of occurrence of ring carbon atoms within 3 Å from Oxygen atom), in model 2. Hence, the frequency of occurrence of ring carbon atoms within 3 Å from Oxygen atom must be kept low for better activity. An example to vindicate this observation is significant difference in activity of **18** ($IC_{50} = 2.8$ μM) with **181** ($IC_{50} = 42$ μM).

Another descriptor which specifies the role of ring Carbon atoms in deciding the activity is **fNringC6B** (frequency of occurrence of ring Carbon atoms within six bonds from Nitrogen atoms) has negative coefficient in model 3. Thereby, such ring Carbon atoms must be avoided to have better activity.

APC2D7_N_X, which represents the presence of N-X (halogen) at a topological distance of 7, has positive coefficient in model 1. Consequently, increasing such pattern of Nitrogen and Halogen atoms will enhance the activity. For example, compare **52** ($IC_{50} = 0.003$ μM) with **53** ($IC_{50} = 0.12$ μM). This observation additionally points out the importance of pyrazole moiety attached to sulphonamide group. Another descriptor which point outs similar pharmacophoric pattern, with positive coefficient (model 3–5), is **AD2D636**. It corresponds to the presence of C and halogen atoms X at a topological distance of nine from each other. To increase the anti-HAT activity, the value of this descriptor must be as high as possible.

In Fig. 4, one of the most active molecule has been used as a reference only for a better visualization and understanding of various molecular descriptors viz. **fOacc9B**, **KRFP3542**, **fSacc8B**, **com_Cplus_7A**, **com_ringC_5A** and **APC2D7_N_X**.

The descriptor **ringC_hy2** (number of ring Carbon atoms possessing partial charge in the range 0 to −0.099) has positive coefficient in the model 1. Henceforth, the number of such Carbon atoms in the molecule must be increased to have better activity profile.

AD2D327, which stands for the presence of N–S at a topological distance of 5, has negative coefficient in model 1. Therefore, increase in number of N–S at a topological distance of 5 will diminish the anti-HAT activity. Another descriptor which provides additional information about the presence of Nitrogen atoms is **com_ringN_6A**, which signifies number of ring Nitrogen atoms present within 6 Å from center of mass, has negative coefficient in model 3. Therefore, any Nitrogen atom which is at a topological distance of 5 and simultaneously present in a ring must be avoided.

The negative coefficient of **fON6B**, which represents frequency of occurrence of Nitrogen and Oxygen within six bonds, in model 2, indicates that higher occurrence of Nitrogen and Oxygen within six bonds could lead to reduced activity for pyrazole-sulphonamides. Same is true for **ringC_O_9B** (number of ring Carbon atoms at a distance from nine bonds from oxygen atoms).

In model 2, for 2D-descriptors **SssCH2** (sum of atom-type E-State $-CH_2-$) and **GGI8** (a topological charge descriptor which stands for topological charge index of order 8) have positive coefficients. Therefore, for an improved activity their values must be augmented as high as possible.

The negative coefficient of **SubFPC1** (number of primary Carbon atoms) in model 4 indicates that lowering the number of such Carbon atoms will be favourable for anti-HAT activity. The descriptor **ringN_don_2Ac**, which denotes the sum of partial charges on donor atoms present within 2 Å from ring Nitrogen atoms.

Although we have compared the anti-HAT activities of pairs of molecules of the dataset in terms of descriptors like **fOacc9B**, **fSacc8B**, **KRFP3542**, **APC2D7_N_X**, etc., we make it clear that the collective or converse effect of confounding factors/descriptors have further influence on the activity profile of the compounds.

As mentioned earlier, metabolism and Blood Brain Barrier (BBB) related optimizations are essential for drug development. Therefore, in the present work, pharmacokinetic and bioavailability associated parameters were estimated for thirty most active compounds of the present dataset using SwissADME server (http://www.swissadme.ch/index.php) [48]. The results for ten compounds have been presented in Table 2. For the rest of the molecules the results are available in supplementary material.

From Table 2, it appears that the compounds are potential

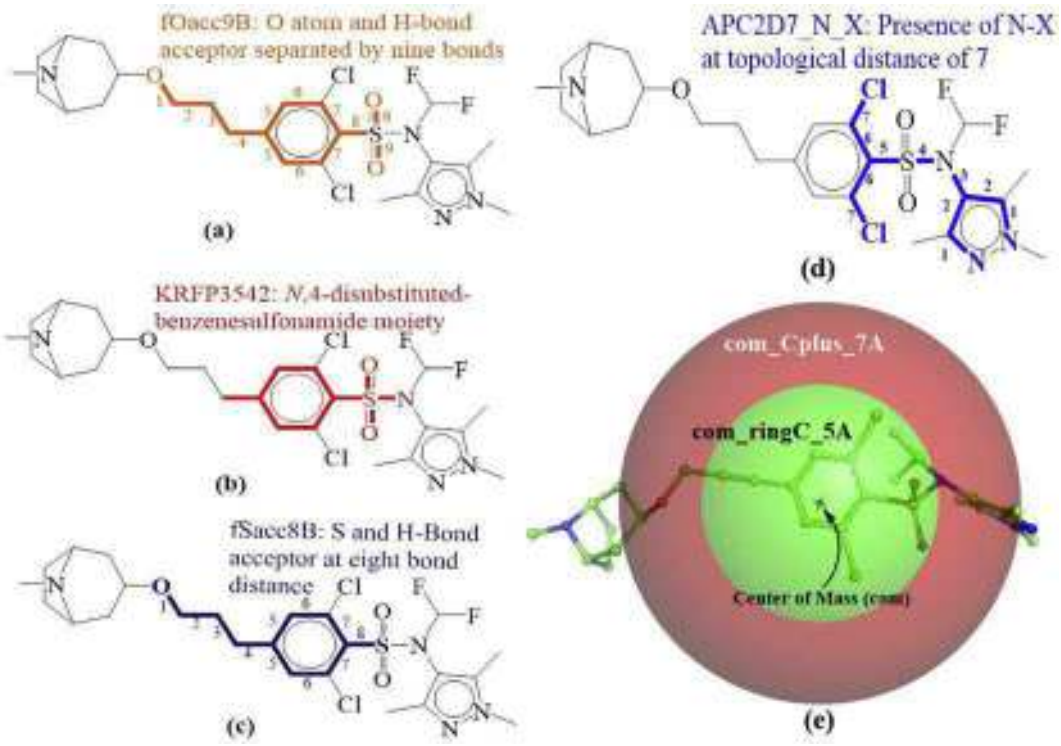

Fig. 4. Pictorial representation of various molecular descriptors viz. (a) **fOacc9B**, (b) **KRFP3542**, (c) **fSacc8B**, (d) **APC2D7_N_X** and (e) **com_Cplus_7A** and **com_ringC_5A**, using (most active) as a reference only.

Table 2
Pharmakokinetic and bioavailability estimations for selected active compounds.[a].

S.N.	GI absorption	BBB permeant	Inhibitor					LogP	Lipinski #violations	Bioavailability Score
			CYP1A2	CYP2C19	CYP2C9	CYP2D6	CYP3A4			
41	High	No	No	Yes	Yes	Yes	Yes	4.63	0	0.55
46	High	No	No	Yes	Yes	Yes	Yes	4.87	1	0.55
52	High	No	No	Yes	Yes	Yes	Yes	3.11	0	0.55
54	High	No	No	Yes	Yes	Yes	Yes	4.56	0	0.55
56	High	No	No	Yes	Yes	Yes	Yes	2.94	0	0.55
58	High	No	No	Yes	Yes	Yes	Yes	3.81	0	0.55
64	High	No	No	Yes	Yes	Yes	Yes	4.29	1	0.55
72	High	No	No	Yes	Yes	Yes	Yes	4.04	0	0.55
74	High	No	No	No	Yes	Yes	Yes	3.13	1	0.55
75	Low	No	No	Yes	Yes	Yes	Yes	4.48	1	0.55

[a] Estimated using SwissADME server (http://www.swissadme.ch/index.php).

CYP3A4 and CYP2D6 inhibitors, but poor BBB permeant, for which a plausible reason pointed out by Brand et al. [16,17,19] is high logP (lipophilicity) and PSA (Polar Surface Area) of the molecules. A good strategy to diminish lipophilicity and increase activity is to decrease number of aromatic carbon atoms that vicinal to center of mass (COM) of molecule (negative coefficient of **com_ringC_5A** in model 2) or reduce number of primary Carbon atoms as suggested by the negative coefficient of **SubFPC1** (number of primary Carbon atoms) in model 4. Thus, the results of the present QSAR work for anti-HAT activity are in consensus with pharmacokinetic and bioavailability estimations.

Conclusion: In the present work, new easily interpretative multiple QSAR models have been successful developed to identify various privileged as well as under-privileged molecular descriptors, which could be highly useful for future use of these models by expert and non-experts of QSAR. The multiple QSAR models have good external predictive ability, which is vindicated by their ability to satisfy threshold values for many statistical parameters such as $R^2_{tr} = 0.80–0.83$, $Q^2_{LOO} = 0.79–0.81$, $CCC_{ext} = 0.82–0.84$, etc. The multiple QSAR and pharmacophoric models successfully identified many pharmacophoric features that govern the anti-HAT activity of pyrazole sulphonamides.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.molstruc.2018.07.080.

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QSAR study of anti-Human African Trypanosomiasis activity for 2-phenylimidazopyridines derivatives using DFT and Lipinski's descriptors

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Abstract

The quantitative structure-activity relationship (QSAR) of sixty 2-phenylimidazopyridines derivatives with anti-Human African Trypanosomiasis (anti-HAT) activity has been studied by using the density functional theory (DFT) and statistical methods. Becke's three-parameter hybrid method and the Lee-Yang-Parr B3LYP functional employing 6−31G(d) basis set are used to calculate quantum chemical descriptors using Gaussian 03W software, and the five Lipinski's parameters were calculated using ChemOffice software.

In order to obtain robust and reliable QSAR model, the original dataset was randomly divided into training and prediction sets comprising 48 and 12 compounds, respectively. An optimal model for the training set with significant

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statistical quality was established. The same model was further applied to predict pEC_{50} values of the 12 compounds in the test set, further showing that this QSAR model has high predictive ability. It is very interesting to find that the anti-HAT of these compounds appear to be mainly governed by four factors, i.e., the number of H-bond donors, the lowest unoccupied molecular orbital energy, the molecular weight and the octanol/water partition coefficient. Here the possible action mechanism of these compounds was analysed and discussed, in particular, important structural requirements for great anti-HAT activity will be by increasing molecular size and substitute the 2-phenylimidazopyridines derivatives with polar, ionic, stronger accepting electron ability group and heteroatoms attached to one or more hydrogen atoms. Based on this proposed QSAR model, some new compounds with higher anti-HAT activities have been theoretically designed. Such results can offer useful theoretical references for future experimental works.

Keyword: Pharmaceutical chemistry

1. Introduction

Human African Trypanosomiasis (HAT) or African sleeping sickness is one of the infectious diseases grouped under the term Neglected Tropical Diseases, which inflict a devastating effect on the health and economy of nearly 150 countries [1, 2, 3]. In Africa, the number of cases has dropped drastically; however, approximately 3,000 new infections of both East and West African Trypanosomiasis have been reported by the World Health Organization in 2015 [4]. HAT-affected 60 zones covering an area of about 8 million square kilometers between 14° north latitude and 20° south latitude [5]. Most cases of HAT are caused by the protozoans *Trypanosoma brucei gambiense* and *Trypanosoma brucei rhodesiense*, which are transmitted to humans through the bite of tsetse flies in rural areas of sub-Saharan Africa.

The disease has two stages: the initial stage is characterized by the spread of the parasite in the blood and the lymphatic system; and in the second stage, the parasite crosses the *blood−brain barrier* (BBB) in which the parasites spread into the central nervous system [6, 7, 8]. Symptoms of this later stage include sleep disturbance, cognitive dysfunction, coma, and death.

Current treatment for the treatment of HAT includes *suramin, pentamidine*, *melarsoprol*, *eflornithine*, or a combination of *nifurtimox* and *eflornithine* (Chemical structures of existing anti-HAT medicines are shown in Fig. 1) [6, 9, 10, 11]. These existing medicines are insufficient, antiquated, toxic, prone to resistance, and require parenteral administration [12, 13, 14, 15, 16, 17]. A new drug, effective for late stage disease that is nontoxic and orally administered, is urgently needed.

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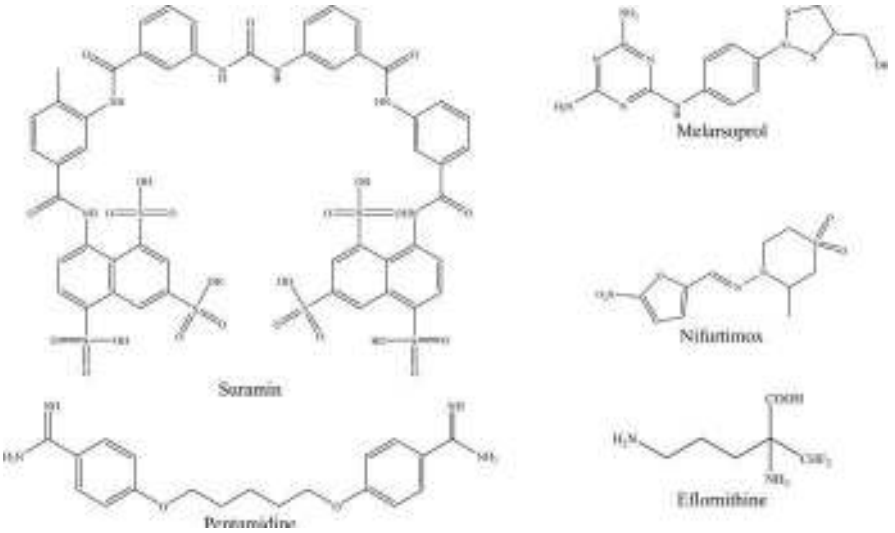

Fig. 1. Chemical structures of existing anti-HAT medicines.

In order to open a new way in anti-HAT drug research, a series of sixty 2-phenylimidazopyridine derivatives were synthesized and studied for their anti-HAT activities by *Tatipaka* et al. [18] to design a better analogue, with rich metabolic stability in liver microsomes, of substituted oxazolopyridine identified as an attractive lead due to good whole-cell activity on *Trypanosoma brucei rhodesiense*, no cytotoxicity on mammalian cell lines, acceptable exposure in the central nervous system, and satisfactory aqueous solubility.

The main focus of the present study is to develop a QSAR model able to correlate the structural features of the 2-phenylimidazopyridine derivatives with their anti-HAT activities.

In general, the QSAR models are based on the assumption that the activity of a certain chemical compound related to its structure through a certain mathematical algorithm. This relationship can be used in the prediction, interpretation, and assessment of new compounds with desired activities, reducing and rationalizing time, efforts, and cost of synthesis as well as new product development. The basic assumption to drive a QSAR model is presented in the form of a mathematical function associating the chemical properties to the effect (activity). Therefore, the effect is like the function *"f"* of the chemical properties *"x": y = (x)*. To find this algorithm, a number of chemical compounds with known values of the studied effect (y) are considered. For each chemical compound, myriad numbers of parameters (called as chemical descriptors) are calculated. Then, QSAR models are built that provides a quite accurate value, similar to the real experimental value. The final step is to check if the obtained QSAR models are able to predict the activity values for other chemicals not used to build up the model (external validation). Indeed, it is very important to generate a model which worked not only for the chemical

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substances used within the training set but also for other similar chemicals. Consequently, the challenge is to define the correct statistical properties of the model [19, 20].

The significance and novelty of findings presented in this work are reflected from the fact that we have used quantum chemistry descriptors which describes electron proprieties of congeneric structures used in this study, and we have used the five Lipinski's descriptors to describes compounds could be potential orally administered drugs. The use of density functional theory (DFT) is justified for the reason that some comparative QSAR studies have shown that the descriptors calculated using the DFT method can improve the accuracy of the results and lead to more reliable QSARs [19].

A flow chart for the development of the QSAR model along with the various validation methods used in this work is demonstrated in Fig. 2.

2. Materials and method

2.1. Selection of dataset and generation of molecular descriptors

2.1.1. Data set

In this stage, the data set of the anti-HAT activities of sixty 2-phenylimidazopyridines derivatives were collected from the literature [18, 35]. The molecular structures of the studied molecules with their activity are presented in Fig. 3 and Table 1. All experimental activity values EC_{50} (of compound required to inhibit growth by 50%) were converted to the negative logarithm of EC_{50} ($pEC_{50} = -\log_{10}(EC_{50})$).

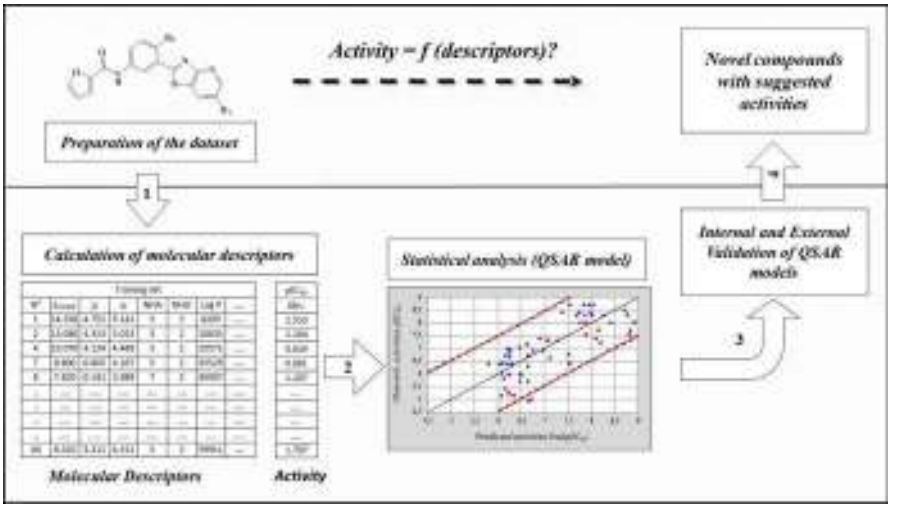

Fig. 2. Flow chart of the methodology used in this work.

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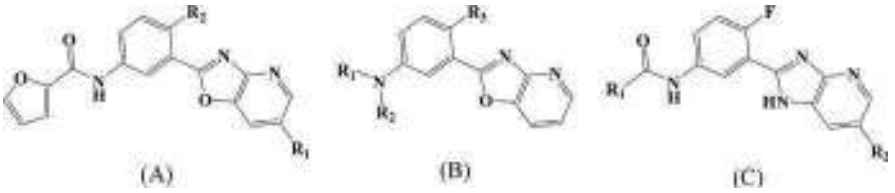

Fig. 3. Chemical structures of the studied compounds skeletons.

2.1.2. Molecular descriptors

Electronic and Lipinski's parameters were calculated using *Gaussian 03W* and *ChemOffice* programs, respectively [21, 22], to predict the correlation between these descriptors of the studied molecules with their anti-HAT activities and to develop linear model. Table 2 shows the used descriptors in this study.

2.2. Data set

In this stage, linear QSAR model was developed and evaluated to predict the studied activities of compounds. The descendent multiple linear regression (MLR) analysis available in *XLSTAT* software [23], based on the elimination of aberrant descriptors (one by one) until a valid model (including the critical probability: *p-value* <0.05 for descriptors and for the model), was employed to find a linear model of the activity of interest, which takes the form below:

$$Y = a_0 + \sum_{i=1}^{n} a_i x_i$$

Where:

Y: the studied activity, which is, the dependent variable; a_0: the intercept of the equation; xi: the molecular descriptors; a_i: the coefficients of those descriptors.

This method is one of the most popular methods of QSAR due to its simplicity in operation, reproducibility and ability to allow easy interpretation of the features used. The important advantage of the linear regression analysis is its transparent nature, therefore, the algorithm is accessible and predictions can be made easily [20].

In order to propose models and to evaluate quantitatively the physicochemical effects of the substituents on the studied activities, we submitted the data matrix constituted obviously from the used variables (descriptors) corresponding to the dataset molecules to a MLR. We use the coefficients R^2, MSE and *p-value* to select the best regression performance [24]. Where:

1. The R-squared (R^2) also called the coefficient of determination, which is the proportion of variance (%) in the dependent variable that can be explained by the independent variable. Since R^2 value is adopted in various research disciplines, there is no standard guideline to determine the level of predictive acceptance.

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Table 1. Chemical structures and anti-HAT activities of studied compounds.

	N°	R_1	R_2	R_3	pEC_{50}
(A)	1	H	Cl		6.658
	2	H	F		6.921
	3	H	CH_3		6.367
	4	H	CN		6.398
	5	Br	F		6.638
	6	CN	F		6.420
	7	Phenyl	F		7.398
	8 (*)	4-fluorophenyl	F		7.301
	9	3-chlorophenyl	F		7.301
	10	4-MeO-phenyl	F		6.770
	11 (*)	4-phenylphenyl	F		6.377
(B)	12	5-methylfuran-2-carbonyl	H	F	6.699
	13	3-methylfuran-2-carbonyl	H	F	7.000
	14	3-furanoyl	H	F	6.824
	15	benzoyl	H	Cl	5.149
	16	oxazole-5-carbonyl	H	F	5.721
	17	2-thiophenyl	H	Cl	5.824
	18 (*)	3-pyridinecarbonyl	H	F	5.155
	19	pyrazine-2-carbonyl	H	F	6.046
	20 (*)	N-methylpyrrole-2-carbonyl	H	F	5.959
	21 (*)	methylsulfonyl	H	Cl	5.215
	22	2-furancarbothioyl	H	F	6.387
	23	2-furanoyl	2-acetyl	F	6.301
	24	2-furanoyl	2-furanoyl	F	6.921
	25	benzyl	Benzyl	F	5.959
	26	methylcarbamoyl	H	F	5.420
	27	isopropylcarbamoyl	H	Cl	6.000
	28	phenylcarbamoyl	H	Cl	4.921
	29	dimethylcarbamoyl	H	Cl	6.398
	30	1-pyrrolidinoyl	H	Cl	7.046
	31	1-piperidinoyl	H	Cl	5.721
(C)	32	2-furanyl	H		6.699
	33 (*)	2-furanyl	Cl		7.155
	34	2-furanyl	F		6.699
	35	2-furanyl	5-Cl		5.000
	36	2-furanyl	7-Cl		6.921

(*continued on next page*)

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Table 1. (*Continued*)

N°	R_1	R_2	R_3	pEC_{50}
37	N-pyrrolidinyl	Cl		7.301
38	N-pyrrolidinyl	phenyl		8.699
39	N-pyrrolidinyl	3-methoxyohenyl		8.000
40 (*)	N-pyrrolidinyl	2-methoxyphenyl		8.301
41	N-pyrrolidinyl	3-chlorophenyl		8.699
42	N-pyrrolidinyl	2-chlorophenyl		8.301
43	N-pyrrolidinyl	3-acetylphenyl		8.523
44	N-pyrrolidinyl	3-methylphenyl		8.699
45 (*)	N-pyrrolidinyl	3-trifluoromethyoxyphenyl		7.523
46 (*)	N-pyrrolidinyl	3-methyl-4-fluorophenyl		7.699
47 (*)	N-pyrrolidinyl	3-NH_2-phenyl		8.000
48	N-pyrrolidinyl	3-furanyl		8.398
49	N-pyrrolidinyl	3-thiophenyl		8.699
50	N-pyrrolidinyl	2-thiophenyl		8.398
51	N-pyrrolidinyl	3-pyridyl		8.301
52 (*)	N-pyrrolidinyl	5-(2-chloropyridyl)		8.000
53	N-pyrrolidinyl	4-(2-chloropyridyl)		8.398
54	N-pyrrolidinyl	5-(3-methylpyridyl)		8.000
55	N-pyrrolidinyl	5-(2-methoxypyridyl)		8.301
56	N-pyrrolidinyl	5-(3-pyrrolidino)		7.699
57	N-pyrrolidinyl	5-(3-chloropyrimidinyl)		8.301
58 (*)	N-pyrrolidinyl	5-pyrimidinyl		7.523
59	N-pyrrolidinyl	5-(2-methoxypyrimidinyl)		7.222
60	N-pyrrolidinyl	5-(2-chloropyrimidinyl)		7.398

(*): Test set compounds. $pEC_{50} = -\log_{10}(EC_{50})$.

Henseler et al. [25] and Hair et al [26, 27] proposed a rule of thumb for acceptable R^2 with 0.75, 0.50, and 0.25 are described as substantial, moderate and weak respectively.

Hence, Zikmund et al. and Moore et al. proposed other rule of thumb for interpreting the strength of a relationship based on its R-squared value (use the absolute value of the R-squared value to make all values positive) [28, 29]:

- If R-squared value $R^2 < 0.3$ this value is generally considered a none or very weak effect size,
- If R-squared value $0.3 < R^2 < 0.5$ this value is generally considered a weak or low effect size,
- If R-squared value $0.5 < R^2 < 0.7$ this value is generally considered a Moderate effect size,

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Table 2. Values of parameters calculated for the studied compounds.

N°	E	μ	E_{HOMO}	E_{LUMO}	MW	NHA	NHD	NRB	log P
1	-40922.340	7.904	-6.113	-1.901	340.049	6	2	3	3.843
2	-31116.982	7.495	-6.062	-1.826	324.079	7	2	3	3.243
3	-29486.806	6.018	-5.939	-1.713	320.104	6	2	3	3.989
4	-30936.391	11.034	-6.432	-2.241	331.083	6	2	3	3.518
5	-101076.674	6.975	-6.153	-2.043	401.990	7	2	3	4.182
6	-33626.856	7.421	-6.348	-2.466	349.074	8	2	4	2.921
7	-37404.050	7.610	-5.949	-1.884	400.110	7	2	4	5.131
8	-40104.179	6.960	-5.983	-1.936	418.101	8	2	4	5.373
9	-49909.639	8.257	-6.067	-2.012	434.071	7	2	4	5.854
10	-40520.225	7.508	-5.686	-1.802	430.121	8	2	5	5.236
11	-43691.129	7.708	-5.839	-1.910	476.142	7	2	5	7.019
12	-32186.636	5.317	-6.146	-1.987	339.102	6	2	3	3.796
13	-32186.624	5.231	-6.245	-2.003	337.086	6	1	7	2.724
14	-31116.792	6.390	-6.030	-1.870	324.079	7	2	3	3.243
15	-40982.768	7.474	-6.166	-1.924	350.070	5	2	3	4.667
16	-31553.426	5.145	-6.267	-1.966	327.090	8	3	3	2.793
17	-49770.221	7.034	-5.890	-2.125	366.047	4	2	2	4.727
18	-31613.730	5.406	-6.222	-1.915	335.095	7	2	3	3.314
19	-32050.206	6.769	-6.173	-2.301	336.090	8	2	3	2.881
20	-31646.188	6.852	-5.952	-1.909	336.102	6	1	4	2.903
21	-47607.896	5.054	-6.359	-2.028	323.013	5	1	3	1.935
22	-39904.311	7.314	-5.869	-2.111	340.056	6	2	3	3.303
23	-35270.067	8.211	-6.247	-1.968	365.081	7	0	5	2.329
24	-40426.686	5.467	-6.361	-1.970	418.084	9	1	5	4.774
25	-36519.016	6.360	-5.499	-1.613	410.167	6	1	5	6.650
26	-27466.414	8.042	-5.960	-1.761	286.087	5	2	4	1.896
27	-39411.369	8.621	-5.993	-1.822	330.088	4	2	5	3.053
28	-42489.155	1.786	-5.891	-1.916	365.081	5	3	4	4.707
29	-38341.359	8.507	-5.957	-1.812	316.073	4	1	4	2.091
30	-40448.111	9.131	-5.884	-1.777	343.097	5	2	3	3.828
31	-41517.874	8.542	-5.927	-1.804	357.112	5	2	3	4.387
32	-30576.266	3.031	-6.117	-1.602	323.095	7	3	3	3.625
33	-43081.767	4.761	-6.292	-1.885	357.056	7	3	3	4.483
34	-33276.260	4.502	-6.216	-1.786	341.086	8	3	3	4.002
35	-43081.927	4.900	-6.281	-1.815	357.056	7	3	3	4.483
36	-43081.878	1.860	-6.339	-1.780	357.056	7	3	3	4.483
37	-42608.017	4.941	-6.020	-1.827	360.103	6	3	3	3.179
38	-36389.529	4.940	-5.774	-1.680	402.174	6	3	4	4.209

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Table 2. (*Continued*)

N°	E	μ	E_{HOMO}	E_{LUMO}	MW	NHA	NHD	NRB	log P
39	-39505.695	4.609	-5.694	-1.673	432.184	7	3	5	4.236
40	-39505.605	4.478	-5.577	-1.544	432.184	7	3	5	3.676
41	-48895.128	5.536	-5.913	-1.803	436.135	6	3	4	4.951
42	-48895.018	5.269	-5.881	-1.704	436.135	6	3	4	4.701
43	-40543.039	6.462	-5.862	-1.776	444.184	7	3	5	3.749
44	-37459.374	4.947	-5.736	-1.655	416.189	6	3	4	4.708
45	-47606.991	5.648	-5.912	-1.805	486.156	10	3	6	5.345
46	-40159.542	4.670	-5.759	-1.699	434.180	7	3	4	4.880
47	-37895.697	6.101	-5.482	-1.614	417.184	7	4	4	3.162
48	-36328.934	4.630	-5.691	-1.680	392.153	7	3	4	3.385
49	-45117.304	5.511	-5.726	-1.688	408.130	6	3	4	5.213
50	-45117.314	5.785	-5.634	-1.763	408.130	6	3	4	5.423
51	-36825.916	3.244	-5.931	-1.806	403.169	7	3	4	4.245
52	-49331.575	4.023	-6.029	-1.933	437.130	7	3	4	5.010
53	-49331.591	4.764	-6.111	-2.046	437.130	7	3	4	5.010
54	-37895.779	2.889	-5.899	-1.776	417.184	7	3	4	4.833
55	-39942.234	2.459	-5.734	-1.714	433.179	8	3	5	5.154
56	-42577.963	2.351	-5.259	-1.654	472.227	8	3	5	5.112
57	-49331.478	4.961	-6.042	-1.940	437.130	7	3	4	5.010
58	-37262.327	5.486	-6.061	-1.960	404.164	8	3	4	3.338
59	-40378.895	3.634	-5.918	-1.830	434.175	9	3	5	4.373
60	-49767.937	6.555	-6.138	-2.084	438.125	8	3	4	4.065

- If R-squared value $R^2 > 0.7$ this value is generally considered strong effect size.

2. The mean square error (MSE): measure the average squared difference between the predicted and experimental activities values.

$$MSE = \frac{1}{N}\sum_{1}^{N}\left(y_i^{pred} - y_i^{obs}\right)$$

N: The number of data points

y_i^{pred}: The predicted (calculated by the model) value for data point i.

y_i^{obs}: The actual (observed) value for data point i.

The MSE is always strictly positive, and a good model will be with MSE values closer to zero, i.e. the good model will be with minimize the sum of the squared difference between the true and estimated values [30].

3. *P-value*: the significance level, which gives an indication of the probability that a QSAR is a significant occurrence.

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In order to assess the significance of the models and its accurate prediction ability for new compounds:

4. The variance inflation factor VIF [31] to detect the absence of the multicollinearity between descriptors was used; models with descriptors correlated with each other are not significant. The VIF was defined as $1/(1-R^2)$, where R is the coefficient of correlation between one descriptor and all other descriptors in model. A VIF value greater than 5.0 indicates that the model is unstable; a value between 1.0 and 4.0 indicates that the model is acceptable [32].
5. In addition, an internal validation procedure (leave-one-out cross validation) was employed, in which one compound is removed and the rebuilt model with the remaining molecules is used to predict the response of the eliminated compound. This one is then returned and a second is removed, and the cycle is repeated, and so on until all compounds have been removed one by one, and an overall correlation coefficient R_{cv} is computed [33]. A model is considered acceptable when the value of R^2_{cv} exceeds 0.6 [27, 32].
6. After the model is built, an external prediction is necessary. This one remains the only way to determine both the generalizability of QSAR model for new chemicals and the true predictive power of the models. In this external validation, the obtained model was used to predict the activities of a test set comprising compounds that are similar to though not used in the training set. This is usually performed by splitting a data set into a training set a test set, typically in a 1:5 ratio [34].
7. A model is valid only within its training domain and new molecules must be considered as belonging to the domain before the model is applied (OECD Principle 3 [35]). Without applicability domain (AD), each model can predict the activity of any compound, even with a completely different structure from those included in the study. Therefore, the AD is a tool to find out compounds that are outside of the built QSAR model and it detects outliers present in the training set compounds. There are several methods for defining the applicability domain (AD) of QSAR models [36], but the most common one is determining the leverage values hi ($hi = x_i^t (X^t X)^{-1} x_i$ ($i = 1,2,\ldots n$)) for each compound, where: x_i: the descriptor row-vector of query compound, X: the n*(k-1) matrix of k model descriptor values for *n* training set compounds and the superscript *t* refers to the transpose of matrix/vector [37]. In this study, we use the *Williams* plot; in this plot, the applicability domain is established inside a squared area within standard deviation $\pm$ x (in this study $x = 2.5$; "three sigma rule" [38]) and a leverage threshold h* ($h^* = 2.5*(k+1)/n$) [39]. Where: n is the number of training set compounds, k is the number of model descriptors. The leverage (h) greater than the warning leverage (h*) suggested that the compound was very influential on the model [40].
8. Further, the y-randomization approach was performed to ensure the robustness of a predictive model. Often, it is used along with the cross-validation. It consists of

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repeating the calculation procedure with randomized activities and subsequent probability assessment of the resultant statistics. The dependent variable vector is randomly shuffled and a new predictive model is developed using the original independent variable matrix. The new predictive models (after several repetitions) are expected to have low R^2 and R^2_{cv} values. If the opposite happens, then an acceptable model cannot be obtained for the specific modelling method and data [41]. Another parameter, cRp^2 is also calculated which should be more than 0.5 for passing this test: $cRp^2 = R^* \sqrt{(R^2 - (Average\ Rr)^2)}$. Where: Average Rr = average 'R' of random models [42].

3. Results and discussions

3.1. Molecular descriptors

From the results of the density functional theory DFT (B3LYP/6-31G (d)) calculations, following quantum chemistry descriptors were obtained for building the model: total energy E, dipole moment μ, highest occupied molecular orbital energy E_{HOMO} and lowest unoccupied molecular orbital energy E_{LUMO}.

The five Lipinski's parameters calculated are: molecular weight MW, number of H-bond acceptors NHA, number of H-bond donors NHD, number of rotatable bonds NRB and octanol/water partition coefficient log P (Table 2).

3.2. Multiple linear regression (MLR)

The QSAR analysis was performed using calculated molecular descriptors and the experimental values of the anti-HAT activities for the forty-eight 2-phenylimidazopyridines derivatives (effect). The established MLR model is represented by the following equation along with the values of the statistical parameters:

$$pEC_{50} = 3.036 + 1.196\ \mathbf{E_{LUMO}} + 0.019\ \mathbf{MW} + 0.301\ \mathbf{NHD} - 0.398\ \mathbf{logP} \quad (1)$$

$R^2 = 0.598$; $R = 0.773$; MSE = 0.508; p-value $< 10^{-4}$

The values of calculated activities from Eq. (1) have been presented in Table 3 and the correlations of calculated and observed activities values are illustrated in Fig. 4.

The *p-value* is lower than 0.0001, it means that we would be taking a lower than 0.01% risk in assuming that the null hypothesis (no effect of the explanatory variables) is wrong D equation has statistically significance. Therefore, we can conclude with confidence that the selected variables do bring a significant amount of information.

The value of R^2 and the MSE indicate that the proposed model is predictive and reliable.

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Table 3. Observed and predicted activities using the MLR models for the training set.

N°	pEC_{50}	MLR	Residues	N	pEC_{50}	MLR	Residues
1	6.658	6.250	0.408	30	7.046	6.463	0.584
2	6.921	6.278	0.643	31	5.721	6.472	-0.751
3	6.367	6.041	0.326	32	6.699	6.676	0.024
4	6.398	5.804	0.595	34	6.699	6.645	0.054
5	6.638	7.115	-0.477	35	5.000	6.720	-1.720
6	6.420	6.112	0.308	36	6.921	6.762	0.159
7	7.398	6.891	0.507	37	7.301	7.283	0.019
9	7.301	7.091	0.210	38	8.699	7.842	0.857
10	6.770	7.514	-0.744	39	8.000	8.406	-0.406
12	6.699	6.148	0.551	41	8.699	8.040	0.660
13	7.000	6.217	0.783	42	8.301	8.258	0.043
14	6.824	6.225	0.599	43	8.523	8.703	-0.180
15	5.149	6.084	-0.935	44	8.699	7.938	0.761
16	5.721	6.647	-0.926	48	8.398	7.981	0.417
17	5.824	6.121	-0.297	49	8.699	7.545	1.154
19	6.046	6.081	-0.035	50	8.398	7.371	1.027
22	6.387	6.214	0.173	51	8.301	7.695	0.606
23	6.301	6.643	-0.342	53	8.398	7.744	0.654
24	6.921	6.968	-0.047	54	8.000	7.762	0.238
25	5.959	6.499	-0.540	55	8.301	8.010	0.291
26	5.420	6.174	-0.754	56	7.699	8.835	-1.136
27	6.000	6.472	-0.472	57	8.301	7.872	0.429
28	4.921	6.661	-1.740	59	7.222	8.201	-0.979
29	6.398	6.301	0.097	60	7.398	8.094	-0.696

The VIF values of all four descriptors in MLR model are smaller than 4.0 (VIF = 1.173, 2.170, 1.270 and 2.094 for E_{LUMO}, MW, NHD and log P, respectively) indicating that there is no collinearity among the selected descriptors and the resulting model has good stability.

The obtained model was validated internally by the *leave-one-out* cross validation technique, the cross-validation coefficient R^2cv for the model was determined based on the predictive ability of the model. The value of R^2cv is higher than 0.5 (R^2cv = 0.509), it indicates the better predictively of the model.

True predictive power of this model is to test their ability to predict perfectly the pEC_{50} of compounds from an external test set (compounds that were not used for the developed model), the pEC_{50} of the remained set of 12 compounds are deduced from the quantitative model proposed with the compounds used in training set by

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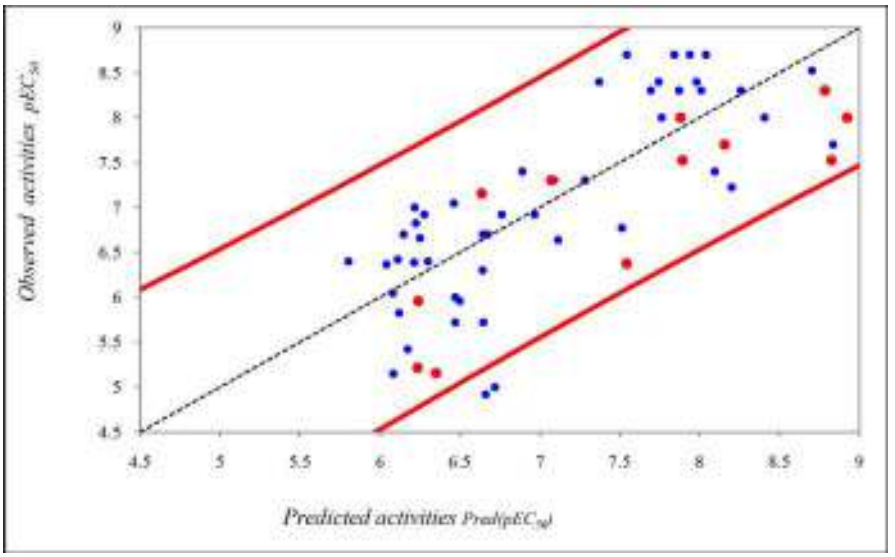

Fig. 4. Correlations of observed and predicted activities (training set in blue and test set in red) values calculated using MLR models.

MLR. This model will be able to predict the activities of test set molecules in agreement with the experimentally determined value. The observed and calculated pEC_{50} values are given in Table 4. The predictive capacity of the models that was judged, the higher value of R^2test (R^2test = 0.700) indicate the improved predictively of the model.

In the Eq. (1), the number of H-bond donors NHD, the lowest unoccupied molecular orbital energy E_{LUMO} and the molecular weight MW influence positively the

Table 4. Chemical descriptors, observed and MLR predicted activities for the test set.

Test Set					pEC_{50}	
N°	E_{HOMO}	MW	NHD	logP	Obs.	MLR
8	-1.936	418.101	2	5.373	7.301	7.072
11	-1.910	476.142	2	7.019	6.377	7.543
18	-1.915	335.095	2	3.314	5.155	6.351
20	-1.909	336.102	1	2.903	5.959	6.239
21	-2.028	323.013	1	1.935	5.215	6.235
33	-1.885	357.056	3	4.483	7.155	6.636
40	-1.544	432.184	3	3.676	8.301	8.783
45	-1.805	486.156	3	5.345	7.523	8.824
46	-1.699	434.180	3	4.880	7.699	8.156
47	-1.614	417.184	4	3.162	8.000	8.922
52	-1.933	437.130	3	5.010	8.000	7.880
58	-1.960	404.164	3	3.338	7.523	7.892

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activities and the octanol/water partition coefficient log P influence negatively the activities.

By definition:

- Molecular weight MW is the sum of the masses of all the atoms in the molecular formula of the molecule. This descriptor has been used as a descriptor in systems such as transport studies where diffusion is the mode of operation. It is an important variable in QSAR studies pertaining to cross resistance of various drugs in multidrug resistant cell lines [43, 44]. For orally delivered drugs, the molecular weight must be less than or equal to 500 Daltons [45].
- Partition coefficient octanol-water (Log P) is the ratio of concentrations of a substance in a mixture of two solvents, octanol and water. Both solvents are immiscible and therefore form two phases [46].

$$\mathrm{LogP} = \log \frac{[\mathrm{Octanol}]}{[\mathrm{Water}]}$$

The LogP is the most useful parameter for the characterization of hydrophobicity (and polarity) of compounds [47]. It is an important variable in QSAR studies because the distribution of chemicals between fatty and aqueous phases of a biological system could totally account for the variation in activities [48]. For orally delivered drugs, the partition coefficient octanol-water must be less than 5 [45].

- The number of H-bond Donors NHD is a crucial descriptor in the description of diverse processes occurring in condensed media such as dissolving, partitioning, solubilisation, etc. Drug action and bioavailability critically depends on aqueous solubility, blood-tissue distribution, and specifically on hydrogen binding to receptor active sites and transport proteins [49]. For orally delivered drugs, the hydrogen bond donors must be less than 5 [45].
- The lowest unoccupied molecular orbital energy, E_{LUMO}: HOMO and LUMO refer to highest occupied molecular orbital and lowest unoccupied molecular orbital. According to the frontier orbital theory, the nucleophilic attack occurs by electron flow from the HOMO of the nucleophile into the LUMO of the electrophile. In stable molecules, occupied electrons always reside into orbitals with negative energies and unoccupied orbitals have positive energies. The energies of HOMO and LUMO are related to the reactivity of the molecule: molecules with electrons at accessible (near-zero) HOMO levels tend to be good nucleophiles because it does not cost much to donate these electrons toward making a new bond. Similarly, molecules with lower LUMO energies tend to be good electrophiles because it does not cost much to place an electron into such an orbital [50, 51].

Comparing the importance of each descriptor on pEC_{50} of 2-phenylimidazopyridines, one must know the standardized coefficient or the *t-test* values of them in the model

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equation. The bigger the absolute value of the *t-test* value is, the greater the influence of the descriptor is. The *t-test* values for our model descriptors are 1.928, 5.714, 1.883 and -2.639 for E_{LUMO}, MW, NHD, and logP, respectively. This means that the *t-test* value of logP is larger than that of other three descriptors, which indicate that in this model, the influence of MW on activity is stronger than that of the others.

Consequently, if we want to increase the value of the activity, we will:

- Decrease the logP (with negative sign in the model) value, for which we must substitute the 2-phenylimidazopyridines derivatives for hydrophilic ("water-loving") substituents. This means that a substitution with a polar and ionic group (such as: -OH, -COOH, $-NH_2$) may lead to high activity values.
- Increase the E_{LUMO} value, for which we suggests the substitution of the 2-phenylimidazopyridines derivatives with a stronger accepting electron ability group, positively charged or neutral species having vacant orbitals that are attracted to an electron rich centre (such as ROX, BH, $-NO_2$).
- Increase the NHD (with positive sign in the model) value, for which substituting the 2-phenylimidazopyridines derivatives by heteroatom attached to one or more hydrogen atoms.
- Increase the MW value, for which increasing the molecular size.

In the conclusion, these results illustrates that to increase the anti-HAT, we will increase the molecular size and substitute the 2-phenylimidazopyridines derivatives with polar, ionic, stronger accepting electron ability group and heteroatoms attached to one or more hydrogen atoms.

This study is in agreement with the conclusions of a previous QSAR studies [52] which revealed the importance the presence of five membered rings, especially the pyrrolidine ring, is beneficial for the HAT activity of the present series of molecules; and the interesting pattern of H-bond donor/acceptor nitrogen atoms in attaining various tautomeric forms, thereby, providing additional flexibility to the molecules to acquire bioactive tautomeric form(s) while interacting with the target receptor.

Further, before performing the external validation of a model, it is very important to check for the presence of systematic error that violates the basic assumptions of the least squares regression model. If high systematic error (bias) is present in the model, then such model should be discarded and performing any external validation test is of no use on such biased model. Xternal Validation Plus is a tool that checks the presence of systematic errors in the model and further computes all the required external validation parameters, while judging the performance of actual prediction quality of a QSAR model based on recently proposed MAE-based criteria [53];

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Table 5. Output file summarize the information including all the external validation parameters that are required to judge the performance of prediction quality of the MLR model.

User Input File Info.	File Name	Sample_TestSet.xlsx
Model biasness test	nPE/nNE	0.3333
	nNE/nPE	3.0000
	|MPE/MNE|	0.3620
	|MNE/MPE|	2.7623
	AAE - |AE|	0.1447
	R'2 (Residuals; serial correlation)	0.0421
	R'2 (Residuals and Yobs values)	0.1383
	R^2Test (100% data)	0.6997
	R_0^2Test (100% data)	0.6978
	$R_0^{2'}$Test (100% data)	0.6123
Classical Metrics	Q2F1 (100% data)	0.4622
(for 100% data)	Q2F2 (100% data)	0.4291
	Scaled Avg.Rm'2 (100% data)	0.5094
	Scaled DeltaRm'2 (100% data)	0.2532
	CCC(100% data)	0.7351
	R'2Test (95% data)	0.7330
	R0'2Test (95% data)	0.7321
Classical Metric	R0"2Test (95% data)	0.4763
(after removing	Q2F1 (95% data)	0.5674
5% data with	Q2F2 (95% data)	0.5506
high residuals)	ScaledAvgRm2 (95% data)	0.5028
	ScaledDeltaRm2 (95% data)	0.2536
	CCC(95% data)	0.7703
Error-based metrics (for 100% data)	RMSEP (100% data)	0.7834
	SD (100% data)	0.4210
	SE (100% data)	0.1215
	MAE (100% data)	0.6718
	RMSEP (95% data)	0.7181
Error-based metric	SD (95% data)	0.3896
(after removing 5% data	SE (95% data)	0.1175
with high residuals)	MAE (95% data)	0.6145
	MAE+3*SD (95% data)	1.7834
	NCompTest	12.0000
Number of test set compounds.	Train range	7.8195

(*continued on next page*)

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Table 5. (*Continued*)

User Input File Info.	File Name	Sample_TestSet.xlsx
Range and Mean (train and test)	TrainYMean	6.7604
	Test range	3.1460
	TestYMean	7.0173
Distribution of observed response values of Test set around Test mean (in %)	%Y (±0.5)TestMean	16.6667
	%Y (±1.0)TestMean	66.6667
	%Y (±1.5)TestMean	83.3333
	%Y (±2.0)TestMean	100.0000
Distribution of observed response values of Test set around Train mean (in %)	%Y (±0.5)TrainMean	16.6667
	%Y (±1.0)TrainMean	58.3333
	%Y (±1.5)TrainMean	75.0000
	%Y (±2.0)TrainMean	100.0000
Distribution of prediction errors (in %)	%NComp>(0.1*TR)	41.6667
	%NComp>(0.15*TR)	16.6667
	%NComp>(0.2*TR)	0.0000
	%NComp>(0.25*TR)	0.0000
Threshold values utilized to judge the model predictions	(0.1*TrainingSetRange)	0.7820
	(0.15*TrainingSetRange)	1.1729
	(0.2*TrainingSetRange)	1.5639
	(0.25*TrainingSetRange)	1.9549
RESULT (MAE-based criteria applied on 95% data)	Prediction Quality	MODERATE

Xternal Validation Plus indicates the absence of systematic errors in the model and a moderate performance of prediction quality of a QSAR model based on proposed MAE-based criteria (Table 5).

In the next step, all calculations were repeated with randomized activities of the training set compounds as well to evaluate model robustness (y-randomization test). In the present case, 100 random trials were run for the MLR model. None of the random trials could match the original model (Table 6). The standalone QSAR-tools ("Programs") available online at http://dtclab.webs.com/software-tools and http://teqip.jdvu.ac.in/QSAR_Tools/ ("Websites") was employed in the y-randomization.

The average value of R, R^2 and R^2_{CV} are 0.282, 0.087 and -0.155 respectively, the cRp^2 value equal a 0.557 (more than 0.5), and all the new QSAR models having significantly low R^2 and R^2_{CV} values for the 100 trials, which confirm that the developed QSAR models are robust.

The applicability domain (AD) of the MLR models was evaluated by leverage analysis expressed as *Williams* plot (Fig. 5), in which the standardized residuals and the

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Table 6. Y-randomization test results for MLR models.

Random	R	R^2	R^2_{CV}	Random	R	R^2	R^2_{CV}	Random	R	R^2	R^2_{CV}	Random	R	R^2	R^2_{CV}
1	0,119	0,014	-0,319	26	0,141	0,020	-0,246	51	0,212	0,045	-0,230	76	0,219	0,048	-0,185
2	0,382	0,146	-0,049	27	0,398	0,158	-0,122	52	0,278	0,077	-0,113	77	0,202	0,041	-0,222
3	0,419	0,176	0,013	28	0,242	0,059	-0,270	53	0,349	0,122	-0,073	78	0,249	0,062	-0,248
4	0,212	0,045	-0,159	29	0,388	0,150	-0,072	54	0,251	0,063	-0,235	79	0,341	0,116	-0,112
5	0,196	0,039	-0,177	30	0,133	0,018	-0,224	55	0,354	0,125	-0,136	80	0,154	0,024	-0,192
6	0,368	0,135	-0,148	31	0,273	0,074	-0,165	56	0,282	0,079	-0,096	81	0,314	0,099	-0,178
7	0,459	0,210	-0,040	32	0,317	0,100	-0,130	57	0,239	0,057	-0,251	82	0,166	0,028	-0,184
8	0,390	0,152	-0,022	33	0,232	0,054	-0,169	58	0,270	0,073	-0,144	83	0,302	0,091	-0,121
9	0,319	0,102	-0,139	34	0,282	0,079	-0,175	59	0,300	0,090	-0,151	84	0,347	0,120	-0,224
10	0,323	0,104	-0,177	35	0,169	0,029	-0,194	60	0,296	0,088	-0,201	85	0,377	0,142	-0,066
11	0,176	0,031	-0,235	36	0,166	0,028	-0,195	61	0,283	0,080	-0,107	86	0,256	0,066	-0,168
12	0,293	0,086	-0,145	37	0,174	0,030	-0,253	62	0,336	0,113	-0,086	87	0,318	0,101	-0,225
13	0,488	0,238	0,104	38	0,403	0,162	-0,072	63	0,404	0,164	-0,007	88	0,398	0,158	-0,057
14	0,377	0,142	-0,052	39	0,243	0,059	-0,145	64	0,442	0,195	0,003	89	0,253	0,064	-0,139
15	0,317	0,101	-0,119	40	0,458	0,210	-0,025	65	0,317	0,101	-0,109	90	0,458	0,210	0,004
16	0,395	0,156	-0,086	41	0,261	0,068	-0,197	66	0,348	0,121	-0,160	91	0,396	0,157	-0,068
17	0,245	0,060	-0,268	42	0,166	0,028	-0,230	67	0,164	0,027	-0,228	92	0,430	0,185	-0,070
18	0,264	0,070	-0,150	43	0,231	0,053	-0,193	68	0,263	0,069	-0,299	93	0,256	0,065	-0,150
19	0,246	0,060	-0,154	44	0,201	0,041	-0,235	69	0,210	0,044	-0,202	94	0,279	0,078	-0,224
20	0,305	0,093	-0,138	45	0,271	0,073	-0,122	70	0,285	0,081	-0,104	95	0,194	0,038	-0,191
21	0,154	0,024	-0,179	46	0,225	0,051	-0,238	71	0,190	0,036	-0,287	96	0,260	0,068	-0,122
22	0,269	0,073	-0,257	47	0,336	0,113	-0,075	72	0,349	0,122	-0,080	97	0,204	0,042	-0,268
23	0,151	0,023	-0,225	48	0,373	0,139	-0,071	73	0,285	0,081	-0,142	98	0,324	0,105	-0,182
24	0,286	0,082	-0,149	49	0,261	0,068	-0,171	74	0,210	0,044	-0,192	99	0,279	0,078	-0,261
25	0,142	0,020	-0,313	50	0,364	0,132	-0,088	75	0,219	0,048	-0,152	100	0,120	0,014	-0,217
Average				R		R^2		R^2_{CV}				cR_p^2			
				0,282		0,087		-0,155				0,557			

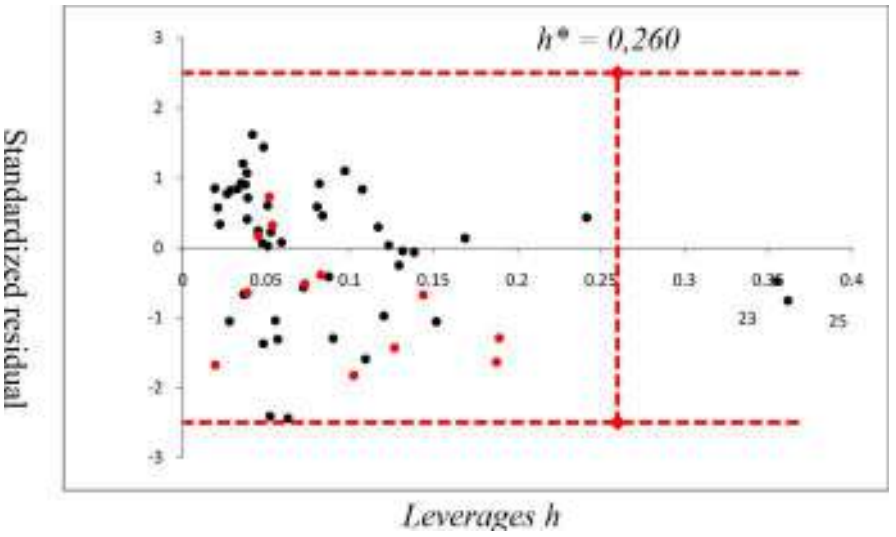

Fig. 5. Williams plot of standardized residual versus leverage for the MLR model (With: h* = 0.260 and residual limits = ±2.5); Train samples in black colour and test samples in red colour).

leverage threshold values (h* = 0.260) were plotted. Any new value of predicted pEC_{50} data must be considered reliable only for those compounds that fall within this AD on which the model was constructed.

From the Fig. 5, it is obvious that all the compounds have a standard deviation into the ±x interval (x = 2.5) and there is two responses outliers both in training set and no response outside in test set. These outliers (compounds 23 and 25) have a higher leverage which is greater than h* value of 0.260. These erroneous predictions could probably be attributed to the structural of these outsides (Fig. 6); maybe the selected

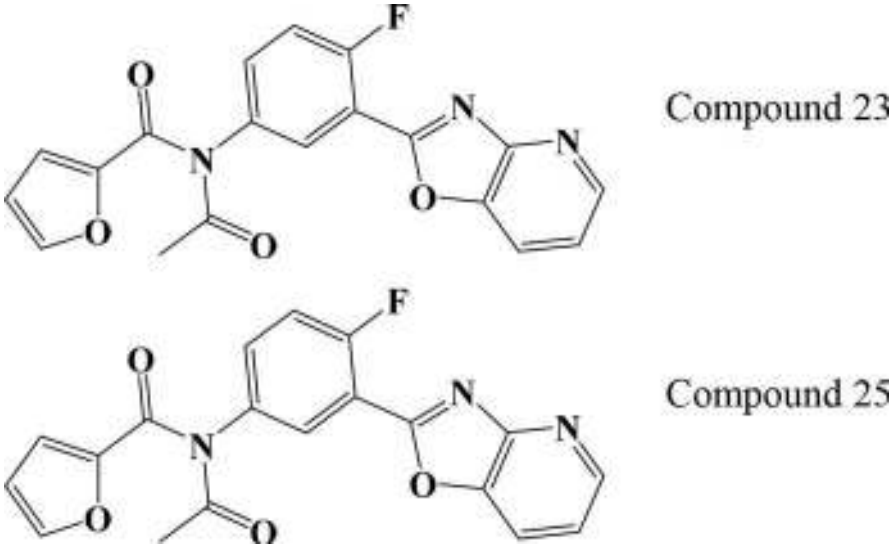

Fig. 6. Chemical structures of the outsides compounds.

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descriptors do not pay much attention to these substructures or their mechanism of action may be different. The predictions of these two compounds are extrapolations of the model, but fortunately they are all ''good leverage'' chemicals.

The results obtained by MLR are very sufficient to conclude the performance of the models. Consequently, we can design new compounds with improved values of activity than the studied compounds using this model.

Taking into account the above results, we added suitable substitutions and then we moved to calculate their activities using the proposed models Eq. (1). Therefore, the suggested model will reduce the time and cost of synthesis as well as the determination of the anti-HAT activity for the 2-phenylimidazopyridines derivatives.

According to the above discussions, the MLR model could be applied to other 2-phenylimidazopyridines derivatives accordingly to Table 1 and could add further knowledge in the improvement of new way in anti-HAT drug research. If we develop a new compound with better values than the existing ones, it may give rise to the development of more active compounds than those currently in use.

In this way, we carried out structural modification starting from compounds having the highest pEC_{50} values as template (38, 41, 44, and 49). The structures of the designed compounds and their parameter values calculated by the same methods, as well as the pEC_{50} values theoretically predicted by the MLR model are listed in Table 7.

Table 7. Values of descriptors, calculated anti-HAT activity pEC_{50} and leverages (h) for the new designed compounds (derivatives of the skeleton (C) of the Fig. 1).

	Designed compounds	E_{LUMO}	MW	NHD	logP	pEC_{50}	leverage
X_1	R_1=COOH; R_2=COOH	-2.129	421.095	5	2.773	8.837	0.436
X_2	R_1=NO_2; R_2= NO_2	-2.658	427.117	7	0.745	9.125	1.596
X_3	R_1=NH_2; R_2= p-PhNH_2	-1.680	363.138	5	1.796	8.669	0.588
X_4	R_1=N-pyrrolidinyl; R_2= m-PhNO_2	-1.780	446.163	4	4.048	8.919	0.170
X_5	R_1=N-pyrrolidinyl; R_2= p-PhNO_2	-1.934	446.163	4	4.048	8.735	0.145
X_6	R_1=N-pyrrolidinyl; R_2= p-PhOH	-1.627	418.168	4	3.733	8.698	0.191
X_7	R_1=N-pyrrolidinyl; R_2= m,p-Ph$(OH)_2$	-1.650	434.163	3	3.327	8.834	0.208
X_8	R_1= N-pyrrolidinyl; R_2=3-thio-2,4-dihydroxyphenyl	-1.493	440.120	5	3.926	9.498	0.395
X_9	R_1= N-pyrrolidinyl; R_2=3-methyl-4-hydroxyphenyl	-1.600	432.184	4	4.182	8.817	0.176
X_{10}	R_1= N-pyrrolidinyl; R_2=3-methyl-6-hydroxyphenyl	-1.543	432.184	4	3.932	8.984	0.214
X_{11}	R_1= N-pyrrolidinyl; R_2=3-methyl-5-hydroxyphenyl	-1.637	432.184	4	4.232	8.753	0.164

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4. Conclusion

The results of the QSAR analysis suggest that derivatives of 2-phenylimidazopyridines with the following structural feature may exhibit great anti-HAT activity by increasing molecular size and substitute the 2-phenylimidazopyridines derivatives with polar, ionic, stronger accepting electron ability group and heteroatoms attached to one or more hydrogen atoms.

According to developed model, the most important findings of this research are that we have designed and suggest some new compounds with possible great activities. Consequently, the proposed models can be used in anti-HAT drug research for the 2-phenylimidazopyridines derivatives. These results encourage the collaboration between theoretical researchers and pharmacologists, academic or industrial, because the last ones many times are groping new drugs.

Declarations

Author contribution statement

Samir Chtita: Analyzed and interpreted the data; Wrote the paper.

Mounir Ghamali, Abdellah Ousaa, Assia Belhassan, Abdelali Idrissi Taourati: Analyzed and interpreted the data.

Adnane Aouidate: Conceived and designed the experiments.

Vijay Hariram Masand: Contributed reagents, materials, analysis tools or data; Wrote the paper.

Mohammed Bouachrine: Contributed reagents, materials, analysis tools or data.

Tahar Lakhlif: Conceived and designed the experiments.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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Quinoxalinones Based Aldose Reductase Inhibitors: 2D and 3D-QSAR Analysis

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This work is dedicated to Dr. Paola Gramatica, Italy for her outstanding contributions toward enrichment of QSAR and Cheminformatics.

Abstract: In the present work, 2D- and 3D-quantitative structure-activity relationship (QSAR) analysis has been employed for a diverse set of eighty-nine quinoxalinones to identify the pharmacophoric features with significant correlation with the aldose reductase inhibitory activity. Using genetic algorithm (GA) as a variable selection method, multivariate linear regression (MLR) models were derived using a pool of molecular descriptors. All the six-descriptor based GA-MLR QSAR models are statistically robust with coefficient of determination (R^2) > 0.80 and cross-validated $R^2 > 0.77$. The derived GA-MLR models were thoroughly validated using internal and external and Y-scrambling techniques. The CoMFA like model, which is based on a combination of steric and electrostatic effects and graphically inferred using contour plots, is highly robust with $R^2 > 0.93$ and cross-validated $R^2 > 0.73$. The established QSAR and CoMFA like models are proficient in identify key pharmacophoric features that govern the aldose reductase inhibitory activity of quinoxalinones.

Keywords: Aldose Reductase Activity · Quinoxalinones · QSAR · CoMFA like model

1 Introduction

Diabetes Mellitus (DM), caused by insulin deficiency or insulin resistance, is a chronic long-term metabolic disorder characterized by high glucose level in blood (Hyperglycemia).[1] DM has global presence with ill-effects on public health. A close link has been revealed between glucose metabolism via the overactive polyol pathway (also known as the sorbitol-aldose reductase pathway) and long-term various diabetic complications such as neuropathy, nephropathy, retinopathy, cataracts, and stroke by damaging blood vessels and peripheral nerves.[1–2]

In the polyol pathway, the enzyme aldose reductase (ALR2, EC 1.1.1.21) is responsible for the catalytic reduction of glucose to sorbitol in the presence of NADPH as a cofactor in the first and rate-controlling step of this metabolic pathway (Figure 1).[1a] Sorbitol is oxidized into fructose by sorbitol dehydrogenase along with reduction of NAD+ to NADH. Under normal conditions (normoglycemia), glucose is mostly phosphorylated to glucose-6-phosphate by hexokinase and then enters the glycolytic pathway, however, due to a relatively low affinity of ALR2 for glucose only a minor amount of glucose (~3% of glucose utilization) is metabolized through the polyol pathway.[1–2] However, the polyol metabolic pathway is activated during hyperglycemia leading to higher flux of glucose (~30% of glucose utilization) through the polyol pathway, thereby, causing higher accumulation of sorbitol, mainly in tissues demonstrating insulin-independent uptake of glucose, such as lens, kidney, retina, and peripheral nerves. Unfortunately, with the increase in concentration of sorbitol, the activity of sorbitol dehydrogenase does not augment proportionately.[1–2]

The enzyme aldose reductase (ALR2), which is a member of the aldo-keto reductase superfamily, has received wide attention from medicinal chemists, as the development and progression of chronic diabetic complications are related to the activation and/or overexpression of ALR2.[1–2] Therefore, inhibition of ALR2 offers an attractive strategy and alternant approach to avert and deferment the progress and increase

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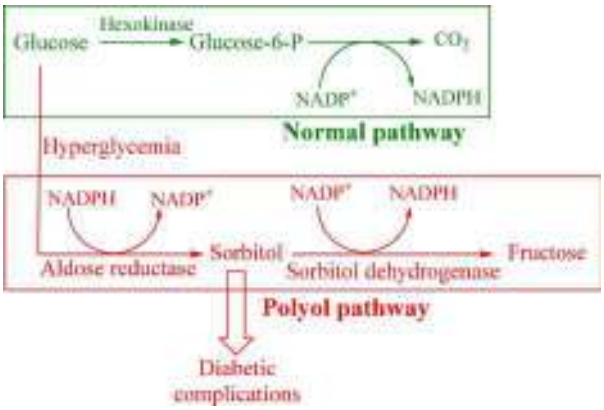


Figure 1. The normal and polyol pathways of glucose metabolism.

significant rational method for recognizing new potent lead/drug candidates and a good alternative to animal testing. CADD is a method of choice in drug designing process due to faster, economical, and result oriented high success. QSAR, molecular docking, pharmacophore modeling, etc. are some of the popular CADD methodologies that are routinely employed for identifying structural features having connection with the activity profile.[3]

Recently, research group of Wang *etal*[1b,2] reported the synthesis and aldose reductase inhibitory activity of diverse quinoxalinones. The quinoxalinones were found to be efficient inhibitors of aldose reductase with activity ranging from μM to nM. In addition, molecular docking and SAR (structure-activity relationship) were performed to under-

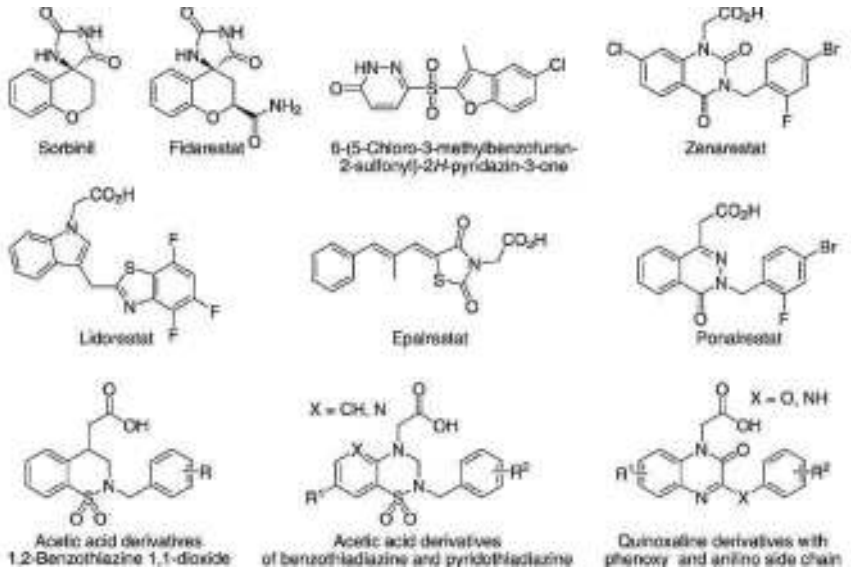


Figure 2. Previously reported aldose reductase inhibitors (ARIs).

of different diabetic complications. At present only one drug 'epalrestat' is marketed for the treatment of neuropathy in Japan, India and China. In past few decades, structurally diverse Aldose reductase inhibitors (ARIs) have been reported (Figure 2).[1b,2] Unfortunately, many of the clinically tested ARIs have been found to be inappropriate as drug candidates because of adverse pharmacokinetics, toxic effects or low efficacy, only few of them have reached advanced clinical stages.[1–2] Therefore, the search for development of highly efficient, safer and potent ARIs still persists.

Modern medicinal chemists go for various strategies to improve the pharmacological and ADMET (Absorption, Distribution, Metabolism, Excretion and Toxicity) profiles and devise a feasible synthetic route for an available lead candidate (i.e. lead optimization). In modern drug designing process, computer-aided drug design (CADD) is a

stand the different structural features that are important to augment the activity profile of quinoxalinones as aldose reductase inhibitors. But, a thorough justification for various SAR results is still required for pharmacophoric feature identification. Surprisingly, till this date, for aldose reductase inhibitory activity of quinoxalinones only one attempt has been made to develop predictive and robust CoMFA like model (ligand based drug design) using a small dataset of thirty-five quinoxalinones only.[4] According to one school of thought,[3b,c,e,f,5] QSAR and CoMFA like modeling are preferable techniques for lead optimization as these techniques not only provide in-depth idea about pharmacophoric features, but, are efficient to predict the activity of a yet to be synthesized drug candidate. Therefore, the main emphasis of the present work was to derive thriving QSAR and CoMFA like models to predict the activity and to

determine the structural features governing the aldose reductase inhibitory activity profile of novel quinoxalinones.

2 Experimental Methodology

Data set: The dataset selected for the present work comprises eighty-nine structurally diverse quinoxalinones with different type of substituents like –F, –Cl, –OH, etc. at various positions.[1b,2] The compounds were assayed against ALR2 and the reported IC_{50} varies from few micro-molar (μM) to single digit nano-molar (nM). The activity expressed as IC_{50} (95% CL) values represent the concentration required to decrease enzymatic activity by 50%. The IC_{50} values were converted to pIC_{50} ($-\log_{10}IC_{50}$) for QSAR and CoMFA like analyses. The experimental activity values IC_{50}, pIC_{50} and structural substituents have been listed in Table 1.

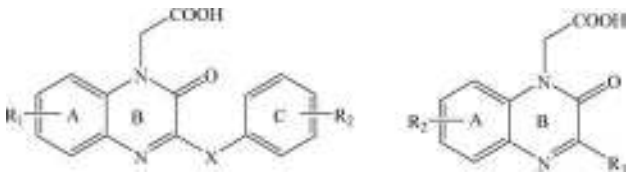


Figure 3. General structure of quinoxalinones used in the present work along with notation for aromatic rings.

3 QSAR Model Building and Validation

The structures were drawn using ChemSketch 12 freeware followed by optimization using TINKER using MMFF94 force field. *PyDescriptor*[6] and PaDEL,[7] were used to calculate a good number of 1D-to 3D-, quantum mechanical and fingerprint descriptors. This resulted in more than 28000 descriptors.[3c–e] Then, objective feature selection was performed to eliminate redundant variables, as a rule highly correlated ($R > 0.90$), constant and nearly constant variables were eliminated.[3c–e] The resultant reduced pool of descriptors consisted of 1122 descriptors only. Subjective feature selection involving genetic algorithm (GA) as a feature selection tool was employed for heuristic search of descriptors for QSAR model building. The search was limited to a set of six descriptors to avoid over-fitting and to develop easy and informative GA-MLR QSAR models. QSARINS 2.2.2 was employed to select optimum number and set of five descriptors with default settings, except for Lack of Fit (*LOF*) which was set to a value of 0.5.[5k,m,n,8] The selected fitness function used to maximize in GA was Q^2, this avoids naive Q^2 also. All the models having poor internal and external predictivity were excluded. The selected descriptors were used to build the statistically acceptable QSAR models followed by exhaustive statistical validation according to the OECD principles for QSAR model validation.[3b–f,5k,n,8c,9]

The developed QSAR models were subjected to extensive internal and external validation along with Y-randomization using QSARINS 2.2.2 to avoid over-fitting and spurious models. The different parameters for internal validation include: determination coefficient R^2, leave-one-out (LOO) cross-validation Q^2, leave-many-out (LMO) cross validation Q^2_{LMO}, coefficient of determination for Y-scrambling R^2_{Yscr}, and root mean squared error (*RMSE*). The LMO were repeated 500 times with 30% of the objects left out randomly from the training set each time; The mean value of Q^2_{LMO} has been reported. The external validation parameters are $RMSE_{ex}$, MAE_{ex}, R^2_{ex}, Q^2_{F1}, Q^2_{F2}, Q^2_{F3}, and CCC_{ex}.[3c–f,5k,n,8c,9d,e]

Applicability domain of models:[3c,e,5k,n,8c] Model validation was carried out also by checking the model applicability domain (AD), which was verified by the Williams plots. AD is a theoretical region defined by the physicochemical, structural or biological space on which the model has been developed using the training set, it's applicable to make predictions for new compounds. Thus, AD is related to interpolation rather than extrapolation. A widely accepted method for AD determination is based on leverage calculation from the diagonal values of the hat matrix using modeling molecular descriptors. It is evaluated by leverage (or hat) analysis using the formula: $h_i = x_i\ (X^T X)^{-1}\ x_i^T$ where (i = 1, …, m), x_i is the descriptor row-vector of the query compound *i*, *m* is the number of query compounds and *X* is the *np* matrix of the training set (*p* is the number of descriptors in the model and *n* is the number of compounds in the training set). The limit of the model domain is quantitatively defined by the leverage cut-off h^* and is set as $3(p+1)/n$. A leverage bigger than h^* for the training set means that the compound is very dominant in determining the model. For the prediction set (*X* outlier), it means that the prediction is the substantial extrapolation of the model and could be unreliable. Also, a compound with a standardized residual greater than 3σ (3x standard deviation units) is recognized as a Y outlier.

CoMFA like analyses: The standard procedure as mentioned in Open3DQSAR was followed to build a database of eighty-nine quinoxalinones. For successful CoMFA like analysis, appropriate alignment of 3D- structures of the molecules is very significant. To improve the success of CoMFA like analysis, Gasteiger-Marsili partial charges were assigned to all the molecules prior to descriptor calculation and alignment. For aligning the complete set of molecules, the lowest energy conformer of most active compound **61** ($IC_{50} = 0.00644$ nM) was used as a template structure in Open3DAlign. The molecules in their respective lowest conformations were superimposed on the template using the atom-based alignment option in Open3DAlign. It was followed by partial least square (PLS) analysis and 3D-contour generation with optimum number of components set to 9. Default settings and procedure as implemented in Open3DQSAR and Open3DGrid were used throughout the work.

Table 1. Substituents, experimental IC_{50} and pIC_{50} for aldose reductase activity of quinoxalinones.

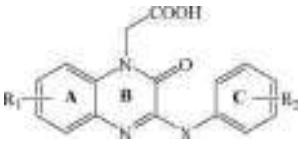
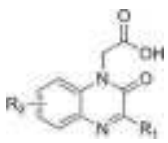
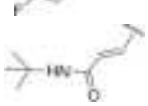
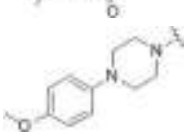
S.N.	R_1	R_2	X	IC_{50}** ALR2	pIC_{50} (M)
					
1.	H	H	–	5.981	5.223
2.	H	4-F	–	3.380	5.471
3.	7-F	4-F	–	0.874	6.058
4.	7-Cl	4-F	–	1.516	5.819
5.	4-fluorophenyl	4-F	–	2.131	5.671
6.	H	4-OH	–	2.592	5.586
7.	H	2,4-$(OH)_2$	–	0.397	6.401
8.	6-F	2,4-$(OH)_2$	–	0.063	7.201
9.	6-Cl	2,4-$(OH)_2$	–	0.095	7.022
10.	6-Br	2,4-$(OH)_2$	–	0.139	6.857
11.	7-F	2,4-$(OH)_2$	–	0.032	7.495
12.	7-Cl	2,4-$(OH)_2$	–	0.069	7.161
13.	7-Br	2,4-$(OH)_2$	–	0.091	7.041
14.	4-fluorobenzyl	2,4-$(OH)_2$	–	3.34	5.476
15.	H	3-indole	–	0.639	6.194
16.	7-Br	3-indole	–	0.368	6.434
17.	7-Cl	2-benzothiophene	–	0.238	6.623
18.	H	H	O	0.468	6.33
19.	H	H	S	0.421	6.376
20.	H	4-Br	S	0.296	6.529
21.	7-F	4-Br	S	0.191	6.719
22.	7-Cl	4-Br	S	0.326	6.487
23.	7-Br	4-Br	S	0.467	6.331
24.	6-Br	4-Br	S	0.319	6.496
25.	H	4-Cl	S	0.273	6.564
26.	7-F	4-Cl	S	0.056	7.252
27.	7-Cl	4-Cl	S	0.158	6.801
28.	7-Br	4-Cl	S	0.395	6.403
29.	H	H	CH_2	1.112	5.954
30.	H	H	CH=CH	0.820	6.086
31.	H	H	CH_2–CH_2	0.143	6.845
32.	H	4-OH	CH=CH	0.182	6.74
33.	7-F	4-OH	CH=CH	0.153	6.815
34.	H	4-OCH_3	CH=CH	4.181	5.379
35.	H	3-OCH_3, 4-OH	CH=CH	0.419	6.378
36.	H	4-OH	CH_2–CH_2	0.798	6.098
37.	7-F	4-OH	CH_2–CH_2	0.652	6.186
					
38.		H	–	1.43	5.845
39.		H	–	1.86	5.73
40.		H	–	7.53	5.123

Table 1. continued

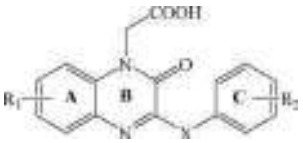
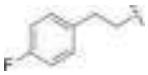
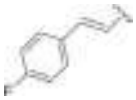
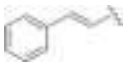
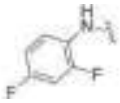
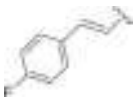
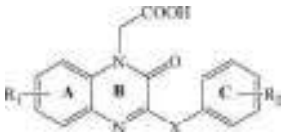
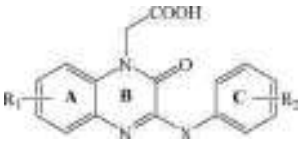
S.N.	R_1	R_2	X	IC_{50}** ALR2	pIC_{50} (M)
					
41.		H	–	1.14	5.943
42.		6-Cl	–	0.66	6.18
43.		7-Cl	–	3.88	5.411
44.		$6\text{-}NO_2$	–	0.362	6.441
45.		$6\text{-}NO_2$	–	0.283	6.548
					
46.	H	$4\text{-}CF_3$	CH_2	0.70167	6.154
47.	H	2,4,5-3F	CH_2	0.44903	6.348
48.	H	4-F	CH_2	0.92487	6.034
49.	H	4-Cl	CH_2	0.1227	6.911
50.	H	4-Br	CH_2	0.05595	7.252
51.	H	2-F,4-Br	CH_2	0.03484	7.458
52.	7-Cl	4-F	CH_2	0.272	6.565
53.	7-Cl	4-Cl	CH_2	0.07495	7.125
54.	7-Cl	4-Br	CH_2	0.02328	7.633
55.	7-Cl	2-F,4-Br	CH_2	0.01025	7.989
56.	6-Cl	4-Br	CH_2	0.10553	6.977
57.	6-Cl	2-F,4-Br	CH_2	0.05856	7.232
58.	7-F	4-F	CH_2	0.3685	6.434
59.	7-F	4-Cl	CH_2	0.03029	7.519
60.	7-F	4-Br	CH_2	0.03359	7.474
61.	7-F	2-F,4-Br	CH_2	0.00644	8.191
62.	6-F	4-Br	CH_2	0.3016	6.521
63.	7-Y[c]	4-F	CH_2	1.7954	5.746
64.	H	2-F,4-Br	O	0.22042	6.657
65.	7-Cl	2-F,4-Br	O	0.15275	6.816
66.	7-F	2-F,4-Br	O	0.12848	6.891
67.	H	4-F	NH	0.4935	6.307
68.	H	4-Br	NH	0.15031	6.823
69.	H	2-F,4-Br	NH	0.12405	6.906
70.	H	2,4-2F	NH	1.20379	5.919
71.	H	3,4,5-3F	NH	0.98685	6.006
72.	H	4-F	O	0.03274	7.485
73.	H	4-Br	O	0.02728	7.564
74.	7-F	4-F	O	0.01906	7.72
75.	7-F	4-Br	O	0.0114	7.943
76.	7-Cl	4-F	O	0.04229	7.374

Table 1. continued

S.N.	R_1	R_2	X	IC_{50}** ALR2	pIC_{50} (M)
					
77.	7-Cl	4-Br	O	0.03299	7.482
78.	7-Br	4-F	O	0.06298	7.201
79.	7-Br	4-Br	O	0.04348	7.362
80.	7-Br	2-F,4-Br	O	0.0471	7.327
81.	6-F	4-F	O	0.06987	7.156
82.	6-F	4-Br	O	0.04925	7.308
83.	6-F	2-F,4-Br	O	0.07479	7.126
84.	6-Cl	4-F	O	0.05039	7.298
85.	6-Cl	4-Br	O	0.02434	7.614
86.	6-Cl	2-F,4-Br	O	0.04633	7.334
87.	6-Br	4-F	O	0.04313	7.365
88.	6-Br	4-Br	O	0.01633	7.787
89.	6-Br	2-F,4-Br	O	0.03822	7.418

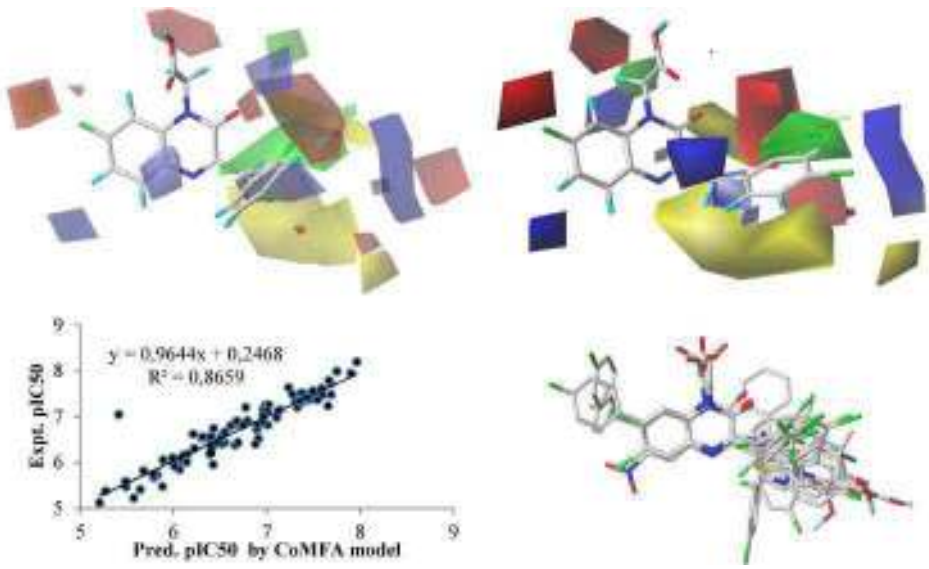


Figure 4. CoMFA like contour maps at different angles for quinoxalinones with compound **61** (most active) as a representative along with graph correlation between experimental and predicted pIC_{50} (CoMFA like model) and alignment of dataset molecules (Red: More negative charge, blue: more positive charge, Green: More bulk and yellow: Less bulky groups favourable).

4 Results and Discussion

CoMFA like analysis: CoMFA like model based on either steric or electrostatic molecular field alone had poor statistical performance with $R^2_{CV}=0.469$ and $R^2_{CV}=0.456$, respectively. However, the present CoMFA like model, comprising a combination of steric, lipophilic and electronic molecular fields, is statistically acceptable with $N_{train}=89$, leave-one-out (LOO) correlation coefficient $R^2_{CV}=0.731$, F value ($n_1=9$, $n_2=78$)$=121.961$, and $R^2=0.934$. A higher value of R^2_{CV} (>0.60) along with R^2 confirms statistical robustness of the CoMFA like model.[3d,e,9e] Further, standard error of estimate was found to be 0.190 with an optimized component of 9. This implies that the model is not only trustworthy in capturing the essence of structural features that govern the aldose reductase activity but it is very good at predicting the activity of quinoxalinones also.[3d,e,9e] The pIC_{50}values predicted by CoMFA like model have been listed in Table 2.

Table 2. Different statistical parameters for goodness of fit, internal validation and external predictive ability for model 1–5.

S. No.	Statistical Parameter	Model-1	Model-2	Model-3	Model-4	Model-5
1.	N_{tr}	89	89	72	72	72
2.	N_{ex}	00	00	17	17	17
3.	*Number of Descriptors*	06	06	06	06	06
Fitting Criteria						
4.	R^2_{tr}	0.82	0.82	0.83	0.84	0.82
5.	$R^2_{adj.}$	0.81	0.80	0.82	0.83	0.81
6.	*LOF*	0.11	0.12	0.11	0.10	0.12
7.	*Kxx*	0.21	0.16	0.25	0.17	0.21
8.	ΔK	0.09	0.11	0.06	0.12	0.09
9.	$RMSE_{tr}$	0.29	0.30	0.27	0.26	0.29
10.	MAE_{tr}	0.22	0.24	0.21	0.21	0.22
11.	RSS_{tr}	7.58	7.87	5.38	5.03	6.22
12.	CCC_{tr}	0.90	0.90	0.91	0.92	0.90
13.	*s*	0.30	0.31	0.29	0.28	0.31
14.	*F*	63.62	60.79	54.54	58.52	49.92
Internal Validation Criteria						
15.	R^2_{cv} (Q^2loo)	0.79	0.79	0.80	0.81	0.79
16.	$RMSE_{cv}$	0.32	0.32	0.30	0.29	0.32
17.	MAE_{cv}	0.24	0.26	0.23	0.23	0.25
18.	$PRESS_{cv}$	9.05	9.10	6.36	6.23	7.48
19.	CCC_{cv}	0.88	0.88	0.89	0.90	0.88
20.	Q^2_{LMO}	0.78	0.78	0.78	0.80	0.78
21.	R^2_{Yscr}	0.07	0.07	0.08	0.09	0.08
22.	Q^2_{Yscr}	−0.10	−0.10	−0.13	−0.13	−0.13
External Validation Criteria						
23.	θ^*	–	–	−8.39°	−6.81°	−7.02°
24.	$RMSE_{ex}$	–	–	0.41	0.38	0.37
25.	MAE_{ex}	–	–	0.30	0.32	0.26
26.	$PRESS_{ext}$	–	–	2.89	2.45	2.34
27.	R^2_{ex}	–	–	0.75	0.77	0.76
28.	Q^2_{F1}	–	–	0.73	0.77	0.71
29.	Q^2_{F2}	–	–	0.70	0.76	0.71
30.	Q^2_{F3}	–	–	0.62	0.68	0.72
31.	CCC_{ex}	–	–	0.83	0.87	0.84
32.	R^2-*ExPy*	0.79	0.79	0.80	0.77	0.76
33.	R'^2_o	0.74	0.74	0.77	0.71	0.69
34.	*k'*	0.99	0.99	0.99	0.99	1.02
35.	$1-(R^2/R'^2_o)$	0.06	0.06	0.04	0.07	0.09
36.	r'^2m	0.62	0.62	0.65	0.59	0.56
37.	R^2_o	0.79	0.79	0.80	0.77	0.76
38.	*k*	0.99	0.99	0.99	1.00	0.98
39.	$1-(R^2\text{-}ExPy/R^2_o)$	0.00	0.00	0.00	0.00	0.00
40.	r^2m	0.77	0.77	0.79	0.74	0.76

The presence of red contour near position number 7 of ring A indicates that the presence of a more negative charge i.e. electron withdrawing group (EWG) at this position is highly favourable for activity augmentation. This observation is supported by comparing the activity values of following quinoxalinones, as representative examples: **3** (IC_{50} = 0.874 μM) with **4** (IC_{50} = 1.516 μM), **11** (IC_{50} = 0.032 μM) with **12** (IC_{50} = 0.069 μM) and **13** ((IC_{50} = 0.091 μM), **21** (IC_{50} = 0.191 μM) with **22** (IC_{50} = 0.326 μM) and **23** (IC_{50} = 0.467 μM), **26** (IC_{50} = 0.056 μM) with **27** (IC_{50} = 0.158 μM) and **28** (IC_{50} = 0.395 μM). Interestingly, this red contour surrounds a yellow contour, which indicates that the EWG must be less bulky in nature. This could be another plausible reason behind the high activity profile of quinoxalinones with –F compared to molecules with –Br as a substituent at this position, as well as for outlier behavior of molecule **13** in CoMFA like model. Similarly, the red contour present in the vicinity of $-CH_2-COOH$ group indicates that

an EWG is favourable at this position, therefore, for better activity this group must be retained. This observation is further supported by the molecular docking analysis performed by Wang *etal*.[1b,2]

A blue contour close to position number 6 of ring A indicates that less electronegative groups are favourable at this position. This observation is reinforced by equating the activity values of following quinoxalinones: **50** (IC_{50} = 0.05595 μM) with **56** (IC_{50} = 0.10553 μM) and **62** (IC_{50} = 0.30160 μM), **72** (IC_{50} = 0.03274 μM) with **87** (IC_{50} = 0.04313 μM), **84** (IC_{50} = 0.05039 μM) and **81** (IC_{50} = 0.06987 μM). A big yellow contour (almost 'U' shaped with higher presence towards quinoxaline ring) spanning the meta and para positions of ring C indicate that the presence of less bulkiness in this region is in support of activity escalation. A big green contour (present opposite to yellow contour and other side of ring C away from quinoxaline ring) and a red contour are present vicinal to the ortho position of ring C representing that the presence of more bulky groups with electron withdrawing ability (i.e. highly electronegative atom) on this side could be activity promoter. This observation is accepted when the activity values of following quinoxalinones are compared: **7** (IC_{50} = 0.397 μM) with **6** (IC_{50} = 2.592 μM), **51** (IC_{50} = 0.03484 μM) with **50** (IC_{50} = 0.05595 μM), **55** (IC_{50} = 0.01025 μM) with **54** (IC_{50} = 0.02328 μM), **57** (IC_{50} = 0.05856 μM) with **56** (IC_{50} = 0.10523 μM), **61** (IC_{50} = 0.00644 μM) with **60** (IC_{50} = 0.03359 μM), a few examples to mention.

A conceivable reason for the presence of yellow and green contours close to each other and spanning the opposite sides of the similar region of ring C could be the huge variations or absence of the linker between ring B and C, which causes good variations in angle and distance for ring C during alignment of all the molecules in the dataset.

A blue contour, which represents the presence of more positive charge is favourable in this region, is present between ring B and C. A comparison of compounds **1** (IC_{50} = 5.981 μM), **18** (IC_{50} = 0.468 μM), **19** (IC_{50} = 0.421 μM), **29** (IC_{50} = 1.112 μM), **30** (IC_{50} = 0.820 μM) and **31** (IC_{50} = 0.143 μM) indicates that $-CH_2-CH_2-$ is a better linker for increasing the activity. Another reason for this could be the additional high flexibility provided by this linker.

5 QSAR Analysis

The principal objective of the present work is to employ conventional QSAR to acquire extensive information about the structural moieties that govern the activity. Recently, our group successfully proved that single splitting based QSAR models are neither best suitable to judge external predictive ability nor getting maximal information.[3c,e] Therefore, multiple models were built using 80% training set and validating them on remaining set (20% prediction set) using random splitting. Furthermore, QSAR model was built using whole dataset (no splitting) to confirm the identification of all the significant structural-activity information.

The GA-MLR analysis resulted in statistically acceptable QSAR models 1–5, which satisfy recommended threshold values for many statistically parameters that are essential to judge the goodness of fit and external predictive ability. The QSAR models are also able to shed light on the structural features that govern the aldose reductase activity. The developed QSAR models are as follow:

Model-1 (Full set model): pIC_{50} = 5.97 (±0.32) + 0.93 (±0.33)****all_F_5Ac*** + 1.26 (±0.37)****MATS8m*** + 20.67 (±5.23)****R2v+*** − 1.99 (±0.56)****O_lipo_2Bc*** − 0.05 (±0.02)****Cplus_AbSA*** − 0.19 (±0.06)****RDF115p***

Model-2 (Full set model): pIC_{50} = 7.30 (±0.24) + 1.03 (±0.34)****all_F_5Ac*** + 1.28 (±0.36)****N_all_3Bc*** + 1.18 (±0.38)****MATS8 m*** + 0.59 (±0.16)****F08[N–Br]*** − 1.64 (±0.59)****O_lipo_2Bc*** − 0.23 (±0.06)****RDF115p***

Model-3 (Divided set model): pIC_{50} = 2.01 (±1.00) + 0.84 (±0.22)****acc_F_5Ac*** + 27.87 (±4.92)****R2v+*** + 0.90 (±0.34)****B10[C–O]*** + 10.48 (±4.10)****HATS1e*** − 0.64 (±0.28)****fBrS10A*** − 2.39 (±0.63)****acc_F_5Bc***

Model-4 (Divided set model): pIC_{50} = 11.66 (±0.77) + 0.72 (±0.34)****all_F_5Ac*** − 0.40 (±0.16)****fCN7B*** − 0.75 (±0.21)****fFO8B*** − 1.02 (±0.24)****GATS8e*** − 3.71 (±0.88)****SPH*** − 1.40 (±0.29)****Mor19e***

Model-5 (Divided set model): pIC_{50} = 6.44 (±0.42) + 1.21 (±0.38)****B10[C–O]*** + 1.08 (±0.32)****lipo_N_5Ac*** + 2.52 (±0.62)****all_N_7Ac*** − 0.41 (±0.18)****B08[O–F]*** − 2.00 (±0.63)****C_F_3Ac*** − 0.26 (±0.07)****RDF115p***

The 3D-descriptor ***all_F_5Ac***, which stands for sum of partial charges on all atoms which are within 5 Å from Fluorine atom, has positive coefficient in model 1, 2, and 4. Therefore, its value must be as high as possible. This descriptor provides information about the role of local environment in the vicinity of F atom in deciding the activity. As the number of positively charged atoms like H-atoms in the vicinity of F atom increases, its value increases. Another similar descriptor with positive coefficient in model 3 is ***acc_F_5Ac***, which corresponds to sum of partial charges on H-bond acceptor present within 5 Å from F atom. These descriptors have been depicted using the molecule **11** as a representative in the Figure 5.

The descriptor ***N_all_3Bc*** stands for sum of partial charges on all atoms which are at a distance of three bonds from Nitrogen atoms. This descriptor has positive coefficient in model 2, thereby increasing it value will increase the bioactivity. This descriptor highlights the role of local environment with three bond distance around N atoms in determining the activity. This descriptor has been depicted using the most active molecule **11** as a representative in the Figure 5. Similarly, the positive coefficient of ***lipo_N_5Ac*** in model 3 highlights the importance of local environment around N atoms. The descriptor ***lipo_N_5Ac*** corresponds to sum of partial charges on all lipophilic atoms which are present within 5 Å from N atoms. Same is true for ***all_N_***

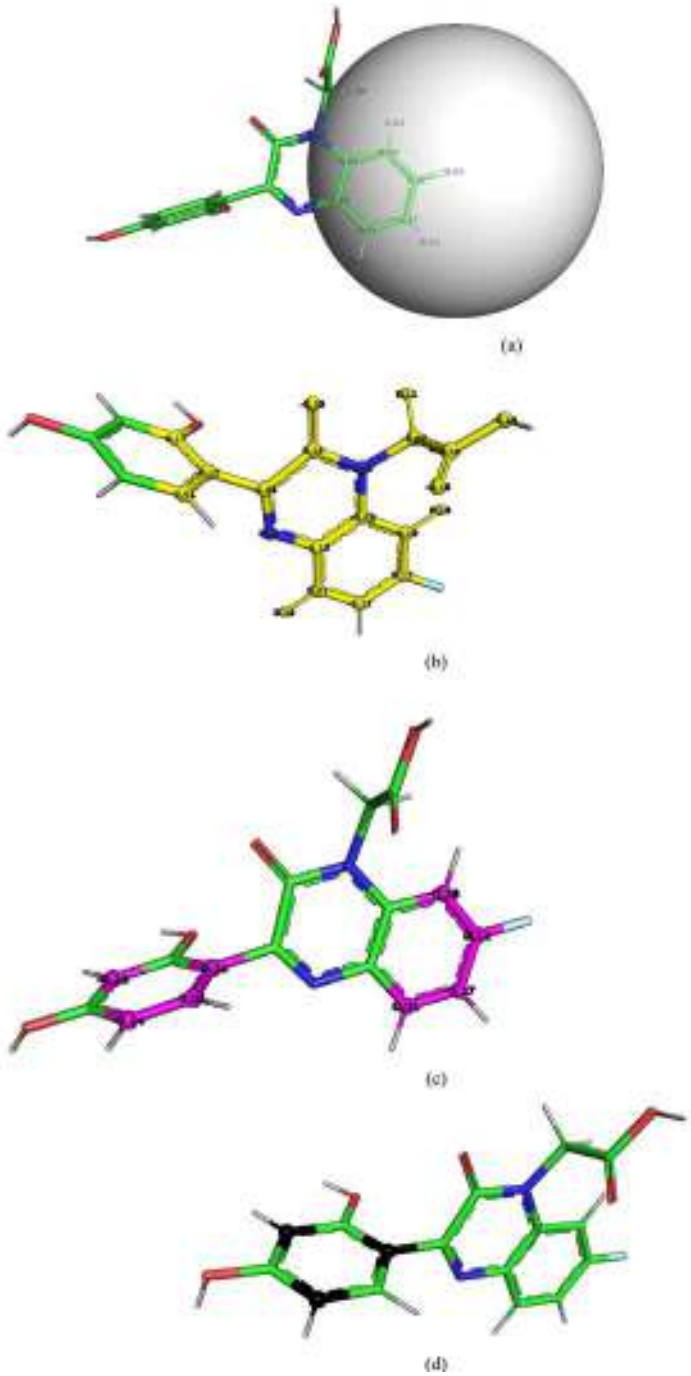


Figure 5. 3D-representation of (a) ***all_F_5Ac*** and ***acc_F_5Ac*** (the gray sphere has radius of 5 Å with F as the center) and (b) ***N_all_3Bc*** (atoms within three bonds from N atoms have been shown with yellow colour) (c) ***lipo_N_5Ac*** (lipophilic atoms within 5 Å from N atoms have been shown with magenta colour) (d) ***O_lipo_2Bc*** (lipophilic atoms which are within two bonds from O atoms have been shown as black) using the molecule **11** (as a representative only).

7Ac (sum of partial charges on all atoms within 7 Å from N atoms).

The 2D frequency fingerprints descriptor ***F08[N–Br]*** has positive coefficient in model 2. This topological descriptor stands for frequency of N and Br at a topological distance of 08. It has positive coefficient in model 2, hence, in future its value must be increased to improve the activity. A comparison of activity of **19** (IC_{50} = 0.421 μM) with **20** (IC_{50} = 0.296 μM), **48** (IC_{50} = 924.87 nM) and **49** (IC_{50} = 122.70 nM) with **50** (IC_{50} = 55.95 nM), **52** (IC_{50} = 272.00 nM) and **53**

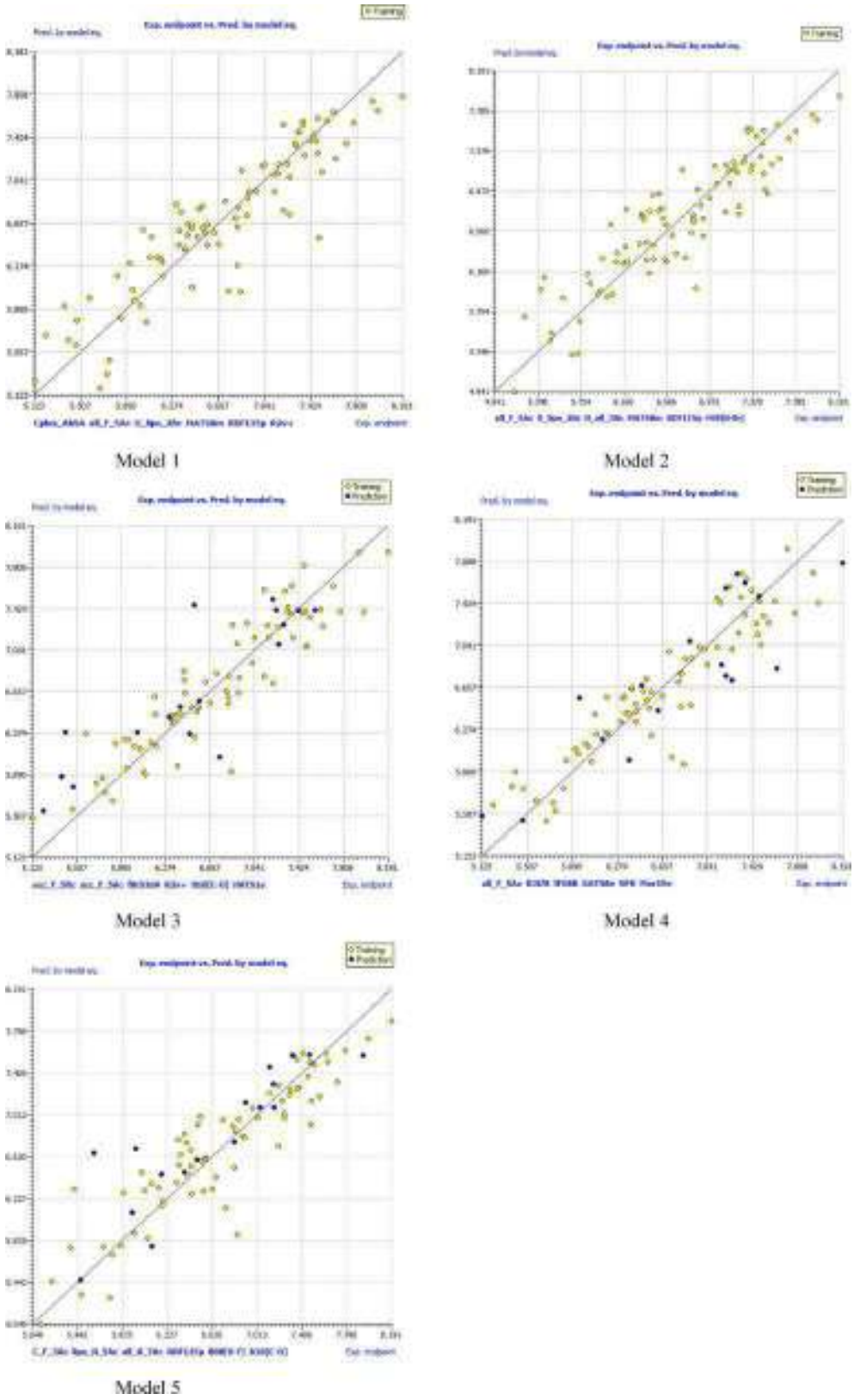


Figure 6. Correlation graph between predicted and experimental pIC_{50} values by QSAR models 1 to 5.

Table 3. Status of the molecule and predicted pIC_{50} values by QSAR and CoMFA like models.

Mol id	Pred. pIC_{50} (CoMFA like model)	Status	Pred. by model 1	Pred. by model 2	Status	Pred. by model 3	Status	Pred. by model 4	Status	Pred. by model 5
1	5.572	Training	5.6607	5.7039	Prediction	5.5551	Training	5.5913	Training	5.4509
2	5.49	Training	5.5711	5.4625	Training	5.5691	Prediction	5.4483	Prediction	5.4694
3	5.888	Training	5.7820	5.9281	Training	6.1262	Training	5.9884	Training	5.8561
4	5.679	Training	6.1909	6.1381	Training	5.6527	Training	5.7382	Training	5.7930
5	5.788	Training	5.1844	5.3122	Training	5.8155	Training	5.4405	Training	5.7728
6	5.484	Training	5.9947	5.8911	Training	6.2693	Training	5.6317	Prediction	6.6589
7	6.875	Training	6.5511	6.7699	Prediction	6.5173	Training	6.6482	Training	6.7559
8	6.773	Training	6.7737	7.1975	Training	6.7320	Prediction	6.7688	Training	6.7283
9	6.96	Training	7.1699	7.2294	Training	6.9216	Training	7.0145	Training	6.9898
10	6.966	Training	7.1314	6.9896	Training	7.2804	Training	6.9246	Training	6.9743
11	7.461	Training	6.5355	6.9874	Training	7.0849	Training	7.0518	Training	7.1438
12	7.159	Training	7.1853	7.0553	Training	7.1584	Prediction	6.8708	Prediction	7.0882
13	6.961	Training	7.1853	7.0553	Training	7.1584	Training	6.8708	Prediction	7.0882
14	5.411	Training	5.7924	5.5363	Prediction	5.7807	Training	5.7419	Training	5.3300
15	5.881	Training	6.1892	6.2641	Training	6.1576	Training	6.2439	Training	6.2050
16	6.403	Training	6.6143	6.4250	Training	6.7709	Training	6.3516	Training	6.5321
17	6.55	Training	6.5710	6.5281	Training	6.7474	Prediction	6.4523	Training	6.3185
18	6.209	Training	6.4655	6.7399	Training	6.3774	Training	6.5651	Training	6.7797
19	6.409	Training	6.4242	6.4543	Training	6.4435	Training	6.4243	Prediction	6.4804
20	6.301	Training	6.6200	6.6987	Training	6.2392	Training	6.5444	Training	6.5848
21	6.892	Training	6.8542	7.1923	Training	6.8277	Training	6.9921	Training	6.9658
22	6.517	Training	6.5373	6.7733	Prediction	6.2706	Prediction	6.6810	Prediction	6.5969
23	6.415	Training	6.5915	6.7177	Training	6.4448	Training	6.5818	Training	6.5405
24	6.393	Training	6.7903	6.9468	Training	6.5110	Training	6.6273	Training	6.9242
25	6.399	Training	6.4654	6.2645	Training	6.5097	Training	6.6172	Training	6.6067
26	6.989	Training	6.7313	6.7428	Prediction	7.0982	Training	7.0124	Training	6.9877
27	6.615	Training	6.7049	6.5544	Training	6.6700	Training	6.7132	Training	6.9128
28	6.514	Training	6.6529	6.1446	Training	6.4553	Training	6.6577	Training	6.4550
29	6.424	Training	5.9709	6.2941	Training	6.2169	Prediction	6.5691	Prediction	6.6963
30	6.077	Training	6.3502	6.2563	Training	5.9203	Training	6.4155	Training	6.3694
31	6.69	Training	6.0451	5.9895	Training	5.9204	Training	5.9590	Training	5.8944
32	6.428	Training	6.0564	6.3016	Prediction	6.0531	Training	6.0297	Training	6.1447
33	7.008	Training	6.2806	6.7346	Training	6.6102	Training	6.4848	Training	6.5237
34	5.27	Training	5.9232	5.9797	Prediction	5.8750	Training	5.7587	Training	5.7680
35	6.658	Training	6.4301	6.2801	Training	5.9762	Prediction	6.0002	Training	6.8368
36	5.989	Training	6.5406	6.3502	Training	5.8926	Training	6.2334	Prediction	5.7823
37	6.387	Training	6.3187	6.7875	Training	6.4497	Training	6.5758	Training	6.1662
38	6.063	Training	5.8121	6.0447	Training	6.1786	Training	5.9911	Training	6.2853
39	5.824	Training	5.3178	5.3295	Training	5.8574	Training	5.6110	Training	5.3034
40	5.205	Training	5.2484	4.9415	Training	5.4876	Prediction	5.4885	Training	5.0493
41	6.008	Training	6.0665	5.9625	Training	5.9519	Training	6.0519	Training	5.9082
42	6.146	Training	6.3373	6.4119	Training	6.6107	Training	6.2528	Prediction	6.4596
43	5.641	Training	5.6202	6.0982	Prediction	6.2865	Training	5.8904	Training	6.3177
44	6.467	Training	6.0907	6.2882	Training	6.6498	Training	6.4419	Training	6.2690
45	6.507	Training	6.5770	6.2855	Training	6.4708	Training	6.4708	Training	6.2993
46	6.099	Training	6.3595	6.2427	Training	6.1892	Prediction	6.1881	Training	6.3312
47	6.4	Training	6.7598	6.6931	Training	6.3827	Training	6.4343	Training	6.6423
48	6.102	Training	6.5970	6.6312	Prediction	6.2833	Training	6.1220	Training	6.3073
49	6.792	Training	6.9459	6.5217	Training	6.7884	Training	6.9267	Prediction	7.1327
50	7.02	Training	7.0675	6.8188	Training	7.2587	Prediction	6.7282	Training	7.0301
51	7.587	Training	7.4543	7.3229	Training	7.3840	Training	7.2450	Training	7.3771
52	6.313	Training	6.6436	6.6374	Prediction	6.5725	Training	6.2228	Training	6.6036
53	7.002	Training	6.9436	6.7640	Training	6.7989	Training	7.0308	Prediction	7.4650
54	7.233	Training	7.2423	7.3010	Training	7.2692	Prediction	6.8384	Training	7.5154
55	7.75	Training	7.6694	7.6979	Training	7.3944	Training	7.4320	Training	7.7321
56	7.103	Training	6.9407	6.9052	Training	7.2902	Training	7.0322	Training	7.0798
57	7.654	Training	7.1941	7.1706	Prediction	7.4154	Training	7.5850	Training	7.1464
58	6.689	Training	6.6498	6.9345	Training	6.8509	Training	6.5155	Training	6.6873
59	7.372	Training	7.1163	6.9498	Training	7.3456	Training	7.3145	Training	7.4872

Table 3. continued

Mol id	Pred. pIC_{50} (CoMFA like model)	Status	Pred. by model 1	Pred. by model 2	Status	Pred. by model 3	Status	Pred. by model 4	Status	Pred. by model 5
60	7.597	Training	7.3951	7.4578	Training	7.8263	Training	7.1475	Prediction	7.5797
61	7.962	Training	7.7967	7.9371	Training	7.9516	Prediction	7.7946	Training	7.8985
62	6.911	Training	6.8114	6.8058	Prediction	7.4629	Training	6.7435	Training	7.0015
63	5.779	Training	5.4339	5.6595	Training	5.7248	Training	5.5374	Training	5.6979
64	6.548	Training	6.4709	6.3384	Training	6.5554	Training	6.5866	Training	6.4340
65	6.745	Training	6.6237	6.6898	Training	6.5554	Training	6.7897	Prediction	6.7607
66	6.959	Training	6.7252	6.8254	Training	7.1020	Prediction	7.0825	Training	6.8191
67	6.221	Training	6.8254	6.4408	Prediction	6.4261	Training	6.3506	Training	6.3854
68	6.9	Training	6.8050	6.6603	Training	6.8023	Training	6.7858	Training	6.8650
69	6.678	Training	6.8860	6.6998	Training	6.6478	Training	6.5001	Training	6.8055
70	6.012	Training	6.3027	5.9284	Training	6.2158	Training	6.1015	Prediction	6.0988
71	6.14	Training	5.9272	5.9071	Training	6.1549	Training	6.1521	Training	6.4803
72	7.275	Training	7.2841	7.1560	Training	7.0776	Prediction	7.4918	Training	6.9279
73	7.492	Training	7.5741	7.2485	Prediction	7.4159	Training	7.2551	Training	7.1878
74	7.684	Training	7.3746	7.5072	Training	7.6348	Training	7.9275	Training	7.3249
75	7.9	Training	7.7501	7.7438	Training	7.9451	Training	7.7084	Prediction	7.5734
76	7.471	Training	7.2626	7.2412	Training	7.1613	Training	7.6520	Training	7.2687
77	7.688	Training	7.5972	7.5911	Training	7.3985	Training	7.4451	Training	7.5124
78	7.327	Training	7.5418	7.2690	Prediction	7.5132	Prediction	7.5655	Training	7.2903
79	7.544	Training	7.5703	7.6001	Training	7.3775	Training	7.3268	Training	7.5352
80	7.307	Training	7.4757	7.6001	Training	7.4014	Training	7.4877	Training	7.5733
81	7.142	Training	7.1067	7.1833	Training	7.2713	Training	7.4344	Prediction	7.3035
82	7.359	Training	7.3541	7.3154	Training	7.5921	Training	7.1613	Training	7.2491
83	7.123	Training	7.0946	7.2416	Training	7.6055	Training	7.4770	Training	7.2229
84	7.368	Training	7.3719	7.2714	Prediction	7.2763	Prediction	7.6933	Training	7.2040
85	7.587	Training	7.6577	7.6465	Training	7.4194	Training	7.4452	Training	7.5931
86	7.349	Training	7.4787	7.5841	Training	7.4433	Training	7.7013	Prediction	7.5733
87	7.448	Training	7.5326	7.1794	Training	7.6351	Prediction	7.6187	Training	7.2658
88	7.666	Training	7.5525	7.5817	Training	7.3985	Training	7.3411	Training	7.6202
89	7.428	Training	7.4023	7.5343	Prediction	7.4118	Training	7.5491	Training	7.5974

(IC_{50} = 74.95 nM) with **54** (IC_{50} = 23.28 nM) supports this observation.

The ***MATS8 m*** is a 2D- autocorrelations descriptor which represents Moran autocorrelation-lag 8/weighted by atomic masses. It has positive coefficient in model 1 and 2. Another descriptor with positive coefficient in model 1 is ***R2v+***, a GETAWAY descriptor that stands for R maximal autocorrelation of lag 2/weighted by atomic van der Waals volumes. Therefore, for better activity profile, the values of ***MATS8m*** and ***R2v+*** must be as high as possible. Same is true for ***HATS1e*** (see model 3), a GETAWAY descriptor, which corresponds to leverage-weighted autocorrelation of lag 1/ weighted by atomic Sanderson electronegativities. In model 3 and 5, the descriptor ***B10[C–O]*** (presence/absence of C–O at a topological distance of 10). This 2D- binary fingerprints descriptor has positive coefficient in both the models. Henceforth, such a combination of C and O is in favour of activity profile.

The descriptor which has negative correlation, indicated by its negative coefficient in model 1 and 2, is ***O_lipo_2Bc.*** ***O_lipo_2Bc*** stands for sum of partial charges on lipophilic atoms which are within two bonds from O atoms. Therefore, in future optimizations, the value of this descriptors must be decreased by introducing electron donating groups as substituents on ring C.

Cplus_AbSA (absolute surface area of positively charged carbon atoms) has negative coefficient in model 1, which indicates that lower its value, better the activity. This could be achieved by reducing the number of positively charged Carbon atoms, which in turn, is achievable if number of electron withdrawing groups attached to Carbon are diminished. Another descriptor with negative association with activity is ***fBrS10A*** (frequency of occurrence of Br and S with a separation of 10 Å). This descriptor has negative coefficient in model 3, which specifies that such a combination of Br and S atoms must be avoided for better activity. A comparison of activity of **24** (IC_{50} = 0.319 μM) with **88** (IC_{50} = 0.01633 μM), **23** (IC_{50} = 0.467 μM) with **79** (IC_{50} = 0.04348 μM), **22** (IC_{50} = 0.326 μM) with **54** (IC_{50} = 0.02328 μM) and **77** (IC_{50} = 0.03299 μM), **21** (IC_{50} = 0.191 μM) with **60** (IC_{50} = 0.03359 μM) and **75** (IC_{50} = 0.0114 μM), and **20** (IC_{50} = 0.296 μM) with **50** (IC_{50} = 0.05595 μM), **68** (IC_{50} = 0.15031 μM) and **73** (IC_{50} = 0.02728 μM) is in favour of this opinion.

Interestingly, ***acc_F_5Bc*** (sum of partial charges on F atoms present within five bonds from H-bond acceptor

atom) has negative coefficient in model 3. Therefore, for better activity profile, its value must be as low as possible. This observation is supported by comparing the activity of following pairs of molecules: **2** (IC_{50} = 3.380 μM) with **3** (IC_{50} = 0.874 μM), **7** (IC_{50} = 0.397 μM) with **8** (IC_{50} = 0.063 μM), **7** (IC_{50} = 0.397 μM) with **11** (IC_{50} = 0.032 μM), **20** (IC_{50} = 0.296 μM) with **21** (IC_{50} = 0.191 μM), **25** (IC_{50} = 0.273 μM) with **26** (IC_{50} = 0.056 μM), and **32** (IC_{50} = 0.182 μM) with **33** (IC_{50} = 0.153 μM). Another negatively associated descriptors, having negative coefficients in model 4, with activity are ***fCN7B*** (frequency of occurrence of C and N atoms with a separation of seven bonds) and ***fFO8B*** (frequency of occurrence of F and O atoms with a separation of eight bonds). Therefore, such a combination of C with N and F with O atoms must be sidestepped to have better activity. This indicate that, in general, the presence of F atom at the position number 4 of ring A is unfavouable for activity. Same is true for the 2D- binary fingerprints descriptor ***B08[O–F]*** (presence/absence of O–F at topological distance of 08), having negative coefficient in model 5, has negative relationship with the activity.

C_F_3Ac, which represents sum of partial charges on C atoms present within 3 Å from F atoms, has negative impact on activity as evident from its negative coefficient in model 5. Therefore, its value must be minimized in future optimization to have superior activity. The difference in activity of following pairs of compounds **64** (IC_{50} = 0.22042 μM) with **73** (IC_{50} = 0.02728 μM), **65** (IC_{50} = 0.15275 μM) with **77** (IC_{50} = 0.03299 μM), and **66** (IC_{50} = 0.12848 μM) with **75** (IC_{50} = 0.0114 μM) is in favour of this observation.

In models 1,2, and 5, the Radial Distribution Function descriptor ***RDF115p*** (Radial Distribution Function – 11.5/ weighted by atomic polarizabilities) has negative coefficient. Similarly, ***GATS8e***, a 2D autocorrelations descriptor which represents Geary autocorrelation-lag 8/weighted by atomic Sanderson electronegativities, has negative influence (negative coefficient in model 4) on activity profile of quinoxalinones as aldose reductase inhibitors. Likewise, the 3D-MoRSE descriptors ***Mor19e*** (3D-MoRSE – signal 19/ weighted by atomic Sanderson electronegativities) and ***SPH*** (spherosity geometrical descriptors) have negative coefficient in model 4. Therefore, the values of ***RDF115p***, ***GATS8e***, ***SPH*** and ***Mor19e*** must be minimal to have better aldose reductase inhibitory activity.

Though we have equated the activities of quinoxalinones as aldose reductase inhibitors in terms of a good number of molecular descriptors like ***all_F_5Ac***, ***acc_F_5Ac***, ***N_all_3Bc***, ***lipo_N_5Ac***, ***O_lipo_2Bc***, etc., we make it clear that the combined or converse effect of confounding factors/descriptors do have added effect on the activity profile of the compounds.

The different statistical parameters for goodness of fit, internal validation and external predictive ability for model 1–5 have been tabulated in the Table 2.

The different statistical parameters for model 1–5, depicted in the Table 2, point out that all the developed models satisfy various statistical parameters like R^2_{tr}, Q^2_{Fn}, R^2_{ex} and CCC_{ex}, etc., which are necessary to establish the internal and external predictive ability of a model.[3c,e,5k,m,n,8,10] The models 1 and 2 are based on undivided dataset (no splitting) whereas models 3–5 have been developed using a divided dataset (80% training and 20% prediction set using random splitting method). The success of the strategy of developing multiple QSAR models is evident from the fact that models 1–5 comprise different descriptors, thereby, capturing most relevant structure-activity information.[3c,e] For all the models, the close value of R^2_{ad} with R^2 indicates that adequate number of descriptors have been used for model building.[3c,e]

The predicted pIC_{50} values by developed QSAR models have been shown in Figure 6 and tabulated in Table 3.

6 Conclusions

In conclusion, multiple QSAR models and thriving CoMFA like model have been reported possessing statistically acceptable internal and external predictive ability. Both analyses provide concurrent and complementary results and are well supported by the molecular docking analysis performed by Wang *etal*. Both analyses indicate that steric repulsion and electrostatic characters have significant correlation with the aldose reductase activity. The developed QSAR and CoMFA like model offer helpful insinuations for optimization of aldose reductase activity of quinoxalinones with improved activity profile. The models could be used to design new ligands with better activity, prior to their actual synthesis.

7 Abbreviations

CoMFA	Comparative Molecular Field Analysis
GA	Genetic Algorithm
MLR	Multiple Linear Regression
QSAR	Quantitative Structure-Activity Relationship
ADMET	Absorption, Distribution, Metabolism, Excretion and Toxicity
CADD	Computer Aided Drug Designing
EWG	Electron withdrawing group
OLS	Ordinary Least Square
QSARINS	QSAR Insubria

Conflict of Interest

None declared.

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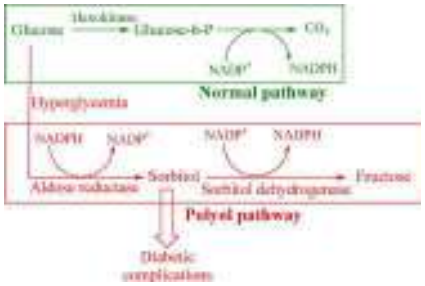
FULL PAPER



V. H. Masand, N. N. Elsayed, S. D. Thakur, N. Gawhale, M. M. Rathore*

Research Paper

Antiinflammatory Activity of Triazine Thiazolidinone Derivatives: Molecular Docking and Pharmacophore Modelling

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Some 3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-phenylthiazolidin-4-one derivatives were prepared by cyclo-condensation reaction between 2-amino-4,6-dichloro-1,3,5-triazine, substituted aromatic aldehyde and ethyl-2-mercaptoacetate, with an yield in the range 76-86 %. Prepared compounds showed antiinflammatory activity. The halogenated electron-withdrawing groups on the phenyl ring of 4-thiazolinone generated antiinflammatory activity. Among the synthesized compounds, 3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-(2,5-difluorophenyl)thiazolidin-4-one showed better antiinflammatory activity with 72 and 79 % inhibition for TNF-α and IL-6, respectively. Also, molecular docking and pharmacophore modelling performed for this active antiinflammatory compound highlighted that hydrophobicity as an important feature for activity optimization.

Key words: Triazine thiazolidinone, antiinflammatory activity, molecular docking, pharmacophore modeling

Medicinal chemistry has an important role in medicine and health care. The leading objective of medicinal chemistry is to design and synthesize therapeutically potential molecules, study their pharmacokinetic and pharmacodynamic properties, and thoroughly test them as human therapeutic agents. It has been established that infections due to multidrug-resistance (MDR) microbes is a serious concern worldwide and an important issue, also. According to AR threat report in 2013, in the USA annually, at least two million infections and 23 000 deaths occurred[1] and in the latest report, according to WHO's new Global Antimicrobial Surveillance System, there is an extensive existence of antibiotic resistance among 500 000 people with suspected bacterial infections across 22 countries[2].

The solution for this is actively look for new drugs with newer mechanisms of action. In this context, fundamentally the focus should be on understanding the principles and ecological factors, which can affect MDR in bacteria[3,4]. Rapid growth of MDR strains of pathogens result in a severe resistance development towards presently available antimicrobial drugs in the market.

In spite of several efforts during the last few decades to develop new antimicrobials, the efforts were not completely successful to control the rapid upsurge of resistance genes evolving among both Gram-positive and Gram-negative pathogens[5]. In this regard, there is an urgent need to develop new and improved antimicrobial drugs. Antimicrobial research is important not only for development of effective treatments but also for the increased business potential of the pharma industry[4,6]. Recently thiazole, a five-membered ring heterocycle with three carbons, one sulphur atom and one nitrogen atom; and its derivatives thiazolidinones having carbonyl group at 2, 4 or 5-position have been a focus of therapeutic interest[7,8]. It has been revealed by Palekar *et al.*[9], Hamama *et al.*[10], Kumar *et al.*[11], Kaminskyy *et al.*[12], Samadhiya *et al.*[13] and others[14] that in different synthetic drugs pharmacological activities are associated with the thiazolidinone ring

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system as a core structure. Substituents at 2, 3 and 5-position are useful for varying the properties but greatest difference in structure and properties has been exerted by groups attached to carbon atom in 2-position[15]. As the thiazolidinone possesses almost all different types of pharmacological activities, it has been considered as supernatural moiety or magic moiety i.e. a wonder nucleus[16-19]. On the other hand, triazine derivatives are another important class of heterocycles having wide range of biological activities including antimicrobial, anticancer, antimalarial, antiviral, antitubercular and antiHIV[20].

Furthermore, several systems of heterocyclic compounds having triazine linked-thiazolidinones have been synthesized and their pharmacological activities were examined[21-23]. The thiazolidinones bearing triazine analogues have been found to be potential bioactive molecules[24-27]. Therefore, it was thought worthwhile to develop a scheme which combines biolabile nuclei, 1,3,5-triazine and thiazolidinones together in a molecular framework so that their additive effect can increase already existing antimicrobial potential. In line with this, our earlier work on aryl substituted 3-(4,6-dichloro-1,3,5-triazin-2-yl)thiazolidin-4-ones contributed for evaluation of the antibacterial and antimicrobial activity[28].

In the present work, aryl substituted 3-(4,6-dichloro-1,3,5-triazin-2-yl)thiazolidin-4-ones (fig. 1) were synthesized from aromatic aldehyde, 4,6-dichloro-1,3,5-triazin-2-amine and ethyl 2-mercaptoacetate using dry ethanol. The structure of these compounds was confirmed on the basis of ^{1}H nuclear magnetic resonance (NMR), and mass spectra. Antiinflammatory activity of all the synthesized compounds was screened. In the structure activity relationship (SAR) study, the biological activity of these molecules was compared with that of a reference compound. Furthermore, in recent years, different computational techniques have gained popularity to get insight into the mechanism of action of small molecules and streamline the future optimizations to achieve required objectives. Therefore, molecular docking, which is a structure-based drug design technique study was performed to determine the pharmacophore model (ligand-based drug design) to understand the key structural features, which could help in further optimization of triazine-thiazolidinone derivatives to obtain better drug candidates.

MATERIAL AND METHODS

For the synthesis of 3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-phenylthiazolidin-4-one derivatives, 2-amino-4,6-dichloro-1,3,5-triazine, substituted aromatic aldehyde and ethyl-2-mercaptoacetate were obtained from commercial sources. The solvent dry ethanol was purified by distillation before use. IR spectra were recorded on a Shimadzu FT-IR-8400 instrument using KBr pellet method at the Department of Chemistry, Dayanand College, Solapur. Mass spectra were recorded on a Shimadzu GC-MS-QP-2010 model using direct injection probe technique and the ^{1}H NMR was determined in $CDCl_3$ solution on a Bruker Ascend-TM 400MHz-NMR spectrometer at S.A.I.F. Division, Indian Institute of Technology, Bombay.

Synthesis of 3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-phenyl thiazolidin-4-one (4a):

The synthesis of the target compounds was accomplished via one-pot multicomponent reaction. A mixture of 2-amino 4,6-dichloro-1,3,5-triazine (1, 1 mmol, 0.164 g), benzaldehyde (3, 1 mmol, 0.106 g) and ethyl-2-mercaptoacetate (2, 1 mmol, 0.120 g) was refluxed for 2 h in dry ethanol (20 ml) as reported in our previous article[23]. The progress of reaction was monitored by TLC (toluene:acetone, 4:6). The excess alcohol was evaporated in the vacuum. The resulting crude product was added to crush ice. The solid obtained was washed with water, dried and recrystallized from ethanol to afford final respective compounds (4a). Similarly remaining compounds (4b-l) were prepared. The synthetic strategy for novel compounds triazine based thiazolidinones is outlined in fig. 2. The structure of all synthesized compounds was confirmed on the basis of ^{1}H NMR, mass spectra and elemental analysis. The products were further ascertained by physical and analytical analyses.

Spectral data:

3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-phenylthiazolidin-4-one (4a), pale yellow solid; yield-

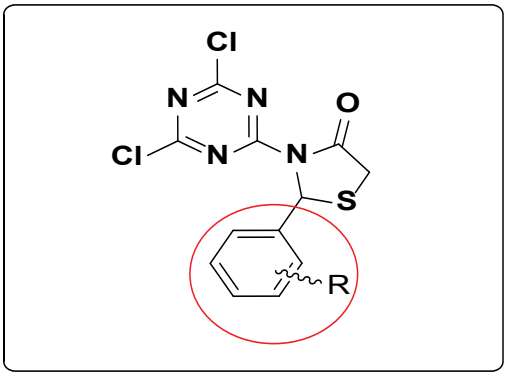

Fig. 1: Design scaffold

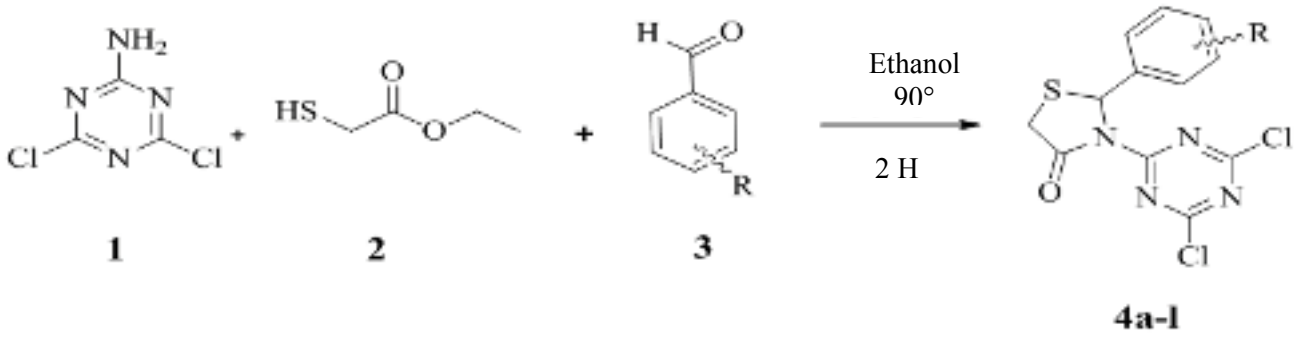

Fig. 2: Synthesis of aryl substituted 3-(4,6-dichloro-1,3,5-triazin-2-yl)thiazolidin-4-one derivatives
R=4a-l; 4a=phenyl, 4b=4-methoxy, 4c=2-fluoro, 4d=2-fluoro-4-bromo, 4e=2-bromo, 4f=2-fluoro-5-chloro, 4g=3-methyl, 4h=4-nitro, 4i=2-hydroxy, 4j=3-methoxy, 4k=2,5-difluoro, 4l=3-CN

80 %, melting point (mp)- 138-140°. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.41-6.85 (m, 5H), 5.33 (s, 1H), 3.40 (d, *J*=7.1 Hz, 2H). IR (KBr): ν (cm^{-1}) 2842 (C-H str. in aromatic ring), 1723 (C=O of thiazolidinone), 1660 (-C=C- str. in aromatic ring), 814 (C-N- str. in s-triazine). MS (70 eV) *m/z*: 325.96 [M^+ 100 %], 327.96 [M+2, 66.66 %], 329.96 [M+4, 11.11 %]. Anal. calcd. for $C_{12}H_8Cl_2N_4OS$: C, 44.05; H, 2.46; N, 17.12: S, 9.80; found: C, 43.98; H, 2.35; N, 17.00: S, 9.60 %.

3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-(4-methoxyphenyl)thiazolidin-4-one (4b), pale yellow solid; yield- 82 %, mp- 140-142°. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.41 (m, 2H), 6.89 (m, 2H), 5.34 (d, 1H), 3.82 (s, 3H), 3.43 (d, *J*=7.2 Hz, 2H). IR (KBr): ν (cm^{-1}) 2838 (C-H str. in aromatic ring), 1720 (C=O of thiazolidinone), 1655 (-C=C- str. in aromatic ring), 813 (C-N- str. in s-triazine). MS (70 eV) *m/z*: 355.98 [M^+, 100 %], 357.98 [M+2, 66.66 %], 358.98 [M+3, 11.66 %], anal. calcd. for $C_{13}H_{10}Cl_2N_4O_2S$: C, 43.71; H, 2.82; N, 15.68: S, 8.98; found: C, 43.30; H, 2.45; N, 15.48: S, 8.40 %.

3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-(2-fluorophenyl) thiazolidin-4-one (4c): pale yellow solid, yield- 78 %, mp- 145-147°. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 (td, *J*=7.5, 1.9 Hz, 1H), 7.32 (td, *J*=6.6, 5.8, 3.7 Hz, 1H), 7.18 (td, *J*=7.6, 1.2 Hz, 1H), 7.06 (ddd, *J*=9.5, 8.3 .1.2 Hz, 1H, Ar-H), 5.94 (d, *J*=7.4 Hz, 1H), 4.25 - 4.10 (m, 2H). IR (KBr): ν (cm^{-1}) 2836 (C-H str. in aromatic ring), 1715 (C=O of thiazolidinone), 1629 (-C=C- str. in aromatic ring), 809 (C-N- str. in s-triazine). MS (70 eV) *m/z*: 343.90 [M^+, 100%], 345.90 [M+2, 66.66 %], 347.11 [M+4, 11.11 %], anal. calcd for $C_{12}H_7F Cl_2N_4OS$: C, 41.75; H, 2.04; N, 16.23: S, 9.29; found: C, 41.55; H, 2.00; N, 16.10: S, 9.10 %.

2-(4-bromo-2-fluorophenyl)-3-(4,6-dichloro-1,3,5-triazin-2-yl)thiazolidin-4-one (4d): pale yellow solid, yield- 76 %, mp- 145-147°. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.48-7.42(m, 1H), 7.33 (dd, *J*=8.4, 2.0 Hz, 1H), 7.25 (dd, *J*=9.4, 1.9 Hz, 1H), 5.86 (s, 1H), 4.20 - 4.13 (m, 2H). IR (KBr): ν (cm^{-1}) 2830 (C-H str. in aromatic ring), 1719 (C=O of thiazolidinone), 1650 (-C=C- str. in aromatic ring), 810 (C-N- str. in s-triazine) cm^{-1}. MS (70 eV) *m/z*: 424.8 [M^+, 60 %], 424.8 [M+2, 100 %], 424.8 [M+4, 46 %], 424.8 [M+6, 6 %], anal. calcd for $C_{12}H_6F Br Cl_2N_4OS$: C, 33.99; H, 1.43; N, 13.21: S, 7.56; found: C, 33.41; H, 1.35; N, 13.10: S, 7.20 %.

2-(4-bromophenyl)-3-(4,6-dichloro-1,3,5-triazin-2-yl) thiazolidin-4-one (4e), pale yellow solid, yield- 80 %, mp- 160-162°. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.53-7.47(m, 2H), 7.41-7.34 (m, 2H), 5.34 (s, 1H), 4.17 (q, *J*=7.2 Hz, 2H). IR (KBr): ν (cm^{-1}) 2830 (C-H str. in aromatic ring), 1721(C=O of thiazolidinone), 1656 (-C=C- str. in aromatic ring), 811 (C-N- str. in s-triazine). MS (70 eV) *m/z*: 403.86 [M^+, 60 %], 405.86 [M+2, 100 %], 407.86 [M+4, 46 %], 409.86 [M+6, 6 %], anal. calcd. for $C_{12}H_7BrCl_2N_4OS$: C, 35.49 ; H, 1.74 ; N, 13.80; S, 7.90, found: C, 35.30; H, 1.45; N, 13.48; S, 7.20 %.

3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-(4-chloro-2-fluorophenyl) thiazolidin-4-one (4f), pale yellow solid, yield- 81%; mp: 155-157°. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69 (dd, *J*=6.4, 2.6 Hz, 1H), 7.41 (ddd, *J*=8.7, 4.6, 2.6 Hz, 1H), 6.95 (dd, *J*=9.6, 8.7 Hz, 1H), 5.86 (s, 1H), 4.17 (m, 2H). IR (KBr): ν (cm^{-1}) 2820 (C-H str. in aromatic ring), 1720 (C=O of thiazolidinone), 1651 (-C=C- str. in aromatic ring), 812(C-N- str. in s-triazine). MS (70 eV) *m/z*: 377.93[M^+, 100 %], 379.93 [M+2, 100 %], 381.93 [M+4, 33 %], 383.93 [M+6, 4 %], anal. calcd. for $C_{12}H_6FCl_3N_4OS$: C, 37.97 ; H, 1.59 ; N, 14.76: S, 8.45; found: C, 37.41; H, 1.35; N, 14.30: S, 8.20 %.

3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-m-tolylthiazolidin-4-one (4g), pale yellow solid, yield- 86 %, mp- 140-142°. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37-7.33(m, 2H), 7.32-7.27 (m, 2H), 5.88 (s, 1H), 2.21 (s, 3H), 4.22-4.27 (d, *J*=7.2 Hz, 2H). IR (KBr): ν (cm^{-1}) 2842 (C-H str. in aromatic ring), 1718 (C=O of thiazolidinone), 1660 (-C=C- str. in aromatic ring), 814(C-N- str. in s-triazine). MS (70 eV) *m/z*: 340.6 [M^+, 100 %], 342.6 [M+2, 66.66 %], 344.6 [M+4, 11.11 %], anal. calcd. for $C_{13}H_{10}Cl_2N_4OS$: C, 45.76; H, 2.95; N, 16.42: S, 9.40; found: C, 45.56; H, 2.65; N, 16.10: S, 9.30 %.

3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-(4-nitrophenyl) thiazolidin-4-one (4h), pale yellow solid, yield- 78 %, mp- 170-172°. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.66 (m, 2H), 6.85(m, 2H), 5.84 (s, 1H), 4.19-4.12 (m, 2H). IR (KBr): ν (cm^{-1}) 2836 (C-H str. in aromatic ring), 1721 (C=O of thiazolidinone), 1641 (-C=C- str. in aromatic ring), 807(C-N- str. in s-triazine). MS (70 eV) *m/z*: 370.8 [M^+, 100 %], 372.8 [M+2, 66.66 %], 374.8 [M+4, 11.11 %], anal. calcd. for $C_{12}H_7Cl_2N_5O_3S$: C, 38.72 ; H, 1.90 ; N, 18.82: S, 8.62; found: C, 38.41; H, 1.65; N, 18.40: S, 8.40 %.

3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-(2-hydroxyphenyl)thiazolidin-4-one (4i), pale yellow solid, yield- 82 %, mp- 160-162°; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 (d, *J*=11 Hz, 1.8 Hz, 1H), 7.32 (d, *J*=6.5, 5.7, 3.6 Hz, 1H), 7.18 (d, *J*=7.5, 1.3 Hz, 1H), 7.06 (dd, *J*=9.4, 8.2 .1.2 Hz, 1H, Ar-H), 5.92 (d, *J*=7.5 Hz, 1H), 4.21 - 4.12 (m, 2H), IR (KBr): ν (cm^{-1}) 2838 (C-H str. in aromatic ring), 1722 (C=O of thiazolidinone), 1630 (-C=C- str. in aromatic ring), 806 (C-N- str. in s-triazine), MS (70 eV) *m/z*: 341.7 [M^+, 100 %], 343.7 [M+2, 66.66 %], 345.7 [M+4, 11.11 %], anal. calcd for $C_{12}H_8Cl_2N_4O_2S$: C, 42.00; H, 2.35; N, 16.33: S, 9.34; found: C, 41.90; H, 2.10; N, 16.10: S, 9.20 %.

3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-(3-methoxyphenyl)thiazolidin-4-one (4j), pale yellow solid, yield- 80 %, mp- 141-143°, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.15 (s, 1H, Ar-H), 7.93 (m, 1H, Ar-H), 7.60 (m, 1H, Ar-H), 7.46 (m, 1H, Ar-H), 5.37 (d, *J*=7.1 Hz, 1H), 3.75(s, 3H), 3.38 (d, 2H); IR (KBr): ν (cm^{-1}) 2834 (C-H str. in aromatic ring), 1717 (C=O of thiazolidinone), 1625 (-C=C- str. in aromatic ring), 806 (C-N- str. in s-triazine), MS (70 eV) *m/z*: 355.7 [M^+, 100%], 357.7 [M+2, 66.66 %], 359.7 [M+4, 11.11 %], anal. calcd for $C_{13}H_{10}Cl_2N_4O_2S$: C, 43.71; H, 2.82; N, 15.68: S, 8.98; found: C, 43.50; H, 2.75; N, 15.42: S, 8.60 %.

3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-(2,5-difluorophenyl)thiazolidin-4-one (4k), pale yellow solid, yield- 75 %, mp- 178-180°. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.72 (dd, *J*=6.3, 2.5 Hz, 1H), 7.39 (dd, *J*=8.6, 4.5,2.5 Hz, 1H), 6.85 (dd, *J*=9.5, 8.6 Hz, 1H), 5.80 (s, 1H), 4.15 (m, 2H), IR (KBr): ν (cm^{-1}) 2825 (C-H str. in aromatic ring), 1725 (C=O of thiazolidinone), 1650 (-C=C- str. in aromatic ring), 813(C-N- str. in s-triazine) cm^{-1}, MS (70 eV) *m/z*: 361.1 [M^+, 100%], 363.1 [M+2, 66.66 %], 365.1 [M+4, 11.11 %], anal. calcd for $C_{12}H_6Cl_2F_2N_4OS$: C, 39.69; H, 1.67 ; N, 15.43: S, 8.83; found: C, 39.50; H, 1.44; N, 15.33; S, 8.32 %.

3-(3-(4,6-dichloro-1,3,5-triazin-2-yl)-4-oxothiazolidin-2-yl)benzonitrile (4l), pale yellow solid, yield- 78 %, mp- 145-147°, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94 (s, 1H, Ar-H), 7.59 (s, 1H, Ar-H), 7.34-7.21 (m, 1H, Ar-H), 7.04-7.02 (m, 1H, Ar-H), 5.78 (s, 1H), 3.40-3.36(m, 2H), IR (KBr): ν (cm^{-1}) 2835 (C-H str. in aromatic ring), 1724 (C=O of thiazolidinone), 1640 (-C=C- str. in aromatic ring), 806(C-N- str. in s-triazine), MS (70 eV) *m/z*: 350.8 [M^+, 100%], 352.8 [M+2, 66.66 %], 354.8 [M+4, 11.11 %], anal. calcd for $C_{13}H_7Cl_2N_5OS$: C, 44.33; H, 2.00 ; N, 19.88; S, 9.10; found: C, 44.10; H, 1.90; N, 19.56: S, 8.89 %.

Antiinflammatory assay:

Proinflammatory cytokine production by lipopolysaccharide (LPS) in THP-1 cells was measured according to the method described by Hwang *et al.*[29]. During the assay, THP-1 cells were cultured in RPMI 1640 culture medium (Gibco BRL, Pasley, UK), containing 100 U/ml penicillin and 100 mg/ml streptomycin containing 10 % foetal bovine serum (JRH). Cells were differentiated with phorbol myristate acetate (PMA, Sigma). Following cell plating, the test compounds 3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-phenylthiazolidin-4-one (4a-l) in 0.5 % dimethyl sulfoxide were added to each well separately and the plate was incubated for 30 min at 37°. Finally, LPS (*Escherichia coli* 0127:B8, Sigma Chemical Co., St. Louis, MO) was added, at a final concentration of 1 µg/ml in each well. Plates were further incubated at 37° for 24 h in 5 % CO_2. After incubation, supernatants were harvested and assayed for tumor necrosis factor (TNF)-α and IL-6 by ELISA as described by

the manufacturer (BD Biosciences). The percent inhibitions were measured at 10 µM concentration. The dexamethasone was used as standard drugs. The results are tabulated in Table 1.

Molecular docking:

Literature and RCSB Protein Data Bank (www.rcsb.org) survey revealed that no TNF-α trimer has been cocrystallized with small molecules; however a TNF-α dimer structure binding with a small molecule SPD304 is available. Therefore, for molecular docking, the 3D-structure of human TNF-α with antagonist SPD-304 (PDB code: 2AZ5, resolution: 2.1 Å) was downloaded and subjected to minimization using UCSF Chimera (http://www.cgl.ucsf.edu/chimera/). Molecular docking was performed using NRG Suite[30,31], a python and C++ based PyMOL plugin, which detects surface cavities in proteins and use them as target binding-sites for docking simulations with the aid of FlexAID[30,31]. In the present work, following default settings were used to get optimum performance of NRGsuite: binding sites input method, spherical shape; spacing of three dimensional grid: 0.375Å; side chain flexibility- no; ligand flexibility- yes; ligand pose as reference- yes; constraints- no; HET groups-included water molecules; vander Walls permeability-0.1; solvent types- no type; number of chromosomes-1000; number of generations- 1000; fitness model-share; reproduction model- population boom; number of TOP complexes- 10.

Pharmacophore modelling:

For pharmacophore modelling, PyMOL 2.1[32] along with its plugin LIQUID and LigFit were used with default settings. The molecules (three most active) were aligned to get consensus pharmacophore model.

TABLE 1: ANTIINFLAMMATORY ACTIVITY OF 3-(4,6-DICHLORO-1,3,5-TRIAZIN-2-YL)-2-PHENYLTHIAZOLIDIN-4-ONE DERIVATIVES

Compounds (4a-l)	Substituent R	% Inhibition at 10 µM	
		TNF-α	IL-6
4a	H	12	20
4b	4-OMe	32	29
4c	2-F	**70**	**76**
4d	2-F, 4-Br	54	57
4e	4-Br	22	23
4f	2-F, 5-Cl	**60**	**67**
4g	3-Me	10	18
4h	4-NO_2	15	20
4i	2-OH	22	29
4j	3-OMe	45	54
4k	2-F, 5-F	**72**	**79**
4l	5-CN	30	29
Reference drug	Dexamethasone (1 µM)	75	81

RESULTS AND DISCUSSION

The synthesis of different 3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-phenyl thiazolidin-4-ones (4a-l) were successfully achieved by the reaction between aromatic aldehyde, 4,6-dichloro-1,3,5-triazin-2-amine and ethyl 2-mercaptoacetate in dry ethanol and yield of the product obtained was from 76 to 86 %. The antiinflammatory activity of 3-(4,6-dichloro-1,3,5-triazin-2-yl)-2 phenylthiazolidin-4-ones were recorded on the basis of reference standard drug dexamethasone and tabulated in Table 1. Some of the compounds showed highest (4c, 4f and 4k) antiinflammatory activity. To understand the structural feature, which steer the activity profile, all the molecules were docked in the active site of TNF-α. For the sake of convenience and representation, herein, we present the docking pose for most active molecule 4k. Fig. 3 shows the molecular docking poses for molecule 4k, as a representative, within the active site of the enzyme TNF-α and fig. 4 shows the consensus pharmacophore model for most active molecules after alignment.

In this multicomponent reaction (fig. 2), synthesis of 3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-phenyl thiazolidin-4-ones was obtained in good to better yield. This cyclo-condensation multicomponent reaction starts with reaction of 4,6-dichloro-1,3,5-triazin-2-amine and aldehyde, which on further reaction with ethyl 2-mercaptoacetate gives the cyclic intermediates and finally results into product. The mechanism of this cyclo-condensation multicomponent reaction is shown is fig. 5.

From antiinflammatory activity data of 3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-phenylthiazolidin-4-ones (Table 1), it was observed that the compounds 4c, 4f, and 4k were found to be comparatively active as TNF-α and IL-6 inhibitor (up to 60-72 % TNF-α and 67-79 % IL-6 inhibitory activity), while compounds 4k (72 % and 79 %) exhibiting highest inhibition against TNF-α and IL-6, respectively at 10 µM. It is to be noted that the compound found to be equieffective to 1 µM dexamethasone. The compounds 4d and 4j exhibited moderate activity (45-57 % inhibition) while other compounds exhibited low (4b, 4e, 4i, 4l) to very low (4a, 4g, 4h) activity at same level of concentration. The substitution of functional group such as $–OCH_3$, -OH, -Cl and –F showed significant activity. The

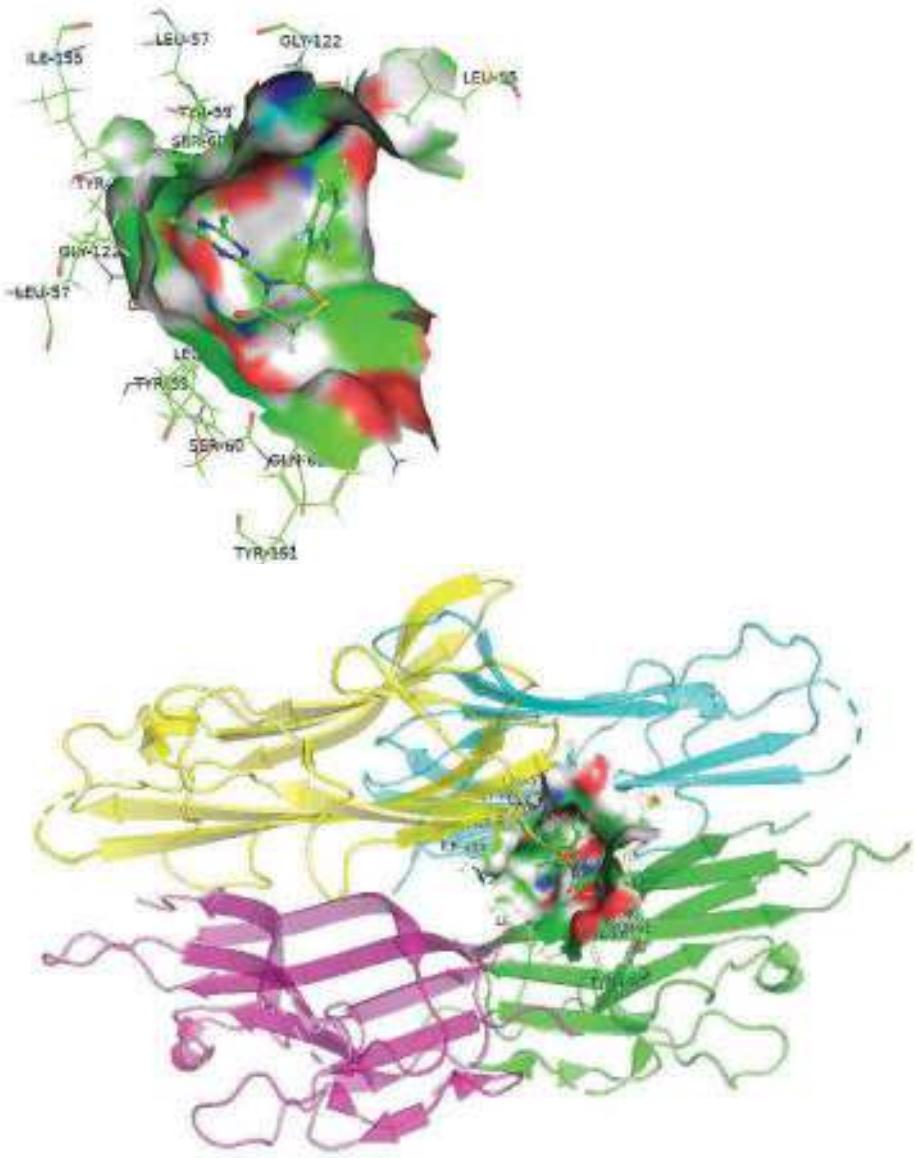

Fig. 3: Docking poses for molecule 4k
Molecular docking poses for the representative molecule 4k within the active site of the enzyme TNF-α

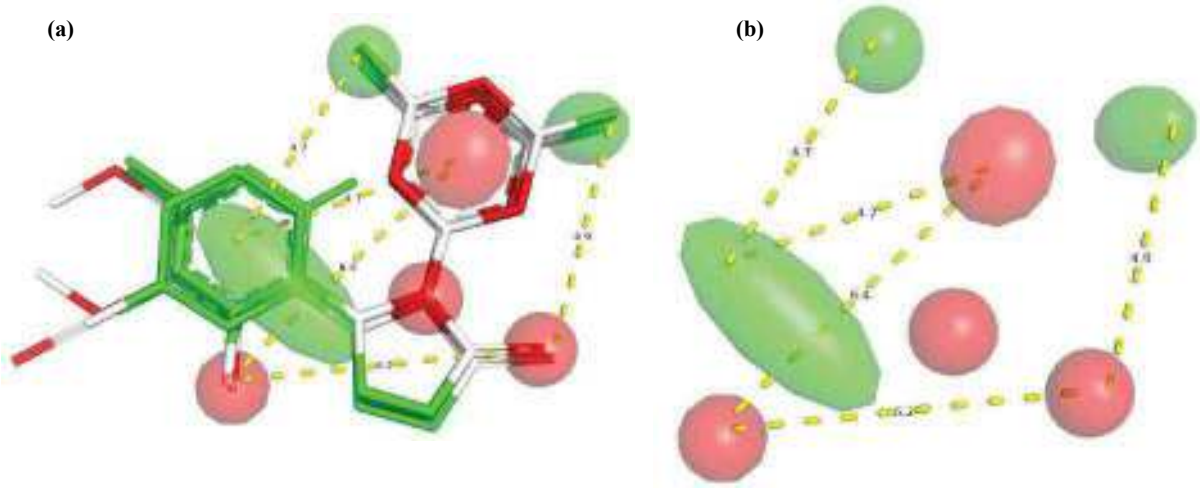

Fig. 4: Consensus pharmacophore model for most active molecules after alignment
(a) Pharmacophore model with molecules as visible, (b) pharmacophore model with molecules made invisible (green contour: hydrophobic, red contour: H-bond acceptor)

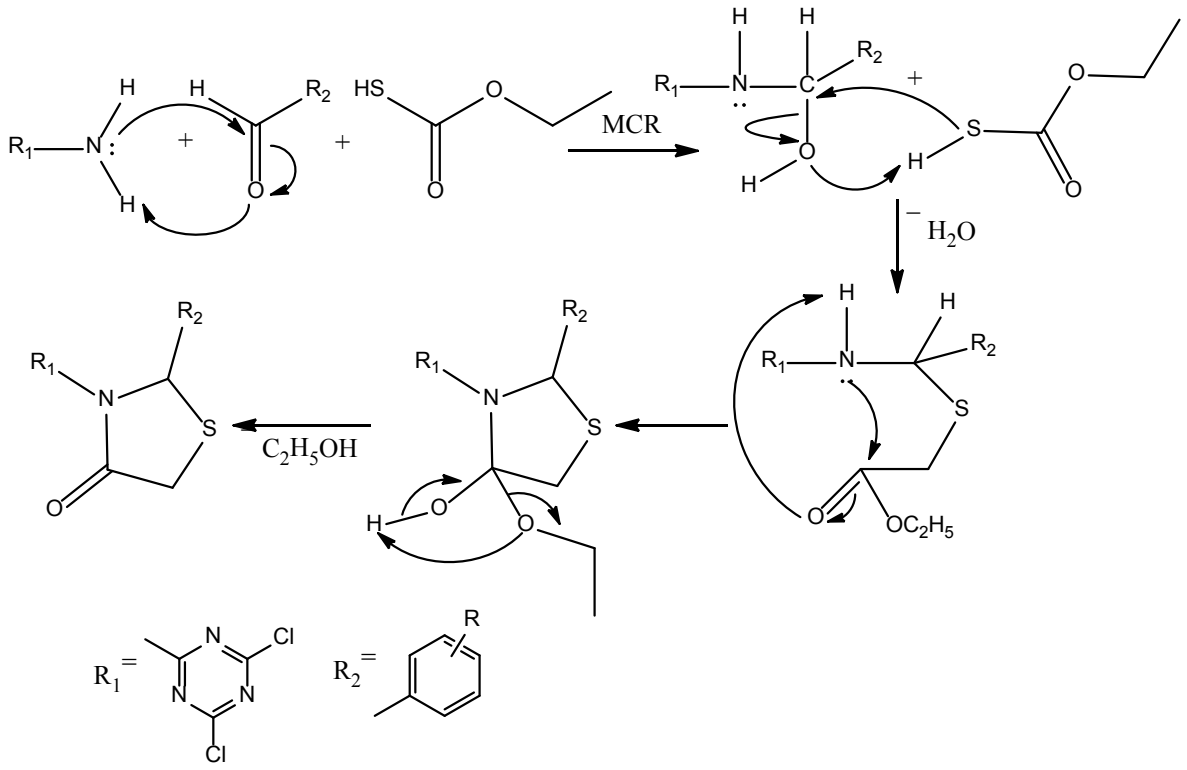

Fig. 5: Mechanism of the multicomponent reaction
Multicomponent reaction involved in the synthesis of aryl substituted 3-(4,6-dichloro-1,3,5-triazin-2-yl) thiazolidin-4-ones

antiinflammatory activity data shows that presence of fluorine group at C-2 and C-5 of phenyl ring plays an important role in the activity. The presence of 'F' group at C-5 enhances the antiinflammatory activity (4k). Because of the presence of chlorine instead of fluorine at C-5 compound (4f) little bit reduces the activity. Further, it was observed that the presence of fluorine at position-2, bromine at position-4 and methoxy group at position-3 on phenyl ring showed moderate activity. Interestingly, the presence of other functional groups on different position on phenyl such as 4-OMe, 4-Br, 3-Me, 2-OH, 4-NO_2 and 5-CN exhibits low to very low activity.

It was revealed from these SAR studies that the presence of a halide (electron donating deactivating group) -F and -Cl at C-5 position tolerates the procytokine activity. It was found that fluorine imparts the special characteristics that enhance therapeutic efficiency and improved pharmacological properties in active molecules. Thus, the compound 4k and 4c were found to be potential antiinflammatory agents amongst the series of compounds studied.

The molecular docking analysis for most active molecule 4k revealed that the molecules have hydrophobic and polar interactions with the receptor residues (fig. 3). From the docking pose, it appeared that the molecule 4k adopted a claw-like shape and presented at the interface of two chains of the enzyme. Its aromatic ring was found to be responsible for hydrophobic interactions with nearby residues viz. Leu55, Leu120, and Tyr59. The importance of hydrophobic part of molecules has also been highlighted by the consensus pharmacophoric analysis (fig. 4).

The two chlorine atoms on the triazine ring also favors hydrophobic interaction with the residues *viz*. SER60, Tyr151, Gly122, and Leu120. Therefore, presence of two chlorine atoms is a good feature for retentions in the future optimizations. The five membered thiazolidinone rings has contributed as a bridge and added additional flexibility to adopt the appropriate conformation inside the active site of the receptor. This ring is closer to chain B of the receptor and responsible for polar interactions with the following residues of chain B *viz*. Ser60 and Gln61. It appeared that docking and pharmacophore analyses provide similar results and highlight hydrophobic as important feature for activity optimization.

In the present work, all molecules (4a-4l) were subjected to molecular docking in the active site of human TNF-α. Table 2 contains the docking scores for the molecules. For the sake of validation of molecular docking, the original ligand (SPD304) was also docked

TABLE 2: DOCKING SCORES FOR MOLECULES 4A-4L AND ORIGINAL LIGAND (SPD304)

ID	SMILES	Docking score
4a	Clc1nc(Cl)nc(N2C(=O)CSC2c2ccccc2)n1	-5.9930043
4b	Clc1nc(Cl)nc(N2C(=O)CSC2c2ccc(OC)cc2)n1	-6.1437421
4c	Clc1nc(Cl)nc(N2C(=O)CSC2c2c(F)cccc2)n1	-5.9163222
4d	Brc1cc(F)c(C2N(c3nc(Cl)nc(Cl)n3)C(=O)CS2)cc1	-6.1437573
4e	Brc1ccc(C2N(c3nc(Cl)nc(Cl)n3)C(=O)CS2)cc1	-5.9886723
4f	Clc1nc(Cl)nc(N2C(=O)CSC2c2c(Cl)cccc2F)n1	-6.1999474
4g	Clc1nc(Cl)nc(N2C(=O)CSC2c2cc(C)ccc2)n1	-6.0782661
4h	Clc1nc(Cl)nc(N2C(=O)CSC2c2ccc([N+](=O)[O-])cc2)n1	-6.4120026
4i	Clc1nc(Cl)nc(N2C(=O)CSC2c2c(O)cccc2)n1	-5.9833794
4j	Clc1nc(Cl)nc(N2C(=O)CSC2c2cc(OC)ccc2)n1	-6.1720862
4k	Clc1nc(Cl)nc(N2C(=O)CSC2c2c(F)cccc2F)n1	-5.9358053
4l	Clc1nc(Cl)nc(N2C(=O)CSC2c2cc(C#N)ccc2)n1	-6.3134403
SPD304	FC(F)(F)c1cc(-n2c3c(c(C[N+](CC[N+](CC4=C(O)c5c(OC4)cc(C)c(C)c5)C)C)c2)cccc3)ccc1	-7.6338243

in the active site of the receptor and its docking score is also tabulated in Table 2. From the Table 2, it is clear that the original ligand (SPD304) has better binding with the receptor than the molecules 4a-4l. Therefore, future modifications are required to increase selectivity and activity profile of triazine thiazolidinone derivatives, synthesized in the present work, for human TNF-α.

In summary, a series of 3-(4,6-dichloro-1,3,5-triazin-2-yl)-2-phenylthiazolidin-4-one derivatives (4a-l) were synthesized in good to better yield by condensation cyclisation reaction between substituted aromatic aldehyde, 4,6-dichloro-1,3,5-triazin-2-amine and ethyl 2-mercaptoacetate using dry ethanol. The SAR study, suggested that the halogenated electron-withdrawing groups imparted greater antiinflammatory activity from the title hybrid skeleton. Furthermore, molecular docking and pharmacophore analyses provided similar results and highlighted hydrophobic moieties as prominent features for activity optimization.

Conflict of interest:

Authors have no conflict of interest.

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SYNTHESIS, SPECTRAL CHARACTERIZATION AND INVESTIGATION OF ANTIMICROBIAL ACTIVITY OF SOME NOVEL SUBSTITUTED PROPANE-1, 3-DIONES DERIVED FROM P-CHLORO-M-CRESOL

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A B S T R A C T

In this study, a series of novel substituted propane-1,3-diones i.e. β-diketones (4a-d) were synthesized in high yields *via* Baker-Venkataraman rearrangement of different substituted 2-benzoyloxy acetophenones (3a-d) with potassium hydroxide in pyridine medium. The structures of titled compounds were established on the basis of spectral data studies of IR and ^{1}H NMR. Furthermore, these compounds were tested *in-vitro* against human pathogens in order to assess their antibacterial and antifungal activity using agar diffusion method.

1. Introduction

In recent years, β-diketones or 1,3-diketones have attracted considerable attention of chemists, biochemists and pharmacologists because of their ready access, predictable reactivity, non-toxicity and serve as precursors for the synthesis of various biologically active heterocyclic compounds[1-2] such as pyrazoles, isoxazoles, imidazoles, benzimidazoles, diazepines and benzodiazepines. They have been used as chelating ligand for various lanthanides and transition metals in material chemistry[3]. Aside from their synthetic importance, they have been found to exhibit significant pharmacological activities like antibacterial[4], antioxidant[5], antiviral[6], systematic insecticidal[7], prophylactic antitumour[8] and breast cancer chemo-preventive blocking agent[9]. In addition, substituted β-diketones like (4-*tert*-butyl-4'-methoxydibenzoylmethane), 1-(4-*tert*-butylphenyl)propane-1,3-dione and 1-p-cumenyl-3-phenylpropane-1,3-dione have been used in UV sunscreen cosmetics that filters ultraviolet rays to protect skin[10] and recently it is reported that β-diketones in its keto-enol form are also the important pharmacophores for the HIV-1 integrase (1N) inhibitors[11]. As β-diketones are having such diverse biological and pharmacological applications, we decided to prepare a new series of substituted propane-1, 3-diones. Hence, in the present work, we have synthesised some novel substituted propane-1,3-diones i.e. β-diketones (4a-d) containing p-chloro-m-cresol moiety by Baker-Venkataraman rearrangement of corresponding substituted 2-benzoyloxyacetophenones (3a-d), characterized them by IR and ^{1}H NMR spectral data and investigate their antimicrobial activity.

2. Materials and Methods

All chemicals and solvents used in this study were of analytical grade obtained from S.D.Fine Chemicals, Merck and Alfa Aesar Company Ltd. The melting points were determined by open tube capillary method and were found uncorrected. The structures of newly synthesized products were characterized by spectral data studies of IR and ^{1}H NMR. The IR spectra were recorded in KBr on Shimadzu (IRAffinity-1) FTIR spectrophotometer. The ^{1}H NMR spectra were recorded on Bruker Avance II 400 MHz NMR spectrometer using DMSO-d_6 as solvent and TMS as an internal standard. All the products were purified by recrystalization and their purity was checked by thin layer chromatography (TLC) on silica gel-G plates.

3. Synthesis of substituted propane-1,3-diones i.e. β-diketones (4a-d)

The synthesis of β-diketones involves following steps:

3.1 General procedure for synthesis of p-chloro-m-cresyl acetate (1)

Initially p-chloro-m-cresol (a) was refluxed with acetic anhydride in presence of anhydrous sodium acetate for 1.5 hour. The reaction mixture was allowed to cool followed by decomposition in cold water. The two layers are formed, out of which lower organic layer was separated by means of separating funnel and purified by distillation to get p-chloro-m-cresyl acetate (1).

3.2 General procedure for synthesis of 5-chloro-2-hydroxy-4-methylacetophenone (2)

The p-chloro-m-cresyl acetate (1) and anhydrous $AlCl_3$ were heated at 120^oC for 1 hour undergone Fries rearrangement followed by decomposition in 10% ice cold HCl to form crude ketone. It was purified by dissolving it in acetic acid and pouring the solution drop wise into cold water with stirring to get 5-chloro-2-hydroxy-4-methylacetophenone (2).

3.3 General procedure for synthesis of substituted 2-benzoyloxy acetophenones (3a-d)

The 5-chloro-2-hydroxy-4-methylacetophenone (2) (0.04 mol) and appropriate substituted benzoic acids (0.05mol) were dissolved in dry pyridine and $POCl_3$ was added drop by drop with stirring till the viscous mass is obtained. Maintain the temperature below 10^oC during the addition of $POCl_3$. The reaction mixture was kept overnight at room temperature and then decomposed by 10% HCl. The solid product thus separated was filtered, washed with water followed by 10% $NaHCO_3$ solution and then again with water. Finally it was crystallized from hot ethanol to get corresponding substituted 2-benzoyloxy acetophenones (3a-d).

3.4 General procedure for synthesis of substituted propane-1,3-diones (4a-d) through Baker-Venkataraman rearrangement

Substituted 2-benzoyloxy acetophenones (3a-d) (0.05mol) was dissolved in dry pyridine (40 ml). The solution was warmed up to 60^oC and pulverized KOH was added slowly with constant stirring. After 6-8 hours the reaction mixture was acidified by ice cold dil.HCl (1:1). The coloured solid product thus separated was filtered, washed with 10% $NaHCO_3$ and finally several times by water. It was then recrystalized from ethanol-acetic acid mixture to get corresponding substituted propane-1, 3-diones i.e. β-diketones (4a-d) as shown in Figure 1. The physical characterization data are given in Table 1.

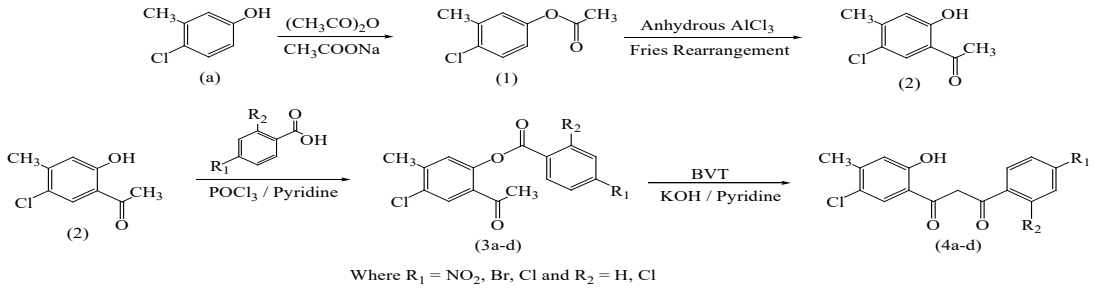

Fig.1: Reaction scheme for synthesis of substituted propane-1,3-diones (4a-d)

4. Spectral data of substituted propane-1, 3-diones (4a-d) *1-(5'-chloro-2'-hydroxy-4'-methylphenyl)-3-(4'-nitrophenyl)propane-1,3-dione (4a)*

IR (KBr): 3388 cm^{-1} (Phenolic -OH stretch), 2918 cm^{-1} (Aromatic C-H stretch), 2848 cm^{-1} (Aliphatic C-H stretch), 1695 cm^{-1} (C=O stretch), 1590 cm^{-1} (Aromatic C=C stretch), 1338 cm^{-1} (C-N stretch), 715 cm^{-1} (C-Cl stretch). ^1H NMR (DMSO-d_6): δ 4.2 (S, 1H of OH), δ 2.5 (S, 3H of CH_3), δ 3.34 (S, 2H of CH_2), δ 6.78-8.33 (m, 6H of Ar-H).

1-(5'-chloro-2'-hydroxy-4'-methylphenyl)-3-(4'-bromophenyl)propane-1,3-dione (4b)

IR (KBr): 3202 cm^{-1} (Phenolic -OH stretch), 3073 cm^{-1} (Aromatic C-H stretch), 2929 cm^{-1} (Aliphatic C-H stretch), 1709 cm^{-1} (C=O stretch), 1564 cm^{-1} (Aromatic C=C stretch), 707 cm^{-1} (C-Cl stretch), 545 cm^{-1} (C-Br stretch). ^1H NMR (DMSO-d_6): δ 4.75 (S, 1H of OH), δ 2.3 (S, 3H of CH_3), δ 2.5 (S, 2H of CH_2), δ 6.91-8.04 (m, 6H of Ar-H).

1-(5'-chloro-2'-hydroxy-4'-methylphenyl)-3-(4'-chlorophenyl)propane-1,3-dione(4c)

IR (KBr): 3413 cm^{-1} (Phenolic -OH stretch), 3136 cm^{-1} (Aromatic C-H stretch), 2950 cm^{-1} (Aliphatic C-H stretch), 1720 cm^{-1} (C=O stretch), 1540 cm^{-1} (Aromatic C=C stretch), 710 cm^{-1} (C-Cl stretch). ^{1}H NMR (DMSO-d_6): δ 4.54 (S, 1H of OH), δ 1.69 (S, 3H of CH_3), δ 2.28 (S, 2H of CH_2), δ 6.69-7.82 (m, 6H of Ar-H).

1-(5'-chloro-2'-hydroxy-4'-methylphenyl)-3-(2',4'-dichlorophenyl)propane-1,3-dione (4d)

IR (KBr): 3734 cm^{-1} (Phenolic -OH stretch), 3096 cm^{-1} (Aromatic C-H stretch), 2919 cm^{-1} (Aliphatic C-H stretch), 1653 cm^{-1} (C=O stretch), 1538 cm^{-1} (Aromatic C=C stretch), 731 cm^{-1} (C-Cl stretch). ^{1}H NMR (DMSO-d_6): δ 4.75 (S, 1H of OH), δ 2.3 (S, 3H of CH_3), δ 2.5 (S, 2H of CH_2), δ 6.95-8.02 (m, 5H of Ar-H).

Table 1: Physical characterization data of substituted propane-1,3-diones (4a-d)

Sr.No.	Compound	R_1	R_2	Mol. Formula	Mol.Wt.	M.P. (^{o}C)	Colour	% Yield
1	4a	NO_2	H	$C_{16}H_{12}ClNO_5$	333.72	218-220	Yellow	70
2	4b	Br	H	$C_{16}H_{12}BrClO_3$	367.62	112-114	Yellow	68
3	4c	Cl	H	$C_{16}H_{12}Cl_2O_3$	323.17	140-142	Yellow	72
4	4d	Cl	Cl	$C_{16}H_{11}Cl_3O_3$	357.62	142-144	Yellow	75

5. Antimicrobial Activity

5.1 Antibacterial activity

The newly synthesized compounds (4a-d) were investigated for their *in-vitro* antibacterial activity against *Escherichia coli* (Gram -ve), *Pseudomonas aeruginosa* (Gram -ve) and *Bacillus subtilis* (Gram +ve) at different concentrations ranging from 25-1000 µg/ml by agar diffusion method[12-13]. DMSO was used as solvent to prepare the solutions of compounds and nutrient agar was used as media. Ciprofloxacin was used as standard antibiotic for reference. Initially the stock cultures of bacteria were revived by inoculating in broth media and grown at 37ºC for 18 hrs. The agar plates of the above media were prepared and wells were made in the plate. Each plate was inoculated with 18 hrs old cultures (100 µl, 10^4 cfu) and spread evenly on the plate. After 20 minutes, the wells were filled with of different concentrations of compounds and antibiotic. All the plates were incubated at 37ºC for 24 hrs and diameter of inhibition zone were noted. The antibacterial activity along with values of MICs of compounds and antibiotic are given in Table 2-5

.

Table 2: Antibacterial activity of substituted propane-1,3-diones (4a-d) against *Escherichia coli*

Compound	25 µg	50 µg	100 µg	250 µg	500µg	1000 µg	MIC µg
4a	0	0	0	0	0	0	NF
4b	0	0	0	0	0	0	NF
4c	0	0	0	0	0	0	NF
4d	0	0	0	0	0	0	NF

Table 3: Antibacterial activity of substituted propane-1,3-diones (4a-d) against *Pseudomonas aeruginosa*

Compound	25 µg	50 µg	100 µg	250 µg	500µg	1000 µg	MIC µg
4a	0	0	0	0	0	5	1000
4b	0	0	0	0	0	0	NF
4c	0	0	0	0	0	0	NF
4d	0	0	0	0	0	5	1000

Table 4: Antibacterial activity of substituted propane-1,3-diones (4a-d) against *Bacillus subtilis*

Compound	25 µg	50 µg	100 µg	250 µg	500µg	1000 µg	MIC µg
4a	0	0	0	0	4	7	500
4b	0	0	0	0	0	0	NF
4c	0	0	0	0	0	0	NF
4d	0	0	0	0	0	4	1000

Table 5: Antibacterial activity of standard Ciprofloxacin against human pathogens

Organism	25 µg	50 µg	100 µg	250 µg	500µg	1000 µg	MIC µg
E.coli	26	29	32	34	38	*	25
P.aeruginosa	30	32	34	35	38	*	25
B.subtilis	20	24	27	30	36	*	25

NF-MIC not found and *Zones could not be measured due to merging.

5.2 Antifungal activity

The antifungal activity of newly synthesized compounds (4a-d) was also investigated in-*vitro* against *Aspergillus flavus*, *Candida albicans* and *Neurospora crassa* at different concentrations ranging from 25-800 µg/ml by agar diffusion method. DMSO was used as solvent to prepare the solutions of compounds and Czapek-Dox agar was used as media. Amphotericin was used as standard antibiotic for reference. Initially the stock cultures of fungi were revived by inoculating in broth media and grown at 27ºC for 48 hrs. The agar plates of the above media were prepared and wells were made in the plate. Each plate was inoculated with 48 hrs old cultures (100 µl, 10^4 cfu) and spread evenly on the plate. After 20 minutes, the wells were filled with of different concentrations of compounds and antibiotic. All the plates were incubated at 27ºC for 96 hrs and diameter of inhibition zone were noted. It is observed that, the compounds have not shown any inhibition zone. The antifungal activity of standard Ampotericin along with their MICs is given in Table 6.

Table 6: Antifungal activity of standard Amphotericin against human pathogens

Organism	25 µg	50 µg	100 µg	200 µg	400µg	800 µg	MIC µg
A.flavus	0	0	0	0	7	10	400
C.albicans	0	2	7	9	13	15	50
N.crassa	0	0	0	0	7	9	400

Result and Discussion

In the present work, a series of novel substituted propane-1,3-diones (4a-d) were synthesized in high yields from corresponding substituted 2-benzoyloxy acetophenones (3a-d) through Baker-Venkataraman rearrangement. The structures of these compounds were established from their physical and spectral data. The IR and ^{1}H NMR spectra showed all the expected signals /peaks which correspond to various groups present in each compound. All the newly synthesized substituted propane-1,3-diones were investigated for their *in vitro* antibacterial and antifungal activities. It was observed that all the compounds 4a, 4b, 4c, and 4d has not showed any zones of inhibition against *E.coli* at all the concentrations tested. The compounds 4a and 4d both showed 5mm of inhibition zones at 1000 µg/ml concentration whereas compounds 4b and 4c has not showed any zones of inhibition at all concentrations against *P.aeurigonosa.* The compound 4a showed 4 and 7mm of zones at 500 and 1000 µg/ml concentrations respectively and also the compound 4d showed 4mm of zone at 1000 µg/ml concentrations against *B.subtilis* whereas for the compound 4b and 4c inhibition zones were not observed against *B.subtilis*. From the results of antifungal activity, it was observed that, all the synthesized compounds 4a-d have not showed any inhibition against *Aspergillus flavus*, *Candida albicans* and *Neurospora crassa.*

Conclusion

In this study, a new series of substituted propane-1,3-diones (4a-d) were successfully derived from p-chloro-m-cresol, analysed for their structures and investigated for their antimicrobial activity. The results of antimicrobial activity reveals that, all the compounds 4a-d showed negative antifungal activity against all the fungi tested and found to be inactive at all the analysed range of concentrations. But in case of antibacterial activity, we concluded that these compounds are poorly active against tested bacteria as compared to standard ciprofloxacin. If the concentration of these synthesized compounds increases, its activity may also increases.

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TO STUDY INTERMOLECULAR INTERACTION OF SUBSTITUTED THIOCARBAMIDOPHENOL AND Cu(II) AND Cd(II) ION IN 70% MIXED SOLVENT MEDIA

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Abstract

Pharmacodynamics and pharmacokinetics of drug received importance in the study of drug potency. Physicochemical parameter of newly synthesized molecules reasonably influence to different steps of pharmacodynamics. Intermolecular interactions and stability constant related to activity synthesized molecules. Present work concerning to the interaction newly synthesized 4-Phenylthiocarbamidophenol (L_1) and 4-(p-Chloro)phenylthiocarbamido phenol (L_2) and Cu(II) and Cd(II) metal ions in 70% ethanol-water mixture. Jobs method of continuous variation is used through this investigation. The stiochiometry of complex formation found to be 1:1. This investigation helps to understand drug effect and drug activity of newly synthesized drugs.

Keywords :- 4-Phenylthiocarbamidophenol (L_1) and 4-(p-Chloro) phenylthiocarbamido phenol (L_2), Stability constant, Jobs Method of Continuous variation.

INTRODUCTION

Drugs Potency closely related to molecular structure and their ionic interactions. Interaction of newly synthesized molecules with deferent metal ions has received some major importance to understand their intra and inter molecular interactions. Solution equilibrium of molecule possible to understood from complex formation ability of ligands and activity of complexes. Physical properties of lignads are relatively corresponding to complexation and its knowledge bear to know composition as well as conformation of complex formation. Drug activity, drug effect, transmission of drug and absorption of drug all these four factors are depending on stability constant of molecule. Absorption directly proportional to concentration and it is alter by different physical parameters of molecules. Spectrophotometric technique more efficiently examines absorption. Thus this technique has a great significance in measurments of stability constant and confirmation of complex formation in solution. Wagh [1] and Deshamukh [2] determined log K value of chalcones pyridine carboxylic acids and hydroxyl ethyl benzene. Galhan et al [3] studied (E)-2-(mercaptophe -nylaminoethylene)-3-oxo-N-p-tolylbutamide with some metal ion by spectrophotometrically. Boldescu et al [4] Spectrophotometrically studied sangurine-bcyclodextrin complex formation. Spectrophotometrically determination of phenylprine hydrochloride and salbutamol sulphate drugs in pharmaceutical preparation using diazotized metacloprine hydrochloride was carried out by Al-Abachi and Abed [5]. Alsamarrai et al [6] investigated ephedrine-hydrochloride by spectrophotometrically. Saleha et al [7] investigated sulphsalazine antibiotics drugs. Investigation of ion complex formation of anti-hypertensive drug mehtyldopal was studied [8]. Meshram [9] studied complexation by interaction of Dy (III) with lincomycine and lyrodoxin in 70%

ethanol-water medium. Spectrophotometric study of diflunisal febuxostate metaxalone, fexofenadine methyl ester and linezolide pharmaceutical dosages using tetracynoethelene was carried out by Shrinivas et al[10] .

Wadekar and Tayade [11] studied conditional stability constants and confirmation of complex formation of Cu (II), Cd (II) and Cr (III) complex with substituted thio- carbamidonaphthols Spectrophotometrically. Valtierra –Alvardo et al [12] investigated complex formation equilibrium of Cu(II). Solvent effect on dissociation of ammonium and pyridinium ion was studied by Ohataki [13]. Investigation of effect of dielectric constant on Cu(II) –Complexes of phthalic acid in various percentage of dioxane-water mixture was carried by Palaskar [14]. To study the interaction of *4-Phenylthiocarbamidophenol* (L_1) and *4-(p-Chloro)phenylthiocarbamido phenol (L_2) and Cu* (II) and Cd(II) metal ions spectrophotometrically. This investigations helps to understand metal-ligand stability constant and confirmation of complexes formation of these interaction at 0.1 M ionic strength. Job method of continuous variation used to through current work. It is specially associated to study of effect of solvents, effect of ligands and group as well as effect of metal ions during formation of complexes.

MATERIALS and METHOD :

Experimental

4-Phenylthiocarbamidophenol (L_1) and *4-(p-Chloro)phenylthiocarbamido phenol (L_2),* has been synthesized in laboratory by standard method. The nitrate salts of Nickel was used & their solutions were prepared in double distilled water. The solutions of potassium nitrate was prepared (1M) & used for maintaining ionic strength constants. Absorption are measured by UV Spectrophotometer model 106, (Systronic make) with an accuracy = ± 0.005 was used.

RESULTS and DISCUSSION

Spectrophotometric Measurement

Job's Method

Jobs method of continuous variation method is reliable to examine formation of complex [15]. Jobs method consist of equimolar solutions of metal and ligand varying proportion in such manner that total concentration of metal plus ligand is constant in resulting mixtures[16]. The compositions of metal ions solution (1 x10 $^{-2}$ M) & ligand (1x 10^{-2}M) were prepared in ten series. Ionic strength was maintained constant (0.1M) by adding an appropriate amount 0f 1M KNO3 solution in 10 ml volume (λmax) was determined using one of the compositions at which there is maximum absorption. The absorption for all the compositions were recorded at a constant wave length (λmax). The data of absorption & % composition of metal ion and ligand solutions at constant pH can be used to construct the curves. It was observed that 1:1 complex formation occurs in the pH range of 3 to 6. Each solution is diluted up to 15 ml and recorded absorption at same (λ max). Conditional stability constants of metal ligand complexes were calculated for all the systems using following expression.

$$K = \frac{X}{(a1-x)(b1-x)} = \frac{X}{(a2-x)(b2-x)}$$

K = Conditional stability constants of complex. X = Concentration of complex.
a1 & a2 = Concentration of metal ions; b1 & b2 = Concentration of ligand.
Conditional stability constants of metal ligand complexes showed in Table-1

Table – 1: Determination of Conditional Stability of Metal Ligand Complexes

System	Conditional stability constant K	Log K
L_1+Cu(II)	1.4930×10^{-3}	0.1741×10^{-3}
L_2+Cu(II)	2.4740×10^{-3}	0.3934×10^{-3}
L_1+Cd(II)	1.8060×10^{-3}	0.2568×10^{-3}
L_2+Cd(II)	1.4590×10^{-3}	0.1641×10^{-3}

CONCLUSION

Table No. 1 reveals that resultant values obtain for L_1 and L_2 are fairly good. There is no appreciably change in log K values. This indicated the simultaneously complex formations.

L_2+Cu(II) interaction has more Log K value than L_1+Cu(II) interaction. It indicate that L_2 able to form more stable complex with Cu(II) than L_1 and L_1+Cd(II) interaction has more Log K value than L_2+Cd(II) interaction. It indicate that L_1 able to form more stable complex with Cd(II) than L_2 .

Variation in Log K values observed due to direct interfere of dielectric constant, solvent-solvent interaction, solute-solvent interaction and solute-solute-solvent interaction. This investigation helps to study of drug activity and drug effect of newly synthesized drugs.

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SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND ANTIMICROBIAL SCREENING OF SOME NEWLY SYNTHESIZED PROPANE-1,3-DIONE (β-DIKETONES) DERIVATIVES

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A B S T R A C T
A simple,efficient and new series of propane-1,3-diones i.e.β-diketone derivatives (4a-d) were prepared via Baker-Venkataraman rearrangement from substituted 2-benzoyloxy acetophenones (3a-d) with potassium hydroxide in pyridine medium and obtained in good yields.The structures of the titled compounds were confirmed by spectral data studies of IR and 1H NMR.The antibacterial and antifungal activity of these newly synthesized compounds (4a-d) were screened by paper disc method and appeared to be significant.
Keywords: 2-Benzoyloxy acetophenones ,Propane-1,3-diones, IR and 1H NMR , Antifungal activity, Antibacterial activity

1.Introduction

Development of simple synthetic steps to widely used organic compounds using readily available of reagents are one of the most important objectives of organic synthesis. In Baker-Venkataraman rearrangement thesynthesis from o-aryloxy acetophenone to β-diketones was utilized. The β-diketones was shows various pharmacological activities like, prophylactic antitumor1, antioxidant2, antisunscreen agents3and biological activity4.The β-diketones have been widely used for the synthesis of heterocyclic compounds such as flavones5,pyrazoles6,2-mercapto pyrimidine7etc.Now recently β-diketones are well known to have keto-enol tautomerism and reported that they have important pharmacophores for the HIV-integrase (1N) inhibitiors8.Substituted propane 1,3-diones are used in various drug containing the heterocyclic moieties, such as isoxazole, carbazole, imidazole and thiazole etc. The β-diketones are used as a ligand in co-ordination chemistry9-10. The synthesis of substituted propane -1,3-diones (β-diketones) are of tremendous important in organic chemistry and medicine, so by focusing on these aspects we are going to synthesized β-diketones asa precursor for different heterocyclic compounds and study their spectroscopic data and antimicrobial properties.

2. Materials and Methods

All solvents and chemicals were of research grade, highest purity and commercially available. The melting points were taken in open capillaries using paraffin Thiele's tube. All the synthesized compounds were purified by recrystallization method. The IR spectra were recorded on Shimadzu IR affinity-1FTIR spectrophotometer in KBr pallets and values were expressed in cm-1.1H NMR spectra were recorded on Bruker Avance II 4000 NMR spectrophotometer in DMSO-d_6 as a solvent and TMS as an internal standard.

3.Synthesis of substituted propane-1,3-diones (β-diketones) (4a-d)

The synthesis involves the following steps.

3.1. General procedure for the synthesis of 4-bromo phenyl acetate (1)

4-bromo phenol (0.05mol) fused with acetic anhydride(5ml) and add sodium acetate. The mixture was refluxed for about 1hr. then cooled for 15 min. and poured in ice crushed water. Acetate layer was separate out by separating funnel and wash several times by water. The product was purified by distillation process to obtained a pure 4-bromo phenyl acetate (1).

3.2. General procedure for the synthesis of5-bromo,2-hydroxy acetophenone (2)

Place anhydrous aluminum chloride (120 g) in kjeldal flask and add 4-bromo phenyl acetate (1) (40 ml) drop wise in a flask. Heat the reaction mixture in oil bath for 60 min at 120^0C temperature. The reaction mixture was cooled and add in to acidified ice crushed water to get crude product. It was purified by dissolving product in acetic acid and decompose in ice cold water to get 5-bromo,2-hydroxy acetophenone (2).

3.3 General procedure for the synthesis of 2-substituted benzoyloxy 5-bromo acetophenone (3a-d)

Place 5-bromo,2-hydroxy acetophenone (2) (0.05mol) and substituted benzoic acid (0.05mol) were dissolved in dry pyridine at 0^0C.Then add $POCl_3$ dropwise with constant stirring bellow 10^0C temperature. The reaction mixture was allowed to stand for overnight at room temperature. The reaction mixture was poured in ice cold acidified 10% HCl. Then the product was wash by 10%$NaHCO_3$ and several times by water. Recrystallized the product by ethanol to obtained a series of 2- substituted benzoyloxy 5-bromo acetophenone (3a-d).

3.4 General procedure for the synthesis of substituted propane-1, 3-diones(β-diketones) (4a-d)

A series of substituted propane-1,3-diones (4a-d) was synthesized by Baker–Venkataraman transformation reaction as shown in **figure 1**. Take 2-substituted benzoyloxy 5-bromo acetophenone (3a-d) (0.05mol) was dissolved in dry pyridine. The reaction mixture was heated up to 60^0C and add pulverized KOH slowly with constant stirring. After 5-6 hr. the reaction mixture was acidified by dil. HCl (1:1) in ice cold water. The crude product was filtered, washed with $NaHCO_3$(10%) and several times by water. Recrystallized the product from ethanol-acetic acid mixture to get substituted propane 1,3-diones (β-diketones) (4a-d) having good yield as shown in **table1**

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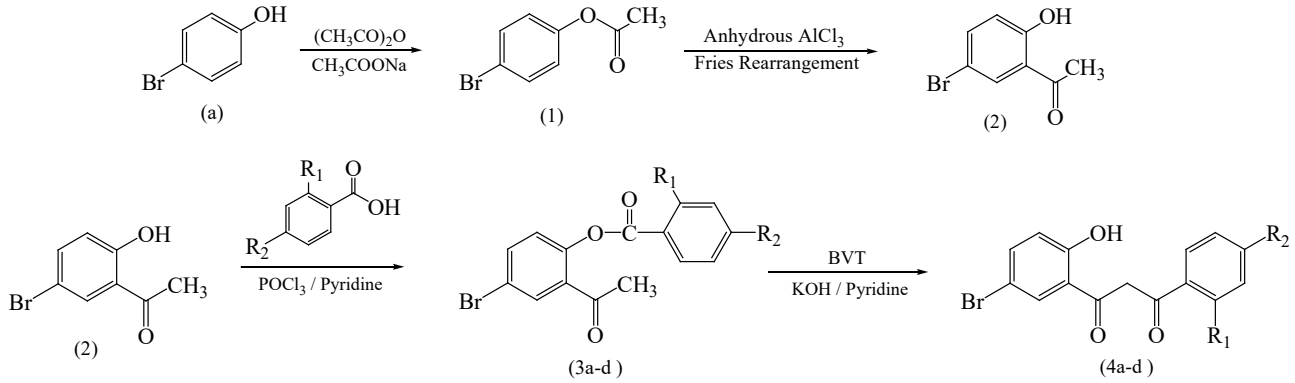
Figure 1. Scheme for the synthesis of substituted propane-1,3-diones (β-diketones) (4a-d)



R_1 – H, Cl R_2 - CH_3, NO_2, H, Cl.

4. Spectral data of all substituted propane -1,3-diones(4a-d)

4.1: 1-(5'-bromo-2'-hydroxy phenyl)-3-(4'-methyl phenyl) propane-1,3-dione(4a)

Solid, dark yellow colour, IR (KBr): 3335 cm^{-1}(Phenolic -OH stretch),3034 cm^{-1}(Aromatic C-H stretch), 2945 cm^{-1}(Aliphatic C-H stretch),1690 cm^{-1}(C=O stretch),1505 cm^{-1}(Aromatic C=C stretch).^{1}H NMR (DMSO-d_6): δ 4.8 (S,1H of OH), δ 2.5 (S, 3H of CH_3), δ 3.44 (S, 2H of CH_2), δ 7.2-8.12(m,7H of Ar C-H).

4.2: 1-(5'-bromo-2'-hydroxy phenyl)-3-(4'nitrophenyl) propane-1,3-dione(4b)

Solid dark yellow colour, IR (KBr):3388 cm^{-1}(Phenolic -OH stretch), 2918 cm^{-1}(Aromatic C-H stretch), 2858 cm^{-1} (Aliphatic C-H stretch),1652 cm^{-1}(C=O stretch),1564 cm^{-1}(Aromatic C=C stretch),1377 cm^{-1}(C-N stretch).^{1}H NMR (DMSO-d_6): δ 6.7 (S, 1H of OH), δ 3.36 (S, 2H of CH_2), δ 6.85-8.30 (m, 7H of Ar C-H).

Table 1 – Physical data of substituted propane-1,3-dione (β-diketones) (4a-d).

Entry	Compound Code	R_1	R_2	M.F.	M.W.	M.P. (^oC)	Yield%
1	4a	H	CH_3	$C_{10}H_{13}BrO_3$	335.18	154-156	72 %
2	4b	H	NO_2	$C_{15}H_{10}B_rNO_5$	364.15	190-192	68%
3	4c	Cl	H	$C_{15}H_{10}BrClO_3$	353.6	112-114	70%
4	4d	H	Cl	$C_{15}H_{10}BrClO_3$	353.6	114-116	74%

M.F.-Molecular formula, M.W.-Molecular weight, M.P.-Melting points

4.3: 1-(5'-bromo-2'-hydroxyphenyl)-3-(2'chlorophenyl) propane-1,3-dione(4c)

Solid dark brown colour,IR (KBr): 3300 cm^{-1} (Phenolic -OH stretch), 3131 cm^{-1}(Aromatic C-H stretch), 2918 cm^{-1} (Aliphatic C-H stretch), 1703 cm^{-1} (C=O stretch),1559 cm^{-1}(Aromatic C=C stretch),766 cm^{-1}(C-Cl stretch).^{1}H NMR (DMSO-d_6): δ 3.53 (S, 1H of OH), δ 2.63 (S, 2H of CH_2), δ 6.92-8.19 (m,7H of Ar C-H).

4..4: 1-(5'-bromo-2'-hydroxyphenyl)-3-(4'chlorophenyl) propane-1,3-dione(4d)

Solid dark yellow colour,IR (KBr): 3310 cm^{-1} (Phenolic -OH stretch), 3124 cm^{-1} (Aromatic C-H stretch), 3042 cm^{-1} (Aliphatic C-H stretch), 1733 cm^{-1} (C=O stretch), 1558 cm-1(Aromatic C=C stretch), 709 cm^{-1}(C-Cl stretch). ^{1}H NMR (DMSO-d_6): δ 4.76 (S, 1H of OH), δ 3.87 (S, 2H of CH_2), δ 6.97-8.11 (m, 7H of Ar C-H).

5.Antimicrobial activity

5.1 Antibacterial Activity

The Synthesized substituted propane-1,3-diones (β-diketones) (4a-d) was screened by antibacterial activity against gram +ve *Staphylococcus aureus* and gram –ve *Salmonella typhi* bacteria by paper disc method[11].The compounds 4a-d was tasted at 50 µg/ml,100 µg/ml and 250µg/ml of concentration in DMSO solvent in which sterile filter paper disc was dipped. Dried the disc and placed the nutrient ager plates spreaded with bacteria. After 24 hr. of incubation at 37^0C the dimeter of zone of inhibition were measured in mm by metric ruler scale and compared with standard ampicillin at 25 µg/ml concentration as antibiotic drug. The results of screening are given in **table 2**.

Table 2 - Antibacterial activity of substituted propane-1, 3-dione (4a-d)

Zone of inhibition (in mm) at µg/ml concentrations							
Entry	Compound Codes	*Staphylococcus aureus* (Gram +ve)			*Salmonella typhi* (Gram –ve)		
		50	100	250	50	100	250
1	4a	--	--	--	--	--	--
2	4b	9.0	7.0	8.0	--	--	--
3	4c	9.0	6.0	7.0	--	--	--
4	4d	8.0	8.0	14.0	7.0	7.0	7.0
5	Std.	24.0	24.0	24.0	24.0	24.0	24.0
6	Control	--	--	--	--	--	--

Std.-Ampicillin, Control-DMSO Solvent," -- "denoted No zone of inhibition

5.2 Antifungal Activity

The synthesized substituted propane-1,3-diones (β-diketones) (4a-d) was also screened for antifungal activity against *candida albican* and *aspergillus niger* by using paper disc method at 50 µg/ml,100 µg/ml and 250 µg/ml concentration in DMSO solvent. The zone of inhibition was measured in mm scale. The antifungal activity of the synthesized compounds was compared with standard Fluconazole at 25 µg/ml concentration as an antibiotic drug. The result of antifungal data was found to be very poor. The β-diketones (4a-d) does not show any zone of inhibition.

Result and Discussion

A series of substituted propane-1,3-diones(β-diketones) (4a-d) was synthesized by Baker–Venkataraman transformation to get good yield. Among the all compounds 4b,4c and 4d shows comparatively better zone of inhibition than 4a against *Staphylococcus aureus*(*Gram +ve)*and 4d show good activity than 4a,4b and 4c against *S. typhi* (Gram –ve). The observed data of antifungal activity were found to be inactive. Compound 4a,4b,4c and 4d does not shows any zone of inhibition at any concentration.

Conclusion

In the present work newly synthesized substituted propane-1,3-diones (β-diketones) (4a-d) involves different steps to get good yield in a short time period. The structure of β-diketones was elucidated on the basis of ^{1}H NMR and IR spectral data. In antibacterial activity only compound 4b,4c and 4d shows zone of inhibition against *s. aureus*. The only compound 4d shows zone of inhibition against *s. typhi*. The result of antifungal activity is negative in which compound 4a-d does not show any zone of inhibition against *candida albican* and *aspergillus nigar.* We are continuing our research work in extending of β-diketones (4a-d) for further synthesis of hetero cyclic compounds

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Synthesis And Characterisation of newly Synthesized Isoxazoline

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Abstract:

A new series of bromo and nitro substituted isoxazolines (3a-d) were synthesized by reacting bromo and nitro substituted chalcones (2a-d) with hydroxyl amine hydrochloride respectively. All these compounds were characterized by means of their UV,IR,^{1}H NMR, spectroscopic data and elemental analysis.

Keywords: Chalcones,Isoxazolines

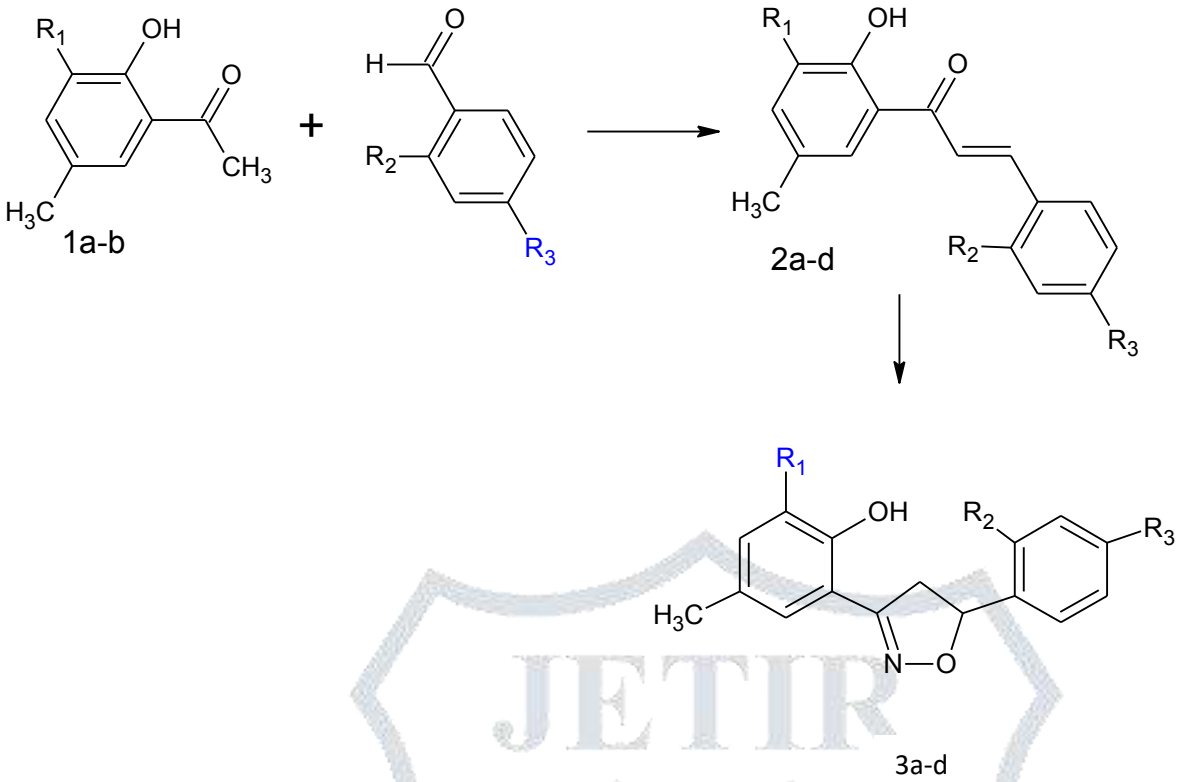
INTRODUCTION:

The dihydroderivatives of isoxazole (a) are known as isoxazolines. A heterocyclic compound is one which possesses a cyclic structure with at least two different kinds of atoms in the ring. Compounds incorporating heterocyclic ring systems continue to attract considerable interest due to the wide range of biological activities. Amongst them five membered heterocyclic compounds occupy a unique place in the realm of natural and synthetic organic chemistry. Five membered heterocycles like isoxazoline have found wide applications pharmaceutical and agrochemical agents.

Experimental

General procedure for synthesis of chalcones (2a-d)

A mixture of substituted acetophenones (0.01 mole) and substituted benzaldehyde (0.01 mole) was stirred in ethanol (15 ml) and to this solution 10% potassium hydroxide added gradually with constant stirring. The reaction mixture was kept overnight at room temperature and then it was poured into crushed ice and acidified with dil. HCI. The product precipitates out was filtered washed with $NaHCO_3$ solution and crystallized from ethanol Scheme 1



General procedure for synthesis of isoxazolines (3a-d)

Bromo and nitro substituted chalcone (2a-d) (0.01 mol) and hydroxyl amine hydrochloride (0.02mol) was refluxed in ethanol (20 ml) and piperidine (0.5ml) for about 1.5 hrs. After cooling; the reaction mixture was acidified with HCl. The solid product thus separated was filtered, washed first with sodium bicarbonate solution (10%) and then with water. Finally it was crystallized from ethanol to get isoxazolines (3a-d). Physical and analytical data of compounds are given in table 1.

Physical and analytical data of compounds (2a-d,3a-d).

table 1.

Compound no.	R_1	R_2	R_3	M.F.	m.p.^{0}C	Yield %	C %	H %	N %
2a	Br	H	Cl	$C_{16}H_{12}O_2BrCl$	101	72	53.98	3.01	--
2b	NO_2	H	Cl	$C_{16}H_{12}O_4NCl$	115	68	59.95	3.01	4.01
2c	Br	Cl	Cl	$C_{16}H_{11}O_2BrCl_2$	82	72	49.01	2.03	--
2d	NO_2	Cl	Cl	$C_{16}H_{11}O_4NCl_2$	102	78	54.02	2.99	3.10
3a	Br	H	Cl	$C_{16}H_{13}BrClNO_2$.	120	60	52.01	3.07	3.00
3b	NO_2	H	Cl	$C_{16}H_{13}ClN_2O_4$.	135	76	56.9	3.02	8.00

3c	Br	Cl	Cl	$C_{16}H_{12}BrNO_2Cl_2$.	160	70	47.00	2.03	3.02
3d	NO_2	Cl	Cl	$C_{16}H_{12}Cl_2N_2O_4$.	145	80	51.90	3.02	7.01

Results and Discussion

The structure of synthesized compounds (2a-d,3a-d) were confirmed on the basis of spectral and elemental analysis .The IR spectrum of **2a-d** exhibited a band due to –OH str.(3350.88cm^{-1}), >C=O str. (1691.59 cm^{-1}),-C=C-str.(1613.84 cm^{-1}), -Cl str.(1135.52 cm^{-1}),-Br str.(1059cm^{-1}).Futher,in^{1}H NMR spectrum, the appearance of a signal at δ 2.4 (s,3H,-CH3), 7.09 to 7.83(m,6H, Ar–H), 7.85(d,1H,-COCH=CH-),8.2(d,1H,-COCH=CH-),11.17(s,1H,-OH)confirms the presence of chalcone.

Similarly ,the structure of compounds **3a-d** was confirmed on the basis of spectral and elemental analysis.The IR spectrum of **3a-d** exhibited a band due to H-bonded O–H stretching (3241.21cm^{-1}), aromatic stretching, >C–H (3087.43 cm^{-1}), Aliphatic C–H stretching 2922.35, –C=N- str.(1582.55cm^{-1}), >C–O stretching (1288.00 cm^{-1}) and -C–Br stretching (1102.97 cm^{-1}). Further, in their in^{1}H NMR spectrum, the appearance of a signal at δ 2.33 (s,3H,Ar-CH_3); δ 3.5 (d, 2H, Heterocyclic –CH_2–CH–) , δ 5.06 (s,1H,-Ar–OH), δ 6.8 (t, 1H, Heterocyclic –CH2–CH–), δ 7.09-7.54 (m,6H,Ar–H) δ 1.2 (s,1H,-CH), δ 2.5(s,1H,-NH), δ 2.3.3 (s,3H,-CH3), δ 6.9(d,1H, =C–H), δ 7.3 to 8.3(m,11H, Ar–H), and δ 12.3(s,1H,-OH) confirms the presence isoxazoline.

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Metal-Ligand Stability Constants of Ni(II) and Co(II) ,Cu(II) Metal Ions Complexes With Some Substituted Isoxazoline Ph –Metrically

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Abstract:

The stepwise stability constant values of substituted isoxazolines with Ni(II) and Co(II) ,Cu(II) metal ion have been studied at 0.1M ionic strength pH-Metrically in 70% Dioxane - Water mixture by Bjerrum method as adopted by Calvin Wilson. The values of proton-ligand stability constant (pK) and metal-ligand stability constant (log K) are calculated and from the data obtained it is observed that metal ions formed 1:1 complexes with ligands L1 and L2 using half integral & pointwise calculation method.

Keywords: Metal ions with Ni(II) and Co(II) ,Cu(II)

L1:- :- (2-hydroxy-3-bromo-5-methylphenyl)-6-(3-Indole)-2-iminophenyl-3,6-dihydro-1,3-thiazine

L_2 :- (2-hydroxy-3-nitro-5-methylphenyl)-6-(3-Indole)-2-iminophenyl-3,6-dihydro-1,3-thiazine

Solvent –70% Dioxane -Water mixture

Introduction:

Substituted isoxazoline are an important class of heterocyclic compound and have attracts many researchers because of its application in medicinal field. The stability constant for the metal complexes are widely used in various fields such as biological processes, pharmaceuticals, analytical processes etc. Metal complexes play a very vital role in nature,with the view to understand the bio-inorganic chemistry of metal ion. Shelke et al.[5] have investigated the interaction between UO_2(II) and Cu(II) with dicarboxylic acids in dioxane-water mixture.

Narwade et al.[1]have studied the equilibrium constant of Fe(III) with substituted chalcones at 0.1 M ionic strength potentiometrically.Sawalakhe and Narwade[2] have studied role of dielectric constants on substituted pyrazoline - complexes potentiometrically.Sawalakhe et al.[3] have studied stability constants of Cu(II) complexes with some substituted diketones at 0.1 M ionic strength by pH-metric technique. Gudadhe et al.[4] have studied the formation constants and stability constants of Thorium(IV) complex with some substituted pyrazolines.Gopal Narain et al.[5] studied characters of some Cobalt(II) complexes with substituted pyrazoles. Raghuwanshi et al.[6] showed confirmation of complex formation of N, O and S containing hetrocycle with Cu(II) metal ion.Tayade V.B. et al7 had studied proton-ligand and metal-ligand stability constants of 3,5-diarylpyrazolines, pyrazoles, isoxazolines and isoxazoles potentiometrically.Ramteke et al.[8]determined stability constants of 4-(2-chlorophenyl)-3-(3-furanoyl-5-(2-hydroxyphenyl) pyrazole with Cu(II), Ni(II), Co(II) and Nd(III) metal ions in 70% dioxane-water mixture.

Experimental:

The solution of ligands L1 and L2 were prepared in 70% dioxane-water mixture. The solution of NaOH, HNO3, KNO3 and metal ions CU (NO3)3,CO(NO3)3, and Ni(NO3)3 were obtained from BDH grade chemicals. The NaOH solution was standardized with oxalic acid, kept in pyrex vessel and used as a titrant for pH titrations. The 1.0 M KNO3 solutions were prepared to maintain the 0.1 M ionic strength of the solution. The metal nitrates were used to prepared the metal solution and were standardized by usual procedure.

Measurements:

All measurements were carried out at 30±0.10C . Systronic microprocessor based pH meter with magnetic stirrer and combined glass and calomel electrode assembly used for pH measurements. The sensitivity of pH is 0.01 units . the instruments could read pH in the range 0.00 to 14.00 in the step of 0.005. The pH meter was switched ON on half an hour before starting the titration for initial warm up of the instrument. It was calibrated before each titration with an aqueous standard buffer solution of pH 7.00 and 9.20 at (30±0.10C) prepared from a 'Qualigens' buffer tablets. The hydrogen ion concentration was measured with combine glass electrode.

Procedure:-

Experimental procedure involves following three set of titrations

- Free acid titration (HNO3 , 1 x 10-2 M)
- Free acid + ligand titration (20 x 10-4M)
- Free acid + ligand + metal ion titration (4 x 10-4 M).

were carried out with standard NaOH solution (0.1M) in presence of inner atmosphere by bubbling a contant flow of nitrogen gas. Data obtained from the titration was used to plot a graph between volume of NaOH and pH values, they are called acid , ligand and metal titration curves.

Result and Discussion:

Substituted isoxazolines is considered as monobasic acid having only one replaceable H+ ion from –OH group.

HL H+ + L

It is observed from titration curve for all the system that ligand curves start deviating from free acid (HNO3) curves at about 3.5 and deviated continuously upto pH-11. The deviation shows that dissociation of –OH group in substituted isoxazoline.

Proton-ligand formation number n_A were calculated from acid titration curve (A) and acid ligand titration curve (A+L) by standard method. It was found that values of n_A decreases with increased pH of solution due to replacement of H+ ion from –OH group. The proton-ligand formation number were calculated by Irving and Rossotti expression.

$$\bar{n}_A = \cdot - \frac{(V_2 - V_1)(N + \cdot^0)}{(V^0 + V_1)(T_L^0)}$$

V0:- is the initial volume of solution, E0 and T0L :- are initial concentrations of mineral acid and ligand respectively. , V_1 and V_2 are the volumes of alkali of a normality N during the acid and ligand titration at a given pH, γ is the number of replaceable proton from the ligand.

Determination of $\bar{n}_A$ Values

System – Ligand (L_1) Medium – 70% Methanol-water

$E° = 1.00 \times 10^{-2}$ M $T_L° = 20.00 \times 10^{-4}$ M Temp. = 30 ± 0.1°C

N = 0.10 N $\mu = 0.1$ M $V^0 = 25$ ml

Table 1

pH	V_1	V_2	$V_2 - V_1$	$\bar{n}_A$
6.00	6.00	5.85	.05	.95
6.25	6.00	6.05	.05	.90
6.50	6.00	6.10	.10	.86
6.75	6.00	6.15	.15	.81
7.00	6.00	6.20	.20	.72
7.25	6.00	6.27	27	.63
7.50	6.00	6.36	.36	.55
7.75	6.00	6.41	.41	.4875

Determination of $\bar{n}_A$ Values System – Ligand (L_2)

Table – 2

pH	V_1	V_2	$V_2 - V_1$	$\bar{n}_A$
5.75	6.00	6.04	0.04	.96
6.00	6.00	6.08	.08	.92
6.25	6.00	6.12	.12	.88
6.50	6.00	6.16	.16	.84
6.75	6.00	6.20	.20	.80
7.00	6.00	6.25	.25	.75
7.25	6.00	6.30	.30	.70
7.50	6.00	6.34	.34	.66
7.75	6.00	6.40	.40	.60
8.00	6.00	6.46	.46	.54
8.25	6.00	6.51	.51	.49
8.50	6.00	6.55	.55	.45

Fig. 1
Plot between n_A Vs pH
System : (L_1)

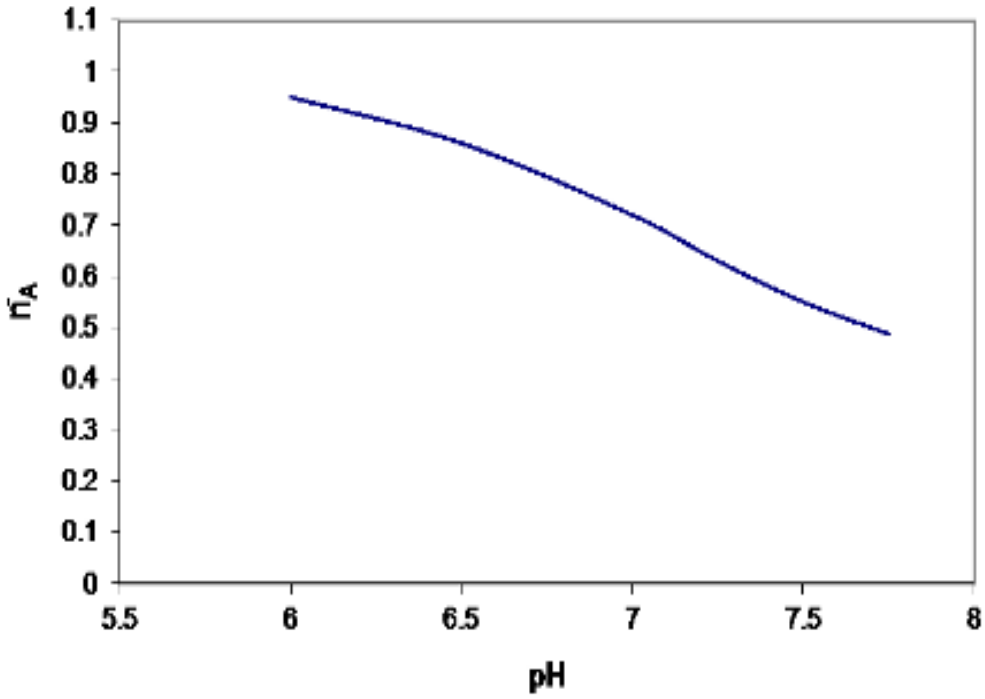

Fig. 2
Plot between π_A Vs pH
System : (L_2)

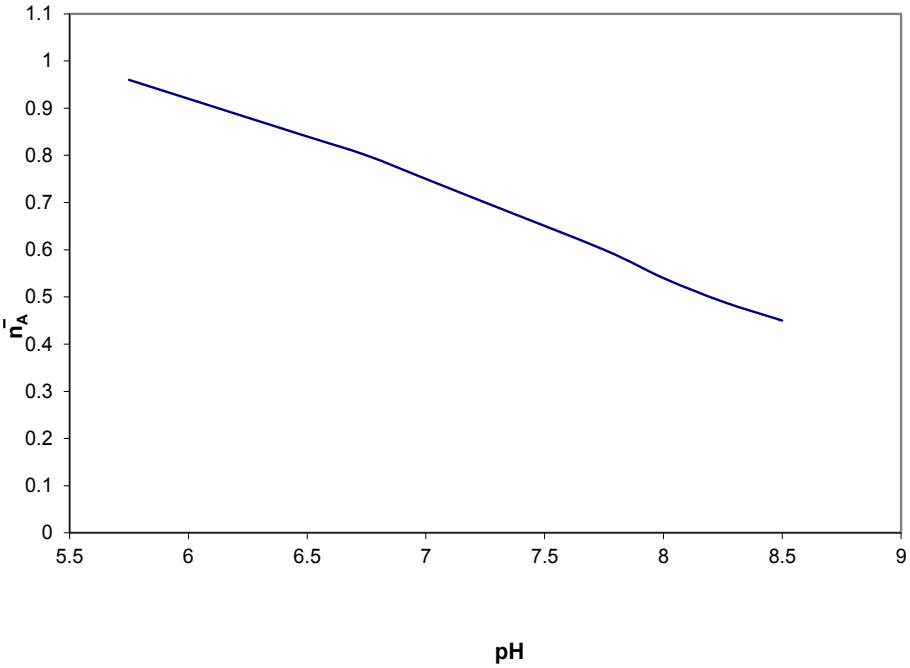

Table 3
Determination of Proton-Ligand Stability Constants (pK)

No.	Ligands	pK Value
L_1	3-(2-hydroxy-3-bromo-5-methyl phenyl)-5-(3-indyl)-isoxazoline	8.78
L_2	3-(2-hydroxy-3-nitro-5-methyl phenyl)-5-(3-indyl)-isoxazoline	8.33

Table 4
Metal-Ligand Stability Constants (log K)

System	Metal-Ligand Stability Constants (Log K)	
	log K_1	**log K_2**
L_1-Ni(II)	6.09	7.36
L_1-Cu(II)	6.13	7.24
L_1-Co(II)	5.62	6.34
L_2-Ni(II)	6.01	7.03
L_2-Cu(II)	6.76	8.51
L_2-Co(II)	7.00	9.21

Conclusion;

It was observed from above table-4 that log K2values are greater than log K1 values for all metal complexes. The difference between log K1 and K2 is greater than 1 which shows the formation of stepwise complex. If the difference is smaller than 1 then that shows the formation of simultaneous complexes. The higher values of ratio (logK1/logK2) indicate the more stable stepwise complex formation.

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Common Pharmacophore Pattern for Anthelmintic Activity of A Pesticide Tolfenpyrad (TFP)

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Abstract:

The present work is based on the technique of pharmacophoric modeling to identify important structural features and their common pattern which is associated with anthelmintic activity of a registered pesticide Tolfenpyrad (TFP) and its derivatives. A dataset of forty derivatives of TFP, covering broad chemical space, was utilized for the present work. The analysis involved a number of steps to arrive at a common pharmacophoric pattern. The results highlight the importance of aromatic rings and local environment in the molecule. The results shall avail deeper understanding of anthelmintic activity of a registered pesticide Tolfenpyrad (TFP) and its derivatives to a greater extent.

Keywords: Common Pharmacophore modeling, Drug designing, anthelmintic activity, Tolfenpyrad

Introduction:

Gastrointestinal roundworms (nematodes) are parasitic worms which cause severe decline in production especially in industries like dairy, meat, etc. Therefore, a variety of chemicals are used for controlling these pathogens. Unfortunately, recent reports have indicated that excessive and uncontrolled use of these drugs has resulted in appearance of resistance and tolerance to many anthelmintic agents. Therefore, repurposing of drug(s) or designing a new drug in time is essential to curb these parasites [1-4]. In last two decades, CADD (Computer Assisted Drug Designing) has appeared a rapid, cheaper and an alternative to traditional approaches like Free-Wilson, Topliss approach, etc. due to fast developments in computers, biochemistry, mathematics and medicinal chemistry.

Pharmacophore modeling, QSAR (Quantitative Structure-Activity relationships), Molecular docking and many branches of CADD are routinely used by medicinal chemists to derive a better drug candidate possessing suitable chemical and biological profiles. Pharmacophore modeling is more popular and used when the 3D- structure of protein (target enzyme) with which a drug and its derivatives interact is unknown. In such a situation, pharmacophore modeling is used to derive a common pattern which is linked with the desired bioactivity [6-8]. Hence, in this work, we have established a consensus pharmacophore model for anthelmintic activity of a registered pesticide Tolfenpyrad (TFP) and its derivatives

In 2019, Le et al [1] described anthelmintic activity of a registered pesticide Tolfenpyrad (TFP) and its analogues. TFP is a pyrazole-5-carboxamide class of complex I inhibitor. The recently synthesized compounds were tested for L3 motility and L4 development of H. contortus larvae and activity values (IC_{50}) varies from micromolar (µM) to nanomolar (nM) range. Though, SAR (Structure Activity Relationships) were conversed in good details by them, but no effort was accomplished to generate consensus pharmacophore model. Hence, in this work, we derived consensus model using Tolfenpyrad (TFP) and its analogues for their activity against L4 development of H. contortus larvae. The results shall a better understanding of structural features and their inter-relationships when developing a new drug for parasites.

Experimental Methodology:

Dataset:

The dataset consists of forty TFP derivatives exhibiting the anthelmintic activity, reported as IC_{50}, in µM to nM range (1.69 to 0.0007 µM). The complete dataset has good alteration with respect to substitution pattern, thereby broadening the chemical space coverage [1]. Hence worth, the carefully chosen dataset is big enough and broad to develop a consensus pharmacophore model. The dataset has been tabulated in table 1.

Table 1. Different TFP derivatives along with reported IC_{50} for L4 used in the present work

S.N.	SMILES notation	L4 (IC_{50})
1.	C18H15Cl2N3O2	0.0007 ± 0.0001
2.	C18H15ClFN3O2	0.0008 ± 0.0001
3.	C19H17Cl2N3O2	0.0008 ± 0.0001
4.	C19H18ClN3O2	0.003 ± 0.004
5.	C20H20ClFN4O2	0.003 ± 0.004
6.	C19H17ClFN3O2	0.004 ± 0.004
7.	C18H16Cl2N4O2	0.008 ± 0.009
8.	C19H18FN3O2	0.01 ± 0.007
9.	C19H19ClN4O2	0.01 ± 0.01
10.	C20H20ClFN4O2	0.019 ± 0.011
11.	C17H14Cl2N4O2	0.02 ± 0.01
12.	C21H22ClN3O2	0.03 ± 0.005
13.	C20H21ClN4O2	0.03 ± 0.01
14.	C18H16ClFN4O2	0.03 ± 0.02
15.	C20H20ClFN4O2	0.03 ±0.02
16.	C20H18Cl2FN3O2	0.035 ± 0.005
17.	C21H21ClFN3O2	0.04 ± 0.005
18.	C20H19ClFN3O2	0.04 ± 0.01
19.	C20H18Cl2FN3O2	0.04 ± 0.01
20.	C20H20ClN3O	0.04 ± 0.01
21.	C21H22ClN3O	0.04 ± 0.02
22.	C18H17ClN4O2	0.04 ± 0.03
23.	C19H19FN4O2	0.05 ± 0.03
24.	C21H23N3O2	0.057 ± 0.002
25.	C21H21ClFN3O2	0.06 ± 0.03
26.	C21H22FN3O	0.07 ± 0.06
27.	C20H20ClN3O2	0.08 ± 0.006
28.	C21H21ClFN3O2	0.08 ± 0.03
29.	C19H19N3O2	0.13 ± 0.10
30.	C21H21ClFN3O2	0.14 ± 0.05
31.	C21H21ClN6O2	0.16 ± 0.11
32.	C17H14ClFN4O2	0.17 ± 0.09
33.	C20H21ClN4O	0.19 ± 0.08
34.	C18H17FN4O2	0.19 ± 0.15
35.	C20H20FN3O	0.19 ± 0.15
36.	C19H19ClN4O	0.23 ± 0.12
37.	C21H19ClN4O3	0.34 ± 0.32

38.	C20H21ClN4O3	0.45 ± 0.04
39.	C20H21FN4O	0.97 ± 0.46
40.	C20H18N4O2	1.69 ± 0.67

Development of Pharmacophore model [6-8]**:**

The complete procedure to derive a consensus model for pharmacophoric pattern identification encompasses many steps like structure drawing, their optimization by suitable method, alignment by appropriate method and creation of model. These steps were accomplished using the standard procedure reported in literature [6-8]. A brief description of these four main steps is as following:

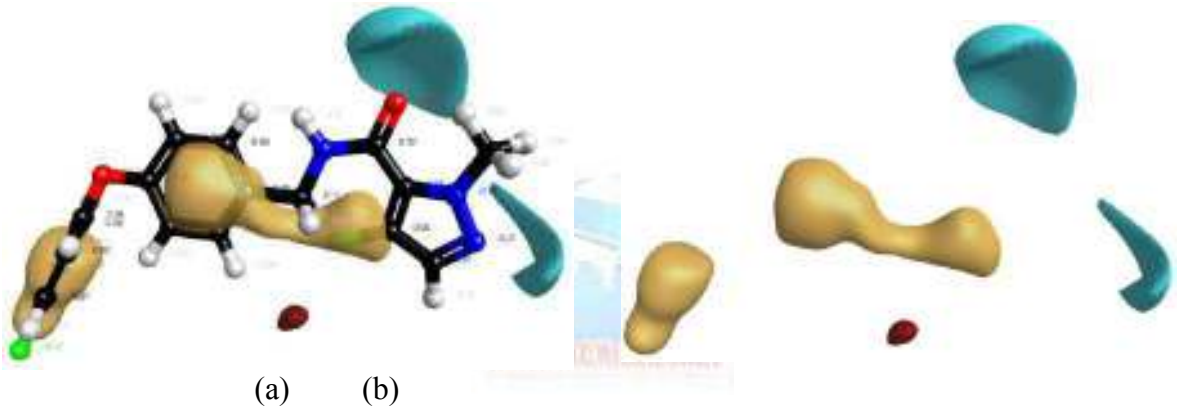
Step-1: The structures were drawn using ChemSketch 2012 freeware

Step-2: PM3 semi-empirical method was used for structure optimization using MOPAC 2012 on Linux

Step-3: Alignment of all the TFP derivatives using Open3dAlign software installed on Linux

Step-4: Using the default settings, consensus pharmacophore model was formed using PyMOl 2.2

Results and Discussion:



(a) (b)

Figure 1. 3D- representation of consensus pharmacophoric pattern using the active molecule **1** as a representative only (Yellow: Hydrophobic, Blue: Negative and Red: Positive charged regions) (a) With molecule and (b) without molecule

The consensus pharmacophore modeling recognized four regions of importance with respect to anthelmintic activity of TFP and its analogues. These four regions are: (1) Two hydrophobic regions (shown by yellow contours): one of the hydrophobic regions extends from benzene ring to a five membered heterocyclic ring whereas the other is due to remaining benzene ring, (2) Two negatively charged regions (shown by blue contour): the first negative region is due to linker -CO-NH- and the other is due to two N atoms of a five membered heterocyclic ring. Thus, the anthelmintic activity of TFP and its analogues varies with hydrophobic/lipophilic and negatively charged regions. The linker -CO-NH- and two N atoms of a five membered heterocyclic ring must be retained in future optimizations along with two benzene rings with appropriate substituents to have optimum logP.

Conclusions:

The present work successfully highlighted the importance of various structural patterns associated with anthelmintic activity of TFP and its analogues.

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Microwave Synthesis and Wound Healing Effect of Δ^2 – Pyrazoles ointment In Albino Rats

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Abstract

Microwave irradiation, as conventional way has been used for variety of applications including pyrazole synthesis. Effect of 3-(3, 5-dichloro-2-hydroxyphenyl)-1-phenyl-5-(pyridin-2-yl)-1H-pyrazol-4-yl) (furan-2-yl) methanone (FP_3) ointment was studied on the wounds of albino rats. The ointment of the Δ^2 –Pyrazoles produced significant result on tested albino rats. The ointment of Δ^2 –Pyrazoles (FP_3) wounds were found to be epithelialise faster and rate of wound contraction was higher, as compare to the control wounds.

Keywords: Δ^2 –Pyrazoles, Microwave synthesis, IR, NMR,Wound healing activity.

Introduction:

Five membered heterocyclic compounds with an additional hetero atom are termed as azoles. The azoles containing two nitrogen atoms in the 1, 2-position is designated as pyrazoles. The generic name pyrazole was given by Knorr[1] et al in 1883. Microwave irradiation, as conventional way has been used for variety of applications including pyrazole synthesis. The short reaction time and expanded reaction range offered by microwave assisted synthesis are suited for the chemist all over the globe. Laurence[2] et al studied microwave assisted pyrazole reactions.

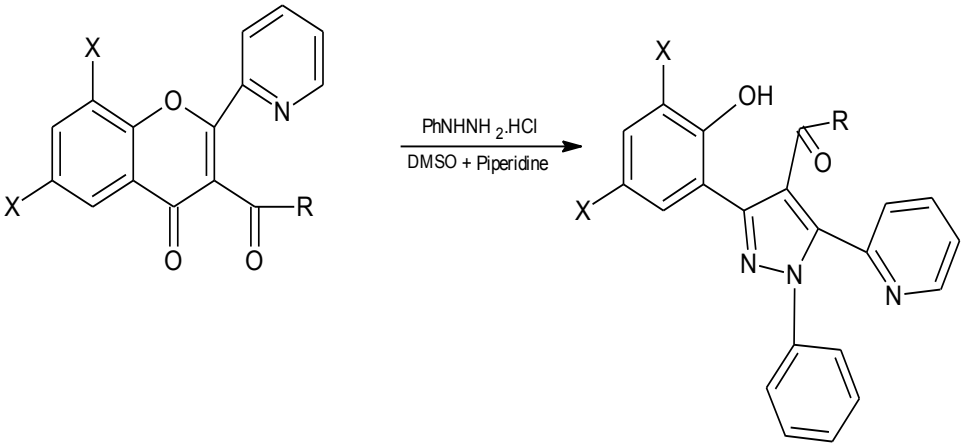
Most of the skin and their related problems heal by pyrazole and their derivatives. The synthetic five membered heterocyclic drugs as pyrazoles is the special type of drugs in pharmaceuticals. Malpani[3] carried out pharmaceutical studies regarding wound healing activity of pyrazole moiety in plant extract. Jha[4] et al reported excision and incision wound healing activity of flower head alcoholic extract of sphaeranthus indicus linn. in albino rats. Hence, the present study was deals the effect of 3-(3, 5-dichloro-2-hydroxyphenyl)-1-phenyl-5-(pyridin-2-yl)-1H-pyrazol-4-yl) (furan-2-yl) methanone (FP_3) on albino rats with special reference to wound healing activity.

Materials And Methods:

Synthesis of (3-(3,5-dichloro-2-hydroxyphenyl)-1-phenyl-5-(pyridin-2-yl)-1H-pyrazol-4-yl) (furan-2-yl) methanone (FP_3)

A mixture of 6,8-Dichloro-3-(furan-2-carbonyl)-2-(pyridin-2-yl)-4H-chromen-4-one (FP_2) (0.01mol) and phenylhydrazine hydrochloride (0.02) was irradiated in DMSO (20 ml)

containing (0.5 ml) piperidine for 3 min.15 sec in microwave. After cooling the mixture was decomposed into the ice and solid product thus obtained crystallized from 50% ethanol-methanol mixture. The black colored shining crystals of the compound (FP_3) were obtained. Yield: 61%, m.p:198 ^{0}C.



Where X = H, Cl and R= C_6H_5, C_4H_4O

MW, 800 W, time: 3 min. 15 sec, Solvent: DMSO.
Microwave: 3 min. 15 sec , Yield: 61%
Conventional: 2 hour, Yield: 60%

The conformation of structure of (3-(3,5-dichloro-2-hydroxyphenyl)-1-phenyl-5-(pyridin-2-yl)-1H-pyrazol-4-yl) (furan-2-yl) methanone (FP_3) compound on the basis of spectral result.

Spectral data for compound (FP_3)

FTIR:- (KBr, cm-1): (FP3):- 3354 (OH – stretching), 3074 (Ar-C-H stretching in CH_3), 1666 (C=O Stretching), 1447 (C=N stretch), 1033 (C-O stretch), 754 (C-Cl stretch),

H1 NMR: - (400MHz, CDCl3, δ ppm): 6.96 to 8.2655 (m, 14H, Ar-H), 11.97 (s, 1H, OH).

(c) UV: - The UV-VIS spectrum of the compound (FP_3) recorded in CHCl3 showed λmax value 410 nm corresponding to n→π*

Synthesis of (3-(3,5-dichloro-2-hydroxyphenyl)-1-phenyl-5-(pyridin-2-yl)-1H-pyrazol-4-yl) (furan-2-yl) methanone (FP_3) ointment

Trituration method (rubbing or reducing to a fine powder) used as the ointment base. 0.5 gm pyrazole (FP_3) compound was taken. 10 g of ointment base was taken (white soft paraffin was used as an ointment base). Ointment base was first melted. The Compound (FP_3) was trituted with the small quantity of ointment base until a homogeneous product was formed. Remaining quantity of ointment base was added step by step at the end of this process we get homogenous ointment. The doses of ointment were prepared once a day and applied within the 12 hours from the preparation

Animals used

The proposed study deals with the incision wound model of albino rats, weighing 250 to 280g were procured and maintained at standard housing conditions. The care of laboratory animals was taken according to the guidelines of CPCSEA, Ministry of Forests and Environment, Government of India (registration number 729/02/a/ CPCSEA). The healthy albino rats were selected for the wound healing activity. This, interdisciplinary part of proposed study

was carried out after getting permission from the Institutional Animal Ethical Committee, Pusad (CPCSEA/IAEC/CP_PL-15/01-02PD02).

Wound Model

The animals of group (I) are considered as the Control Group rat which is treated with simple ointment base. Group (II) are considered as Reference or Standard Group where rats were treated with 5 % w/w povidine iodine. Group (III) animals were treated with Low Dose of pyrazole (FP_3) ointment and group (IV) were treated with High Dose of compounds pyrazole (FP_3) 2.5 % w/w ointment tropically on wound created on dorsal side of rats. Full thickness excision wound was made on the shaved back of the rat by removing a 500sq mm piece of skin and the day on which wound was made considered as the day zero.

Group I:

Group I was the Control Group rats in which the rats were immediately after cutting and cutting areas were covered with propylene glycol as a simple ointment base once in a day for 24 days.

Group II:

Group II was the Standard Group rats. They were treated with reference standard (5% w/w) povidine iodine once a day for 24 days.

Group III:

Group III was the Low Dose group of rats which were treated with low dose of chlorosubstituted pyrazole (FP_3) ointment once a day for 20 days.

Group IV:

Group IV was the high dose group of rats were immediately after cutting, cutting areas were covered with high dose chlorosubstituted pyrazole (FP_3) ointment once a day for 24 days.The wounds were observed in all groups every day. After 8 ^{th,} 16th days and 24 th days, the rats were evaluated.

Result and discussion

The representations of experimental data related to wounds were shown in Table 1.1 and graph 1.2. The contraction rates of group I to group III of experimental wounds were found to contract much faster as compared to control wound. Finally on 24th day after cut wound creation, the control group rats showed 64.26 % of wound contraction indicating the natural healing property of skin. The standard drug povidine iodine treated rat shows 96.6% of wound contraction. The group III of low dose of pyrazole (FP_3) ointment shows 97.66% wound contraction and high dose of pyrazole (FP_3) ointment shows 97.79% indicating faster wound healing

Measurement of wound Contraction:

The test animals were observed daily and the evaluation of percentage wound closure were made on 8 th, 16th and 24 th wounding days percentage was determined using the formula:

$$\text{Percent of Wound Contraction} = \left[\quad\right]$$

Where, A_d = Wound area on corresponding days. A_o = Wound area on zero day.

Group I: Control Group of rats treated with simple ointment base




Fig. (a) 0 day Fig. (b) 8 days Fig. (c) 16 days Fig. (d) 24 days

Group II: Standard drug (5% w/w povidine iodine)




Fig. (a) 0 day Fig. (b) 8 days Fig. (c) 16 days Fig. (d) 24 days

Group III: Low dose of pyrazole (FP_3) ointment




Fig. (a) 0 day Fig. (b) 8 days Fig. (c) 16 days Fig. (d) 24 days

Group IV: High dose of pyrazole (FP_3) ointment




Fig. (a) 0 day Fig. (b) 8 days Fig. (c) 16 days Fig. (d) 24 days

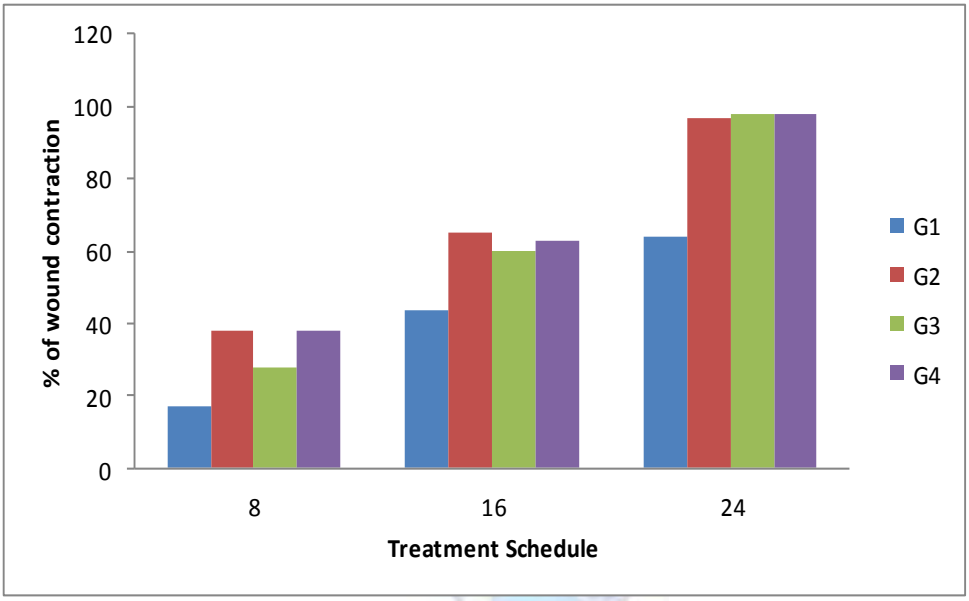
Table 1.1 :- Percentagewise effect of treatments on wound contraction

Treatments	0^{th} day	8^{th} day	16^{th} day	24^{th} day	Epithelia-lization time in days
Group I (Control)	0% ±2.76	17.21 % ±1.62	43.85% ±1.90	64.26% ±1.36	24 ±0.42
Group II (Povidine iodine)	0% ±2.80	38% ±1.30	65% ±1.42	96.6% ±1.12	17 ±0.64
Group III Low dose of pyrazole (FP_3) ointment	0% ±0.85	28% ±2.00	60% ±1.41	97.66% ±0.41	21 ±0.66

Group III **High dose of pyrazole (FP_3) ointment**	**0%** ±1.2	**38%** ±2.22	**62.78%** ±1.53	**97.79%** ±0.30	**18** ±0.66

Graph 1.2 :- Variation of wound contraction % with treatment schedule

Where, G1= Group I, G2= Group II, G3= Low dose (FP_3) Group III, G4= High dose (FP_3) Group IV.



Concusion:-

From the tabulated data was concluded that the wound healing activity of the compound (3-(3,5-dichloro-2-hydroxyphenyl)-1-phenyl-5-(pyridin-2-yl)-1H-pyrazol-4-yl) (furan-2-yl) methanone (FP_3) high dose was found closer (wound contraction 97.79% onday 24thday and epithelization time on day 18) to that of standard drug povidine iodine (96.6%) wound contraction on 24thday and epithelization period on day 17). The presence pyrazole compound might have been favoured a significant wound healing activity. It is observed that the p-value for rows among the four groups is 0.000316* and calculated thought the days is 0.002477** both the values of * and ** is less than 0.05 ($p < 0.05$). The investigation prove that reatment of pyrazole (FP_3) compound has increased healing potential of cut wounds in albino rats.

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Research Article

Synthesis and growth promoting effects of some newly synthesized bromo and nitro substituted isoxazolines on some edible mushroom.

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ABSTRACT
A mushroom (*Agaricus bisporus*) is one of the many species of fungi. About 3,000 different species of fungi can be found in Western Europe, approximately 50 of which are edible fungi, the mushroom is by far the most familiar one. A fungus is actually the visible fruit body of a mould and as such only a small part of that mould. The mould fungus, or mycelium, grows under the ground, invisible to the naked eye. This is a tight network of fine threads, which with some species can even extend across a surface area of several hectares. The present study deals with the effect of newly synthesized bromo and nitro substituted isoxazolines for their growth promoting impact on oyster mushrooms.

KEYWORDS
Oyster mushrooms, bromo and nitro substituted isoxazolines.

1. INTRODUCTION

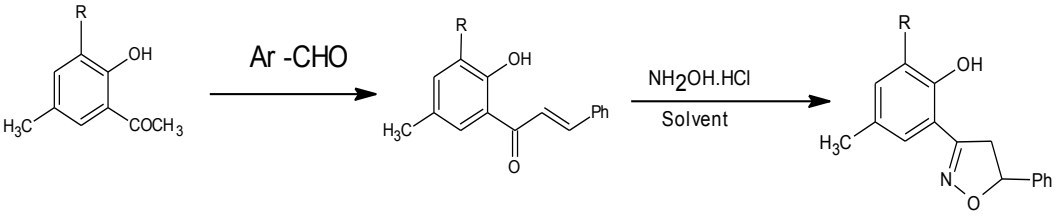
Mushroom cultivation is a profitable agribusiness world-wide. More than 2000 species of edible mushrooms exist in nature, but only approximately 22 species are intensively cultivated [1] could be employed for foods and medicines. In the fungal classification system proposed by Ainsworth and followed by J. Webster [2], almost edible mushrooms are members of the subdivision Basidio mycotina and Ascomycotina [3]. Mushrooms are a good source of protein, vitamins and minerals and are known to have a broad range of uses both as food and medicine. A high nutritional value of oyster mushrooms has been reported with protein (25-50%), fat (2-5%), sugars (17-47%), mycocellulose (7-38%) and minerals (potassium, phosphorus, calcium, sodium) of about 8-12% [4]. The cultivation of edible mushrooms has become an attractive economic alternative over past few years, mainly due to increase in its demand and market value [5,6]. Oyster mushrooms are one among the cultivable varieties. They are wide spread in temperate zones, can grow at moderate temperature and are suitable to grow in most places in India [7,8]. Oyster mushrooms are grown from hyphae (threadlike filaments) that become interwoven into mycelium and propagated on a base of steam sterilized cereal grain usually Wheat grains. This mycelium-impregnated cereal grain is called spawn and is used to inoculate mushroom substrate [8].

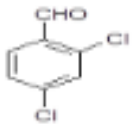
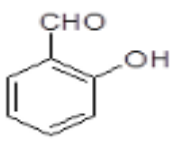
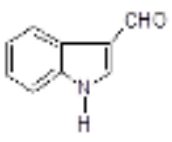
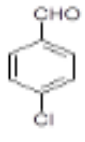
In the present study, the newly synthesized bromo and nitro substituted isoxazolines were assayed for their growth promoting impact on oyster mushrooms with predetermined periodicity.

2. MATERIALS AND METHODS

2.1. Synthesis of bromo and nitro substituted isoxazolines

A mixture of 1-(2-hydroxy-3- bromo and nitro -5-methyl phenyl-3-(4-chlorophenyl)-chalcone (Iva) (0.01 mole) and hydroxyl amine hydrochloride (0.02 mole) was refluxed in ethanol (20ml) and piperidine (0.5ml) for about 1.5 hrs. After cooling the reaction mixture was acidified with HCl (1:1).The solid product thus separated was filtered, washed first with sodium bicarbonate solution (10%) and then with water. Finally it was crystallized from ethanol to get the compound.



R=  ,  ,  , 

Spectral analysis of final compound is given below:

A) IR, 3241.21, (Vb);O-H stretching, 3087.43 (m), Aromatic C-H stretching; 2922.35 (s) Aliphatic C-H stretching; 1582.55, (s), >C=N stretching; 1288.00(s),>CO stretching; 1102.97, (s),>C-Br stretching

B) PMR : 2.3,s,3H,Ar-CH_3; 6.5,t ,1H, Heterocyclic -CH_2-CH-,6.9,d,2H, Heterocyclic -CH_2-CH-,7.1 - 8.4,m,5H,Ar-H, 12.4,s,1H,Ar-OH

2.1. Classification of Oyster Mushroom

Scientific classification

Kingdom – Fungi
Phylum – Basidiomycota
Class – Agaricomycetes
Order – Agaricales
Family – Pleurotaceae
Genus – Pleurotus
Species – ostreatus

2.2. Materials

1. Spawn (Source:- Agriculture College, Amravati)
2. Soya bean Straws.
3. Water bath
4. Hot Air Oven
5. Plastic Bags

2.3. Substrate Preparation

Oyster mushroom was grown on substrates soyabean straw. Since soyabean straw is easily available, cheap and widely used. It is used was fresh and well dried. It was chopped into 3-5 cm pieces and soaked in fresh water for 15-16 hours. Excess water was drained off. This was subjected for sterilization to minimizing contamination problem and gives higher and almost constant yields using hot water treatment maintained at 60-80°C for 1 hour. The sterilized substrate was taken out and allowed to lower down the temperature. When the sterilized substrate had cooled down to room temperature, it was ready for filling and spawning. At this stage, substrate moisture content was about 70%. Polythene bags were used for its cultivation. The spawns of experimental species P. sajor-cajuie, P. pulmonarius were procured from Shivaji agricultural agencies and cultivated in the culture house of the ICAR affiliated Krushi Vidyan Kendra, Durgapur (Badnera) Dist. Amravati. Spawning can be done in layer spawning. The experimental setup was divided into two parts i.e. 'A'-control group plants and 'B'-treated group plants. The spawns were inoculated and cultivated by the conventional methods. Substrate was filled in bag, pressed to a depth of 8-10 cm and broadcasted with a handful of treated spawn above it. Similarly, 2^{nd} and 3^{rd} layers of substrate were put and simultaneously after spawning, the bags were closed and 20-25 pin-holes were made on all sides of the packets. Similarly the untreated spawns were filled in control group beds (bags). After proper labeling, spawned bags were stacked on racks in neat and clean place, in closed position. Temperature at 25-35°C and

humidity at 70-85% was maintained by spraying water twice a day on walls and floor. It took 20-25 days when bags were fully covered. During this incubation period, appropriate temperature of the incubation room was maintained. After the complete development of mycelium, the packets were taken out of the incubation room and shifted to growing room, where the packets were hanged to bamboo frame. During the harvesting of mushroom beds were irrigated according to need. When the first primordial initiation was observed, the test compounds were sprayed on the mushroom with specific intervals. Mushroom crop was harvested before the fruiting body showed any splitting on the edges. The yields of mushroom crop from various bags with different parameters viz. length, diameter, weight and colour were recorded. The results of field experiments with test compounds are tabulated and shown in Fig. no. 1 and 2:

Table 1. Effect of titled compounds (Va-h) on oyster mushroom:-Pleurotussajor-caju spp.

Treated Bags	**Compound**	**D (cm)**	**T (cm)**	**L (cm)**	**Weight of Dry Bag (g) (After Harvesting)**	**Total**		**Colour**
						Fresh	**Dry**	
1	Va	7.7	0.5	5.8	0.925	211	20.43	White
2	Vb	8.4	0.4	5.8	0.982	195	17.59	White
3	Vc	10.9	0.6	6.9	0.975	225	21.31	Creamy
4	Vd	11.01	0.5	6.3	0.955	205	18.89	White
5	Ve	9.92	0.4	5.5	0.966	208	21.22	White
6	Vf	9.84	.0.5	6.2	0.978	209	20.45	White
7	Vg	8.64	0.6	6.4	0.976	207	20.99	Creamy
8	Vh	9.43	0.6	5.7	0.967	208	21.89	Creamy
9	1,4 Dioxane	6.0	0.4	6.1	0.895	174	19.13	White
10	Control	6.8	0.3	5.5	0.853	204	20.00	White

D=Diameter, T=Thickness, L=Length

2.4. Analysis of Mushroom Samples Treated With Test Compounds

The samples of P. sajor-caju collected during the experimental study of growth promoting impact were sun-dried and immediately proceeded for analysis of % crude fibre, % crude protein and elemental detection with special reference to N, P, K and S. The analysis of crude fibre percentage of the samples was carried out at Food Testing Laboratory, Krishi Vigyan Kendra, Durgapur (Badnera) Dist. Amravati using Pelicans FBS-06 (P) Laboratory Manuals & AOAC Method, whereas percentage of crude protein and element detection were determined at Analytical Lab, using Leaf method of analysis. The Kjeldahls method, UV spectrophotometer and Flame photometer were used for the analysis of N, P, K and S elements. The results of analysis obtained for treated mushroom samples are tabulated in table no. 2:

Table 2. Analytical results of dry oyster mushroom:-Pleurotussajor-caju spp. Treated with titled compound.

Sr. No.	Sample	% of Crude Fibre	% of Crude Protein	% N	% P	% K	% S
1	Va	8.0	15.13	2.421	0.3040	2.558	0.1262
2	Vb	8.72	16.00	2.560	0.3111	2.934	0.1367
3	Vc	10.3	20.27	3.246	0.3232	2.760	0.1320
4	Vd	9.83	18.90	3.024	0.2975	2.441	0.1314
5	Ve	10.65	17.05	2.574	0.2745	2.567	0.1378
6	Vf	9.67	18.01	2.654	3.1943	2.647	0.1475
7	Vg	7.89	16.77	3.143	0.3953	2.849	0.1541
8	Vh	8.44	17.23	3.143	0.3173	2.563	0.1498
9	1,4 Dioxane	8.06	13.25	2.122	0.272	2.344	0.1356
10	Control	5.64	15.95	2.554	0.364	2.741	0.1410

3. RESULTS AND DISCUSSION

A species of Oyster mushroom was treated with test compounds to examine the efficacy of the newly synthesized compounds (Va-h) on the morphology of treated mushroom species with inclusion of analysis of treated samples. When the treated and control species of mushroom were compared with reference to their morphological characters, it was interesting to note that the treated species exhibited significant growth in diameter and thickness of caps as well as lengthening of stripes. In addition to this, there was remarkable increase in the yields because of that healthy growth and disease free environment. The analytical results obtained for all the treated mushroom samples clearly show the increase in the value of crude fibre percentage as well as the crude protein percentage. The presence of elements like N, P, K and S were also analysed in the treated mushroom samples.. However, further investigation and a systematic approach in the light of agricultural science would certainly prove to be a potential tool for the growth promoting and creating ecofriendly environment for mushroom cultivation.

4. CONCLUSION

On the basis of chemical analysis and spectral data, it is concluded that, the synthesis of titled compounds was achieved successfully. Besides this, enhancement of the yields reveals the healthy growth due disease free environment. The newly synthesized compounds also showed noticeable enhancement in the nutritive values i.e. increase in crude fibre percentage and crude protein percentage. In this regard, the nitro substituted isoxazolines were found more effective in the enhancement of nutritive value.

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Assessment of Molecular Interactions of 4-Ethyl Thiocarbamidophenol on Acoustic Parameters Base

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ABSTRACT

Acoustic parameters assessment significantly able to disclose molecular and intermolecular interaction briefly. These parameters measured more significant by ultrasonic interferometer. Present research scheme concern to measurements of ultrasonic velocity and density for solutions of 4-ethylthiocarbamidophenol (ETP) at different molar concentrations (i.e. 0.1M, 0.075M, 0.050M and 0.025M) and 300 K, in 70% compositions of ethanol-water mixtures. These determinations sustain estimation of adiabatic compressibility (β), apparent molal compressibility (k), apparent molal volume (v), intermolecular free length (Lf), relative association (RA) and specific acoustic impedance (Z). These properties were help to know about solute-solute and solute-solvent interactions in solvent. Internal structure and molecular association can be possible to understand through current investigation.

Keywords: 4-ethylthiocarbamidophenol (ETP), Interferometric measurements, Intermolecular interactions and acoustic parameters.

INTRODUCTION

Molecular structure and their interactions in solution is always received importance in various field of sciences. Ultra sound and ultrasonic interferometer significantly used in

estimation of molecule interactions such as inter and intra ionic or molecular interactions. Since from last few decades ultra sound and ultrasonic interferometric investigation extensively used to understand molecular interactions in liquid. This investigation has important to know the properties and significances of molecules. Ultra sound and ultrasonic wave's measurements widely applicable in many evolutions and new concepts in engineering, applied, industrial, mechanics, agricultural, medicinal, forensic sciences and space research development and updating. Ultrasonic is a branch of science, which deals with waves of high frequencies. A Thiocarbamido phenol nucleus has various significances in different industrial and life sciences. Valuable information regarding internal structure, molecular association, complex formation, internal pressure and stability[1] obtained from the study of ultrasonic parameters investigation in liquid phase[2-4], liquid mixture[5-6] and electrolyte solution[7-9]. Ultrasonic interferometric study of 4-(p-chloro)phenylthiocarbamido phenol in mixed solvent media carried out by Isankar *et al*[10]. Comparative study of intermolecular interaction by inteferometric measurements of α-bromoacetophenones and cumaran-3-ones in ethanol and dioxan solvents was studied by Aswale *et al*[11] and acoustical studies on ternary mixture of toluene in cyclohexane and nitrobenzene at 308 K was studied[12]. Ultrasonic velocity and density of binary liquid mixture of diethyl ether with three non-polar solvents such as CCl_4, CS_2 and C_6H_6 at 303.15K were investigated[13] and interferometric investigated 4-ethylthiocarbamdiophenol in 60% mixed solvent media[14].

Ultrasonic investigation received more important to understand the ion solvent and solvent-solvent and structure breaking and making properties of solutes. Organic ligands solutions used through the current investigation and this study provide an excellent information concern to intra as well as intermolecular interactions. In present investigation, mainly concentrate on the assessment of ultrasonic velocity and density for solutions of 4-ethylthiocarbamidophenol (ETP) at different molar concentrations and 300K, in 70% compositions ethanol-water mixtures and estimation of adiabatic compressibility (β), apparent molal compressibility (k), apparent molal volume (v), intermolecular free length (Lf), relative association (RA) and specific acoustic impedance (Z). In the view of above current research scheme designed as "Assessment of molecular interactions of 4-ethylthiocarbamidophenol on acoustic parameters base". This investigation regarding to know effect of concentrations on various acoustical properties and effect of acoustic parameters on molecular interactions.

MATERIAL AND METHODS

All AR grade chemicals used through current work. Freshly prepared solution used during study. The solvents were purified by standard method. 0.1M, 0.075M, 0.050M and 0.025M solutions of ETP in 70% ethanol-water mixture were prepared. Ethanol was purified by standard procedure[15]. Densities were measured with the help of bicapillary pyknometer (10.1 % kg m^{-3}). Pyknometer used is of Borosil make. Weighing was made on Citizen CY 104 one pan digital balance (± 0.0001 gm). A special thermostatic arrangement was done for density and ultrasonic velocity measurements. Elite thermostatic bath was used in which continuous stirring of water was carried out with the help of electric stirrer and temperature

variation was maintained within ± 0.1 ^{0}C. The speed of sound waves was obtained by using variable path, Single crystal interferometer (Mittal Enterprises, Model MX-3) with accuracy ± 0.03% and frequency 1 MHz was used in the present work. The densities and ultrasonic velocity of liquids in ethanol solvent were measured at 300 K for the calculation of intermolecular free length and the value of Jacobson's constant[16] (K = 631) was taken.

RESULTS AND DISCUSSION

Ultrasonic velocities and densities of ETP in 70% ethanol-water mixture investigated through present work and it is tabulated in following Table No.1.

Table-1.1: Average Ultrasonic Velocity of Water at 300K.

Sr. No.	No. of Rotation of Screw	Micrometer Reading (mm)	Difference Between Reading (mm)	Distance Travelled By Screw in One Rotation	Average Ultrasonic Velocity (m/sec)
1	5	26.4705	1.6105	0.61465	1398.708956
2	10	24.8642	5.5300	2.18285	
3	15	19.3372	3.0708	1.20041	
4	20	16.2664	4.4071	1.73277	
5	25	11.8593	4.5219	1.78301	
6	30	7.3374	4.0715	1.6004	
7	35	3.2659	2.0059	1.17213	
8	40	1.2663		10.45377	

Table-1.2: Average Ultrasonic Velocity of Pure Ethanol 300K (β_0)

Sr. No.	No. of Rotation of Screw	Micrometer Reading (mm)	Difference Between Reading (mm)	Distance Travelled By Screw in One Rotation	Average Ultrasonic Velocity (v_0) (m/sec)	Density (d_0) (Kg. m^{-3})	$\beta_0 \times 10^{-10}$ (Pa^{-1})
1	5	15.2623	4.9016	1.9321	1243.64	1030.00	5.843517555
2	10	10.3686	2.0211	0.7845			
3	15	8.3374	3.1108	1.2161			
4	20	5.2265	3.3795	1.3199			
5	25	1.8569		5.4374			

Table-1.3: Average Ultrasonic Velocity of 70% Ethanol 300K (β_0)

Sr. No.	No. of Rotation of Screw	Micrometer Reading (mm)	Difference Between Reading (mm)	Distance Travelled By Screw in One Rotation	Average Ultrasonic Velocity (v_0) (m/sec)	Density (d_0) (Kg. m^{-3})	$\beta_0 \times 10^{-10}$ (Pa^{-1})
1	5	16.8193	3.5422	1.39301	1336.98	1030.52	5.172074651
2	10	13.2705	3.9280	1.52925			
3	15	9.3775	3.1075	1.21513			
4	20	6.2752	3.8942	1.48981			
5	25	2.4757		6.65083			

Table-1.4: Acoustic Parameters at Different Concentration of [ETP] at 300 K in 70% E-W

Conc. C (Mole/lit)	Average Ultrasonic Velocity Us (m/sec)	Density d_s ($Kg.m^{-3}$)	$\beta s x10^{-10}$ (pa^{-1})	ϕ_V (m^3mol^{-1})	ϕ_k $x10^{-10}$	L_f (A_0)	R_A	$Z * 10^4$ ($Kgm^{-2} sec^{-1}$)
0.1	1593.587	1034.32	3.7714	0.1885	-8.9981	0.0155	0.982	161.741
0.075	1445.427	1027.52	4.6011	0.256	-1.0204	0.0168	1.007	145.301
0.050	1270.737	1025.12	5.941	0.2771	21.855	0.0186	1.048	126.999
0.025	1172.687	1021.12	6.9857	0.3158	53.761	0.0199	1.072	116.430

CONCLUSION

Table-1.4 reveals acoustic parameters of ETP at different concentration such as 0.1M, 0.075M, 0.050Mand 0.025M and 300K in 70% ethanol-water mixture. Table-1.4 reveals that Ultrasonic Velocity (Us), Density (ds) and decreases along with decreasing concentration from 0.1M to 0.025M. Acoustic parameters such as adiabatic compressibility (βs), Apparent molar volume (φv), Apparent molar compressibility (φk), Intermolecular free length (Lf), Relative association (RA) increases and Specific acoustic impedance (Z) decreases along with decreasing concentration from 0.1M to 0.025M. This acoustic parameters investigation help to understand molecular interactions occur and responsible for breaking and making of their structure in solution.

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Viscometric Measurements of (2e)-1-(4-Thiocarbamido Phenyl)-3-(3,4-Dimethoxyphenyl)Prop-2-En-1-one in 60% Ethanol-Water Mixture at Various Temperatures and Constant Concentration.

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Abstract :

Present investigation are carried out viscometric measurements of (2E)-1-(4-thiocarbamidophenyl)-3-(3,4-dimethoxyphenyl)prop-2-en-1-one at various temperatures and constant concentration to evaluate the dilution effect on solute-sovent interation.

Keywords :

Ethanol-water mixture, viscometric measurements, 2E)-1-(4-thiocarbamidophenyl)-3-(3,4-dimethoxyphenyl)prop-2-en-1-one etc.

Introduction:

Viscosity is one of the important physical properties of liquid. By knowing viscosity, it becomes easy to find out the behavior of solution in vivo. It briefs the information regarding the interaction of solute and solvent interaction also the ability or action of drug in the human body to react. Viscosity measurements play a crucial role in biochemical, agricultural, pharmaceutical, medicinal, and industrial and drug sciences. We get valuable suggestions regarding solvent-solvent, solvent-solute and solute-solute interactions by viscometric measurements in drug sciences. Drug behavior like absorption, transmission and its effect will directly relate to its viscosity measurements and solvent interactions in the human body.

Literature survey reveals that, drugs which are excellently consumable and highly reactive against the revelatory bacterias. Hense, it's the need of todays era to find the drugs and

also know the activity of the drug suddenly in vivo. Its is the need of chemist to find their physical properties viz, viscosity, refractive index, acoustic study and others .

Thocarbamides are the important class of drugs against various disease causing bacteria's. These are widely synthesized screened against class of pathogens. Here, in the present investigation, (2E)-1-(4-thiocarbamidophenyl)-3-(3,4-dimethoxyphenyl)prop-2-en-1-one is selected or their viscometric studies to find its probable activity in vivo.

Experimental:

Chemicals used in the present investigation are MERKS PVT. LTD. Water used for the preparation of solution was double distilled. Electronic balance used was Mechaniki Zaktady Precyzyjnej Gdansk balance (Poland make [±0.001gm]) to weigh our compounds. Viscosity was measured by Ostwald's viscometer. It was kept in Elite thermostatic water bath and temperature variation was maintained at 28^0C (±0.1) for each measurement. Densities were determined by bicapillary with a 1 mm internal diameter. Special care about to maintain thermal equilibrium in between viscometer and water bath, by sufficient time.

The present study deals with the viscosity investigation of (2E)-1-(4-thiocarbamidophenyl)-3-(3,4-dimethoxyphenyl)prop-2-en-1-one at 0.1M concentration in 60% ethanol-water system separately at varying temperatures. Freshly preparedly solutions were employed or every reading. The viscometric readings were taken as described in literature

Observations And Calculations:

Molecular interactions in terms of β-coefficient of solute is figured with the help of data obtained in our work. The results obtained are stated in Table No. 1. According to Jone's-Dole equation, $(\eta r-1)/\sqrt{C} = A+\beta\sqrt{C}$ at different temperatures keeping the concentration 0.1 M. A and β-coefficient values calculated are enlisted in Table No.2.

Table No.1

Viscosity Measurements At Different Concentrations And Determination Of Relative And Specific Viscosities At Different Temperatures At 0.1m

Medium - 60% Ethanol-Water							
Conc.	**Temp. (°C)**	**√C**	**Time t (sec.)**	**Density ρx10^3 (kg.cm^{-3})**	**η_r**	**$\eta_{sp}=\eta_r-1$**	**$(\eta_r-1)/\sqrt{C}$ (pa's)**
0.1 M	25	0.316	51	1.0375	1.799745	0.799745	2.530838
	30	0.316	51	1.0315	1.789337	0.789337	2.497901
	35	0.316	48	1.0294	1.680653	0.680653	2.153965
	40	0.316	40	1.015	1.27193	0.27193	0.860537

TABLE – 2

A and β Co-Efficient Values from Graphs for 60%.

FOR (2E)-1-(4-thiocarbamidophenyl)-3-(3,4-dimethoxyphenyl)prop-2-en-1-one

"A"	β (Slope "m")
2.010811	0.05109

Result And Discussion:

The relative viscosity was determined by using following formula

η_r = Ds x ts / Dw x tw.:

While,the relative viscosities have been analyzed by Jone's-Doles equation as,

$(\eta r-1)/\sqrt{C} = A+\beta\sqrt{C}$

The graph are plotted in between $(\eta r-1)/\sqrt{C}$ versus$\sqrt{C}$. The graph for each system gave linear straight line gave value of β-coefficient.

It was conclude from this research that, density and relative viscosity decreases with decrease in concentration. This is supported by the information that as the concentration decreases the number of solute molecule decreases as well as percentage of solvent molecules increases in the solution due to which solvation effect increases.

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Synthesis and Antimicrobial Screening of Some 6-Substituted Derivatives of 2-Phenyl-4h-Chromen-4-one

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Abstract:

The present research work deals with the synthesis of some 6-substituted-2-phenyl-4H-chromen-4ones i.e. substituted flavones by cyclization of corresponding 1-substituted-3-substituted propane-1,3-diones in glacial acetic acid with small amount of conc.H_2SO_4. The structures of synthesized compounds were established on the basis of spectral data studies o IR and ^1H NMR and were screened for their in vitro antimicrobial activity by performing disc diffusion method.

Keywords: 2-Phenyl-4H-chromen-4-ones, Flavones, Propane-1,3-diones, Antimicrobial.

Introduction:

Flavonoids are group of aromatic oxygen-bearing heterocyclic pigments widely distributed in lower and higher plants. Flavones (flavus = yellow) are the class of flavonoids family. These 'yellow' colored compounds have 2-phenylchromen-4-one backbone structure and usually found in human diet especially in fruits, vegetables, flowers, tea, red wine, and juices. They are also found in variety of medicines and natural products. Due to unique and flexible structure, these compounds could exert direct and indirect beneficial effects on health. In recent years, synthesis of flavones has attracted considerable attention of researchers worldwide due to their dominant medicinal properties such as biocidal[1-3], pharmaceutical[4-7], anti-oxidant[8-10] anti-HIV[11], anti-cancer[12], anti-inflammatory[13], anti-osteoporotics[14] and anti-diabetic[15]. A literature survey clearly indicates that, flavones are synthesized by cyclodehydration of 1-(2'-hydroxyphenyl)-3-phenylpropane-1,3-dione[16], by oxidative cyclization of 2'-hydroxy chalcones[17], by Auwers method[18] and via intermolecular Witting reaction[19]. It has been observed that substituted propane-1,3-diones are the best intermediate for the synthesis of flavones. Hence, in the present work, we describe the synthesis of some 6-substituted-2-phenyl-4H-chromen-4-ones from corresponding 1-(5'-substituted-2'-hydroxyl phenyl)-3-phenylpropane-1,3-diones in acidic condition and explored them for their in vitro antibacterial and antifungal activities.

Materials And Methods:

The chemicals used were of highest purity obtained from Merck, Loba and S.D Fine chemicals Ltd. Melting points (uncorrected) were measured by Thiele's melting point apparatus. The synthesized compounds were characterized by IR and ^1H NMR spectroscopic techniques. IR spectra were recorded in KBr using a Shimadzu IRAffinity-1 spectrophotometer and ^1H NMR spectra on a Brucker Avance II 400MHz NMR instrument in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard.

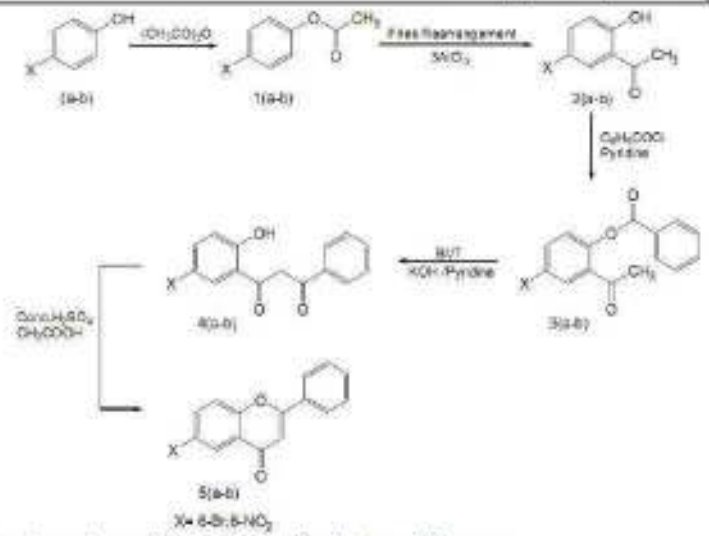

Figure 1: Reaction scheme for synthesis of substituted flavones

General procedure for synthesis of substituted flavones:

Initially, 4-substituted phenol (a-b) was refluxed with acetic anhydride in presence of dry anhydrous sodium acetate for 1.5 hr and then it was allowed to cool followed by their decomposition in water. The two layers were formed out of which separate lower acetate layer by means of separating funnel and then purified by distillation. The resultant product 1(a-b) undergone through Fries rearrangement with anhydrous $AlCl_3$ and then decomposed by 10% ice-cold HCl, which was filtered and crystallized by glacial acetic acid to get substituted acetophenones 2(a-b). The prepared substituted acetophenone 2(a-b) and benzoyl chloride were dissolved in dry pyridine. The reaction mixture was shacked vigorously for about 30 min. The warmed reaction mixture was poured over crushed ice containing 1M HCl. The product thus obtained was filtered, washed with ice-cold methanol and then with water to get 2-benzoyloxy-5-substituted acetophenones 3(a-b) which was heated with pulverized KOH in pyridine at 60^{0}C for 15 minutes and acidified with 10 % glacial acetic acid resulting in the formation 1-(5'-substituted-2'-hydroxy phenyl)-3-phenylpropan-1,3-diones 4(a-b) by Baker-Venkatraman Transformation[20-21]. Finally, the obtained 1-substituted-3-substituted propane-1,3-diones 4(a-b) was refluxed in glacial acetic acid with 3-4 drops of conc. H_2SO_4 at 100^{0}C for about 1hr. After cooling, the reaction mixture was poured over crushed ice, filtered the separated product and washed with plenty of water. The obtained crude products were recrystalized by petroleum ether to get respective 6-substituted-2-phenyl-4H-chromen-4-ones 5(a-b) i.e. substituted flavones. The reaction scheme for synthesis of substituted flavones is shown in Figure 1 and their physical data are given in Table 1.

Table 1: Physical characteristic data of substituted flavones

Compound Code	Compound Name	Mol. Formula	Mol. Weight	M.P. (^{0}C)	Yield (%)
5a	6-bromo-2-phenyl-4H-chromen-4-one	$C_{15}H_9BrO_2$	301.14	192-194	74

5b	6-nitro-2-phenyl-4H-chromen-4-one	$C_{15}H_9NO_4$	267.24	170-172	82

Results And Discussion:

The 6-substituted-2-phenyl-4H-chromen-4-ones 5(a-b) were synthesized successfully in good yields (Table 1). The synthesized compounds were characterized by spectral data studies of IR and ^{1}H NMR. The IR and ^{1}H NMR spectra showed all the expected peaks which correspond to various groups present in each compound.

The Spectral data of synthesized substituted flavones are shown below:

(5a)-6-bromo-2-phenyl-4H- chromen-4-one:

IR (KBr) in cm^{-1} : 526 (C-Br stretch),1118(C-O linkage), 1620 (C=C Aromatic), 1697(C=O stretch), 3059 (C-H Alkene stretch), 3059 (C-H Aromatic).^{1}H NMR in δ ppm: 2.5 (s,1H,C=C-H), 7.26-7.5 (m,5H,Ar-H), 6.9 (d,1H,Ar-H), 8.0 (d,1H,Ar-H), 8.1(d,1H,Ar-H), 2.52 (s,Impurity).

(5b)-6-nitro-2-phenyl-4H-chromen-4-one:

IR (KBr) in cm^{-1}: 852 (p-substituted benzene), 1053(C-O linkage), 1321 (-NO_2 symmetric), 1508 (C=C Aromatic), 1616 (C=O stretch), 3085 (C-H Alkene stretch), 3085 (C-H Aromatic stretch). ^{1}H NMR in δ ppm: 2.54 (s,1H,C=C-H), 6.8-7.8 (m,3H,Ar-H),7.9-8.6 (m,5H,Ar-H), 4.9 (broadpeak,1H,O-H (H_2O),1.24 (s,1H,Impurity).

Antimicrobial screening :

The synthesized compounds 5(a-b) were purified, characterized and screened for their antimicrobial activity against Escherichia coli, Staphylococcus aureus and Candida albicans by disc diffusion method[22] using standard Tetracycline and Griseofulvin for bacteria and fungus respectively for comparison of activity. Compounds and standards were dissolved in DMSO to form a solution of 100µg/ml and used. The following Table 2 indicates the antimicrobial activity of test compounds 5(a-b) with their zones of inhibition in mm. From the results it was found that, the compounds 5a and 5b showed better zones of inhibition against Escherichia coli and Staphylococcus aureus as compared to Candida albicans.

Table 2: Anti-microbial activity of substituted flavones :

Compound Code	Zone of inhibition in mm		
	E.coli	S.aureus	C.albicans
5a	11	09	08
5b	13	12	10
Tetracycline	13	21	-
Griseofulvin	-	-	21

Conclusion:

In summary, we have synthesized some 1-substituted-3-substituted propane-1,3-diones from 4-substituted phenols and convert them to respective substituted flavones. The antimicrobial activity reveals that, the synthesized flavones 5a and 5b were found to be active and inhibits the growth of both bacteria as well as fungus but shows more activity towards bacteria E.coli and S.aureus as compared to fungus C.albicans. This increase in activity may be due to bromo and nitro substitution in flavones ring. As the concentration increases its activity may also increases.

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Impact of Information Technology for Business Success

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Abstract:

We have witnessed a true revolution with the growth of the Internet. One can see evidence of Information Technology everywhere on the worldwide web (www). Many commercial websites have catalogues and support online transactions. It includes everything from sourcing to settlement and all the processes that underlie trading. Information Technology is the process of conducting business electronically among various entities in order to satisfy an organizational or individual objective. A key ingredient of Information Technology, sometimes referred to as electronic trading, is the advertisement and procurement of goods and services over the Internet. Information Technology is possibly the most promising application witnessed in recent years. It is revolutionizing business management and has enormous potential. We have attempted to define Information Technology and examine major Internet elements that link organizational systems. The application of Information Technology from manufacturing to service and a framework for describing Information Technology role in business. For businesses to survive and prosper in the 21st century and beyond, they must develop business models that give Information Technology the prominence it deserves as a key ingredient in business success.
Keywords: Information, technology; Elements; Applications; Benefits.

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1. Scope of Information Technology

Information Technology encompasses all forms of interactive business transactions, which are facilitated by networks of computers. Information Technologyis expanding because of the greater number of businesses and individuals who are able to use these networks and the growing number of ways in which businesses can conduct transactions electronically with other organizations and directly with consumers. These trends are important to the global economy and to the economy of individual countries because Information Technology contributes to economic efficiency. Information Technology contributes to economic efficiency in five important ways. They are as follows:

(a) Shrinking distances and timescale,
(b) Lowering distribution and transaction costs,
(c) Speeding product development,
(d) Providing more information to buyers and sellers and
(e) Enlarging customer choice and supplier reach.

The organization of this paper is as follows:
Section 2 presents the definition and major elements of information technology,
Section 3 examines the application of IT in different areas from manufacturing to service in the organizations,
Section 4 framework describing the business benefits of information technology,
Finally, Section 5 presents a summary of conclusions.

2. Definition of and major elements of Information Technology

Information technology (IT) is the application of computers and telecommunications equipment to store, retrieve, transmit and manipulate data, often in the context of a business or other enterprise.

In a business context, the Information Technology Association of America has defined information technology as "the study, design, development, application, implementation, support or management of computer-based information systems".

2.1. Electronic mail

E-mail is a cheap and convenient way for people to communicate. E-mail is the exchange of messages via a telecommunications network. E-mail is well established as a fast, flexible and cost-effective means of communication. One need only few steps to send, reply, and forward a message to one or many recipients, regardless of the geographic location. For many companies, email is the principal means of communication between employees, suppliers and customers. Email was one of the early drivers of the Internet, providing a simple and inexpensive means to communicate. Over the years, a number of other communications tools have also evolved, allowing staff to communicate using live chat systems, online meeting tools and video-conferencing systems. Under such conditions, groupware becomes a viable option to facilitate electronic interaction among groups of people who must communicate to accomplish group tasks. Voice over internet protocol (VOIP) telephones and smart-phones offer even more high-tech ways for employees to communicate.

2.2. Internet

The Internet an on-line global marketplace that operates 24 hours a day, with millions of sellers, buyers, products and services. The Internet and its capabilities also provide companies with new, more cost effective and time-efficient means for working with customers, suppliers and development partners. Information Technology will enable companies to: shorten procurement cycles through the use of on-line catalogues, ordering, and payment; cut costs on both stock and manufactured parts through competitive bidding; product, marketing information, and prices are always up to date; increase the speed and reduce the cost of communications, promote closer relationship with customers and suppliers, provide a quick and easy way of exchanging information about a company and its products, internally and externally e.g. WWW sites, Intranets, and extranets. The WWW enables B2B and B2C transactions. These developments, along with the Internet, contributed to the growth of global procurement of goods and services and allowed firms to better manage customer relationships.

2.3. Electronic Data Interchange (EDI)

EDI is computer- to- computer exchange of business documents. EDI enables enterprises to exchange precisely formatted business orders, payments, or even engineering drawings, electronically via a direct communication link. EDI help to reduce inventories, foster JIT management, promote engineering interchange, and improve work scheduling. Companies that have successfully implemented EDI have reported

general benefits of expedited purchasing processes, reduced transaction cycle times, higher inventory turnovers, faster response times and overall improved service. EDI provides quick order responses from suppliers and automatic ordering from customers. Information Technology is changing manufacturing systems from mass production to demand-driven, possibly customized, just-in-time manufacturing systems. Companies like IBM, General Motors, General Electric and Boeing are assembling products for which the components are manufactured in many locations. Sub-assemblers gather materials and parts from their vendors and they may use one or more tiers of manufacturers. Communication, collaboration and coordination become critical in such multitier systems. Using electronic bidding, assemblers get sub-assemblies 15–20 percent cheaper than before, and up to 80 percent faster. These systems are flexible and adaptable, allowing fast changes with minimum cost. Costly inventories, once inherent in mass production systems, can be minimized.

3. Application of Information Technology in Business (Manufacturing and Services)

3.1. Purchasing

Automated purchasing and logistics are carried out between trading partners with well established relationships – this is a primary application of EDI. Direct selling offers the prospect of large-scale disintermediation –eliminating middle-men from supply chains. Trading patterns in response to new Information Technology opportunities; however, eliminating the need for intermediaries, the Internet is currently generating a wide range of new opportunities in the facilitation and mediation of electronic trading environments.

3.2. Production

The implementation of e-manufacturing necessitates business-to-business (B2B) e-commerce. There are numerous Internet enabled supply chain management (SCM) systems and enterprise resource planning (ERP) systems available today. Using database management, data warehouse and data mining technologies, the Web can facilitate interaction with customers and suppliers, data collection, and data analysis processes. Outsourcing of service functions is becoming popular.

3.3. Design

Various computer-based technologies have helped to improve the quality of product designs. Design engineers located in different parts of the country or world can exchange information using the Internet and WWW. This can reduce design time and improve the accuracy of the information on product design, and at the same time help to design products that will capture good market share. Companies are using an approach for marketing that uses continuously refined information about current and potential customers to anticipate and respond to their needs.

3.4. Warehousing

EDI can help to minimize warehousing cost. EDI enables minimal stocks to be held with the resultant saving in the costs of storage, insurance, warehousing and security. Reduction in manual processing reduces the need for people, thus labour cost savings are possible. Just-in-time manufacturing refers to the ability to produce minimal sized batches of finished goods, only when needed, i.e. responding to market pull; in an extended supply chain, EDI leads to minimal stock holdings by all parties and hence a reduced supply chain system operating costs. Reduced stock handling saves money.

3.5. Sales and Distribution

Information Technology provides manufacturers with a great opportunity to sell and distribute directly to final customers. Teleshopping, offer great promise in changing the modern retailing. The Internet can actually be used to distribute many informational products, as well as products like software and music that can also be digitized. Internet distribution can produce significant savings in shipping, and it facilitates delivery at speeds only hoped for by those using other, more traditional delivery modes such as truck, air, and rail. Even those who use traditional modes of transportation can use Internet based tools to increase customer service. Web-based order tracking has become common place. It allows customers to trace the shipment of their orders without having to contact the shipper directly.

3.6. Marketing

The advent of Information Technology is changing marketing practice. Information Technology systems has provided easy access, be easy to use, help overcome differences in time of business, location, and language between suppliers and customers, and at the same time support the entire trading process. The cost of delivering information to customers over the Internet results in substantial savings to senders. Major savings are also realized in the direct delivery of digitized products (such as music and software) as compared to the costs of

traditional delivery. Also, the administrative work related to physical delivery, especially across international borders, can be reduced significantly. Customer service can be greatly enhanced by enabling customers to find detailed information online.

3.7. Human Resource Management

The web is now a good place for recruiters to go in search of employees, and for job hunters to go in search of jobs. Many manufacturers, retailers, and service providers now advertise job openings on their own sites, making it easy for qualified applicants to contact them. Some companies have database for employees to manage their benefits and retirement accounts via the web. This is convenient for employees and it is a time saver for HRM employees, who are relieved of some of the tasks related to supplying information to employees about benefits, retirement, policies, and more.

4. Business Benefits of Information Technology

4.1. Data Management

The days of large file rooms, rows of filing cabinets and the mailing of documents is fading fast. Today, most companies store digital versions of documents on servers and storage devices. These documents become instantly available to everyone in the company, regardless of their geographical location. Companies are able to store and maintain a tremendous amount of historical data economically, and employees benefit from immediate access to the documents they need.

4.2. Management Information Systems

Storing data is only a benefit if that data can be used effectively. Progressive companies use that data as part of their strategic planning process as well as the tactical execution of that strategy. Management Information Systems (MIS) enable companies to track sales data, expenses and productivity levels. The information can be used to track profitability over time, maximize return on investment and identify areas of improvement. Managers can track sales on a daily basis, allowing them to immediately react to lower-than-expected numbers by boosting employee productivity or reducing the cost of an item.

4.3. Product Development

Information technology can speed up the time it takes new products to reach the market. Companies can write product requirement documents by gathering market intelligence from proprietary databases, customers and sales representatives. Computer-assisted design and manufacturing software speed up decision making, while collaborative technologies allow global teams to work on different components of a product simultaneously. From innovations in microprocessors to efficient drug delivery systems, information technology helps businesses respond quickly to changing customer requirements.

4.4. Cost Efficiencies

Although the initial IT implementation costs can be substantial, the resulting long-term cost savings are usually worth the investment. IT allows companies to reduce transaction and implementation costs. For example, the cost of a desktop computer today is a fraction of what it was in the early 1980s, and yet the computers are considerably more powerful. IT-based productivity solutions, from word processing to email, have allowed companies to save on the costs of duplication and postage, while maintaining and improving product quality and customer service.

4.5. Inventory Management

When it comes to managing inventory, organizations need to maintain enough stock to meet demand without investing in more than they require. Inventory management systems track the quantity of each item a company maintains, triggering an order of additional stock when the quantities fall below a pre-determined amount. These systems are best used when the inventory management system is connected to the point-of-sale (POS) system. The POS system ensures that each time an item is sold, one of that item is removed from the inventory count, creating a closed information loop between all departments.

4.6. Customer Relationship Management

Companies are using IT to improve the way they design and manage customer relationships. Customer Relationship Management (CRM) systems capture every interaction a company has with a customer, so that a more enriching experience is possible. If a customer calls a call center with an issue, the customer support representative will be able to see what the customer has purchased, view shipping information, call up the training manual for that item and effectively respond to the issue. The entire interaction is stored in the CRM system, ready to be recalled if the customer calls again. The customer has a better, more focused experience and the company benefits from improved productivity.

4.7. Stakeholder Integration

Stakeholder integration is another important objective of information technology. Using global 24/7 interconnectivity, a customer service call originating in Des Moines, Iowa, ends up in a call center in Manila, Philippines, where a service agent could look up the relevant information on severs based in corporate headquarters in Dallas, Texas, or in Frankfurt, Germany. Public companies use their investor relations websites to communicate with shareholders, research analysts and other market participants.

4.7. Competitive Advantage

Cost savings, rapid product development and process improvements help companies gain and maintain a competitive advantage in the marketplace. If a smartphone competitor announces a new device with innovative touch-screen features, the competitors must quickly follow suit with similar products or risk losing market share. Companies can use rapid prototyping, software simulations and other IT-based systems to bring a product to market cost effectively and quickly.

4.8. Globalization

Companies that survive in a competitive environment usually have the operational and financial flexibility to grow locally and then internationally. IT is at the core of operating models essential for globalization, such as telecommuting and outsourcing. A company can outsource most of its noncore functions, such as human resources and finances, to offshore companies and use network technologies to stay in contact with its overseas employees, customers and suppliers.

5. Conclusion

There are dozens of applications of Information Technology. To execute these applications, it is necessary to have supporting information and organizational infrastructure and systems. Websites to promote products or services, develop sales channels, achieve direct cost savings, reduce cycle time, and enhance and expand customer services. We have examined the evolving role of Information Technology in manufacturers to service providers. To reap the benefits of IT, firms must develop and use the Information Technology infrastructure that will empower their business to take advantage of new business opportunities. Development of effective strategies for achieving competitive advantage through Information Technology will be necessary for success in the 21st century. The infrastructure must be designed with sufficient flexibility to allow for adaptive change, as will be surely mandated with the continued evolution of Information Technology. The Internet have the potential to radically change the ways in which we communicate, interact, receive information and entertainment, and acquire goods and services.For businesses to survive and prosper in the 21st century and beyond, they must develop business models that give Information Technologythe prominence it deserves as a key ingredient in business success.

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