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[CICPM-2022]

Organized By
Department of Chemistry, Physics & Mathematics
Sunderrao Solanke Mahavidyalaya, Maharashtra, India
[(M.S.) (NAAC Reaccredited 'A' Grade with CGPA 3.21) (ISO 9001:2015)]

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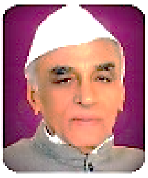

M.S.P.Mandal's

Sunderrao Solanke Mahavidyalaya, Majalgaon, Dist.Beed. (M.S.)

(NAAC Reaccredited 'A' Grade with CGPA 3.21) (ISO 9001:2015)

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(CICPM-2022)

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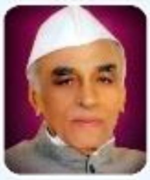

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National Conference

On

" Current Innovations in Chemistry, Physics & Mathematics (CICPM-2022)" 20th December 2022

Organized By

Department of Chemistry, Physics & Mathematics

To.
Mr./Miss/Dr.____
____

Dr.S.N.Ipper	**Prof. Dr.S.K.Vyawahare**	**Prof. Dr.G.K.Sanap**
Convener	Organizing Secretary	Principal & Chief Organizer

E-mail- ssmmmsc@gmail.com Website: www.majalgaonscollege.com

President's Message

Hon. Shri. Prakash Sunderrao Solanke
(MLA & President)
Marathwada Shikshan Prasarak Mandal, Aurangabad

Marathwada Shikshan Prasarak Mandal consistently works for enrichment of educational services for poor and needy people from rural background with the motto 'Tamso ma Jyotirgamay'. Sunderrao Solanke Mahavidyalaya, Majalgaon, Dist. Beed is one of the embodiments of the efforts of the institution through which such efforts are realized at a more systematic level. The present national conference is also an indication of such fruitful effort put together by the Physics, Chemistry and Mathematics Department of College.

The conference entitled "**Current Innovations in Chemistry, Physics & Mathematics (CICPM-2022)**" is going to cover the research areas like Physical Sciences, Chemical Sciences and Mathematics and multidisciplinary approach in Sciences. Such approaches are required in today's research world. It is a matter of happiness and pride for me to write this piece of message to congratulate and offer my wishes for grand success of this national conference.

I deeply feel assured that this conference would prove a very helpful tool and experience for the researchers around the globe for their endeavours at research. I convey my best wishes to the conference.

Secretary's Message

Hon. Shri. Satish Bhanudasrao Chavan
(MLC & Secretary)
Marathwada Shikshan Prasarak Mandal, Aurangabad

Marathwada Shikshan Prasarak Mandal has always been conscious regarding its contribution in the areas like social responsibilities, student centric activities, quality education and research promotion. It ensures achieving landmarks in the areas with constant efforts. It has been reflected in the NAAC accreditation results of the colleges under Marathwada Shikshan Prasarak Mandal. Seven colleges received 'A' grade in the third cycle of accreditation; four colleges are recognized by UGC as College with Potential for Excellence. The journey of achieving excellence is never a sudden process. It takes years to reach at goal of quality education in which every stakeholder has to contribute whole heartedly. Such are the positive efforts executed by the stakeholders. The present National conference entitled "**Current Innovations in Chemistry, Physics & Mathematics (CICPM-2022)**" addresses current issues in Physical Sciences, Chemical Sciences, Mathematics and multidisciplinary approach in Sciences.

I am more than sure that this national conference would provide all budding researchers a good platform to showcase their research ideas, to discuss and interact with the expert coming from different parts of the country. I also would expect you all to make best use of this opportunity for your research and career development. I convey my best wishes to the conference.

College Development Committee Member's Message

Hon. Adv. B. R. Dak
Member, College Development Committee,
Sunderrao Solanke Mahavidyalaya, Majalgaon, Dist. Beed

Dear Participants,

On behalf of Marathwada Shikshan Prasarak Mandal, Sunderrao Solanke Mahavidyalaya, Majalgaon, it is my pleasure to invite all of the great scientists, academicians, young researchers, delegates and students from all over the nation to attend the National Conference on **"Current Innovations in Chemistry, Physics & Mathematics (CICPM-2022)"** on 20th December, 2022. This conference shares an insight into the recent research and cutting edge technologies, which gains immense interest with the colossal and exuberant presence of adepts, young and brilliant researchers, delegates and talented student communities.

We're looking forward to an excellent meeting with researchers from different states. It will be a privilege and honour to have such an imminent personality like you in our institution.

Best wishes!

Principal's Message

Dr. G. K. Sanap
(Principal)
Sunderrao Solanke Mahavidyalaya, Majalgaon, Dist. Beed

Marathwada Shikshan Prasarak Mandal's Sunderrao Solanke Mahavidyalaya, Majalgaon has consistently kept its promises for quality education for the masses in the region addressing to the issues of social responsibility, students development and progression and research. Research has been one of the most prominent activities undertaken by the faculties on the campus. College has 'A' grade with CGPA 3.21 in its third cycle of accreditation by NAAC.

Physics, Chemistry and Mathematics departments of college are the best establishments with its outstanding research output and effective teaching-learning process. It has always been proactive in all student centric activities. The present National conference entitled **"Current Innovations in Chemistry, Physics & Mathematics (CICPM-2022)"** is also a part of its efforts for bringing about academic discussion on the recent development in Physical Sciences, Chemical Sciences, Mathematics and multidisciplinary approach in Sciences.

I feel doubly happy to write this message as I also happen to be a part of the department. I take this privilege to welcome all the participants to the National Conference.

Best wishes!

Convener's Message

Dr. S. N. Ipper
(Convener)
Sunderrao Solanke Mahavidyalaya, Majalgaon, Dist. Beed

It is a great matter of happiness for me as a convener to welcome all the delegates to this national conference. I personally feel that such academic events are essentials not only for the academic purposes but also it is a great source of finding inter and intra personal interactions that enhance our attitude towards whole process of research.

Department of Physics, Chemistry and Mathematics of Sunderrao Solanke Mahavidyalaya takes pride in its galaxy of prominent alumni who bear significant academic and administrative positions across the globe. The faculties of the department have always engaged themselves in the academic and research work of great stature. The present National Conference entitled **"Current Innovations in Chemistry, Physics & Mathematics (CICPM-2022)"** is envisaged by the department keeping in view the need of bringing about fruitful discussions on the thematic concerns.

I feel very happy to welcome you all to this campus for fruitful academic discussions in the sessions to follow.

Best wishes!

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Solvent Free CSA Catalyzed Synthesis of Benzimidazole Derivatives By Microwave Irradiation

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Department of Chemistry, KES Anandibai Pradhan Science College, Nagothane– 402106, Maharashtra, India

ABSTRACT

Due to the diversity of their biological actions, there have recently been many publications on the synthesis of heterocyclic compounds including nitrogen, oxygen, and sulphur. Different substituted Benzimidazoles have regulated and prospective medicinal effects.

Numerous findings on the synthesis of heterocyclic compounds in a variety of settings, including solvent-free, with reactants immobilized on a solid support, with microwave irradiation, with a green catalyst, and with a green solvent, have been published in the literature. Modern drug discovery investigations have recently paid a lot of attention to microwave-assisted heterocyclic synthesis. In the current research, we concentrated on studying the microbial activity while synthesizing benzimidazole utilizing CSA (Camphor Sulphuric Acid) as a catalyst in a domestic microwave. The present method is simple, efficient, cost-effective, and eco-friendly.

Keywords: Bioactive, Benzimidazole, Imidazolium, pharmacologically.

I. INTRODUCTION

The class of biologically active chemicals known as benzimidazole derivatives has emerged during the past decade as a flexible nitrogen-containing heterocyclic compound with a variety of biological and pharmacological activities. Because molecules containing the benzimidazole moiety are so important and display such a wide range of activities, efforts have been made to create libraries of benzimidazole derivatives and screen them for potential biological activities.

Benzimidazole is a white to barely solid substance. It has a melting point of 172 °C, a boiling temperature of 360 °C, is soluble in water to a limited extent, and is totally soluble in ethanol. It is a bicyclic molecule with an imidazoles ring fused to benzene, which has two nitrogen atoms in a nonadjacent position. A phenyl ring is joined to an Imidazole ring via the benzimidazole. The Benzimidazoles are also referred to as benzoglyoxalines or Benzimidazoles. They have also been referred to as o-phenylenediamine derivatives, particularly in earlier literature. This terminology would therefore refer to benzimidazole as methenyl-o-phenylenediamine and 2-methyl benzimidazole as ethenyl-o-phenylenediamine.

The field of study known as medicinal chemistry is focused on figuring out how chemical structure affects biological activity. The practice of medicinal chemistry evolved from an empirical one that involved creating new compounds by organic synthesis, mostly by altering the system, and then determining their biological activity. A review of the literature found that medicinal chemistry has shown a lot of interest in benzimidazole derivatives. Its wide range of pharmacological activity and synthetic utility are the reasons.[1] Ahmad Khorramabadi-zad et al. synthesized Triaryl-1H-imidazole with hydroxy ketone, aromatic aldehyde, ammonium acetate, and the mixture of KMnO4/ CuSO4 were stirred and refluxed in ethanol.[2]

The O-phenylene diamine is condensed with carbonyl molecules during the benzimidazole synthesis.[3] Using o-phenylenediamine and aldehydes as starting materials, C. P. Rushi *et al.* reported good yields of 2-substituted Benzimidazoles synthesized in a single pot under solvent-free conditions at room temperature in the presence of a catalytic quantity of indium triflate [In (OTf)3].[4] Similar to this, Rathod *et al.* produced benzimidazole by heating o-phenylene diamine and aldehydes together while maintaining reflux.[5] By reacting o-Phenylenediamine with various aromatic aldehydes in the presence of sodium hexafluoro aluminate, Na_3AlF_6, as an effective catalyst at 50 °C, a range of benzimidazole derivatives were created in good to high yields. By using water extracts of papaya bark ash (WEPBA) as a green catalyst in the reaction of substituted o-phenylenediamine with various substituted benzoyl chlorides at room temperature, K. Kantharaju *et al.* have developed a quicker, more environmentally friendly method for making 2-substituted benzimidazole. This technique offers a number of benefits, including being entirely green and inexpensive, in high yield.[6] Synthesis of 2-Aryl Substituted Benzimidazole Derivatives in One Pot Using a Green Method Catalyzed by Papaya Bark Ash Water Extract. Anju V. Mishra *et al.* developed a method for producing 2-substituted benzimidazole by starting with 2-nitro aniline, reducing it in the presence of silver nanoparticles and sodium borohydride to produce o-phenylenediamine, and then cyclizing it with a number of different aldehydes to produce 2-aryl benzimidazole, which was then suspended in an ethanol-water mixture. They came to the conclusion that it is a straightforward, environmentally benign, non-polluting, non-toxic, and inexpensive method for biocatalytic pot conversion of 2-nitro aniline to physiologically significant 2-arylbenzimidazoles.[7] The use of silver nanoparticles as a catalyst in the synthesis of 2-substituted Benzimidazoles. In the presence of benzaldehyde, M. L. Di Gioia and colleagues created a green synthesis of 2-substituted benzimidazole starting with o-phenylenediamine.[8]

Devi *et al.* using an equivalent ratio of benzimidazole from 60 °C to 80 °C, the refluxing mixture was kept on the magnetic stirrer. TLC was used to monitor it. It produces derivatives of benzimidazole. Without using an external solvent, using deep eutectic solvent as the reaction medium and reagent has benefits for both the yields and the reaction's setup.[9] N Kaur and others OPD was converted into benzimidazole utilizing a green catalyst and a green solvent. To the R.B.F solution containing CuMVS, o-phenylenediamine and aromatic aldehydes were added. As the reaction reached its culmination and the result precipitated, the mixture was agitated. To separate the product that was recrystallized in ethanol, the reaction mixture was filtered. Sustainable and greener catalytic method.[10] Synthesis of benzimidazole from OPD by using green catalyst and green solvent.

By altering the groups on the core structure, medications that exhibit a variety of diverse biological activities, such as antibacterial [11], antifungal [12], anti-analgesic & antiviral [13], herbicides [14], anti-inflammatory and antithrombotic agents [15-16], plant growth regulators [17], and therapeutic agents.[18] are found in Benzimidazole rings. The synthesis of benzimidazoles could be done in a variety of ways. More recently, the treatment potency of benzimidazoles in diseases such as ischemia-reperfusion injury or hypertension, has also been reported [19] due to their properties and roles in various diseases; special interest has been devoted to benzimidazole-based chemistry [20–23]. A lot of synthetic methodologies are available for the preparation of benzimidazole and its derivatives. Generally, the reaction between o-phenylenediamine and carboxylic acids or their derivatives has been used [24-25]. Equimolecular amounts of the reactants are combined in an aqueous suspension to carry out the reaction. However, the literature review does not place much emphasis on its variants that employ camphor sulphuric acid as a more environmentally friendly catalyst and have a benzene moiety.

Schematic work

II. MATERIAL AND METHODS

2.1 MATERIALS:

All chemicals and reagents used were of analytical grade and laboratory grade. O-Phenylenediamine, Camphor sulfuric acid, aromatic aldehydes, chloroform, ammonium chloride, ethanol, THF, ethyl acetate, borosil-made glassware, domestic microwave, etc.

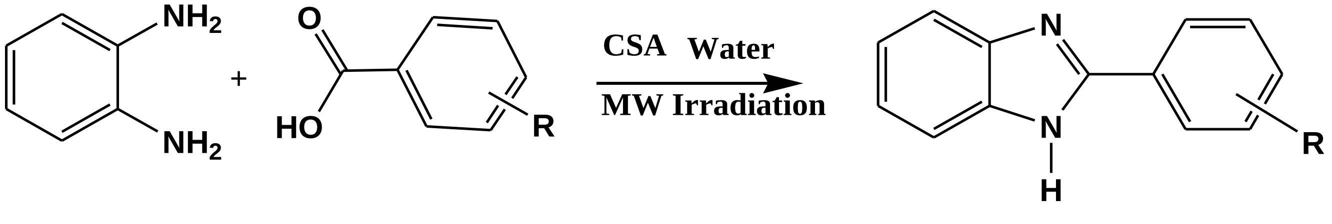
2.2 METHODS:

Melting points were determined in open capillaries in the laboratory and were uncorrected. IR spectra were recorded in KBr pellets on a Perkin Elmer FT-IR spectrophotometer ^{1}H - NMR spectra were measured on a Varian 4 spectrometer using DMSO d^6 as solvent and TMS as an internal standard. Mass spectra were taken in H- ESI mode on Thermo Quantum Mars. All experiments were done in the microwave process in the household microwave oven.

2.3 General procedure for the synthesis of benzimidazole:

O-phenylene diamine (0.01 mmol) and 4 - Chloro benzoic acid (0.01 mmol) (3b) are combined in a beaker containing a 20% solution of camphor sulfuric acid. It starred well and was irradiated in a domestic microwave for 3-4 minutes at 180W maximum power. TLC monitored the reaction. The reaction mixture was then gradually cooled, and this mixture was made essential by the gradual addition of concentrated ammonia solution and stirred for 5-10 minutes. The obtained solid was filtered and recrystallized in aqueous ethanol.

IR, NMR, and mass spectra are used to confirm all compounds.



1 2 3a-g

Where R = **-OH, -OCH$_3$, -NO$_2$, -CH$_3$, -Cl, -Br, etc.**

2.4 Antibacterial evaluation of benzimidazole:

2.4.1. Agar cup method [26]:

Antibacterial activity of benzimidazole was checked with the help of two human pathogens, Escherichia coli and staphylococcus arenas. It was studied at a DMSO concentration of 100 µg/ 10 µL. The diameter of the inhibitory zone was measured in millimeters, and the results of their antibacterial activity have presented in Table 2. Benzimidazole shows similar values of antibacterial activity when compared with standard Streptomycin for the two pathogenic bacteria. Among all the synthesized complexes, 3a & 3d showed good antibacterial activity against Escherichia coli, and 3e showed good activity against S. arenas when compared with other synthesized compounds.

III. RESULTS AND DISCUSSION

Synthesis of benzimidazole from o-phenylene diamine and aromatic carboxylic acid using camphor sulphuric acid as a catalyst in domestic microwave irradiation save time, high yield of the product and save electricity. When they were screened for antibacterial activities many of the products found active and gave good values with human pathogen. All detailed are mention in table 2.

Table. 1. Physical Data of newly Synthesized Compounds:

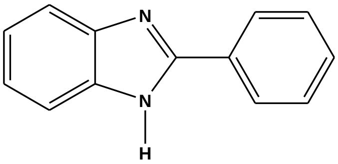
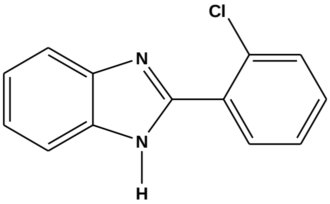
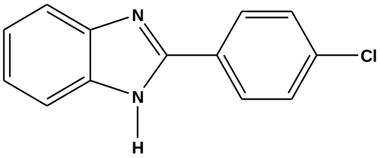
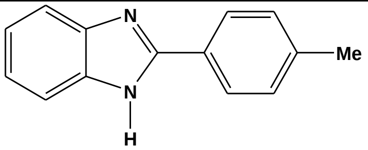
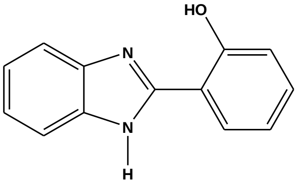
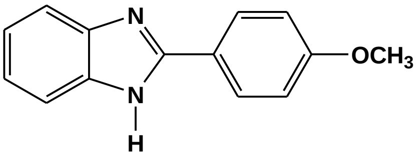
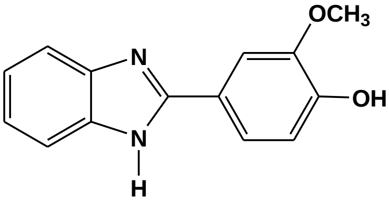
Sr. No.	Structure	Reaction time in Minutes	Yield in %	Melting points (°C)
3a		3.5	65	215
3b		4	57	222
3c		4	62	255
3d		3.0	68	231
3e		3.5	60	245
3f		3.0	78	224
3g		4.5	85	147

Table 2: Antibacterial activities of newly synthesized benzimidazole compounds.

Entry	Human pathogen	
	Escherichia coli	*Staphylococcus arenas*
3a	**21**	17
3b	14	16
3c	14	15
3d	**20**	16
3e	19	**18**
3f	**21**	17
3g	**23**	**19**
Streptomycin (Ref.)	**22**	**20**

3.1 Spectral Analysis:

3.1.1. Compound 3b

Molecular Formula $C_{13}H_9ClN_2$; Pale yellow; **IR** Spectra: 1598 (C=N), N-H 2490 cm^{-1} (stret. vib.), 760 cm-1 due to Cl

3000 cm^{-1} Aromatic C-C; ^{1}**HNMR (CdCl$_3$) :** dd 7.70 aromatic stretching, dd 7.45 aromatic stretching, d 5 due to N-H stretching; **Mass:** m/e 228.

3.1.2. Compound 3c

Molecular Formula $C_{13}H_9ClN_2$; Pale yellow; **FTIR** Spectra: 1645 (C=N), N-H 2489 cm^{-1} (stret. vib.), 740 cm^{-1-} -Cl, 3100 cm^{-1} Aromatic C-C; ^{1}**HNMR (CdCl$_3$) :**dd 7.70, dd 7.45 (Ar. Stret.), d 5 - N-H (cyclic stret.); **Mass:** m/e 228.

3.1.3. Compound 3d

Molecular Formula $C_{14}H_{12}N_2$; Faint yellow; **FTIR** Spectra: 1670 (C=N), N-H 2488 cm^{-1} (stret. vib.), 3060 cm^{-1} (Aromatic C-C).; ^{1}**HNMR (CdCl$_3$) :** 2.4 due to free -CH_3, dd 7.70 (Ar. Stret.), dd 7.45, (Ar. Stret.), dd 7.1, (Ar. Stret.), d 4.9 due to N-H (cyclic stret.); **Mass:** m/e 208.

3.1.4. Compound 3e

Molecular Formula $C_{13}H_{10}N_2O$; Yellow; **Mp** 245°C; **Yield** 60%; **FTIR** Spectra: 1599 (C=N), N-H 2486 cm^{-1} (stret. vib.), 3000 cm^{-1} Aromatic C-C ^{1}**HNMR (CdCl$_3$):** dd 7.7 (Ar. Stret.), dd 7.5 (Ar. Stret.), d 5 due to N-H cyclic stretching. **Mass:** m/e 210.

3.1.5. Compound 3f

Molecular formula $C_{14}H_{12}N_2O$; Yellow; **Mp** 224°C; **Yield** 78%;

FTIR: (KBr) :3400-3300 cm^{-1} N-H 2480 cm^{-1} (stret. vib.), 3055 cm^{-1} , 1697 cm^{-1}, 1436 cm^{-1} -OCH$_3$; ^{1}**HNMR (CdCl$_3$):** dd 7.7 dd 7.7,dd 7.4, dd 7.3, dd 6.9 (Ar. Stret.), dd 6.9(Ar. Stret.), d 5 due to N-H cyclic stretching. **Mass:** m/e 224.

3.1.6. Compound 3g

Molecular formula $C_{14}H_{13}N_2O_2$; Dark yellow; **M.p.** 297°C; **Yield** 85 %;

FTIR (KBr): 3250 cm^{-1}, 3000 cm^{-1} N-H stretching vibration; 1622 cm^{-1}, 1421 cm^{-1} -OCH$_3$ stretching; 1246, ; C=C Stretching; ^{1}**HNMR (CdCl$_3$):** dd 7.71, dd 7.7, dd 7.4, dd, dd 6.9 (Ar. Stret.), d 5 N-H (cyclic stret.) & Free –OH (exchangeable –OH) .; **Mass:** m/e 224

IV. CONCLUSION

This process for making benzimidazoles is simple and does not use organic solvents. It is discovered that, in the presence of camphor sulfuric acid as a catalyst, O-phenylene diamine reacts quickly with carboxylic acid to produce 2-substituted benzimidazole, usually in good quantities. Because it reduces the response time, microwave irradiation is also regarded as environmentally friendly. When tested for microbial activity, they show moderate to good characteristics for several antibacterial species. It is used for a variety of medicinal purposes, including anti-inflammatory and anti-anxiety treatments.

V. ACKNOWLEDGEMENT

The author would like to express his gratitude to the University of Mumbai for funding under the Minor Research Project Management, as well as to our college's principal, Dr. Sandesh S. Gurav, the head of the chemistry department, and the entire chemistry department staff for providing the lab and helping me throughout my research.

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Densities, Viscosities, Excess Molar Volumes and Excess Gibbs Free Energy of Activation of Binary Mixtures of Propionaldehyde with Methanol Over the Entire Range of All Compositions at 298.15, 308.15 and 318.15 K

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ABSTRACT

Densities and viscosities of the binary mixtures of propionaldehyde with methanol, ethanol n-propanol and n-butanol at 298.15, 308.15 and 318.15 K over the entire range of all compositions have beem studied in this paper. Viscosity deviations (Δŋ), molar volumes Vm, excess molar volumes VE and excess free energies of activation of viscous flow ΔG*E have been determined by using experimental data. Viscosity deviations, excess molar volumes and excess free energies of activation of viscous flow have been calculated and correlated with Redlich-Kister polynomial equation.

Keywords: Density, Viscosity, Viscosity deviation, Excess molar volume, Binary system, propionaldehyde.

I. INTRODUCTION

It is general finding that there is a little information of the viscosity of binary mixtures propionaldehyde with methanol and effect of temperature on it. Study of effect of temperature on the viscosity of a liquid is important and has been studied by some researchers. However, study of the effect of temperature on viscosity and density of binary liquid mixtures of propionaldehyde with methanol is rarely reported. Therefore, the main aim of this study was to produce the data on the effect of temperature on the viscosity of binary liquid mixtures. Further, the thermo-physical properties of binary liquid mixtures and their analysis in terms of interpretative models constitute a very interesting subject [1-2]. The characterization of mixtures through their thermodynamic and transport properties is important from the fundamental viewpoint of understand their mixing behavior [3-7]. Liquid mixtures consisting of aldehydes and alcohols are of great importance in the field of industries such as in Petrochemical, Pharmaceutical and Dye [8, 9]. A thorough knowledge of transport properties of non-aqueous solutions is essential in many chemical and industrial applications [10]. The studies of excess properties such as deviation in viscosity, excess molar volume, excess Gibbs free energy of activation of viscous flow molecular interactions of binary mixtures are useful in understanding the nature of intermolecular interactions between two liquids [11-12]. Binary liquid mixtures due to their unusual behavior have attracted considerable attention due to their importance from both theoretical and practical point of view because these mixtures are used in titration, calorimetry and reaction calorimetry, among other uses [14].

In this present paper, density (ρ) and viscosity (ŋ) of binary mixtures of propionaldehyde methanol are reported at various temperatures i.e. 298.15, 308.15 and 318.15 K. Deviation in viscosity (Δŋ), molar volume (V_m), excess molar volume (V^E) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) have been calculated from the density ((ρ) , and viscosity (ŋ), data. Calculated deviation in viscosity and excess functions were fitted to the Redlich-Kister polynomial equation and the results analyzed in terms of molecular interactions.

II. EXPERIMENTAL METHODS

The chemicals such as propionaldehyde and methanol used for the current investigation were obtained from SD fine chemicals India. Propionaldehyde and methanol used were of analytical grade (AR) of minimum purity of 99.9 %. The purities of propionaldehyde and methanol were cross checked by density determination at different temperatures. The densities of pure propionaldehyde & methanol and their binary mixtures were measured by using a single-arm pycometer which was calibrated at the working temperatures with doubly distilled water. The sensitivity of the pycnometer corresponded to a precision in density of $1x10^{-3}$ gm cm^{-3}. The binary liquid mixtures of different known concentrations were prepared in stopper measuring flasks. The weight of the sample was measured using electronic digital balance with an accuracy of ± 0.0001 gm. An Ubbelohde viscometer (of 20 ml capacity) was used in the viscosity measurement and efflux time was determined using a digital clock to within ± 0.01 Sec. The experimental temperature was controlled using kinematic viscosity bath with an accuracy of ± 0.10K.

III. RESULTS AND DISCUSSION

The variations in viscosity of different binary mixtures of propionaldehyde with methanol with temperature and calculated data of deviation in viscosity (Δŋ), molar volume (V_m), excess molar volume (V^E) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) are given in tables below.

Propionaldehyde with Methanol at 298.15, 308.15 and 318.15 K.

Table: 1-a At 298.15:

x1	P (g cm^{-3})	H (mPa.s)	Δŋ (mPa.s)	Vm cm^3mol^{-1}	VE cm^3mol^{-1}	ΔG*E $J.mol^{-1}$
0	0.7864	0.5549	0	40.7426	0	1512.201
0.0590	0.7883	0.5378	-0.0225	42.5960	0.0123	1662.324
0.1237	0.7902	0.5189	-0.0396	44.6260	0.0184	1822.321
0.1945	0.7915	0.5019	-0.0505	46.8817	0.0235	1972.254
0.2736	0.7941	0.4848	-0.0543	49.3210	0.0289	2121.354
0.3610	0.7961	0.4692	-0.0525	52.0566	0.0348	2268.214
0.4587	0.7979	0.4491	-0.0487	55.1281	0.0326	2382.254
0.5687	0.7998	0.4326	-0.0388	58.5760	0.0278	2462.254
0.6932	0.8017	0.4178	-0.0291	62.4840	0.0177	2317.258
0.8356	0.8037	0.3912	-0.0207	66.9421	0.0112	2117.365
1	0.8056	0.3765	0	72.0953	0	2011.354

Table: 1-b At 308.15:

x1	ρ (g cm^{-3})	η (mPa.s)	Δŋ (mPa.s)	Vm cm^{3}mol^{-1}	VE cm^{3}mol^{-1}	ΔG*E J.mol^{-1}
0	0.7764	0.4782	0	41.6391	0	1569.436
0.0590	0.7779	0.4647	-0.0189	43.4925	0.0186	1719.559
0.1237	0.7793	0.4515	-0.0361	45.5225	0.0247	1879.556
0.1945	0.7808	0.4392	-0.0469	47.7782	0.0298	2029.489
0.2736	0.7823	0.4251	-0.0507	50.2175	0.0352	2178.589
0.3610	0.7837	0.4125	-0.0489	52.9531	0.0411	2325.449
0.4587	0.7852	0.3982	-0.0451	56.0246	0.0389	2439.489
0.5687	0.7867	0.3859	-0.0352	59.4725	0.0341	2519.489
0.6932	0.7881	0.3736	-0.0255	63.3805	0.024	2374.493
0.8356	0.7896	0.3604	-0.0171	67.8386	0.0175	2174.612
1	0.7913	0.3461	0	72.9918	0	2068.589

Table: 1-c At 318.15:

x1	ρ (g cm^{-3})	η (mPa.s)	Δŋ (mPa.s)	Vm cm^{3}mol^{-1}	VE cm^{3}mol^{-1}	ΔG*E J.mol^{-1}
0	0.7711	0.4195	0	42.5803	0	1642.088
0.0590	0.7720	0.4083	-0.0146	44.4337	0.0273	1792.211
0.1237	0.7730	0.3965	-0.0317	46.4637	0.0334	1952.208
0.1945	0.7739	0.3823	-0.0426	48.7194	0.0385	2102.141
0.2736	0.7748	0.3704	-0.0464	51.1587	0.0439	2251.241
0.3610	0.7758	0.3591	-0.0446	53.8943	0.0498	2398.101
0.4587	0.7767	0.3472	-0.0408	56.9658	0.0476	2512.141
0.5687	0.7777	0.3348	-0.0309	60.4137	0.0428	2592.141
0.6932	0.7786	0.3217	-0.0212	64.3217	0.0327	2447.145
0.8356	0.7795	0.3098	-0.0128	68.7798	0.0262	2247.252
1	0.7805	0.3041	0	73.933	0	2141.241

To investigate the molecular interaction between Propionaldehyde and the alcohols, (methanol, ethanol, n-propanol and n-butanol), viscosity deviation, excess molar volumes and excess Gibbs free energy of activation of viscous flow have been evaluated from experimental density and viscosity using equations 1 and 2 respectively.

$$V^E = \frac{x_1M_1+x_2M_2}{\rho_m} - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \quad \text{------------ (1)}$$

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \quad \text{--------------- (2)}$$

where x_1 and x_2 are the mole fractions calculated from mass fractions. M_1 and M_2 are molar masses, ρ_1 and ρ_2 are densities, η_1 and η_2 are the viscosities of pure components 1 and 2 respectively. ρ_m and η_m are the density and viscosity of the mixture.

The excess Gibbs free energy of activation of viscous flow was obtained from equation 3.

$$\Delta G^{*E} = RT[ln\eta_m V_m - (x_1 ln\eta_1 V_1 + x_2 ln\eta_2 V_2)] \qquad \text{---------------------- (3)}$$

where R is the universal constant of gases, T is the absolute temperature, V_1 and V_2 are the molar volumes of component 1 and 2, x_1 and x_2 represents the mole fraction of component 1 and 2.

Vm is obtained from equation 4 below.

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho_m} \qquad \text{------------------ (4)}$$

Where η_1, η_2 and η_m are the viscosity of component 1 and 2 and mixture respectively

Figure 1-a: The plots of deviation in viscosity against mole fraction at 298.15, 308.15 and 318.15 K for binary mixtures of **Propionaldehyde with methanol**.

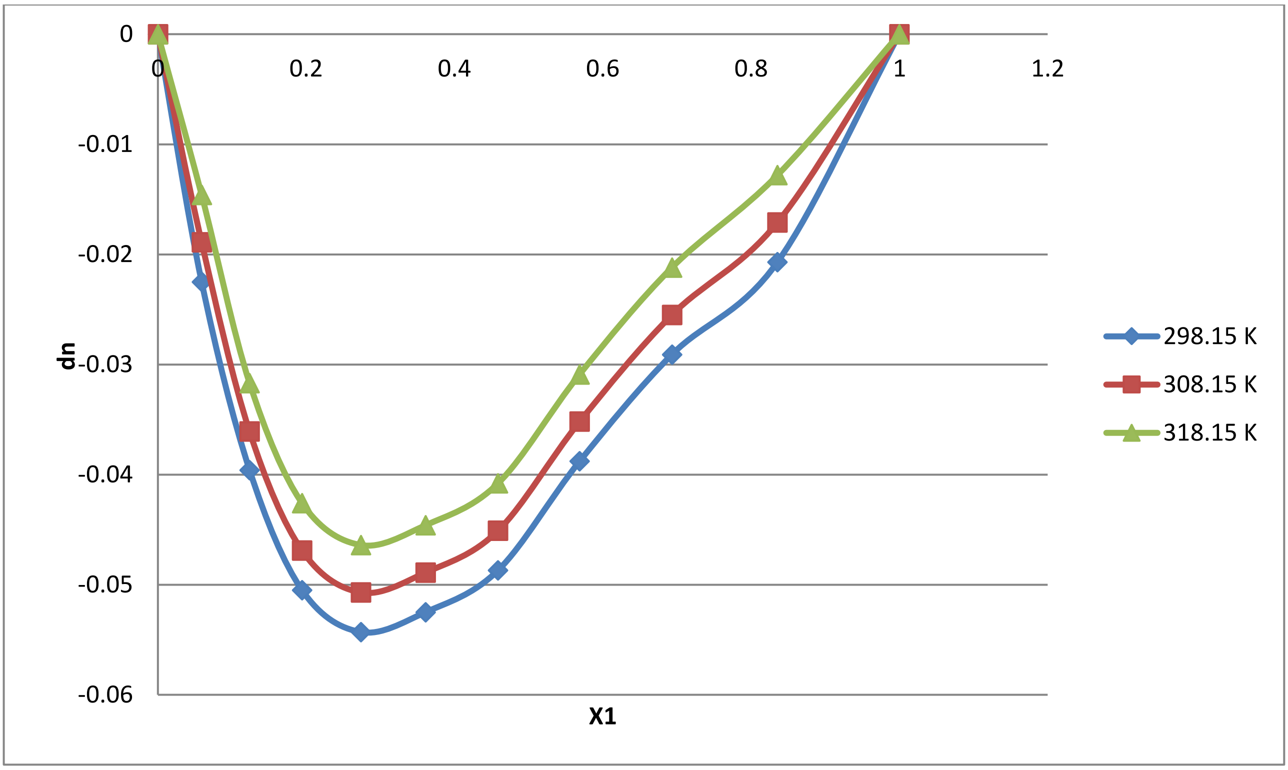
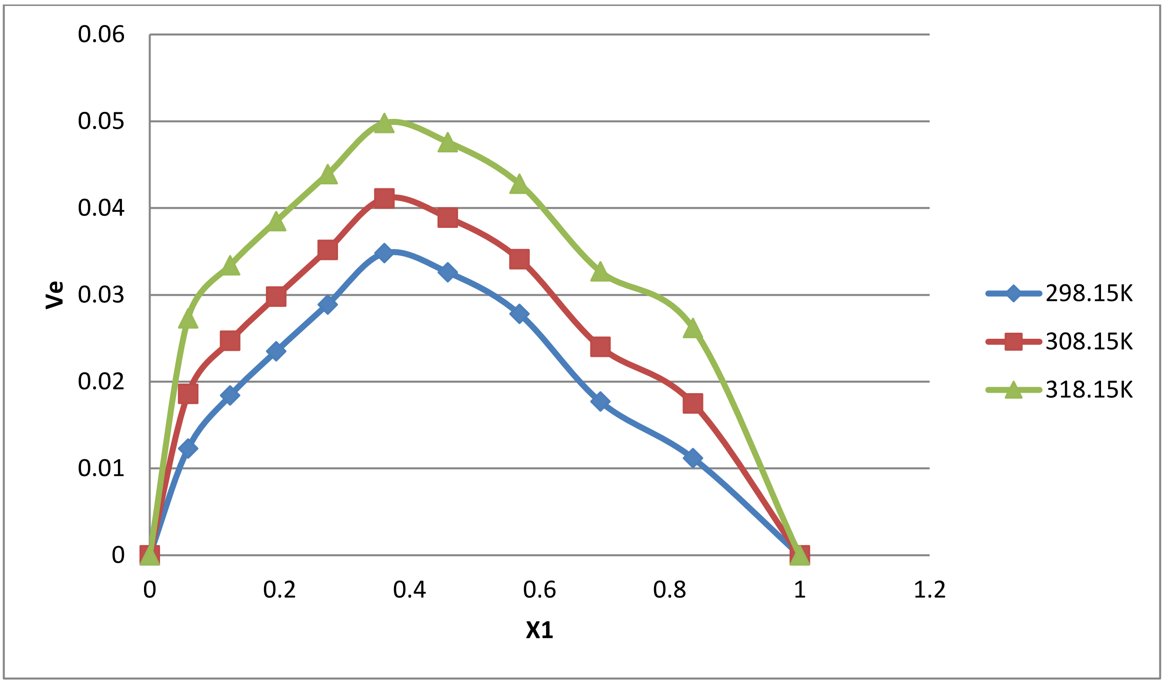
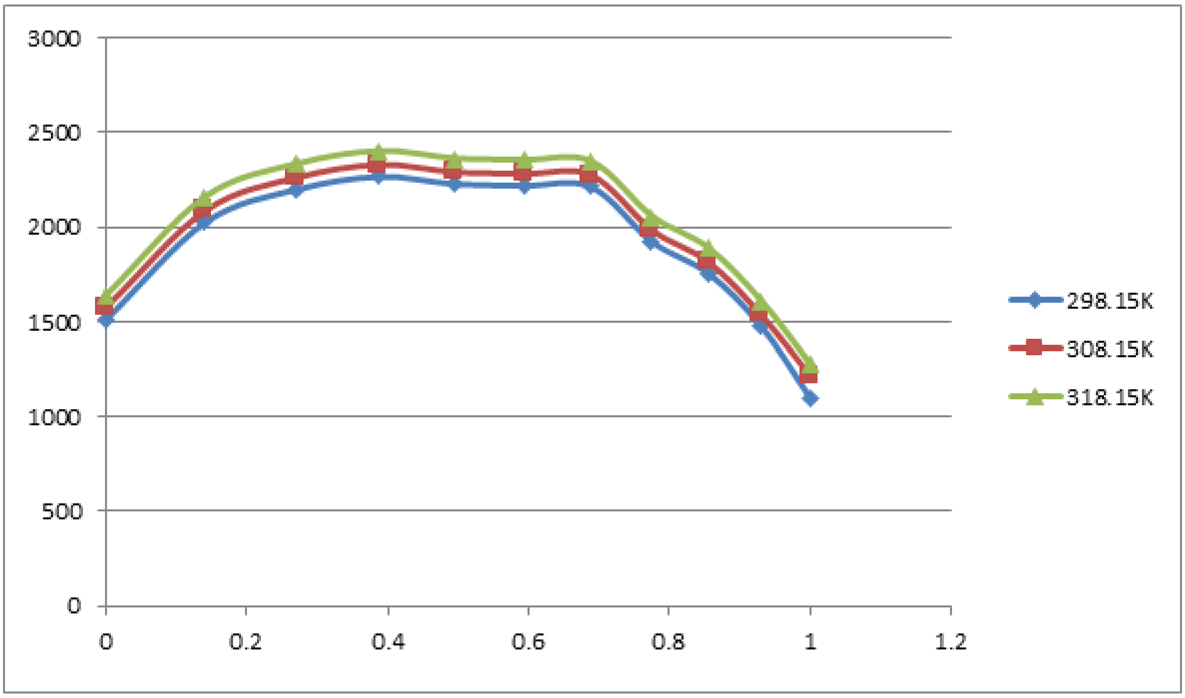


Figure: 1-b. The plots of excess molar volumes against mole fraction for binary mixtures of **Propionaldehyde with methanol** at 298.15, 308.15 and 318.15 K.



Figures 1-c: The plots of **excess free energies of activation of viscous flow, ΔG*E** against mole fraction at 298.15, 308.15 and 318.15 K for binary mixtures of propinaldehyde with methanol.



The experimental values of densities and viscosities of studied binary mixtures of propionaldehyde with methanol at 298.15 K, 308.15 K and 318.15 K over the entire composition range expressed by mole fraction x_1 of propionaldehyde are listed in Tables -(a-c). The densities and viscosities of the studied binary mixtures are found decreased with increasing temperature and increased with increasing of mole fraction of propionaldehyde. Qualitative explanation for the behavior of binary mixtures with the change in mole fraction can be suggested from the experimental data obtained under study. Deviations in viscosity can be explained by means of relative strength of molecular interaction between like and unlike molecules. The sign and extent of dη depends on the combined effect of factors like molecular size and shape of the propionaldehyde and alcohol in addition to intermolecular forces. For the systems where dispersion, induction and dipolar forces are operating, the values of viscosity deviations are found to be negative, whereas the existence of specific interactions between the mixing components of the various binary systems tends to make viscosity deviations positive. Figure 1-a show the graphical variations of dη for binary mixtures of propionaldehyde with methanol at 298.15, 308.15 and 318.15 K. The values of dη are found negative for binary mixtures of propionaldehyde with methanol at all experimental temperatures. As temperature increases dη values became more negative in case of methanol. A minima of plot x_1 Vs dη values for all binary mixtures occurs at equimolar concentrations at all experimental temperatures. Furthermore negative dη values for all the binary mixtures indicate that the dispersion forces are dominant and furthermore the existence of dispersion forces indicates that the component molecules have different molecular size and shapes (10).

Figure 1-b shows graphical variation of V^E for binary mixtures of propionaldehyde with methanol at 298.15, 308.15 and 318.15 K. In the investigation V^E are found positive for all the binary mixtures of propionaldehyde with methanol at all experimental temperatures. The maxima of plot x_1 against V^E is obtained at equimolar concentration for all binary mixtures. The V^E values are found increased with increase in the temperature for all binary mixtures. As the temperature increases V^E also increases because of inconvenient interstitial accommodation due to thermal agitations among propionaldehyde and alcohol. The positive values of V^E in the present investigation are resultant of specific interactions formation of hydrogen bonds resulting in positive contribution (3, 4).

Figures 1-c show the variation of excess Gibb's free energy of activation of viscous flow ΔG^{*E}. The vales of excess Gibb's free energy of activation of viscous flow ΔG^{*E} for all binary mixture are found positive which attributes the dominance of specific interaction between propionaldehyde and alcohol and size effect of the mixing components (11). Positive values of ΔG^{*E} represents hydrogen bonding between the molecules are dominant (13). ΔG^{*E} values increased with increase in temperature in all cases however ΔG^{*E} values are found almost constant for methanol at all studied temperatures.

IV. CONCLUSION

The deviation in viscosity, excess molar volume and excess Gibbs free energy of activation of viscous flow for the systems Propionaldehyde + methanol at 298.15, 308.15 and 318.15 K has been reported. The deviation in viscosity of the binary systems Propionaldehyde + methanol are found to be negative and increases with temperature while excess molar volumes are positive for all binary systems. There is intermolecular interaction among the components of the binary mixtures leading to possible hydrogen bond formation of the type Ō̈---H-O between unlike molecules confirming intermolecular hydrogen bond formation between Propionaldehyde and the alcohol mixtures(14-20).

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Physico-Chemical Analysis of Water Quality of Shivana-Takali Dam, Kannad, Dist.-Aurangabad

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ABSTRACT

Water quality of Shivana-Takali dam of Kannad, Dist- Aurangabad (MH) has been analyzed seasonally by using various physico-chemical parameters like pH, water temperature, alkalinity, dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), chloride, sulphate, phosphorous etc. during 2021-2022 and the results obtained varied seasonally. Maximum value of TDS was recorded during monsoon season. In case of some physico-chemical parameters like COD and BOD maximum values were recorded during winter season while maximum values of pH, water temperature, alkalinity, DO, chlorides, sulphate and phosphorus were recorded during summer season. Most of the physico-chemical parameters showed their maximum values in the summer season followed by winter and monsoon season.

KEYWORDS-Water Quality, DO, BOD, COD, TDS, Physico-Chemical Parameter.

I. INTRODUCTION

The study of fresh water contained within continental boundaries is known as limnology (Roberto Bertoni; 2011). Shivana-Takali dam is constructed across the Shivana river in Kannad Tehsil of Aurangabad district, Maharashtra for different purposes like irrigation, domestic water supply, fish farming as well as industrial purposes. This water reservoir is getting polluted due to increased man made activities in the dam, use of fertilizers in agriculture which affected the water quality of the Shivana-Takali dam very badly and decrease in number of aquatic organisms also observed. Therefore, it is necessary to check the water quality of selected water reservoir seasonally.

Various researchers carried out the limnological study of fresh water including Kadam *et al.,* (2007), Salve and Hiware (2008), Mahor (2011), Khan *et al.,* (2012), Mule *et al.,* (2019) etc.

The study area selected for Shivana-Takali dam which is situated on the Shivna river near Kannad, Dist.-Aurangabad, Maharashtra. In present investigation, an attempt has been made to study seasonal water quality of Shivana-Takali dam by using various physico-chemical parameters during 2021-22.

II. MATERIAL AND METHODS

i. COLLECTION OF WATER SAMPLES-

The water samples were collected from 03 different stations of Shivana-Takali dam in plastic transparent bottles in the morning hours between 9 to 11 am regularly during monsoon, winter and summer seasons. The collected water samples were brought to the laboratory to study various physico-chemical parameters. Some physical parameters such as pH and water temperature were recorded on the collection sites of 03 different stations by using pH paper and thermometer respectively.

ii. PHYSICO-CHEMICAL ANALYSIS

Various physico-chemical parameters like pH, water temperature, alkalinity, dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), chloride, sulphate and phosphorous were studied as per standard procedures (APHA; 2005) for water quality analysis.

III. RESULTS AND DISCUSSION

The water quality analysis by using some physico-chemical parameters was carried out seasonally during June 2021 to May 2022 and the results obtained are summarized in table-1.

3.1. pH

pH can affect most of the chemical and biochemical reactions. During monsoon season maximum pH value 7.7 was observed in the month of July while the minimum pH value 7.3 was recorded in the month of September. During present study, maximum pH value 8.2 was recorded in the month of May during summer season while the minimum pH value 7.2 was recorded in the month of October during winter season. It was observed that the pH values observed higher in summer season. Similar type of study was carried out by Kamble *et al.,* (2009).

3.2. Water temperature

The chemical, biochemical and biological characteristics of the water reservoir are determined by water temperature. During monsoon season the maximum water temperature 33.5^{0}C was recorded in the month of June while minimum temperature 31.3^{0}C was observed in the month of September.

During present investigation, the maximum temperature 36.5^{0}C was observed in the month of May during summer season while minimum temperature 25^{0}C was recorded in the month of January during winter season.

3.3. Alkalinity

During monsoon season the maximum alkalinity recorded was 158 mg/L in the month of July while the minimum alkalinity 138 mg/L was observed in the month of August. During present study, maximum alkalinity 172 mg/L was recorded in the month of May during summer season while minimum alkalinity 134 mg/L was observed in the month of November during winter season.

3.4. Dissolved Oxygen (DO)

During monsoon season maximum DO 5.5 mg/L was observed in the month of June while minimum DO 4.5 mg/L was recorded in the month of August. During present investigation maximum DO 6.5 mg/L was recorded in the month of May during summer season while the minimum DO 4.1 mg/L was observed in the month of November. Kadam *et al.,* (2007) carried out similar study.

3.5. Biological oxygen demand (BOD)

Maximum BOD value was recorded 3.60 mg/L in the month of December during winter season while minimum value was recorded 2.25 mg/L in the month of April during summer season.

3.6. Chemical oxygen demand (COD)

Maximum COD value was recorded 39 mg/L in the month of January during winter season while minimum value 29 mg/L was recorded in the month of July during monsoon season.

3.7. Total Dissolved Solids (TDS)

During present study maximum TDS value 133 mg/L was observed in the month of June during monsoon season while minimum TDS value 111 mg/L was recorded in the month of April during summer season.

3.8. Chloride

Maximum value 34 mg/L was recorded in the month of April during summer season while minimum value 23 mg/L was observed in the month of November during winter season.

3.9. Sulphate

Maximum value 179 mg/L was observed in the month of May during summer season while minimum value 129 mg/L was recorded in the month of November during winter season.

3.10. Phosphorus

Maximum value 1.3 mg/L was observed in the month of May during summer season while minimum value 0.6 mg/L was recorded in the month of July during monsoon season.

Table-1: Physico-Chemical Parameters of Seasonal Water Quality Analysis of Shivana-Takali Dam.

Parameter	Monsoon				Winter				Summer			
	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May
pH	7.5	7.7	7.4	7.3	7.2	7.6	7.7	7.8	7.7	8.0	7.9	8.2
Water Temp. (^{0}C)	33.5	32	31.4	31.3	32.2	28.5	28	25	26	31	34	36.5
Alkalinity (mg/L)	148	158	138	143	149	134	139	144	150	170	158	172
DO (mg/L)	5.5	4.7	4.5	4.8	5.0	4.1	5.3	5.8	6.0	6.4	6.3	6.5
BOD (mg/L)	2.65	2.75	2.80	2.85	2.90	3.0	3.60	3.40	2.70	2.60	2.25	2.40
COD (mg/L)	30	29	31	32.5	35	37	36	39	33	33.5	34	34.5
TDS (mg/L)	133	121	127	131	125	126	118	115	120	116	111	113
Chloride (mg/L)	30.5	30	29	31	24	23	26	25	33	33.7	34	33.9
Sulphate (mg/L)	159	149	144	139	134	129	139	144	159	164	174	179
Phosphorus (mg/L)	0.8	0.6	0.9	1.1	1	0.9	1	0.9	0.7	0.9	1.2	1.3

IV. CONCLUSION

In the present investigation, maximum value of TDS was recorded during monsoon season. In case of some physico-chemical parameters like COD and BOD maximum values were recorded during winter season while maximum values of pH, water temperature, alkalinity, DO, chlorides, sulphate and phosphorus were recorded during summer season.

During present investigation, most of the physico-chemical parameters showed their maximum values in the summer season followed by winter and monsoon season.

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Green Approach for the Synthesis of Schiff Bases Catalyzed by Scolecite Zeolite

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ABSTRACT

Scolecite zeolite is natural zeolite used to convert many organic transformations. A series of Schiff bases have been synthesized by condensing various aromatic aldehydes with 3-(1-(2-aminophenylimino)ethyl)-4-hydroxy-6-methyl-2H-pyran-2-one or 3-(1-(2-amino-4-methylphenylimino)ethyl)-4-hydroxy-6-methyl-2H-pyran-2-one in the presence of natural zeolite i.e. scolecite as a catalyst. The reaction was carried out under solvent free condition by microwave irradiation. The simple experimental procedure, short reaction times, reusability of the catalyst is the advantages of the present method.

Keywords: Scolecite zeolite, Catalyst, Microwave, Green Approach.

I. INTRODUCTION

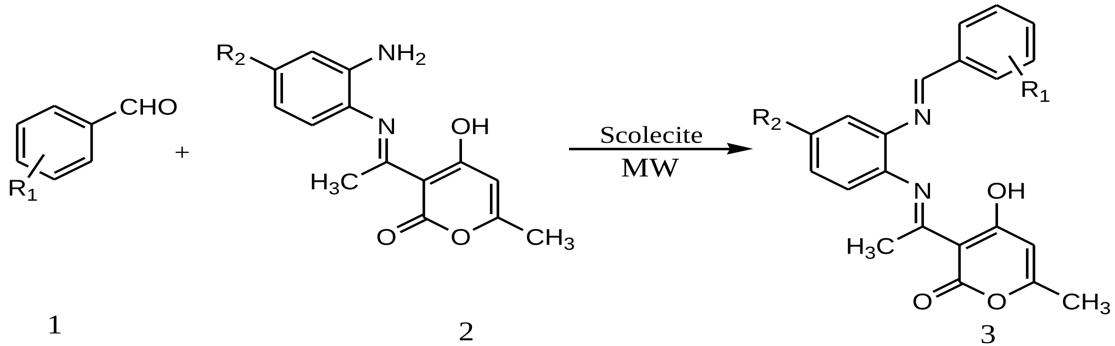
To plan and conduct chemical transformation with “green” experimental protocol is a great challenge that chemists have to confront for improving the quality of the environment for present and future generations. To achieve this target, the exploration of alternative reaction conditions and reaction media to accomplish the desired chemical transformations with minimized side products or waste, including organic solvents whose recovery is mandated by ever more strict laws. Hence, the use of neat and clean procedures which can avoid the use of harmful solvents is needed. The emergence of microwave reaction for synthesis is a step forward in this direction. Microwave irradiation has become an established tool in organic synthesis, because of the rate enhancements, higher yields, and often improved selectivity, with respect to the conventional reaction conditions [1-6].

Many schiff’s bases are considered privileged ligands which are active and well-designed as precursor. These ligands have been extensively studied in coordination chemistry, and are found to be stable under a variety of oxidative and reductive conditions [7]. Schiff bases are actually able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations [8, 9]. It has the potentials to be used in different areas such as electrochemistry, bioinorganic, catalysis, metallic deactivators, separation processes and environmental chemistry [9] and they are becoming increasingly important in the pharmaceutical, dye and plastic industries as well as in the field of liquid-crystal technology [10].

Generally the Schiff bases are prepared by simply refluxing the amines and aldehydes for 2-6 hours but yield of products was less, requires longer reaction time and harsh reaction condition. So here the attempt was made to minimize the time and increase the yield of schiff bases by using solid acid catalyst in mono made microwave oven under solvent free condition. Similar effort was done by M. Gopalakrishnan et al. using activated fly ash for the synthesis of schiff bases [11].

The use of acid catalysts is very common in the chemical and refinery industries, and those technologies employing highly corrosive, hazardous and polluting liquid acids are being replaced with solid acids like clays, zeolites and metal oxide is desirable to achieve effective catalyst handling, product purification and to decrease waste production [12]. Recent decades have witnessed an exponential growth in the applications of heterogeneous catalysis to carry out synthetic transformations as a consequence of its significance in terms of enviro-economical and practical aspects [13,14].

In this research, scolecite zeolite as the solid heterogeneous acid catalyst deserves special mention. This reusable catalyst is safe, world wide available, easy to handle and eco-friendly benign, presents fewer disposal problems and is stable in reaction media. Scolecite has been demonstrated to be efficient catalyst for synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones [15], 2,4,5-triarylimidazoles [16]. In continuation to our investigation of heterogeneous environmentally friendly catalyst [15-20]. In this paper, we report an efficient method for the preparation of Schiff bases using scolecite zeolite (Scheme 1). Our method shows the following advantages: i) cleaner synthesis, ii) shorter time, iii) high yields, iv) ecofriendly, v) reusability of catalyst. Thus, this is an excellent method for the preparation of schiff bases.



Scheme 1

II. EXPERIMENTAL

All the reagents and aldehydes are purchased from Rankem and S. D. Fine (Mumbai). Melting points were measured in open capillaries in a paraffin bath and are uncorrected. The reactions were monitored by TLC [n-hexane: ethyl acetate (7:3)]. IR spectra were recorded with dry KBr on FTIR-4100, Jasco. ^{1}H NMR spectra were recorded on 300 MHz instrument with $CDCl_3$ as a solvent and TMS as an internal standard, Mass spectra were run on a Jeol AX500 instrument.

The naturally occurring scolecite zeolite was collected from the Ellora valley, village Satara, Aurangabad, Maharashtra, Deccan traps of India. It was subsequently washed with distilled water and acetone for several times, dried and crushed into fine powder which was further washed with distilled water 3–4 times and dried at 110°C in an oven. The resulting sample was heated at 500°C in high temperature muffle furnace (SONAR) for

1 h at rate 3°C per minute. The sample was naturally cooled and used in organic synthesis. We have shown its application earlier in the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones [15]. The surface area, pore volume, pore diameter of catalyst was determined by the nitrogen adsorption on Quantachrome Autosorb Instrument and acidity of the sample measured by Temperature Programmed Desorption (TPD) of ammonia on Quantachrome TPR [16].

General procedure for the synthesis of Schiff bases

Aromatic aldehydes (5 mmol), 3-(1-(2-aminophenylimino)ethyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one or 3-(1-(2-amino-4-methylphenylimino)ethyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (5 mmol) and 2 % catalyst with respective to initial concentration of reactant were well mixed in a 25 ml beaker at room temperature and then irradiated at 300 watt for 2-5 minutes in microwave oven (scheme 1). The progress of reaction monitored by TLC. After completion of the reaction, the reaction mixture poured on ice, filtered, washed with cold water to remove excess of impurities. The crude product obtained was recrystallized from ethanol to afford high purity of the product.

The required starting material 3-(1-(2-aminophenylimino)ethyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one and 3-(1-(2-amino-4-methylphenylimino)ethyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one was prepared according to literature procedure [21].

Spectral data of representative compounds

1) 3-((1E)-1-((E)-2-(benzylideneamino)phenylimino)ethyl)-4-hydroxy-6-methyl-*2H*-pyran-2-one **(1).** IR (KBr, cm^{-1}): 3059, 1698,1657, 1579, 1354, 1212, 1146 cm^{-1}. ^{1}H NMR (CDCl$_3$,80 MHz,δ,ppm): 2.11 (s, 3H), 2.54 (s, 3H), 5.83 (s, 1H), 6.9 – 7.9 (m, 9H), 8.71 (s, 1H), 15.86 (s, 1H).

EIMS (m/z, %): 346.38 (M+1).

2) 3-((1E)-1-((E)-2-(4-chlorobenzylideneamino)phenylimino)ethyl)-4-hydroxy-6-methyl-*2H*-pyran-2-one **(2)** IR (KBr, cm^{-1}): 3067,1697, 1657, 1585, 1474, 1354, 1248, 717 cm^{-1}. ^{1}H NMR (CDCl$_3$,80 MHz,δ,ppm): 2.12 (s, 3H), 2.55 (s, 3H), 5.84 (s, 1H), 7.4 – 8.0 (m, 8H), 8.8 (s, 1H), 15.88 (s, 1H).

EIMS (m/z, %): 380.09 (M+1).

III. RESULTS AND DISCUSSION:

The cumulative desorption surface area of catalyst from adsorption-desorption isotherm of nitrogen, pore volume at $p/p_0 = 0.993$ and pore diameter was determined by BJH method and it was found to be $S_{BJH}= 26.39$ m^2/gm, $P_v = 0.0344$ cm^3/gm and $P_d = 11.08$ A° respectively. Temperature Programmed Desorption method (TPD) was used to determine the acidic properties of solid catalyst. This provides information about the total concentration and strength of acidic sites (Bronsted and Lewis). It was found that the total ammonia desorbed is 0.376 mmol/gm of the catalyst.

In order to find the optimum reaction conditions for ecofriendly synthesis of Schiff bases, we have selected 4-chlorobenzaldehyde and 3-(1-(2-aminophenylimino)ethyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one as a model reaction in presence of scolecite catalyst. The reaction was carried out using 1:1 molar ratio of reactants and the conditions are optimized by varying the catalyst amounts (Table 1). Generally, the reaction rate and yield were increased over the amount of catalyst. It was found that 150 mg of catalyst was the appropriate amount for the reaction at 300 watt in microwave oven. The fewer amounts gave a low yield even after long reaction time and the more amounts could not cause the obvious increase for the yield of product. By getting this result, we have extended this protocol to a variety of aldehydes and the results are summarized in Table 2. This protocol is rapid and efficient for the preparation of several Schiff bases from both electrons efficient as well as electron deficient aromatic aldehydes.

The separated catalyst was again reused in same reaction and this was repeated three times. In these cases, the yield of (Entry 2, Table 2) was found to be 93, 90, 89% in each successive reaction. Thus the activity of the catalyst was remains almost same. The presence of strong bronsted and lewis acid sites on the catalyst surface are primarily responsible for rapid reaction leading to high yield of products.

Table 1. Reaction of 4-chlorobenzaldehyde and 3-(1-(2-aminophenylimino)ethyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one

Catalyst in mg	Time (sec)	Yield (%)[a]
No catalyst	420	71
50	90	78
100	90	82
150	90	93
200	90	93

[a]The yields refer to isolated product

Table 2. Scolecite catalyzed synthesis of schiff bases.

Entry	R1	R2	Time (sec)	Yield (%)[a,b]	M. P. (°C)
1	H	H	80	89	162-163
2	4-Cl	H	90	93	196-197
3	4-F	H	80	91	182-183
4	4-OCH_3	H	95	89	217-218
5	H	CH_3	110	91	137-138
6	4-Cl	CH_3	115	90	178-179
7	4-F	CH_3	110	93	161-162
8	4-OCH_3	CH_3	130	85	194-194
9	2-OH	H	140	87	185-186
10	2-OH, 4-OH	H	160	83	201-202
11	2-OH	CH_3	120	91	178-179
12	2-OH, 4-OH	CH_3	160	85	218-219

[a]The yields refer to isolated product. b-All products are known and spectroscopic data matched with authentic sample.

IV. CONCLUSIONS

In conclusion, scolecite catalyst was found to be a mild and effective catalyst for the formation of Schiff bases in moderate to excellent yield. The uses of this inexpensive and easily available catalyst under solvent free conditions make this protocol practical and economically attractive. The simple work-up procedure, mild reaction conditions, selectivity, very good yields and above all, the ease in purification of products simply by recrystallization make our methodology a valid contribution to the existing processes in the field of Schiff bases synthesis.

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A Comparative Study on the Oxidation of Acetic, n-butyric, n-Valeric acid hydrazides to their Corresponding Acid by Thallium (III) in 1, 4-Dioxane Medium - A Kinetic and Mechanistic Approach

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ABSTRACT

The reaction between Thallium (III) and Acetic, n-Butyric acid and n-Valeric acid hydrazides was carried out in a mixture of perchloric and hydrochloric acid medium. The reaction proceeds through formation of complex with reactant, which decomposes in subsequent steps to give product. Effect of acrylonitrile shows, that there is no formation of free radicals. The increase in [H+] and [Cl-] decreases the rate of the reaction. The increase in ionic strength does not affect the rate of reaction. The effect of temperature was studied at four different temperatures ranging from 150C to 300C. The activation parameters were also determined and a mechanism is predicted.

Keywords: kinetics, Thallium(III), Oxidation, Acetic acid hydrazide (AAH), n-Butyric acid hydrazide(n-BuAH), n-Valeric acid hydrazide(n-VAH).

I. INTRODUCTION

Chemical kinetics is the branch of physical chemistry which deals with a study of the speed of chemical reactions. Such studies also enable us to understand the mechanism by which the reaction occurs. Thus, in chemical kinetics we can also determine the rate of chemical reaction.

In recent years, a lot of biologically important hydrazide–hydrazone derivatives with a number of functional groups have been synthesized from many different carbonyl compounds. They were found to possess anticancer[1], anti-inflammatory[2-3], anticonvulsant[4], antiviral,[5] Şenkardes and antiprotozoal[6] activities. Among the biological properties of this class of compounds, the antimicrobial activity is the most frequently encountered one in scientific literature.

Recently thallium(III) nitrate trihydrate6 (TTN), ceric(IV) ammonium nitrate[7] (CAN) and iodobenzene diacetate[8] have been reported for the oxidation of hydrazides to esters / acids. However, most of the methods for this transformation have several limitations, such as the reagents used are often toxic, expensive, hazardous and incompatible with other functional groups present in the substrate. In order to circumvent some of the problems associated with earlier methods, a mild and efficient method is still needed for this transformation.

Interest in the use of thallium(III) in the oxidation of organic compounds has increased only recently and research in this regard is not been extensive. The potential of this oxidant is realized more and more as is evident from the considerable amount of work that is lately being done. Thus, the selectivity of thallium (III) is higher than its neighbours in the periodic table, mercury(II) and lead (IV) and also thallium (III) is a better oxidant than the other two. The kinetics of oxidation of simple olefins was studied in detail by Henry[9].

Hence, the present work deals with the kinetics and mechanism of oxidation of Acetic, n-Butyric, n-Valeric acid hydrazides by thallium(III) in acidic medium.

II. EXPERIMENTAL

Thallium (III) solution was prepared by dissolving Tl_2O_3 (ACROS) in 1.0 mol dm^{-3} HCl and the concentration was ascertained by iodometric titration. The oxidation of Acetic, n-Butyric, n-Valeric acid hydrazides was prepared from reported[10] procedure and characterized by determining their melting points. Stock solution of oxidation of Acetic, n-Butyric, n-Valeric acid hydrazides were prepared in 50 % v/v, 1,4-dioxan. Ionic strength was kept constant.

The reactions were carried out in 50 % v/v 1-4 dioxane (s.d.fine.chem) under pseudo first order conditions keeping concentration of hydrazide in large excess over that of the oxidant. The solutions containing the reactants and all other constituents were thermally equilibrated separately, mixed and the reaction mixture was analysed for unreacted thallium (III) iodometrically by titrating against standard thiosulphate. The pseudo-first order rate constants were determined from the slopes of linear log[Tl(III)] versus time plots. The results were reproducible up to ± 5 %. Kinetic runs were followed to about three half-lives of the reactions. Under the experimental condition oxidation of 1,4-dioxan did not occur.

End Product Analysis

For identification of products the reaction was carried out by using aqueous solution of hydrazide, Thallium(III), HCl and $HClO_4$. The flask containing reaction mixture was kept in thermostated water bath maintained at 50^0C for 24 hours to complete the reaction, the residue obtained after filtration was analysed for acid as follows

i. The presence of oxidation of Acetic, n-Butyric, n-Valeric acid were detected by testing with bicarbonate.

ii. The formation of acid was confirmed by IR and its melting point.

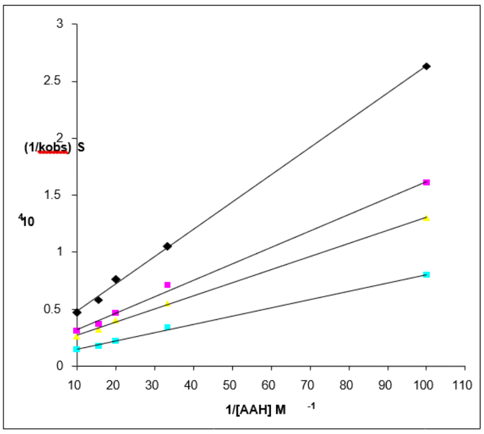
$$\mathrm{RCONHNH_2 + 2\,Tl(III) + H_2O \rightarrow R\text{-}COOH + N_2 + 4H^+ + 2\,Tl(I)} \qquad \text{... (1)}$$

III. RESULTS AND DISCUSSION

The reaction occurs rapidly in perchloric acid medium but in the presence of hydrochloric acid the rate is measurable. Therefore, the reaction was carried out in a mixture of both the acids. The effect of reactants on the reaction was studied at constant [HCl] and [$HClO_4$] of 0.1 mol dm^{-3} each and ionic strength of 0.6 mol dm^{-3}. Concentration of oxidant was varied from $6.4x10^{-4}$ to $6.4x10^{-3}$ mol dm^{-3} keeping the [hydrazide] constant at $1x10^{-1}$ mol dm^{-3}.Since,the pseudo first order rate constants were fairly constant($3.4 \pm 0.1x10^{-4} s^{-1}$ for AAH, n-BuAH, n-VAH at, the order with respect to [oxidant] is unity. The effect of [hydrazide] was studied between the concentration range from $1x10^{-2}$ to $1x10^{-1}$ mol dm^{-3} keeping the [oxidant] constant at $3.0x10^{-3}$ mol dm^{-3}.The pseudo first order rate constants increases with increase in concentration and the order with respect to hydrazide is found to be fractional.

To study the effect of [H^+] and [Cl^-],[oxidant], [hydrazide] and ionic strength were kept as $3.0x10^{-3}$,$1x10^{-1}$ and 0.6 mol dm^{-3} respectively. To vary [H^+] and [Cl^-], $HClO_4$ and NaCl were used. Increase in [H^+] from 0.13 to 0.60 mol dm^{-3} decreases 10^{-4} k(s^{-1}) from 18.71 to 0.11 for AAH from 25.45 to 0.26 for n-BuAH from 35.85 to 0.40 for n-VAH at 25^0C. Increase in [Cl^-] from 0.13 to 0.60 mol dm^{-3} decreases 10^{-4} k(S^{-1}) from 1.03 to 0.05 for AAH from 2.10 to 0.15 for n-BuAH from 6.10 to 0.28 for n-VAH at 25^0C. The relative permittivity was varied by changing the 1,4-dioxan content from 5 to 40 % v/v. The rate was found to decrease with decrease in relative permittivity.

Added acrylonitrile in the concentration range 0.5 to 2.5vol.% by keeping concentrations of oxidant,reductant,perchloric acid,hydrochloric acid and ionic strength fixed did not produce any precipitate due to polymerization of the added acrylonitrile on the pseudofirst order rate constants indicating absence of free radical .



Michalie's-Menten plot

Since there is no formation of free radicals in the reaction, the reaction proceeds with two-electron transfer step. The order in thallium (III) was found to be unity and the order in hydrazide was found to be fractional. Such fractional order in substrate concentration is due to prior complex formation equilibrium between the reactants.

Tl^{III} + Hydrazide Complex $\rightleftharpoons$ K_c
Complex → Tl^I + Intermediate k_1
Tl^{III}+Intermediate → Tl^I + Products fast

Scheme 1

The Michealis - Menten plots of $1/k_{obs}$ versus 1/[Hydrazide] were linear with an intercept in support of the complex formation. Therefore, in agreement with the results obtained the mechanism of the reaction can be represented as in Scheme 1. Equation 2 gives the rate according to Scheme1. Since, total [Tl^{III}] exists in the form of free [Tl^{III}] and the complex (Equation 3) therefore, the [Tl^{III}] free is given by Equation 6. The overall rate law is now expressed by Equation 7 and the Pseudo-first order rate constant k_{obs}, by Equation 8.

Rate = k_1 [Complex] = k_1K_c $[Hydrazide]_{free}$ $[TI^{III}]_{free}$ (1)

$[TI^{III}]_{total}$ = $[T1^{III}]_{free}$ + [Complex] (2)

$[TI^{III}]$ total = $[T1^{III}]_{free}$ + K_c [Hydrazide] $[TI^{III}]_{free}$ (3)

$[T1^{III}]_{free}$ = $[TI^{III}]_{total}$/(1 + K_c [Hydrazide]) (4)

Rate = k_1K_c [Hydrazide] [TI^{III}]$_{free}$ (5)

$k_{obs} = k_1K_c$ [Hydrazide]/(1 + K_c [Hydrazide]) (6)

Rate law 8 is verified by plotting 1/kobs against 1/[Hydrazide] at four different temperatures and from the slopes and intercepts of these plots the values of k_1 and K_c were calculated and are given in Table 1.

The effect of hydrogen and chloride ion concentrations on the reaction is due to the protonation of hydrazides[11] and different chloro – complexes[12] of thallium (III) present in the solution. in acid medium according to Equation 9. Hydrazides are known to be protonated, therefore, total [Hydrazide] can be expressed by Equation 10 and thereby the fact that there was no effect of free [Hydrazide] by Eq. 12. Since the rates of reaction decreases as the [H^+] increases, free hydrazide is the active species, this is in support of ionic strength on the reactions indicating one of the reactant is neutral.

$RCONHNH_2 + H^+ \rightleftharpoons RCONHNH_3^+$ K_H (07)

$[Hydrazide]_{total} = [Hydrazide]_{free} + [Hydrazide]_{protonated}$ (08)

$[Hydrazide]_{total} = [Hydrazide]_{free} + K_H\,[Hydrazide]_{free}$ (09)

$[Hydrazide]_{free} = [Hydrazide]_{total} /(I+ K_H\,[H^+])$ (10)

Thallium (III) forms strong complexes with chloride ions of the formula $TlCl_n^{3-n}$ where n is the number of chlorides complexes with thallium(III) as represented in equilibrium 13 to 16. The values of respective stability constants[13] are $K_1 = 1.38 X 10^8$, $K_2 = 3.98 X 10^{13}$, $K_3 = 6.02 X 10^{15}$ and $K_4 = 1.0 X 10^{18}$ $mol^{-1}dm^3$.

$T1^{3+} + C1^- \rightleftharpoons TICl^{2+}$ K_1 (11)

$TlCl^{2+} + Cl^- \rightleftharpoons TlCl_2^+$ K_2 (12)

$TlCl_2^+ + Cl^- \rightleftharpoons TlCl_3^+$ K_3 (13)

$TlCl_3 + Cl^- \rightleftharpoons TlCl_4^+$ K_4 (14)

All the thallium(III) will exists as $TlCl_2^+$ and its concentration can be expressed by Equation 17. The $[TlCl_2]^+_{free}$ can now be given by eq. 19 where, $\beta_1 = K_3/K_2 = 151$ and $\beta_2 = K_4/K_3 = 166$, further, using Equations 18 and 19 the concentrations of $[TlCl_2]^+_{free}$, $TlCl_3$ and $TlCl_4^-$ were calculated at different chloride ion concentrations and compared with the change in rate constant as the chloride ion concentration varied.

$[TI\,(III)]_{total} = [T1CI_2^+]_{total} = [T1C1_2^+]_{free} + [T1C1_3] + [T1C1_4]$ (15)

$[T1C1_2^+]_{total} = [T1C1_2^+]_{free}\,(1+\beta_1[Cl^-] + \beta_2[Cl^-]^2)$ (16)

$[T1C1_2^+]_{free} = [T1Cl_2^+]_{total} / (1 + \beta_1\,[Cl^-] + \beta_2[Cl^-]^2)$ (17)

The concentration of both of $[TlCl_2^+]_{free}$ and $TlCl_3$ parallel the values of rate constants as [Cl^-] changes but the order [Cl^-] is – 1.5, which makes $[TlCl_2^+]_{free}$ as the only active species.

$TIC1_2^+ + Hydrazide \rightleftharpoons Complex$ K_c

$Complex \rightarrow RCONHNH + T1C1_2- + H^+$ k_1

$RCONHNH+H_20+T1C1_2^+ \rightarrow RCOOH+N_2+2H^+ + T1C1_2^-$ fast

where R –Alkyl group

Scheme 2

The mechanism considering $TlCl_2^+$ of oxidant and free hydrazide of the substrate as the active species can now be represented by scheme 2 with respective rate law and the expression for the pseudo-first order rate constants by Equations 20 and 21. The rate law 21 was verified by plotting $1/k_{obs}$ against 1/[Hydrazide] and $1/k_{obs}$ against [H^+] which were found to be linear. From the slopes and intercepts of these plots the values of K_c and K_H were determined. The values of K_c are given in Table 1 and those of K_H were found to be 13 and 16 $mol^{-1}\ dm^3$ for heterocyclic acid hydrazides respectively.

$$\text{Rate} = \frac{k_1K_c\ [\text{Hydrazide}]_{total}\ [T1C1_2^+]_{total}}{(1+K_c[\text{Hydrazide}])\ (1+K_H[H^+])\ (1+\beta_1[Cl^-]+\beta_2\ [Cl^-]^2)} \qquad (18)$$

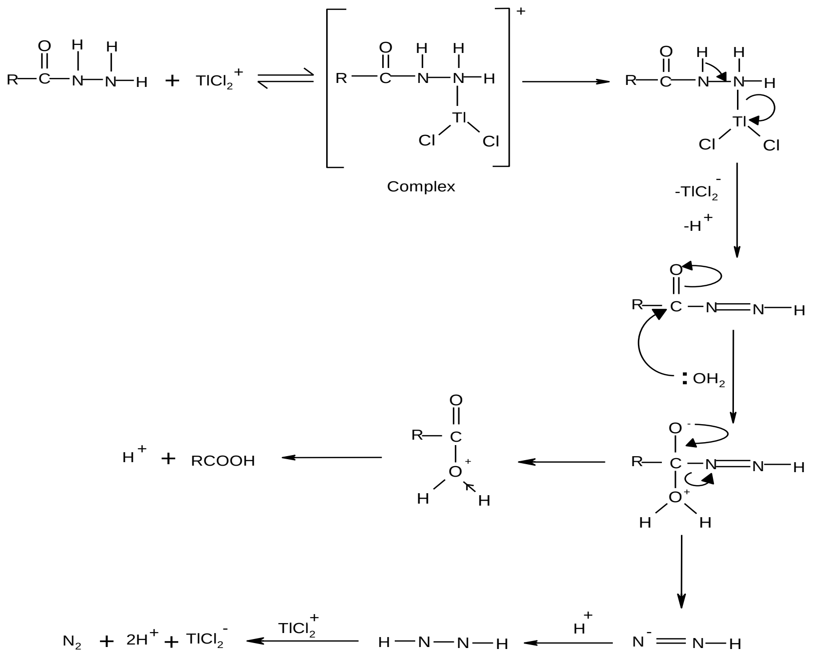
$$k_{obs} = \frac{k_1K_C\ [\text{Hydrazide}]_{total}}{(1+K_c\ [\text{Hydrazide}])\ (1+K_H[H^+])\ (1+\beta_1\ [Cl^-]+\beta_2[Cl^-]^2)} \qquad (19)$$

The electrophilic character of $TlCl_2^+$ among the thallium (III) chlorocomplexes is highest thus making it the reactive species.

Table 1 – values of Kc and k_1 [HCl] = 0.1 $moldm^{-3}$, [$HClO_4$] = 0.1 mol dm^{-3} [Tl^{III}] = 3.0 X 10^{-3} mol dm^{-3}, I = 0.6 mol dm^{-3}

Hydrazide	Kc. (mol dm $^{-3}$)			
	15°C	20°C	25°C	30°C
n-AAH	7.00	6.92	7.23	7.25
n-BuAH	8.35	8.87	8.57	8.45
n-VAH	9.45	9.48	9.48	9.46

IV. MECHANISM



R=Alkyl group for acid hydrazides

Scheme 3

The detailed mechanism involves electrophilic substitution on the nitrogen of the hydrazide with the formation of N-Tl bond, which decomposes in the subsequent step with, direct two-electron transfer from hydrazide to thallium to give an intermediate followed by fast steps. (Scheme 3). Such N-T1 bond formation has been postulated during thallium (III) oxidation of nitrogen[14] containing compounds.

The activation parameters, with respect to slow step, k_1, $\Delta H^{\#}$ (KJ mol^{-1}), $\Delta G^{\#}$ (KJ mol^{-1}) and $\Delta S^{\#}$ ($JK^{-1}mol^{-1}$) were found to be 28.54, 105.16 and -113.50 respectively for AAH, 36.22, 54.16 and -120.45 respectively for n-BuAH, 48.44, 127.16 and -115.50 respectively for n-VAH. Considerable decrease in the entropy of activation is due to formation of more ordered transition state as shown in scheme 3. The mechanism involves neutral hydrazide as the active substrate thus the reaction is unaffected by the change in the ionic strength. The increase in 1,4-dioxan content in the reaction medium decreases; the rate such an effect of the solvent is due to the stabilization of the complex formed between reactants[15] in a medium of low relative permittivity[16-24].

V. CONCLUSION

The order of reactivity of Selected hydrazides under investigation is -

AAH < n-BuAH < n-VAH

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Synthesis of Oxochromenyl Xanthenone and Indolyl Xanthenone Derivatives Using Triazole-Thione Based L-Proline Organocatalyst

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ABSTRACT

A series of novel oxochromenyl xanthenone and indolyl xanthenone derivatives were obtained by one- pot reaction of substituted salicylaldehyde, 4-hydroxy coumarin/indole and dimedone at ambient temperature condition using 1, 2-dihydro-1-phenyl-5-((S)-pyrrolidin-2-yl)-1, 2, 4-triazole-3-thione (DPPTT) as organocatalyst in ethanol solvent. Excellent yields, mild reaction condition, and simple experimental work-up procedure are some of the advantages of this method.

Keywords: Oxochromenyl xanthenone, Indolyl xanthenone, L-Proline, Organocatalyst,

I. INTRODUCTION

Now days, because of environmentally proposition, one-pot multi-component reactions are gaining more significance [1]. MCRs are economically and environmentally very valuable as multi-step synthesis produce considerable amounts of waste mainly due to complex isolation procedures often involving costly, toxic and harmful solvents after each step. Due to these advantages these reactions are perfectly suited for combinatorial laboratory synthesis, and thus are finding increasing use in the discovery process for new drugs and agrochemicals [2]. The synthesis of variety of significant heterocycles could be synthesized by MCRs. One of the advantages of synthesizing heterocycles via MCRs is the great ability of creating molecular complexicity and diversity.

Chromene derivatives are important class of heterocycles, generally used as food additives, cosmetic agents and potential biodegradable agrochemicals and are the chief components of many naturally occurring products [3-5]. Recently, the synthesis of chromene derivatives has more attention due to their biological and pharmacological applications. The chromene derivatives present the various pharmacological properties such as anti-coagulant, anti-cancer [6], diuretic[7], anti-HIV[8], antitumor[9], anti-malarial activities[10], anti-leukemic[11], antibacterial[12], anti-malarial[13] and anti-anaphylactic activities[14]. Moreover chromene derivatives are components of several natural products like calanolides, calanone, calophyllolides[15]. In addition, they can be used as cognitive enhancers for the treatment of neurodegenerative disease, including

Alzheimer's disease, amyotrophic lateral sclerosis, Huntington's diseases, Parkinson's disease, AIDS-associated dementia and Down syndrome as well as for the treatment of schizophrenia and myoclonus[16]. A number of chromene derivatives are valuable as photoactive materials [17]. In previous studies, observed that a chromene derivative has high potency against wild-type HIV-1 replication. DCP8 (3`R, 4`R-Di-O-(-)-camphanoyl-2-ethyl-2`,2`-dimethyldihydro-pyrano [2,3-f]chromone), analogs also showed capable anti-HIV potency against drug-resistant HIV strains. Among previously reported DCP analogs, 2-ethyl DCP (2-EDCP,) and 2, 5-dimethyl DCP exhibited the best anti-HIV activity against both wild type and drug-resistant strains [18-19].

Xanthenes and their derivatives have been received special attention due to their diverse array of biological activities such as anti-inflammatory, antibacterial and antiviral activities. Various methods are found in literature for the synthesis of xanthenes derivatives [20-28].

The most attractive method to produce chiral compounds is catalytic enantioselective processes [29] that gives the compounds with high selectivity and efficiency [30]. In this field, at the end of the last century the use of transition metal catalysts was the preferred option. Nowadays, organocatalysis is used as the metal-free processes [31] and is regarded as an environmentally benign strategy due to the advantages related to handling, cost, and safety issues. Several strategies such as heterogeneous catalysis, Bonsted or Lewis acid base catalysis, homogeneous transition metal acid base catalysis, and biocatalysis are available for enantioselective catalysis. Instead of these, the amino acid Proline is one of the important components for enantioselective catalysis. Proline is the bifunctional molecule with a carboxylic acid and an amine portion. Similar to enzymatic catalysis, proline acts as acids as well as base and can facilitate chemical transformations in concert. Bifunctional asymmetric catalysis has become a very successful strategy in the laboratory [32]. There are the several ways that proline gives different asymmetric transformations, through iminium intermediate, hydrogen bonding formation etc [33]. Now a days, triazole based organocatalyst are mostly used for asymmetric aldol reaction, Mannich reaction and Micheal reaction. Therefore, the triazole-thione based organocatalyst reported in this article provide a new opportunity.

In order to develop a general, practicable and an environmentally benign method for the synthesis of 4H-chromenes, we started a research program on this topic. During our investigation, we viewed that it might be possible to prepare 4H-chromenes through a one-pot three-component reaction of salicylaldehyde, cyclo-1, 3-dicarbonyl compound and a nucleophile. However, in view of the fact that cyclo-1,3-dicarbonyl compounds and nucleophiles are both reactive in the electrophilic alkylation of salicylaldehyde, in order to get the desired three-component adduct, extra effort should be paid to control the reaction selectivity.

Herein, we disclose the successful outcome of this endeavor in which a new class of densely substituted 4H-chromenes was prepared in good to excellent yields via a three-component reaction of salicylaldehyde, 1,3-cyclohexanedione and a suitable nucleophile. In our system, the use of 1, 2-dihydro-1-phenyl-5-((S)-pyrrolidin-2-yl)-1, 2, 4-triazole-3-thione (DPPTT) as organocatalyst is the key for rendering the three-component reactions possible. All the reactions were performed in ethanol under mild and metal-free conditions.

II. EXPERIMENTAL

General details:

All solvents were used as commercial anhydrous grade without further purification. Aluminium sheets 20 x 20cm, Silica gel 60 F_{254}, Merck grade was used for thin layer chromatography to determine progress of reaction.

The column chromatography was carried out over silica gel (80–120 mesh). Optical rotations were measured on a Polax-2L digital polarimeter. Melting points were determined in open capillary tube and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer in $CDCl_3$ solvent. Mass spectra were taken on Polaris-Q Thermoscintific GC-MS. Enantiomeric purity is determined on PerkinElmer Series 200 HPLC Systems with chiral HPLC [Whelk-O1 (25 cm x 4.6 mm), EtOAC /Hexane (20/80), Flow rate 1.0 mL/min, ƛ = 254 nm].

Preparation of (S)-N-(4-Fluorophenyl)-1-tosylpyrrolidine-2-carboxamide (DPPTT):

(S)-tert-butyl 2-(chlorocarbonyl)pyrrolidine-1-carboxylate (10 mmol) is dissolved in anhydrous acetonitrile (30ml), added to a solution of ammonium thiocyanate (10 mmol) and refluxed for 1h. The ammonium chloride is removed by filtration and an acetonitrile solution of henylhydrazine (10mmol) is added. The mixture is heated under reflux for 1h .The mixture was extracted with CH_2Cl_2 (2× 20ml) and the combined organic layer was washed with brine (20ml) dried over $MgSO_4$, and filtered. The solvent was removed under vacuo. The resulting crude product, i.e (S)-tert-butyl 2-(2,5-dihydro-2-phenyl-5-thioxo-1H-1,2,4-triazol-3-yl)pyrrolidine-1-carboxylate was dissolved in CH_2Cl_2 (10 mL) and was added TFA (2 mL) dropwise with stirring for 1h at 0°C. After the consumption of the starting material as indicated by TLC analysis, the reaction mixture was diluted with H_2O (10 mL) and the resulting solution was adjusted to pH= ˜7 with aqueous $NaHCO_3$. The reaction mixture was extracted with CH_2Cl_2 (2 × 20 mL), the combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The purification of residue by column chromatography (EtOAC/ hexane, 1:1) afforded 80-85% of 59 as yellow solid.

Enantiomeric purity is determined on PerkinElmer Series 200 HPLC Systems with chiral HPLC [Whelk-O1 (25 cm x 4.6 mm), EtOAC /Hexane (20/80), Flow rate 1.0 mL/min, ƛ = 254 nm].

Characterization data for organocatalyst 1, 2-dihydro-1-phenyl-5-((S)-pyrrolidin-2-yl)-1, 2, 4-triazole-3-thione (DPPTT): Yellowish Solid **M.P. (°C):** 160-162°C.

Optical rotation $[\alpha]^{20}_D$ **:** -80.7 (c 0.42, $CHCl_3$). **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.70 (s, 1H, NH), 7.20-7.61(m, 5H), 3.12 (s, 1H), 2.5 (s, 1H), 1.5-1.9 (m, 6H). **^{13}C-NMR (300 MHz, $CDCl_3$):** δ 187.56, 165.78, 140.08, 130.00, 120.03, 114.12, 58.03, 47.01, 28.45, 23.01.

GC-MS: *m/z* 246 (M+).**Elemental Analysis:** Anal. Calcd for $C_{12}H_{14}N_4S$: C, 58.51; H, 5.73; N, 22.74; S, 13.02 Found C, 58.24; H, 5.35; N, 22.50; S, 12.90. **HPLC:** 99.80 % *ee*. Enantiomeric purity is determined by chiral HPLC Systems using chiral column Whelk-O1 (25 cm x 4.6 mm), EtOAc / Hexane (80/20), Flow rate 1.0 mL /min, ƛ = 254; t_R (minor) = 10.5 min, t_R (major) = 17.8 min].

Typical procedure for synthesis of Oxochromenylxanthenone and Indolyl xanthenone derivatives (9a-9r): To a mixture of salicylaldehyde (1mmol), dimedone (1.0 mmol) and (S)-N-(4-Fluorophenyl)-1-tosylpyrrolidine-2-carboxamide (DPPTT) (0.1 mmol) in solvent ethanol (5 ml), 4-hydorxy coumarin /indole (1mmol) was added. The reaction mixture was vigorously stirred at 60°C for 30-90 minutes (monitored by TLC). Then white crystals were appeared. It was filtered washed with ethanol then with water to afford analytically pure product.

5,7-dibromo-3,4-dihydro-9-(4-hydroxy-2-oxo-2H-chromen-3-yl)-3,3-dimethyl-2H-xanthen-1(9H)-one (9c): White solid, **M.P. 252°C. IR (cm^{-1}):** 3417, 2953, 2870, 1672, 1622, 1565, 1499, 1451, 1335, 1236, 1172, 763, 457. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 1.06 (s, 3H), 1.16 (s, 3H), 2.38 (d, 2H), 2.64 (q, 2H), 5.00 (s, 1H) 7.09 (d, 1H), 7.21(d,1H), 7.30 (m, 1H), 7.48(m, 1H), 7.57(d,1H), 8.00(q, 1H), 10.85(s, 1H); **^{13}C-NMR (300 MHz, $CDCl_3$):** δ 27.22, 29.06, 29.37, 32.53, 41.44, 50.03, 108.49, 110.15, 111.30, 116.50, 116.98, 117.28, 124.04, 124.48, 126.02, 130.41, 132.14, 134.51, 147.79, 153.24, 161.24, 161.46, 169.54, 201.43; **MS:** *m/z* 546.6 (M^+). **Elemental Analysis:** $C_{24}H_{18}Br_2O_5$: C, 52.77; H, 3.32; Found C, 52.75; H, 3.34.

3,4-dihydro-9-(4-hydroxy-2-oxo-2H-chromen-3-yl)-3,3-dimethyl-7-nitro-2H-xanthen-1(9H)-one (9h): White solid, **M.P.239°C. IR (cm^{1}):** 3418, 2942, 2878, 2071, 1674, 1621, 1572, 1522, 1488, 1455, 1387, 1339, 1234, 1156, 750, 440.**^{1}H NMR (300 MHz, $CDCl_3$):** δ 1.04 (s, 3H), 1.15 (s,3H), 2.40 (q, 2H), 2.61 (q, 2H), 5.06 (s, 1H), 7.18 (d, 2H), 7.30 (t, 1H),7.51(m, 1H),7.95(d, 1H), 8.04 (q, 1H), 8.08 (q, 1H), 10.84 (s, 1H). **^{13}C-NMR (300 MHz, $CDCl_3$):** δ , 201.44, 169.56, 161.43, 160.23, 152.25,148.74, 133.50, 131.31, 130.43, 124.58, 124.31, 124.20, 117.28, 116.98, 116.50, 110.41, 110.17, 106.51, 51.03, 42.50, 32.58 ,29.30, 28.71, 27.31. **MS:** *m/z* 432.1 (M^+). **Elemental Analysis:** C, 66.51; H, 4.42; N, 3.23; Found C, 66.50; H, 4.44; N, 3.20.

5, 7-dibromo-3,4-dihydro-9-(1H-indol-3-yl)-3,3-dimethyl-2H-xanthen-1(9H)-one (9l):

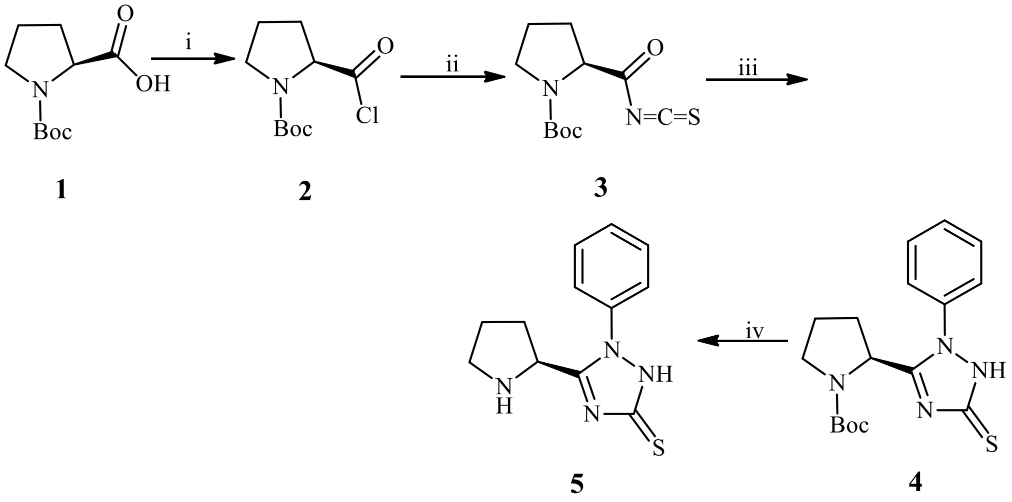
White solid, **M. P. 227°C. IR (cm^{-1}):** 3416, 3071, 2970, 2920, 2866, 2036, 1637, 1621, 1556, 1452, 1376, 1232, 1202, 1165, 742, 622, 426. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 0.97 (s, 3H), 1.14 (s,3H), 2.22 (q,2H), 2.65 (q,2H), 5.21 (s,1H), 7.01 (t,1H), 7.10 (t,1H), 7.12(d,1H), 7.15 (s,1H), 7.25 (d,1H), 7.34(d,1H), 7.50(d,1H),8.08(s,1H). **^{13}C-NMR (300 MHz, $CDCl_3$):** δ 195.96, 163.82, 144.94, 135.64, 133.70, 132.14, 128.85, 125.48, 122.70, 122.11, 119.81, 119.53, 118.64, 117.21, 111.81, 110.51, 50.94, 41.28, 31.21, 30.21, 28.25, 26.66.

MS: *m/z* 520.93 (M^+), 523(M^++2). **Elemental Analysis:** $C_{23}H_{19}Br_2NO_2$; C, 55.12, H, 3.82; N, 2.79; Found C, 55.11; H, 3.80; N, 2.78.

III. RESULT AND DISCUSSION

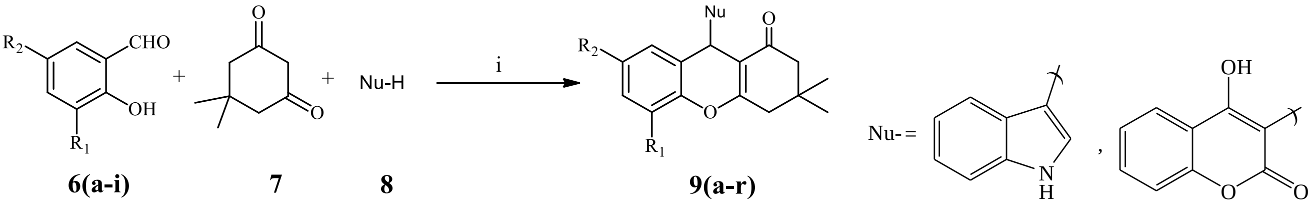
Synthesis of 1, 2-dihydro-1-phenyl-5-((S)-pyrrolidin-2-yl)-1, 2, 4-triazole-3-thione (DPPTT):

The synthesis of organocatalysts 1, 2-dihydro-1-phenyl-5-((S)-pyrrolidin-2-yl)-1, 2, 4-triazole-3-thione (DPPTT) **5** began with (S)-tert-butyl 2-carbonylpyrrolidine-1-carboxylate **3**, which was readily prepared from the Boc-protected L-proline **1**. The precursor Boc-protected L-proline **1** was converted in to the (S)-tert-butyl 2-(chlorocarbonyl)pyrrolidine-1-carboxylate **2** using thionyl chloride as chlorinating reagent and was treated with ammonium thiocyanate to afford (S)-tert-butyl 2-carbonylpyrrolidine-1-carboxylate**3**.(S)-tert-butyl2-(2,5-dihydro-2-phenyl-5-thioxo-1H-1,2,4-triazol-3-yl)pyrrolidine-1-carboxylate **4** was obtained in one step reaction from (S)-tert-butyl 2-carbonylpyrrolidine-1-carboxylate **3** and phenyl hydrazine. The boc-protected compounds was deprotected in CH_2Cl_2 using TFA to obtained 1, 2-dihydro-1-phenyl-5-((S)-pyrrolidin-2-yl)-1, 2, 4-triazole-3-thione (DPPTT) with overall 70-85% yield.



Scheme 1. *Reaction conditions*: i) $SOCl_2$, $C_2H_4Cl_2$, reflux, 3hrs; ii) NH_4SCN, acetonitrile , reflux, 1hr; iii) $C_6H_5NHNH_2$, CH_3CN, reflux,1hr; iv) MDC, TFA, Stirr, 1hr, 70-85%

The synthesis of organocatalysts **5** began with (S)-tert-butyl 2-carbonylpyrrolidine-1-carboxylate **3**, which was readily prepared from the Boc-protected L-proline **1**. The precursor Boc-protected L-proline **1** was converted in to the (S)-tert-butyl 2-(chlorocarbonyl)pyrrolidine-1-carboxylate **2** using thionyl chloride as chlorinating reagent and was treated with ammonium thiocyanate to afford (S)-tert-butyl 2-carbonylpyrrolidine-1-carboxylate **3**.



Scheme 2: Synthesis of Oxochromenyl xanthenone and Indolyl xanthenone derivatives[a] i) DPPTT, EtOH, stir, 60°C.

Synthesis of Oxochromenyl xanthenone and Indolyl xanthenone derivatives: Initially, in search of an effective catalyst, various catalysts were tested as catalysts using the reaction of 2-hydroxycoumarine, 3,5dibromosalicylaldehyde and dimedone as model reaction. A summary of the experiment optimization is provided in Table 1. It was found that was the 1, 2-dihydro-1-phenyl-5-((S)-pyrrolidin-2-yl)-1, 2, 4-triazole-3-thione (DPPTT) most efficient catalyst compared with $SnCl_4$, $InCl_3$, DMAP and *L*-Proline, which exhibited from moderate to poor catalytic properties. We used both *L*-Proline and triazole-thione based L-proline derived catalyst but out of these two organocatalyst triazole-thione based L-proline organocatalyst was more effective than L-proline. The effect of the amount of catalyst was examined in this reaction. The results showed that a 10% mol amount 1, 2-dihydro-1-phenyl-5-((S)-pyrrolidin-2-yl)-1, 2, 4-triazole-3-thione (DPPTT) was sufficient to promote the reaction and larger amounts of the catalyst did not lead to any significant changes in the reaction yield. Also we studied the model reaction catalyzed 1, 2-dihydro-1-phenyl-5-((S)-pyrrolidin-2-yl)-1, 2, 4-triazole-3-thione (DPPTT) in different solvent. The yields increased as the solvent was EtOH. When reaction was carried out in EtOH at 60°C, the good yield could be obtained in a short time. The reaction was also carried out at room temperature and above 60 °C, but the yield and time of the expected product was not further improved at this temperature. Thus, based on an overall consideration, 60°C should be reasonable choice. Finally, it should be mentioned that when the reactions were carried out without catalyst, almost no conversion occurred.

Table 1: Optimization condition for the synthesis of 5,7-dibromo-3,4-dihydro-9-(4-hydroxy-2-oxo-2H-chromen-3-yl)-3,3-dimethyl-2H-xanthen-1(9H)-one [a]

Catalyst	Solvent	Catalyst loading (mol %)	Time (min)	Yield %
-	EtOH	-	-	NR
$SnCl_2$	EtOH	10	192	45
$SnCl_2$	Toluene	10	211	40
L-Proline	EtOH	10	165	75
L-Proline	Toluene	10	198	65
$InCl_3$	EtOH	10	210	71
$InCl_3$	Toluene	10	205	65

DMAP	Toluene	10	250	38
DMAP	EtOH	10	230	10
DPPTT	**EtOH**	**10**	**50**	**95**
DPPTT	DCM	10	75	55
DPPTT	Toluene	10	80	68
DPPTT	EtOH	5	52	70
DPPTT	EtOH	15	40	85
DPPTT	EtOH	20	45	88

[a] 3,5-Dibromo salicylaldehyde (1 mmol), dimedone (1.0 mmol), Solvent (5 mL), 4-hydorxy coumarin (1mmol) at 50 °C.

With this optimized procedure in hand, a range of 2, 3, 4, 4a, 9, 9a hexahydro-9-(4hydroxy-2-oxo-2H-chromen-3-yl)-3,3-dimethylxanthen-1-one were synthesized by the one-pot condensation of substituted salicylaldehyde ,4-hydroxy coumarin and dimedone under eco-friendly condition. The reaction preceded about 30-90 min in excellent yields at 60°C after the addition of the catalyst 1, 2-dihydro-1-phenyl-5-((S)-pyrrolidin-2-yl)-1, 2, 4-triazole-3-thione (DPPTT) (see Table2).

Table 2. Exploration of the substrate scope for the synthesis of oxochromenyl xanthenone and Indolyl xanthenone derivatives[a]

Entry	Nu H	R_1	R_2	Time (min)	Product	M.P. (°c)	Yield %
1	4-Hydroxy Coumarin	H	H	45	9a	235	86
2	4-Hydroxy Coumarin	H	Br	42	9b	240	88
3	4-Hydroxy Coumarin	Br	Br	35	9c	252	95
4	4-Hydroxy Coumarin	I	Br	40	9d	248	88
5	4-Hydroxy Coumarin	H	Cl	38	9e	239	90
6	4-Hydroxy Coumarin	I	Cl	45	9f	246	89
7	4-Hydroxy Coumarin	I	I	40	9g	256	86
8	4-Hydroxy Coumarin	H	NO_2	43	9h	239	85
9	4-Hydroxy Coumarin	H	OCH_3	55	9i	243	88
10	Indole	H	H	45	9j	221	84
11	Indole	H	Br	43	9k	224	83
12	Indole	Br	Br	40	9l	227	90

13	Indole	I	Br	42	9m	231	86
14	Indole	H	Cl	52	9n	229	84
15	Indole	I	Cl	48	9o	234	89
16	Indole	I	I	50	9p	239	85
17	Indole	H	NO_2	54	9q	223	87
18	Indole	H	OCH_3	56	9r	213	80

[a] Substituted saliycylaldehyde (1 mmol), dimedone (1.0 mmol), EtOH (5 mL), 4-hydorxy coumarin/Indole (1mmol) at room temperature.

4-hydroxychromenes are an important class of carbon-based nucleophiles. In view of the fact that a 4-hydroxy chromenes fragment is found in many biologically active compounds. We therefore investigated the feasibility of using 4-hydroxy chromenes as a nucleophile to react with salicylaldehyde and dimedone. As shown in Scheme 1, the multi-component reaction of 4-hydroxy chromenes proceeded very well, and importantly, it displayed very good substrate compatibility. 4-hydroxy chromenes, cyclo-1,3-hexanediones or salicylaldehyde containing various substituents could all be successfully used in this reaction, producing the corresponding products in good to excellent yields. It should be noted that the products in the reactions of 4-hydroxy chromenes could be easily isolated without the use of silica column chromatography.

All reactants dissolved well in ethanol in the beginning of the reaction. As the reaction progressed, some insoluble species were gradually precipitated out, and at the end of the reaction, a large amount of solid accumulated in the bottom of the vessel. As a result of this behavior, all the products (9a-9r) could be obtained by filtration. This procedure imbues the synthetic methodology with green credentials. With these results in hand, we examined the possibility of synthesizing xanthenes via this method. Other nucleophiles, such as indole could also be successfully employed to react with substituted salicylaldehyde and dimedone.

Various substituted salicylaldehydes with the both electron donating and withdrawing groups have been used. The electron donating group on salicyaldehydes resulted in excellent yields. However, good yields are obtained for salicylaldehyde with electron withdrawing groups (Table 2). Therefore, the method in Scheme 1 not only expands the synthetic capacity of the three-component reaction, but also opens an effective way for accessing some valuable compounds.

IV. CONCLUSION

In conclusion, An expeditious and forceful method has been devised for the synthesis of highly functionalized 2,3,4,4a,9,9a-hexahydro-9-(4-hydroxy-2-oxo-2H-chromen-3-yl)-3,3-dimethyl-xanthen-1-one and 2,3,4,4a,9,9a-hexahydro-9-(1H-indol-3-yl)-3,3-dimethylxanthen -1-one. The newly developed method expanded the scope of the tandem Knoevenagel–Michael reaction. The organocatalyst such as DPPTT are an excellent catalyst for the preparation of 2,3,4,4a,9,9a-hexahydro-9-(4-hydroxy-2-oxo-2H-chromen-3-yl)-3,3-dimethyl-xanthen-1-one and 2,3,4,4a,9,9a-hexahydro-9-(1H-indol-3-yl)-3,3-dimethylxanthen -1-one. Extensive studies are required to fully explore the potential of organocatalyst in synthetic organic chemistry.

To the best of our knowledge, DPPTT was used in multi-component reactions for the first time, and this is the first report on the synthesis of 2,3,4,4a,9,9a-hexahydro-9-(4-hydroxy-2-oxo-2H-chromen-3-yl)-3,3-dimethylxanthen-1-one and 2,3,4,4a , 9,9a-hexahydro-9-(1H-indol-3-yl)-3,3-dimethylxanthen-1-one.

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Application of Carboxylic Acid in Organic Synthesis of Nano Technology

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ABSTRACT

Carboxylic acid are versatile organic compounds carboxylic acid in a different area as organic synthesis nanotechnology. The application Carboxylic acid in these areas are obtained of small molecules macro molecules synthetic modifications surface of nanoparticles metallic modification surface of nanostructure such as carbon nanotubes and graphene, nanomaterials, medical field pharmacy etc. Carboxylic acid can be natural and synthetic can be extracted present chemical structure highly polar active in organic reaction, substitution, elimination, oxidation, coupling etc. In nanotechnology the use of acid Carboxylic as surface modifier to promote the dispersion and incorporation of metallic nanoparticles the importance of Carboxylic acid in different area highlighting the area of organic synthetic nanotechnology its application

I. INTRODUCTION

Carboxylic acids are compounds with excellent chemical and physical properties. The most particular characteristics of this type of organic compounds is high solubility in polar solvent as water or alcohol, methanol, ethanol etc chemical structure contains a Carboxylic functions(>C=O) as a hydroxy group(OH).These groups interact easily with polar compounds the carbonyl group(>C=O) is considered one of the most functional group involved in many important reaction this type of organic compounds can be obtained by different routes, Carboxylic acids , citric acid, lactic acid or fumaric acid are produced formed by fermentation, most of this type of Carboxylic acids are applied in the food industries. Carboxylic acids are different synthetic reactions such as reaction of oxidation from alcohol in this the presence of strong oxidants such $KMNO_4$ oxidation of aromatic compounds.[1]

Derivatives of Carboxylic acids, as alkali halides, Ester and amide present different and important application in diverse area. the reaction between Carboxylic acids and alcohol in presence of an acid catalyst H_2SO_4 with heat, this type of reaction is known as Esterification. In the in the case of amides, it is obtained in the presence of amines may be primary and secondary with Carboxylic acids in this reaction also can be used catalyst and heat to accelerate the reaction. Their chemical and physical characteristics this type of organic compounds present in numerical applications in the different areas medicine, pharmacy, organometallic, food among other. To study Carboxylic acids in the area organic synthesis in 2008 Lazzarato.et al, reported the use of Carboxylic acids, salicylic acid type of aspirin like molecules obtained through a novel approach, where phenol reactions to Nitro oxy-acyl these molecule present pharmaceutical properties [2].

II. ORGANIC SYNTHESIS

The use of Carboxylic acids in organic synthesis is very wide area and the chemical transformation of this type to other have made it very versatile functional group. this chemical transformation have seen improvement when they carry out through green chemistry process. These methods to aim for energy efficiency to make reaction under microwave irradiation this methology was an esterification reaction with Carboxylic acids and alcohol obtaining high yield in the short reaction [3]. new direct amidation reaction is important [4,5] one of those direct methodology of amide formation is by reaction amides with the Carboxylic acids using toluene solvent Radio frequency heating under neat conditions [6]. these reagents free pathway has limitation in the substance scope. Lonigon et.al reported the metrology in which they used the simple borate Ester that are different reagents for the direct synthesis of amide using a variety of Carboxylic acids and amides [7]. this reaction can be carried out openly to the air under acetonitrile flux. the amidation products can be purified in very simple way in the most cases, it only needs simple filtration procedure using commercial availability resins giving excellent yield [fig.1]

Ojeda-parras et al [8] describe a green methodology from direct amidation of Carboxylic acids and amines using silica gel as a solid support [fig.2] An example is the reaction between an oxazolidine an isocyanide and a Carboxylic acid to provide N-acyl oxy ethyl amino acid derivatives [fig.3][09] it can be completed with those structures that are produced by the will established a reaction and they allow the generation of chemicals Carboxylic acids can be used in organocatalytic reactions in this case Carboxylic acid can be used directly to obtain the alpha hydroxy phosphonates the reaction was carried out in the simple way with a variety of aldehydes and ketones with a trimethyl phosphate in the presence of catalytic amount of pyridine 2,6-di Carboxylic acid in water as a solvent these generated a low cost and environmentally friendly methodology [fig.4][10]

Carboxylic acid present important applications on in the pharmaceutical area due to their chemical structure different methods have been developed for their detection in medicine in cosmetics in food additives. in 2015 Soham et al reported a selective chromogenic system which not only can discriminate Maleic acid vs fumaric acid but can also differentiate maleic acid among diverse Carboxylic acid the detection of this type of organic acid is very important

III. NANO TECHNOLOGY

Carboxylic acid have been extensively due to their important application in petrochemical, food industries, dyes stabilizer and currently on nanotechnology[11] one of the most important application today of the Carboxylic acid is the surface modification of the nano part particles, this because during this synthesis of the nanoparticles by any methodology this tends to agglomerate due to the Vander walls forces and the absence of repulsive forces in this sense in 2008 yong et al obtained nanoparticles of Fe_3O_4 with a of 6-13 nm using olic acid as a surfactant this group of researchers functionalized the nanoparticles with Carboxylic acids obtaining acid catalyst for the hydrolysis of carbohydrates being able to observe that the acid functionalization can have large advantages in producing more active catalyst and thus an application in green process[12]

Hojjati et.al modifier TiO_2 nanoparticles with carboxylic acid followed by edition with acrylic acid to obtain a well dispersed nanoparticle in polyacrylic acid [13] the chemical modification of nanoparticles TiO_2 with Carboxylic acid by the thermal methods finding improvement in the photovoltaic performance of the TiO_2 nanoparticle despite being coated with carboxylic acid[14]

In other studies it has been shown that this use of carboxylic acid as a surface modifier of nanoparticles can be easily we redispersed in diverse matrix also or solvent and improves properties as antibacterial activity[15] in recent years inorganic nanoparticles have been widely studied due to the excellent properties that they provide due to their large surface area emphasizing applications such as optical, catalytic, electrical sensing, transport, magnetic, thermal conductivity, electromagnetic these properties are the result of the large surface area that they possess metals such as gold, silver, palladium and copper have been used to make inorganic nanoparticles of various shapes and size. A wide variety of methods have been developed to synthesize metallic nanoparticles with different method chemical method, physical and biological methods.

chemical methods are the most used, due to their ease of climbing [16] the chemical reduction of metal salts in the solution the most commonly used method [17]. In aqueous the reducing agent is added or generated among the most commonly used reducing agents or sodium borohydride, hydrazine and dimethyl formamide, however in the recent years monotoxic and equally effective substances have been used sodium citrate and glucose[18] non-aqueous system, the solvent can also act as a reducing agent such solvent can be alcohols such as a polyethylene glycol, glycerol and ethylene glycol through which colloidal nanoparticles obtained. physical methods included electrochemical method laser ablation, thermolysis, microwave irradiations and Sonochemistry for example the decomposition of solid at a high temperature through this process it is a possible to obtain particles smaller than 5nm.biological methods are developed using a metal salt and a reducing agent, which may be micro-organism enzyme or plant extract [19]

The nanoparticles can also be functionalized with the organic molecules with the biological functions example lipids, vitamins, peptides and sugars in addition to their other macromolecules such as the proteins, enzymes, DNA and RNA the combinations of inorganic nano particles and biomolecules allows the use of these in biological system because they combine unique properties for applications such as molecular recognition [20]. organic molecules such as acrylic acid, pyrrole and styrene have been used in a plasma to modify nanoparticles of zinc oxide, alumina and carbon nanofibers by this process it is possible to form a thin layer ranging from 1 to 3 nm in thickness silver nanoparticles are recognized with antifungal and antibacterial properties and have application in biosensing antiviral agents HIV-I, in water purification system and paint products. In case Au nanoparticles these are used in cancer diagnosis and therapy, antiviral and antibacterial MRI, biosensing application.

carboxylic acids are currently used as a surface modifiers in carbon based nanostructure, carbon nanotube, single wall and multiple wall graphene, nano fibres etc this type of superficial modification can be carried out through different alternative making use of green chemistry which recommend the use of sustainable activation energies such as ultrasound, microwaves, plasma, that helps to reduce the energy consumption and decrease the time of reaction in the surface modification.

IV. CONCLUSION

The carboxylic acid have been widely applied in different areas highlighting organic synthesis nanotechnology have been used basic application anti relevant application in organic synthesis, carboxylic acid can act as organic substrate reagent in the reaction one step which are considered green reaction are used as a catalyst in substitution, addition, condensation, polymerization reaction. organic synthesis is directed towards green reactions easy fast economical, sustainable process. the carboxylic acids highly reactive due to the chemical nature of carbonyl group.

In nanotechnology the carboxylic acids are used as modifier substrate in the surface modification of the nanostructure of carbon. the chemical nature of the carboxylic acid allows to carry out this type of application of the carboxylic acids is due to nature chemical, specifically by hydrophilic characteristic provided by the functional group. The research on the carboxylic acids, is very interesting described some recent report. there are still challenges with in this field that remain to explored.

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A Review Synthesis and Biological Activity of Thiazolyl Derivatives

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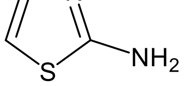
ABSTRACT

1,3-Thiazole is one of the most important scaffolds in heterocyclic chemistry and drug design and discovery. It is widely found in diverse pharmacologically active substances and in some naturally-occurring compounds. Thiazole is a versatile building-block for lead generation, and is easily access of diverse derivatives for subsequent lead optimization. In the recent years, many thiazole derivatives have been synthesized and subjected to varied biological activities. In this article we intended to review the most important biological effects of thiazole-based compounds and highlight their roles in new leads identification and drug discovery. This article is also intended to help researches for finding potential future directions on the development of more potent and specific analogs of thiazole-based compounds for various biological targets.

I. INTRODUCTION

Thiazole is of five-membered heterocyclic compounds having molecular formula C_3H_3NS with sulphar and nitrogen set at 1 and 3 position, it is also known as 1,3 thiazole. It is a clear to pale yellow flammable liquid with a pyridine like odour. Thiazole is aromatic compound, confirmed on the basis of delocalization of a lone pair of electrons from the sulfur atom completing the needed 6 π electrons to satisfy Huckel's rule. It is found in many natural and synthetic agents. Naturally, thiazole is available in a large number of terrestrial and marine compounds with different pharmacological activities. Thiazole is also present in the vitamin B1 (Thiamine). In synthetic substituted thiazole derivatives, 2-aminothiazoles have shown a variety of biological activities and found as main constituents of various synthetic medicines. Thus, thiazole is an entity of great interest, and the synthesis of its derivatives from long-past and recent years has received the attention of synthetic and medicinal chemists to develop new derivatives and explore their biological and pharmacological potentials. Historically, thiazoles were first synthesized from condensation of haloketones and thiourea or thioamides in refluxing alcohol by Hantzch in 1887 [1].



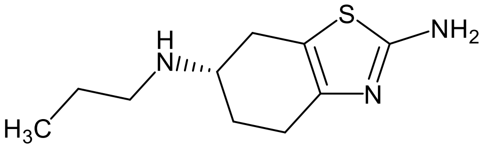
2-Amino thiazole

Because of its wide application in medicinal chemistry. 2-amino thiazoles have created great interest among the researcher worldwide. A literature survey revealed several useful methods for the synthesis of 2-amino thiazoles by using various catalyst, methods and environmentally benign chemical procedure. In addition, this review outlines and discusses data regarding the biological activities of these heterocycles to make it more useful for medicinal chemists, pharmacists, and pharmacologists.

Importance of 2-Aminothiazole

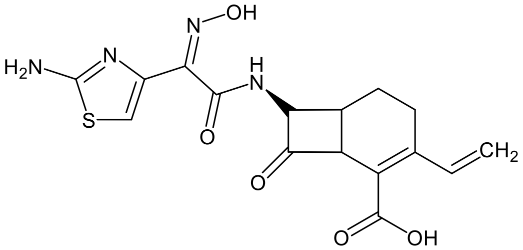
2-aminothiazoles have shown a variety of biological activities such as antibacterial, antifungal, antitubercular, anti-HIV, anti-inflammatory, anticancer, anticonvulsant, antidiabetic,antihypertensive, antiprotozoal, dopaminergic, plasminogen activator inhibitor-1, neuroprotective and antioxidant. This broad spectrum of activities makes 2-aminothiazole as an attractive moiety in medicinal chemistry.

There are various well known drugs which containing 2-aminothiazole moiety. Such as, Pramipexole which is used for the treatment of Parkinson's disease, restless legs syndrome and sometimes used in clusterheadache. [2]



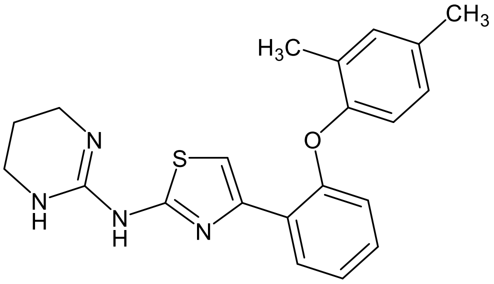
Pramipexole

Cefdinir is a third generation broad spectrum cephalosporin antibiotic used to treat some bacterial infections such as pneumonia, chronic bronchitis, sinusitis, pharyngitis, tonsillitis and some skin infections.[3]



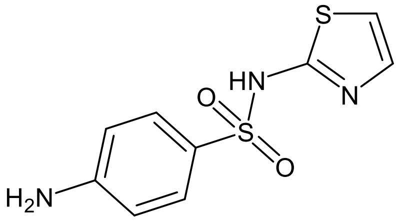
Cefdinir

Abafungin is an antimicrobial agent used for the treatment of dermatomycoses. It prevents the conversion oflanosterol to ergosterol [4]



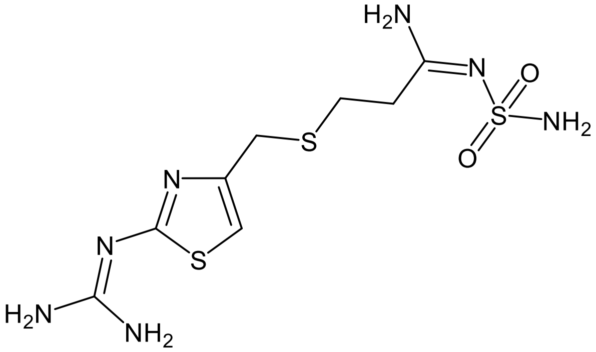
Abafungin

Sulfathiazole is a sulpha drug used as an antimicrobial agent. It acts by inhibition of folic acid synthesis in prokaryotes. Now-a-days it is used in combination with sulfabenzamide and sulfacetamide to treat vaginal infections. [3,5]



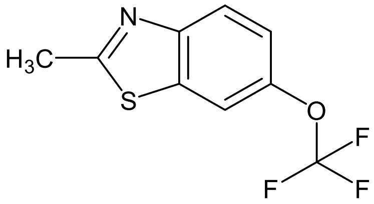
Sulfathiazole

Famotidine is a H_2-receptor antagonist used in the treatment of peptic ulcer disease and gastroesophageal reflux disease. It acts by inhibition of stomach acid production.[6]



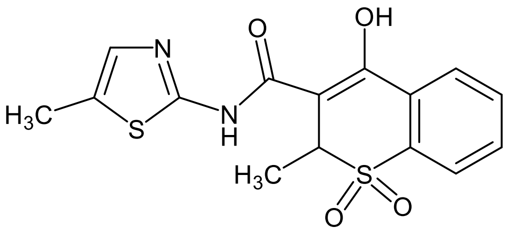
Famotidine

Riluzole is used as an anticonvulsant drug. The mechanism of action of Riluzole is still unknown but it is considered that it indirectly prevents glutamate receptor activation [2]



Riluzole

Meloxicam is a nonsteroidal anti-inflammatory drug (NSAID) used in arthritis, dysmenorrhea and fever. [2]

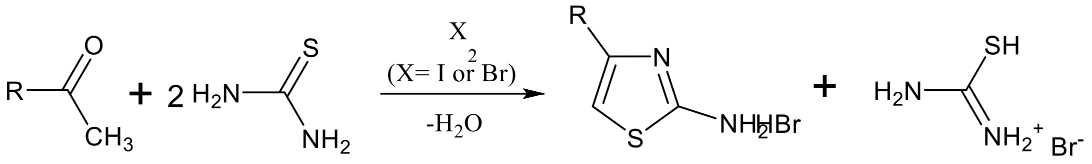


Meloxicam

Synthesis of 2-Amino-4-substituted Thiazole

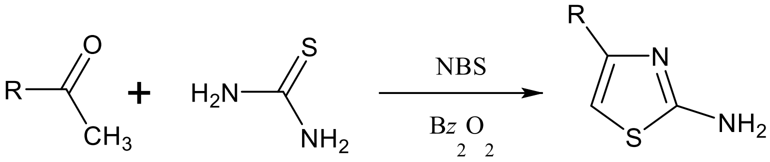
1) Dodson R.M. et al [7]

Dodson R.M. et al reported Methyl Ketones reaction with thiourea and halogen to give 2- Amino thiazole in excellent yield.



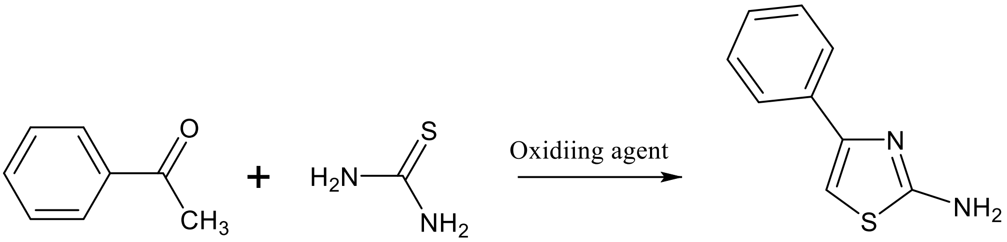
2) Dahiya R. et al [8]

Dahiya R. and his co-workers have reported the synthesis of 2-amino 4-substituted thiazole by condensation of methyl ketone and thiourea using N-bromosuccinamide (NBS) and Benzoyl peroxide as a initiator.



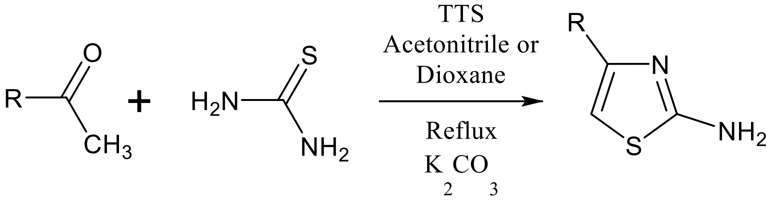
3) Dodson R.M. and King, L. C.[9]

Dodson R.M. and King, L. C. *et al* Formation of 2-aminothiazoles from acetophenone and thiourea by using various oxidizing agent such sulfuryl chloride, chlorosulfonic acid, thionyl chloride, sulfur monochloride,sulfur trioxide, sulfuric acid, nitric acid and sulfur.



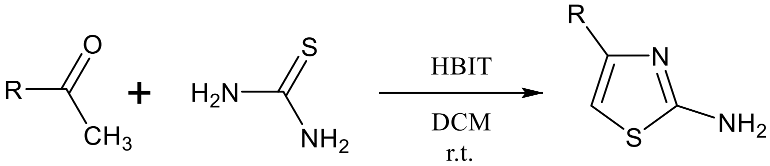
4) Rao, V. R. et al [10]

Methyl Ketones on oxidation with thallium(III)-*p*-tosylsulfonate (TTS) in refluxing acetonitrile or dioxane followed by additional refluxing of the reaction mixture with thiourea yielded 2-amino-4-substituted-thiazoles as *p*-toluenesulfonates salt which on basification with pottasium carbonate gives 2-amino 4-substituted thiazole.



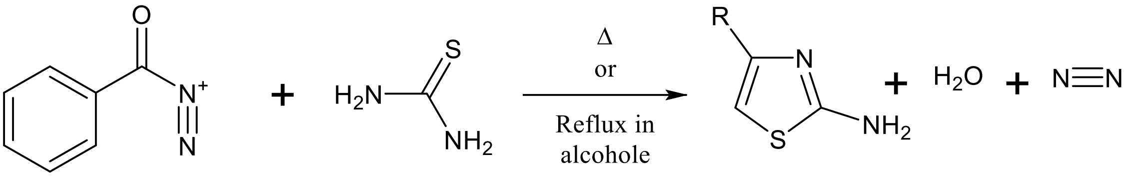
5) Singh, S. P et al [11]

A facile and eco-friendly synthesis of 2-amino4-substituted thiazole by the condensation of methyl ketone with thiourea in presence of [hydroxyl-(tosyloxy)-iodo]benzene(HTIB) in dichloromethane at room temperature gives excellent yield.



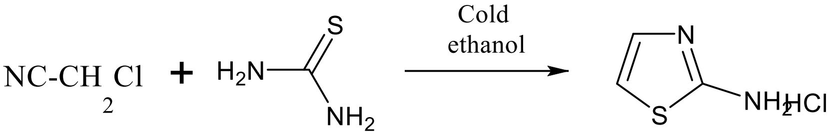
6) King, L. C. et al [12]

Diazoacetophenone on heating or refluxing in alcoholic solution with thiourea gives 2-amino-4-phenyl thiazole.



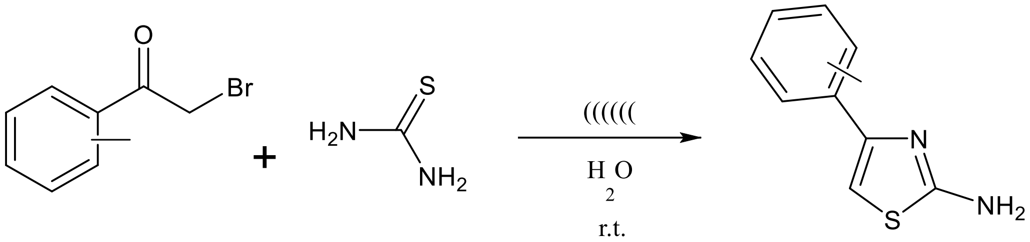
7) Gewald, K. et al [13]

The condensation of thiourea and halogeno-nitriles in cold ethanol to form hydrochloride salt of 2-amino thiazole.



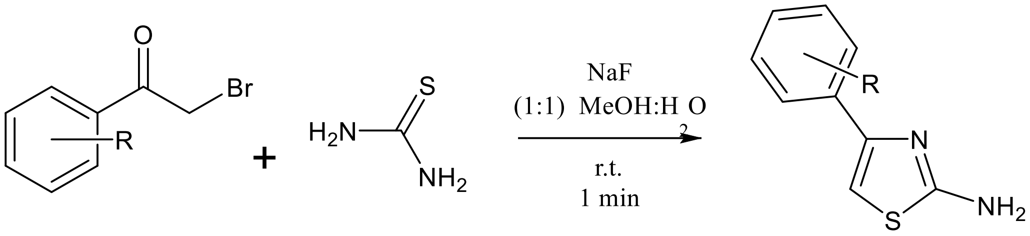
8) Ramesh, Gondru et al [14]

This method reports an efficient synthesis of 2-amino 4-substituted thiazole via condensation of α-halo ketone and thiourea in aqueous medium under ultrasonic irradiation. This method gives an excellent yield (98%) within short reaction time of 10s and aqueous medium explain the green approach of methodology.



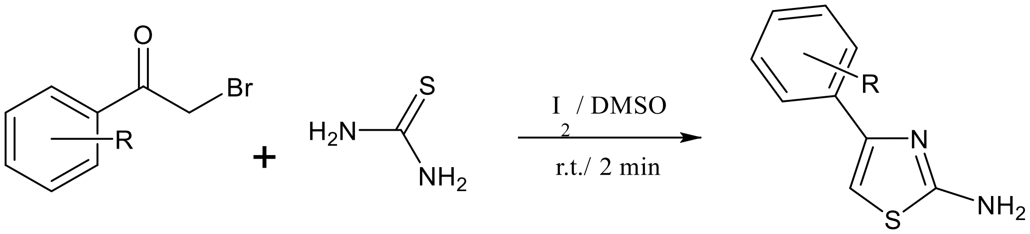
9) Banothu, Janardhan et al [15]

Condensation of α-halo ketone and thiourea by using sodium fluoride as a catalyst in (1:1) methanol water as solvent at ambient temperature gave 2-amino 4-substituted 1,3 thiazole in excellent yield (98%) within short reaction time of 1 min.



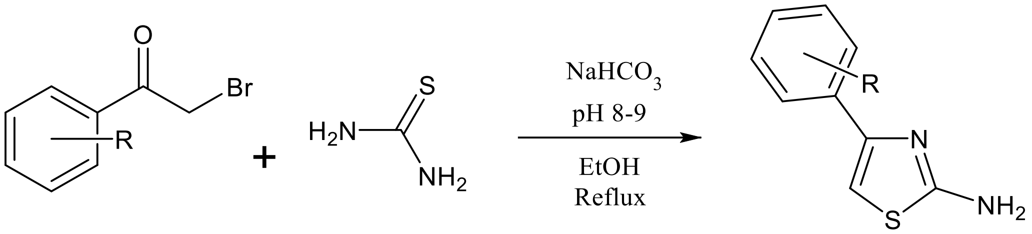
10) Kottawar, Shrinivas S. et al [16]

Remarkebaly fast and mild conversion of phenyacyl bromide to 2-amino thiazole in excellent yield (97%) within short reaction time of 2 min via condensation of phenylacyl bromide and thiourea catalyzed by molecular iodine by using DMSO as solvent at room temperature.



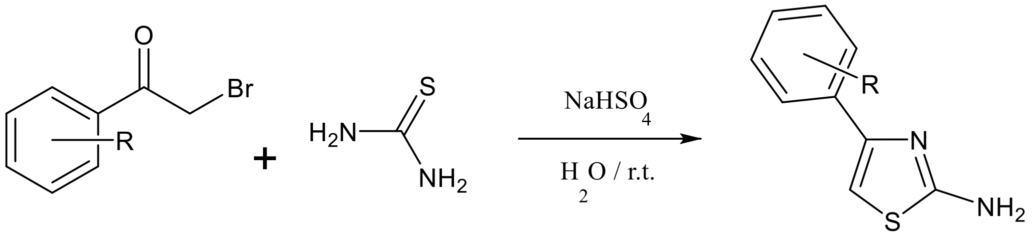
11) Zheng, Shilong et al [17]

This method report a synthesis of 2-amino thiazole in excellent yield (97%) by using aq $NaHCO_3$ as a reagent to keep reaction mass pH 8-9 via condensation of α-haloketon and thiourea by using ethol as solvent at reflux condition.



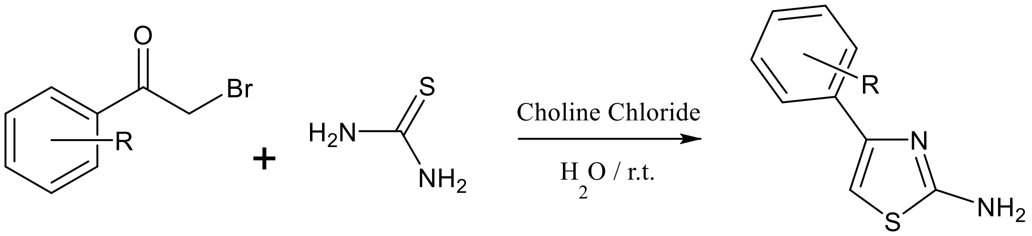
12) Rostamizadeh, Shahnaz et al [18]

Aqueous $NaHSO_4$ catalyzed regioselective and versatile synthesis of 2-thiazolamines via condensation of α-haloketone and thiourea in aqueous medium at room temperature. This method reports excellent conversion.



13) Shankarling, Ganapati S. et al [19]

Cholin Chloride catalyzed condensation of α-haloketone and thiourea in aqueous medium at room temperature reports 96% yield within 20 min of reaction time.

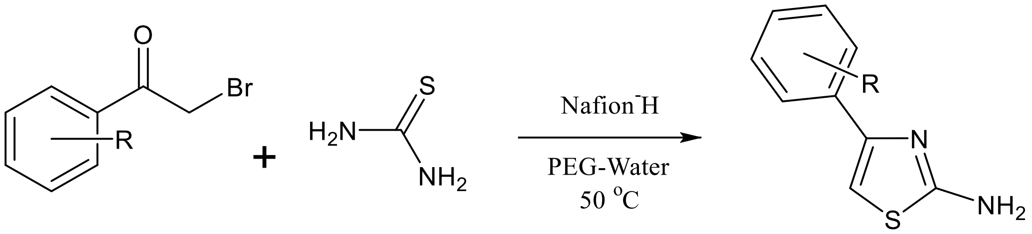


14) Dighe, Satish N. et al [20]

A high-speed, solution-phase and combinatorial synthesis of 2-substituted amino-4-aryl thiazoles in polar solvents in absence of catalyst under ambient conditions.

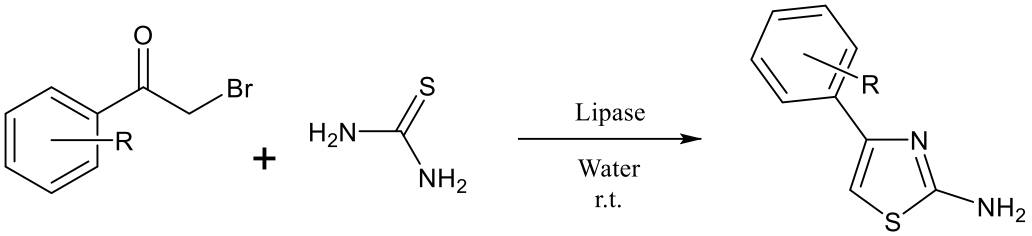
15) Kidwai, Mazaahir et al [21]

Eco-friendly synthesis of 2-amino thiazoles catalyzed by Nafion-H as recyclable catalyst under PEG-Water as solvent system at 50°C in 10 min reports 96% yield.



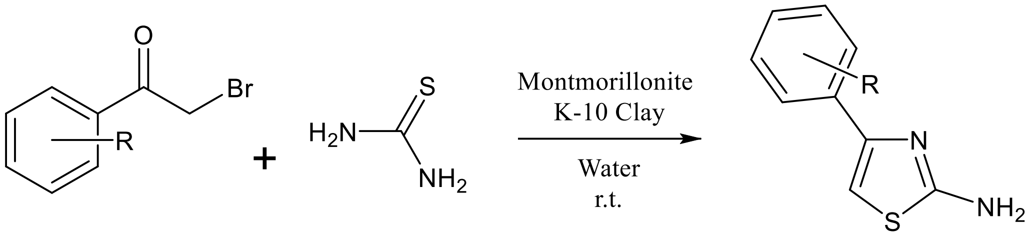
16) Lobo, Hyacintha Rennet et al [22]

This method report Lipase and Deep Eutectic Mixture catalyzed efficient synthesis of thiazoles in water at room temperature via condensation of α-haloketon and thiourea.



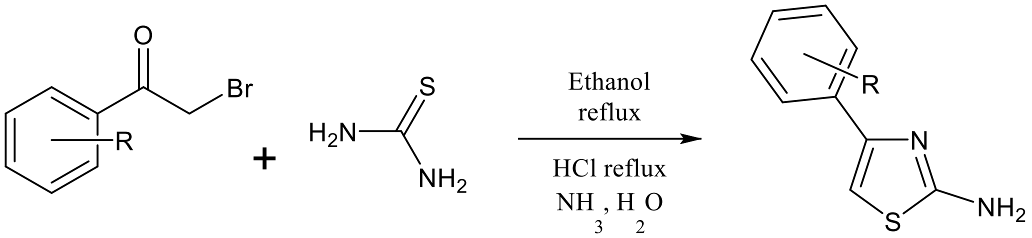
17) Mohinuddin, Pinjari Md. K. et al [23]

This method reports Montmorillonite K-10 Clay Mediated GreenSynthesis of 2-Amino-4-aryl thiazole Derivatives from a-Brominated Aralkyl Ketones in Water within short reaction time of 20 min and excellent yield (92%)



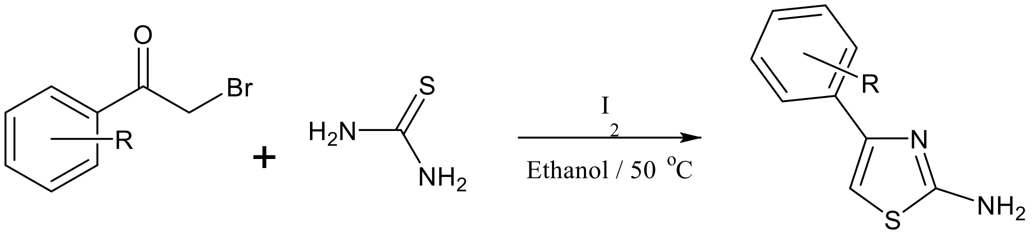
18) Sharma, Sunil et al [24]

α-haloketone treated with thiourea and refluxed in ethanol, resulted salt is treated with 1N HCl and then with ammonia solution to give 2-amino 4-aryl substituted thizole in excellent yield (94%).



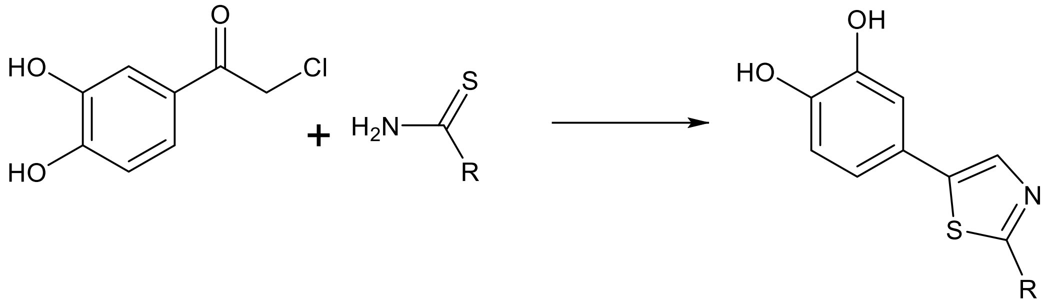
19) Kidwai, Mazaahir et al [25]

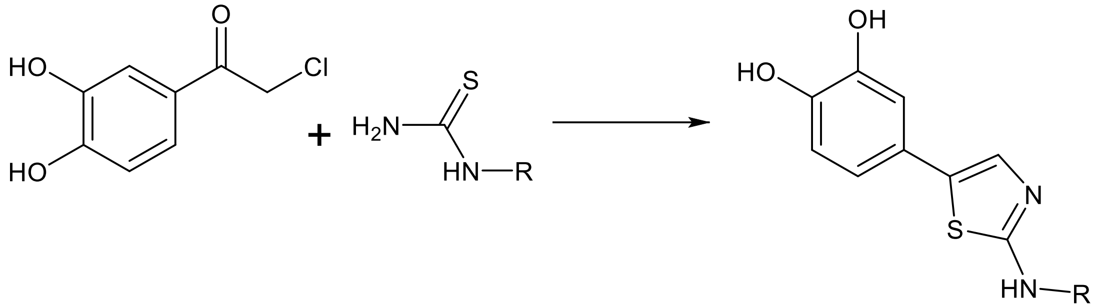
A facile synthesis of 2-amino 4-substituted thiazole by using molecular iodine as a versatile catalyst via condensation of α-haloketone and thiourea using ethanol as a solvent at 50°C. This method report excellent yield i.e 98%.



20) B. Narayana et al [26]

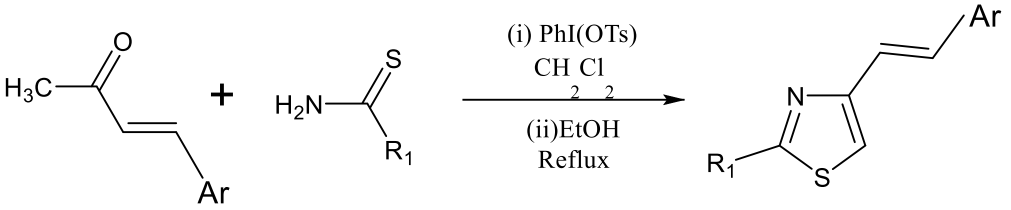
This method gives synthesis of some new 4-{2-[(Aryl)amino]-1,3-thiazol4-yl}benzene-1,2- diols as possible antibacterial and antifungal agents.





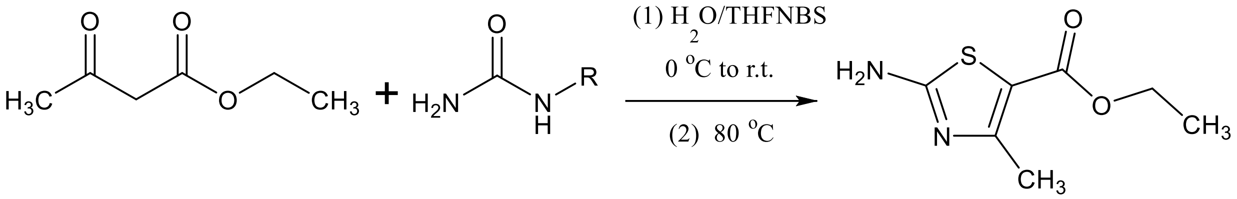
21) Om Prakash et al [27]

The reaction of (E)-4-arylbut-3-en-2-ones with [(hydroxy(tosyloxy)iodo]benzene(HTIB) followed by the treatment with thiourea, thioamide, and thiobenzamide has offered one-pot synthesis of 2-substituted 4-styrylthiazoles.



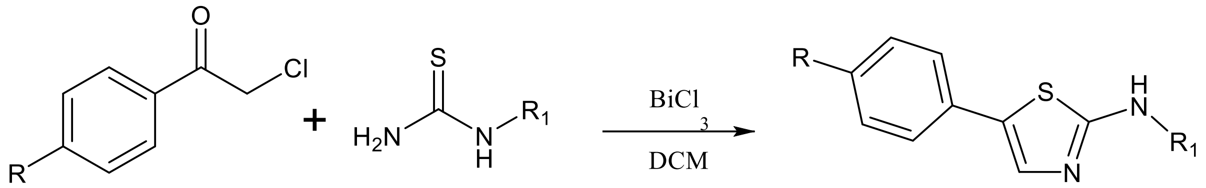
22) Ge Meng et al [28]

A new and practical one-pot procedure for the synthesis of several 2-sustituted-4-methyl thiazole-5-carboxylates from commercially available starting materials is described. Under mild reaction conditions, various 2-substituted phenyl ring derivatives were obtained in good yields from ethyl acetoacetate, N-bromosuccinimide, thiourea, or its N-substituted derivatives in efficient way instead of the traditional two-step reaction.



23) T. Giridhar et al [29]

Synthesis of 4-aryl-2-Amino thiazoles was achieved from the reaction of 4-butyl phenacyl chlorides with N-substituted thiourea in the presence of Bismuth Chloride.



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Formal Synthesis of Antihistaminic Drug Olopatadine Hydrochloride via DDQ-Oxidation

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ABSTRACT

A formal synthesis for the olopatadine hydrochloride is described. The present strategy involves DDQ mediated dehydrogenation for the construction of the key side chain (3-(dimethylamino)propylidene group).

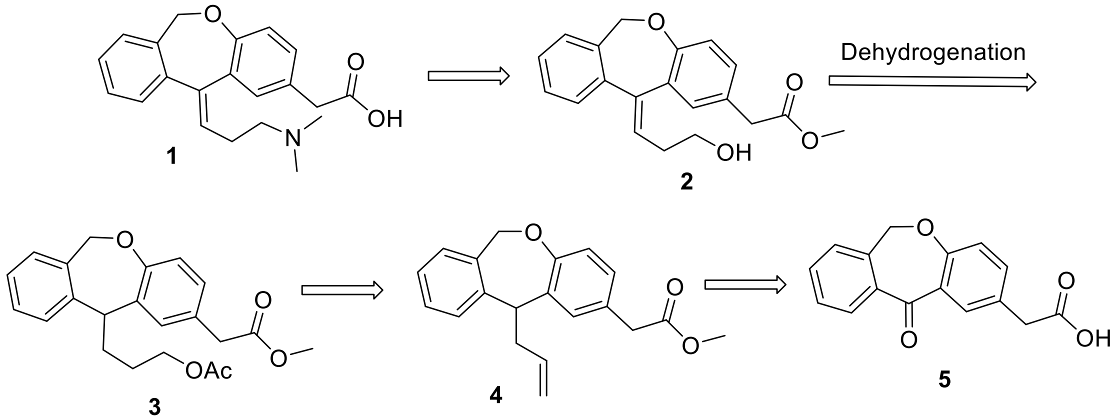
Keywords: Antihistaminic Drugs, Dehydrogenation, DDQ, Olopatadine, Isoxepac.

I. INTRODUCTION

Olopatadine hydrochloride is a selective histamine H_1 receptor antagonist *in vitro* and *in vivo* as demonstrated by its ability to inhibit binding and histamine-stimulated vascular permeability in the conjunctiva following topical ocular administration. Olopatadine is devoid of effects on alpha-adrenergic, dopamine, muscuarinic type 1 and 2, and serotonin receptors. Only cis isomer of olopatadine being useful in treating allergic eyes diseases in humans, which comprises of stabilizing conjuctival mast cells by topical administration to the human eye. Literature review reveals a number of synthetic strategies to access olopatadine, mostly in the form of patents.[1] In most of the synthesis, the key side chain has been introduced *via* 'Grignard reaction' or 'Wittig olefination'.[1d,2] In most of the previous approaches, the main drawback has been the low *E*/*Z* stereoselectivity. Recently, Bosch *et al.* have utilized a stereoselective Heck reaction for the selective generation of *Z*-isomer *via* the intramolecular cyclization of an *E*-alkene intermediate.[3] Nishimura *et al.* too reported a stereospecific route to **1** under palladium catalysis. In their synthetic route, the *Z*-stereoselectivity was controlled by an intramolecular stereospecific seven-membered ring cyclization from an alkyne intermediate using palladium catalyst.[4] Unfortunately most of the reported syntheses involves expensive reagents and harsh reaction conditions which are operationally difficult to perform on a large scale.

II. PRESENT WORK

The envisaged retrosynthetic strategy for olopatadine **1** is delineated in Scheme 1. A linear synthetic strategy was invoked wherein homoallyl alcohol **2** was conceived as the ideal precursor to **1**. Elaboration of the intermediate **2** to **1** is well documented in the literature.[4] Homoallyl alcohol **2** upon mesylation, dimethylamination and hydrochlorination would lead to olopatadine hydrochloride salt. In turn the focus was the construction of the key side chain. The homoallyl alcohol **2** could be accessed from intemediate **3** by DDQ mediated dehydrogenation, which in turn can be synthesized from allyl compound **4** by hydroboration and protection. The allyl compound **4** could be accessed from known intermediate 2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetic acid (**5**, also known as Isoxepac) through reduction followed by allylation.

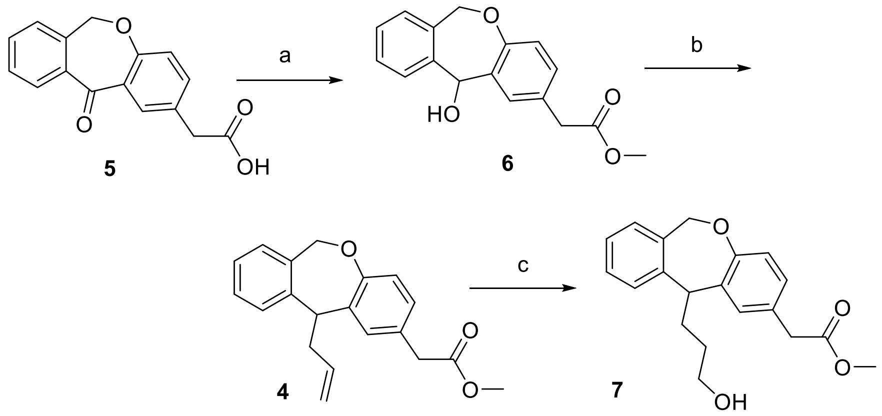


Scheme 1. Retrosynthetic analysis for olopatadine ***1***

III. RESULTS AND DISCUSSION

According to retrosynthetic plan (Scheme 1), synthesis of olopatadine (**1**) began from Isoxepac (**5**).[5] **5** on treatment with thionyl chloride in methanol gave the corresponding Isoxepac methyl ester in quantitative yield. This methyl ester was reduced using sodium borohydride in methanol furnished alcohol **6** in 93% yield. The IR spectrum of compound **6** showed strong bands at 3462 and 1739 cm^{-1} indicating the presence of hydroxyl and ester functionalities. The ^1H NMR spectrum of compound **6** showed peak at δ 3.64 as singlet corresponding to the three protons indicating the presence of a methyl ester compound. Peak at δ 5.55 appeared as a singlet accounting for one proton adjacent to hydroxyl group. The ^{13}C NMR spectrum showed peak at δ 172.2 corresponding to ester functional group. Its DEPT NMR spectrum showed presence of peak at δ 76.1 corresponding to characteristic benzylic methine carbon. MS spectrum of compound **6** showed signal appearing at *m/z*: 307 (M + Na), further confirmed its molecular formula (Scheme 2).

Alcohol **6** was converted into allyl compound **4** using allyltrimethylsilane and $BF_3 \cdot OEt_2$ in DCM in 83% yield. The IR spectrum of compound **4** showed absence of band at 3462 cm^{-1} indicating the absence of hydroxyl group. ^1H NMR spectrum showed signals that appeared in olefinic region at δ 5.63-5.87 (m, 1 H), as multiplet integrating for one proton ($-\underline{CH}=CH_2$) and the multiplet which appeared at 2.78-3.13 (m, 2 H) integrating for two protons ($-\underline{CH_2}-CH=CH_2$) was attributed to the allylic methylene protons while rest of the proton peaks associated with the compound resonated at expected positions. ^{13}C NMR and DEPT NMR spectra of compound **4** showed the signals that appeared at δ 136.6 ($CH_2-\underline{CH}=CH_2$), 116.3 ($CH_2-CH=\underline{CH_2}$) and 43.6 ($\underline{CH_2}-CH=CH_2$) corresponding to allyl chain carbons while rest of the carbons associated with the compound resonated at their expected positions. Finally, HRMS analysis (calculated for $C_{20}H_{21}O_3$-309.1485, observed-309.1480) confirmed the formation of **4**.

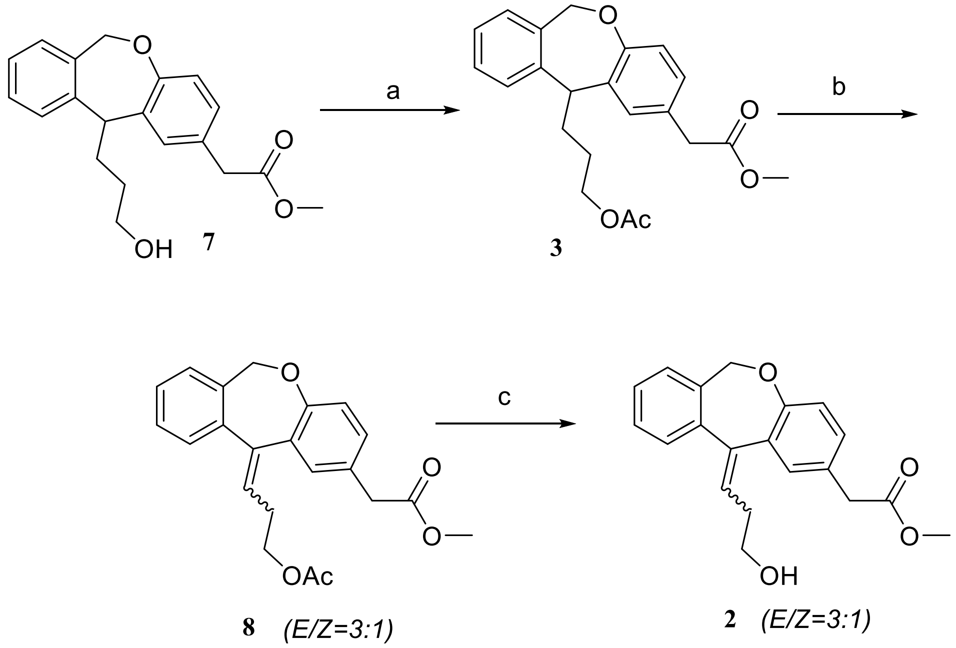


Scheme 2. *Reagents and conditions: a) i) $SOCl_2$, MeOH, 24 h, rt, quent; ii) $NaBH_4$, MeOH, 0 ºC, 2 h, 93%; b) Allyl-TMS, $BF_3 \cdot Et_2O$, 0 ºC-rt, DCM, 4 h, 83%; c) $BH_3 \cdot DMS$, NaOH, H_2O_2, THF, 0 ºC-rt, 12 h, 81%.*

Hydroboration was carried out on **4** using $BH_3 \cdot DMS$ which was quenched by sodium hydroxide and hydrogen peroxide, afforded alcohol **7** in 81% yield.[6] IR spectrum of the product **7** indicated the presence of a hydroxyl group by revealing broad absorption at 3444 cm^{-1} confirming hydroboration-oxidation. ^1H NMR spectrum showed no peak in the olefinic region corresponding to allyl protons and ^{13}C NMR and DEPT NMR spectra of compound **7** showed signals that appeared at δ 31.6, 35.4, 40.3, 62.5 and 72.7 corresponding to methylene (-CH_2-) carbon confirming hydroboration-oxidation. Finally, the structure of compound **7** was confirmed by HRMS analysis (calculated for $C_{20}H_{23}O_4$-327.1591, observed-327.1584).

The primary hydroxyl group of **7** was protected as its acetate using pyridine and acetic anhydride, afforded acetate **3** in 96% yield. The IR spectrum of compound **3** showed absorption bands at 1742 and 1732 cm^{-1} for the corresponding ester and acetate functionalities respectively. ^1H NMR spectrum of compound **3** showed singlet at δ 2.02 which indicated the formation of acetate compound **3**. Its ^{13}C NMR and DEPT NMR spectra showed peaks at δ 170.6 and δ 20.8 corresponding carbonyl group ($CH_3\underline{CO}$-) and methyl group ($\underline{CH_3}CO$-) of acetate respectively. Finally, the structure of compound **3** was confirmed by HRMS analysis.

Next job was the introduction of key double bond. Accordingly, compound **3** was subjected to DDQ oxidation.[7] Here although desired compound **8** (*E/Z*=3/1) was obtained, but in low (40%) yield. ^1H NMR spectrum of compound **8** showed characteristic triplet at δ 5.69 (t, *J*=7.1 Hz) and 6.02 (t, *J*=7.1 Hz) integrated for 0.25 H and 0.75 H corresponding to *Z*-isomer and *E*-isomer respectively. Interestigly, ^1H NMR spectrum of compound **8** showed a broad peak at δ 5.16 (brs, 2 H) as a hump corrosponding to two protons (benzylic proton of oxepin ring) indicating presence of a double bond at C-11. Acetate deprotection smoothly worked in potassium carbonate and methanol in 30 min resulted in the formation of hydroxyl compound **2** (*E/Z*=3/1) in quantitative yield (Scheme 3).



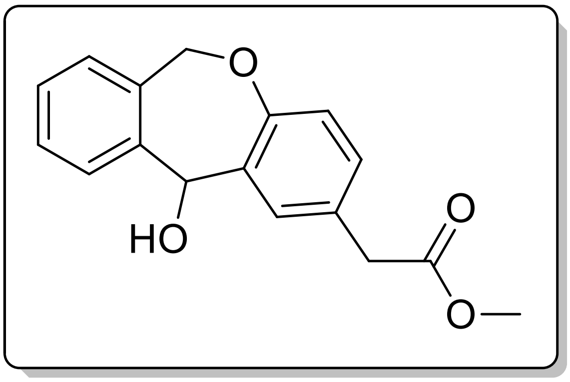
Scheme 3*. Reagents and conditions: a) Py, Ac_2O, 0 ºC-rt, DCM, 4 h, 96%; b) DDQ, Dioxane, Reflux, 12 h, 40%; c) K_2CO_3, MeOH, 30 min, 90 %.*

Elaboration of the intermediate **2** upon mesylation, dimethylamination and hydrochlorination would lead to olopatadine hydrochloride salt is well documented in the literature.[4]

IV. EXPERIMENTAL SECTION

General remarks: All reagents and solvents were used as received from the manufacturer. Melting points are recorded using Buchi B-540 melting point apparatus in capillary tubes and are uncorrected. The temperatures are reported in centigrade scale. The reaction progress was monitored by the TLC analysis on thin layer plates precoated with silica gel 60 F254 (Merck) and visualized by fluorescence quenching or iodine or by charring after treatment with p-anisaldehyde and also 2,4-DNP. Merck's flash silica gel (230-400 mesh) was used for column chromatography.

Methyl 2-(11-hydroxy-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetate (6):



2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetic acid (5 g, 18.65 mmol) was dissolved in methanol (100 mL) and cooled at 0 ˚C. Thionyl chloride (2.06 mL, 27.98 mmol) was added dropwise during a half hour period and the solution was stirred at room temperature for 24 h. The solvent was evaporated almost to dryness and the residue was partitioned between dichloromethane (50 mL) and saturated sodium bicarbonate solution (50 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, giving ketoester, which was used without further purification.

Ketoester (5 g, 17.66 mmol) was dissolved in methanol (50 mL) and cooled to 0 ˚C. Sodium borohydride (0.65 g, 17.66 mmol) was added portionwise over a period of half hour. After complete addition, the reaction mixture was stirred for additional 2 h. After completion of the raction (TLC), the reaction mixture was quenched by addition of 10% HCl solution and evaporated almost to dryness and then extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine solution were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure and purified by flash column chromatography (silica gel, pet. ether: EtOAc, 7:3) to furnish **6** as colorless liquid.

R*f* = 0.3 (pet. ether-ethyl acetate, 7:3)

Yield: 4.8 g, 96% over two steps.

MF: $C_{17}H_{16}O_4$, **MW:** 284.30.

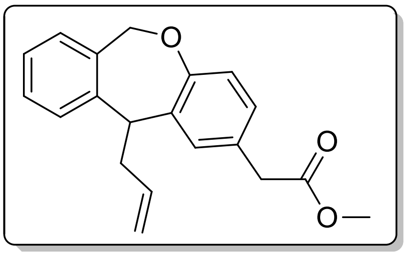
IR ($CHCl_3$, cm^{-1}): νmax 3462, 2951, 1739, 1496.

^{1}H NMR (200 MHz, $CDCl_3 + CCl_4$): δ 3.01 (brs, 1 H), 3.51 (s, 2 H), 3.64 (s, 3 H), 4.93 (d, *J* = 12.8 Hz, 1 H), 5.55 (s, 1 H), 5.83 (d, *J* = 12.8 Hz, 1 H), 6.83 (d, *J* = 8.3 Hz, 1 H), 7.09 (dd, *J* = 8.3 Hz and 2.2 Hz, 1 H), 7.17-7.37 (m, 3 H).

^{13}C NMR (50 MHz, $CDCl_3 + CCl_4$): δ 39.9, 51.9, 70.6, 76.1, 120.5, 126.5, 127.4, 127.9, 128.4 (2 C), 128.6, 130.6, 131.6, 134.7, 140.6, 155.8, 172.2.

MS (ESI): *m/z*: 307.00 $(M+Na)^+$.

Methyl 2-(11-allyl-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetate (4):



To a stirred solution of **6** (4 gm, 14.08 mmol) in dry CH_2Cl_2 (40 mL) was added Allyl-TMS (3.34 mL, 3.59 mmol) at 0 °C, after 10 min $BF_3 \cdot Et_2O$ was added slowly over period of 15 min and stirred for another 15 min. TLC showed complete conversion of hydroxyl to allyl. Reaction mixture was quenched by careful addition of saturated solution of NH_4Cl, after which organic layer was separated and aqueous layer was washed with CH_2Cl_2 (3 × 40 mL). Combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, to yield colorless oil of **4** which was purified using flash chomatography (silica gel, pet. ether: ethyl acetate, 2:8) furnished allyl compound **4** as colorless liquid.

R*f* = 0.6 (pet. ether-ethyl acetate, 2:8)

Yield: 4.03 g, 93%.

MF: $C_{20}H_{20}O_3$, **MW:** 308.37.

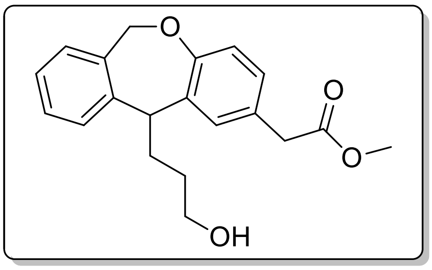
IR ($CHCl_3$, cm^{-1}): νmax 2950, 1732, 1500.

^{1}H NMR (200 MHz, $CDCl_3 + CCl_4$): δ 2.78-3.13 (m, 2 H), 3.63 (s, 2 H), 3.76 (s, 3 H), 3.90 (t, *J* = 7.8 Hz, 1 H), 4.90-5.14 (m, 3 H), 5.57 (d, *J* = 14.6 Hz, 1 H), 5.63-5.87 (m, 1 H), 6.98-7.08 (m, 1 H), 7.08-7.21 (m, 3 H), 7.21-7.33 (m, 3 H).

^{13}C NMR (50 MHz, $CDCl_3 + CCl_4$): δ 40.4, 43.6, 51.9, 52.6, 72.8, 116.3, 121.3, 126.7, 127.2, 127.4, 128.4, 128.9, 130.4, 131.5, 133.6, 135.8, 136.6, 140.1, 156.8, 171.8.

HRMS (ESI) $[M + H]^+$ Calculated for $C_{20}H_{21}O_3$-309.1485, observed-309.1480.

Methyl 2-(11-(3-hydroxypropyl)-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetate (7):



The allyl compound **4** (2 g, 6.49 mmol) was dissolved in dry THF (15 mL) in an oven-dried flask under a nitrogen atmosphere, then $BH_3 \cdot DMS$ (1.31 mL, 12.98 mmol) was added dropwise *via* syringe at 0 °C, stir it for 4 h. Then the reaction mixture was quenched with 3 M NaOH (2.4 mL) at 0 °C, followed by the dropwise addition of 30% H_2O_2 (2.2 mL) and the resulting solution was stirred for additional 6 h at room temperature. The organic phase was separated and the aqueous layer extracted with ethyl acetate (3 × 20 mL). The combined organic phase was washed with brine (30 mL), dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was subjected to flash column chromatography (silica gel, pet. ether: ethyl acetate, 7:3) to obtain primary alcohol **7** as liquid.

R$_f$ = 0.5 (pet. ether-ethyl acetate, 1:1)

Yield: 1.9 g, 90 %.

MF: $C_{20}H_{22}O_4$, **MW:** 326.38.

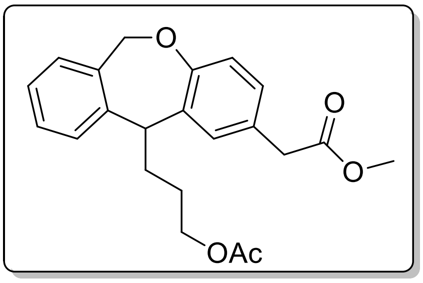
IR ($CHCl_3$, cm^{-1}): vmax 3444 (broad), 2952, 1738, 1500.

^{1}**H NMR** (200 MHz, $CDCl_3$ + CCl_4): δ 1.35-1.58 (m, 2 H), 1.96-2.35 (m, 3 H), 3.46-3.61 (m, 4 H), 3.68 (s, 3 H), 3.74 (t, *J* = 7.8 Hz, 1 H), 4.95 (d, *J* = 14.5 Hz, 1 H), 5.48 (d, *J* = 14.5 Hz, 1 H), 6.98-6.87 (m, 1 H), 6.99-7.11 (m, 3 H), 7.11-7.23 (m, 3 H).

^{13}**C NMR** (50 MHz, $CDCl_3$ + CCl_4): δ 31.6, 35.4, 40.3, 51.9, 52.2, 62.5, 72.7, 121.3, 126.7, 127.2, 127.5, 128.4, 128.9, 130.2, 131.5, 134.0, 135.7, 140.6, 156.7, 172.0.

HRMS (ESI) $[M + H]^+$ Calculated for $C_{20}H_{23}O_4$-327.1591, observed-327.1584.

Methyl 2-(11-(3-acetoxypropyl)-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetate (3):



1 g (3.08 mmol) of alcohol **7** was dissolved in dry DCM (10 mL) and the solution was stirred. To the stirred solution was added 0.49 mL (6.16 mmol) of pyridine at 0 °C and the mixture was stirred for five minutes. Acetic anhydride (0.72 mL, 7.71 mmol) was added dropwise, and stirred well while warming to room temperature for 4 h. Reaction mixture was quenched by saturated solution of $NaHCO_3$ (10 mL), The organic phase was separated and the aqueous layer extracted with DCM (3 × 10 mL). The combined organic phase was washed with brine (30 mL), dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was subjected to flash column chromatography (silica gel, pet. ether: ethyl acetate, 8:2) to obtain acetate **3** as sticky liquid.

R$_f$ = 0.6 (pet. ether-ethyl acetate, 7:3)

Yield: 1.1 g, 98 %

MF: $C_{22}H_{24}O_5$, **MW:** 368.42.

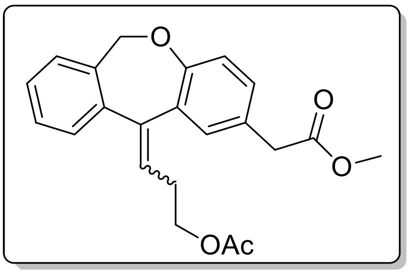
IR ($CHCl_3$, cm^{-1}): vmax 2950, 1742, 1732, 1503.

^{1}**H NMR** (400 MHz, $CDCl_3$ + CCl_4): δ 1.49-1.62 (m, 2 H), 2.02 (s, 3 H), 2.05-2.17 (m, 1 H), 2.17-2.30 (m, 1 H), 3.55 (s, 2 H), 3.68 (s, 3 H), 3.74 (t, 1 H), 4.02 (t, 2 H), 4.95 (d, *J* = 14.5 Hz, 1 H), 5.47 (d, *J* = 14.5 Hz, 1 H), 6.96 (d, *J* = 8.7 Hz, 1 H), 7.01-7.11 (m, 3 H), 7.13-7.24 (m, 3 H).

^{13}**C NMR** (100 MHz, $CDCl_3$ + CCl_4): δ 20.8, 27.4, 35.2, 40.2, 51.8, 51.9, 64.0, 72.6, 121.3, 126.7, 127.1, 127.3, 128.5, 128.9, 130.1, 131.3, 133.9, 135.6, 140.1, 156.6, 170.6, 171.7.

HRMS (ESI) $[M + H]^+$ Calculated for $C_{22}H_{25}O_5$-369.1697, observed-369.1692.

Methyl 2-(11-(3-acetoxypropylidene)-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetate (8): To a solution of acetate **7** (1 g, 2.71 mmol) in dry dioxane (10 mL), DDQ (2.98 mmol) was added. The reaction mixture was refluxed for 6 h. After completion of the reaction, the precipitated solid $DDQH_2$ was removed by filtration and the filtrate was evaporated. The residue was taken in ethyl acetate (20 mL) and was washed with water (2 × 10 mL), saturated solution of $NaHCO_3$ (2 × 5 mL), brine (2 × 10 mL), dried over Na_2SO_4 and filtered. The filtrate was evaporated under reduced pressure to afford a crude yellow liquid. The crude product was



subjected to purification by flash column chromatography (silica gel, pet. ether: ethyl acetate, 8:2) to furnish acetate **8** as an oil (*E/Z* = 3:1).

R_f = 0.6 (pet. ether-ethyl acetate, 7:3)

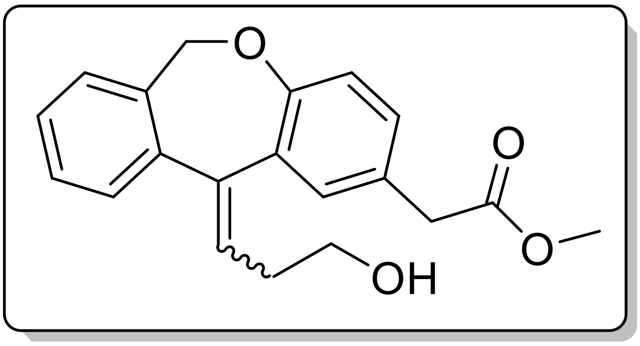
Yield: 0.39 g, 40 %

MF: $C_{22}H_{22}O_5$, **MW:** 366.14.

IR ($CHCl_3$, cm^{-1}): νmax 2950, 1742, 1732, 1503.

^{1}H NMR (500 MHz, $CDCl_3$ + CCl_4) (*E/Z* = 3:1): δ 2.04 (s, 2.25 H, for *E*-isomer), 2.07 (s, 0.75 H, for *Z*-isomer), 2.51 (dt, *J* = 7.1 and 6.7 Hz, for *E*-isomer), 2.77 (dt, *J* = 7.1 and 6.7 Hz, for *Z*-isomer), 3.54 (s, 2 H), 3.69 (s, 3 H), 4.13-4.23 (m, 2 H), 5.16 (brs, 2 H), 5.69 (t, *J* = 7.1 Hz, 0.25 H, for *Z*-isomer), 6.02 (t, *J* = 7.1 Hz, 0.75 H, for *E*-isomer), 6.71 (d, *J* = 8.24 Hz, 0.75 H, for *E*-isomer), 6.81 (d, *J* = 8.24 Hz, 0.25 H, for *Z*-isomer), 7.03-7.40 (m, 6 H).

Methyl 2-(11-(3-hydroxypropylidene)-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (2): To a stirred solution of acetate **8** (0.3 g, 0.81 mmol) in MeOH was added K_2CO_3 (0.22 g, 1.63 mmol) at room temperature and stirred for 30 min. The MeOH was evaporated, diluted with EtOAc (10 mL) and solid K_2CO_3 was filtered. The filtrate was washed with water (20 mL), brine (10 mL), dried over Na_2SO_4 and filtered. The filtrate was evaporated under reduced pressure to afford a crude product. The crude product was subjected to flash column chromatography (silica gel, pet. ether: ethyl acetate, 7:3) to obtain homoallyl alcohol **2** as a white solid (*E/Z* = 3:1).



R_f = 0.4 (pet. ether-ethyl acetate, 6:4)

Yield: 0.25 g, 96 %

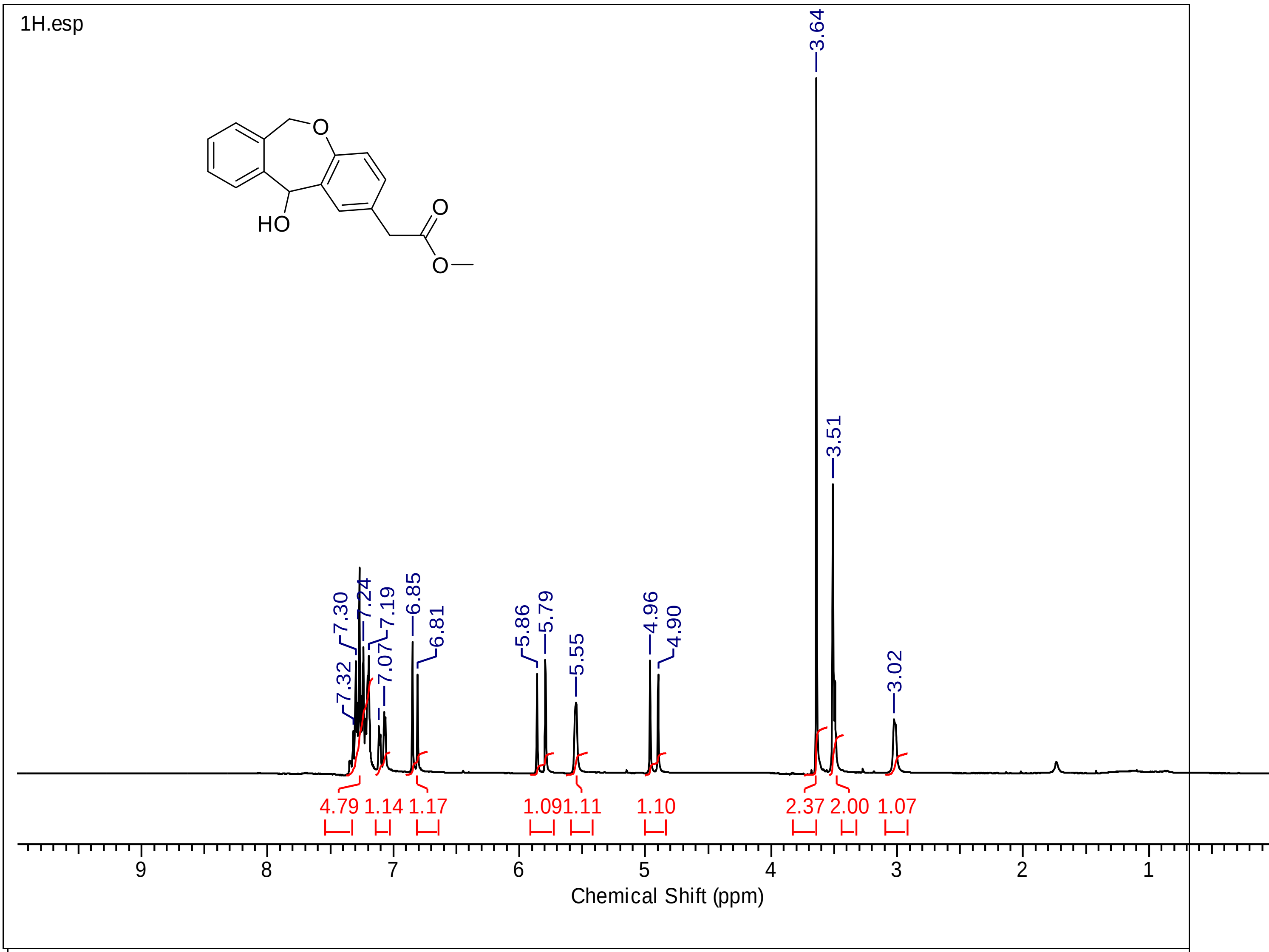
MF: $C_{20}H_{20}O_4$, **MW:** 324.13.

IR ($CHCl_3$, cm^{-1}): νmax 3446, 2921, 1736, 1463.

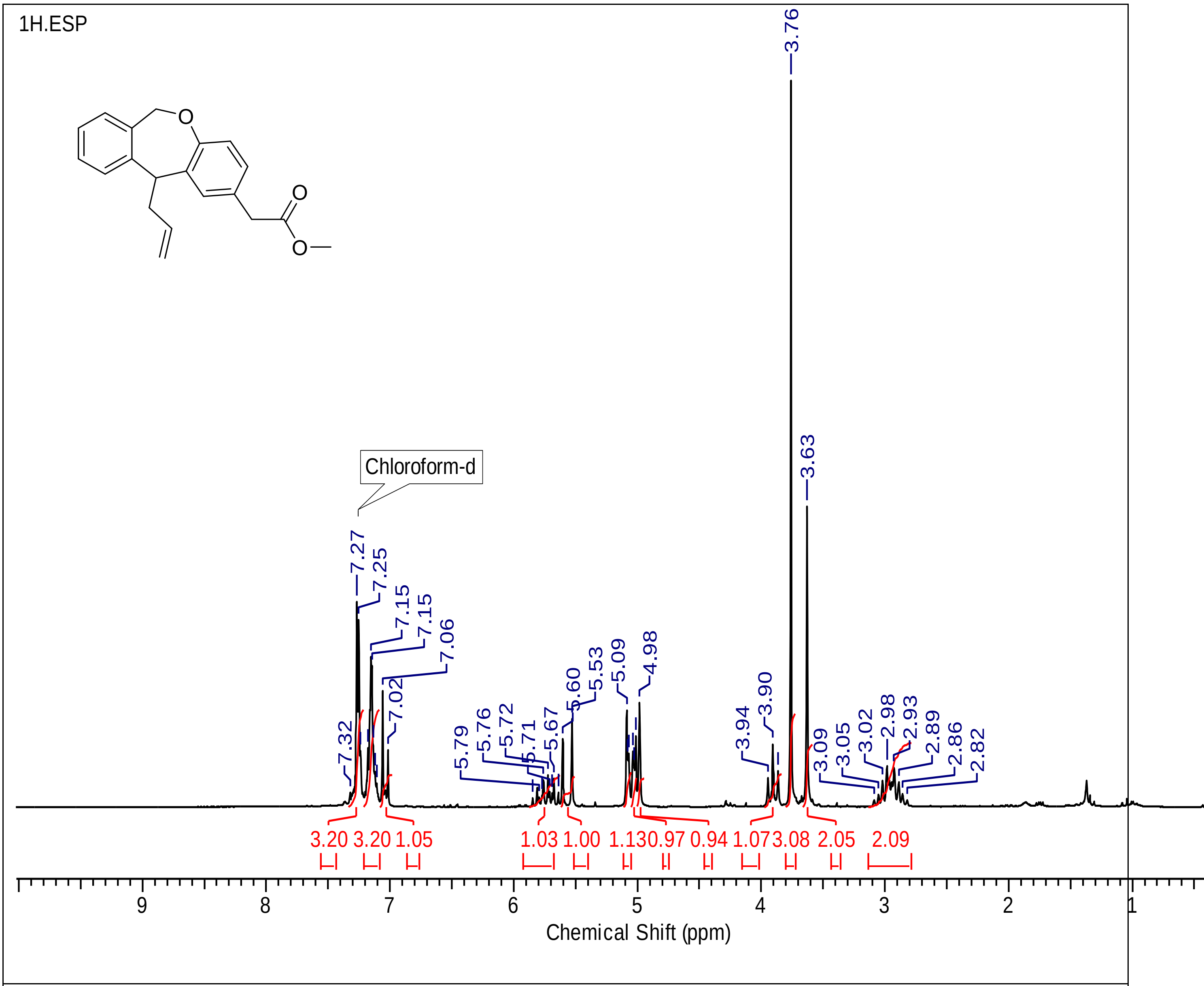
^{1}H NMR (200 MHz, $CDCl_3$ + CCl_4): δ 2.38-2.49 (m,0.8 H, *E*-Form), 2.63-2.73 (m,1.2 H, *Z*-Form), 3.53 (s, 2 H), 3.68 (s, 3 H), 3.75 (m, 0.8 H, *E*-Form), 3.81 (t, *J*=6.3 Hz, 1.2 H), 5.19 (brs, 2 H), 5.73 (t, *J*=7.8 Hz, 0.6 H, *Z*-Form), 6.06 (t, *J*=7.8 Hz, 0.4 H, *E*-Form), 6.70 (d, *J*=8.2 Hz, 0.4 H, *E*-Form), 6.79 (d, *J*=8.2 Hz, 0.6H, *Z*-Form), 7.00-7.34 (m, 6H).

V. SPECTRA

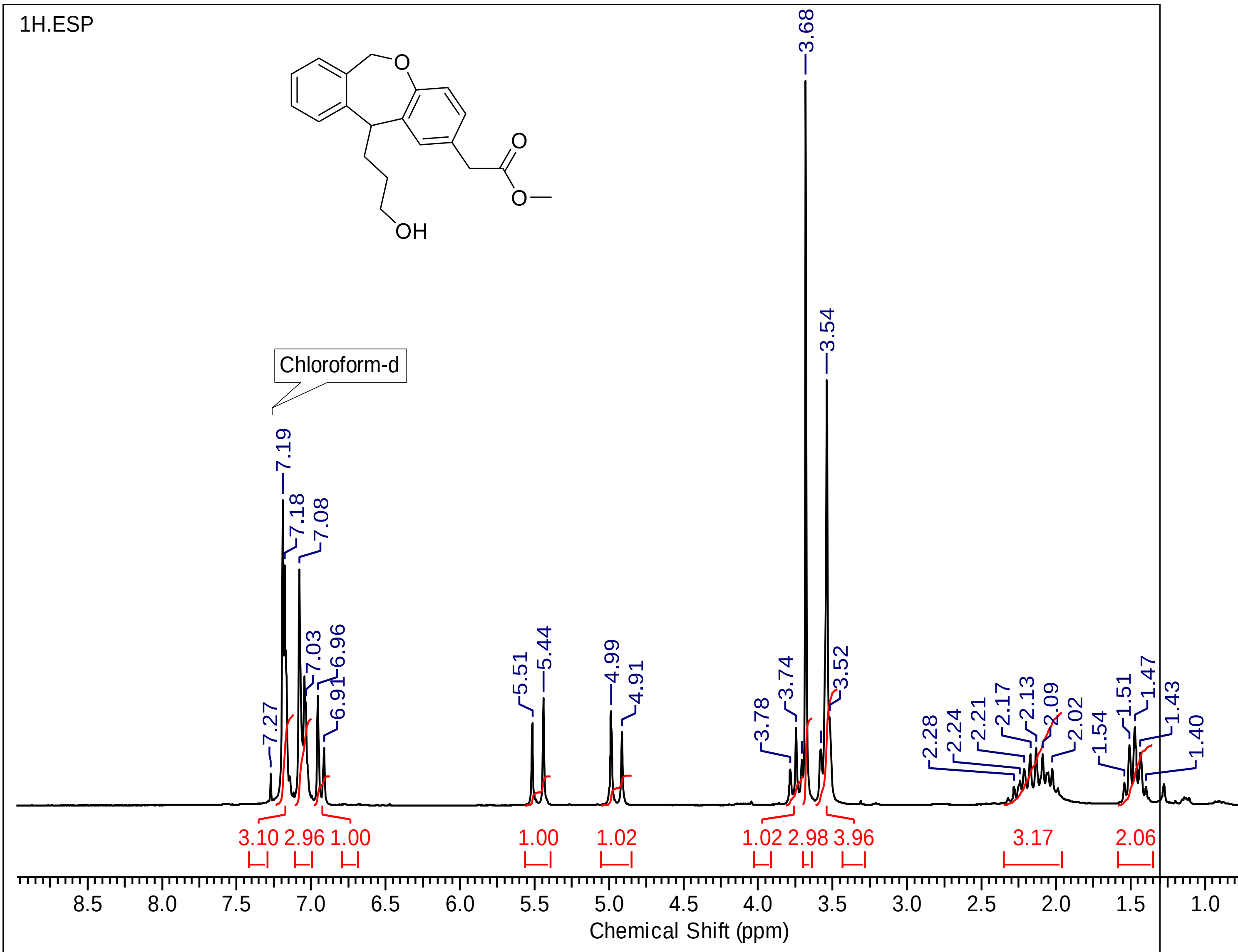
^{1}H NMR spectrum of compound 6 ($CDCl_3$ + CCl_4, 200 MHz)



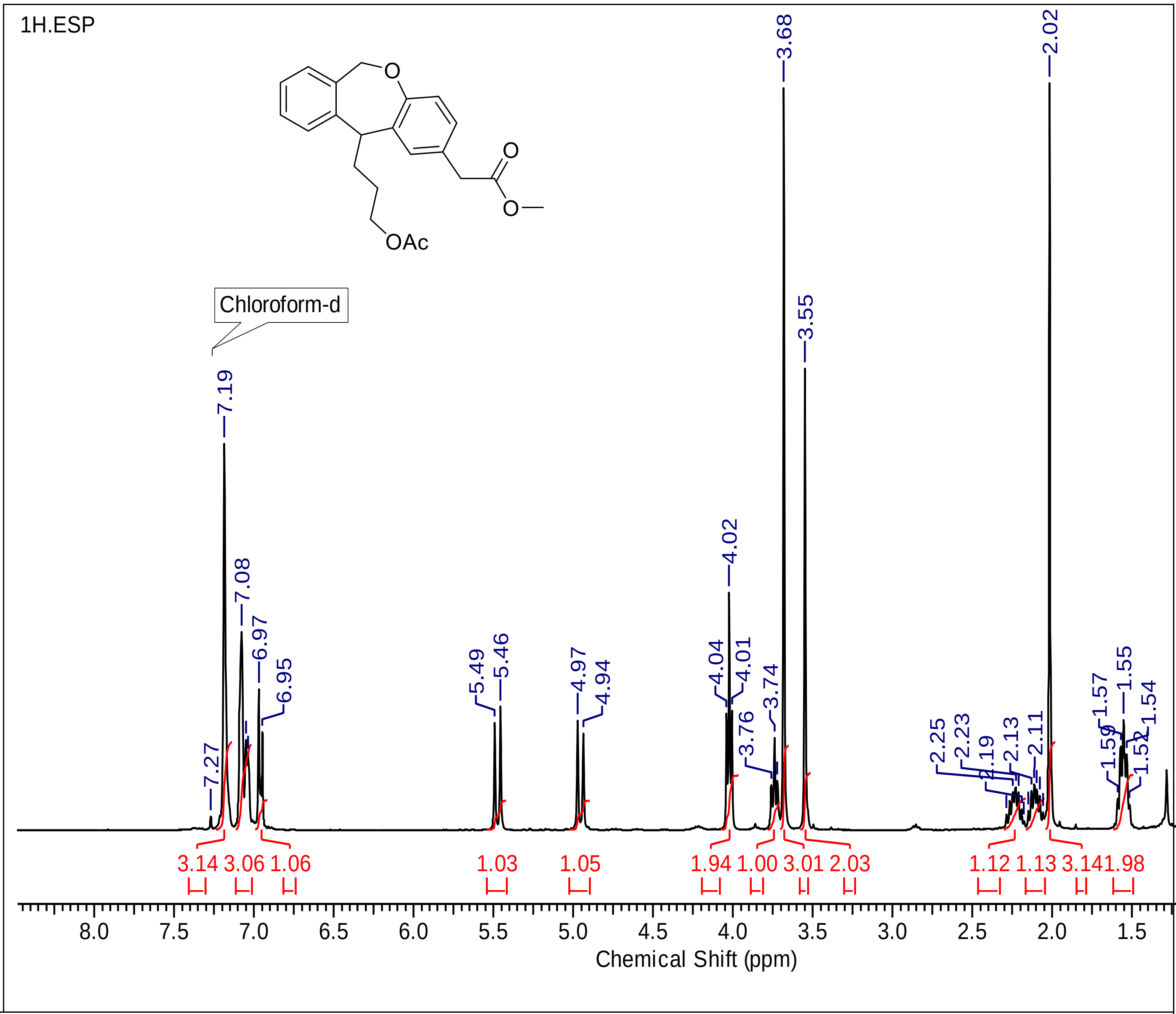
^{1}H NMR spectrum of compound 4 ($CDCl_3$ + CCl_4, 200 MHz)



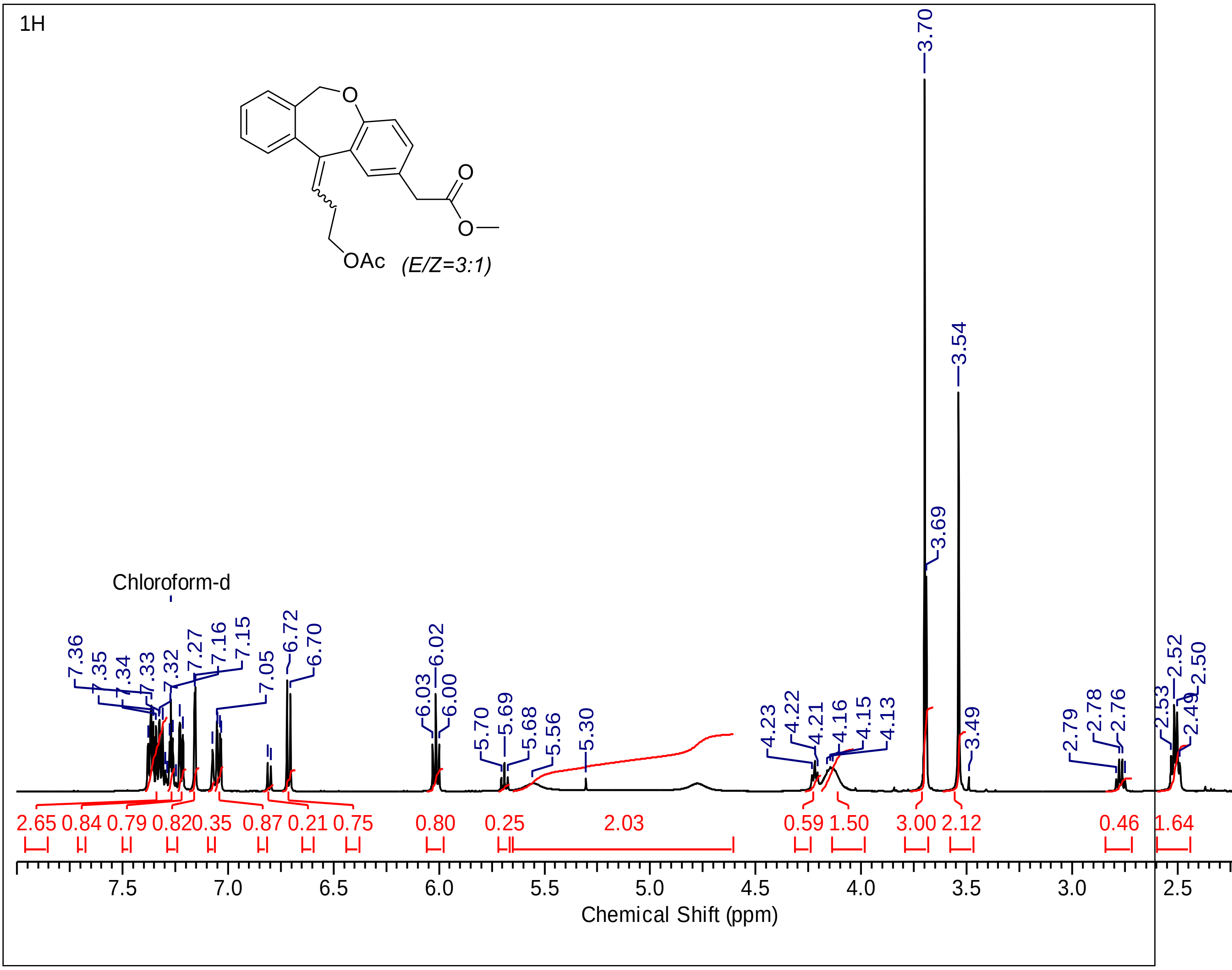
^{1}H NMR spectrum of compound 7 ($CDCl_3$ + CCl_4, 200 MHz)



^{1}H NMR spectrum of compound 3 ($CDCl_3 + CCl_4$, 200 MHz)



^{1}H NMR spectrum of compound 8 ($CDCl_3 + CCl_4$, 400 MHz)



VI. CONCLUSIONS:

In the present investigation we have developed a formal synthesis for antihistaminic drug, olopatadine hydrochloride using DDQ-oxidation. The research involves DDQ mediated dehydrogenation for the synthesis of the key side chain (3-(dimethylamino)propylidene group).

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The Seasonal Variations in Physico-Chemical Parameters in Ground Water Quality of Vaijapur Tehsil of Aurangabad District Duringpre-Monsoon and Post Monsoon

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I. INTRODUCTION

Water is a prime natural resource, a basic human need, and a precious asset, in the absence of which no socio-economic developmental activities can sustain. The water in oceans and seas is highly saline, the estimated 1011 million cubic km of the total water present on earth, and only 33400 cubic meters of water is available for drinking, industrial consumption, and waste disposal[1]. The main objective of the water resources development in India was to ensure adequate supplies of water for various uses such as irrigation, urban and rural drinking water, sanitation, industrial water, and others while preserving the ecosystem. Water is an important source of generating energy and electricity, be it hydropower generation, thermal power generation, or nuclear power generation. Thus, the development of water resources plays an important role in the energy sector, particularly for hydropower generation, where there is no conjunctive use of water and no environmental pollution. The other important uses of water relate to navigation, industrial use, and forestry.

India's finite water resources, however, are under pressure with declining per capita water availability and deteriorating water quality due to rapid growth of population, urbanization, and Industrialization. At the time of Independence, the population was less than 40 crore and per capita, water availability was over 5,500 cubic meters per year. Now after 70 years of Independence, India's population has gone up to about 137.8 crores and per capita, water availability in 2021 has fallen to about 1486 cubic meters per year. This per capita water availability will further fall to about 1367 cubic meters per year by the year 2031 due to the increasing population[2]. Thus, growing pressure on water availability is resulting in competing demands for diverse uses of water. Inter-sectoral allocation, planning, and management of increasingly fragile water resources for diverse uses on a sustainable basis are emerging as a major challenge for the nation.

India is rich in surface water resources. The average annual precipitation is nearly 4000 cubic km. and the average flow in the river system is estimated to be 1880 cubic km. Because of the concentration of rains only in the three monsoon months, the utilizable quantum of water is about 690 cubic km. However, conditions vary widely from region to region. Whereas, some are drought-affected, others are frequently flooded. With the rapid increase in the population, the demand for irrigation, human and industrial consumption of water has increased considerably, thereby causing depletion of water resources. Increased population density, industrialization, agricultural practices, disposal of domestic sewage, and industrial runoffs all contaminate the groundwater and water resources[3].

The issue of groundwater availability is critical as one-third world population uses it for drinking purposes[4]. Groundwater that occurs beneath the earth's surface is considered free from contamination, hence usable but anthropogenic as well as natural factors are affecting the quality as well as quantity of this valuable resource[5]. Groundwater is one of the most reliable and vital sources of drinking water because of its widespread availability, occurring in natural conditions, and being less susceptible to water contamination as compared to fresh water [6-8].

There is a need for proper planning, development, and management of the greatest assets of the country like water [9]. Water requirements for industrial and domestic use are met partly from reservoirs constructed and managed by the irrigation department. Groundwater is one of the most important natural resources required for human consumption, domestic purposes, irrigation, industrialization, and urbanization[10]. The agriculture production technologies have put a lot of stress on groundwater resources in a few areas.

The statistics on water quality derivations into simple ratings in the form of comprehensive conclusions as good, best, poor or excellent for the public assessment that helps to manage their groundwater resources prudently for the near future[11].

Physico-chemical characteristics are indeed vital parameters for monitoring and assessing water quality due to their instability[12]. The chemical composition of groundwater plays a significant role in determining the water quality for various utility purposes[13].Suitability of Ground Water for Drinking Purpose is determined keeping in view the effects of various chemical constituents in water on the biological system of the human being. Though many ions are very essential for the growth of human being, when present in excess, have an adverse effect on human body.

India’s agricultural and drinking water requirements are partly met by aquifers and groundwater that supply roughly 62% towards irrigation, 85% towards water supply in rural areas, and 45% in urban areas[14]. Overexploitation and unabated pollution of this vital resource is threatening our ecosystems and even the life of the future generation[15]. The standards proposed by the Bureau of Indian Standards (BIS) for drinking water (IS-10500-91, Revised 2015) were used to decide the suitability of ground water[16]. The classification of groundwater samples was carried out based on the desirable and maximum permissible limits for the parameters. Many researchers have reported seasonal Physico-chemical parameters studies in India[17-20].

Climate and Rainfall:

The climate of the Vaijapur Tehsil is characterized by a hot summer and a general dryness throughout the year except during the southwest monsoon season, which is from June to September while October and November constitute the post-monsoon season. The winter season commences towards the end of November when temperatures begin to fall rapidly. December is the coldest month with the lowest temperature. From the beginning of March, the daily temperature increases continuously. May is the hottest month with the highest maximum temperature. With the onset of the southwest monsoon by about the second week of June, the temperature falls appreciably. Except during the southwest monsoon season, when the relative humidity is high, the air is generally dry over the Tehsil. The summer months are the driest when the relative humidity is generally between 20 and 25% in the afternoon. Winds are generally light to moderate with the increase in speed during the latter half of the hot season and in the monsoon season. The winds flow predominantly from directions between west and north during the hot season. They are mostly from directions between southwest and northwest during the southwest monsoon season. They blow mostly from the directions between northeast and southeast during the rest of the year becoming south-westerly to north-westerly in January and February.

The average annual rainfall of the Vaijapur Tehsil for the period 2002 to 2011 is 634.23 the average annual rainfall of the district for the period 2002 to 2011 is 705 mm. The average annual rainfall of the Vaijapur Tehsil for the period 2008 to 2017 is 561.13 mm.

II. EXPERIMENTAL- MATERIALS AND METHODS:

The current study is monitoring the pre and post-monsoon groundwater quality of the Vaijapur Tehsil for the last six months through its established monitoring dug wells and borewells. The objectives behind the monitoring are to study the seasonal variation of quality of the Tehsil. The sampling of groundwater from these sites was carried out in May (pre-monsoon period). The water samples after collection were immediately subjected to the analysis of various parameters in the Laboratory of Vinayakrao Patil College, Vaijapur. The parameters analyzed, include pH, Total Dissolved Solids (TDS), Electrical Conductivity (EC), Total Hardness (TH), Calcium (Ca^{2+}), and Magnesium (Mg^{2+}).

Water samples have been collected in 2 litre capacity polythene bottles (soaked overnight in 2% nitric acid and washed well in distilled water) from each location. The collected samples were properly labelled which indicates the source of the sample time and date of collection. Proper care taken in the storage of the sample, in such a way that their composition does not change between the period of collection and analysis. The samples are sealed and stores under cool and dry condition.The samples were brought to the laboratory and analyzed for the parameters within the 48 hours of collection; which has been carried out using the Standard methods of water analysis is employed to analyze the physico- chemical parameters of the water following APHA[21].The groundwater quality data thus generated was first checked for completeness and then the validation of data was carried out using standard checks. Subsequently, the interpretation of data was carried out to develop the overall picture of groundwater quality in the tehsil in the year 2020-21.

Table 1: Sampling Stations:

S1- Dug Well Vadji
S2- Bore Well Vadji
S3- Dug Well Jarul
S4- Bore Well Jarul
S5- Dug Well Sirasgaon
S6- Bore Well Sirasgaon
S7- Dug Well Khandala
S8- Bore Well Khandala
S9- Dug Well Waghala
S10- Bore Well Waghala
S11- Dug Well Shioor

S12- Bore Well Shioor
S13- Dug Well - Chor waghalgaon
S14- Bore Well Chor waghalgaon
S15- Dug Well Kavitkhed
S16- Bore Well Kavitkhed
S17- Dug Well Malegaon Kannad
S18- Bore Well Malegaon Kannad

Estimation of following Physico-Chemical parameters was brought about.

1. Temperature
2. Hydrogen Ion Concentration (pH)
3. Dissolved oxygen (DO)
4. Total Dissolved Solids (TDS)
5. Total Hardness
6. Magnesium (Mg)
7. Calcium (Ca)
8. Electrical Conductivity (EC)

1. Temperature:

Temperature-dependent solubility affects the DO levels in streams. Temperature governs many biochemical and physiological processes in aquatic organisms and increases metabolic and reproductive rates throughout the flood chain. Temperature also affects abiotic chemical processes, such as re-aeration rate, sorption of organic chemicals to particulate matter, and volatilization rates.

2. pH:

The pH of a solution is a measure of its hydrogen ion activity and is the logarithm of the reciprocal of the hydrogen ion concentration. Thus it is important to remember that a change of one pH unit represents a tenfold change in hydrogen ion concentration. The pH of water is a measure of acidity or alkalinity. The pH is a logarithmic scale based on a measure of the free hydrogen ions in the water. The scale runs from 0 to 14, where 7 is considered neutral, 0 to 7 is acidic and 7 to 14 is alkaline. Because pH can be affected by dissolved minerals and chemicals, it is an important indicator of the change in water chemistry.

The drinking water with a pH between 6.0 and 9.5 generally is considered satisfactory. Water with a pH below 6 or above 9.5 can be corrosive to metal plumbing pipes and fixtures.

The following methods were used for measurement of hydrogen-ion-concentration: pH meter Method: Apparatus: (i) pH meter (ii) Centigrade thermometer (iii) Beakers (iv) Blot paper. Reagents: (i) pH buffer solution in the range of water sample being analyzed. (ii) Distilled water. Procedure: A buffer solution was prepared with a pH near the expected pH of the water sample. 25 ml of buffer solution was poured in a small beaker. The vent of glass reservoir of the fiber junction electrode was opened. The electrodes were rinsed in distilled water, and blotted with soft paper. The electrodes were immersed in the buffer solution.

3. Dissolved Oxygen:

There are two main routes for oxygen input in surface waters: transfer of oxygen directly from the atmosphere (a process called re-aeration), and from plants as a result of photosynthesis. Re-aeration is the primary route for introducing oxygen into most waters. Oxygen gas (O2) constitutes about 21% of the atmosphere and readily dissolves in water. The ability of water to hold oxygen is influenced by temperature and salinity. The saturation concentration of DO in water is a measure of the maximum amount of oxygen that water can hold at a given temperature. As the salinity of water increases, the saturation concentration decreases. When oxygen is below the saturation concentration, it tends to diffuse from the atmosphere to water. Apart from these physical processes that influence the DO concentration in surface waters, biological processes like photosynthesis and respiration also influence the DO content. Daytime photosynthesis, influenced by the solar photo cycle, increases the productivity of autotrophs causing the increase of oxygen. In the night time, in the absence of photosynthesis, respiration is active in the streams causing the removal of oxygen. Some fish and aquatic organisms, such as carp and sludge worms, are adapted to 5 low oxygen conditions, but most fish species, such as trout and salmon, suffer if DO concentrations fall below 3 to 4 mg/l.

4. Total Dissolved Solids (TDS):

The high concentrations of TDS may affect taste adversely and deteriorate plumbing and appliances. The EPA recommends that water containing more than 500 mg/l of dissolved solids not be used if other less mineralized supplies are available. However, water containing more than 500 mg/l of TDS is not dangerous to drink.

5. Total Hardness:

The hardness is the property that makes water form an insoluble curd with soap and primarily is due to the presence of calcium and magnesium. Very hard waters have no known adverse health effects and may be more palatable than soft waters. Hard water is primarily of concern because it requires more soap for effective cleaning; forms scum and curd; causes yellowing of fabrics; toughens vegetables cooked in the water; and forms scale in boilers, water heaters, pipes and cooking utensils. The hardness of high-quality water should not exceed 270 mg/l measured as calcium carbonate. Water softer than 30 to 50 mg/l may be corrosive to piping, depending on pH, alkalinity and dissolved oxygen. Water softeners will correct hard water of more than 270 mg/l.

6. Calcium (Ca):

Calcium can be leached from practically all rocks but is much more prevalent in water from regions with deposits of limestone, dolomite and gypsum. Regions where granite or siliceous sand predominates have very low calcium levels in the waters. Waters with a concentration of 10 mg of less per litre are usually oligotrophic, while waters with 25 mg or more per litre are usually distinctly eutrophic.

Calcium is estimated complexometrically by titrating with EDTA using murexide indicator.

7. Magnesium (Mg):

Magnesium in natural water comes mainly from the leaching ofigneous and carbonates rocks. In areas where these sources are common, magnesium concentrations in water often ranges from 5 to 50 mg per litre. Magnesium is related to water hardness in thesame manner as calcium and it is also an essential nutrient forplant growth and development.

Magnesium is estimated complexometrically by titrating with EDTA using EBT indicator.

8. Electrical Conductivity (EC):

Conductivity is a measure of the conductance of an electric current in water. This is an easy measurement to make and relates closely to the total dissolved solids (mineral) content of water. The maximum contaminant level is 0.4 to 0.85 micro Siemens per centimetre. Treatment with reverse osmosis is effective for drinking water purposes.Specific Conductance or Conductivity as mentioned above, dissolved ionic substances can be measured by electrical conductance. On laboratory reports this may be shown as specific conductivity. Conductivity is reported as micromhos/cm.

Natural surface waters would be expected to have conductivities that measure from 50 to 1500. Where, well waters from saline ground water strata are used, the conductivity could run higher.The electrical conductivity or EC of a soil or water sample is influenced by the concentration and composition of dissolved salts. Salts increase the ability of a solution to conduct an electrical current, so a high EC value indicates a high salinity level.

Electrical Conductivity (EC) The amount of dissolved ions in the water is best represented by the parameter electrical conductivity. The classification of water for irrigation based on the EC values is as follows. Low Salinity Water (EC: 100-250 µS/cm): This water can be used for irrigation with most crops on most soils with little likelihood that salinity will develop. Medium Salinity Water (EC: 250 – 750 µS/cm): This water can be used if moderate amount of leaching occurs. Plants with moderate salt tolerance can be grown in most cases without special practices for salinity control. High Salinity Water (EC: 750 – 2250 µS/cm): This water cannot be used on soils with restricted drainage. Even with adequate drainage, special management for salinity control may be required and plants with good salt tolerance should be selected. Very High Salinity Water (EC: >2250 µS/cm): This water is not suitable for irrigation under ordinary condition. The soils must be permeable, drainage must be adequate, irrigation water must be applied in excess to provide considerable leaching and very salt tolerant crops should be selected. The classification of ground water samples collected from monitoring wells for was carried outin Table-3.

III. RESULTS AND DISCUSSIONS:

The physico-chemical parameters of the ground water which are essential for potable purpose like pH, EC, TDS, TH, Calcium, Magnesium, DO, were analysed and presented in Tables. 3. The sampling stations, source of the water from where sampling has been done is given in Table.1 and Indian Standards for drinking water specification: Bureau of Indian Standards[15] New Delhi 2015 is given in Table 2.

Table:2 Standards for quality of drinking water

Sr. No.	Parameter	Acceptable limit	Permissible limit
1.	Calcium (Ca)*mg/l*	75	200
2.	Dissolved oxygen (DO)	6.0	4.0
3.	Electrical Conductivity (EC)	1500 mmho/cm drinking (WHO)	2250 mhos/cm Irrigation
4.	Hydrogen Ion Concentration (pH)	6.5 to 8.5	No relaxation
5.	Magnesium (Mg) *mg/l*	30	100
6.	Total Dissolved Solids (TDS) mg/l	500	2000
7.	Total Hardness *mg/l*	200	600

Table -3: Critical parameter exceeding the permissible limit

Sr. No.	Parameter	BIS Permissible limit	No. of sample exceeding permissible limit		Percentage of sample exceeding permissible limit	
			Pre-Monson	Post Monson	Pre-Monson	Post Monson
1.	pH	6.5 to 8.5	00	00	00	00

2.	TDS	2000	02	01	11	05
3.	TH	600	07	04	39	22
4.	Magnesium	100	16	13	89	72
5.	Calcium	200	07	06	33	22
6.	EC	1500	06	06	33	33

Table: 4. Physico-chemical parameters of bore well and dug well in Vaijapur Tehsil of Aurangabad district

Sample sites	Temperature		pH		DO		EC µ Siemens		TDS mg/l		TH mg/l		Ca^{+2} mg/l		Mg^{+2} mg/l	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post
S1	30.3	25.4	7.35	7.10	6.25	6.50	480	215	353	142	147	98	56	34	98	59
S2	30.1	26.0	8.16	8.07	6.40	6.62	587	246	382	160	179	114	68	43	111	71
S3	29.8	25.6	8.55	8.43	6.17	6.43	580	350	378	127	136	82	51	31	84	51
S4	30.2	25.3	7.87	7.42	6.50	6.70	1244	1090	810	250	350	271	133	103	217	169
S5	29.9	26.0	8.21	7.74	6.30	6.42	2720	2450	1749	1350	1214	857	460	325	754	532
S6	29.7	26.1	7.92	7.35	6.61	6.80	1138	590	741	380	657	393	249	149	408	244
S7	29.8	25.9	8.30	7.76	6.23	6.65	573	950	373	230	229	136	87	51	142	84
S8	29.4	25.6	7.87	7.42	6.80	7.15	1305	750	453	325	405	271	135	110	245	167
S9	30.1	26.2	7.25	7.10	7.13	7.52	525	212	354	254	202	175	75	42	115	101
S10	29.7	25.4	7.90	7.81	6.37	6.58	665	270	433	350	286	207	108	78	177	129
S11	29.8	25.6	7.85	7.52	6.01	6.33	895	593	1117	897	985	879	427	376	457	384
S12	30.2	25.7	7.40	7.25	6.44	6.76	3980	2440	2505	1892	1329	1107	503	419	825	688
S13	30.1	25.5	8.35	8.21	6.72	7.02	1920	1690	1328	1100	250	207	95	78	155	129
S14	29.4	25.8	8.25	8.00	6.15	6.38	2531	1985	1543	987	325	258	123	117	104	98
S15	29.6	25.4	7.75	7.62	6.21	6.60	744	650	485	350	357	279	135	106	222	173

S16	29.7	25.9	8.21	7.51	6.46	6.77	1918	1780	589	1387	786	579	298	219	488	359
S17	30.3	26.2	7.95	7.76	6.54	6.89	419	328	272	214	929	571	352	216	577	444
S18	29.7	25.7	7.35	7.23	6.32	6.67	4120	3190	2690	2350	1521	986	576	350	945	532

Table-5: Classification of water samples on the basis of conductivity values

Sr. No.	**Conductivity range µS/cm**	**Classification**	**No. of sample**	**Percentage of samples**
1.	100-250	Low Salinity	00	00
2.	250-750	Medium Salinity	08	44
3.	750 – 2250	High Salinity	06	33
4.	>2250	Very High Salinity	04	22

3.1. Physical Parameters

3.1.1. Temperature:

The values of temperatures during pre-monsoon season vary in range 29.4 ^{0}C to 30.3 ^{0}C and in past monsoon season it is found to be in the range 25.3 ^{0}C to 26.1^{0}C. The minimum and maximum values recorded in the same field stations, as shown in Table 4. From the Table 4 it is observed that the temperature values are higher during pre-monsoon season than post monsoon season due seasonal temperature variation.

3.1.2. Electrical Conductivity:

The Electrical Conductivity of the sampling waters for pre-monsoon seasons is ranging from 480 to 4140 µS/cm and for post-monsoon seasons it is in the range of 215 to 3190 µS/cm. The values of minimum and maximum have recorded in the same field stations, given in Table. 4. The EC values from all the sampling stations recoded at higher in pre monsoon season than post monsoon season. The electrical conductance values of sampling sites S13, S14 and S16 are above acceptable limits (1500 µS/cm) and at sites S5, S12, S13, S14, S16 and S18 the values are are higher than permissible limit in both pre and post monsoon seasons[14]. The electrical conductance values (Table 5) suggest that in pre-monsoon season 33% water samples are in the category of medium water and only 17% samples shows very high water salinity.

3.2. Chemical Parameters

3.2.1. pH:

The pH values of study area are ranged from 7.35 to 8.55during pre-monsoon and 7.10 to 8.35 during post monsoon. The minimum and maximum values have recorded during post and pre monsoon seasons at the same field stations. The pH values of all the stations indicating alkaline condition and within permissible limits (6.5 to 8.5 pH) as per the Indian Standards, given in Table. 2. The pH values of the sampling stations show that higher values are recorded during pre-monsoon season than post monsoon due to dilution effect. (Table 4,).

3.2.2. Dissolved Oxygen:

In pre-monsoon season the Dissolved Oxygen of the sampling sites is ranging from 6.42 mg/l to 7.52 mg/l and this was 6.01 mg/l to 7.13 mg/l during summer. The minimum and maximum values recorded in the same field stations, is shown in Table.4. The Dissolved Oxygen concentration from all the stations is recorded at more or equal during pre-monsoon season than post monsoon.

3.2.3. Total Dissolved Solids:

The Total Dissolved Solids of the samples in pre-monsoon season is ranging from 272 mg/l to 2690 mg/l and 450 mg/l to 1600 mg/l in post monsoon season. The minimum and maximum values have recorded in the same field stations and data given in Table. 4

During the pre-monsoon season it is observed that the half of the sampling stations are found to be in acceptable limit while remaining sampling sites records the TDS value above acceptable limit except the sites S12, and S18 whose TDS value is above permissible limit. However the values are within the maximum permissible limits (2000 mg/l). It is observed that the TDS values are recorded at higher during pre-monsoon than post monsoon season.

3.2.4. Total Hardness:

During pre-monsoon season the Total Hardness expressed as $CaCO_3$ of water samples under study is recorded in the range 147 mg/l to 1521 mg/l and its value in post monsoon season is found to be 98 mg/l to 1107 mg/l. The minimum and maximum hardness has recorded from the same sampling stations, are given in Table. 3. It is noticed that the concentration of Total Hardness recorded in pre monsoon season is more than the post monsoon season. The Total Hardness of only three water samples (S1, S2, S3 and S9) in pre-monsoon is found in acceptable limit and all other sampling sites recorded the TH above acceptable limit except S5, S11, S12, S16, S17 and S18 whose TH is recorded above the permissible limit. Near about same trend is followed by post monsoon season. It is observed that the Total Hardness recorded in pre monsoon season is more than the post monsoon season.

3.2.5. Magnesium:

The values of Magnesium have been recorded from the study area is ranging from 84 mg/l to 945 mg/l in Pre-Monsoon season and 51 mg/l to 688 mg/l during summer expressed as Mg. The minimum and maximum values recorded from the same field stations, were discussed in Table. 4. From Table 4 it is observed that the concentrations of Magnesium are recorded at higher during pre-monsoon than post monsoon season. All the water samples show the Magnesium concentrations more than acceptable and permissible limits.

3.2.6. Calcium:

In Pre-Monsoon season the Calcium values from the sampling stations were ranging from 56 mg/l to 576 mg/l and this was 34 mg/l to 376 mg/l during Post Monsoon season. The minimum and maximum values recorded from the same field stations, were discussed in Table 4. The sampling station of S1, S2, S9 and S3 recorded Calcium values within acceptable limit while sampling station S4, S8, S10, S14, S15 shows the values above acceptable limit and Calcium values of sampling station S5, S6, S11, S12, S15 and S16 are found to be above permissible limit as shown in Table.4. The Calcium values are recorded at higher concentration during pre-monsoon than post monsoon season.

3.3. Correlation Matrix of Various Physicochemical Parameters During Pre - as well as Post-Monsoon

The systematic studies of correlation and regression coefficients were found to be useful to measure the overall groundwater. Pearson's correlation coefficient (indicated 'r') is normally useful to find the relationship between the two variables. The parameters having r > 0.5 or < - 0.5 are considered important. The correlation coefficients of the physicochemical parameters data of pre-monsoon as well as post-monsoon have been given in Table-5 and Table-6, respectively.

Table-5: Correlation Matrix between Water Quality Parameters: Pre-Monsoon

	pH	DO	EC	TDS	TH	Ca^{2+}	Mg^{2+}
pH	1						
DO	-0.2880	1					
EC	-0.2007	-0.0803	1				
TDS	-0.2465	-0.1798	0.9552	1			
TH	-0.3016	-0.1554	0.7343	0.7532	1		
Ca^{2+}	-0.2964	-0.1902	0.7099	0.7453	0.9973	1	
Mg^{2+}	-0.3143	-0.0936	0.7364	0.7343	0.9884	0.9764	1

Table-6: Correlation Matrix between Water Quality Parameters: Post-Monsoon

	pH	DO	EC	TDS	TH	Ca^{2+}	Mg^{2+}
pH	1						
DO	-0.2882	1					
EC	-0.2008	-0.0801	1				
TDS	-0.2465	-0.1799	0.9550	1			
TH	-0.3016	-0.1556	0.7341	0.7536	1		
Ca^{2+}	-0.2965	-0.1903	0.7098	0.7455	0.9971	1	
Mg^{2+}	-0.3142	-0.0937	0.7367	0.7341	0.9885	0.9765	1

In both the pre as well as postmonsoon periods, strong positive correlations exist between TDS with EC (0.9552), Ca^{2+} with TH (0.9884) and Mg^{2+} with Ca^{2+}(0.9764) which represents that these ions contribute considerably to TDS, TH in the groundwater of this study region. The parameters that moderately correlated with each other were, TH with EC (0.7343) and TDS (0.7532), Ca^{2+} with EC (0.7099) and TDS (0.7453), and Mg^{2+} with EC (0.7364) and TDS. The pH and DO is negatively correlated with all the other physico-chemical parameters namely, EC, TDS, TH Ca^{2+} and Mg^{2+}.

IV. CONCLUSION

The physico-chemical parameters of the ground water have been assessed in order to study the pre-monsoon and post monsoon effect on the quality of water in Vaijapur Tehsil of Aurangabad district in the current study area of eighteensampling stations. Based on the study some results showed that the water quality is poor and majority of the waters doesn't meeting the standards as per Indian Standards for drinking water (BIS: 10500, 2015). It is observed that the water quality parameters recorded at higher concentration during pre-monsoon season than post monsoon season may be due to the influence of monsoon rains. The pH of all the study stations is at alkaline condition but within the range of 6.5 to 8.5. It is observed that the TDS from the majority sampling stations is recorded within acceptable limit with some exceptions during both post and pre monsoon seasons.

The TH is recorded in majority the study stations is more than the permissible limit and some sites recorded more than the maximum permissible limit for both pre and post monsoon seasons. It is noticed that the Calcium concentration in majoritysample stations are less than the permissible limit for both pre and post monsoon seasons. The Magnesium values nearly all the samples records concentration more than the permissible limit during pre and post monsoon seasons. From Table 4 it is observed that electrical conductance values suggest that 33% water samples were in the medium water salinity category. Table 5 and 6 shows the strong positive correlation TDS with EC, Ca^{2+} with TH and $Mg^{2+}$with Ca^{2+}. The pH and DO is negatively correlated with all the other physico-chemical parameters namely, EC, TDS, TH Ca^{2+} and Mg^{2+}.

Declarations

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Synthesis, Characterization and Antimicrobial study of Manganese (II) Complex of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl) prop-2-en-1-one

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ABSTRACT

The synthesis of Manganese (II) metal complex **1** has been synthesized by using novel (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one ligand. The ligand was prepared by the Claisen-Schmidt condensation method of 2,6-dihydroxy acetophenone and 2-furaldehyde. The structure of the complex has been characterized by the analytical data, conductivity measurement, magnetic moment, UV-Vis spectra, and thermal studies. Analytical data shows 1:2 stoichiometry and the magnetic moment, TG-DTA suggests that Mn(II) complex has octahedral geometry. The presence of coordinated water molecules in Mn (II) complex **1** is confirmed by thermal studies. The conductivity data revels that the complex is non electrolyte. Antimicrobial study of complex with selected bacterial strain and fungal strain carried out and the results have been compared with commercial standards. The Mn (II) complex **1** shows moderate to good Antibacterial and Antifungal activity.

Keywords: Antimicrobial activities, TG-DTA study, Physico-chemical property, Magnetic Susceptibility and Conductivity.

I. INTRODUCTION

Chalcones and their metal complexes play an important role in modern coordination chemistry. These compounds possessing novel structural features, interesting spectral and magnetic properties, have been observed of intensive research due to their importance in medical, agriculture, analytical, biological and industrial fields. In recent years a number of β-dicarbonyl compounds in which the carbonyl function bonded to olefinic linkage have gained considerable importance mainly because of the fact that such compounds are structurally related to the active chemical constituents of several traditional medicinal plants[1-3].

Chalcones constitute an important group of natural products, which has two aromatic rings joined by α, β unsaturated carbonyl system. The name chalcone is given by Kostanecki and Tambar [4]. The metal complexes possess interesting biochemical properties, such as antitumor, antioxidant, and antimalerial, anti-fungal and antimicrobial activities [5]. The magnetic moment, TG-DTA supports the octahedral geometry of the metal complex of chalcone.

II. MATERIALS AND METHODS

2.1. Synthesis of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl) prop-2-en-1-one ligand:

The reagents used for preparation of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl) prop-2-en-1-one are of A.R. grade. A mixture of 2,6-dihydroxy acetophenone (0.01 mol) and 2-furaldehyde (0.01 mol) are dissolved in ethanol (20 mL) and then solution of potassium hydroxide 10 mL (15%) were added to it. The mixture was stirred for overnight. The progress of the reaction was monitored by TLC. It was then poured on ice cold water and acidified with dilute HCl. The coffee brown solid was precipitates, filtered and washed with water and recrystallized from ethanol to give the chalcone [6].

2.2. Synthesis of Metal Complex:

The solution of 0.02 mole of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one was taken in round bottom flask containing 30 ml of anhydrous methanolic solution and boiled for 10 minutes. A hot solution of 0.01 mole, of Manganese Acetate in 20 ml of methanol was added drop wise to the solution of the chalcone of 5-methylfurfural to this reaction mixture, 10% alcoholic ammonia was added up to slightly alkaline pH. The complex was precipitated at 8 pH range. The pH 8-10 range was definite for these complexes [7]. The content was stirred on magnetic stirrer for one hour. The solid metal complex separated out and washed with methanol three to four times. The melting point of the complex was determined by Thiele's melting apparatus. The reactions of formation of Mn (II) complex **1** is shown in **Figure-1**.

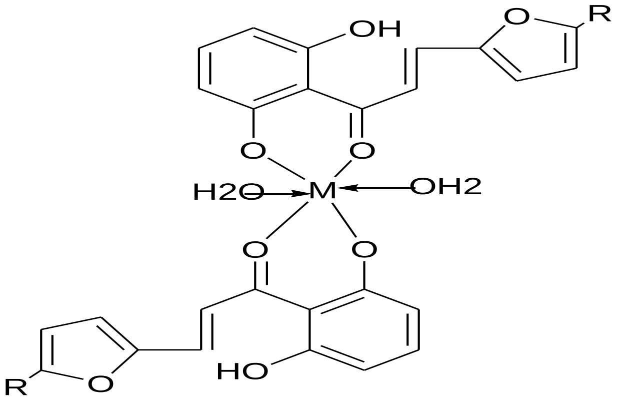

Figure-1: Metal complex **1** of Manganese (II) with (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one
R= -H, M= Mn(II)

III. RESULTS AND DISCUSSION

3.1. Physical parameters:

Metal complex **1** of Manganese (II) with (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one was brown in color. The complex was precipitated at 8 pH range, having Melting point 320°C. The complex is insoluble in water and soluble in DMSO, DMF [8].

3.2. CHO analysis:

The carbon, hydrogen, oxygen, Manganese metal percentage in Mn (II) complex **1** of chalcone measured at SAIF Cochin, Kerala. The calculated and measured values of CHO analysis are matching and are given in the **Table-1**.

Table-1: Study CHO analysis of synthesized Mn (II) complex **1**

Metal complex	**Chemical formula**	**Mol. Wt.**	**Elemental analysis : % found (calculated)**						
			C	**H**	**N**	**O**	**S**	**X(Br)**	**M**
Mn (II) Complex	[$C_{26}H_{22}O_{10}Mn$]	549	56.84 (64.33)	4.03 (4.57)	-	29.12 (19.78)	-	-	9.99 (11.32)

3.3. Magnetic susceptibility, solution conductivity and electronic absorption spectral data Magnetic susceptibility:

The magnetic moment of Mn (II) complex **1** in the present investigation are in the range which is almost close to the spin only value of 5.92 B.M. These values are in good agreement with the moment reported for mononuclear high spin octahedral Mn (II) complex **1** by earlier workers [9].

Table-2: Study magnetic susceptibility, solution conductivity and electronic absorption of synthesized Mn (II) complex 1 of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one

Mn(II) Complex	**Molar Conductance Ohm^{-1} cm^{2}mol^{-1}**	**μ_{eff} (B.M.)**	**Absorption Maxima cm^{-1} (nm)**		
			$^6A_{1g} \rightarrow ^4T_{2g}$ (G)	$^6A_{1g} \rightarrow ^4A_{1g}$ (G), ^4E_g	Charge Transfer
1	2.12	5.86	24937(401)	28571(350)	32154(311)

Solution conductivity and electronic absorption spectral data:

The solution conductivities of 10^{-3} M solution of metal complex in DMSO were measured on EQUIPTRONICS digital conductivity meter EQ - 660 with 20 μΩ to 200 μΩ at 298K temperature. They are insoluble in water and soluble in DMSO, DMF. The low solution conductivity of 10^{-3} M solutions of Mn (II) complex **1** in DMSO indicates their non-electrolytic nature.

Figure-2.

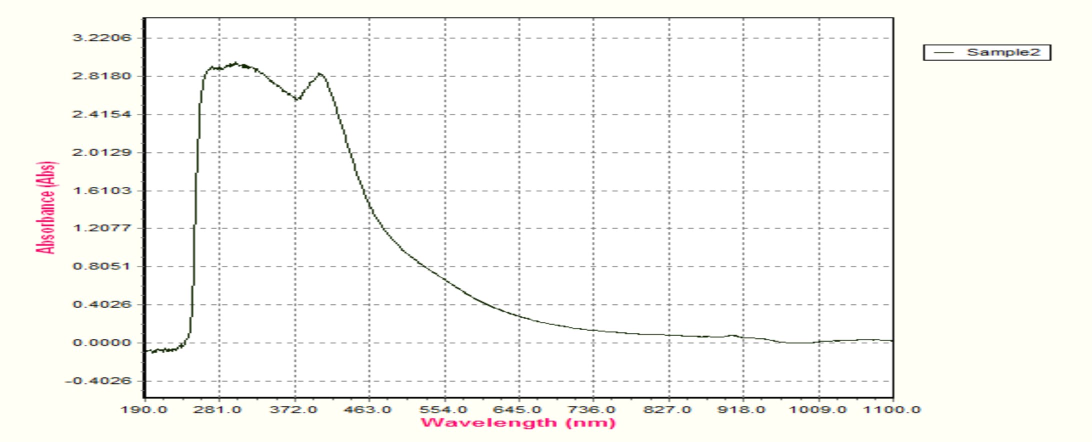

Figure-2: Electronic absorption spectrum of Mn (II) complex **1** of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one

The electronic absorption spectra of Mn(II) complex **1** **Table-1:** Study CHO analysis synthesized Mn (II) complex **1** were showed three bands at 19,120 to 25000 cm^{-1}, 25125 to 27700 cm^{-1}, and 28993 to 30581 cm^{-1} assignable to $^6A_{1g}\rightarrow{}^4T_{2g}$(G), $^6A_{1g}\rightarrow{}^4E_{1g}$ or $^6A_{1g}\rightarrow{}^4T_{1g}$ (G) and charge transfer indicating octahedral geometry around the metal ion [10-11].

3.4. Infra-red spectrum:

The IR spectrum of α, β-unsaturated carbonyl group has characteristic bands of chalcone at prominent bands between 1625 to 1650 cm^{-1}. The characteristic peaks in infra red spectrum give the presence of particular functional group. The region at which other absorption bands appear depends on the type of aromatic / hetero-aromatic rings as well as the substituent present on these rings. The infrared spectrum of Mn (II) complex **1** of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one was recorded on a Perkin- Elmer Spectrum RX-IFTIR Spectrophotometer in the range 4000-400 cm^{-1} (**Table-2**) using potassium bromide pellet at CIL, Chandigarh, Punjab. The stretching frequency of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one is represented in table number (2) and the IR spectrum in **Figure-3.**

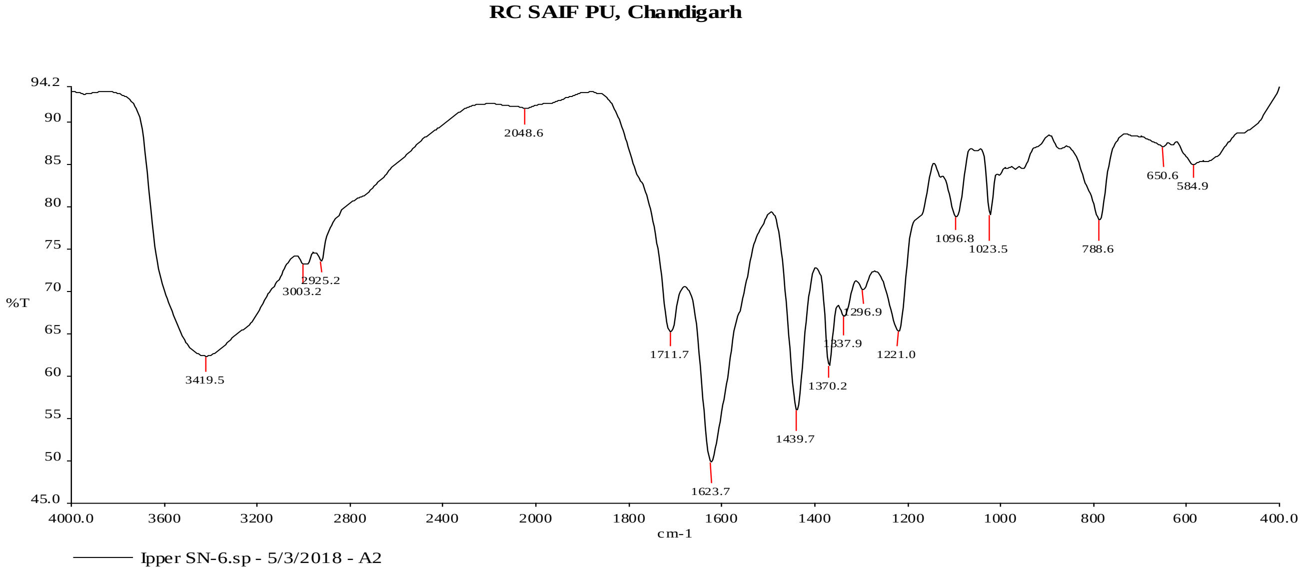

Figure-3: IR spectrum of Mn (II) complex **1** of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one

Table-3: IR spectral data of Mn (II) complex **1** of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one

Molecule	υ(OH) Enolic	(-CO-CH=CH-) α,β-unsaturated carbonyl group	Carbonyl group (-C=O in pyron ring)	(C-O-C) Stretching Frequency	(C=C) Stretching Frequency	Aromatic Ring (C=C) Stretching Frequency	Ar-H Stretching Frequency	$-NO_2$ stretching frequency
Ligand	3420	1652	-	1096	1575	1457	2920	-

3.5. Thermal analysis Mn (II) complex 1 of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one

The simultaneous thermo gravimetric, differential thermal analysis of Mn (II) complex **1** of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one was performed in an inert nitrogen atmosphere on Perkin Elmer STA

6000 at SAIF, Cochin, Kerala. The heating rate was 10˚/min and flow rate of nitrogen 50 ml/min. The reference substance used was α Al_2O_3 in platinum crucible and sample weighted in the range of 4-12 mg. The thermogram of Mn (II) complex (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one is presented in figure-2. This curve reveals that there is presence of lattice as well as coordinated water in the complex.

The thermogram of Mn (II) complex **1** of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one shows first weight loss at 60˚C indicating presence of lattice water. The second loss due to the coordinated water molecule liberated, from the complex. The anhydrous compound undergoes four step decomposition. In the first two steps, decomposition occurs due to loss of non-coordinated part of ligand. The first step shows decomposition within a temperature of range from 240-330˚C with mass loss of 39.29%, which is supported by a sharp an endothermic peak at 259˚C in DTA curve. It may be due to half decomposition of non-coordinated part of ligand. In the second step, decomposition observed at about 350-400˚C with the weight loss of 33.78% in TG curve. This is supported by an endothermic peak at 380˚C. This may be due to decomposition of remaining coordinated part of ligand. Beyond 600˚C there is a formation of MnO as indicated by constant weight loss of in TG-DTA curve.

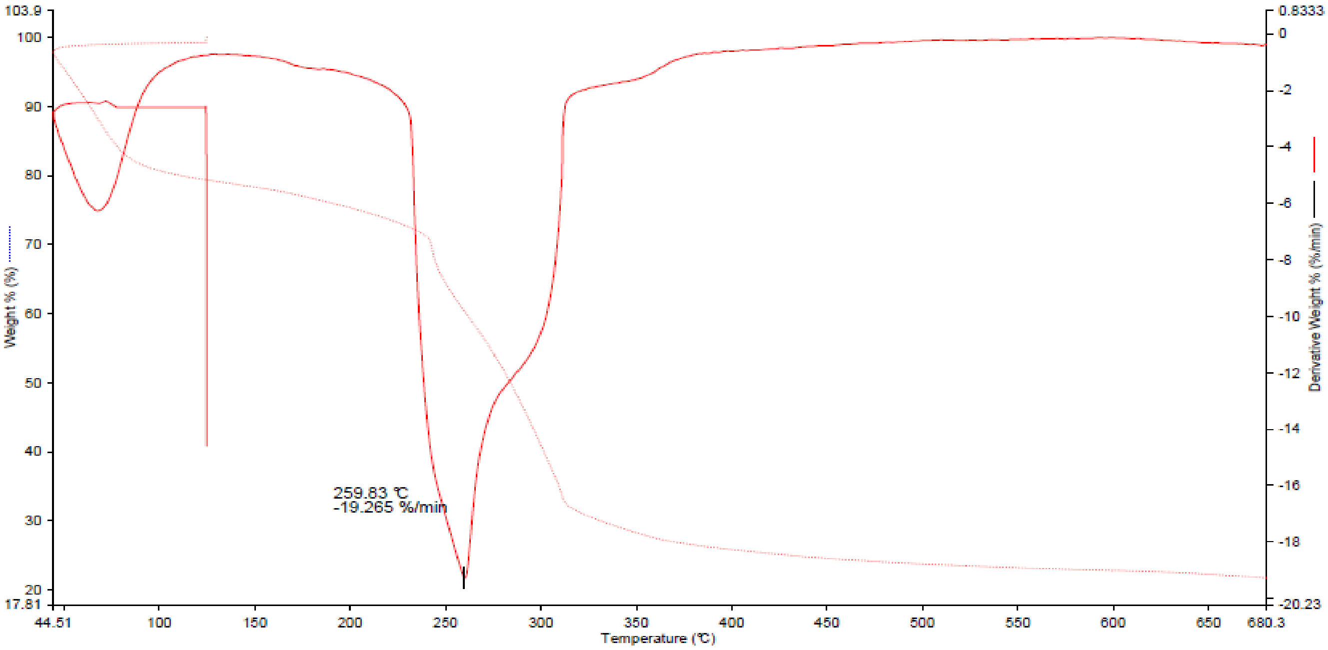

Figure-4: TG-DTA curve of Mn (II) complex **1** of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one

3.6. Thermodynamic and Kinetic Parameters

Akahira [12], first introduced that decomposition and kinetic studies of thermal reactions are useful in determining thermodynamic and kinetic parameters like free energy, entropy change, activation energy, pre-exponential factor. Thermal decomposition studies of materials are useful in predicting thermal stability (**Table-3**).

The negative values of the entropy of activation (ΔS) indicate that the metal complex is thermally stable. ΔG is positive for the complexes revealing that the free energy of the final residue is higher than that of the initial complex, and all decomposition steps are non-spontaneous processes. Also, the value of free energy of activation, ΔG increases significantly for the subsequent decomposition stages of a given complex [13]

Table-3: Thermodynamic and Kinetic Parameters of Mn (II) complex 1 of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one

Metal complex	**Method**	**Step**	**Decomp. Temp.**	**Order of Reaction**	**Ea(KJ mol^{-1})**	**ΔS(KJ mol^{-1})**	**ΔG(KJ mol^{-1})**	**Z (S^{-1})**	**Correlation Coefficient (r)**
Mn (II) complex	H-M C-R	I	300	0.5	26.84 21.75	-153.91 -97.64	37.80 28.70	112973.9 98100737	0.907 0.989
	H-M C-R	II	450	0.5	6.73 4.09	-172.89 -83.66	19.06 9.96	11545.4 527754555.2	0.999 0.997

3.7. Antimicrobial activity:

Antimicrobial activity was assayed by cup plate agar diffusion method by measuring inhibition zones in mm. In vitro antimicrobial activity of all synthesized compounds and standard have been evaluated against strains of The fungal toxicity of Mn (II) complex **1** was studied *in vitro* against *Aspergillus niger* ATCC 16404, *Saccharomyces cerevisiae* ATCC 9763, *Candida albicans* ATCC10231 fungal pathogens at fixed 1% concentration.

The antibacterial activity of Mn (II) complex **1** was studied, for evaluating antibacterial activity Gram positive and Gram negative bacterial pathogens were used. *Staphylococcus aureus* ATCC 6538*, Bacillus megaterium* ATCC 2326, *Bacillus subtilis* ATCC 6633 were Gram positive pathogens used in this study. *Escherichia coli* ATCC8739*, Salmonella typhi* ATCC9207*, Shigella boydii* ATCC 12034*, Enterobacter aerogenes* ATCC13048*, Pseudomonas aerogenosa* ATCC9027, *Salmonella abony* NCTC6017 were the Gram-negative pathogens used in this study.

From the results of antimicrobial activity of ligands and complex it is clear that the complex shows enhanced activity than ligand. The increase in antimicrobial activity is due to faster diffusion of metal complexes as a whole through the cell membrane or due to the combined activity of the metal and ligands [14].

IV. CONCLUSION

The Mn (II) complex **1** was colored, soluble in most of the organic solvent. The stoichiometry ratios of the metal complexes are obtained has been found to be 1:2.Solution conductivity of this metal complex reveals non-electrolytic nature. The electronic spectral data, magnetic moment, TG-DTA suggests that Mn (II) has Octahedral geometry. The CHO analysis gives C, H, and O percentage in the metal complex. From the antimicrobial activity of ligand and complex it is clear that the complex shows enhanced antimicrobial activity than ligand.

V. ACKNOWLEDGEMENT

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Chalcone Biological Significance and Synthesis A Review

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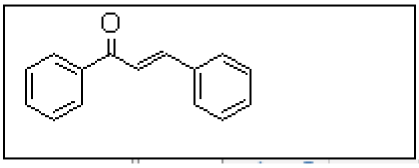
ABSTRACT

Chalcone is an aromatic ketone that forms the central core of many important biological compounds. The biogenetic building blocks of favonoids and isofavonoids, which are abundant in plants, are called chalcones. Chalcones are active lead molecules in the search for new drugs in medicinal chemistry. Here, we review the biological significance and synthesis of natural and synthetic chalcones.

Keywords: Chalcones, Antibacterial activity, Antidiabetic activity, Claisen–Schmidt condensation, Witting reaction

I. INTRODUCTION

Chalcones are the building blocks of several natural compounds.[1-2] The word "chalcone" is derived from the Greek word "chalcos", meaning "bronze", which results from the colors of most natural chalcones.[3] Chalcones are 1, 3-diaryl-2-propen-1-ones with various substitution patterns that exist in cis and trans isomeric forms, with the trans form being thermodynamically advantageous.They are represented as



On their aryl rings, they have different substituents. Some of these substitutes affect the biological properties that chalcones have. However, the key pharmacophore is believed to be the, α,β -unsaturated ketone moiety.[4] Naturally occurring chalcones and their synthetic analogues have been documented to comprise a wide range the biological activity. They are therefore high in demand as the starting components in the synthesis of a number of different heterocyclic compounds. Chalcones have been utilized as medicine for thousands of years to treat a variety of pharmacological conditions through the use of plants and herbs. There are many chalcone-containing drugs that have received clinical use approval. Metochalcone was previously employed as a choleretic medication, whereas sofalcone was used as an antiulcer and mucoprotective medicine (Figure 1)[5, 6]

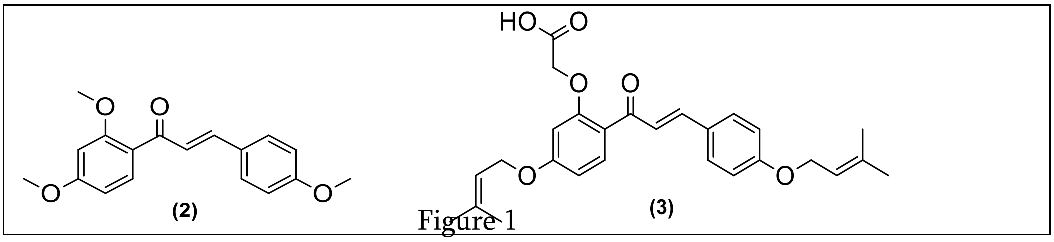


Figure 1

Many novel compounds with chalcone scaffolds are reported each year since most chalcones are easy to produce. The majority of them are employed to generate new, effective medications based on the chalcone skeleton after being subjected to biological activity.[7]

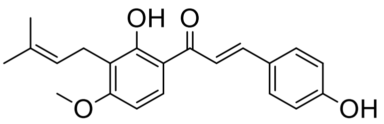
II. BIOLOGICAL SIGNIFICANCE:

Chalcones as antibacterial agents:

Kazuhiro Sugamoto *et al* reported chalcones derivatives (1) and (2) bearing prenyl or geranyl groups and their antibacterial activity was assessed. All compounds demonstrated good antibacterial activity against Gram-positive bacteria, with the prenyl group contributing to an increase in antibacterial activity.[8]

Hybrids of chalcone metronidazole (3) were constructed by Amit Anthwal *et al* and tested for anti-trichomonas efficacy against both metronidazole susceptible and resistant strains (3). Some substances were discovered to be more effective than metronizole against resistant strains.[9] Kant *et al* screened the antibacterial, antifungal, and antiplasmodial activities of chalcones (4).

Some of the compounds shown good activity against *E.coli, P. aeruginosa,* and *S. boydii* with MIC 12.5 g/mL and demonstrated substantial inhibitory activity against *S. aureus* and *E. faecalis* with MIC 6.25 g/mL, which were comparable to the standard medication ciprofloxacin.[10] The antibacterial and antibiotic activity of compound (5) with a furan ring against multi resistant strains of *E. coli* and *S. aureus* has been studied by C.A.N. Ferraz. By exhibiting synergistic effects with all the antibiotics and lowering the necessary concentrations, target chalcone altered the antibiotics' ability to combat multi-resistant strains of *S. aureus.*[11]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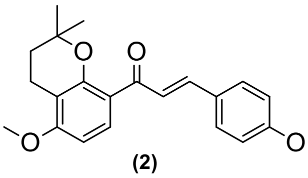
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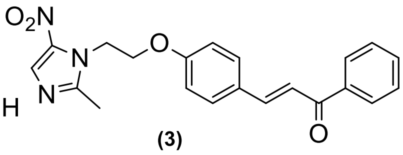
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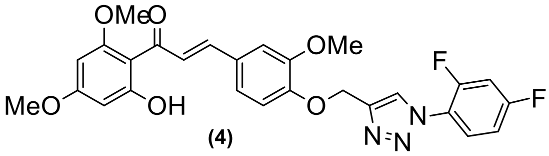
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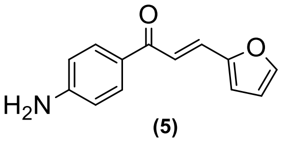
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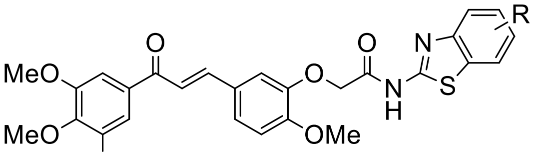
Chalcones as anticancer agents:

Chalcone-amido benzothiazole conjugates (6) were tested for their anticancer efficacy against five different human cancer cell lines by A. Kamal *et al.* Some of these substances have strong anticancer properties.[12] Wamg *et al* reported compound (7) as novel HIF-1 inhibitor and may possess potential for cancer treatment.[13] Chalcone polyamine conjugates (8) found to possess a marked cytotoxic activity.[14]

The anti-cancer potential of compounds (9) was examined, and some of these conjugates with hydroxyl and methoxy groups demonstrated substantial action with an IC_{50} value of 1.3 and 1.2 mM against MDA MB-231 cells. Detailed biological study showed that they inhibit tubulin assembly.[15] Yu Wang *et al* reported compound (10) as thioredoxin reductases inhibitors. Most of them showed potent anticancer activity than xanthohumol.[16]



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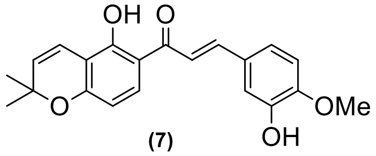

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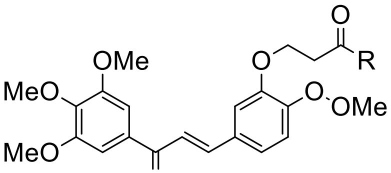

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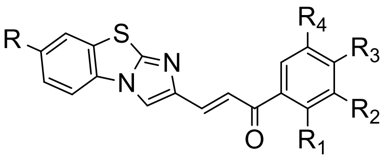

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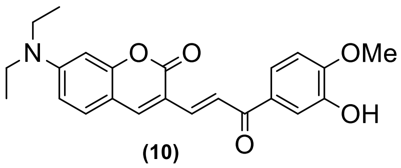
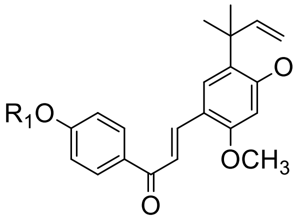


(10)

Chalcones as antidiabetic agents:

Compounds (11) were shown to exibit significant protein tyrosine phosphatase 1B (PTP1B) inhibitory activities. Allyl groups in the B ring of licochalcones produced pronounced inhibitory effects.[17] Chalcone-triazole derivative (12) was tested for inhibition effect against rat intestinal -glucosidase and in vitro anticancer activity on human cancer cell lines.[18] Inhibiting -glucosidase, chalcones and bis-chalcones (13) and (14) significantly decreased the glucose level in HepG-2 cells.[19] By lowering inflammation and oxidative stress, isoliquiritigenin (15) prevented HG-induced hypertrophy, fibrosis, and apoptosis in H9c2 cells and found as a prospective drug for the therapy of diabetic cardiomyopathy.[20]



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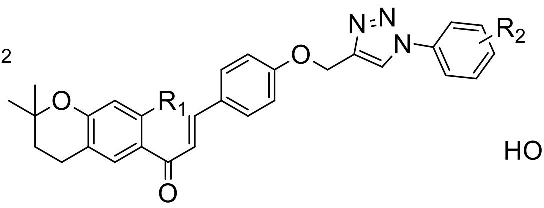

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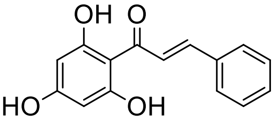

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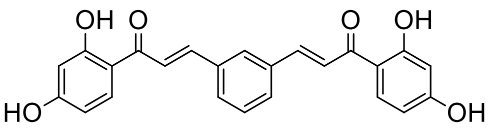

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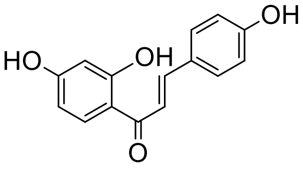
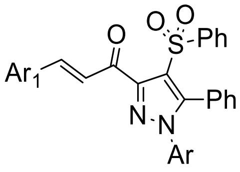


(15)

Chalcones as anti-inflammatory agents:

Ekhlass Nassar *et al* studied compounds (16) for the anti-inflammatory activity and ulcerogenic effect and were found some of the obtained products possessed a significant anti-inflammatory activity.[21] A number of compounds (17) were developed by Nitesh Tamang *et al* and their cytotoxicity and anti-inflammatory effects were evaluated. By preventing the synthesis of PGE2, one molecule was shown to have the highest anti-inflammatory activity, while three other compounds were shown to have significant cytotoxicity.[22]

Novel allylated or prenylated mono-carbonyl analogues of curcumin(18) were produced by Zhiguo Liu *et al* and their anti-inflammatory properties in RAW 264.7 macrophages were investigated. The majority of them successfully reduced TNF-a and IL-6 expression.[23] K.V. Sashidhara *et al* evaluated novel chalcones with biscoumarine moiety (19) and (20) for their antioxidant and anti-inflammatory properties. The examined substances demonstrated significant scavenging activity.[24]



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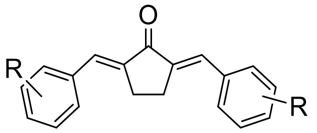

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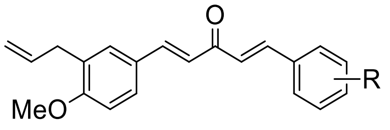

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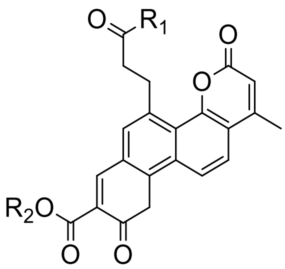

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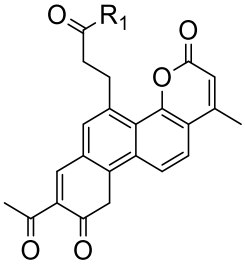
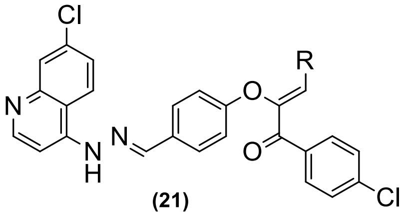


(20)

Chalcones as antimalerial agents:

Chloroquine-based hybrid chalcones (21) were shown to be effective against the 3D7 and K1 strains of *P. falciparum* in vitro by K. V. Sashidhara *et al* Most of the compounds had comparable antimalarial activity to chloroquine against the 3D7 strain and considerable antimalarial activity against the K1 strain.[25] Michael Eder de Oliveira *et al* were examined nine 4-methoxychalcone derivatives (22) for their ADMET properties and shown to have antimalarial activity against the *P. falciparum* chloroquine-resistant clone W2.[26]

Chalcones amides (23) and (24) were reported by F. J. Smit *et al* as being anti-malarial against strains of *P. falciparum*, and the action was discovered to depend on the chain length.[27] H. Kumar *et al* synthesized quinoline-containing chalcones (25) and tested them for DNA cleavage activity. According to the findings, the compound can effectively cleave pBR 322 DNA and can be used to target nucleic acids.[28]



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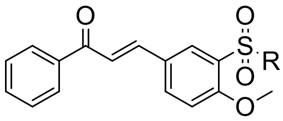

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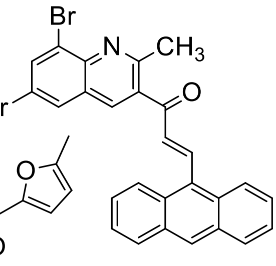

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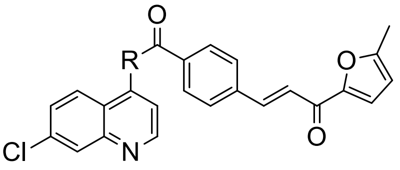

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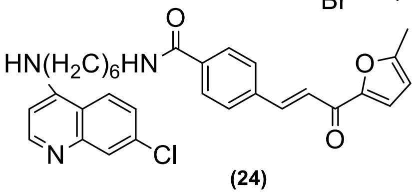
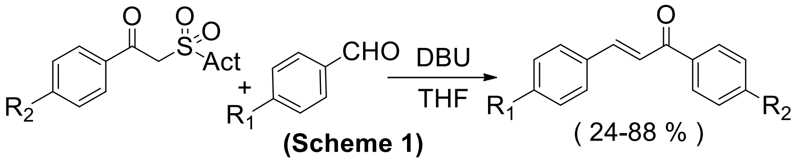


(24)

III. METHODS OF SYNTHESIS

A. Kumar approach (2010)[29]

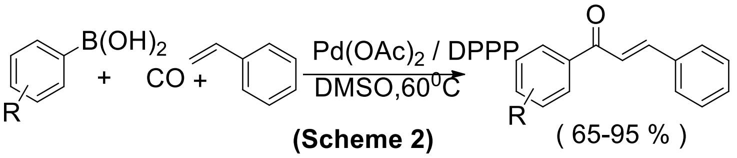
A. Kumar's method reveals an efficient direct Julia-Kocienski olefination method for the preparation of chalcones deivatives (3) in tetrahydrofuran using 2-(Benzo[d]thiazol-2-ylsulfonyl)-1-phenylethanones (1) and benzaldehydes (2) in the presence of DBU **(Scheme 1).**



(Scheme 1)

X. Wu approach (2010)[30]

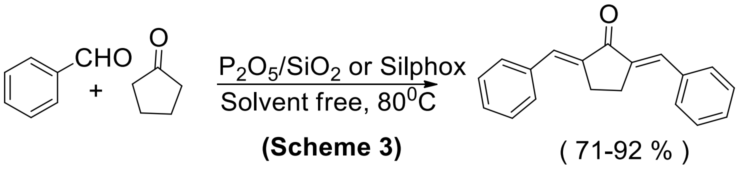
A palladium-catalyzed oxidative carbonylative coupling process was used to synthesize chalcone using arylboronic acid and styrenes. The reactions require mild conditions and air act as the terminal oxidant reagent **(Scheme 2).**



(Scheme 2)

A. Hasaninejad approach (2010)[31]

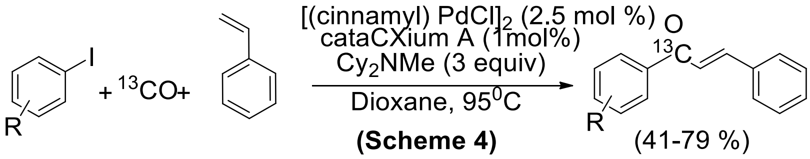
A. Hasaninejad approach developed silica supported phosphorus pentoxide or silicaphosphinoxide catalyst for reaction of benzaldehyde and cyclopentanone under solvent free condition. This protocol provides bischalcone derivatives, which possess important biological activities, in good yields **(Scheme 3).**



(Scheme 3)

P. Hermange approach (2011)[32]

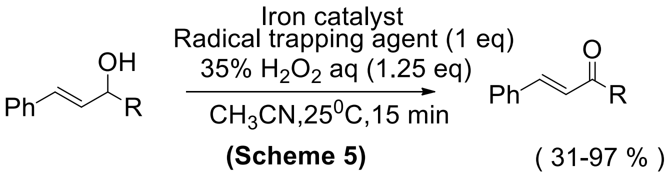
P Hermange approach developed cinnamyl palladium chloride catalyst for the carbonylative Heck reaction of styrene and various aryl iodides to provide chalcones derivatives in dioxane at 80°C. Isotope labeling incorporating ^{13}CO was also established **(Scheme 4).**



(Scheme 4)

S. Tanaka approach (2014)[33]

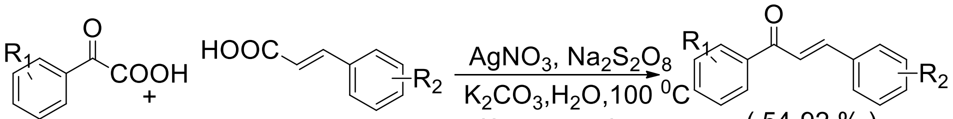
S. Tanaka developed a productive method for creating chalcone derivatives by oxidising allylic alcohols using hydrogen peroxide and iron-picolinate catalysts in acetonitrile at 25°C **(Scheme 5).**



(Scheme 5)

N. Zhang approach (2015)[34]

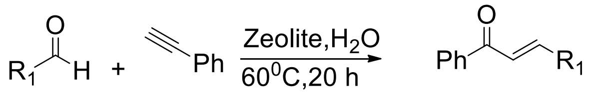
The K. Hu strategy outlines the development of a coupling reaction between cinnamic acid and keto acids at 100 °C in water. The procedure allows access to highly valuable chalcones derivatives for pharmaceutical use **(Scheme 6).**



(Scheme 6)

M. Naresh approach (2016)[35]

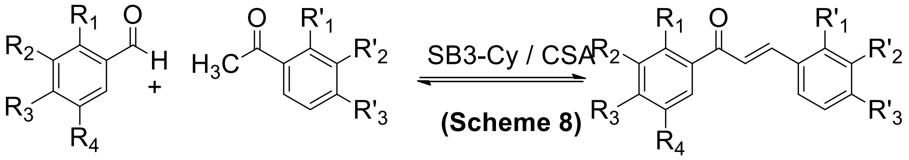
M. Naresh approach explains tandem hydration / condensation of alkynes and aldehydes to afford chalcones. In this study, alkynes were reacted with aldehydes in the presence of H zeolite, yielding good results **(Scheme 7).**



(Scheme 7) (59-96 %)

M. Tiecco approach (2016)[36]

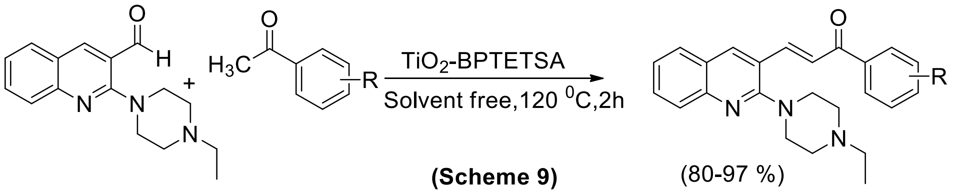
Use of deep eutectic solvent as green and reusable reaction media has been proposed by Matteo Tieccoet et al for the construction of chalcone derivative via Claisen–Schmidt condensation with mild condition and excellent yields **(Scheme 8).**



(Scheme 8)

A. Murugesana approach (2017)[37]

A. Murugesana approach describes TiO_2-BPTETSA promoted aldol condensation between piperazine bearing quinoline-3-carbazide moiety and several acetophenones. The protocol afford quinoline chalcones with piperazine moiety under solvent free condition at 120°C **(Scheme 9).**

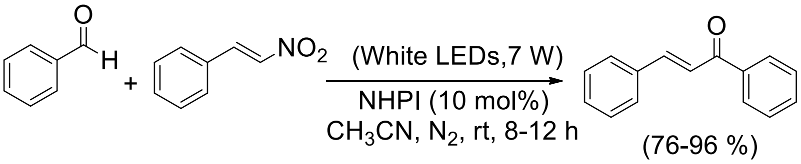


(Scheme 9)

S. Tripathi approach (2018)[38]

S. Tripathi described visible light as a catalyst to promote reaction between various benzaldehyde and β-nitrostyrenes at room temperature to form chalcones

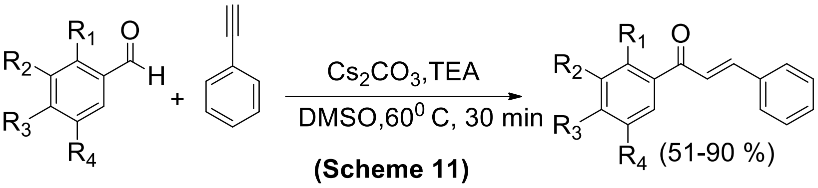
(Scheme 10).



(Scheme 10)

M. Tiwari approach (2019)[39]

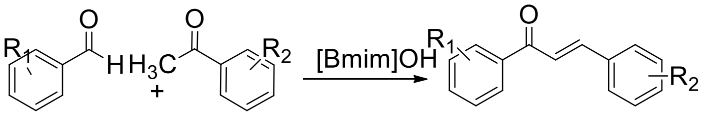
M. Tiwari developed simple and metal free protocol for the synthesis of chalcones by alkenylation of carbonyl compounds by employing Cs_2CO_3 and Et_3N as catalyst in DMSO at 60°C **(Scheme 11).**



(Scheme 11)

Q. Zhao approach (2021) [40]

Q. Zhao was observed that an ionic liquid works well as a catalyst for the aldol reaction between benzaldehyde and a number of acetophenones to produce chalcone in the absence of a solvent **(Scheme 12).**



(Scheme 12) (70-100 %)

IV. CONCLUSION

In conclusion, the current review focuses primarily on the novel chalcones with promising applications that have been reported from both synthetic and natural sources. The synthesis of chalcones, various synthetic methods for their preparation, and their medical applications are also covered in this review. The fact that the chalcones have a privileged template with an, -unsaturated carbonyl system and easily permit structural modifications is interesting to note. As a result, when designing new and innovative materials with a variety of applications, researchers concentrate their attention to chalcones' skeletal modifications.

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Evaluation of Acoustical Parameters of Some Substituted Ketimine Drugs Under Different % Composition In 75 % Dichloromethane (DCM)–Water Mixture At 30⁰C.

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ABSTRACT

In the present investigation ultrasonic velocity of binary mixture of aromatic substituted ketimines and dichloromethane (DCM) under different percentage composition at 30⁰C were evaluated using ultrasonic interferometer having 2MHz frequency. The obtained data was used to investigate the different acoustical parameters such as adiabatic compressibility, apparent molar compressibility, acoustic impedance, relative association, solvation number and intermolecular free length. The result is interpreted in terms of molecular interaction such as dipole-dipole interaction through hydrogen bonding between components of mixtures.

Keywords: Ultrasonic velocity, Dichloromethane (DCM), adiabatic compressibility, ketimines etc.

I. INTRODUCTION

The various techniques available to study molecular interactions in liquid are nuclear magnetic resonance, microwave, ultraviolet and infrared spectroscopy, neutron and X-ray scattering and ultrasonic investigation. NMR technique reflects effect on the proton bearing molecules, whereas microwave absorption provides information through dielectric constant. Neutron and X-ray scattering help in the study of molecular motion. The spectroscopic techniques provide useful information of interactions when the interaction energies involved are large. Weak molecular interactions cannot be resolved from the observed spectra. Ultrasonic techniques reveal very weak intermolecular interactions due to its useful wavelength range. In the recent years, determination of ultrasonic velocity evaluates various parameters of liquids for studying molecular and structural properties. There is an intimate relationship between the ultrasonic velocity on chemical and structural characteristics of molecule of liquids; this gives a property of basic importance to ultrasonic velocity in molecular theory of liquids. At present, the ultrasonic and absorption studies especially in case of electrolyte solutions have led to new insight into the process of ion-association and complex-formation[1-2]. Many researchers such as M.S. Chouhan[3], S. Sasikumar[4], Shashi Kant[5], T. Sumathi[6], Chandami A. S.[7] and Azhagiri S.[8] have made ultrasonic study of electrolytic solutions and discussed about the variation of ultrasonic velocity with ion concentration. It has already been observed that extent of a lowering of compressibility and an increase in ultrasonic velocity with reference to that of water are proportionate to the number of ions existing in that medium. Most of the ultrasonic work in non-aqueous systems possesses an interpretation of solute-solvent interactions[9]. Solvation numbers have been obtained from the study of non-aqueous solutions by K.Kannagi et.al.[10], Harish Kumar[11].

In the present investigation, study of the interaction between solute-solute and solute-solvent of substituted ketimine in 75%, 80% and 85% (DCM+water) solvents by measuring ultrasonic velocity and density in different concentration of solute in different percentage of solvent has been done.

II. EXPERIMENTAL

All the chemicals used were of AR grade. The density measurements all the solutions were made with the precalibrated bicapillary pyknometer. All the weighings were made on one pan digital balance (petit balance AD-50B) with an accuracy of + 0.001 gm. The ultrasonic velocity was measured by using variable path crystal interferrometer (Mittal Enterprises, Model F-81) with accuracy of + 0.03 % and frequency 2MHz. The instrument was calibrated by measuring ultrasonic velocity of 75 % DCM-water mixture at 303 K. Elite thermostatic water 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 oC. The ligands used in the present study are

5- Bromo-2-hydroxy-4-chloro (p-methyl phenyl) ketimine (LA)
5- Bromo-2-hydroxy-4-chloro (p-amino phenol) ketimine (LB)

III. THEORY AND FORMULATION

The distance traveled by micrometer screw get one maximum in ammeter (D), from the value of D, wavelength of ultrasonic wave is calculated using relation.

$2D = \lambda$ ………… (1)

Where λ is wave length and D is distance in mm. The ultrasonic velocity is calculated by using relation.

Ultrasonic velocity $(U) = \lambda \times \text{Frequency} \times 10^3$ ……….(2)

Using the measured data some acoustical parameters have been calculated using the standard relations.

The adiabatic compressibility of solvent and solution are calculated by using equations

Adiabatic compressibility $(\beta s) = 1/ Us^2 x\ ds$ …………….. (3)

Adiabatic compressibility $(\beta_0) = 1/ U_0^2 x\ d_0$ ………………. (4)

Acoustic impedance $(Z) = Us \times ds$ ……………………… (5)

Where U_0, Us are ultrasonic velocity in solvent and solution respectively. d_0 and ds are density of solvent and solution respectively

The apparent molal volume (ϕ_v) and apparent molal adiabatic compressibilities ($\phi_{k(s)}$) of substituted ketimines in solutions are determined respectively, from density (d_s) and adiabatic compressibility(β_s) of solution using the equations

$\phi_v = (M/d_s) + [(d_o-d_s)\ 10^3] / m d_s d_o$ .... (6) and

$\phi_{k(s)} = [1000(\beta_s d_o-\beta_o d_s) / m d_s d_o] + (\beta_s M / d_s)$ …………….. (7)

Where, d_o and d_s are the densities of the pure solvent and solution, respectively. m is the molality and M is the molecular weight of solute. β_o and β_s are the adiabatic compressibility's of pure solvent and solution respectively.

Intermolecular free length (Lf) = $K\sqrt{\beta s}$ …………… (8)

Relative association (RA) = $(ds/d0) \times (U0/Us)^{1/3}$ .... (9)

Solvation number (Sn) = $\varphi^{\kappa} / \beta 0 \times (M/d0)$ ………….. (10)

The value of Jacobson's constant is calculated by using relation

$K=(93.875+0.375 \times T)\times 10^{-8}$ …………….. (11)

Where T is temperature at which experiment is carried out. The present investigation is carried out at temperature (T = 303K).

Table 1: Ultrasonic velocity, density, adiabatic compressibility (βS), Specific acoustic impedance (Z) Intermolecular free length (Lf) in 75% DCM solvent at 303K.

Conc. (m) Moles lit^{-1}	Density (ds) Kg m^{-3}	Ultrasonic Velocity(Us) m s^{-1}	Adiabatic Compressibility (β_s) $\times 10^{-9}$ m^2N^{-1}	Inter molecular free length (Lf) $\times 10^{-11}$ m	Specific acoustic impedance (Z) $\times 10^5$ kg $m^{-2}s^{-1}$
Ligand LA in 75% (DCM +water) solvent					
0.01	1224.1	3630.4	6.1983	5.1660	4.44397
0.008	1223.9	3529.6	6.5622	5.3155	4.31741
0.006	1222.3	3433.6	6.9394	5.4661	4.19689
0.004	1221.8	3342.4	7.3287	5.6173	4.08241
0.002	1216.0	3273.6	7.6739	5.7399	3.98070
Ligand LB in 75% (DCM +water) solvent					
0.01	1220.5	3504.0	6.6732	5.3602	4.27663
0.008	1219.6	3438.4	6.9354	5.4645	4.19347
0.006	1219.6	3401.6	7.0862	5.5236	4.14859
0.004	1218.7	3337.6	7.3660	5.6316	4.06753
0.002	1217.8	3188.8	8.0755	5.8966	3.88332
Ligand LA in 80% (DCM +water) solvent					
0.01	1225.3	3604.8	6.2805	5.2001	4.41696
0.008	1224.4	3483.2	6.7316	5.3836	4.26483
0.006	1223.5	3302.4	7.4940	5.6805	4.04048
0.004	1222.5	3158.4	8.2000	5.9419	3.86114
0.002	1217.1	3072.0	8.7062	6.1190	3.73893
Ligand LB in 80% (DCM +water) solvent					
0.01	1221.7	3371.2	7.2022	5.5686	4.11859
0.008	1220.8	3243.2	7.7876	5.7905	3.95929
0.006	1220.7	3236.8	7.8191	5.8022	3.95116
0.004	1219.9	3201.6	7.9500	5.8504	3.91734
0.002	1218.5	3211.2	8.006	5.8706	3.90115

Ligand LA in 85% (DCM +water) solvent					
0.01	1226.5	3371.2	7.1740	5.5577	4.13477
0.008	1225.7	3249.6	7.7260	5.7676	3.98303
0.006	1224.6	3211.2	7.9190	5.8392	3.93243
0.004	1223.7	3188.8	8.0365	5.8823	3.90213
0.002	1218.3	3172.8	8.1538	5.9251	3.86542
Ligand LB in 85% (DCM +water) solvent					
0.01	1222.9	3320.0	7.4187	5.6517	4.06002
0.008	1221.9	3284.8	7.5848	5.7146	4.01369
0.006	1221.7	3236.8	7.1812	5.7998	3.95439
0.004	1220.9	3212.8	7.9351	5.8451	3.92250
0.002	1220.3	3192.0	8.0428	5.8846	3.89519

Plots of adiabatic compressibility β_s of different ligand at different concentration in a 75%, 80%, 85% (DCM +water) solvent

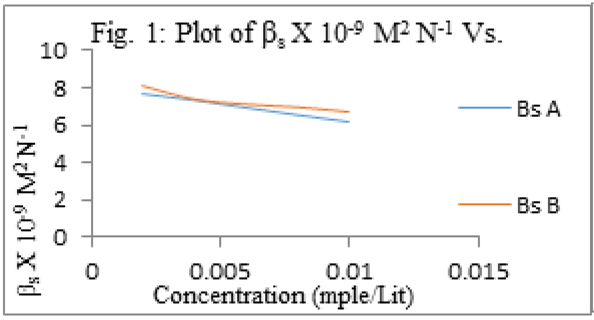


Fig. 1: Plot of β_s X 10^{-9} $M^2 N^{-1}$ Vs.

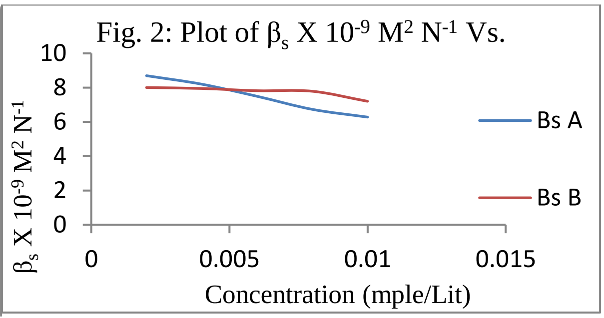


Fig. 2: Plot of β_s X 10^{-9} $M^2 N^{-1}$ Vs.

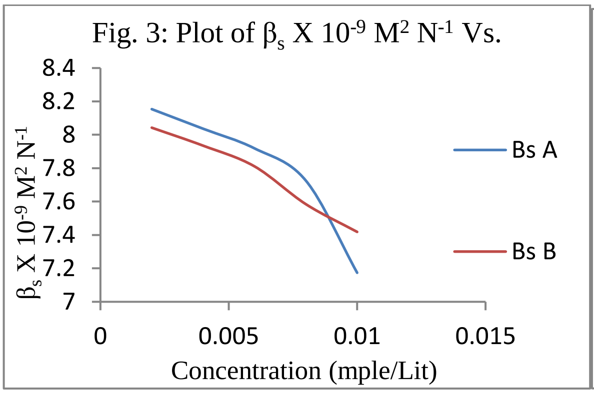


Fig. 3: Plot of β_s X 10^{-9} $M^2 N^{-1}$ Vs.

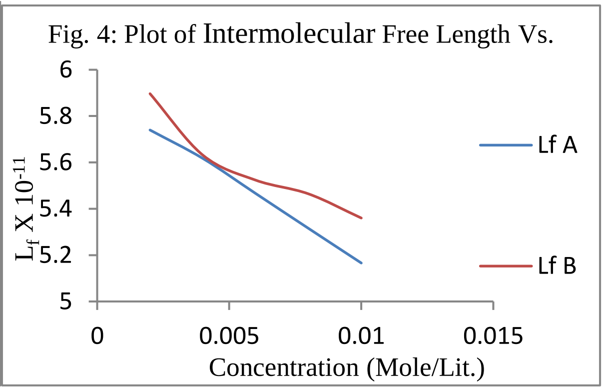


Fig. 4: Plot of Intermolecular Free Length Vs.

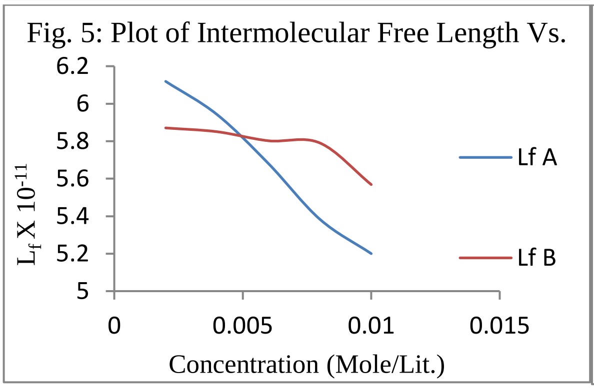


Fig. 5: Plot of Intermolecular Free Length Vs.

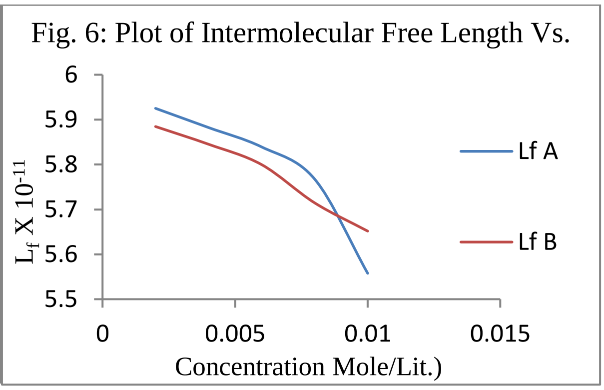


Fig. 6: Plot of Intermolecular Free Length Vs.

Fig. 7: Plot of Specific acoustic impendance

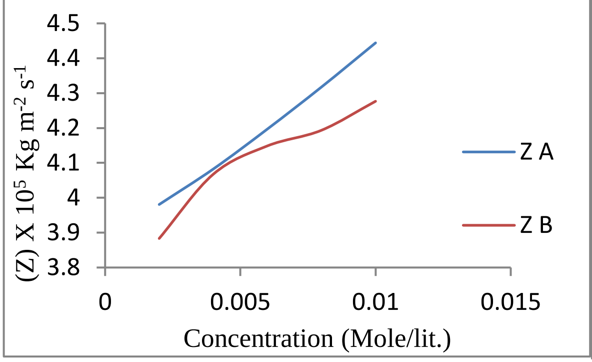


Fig. 8: Plot of Specific acoustic impendance

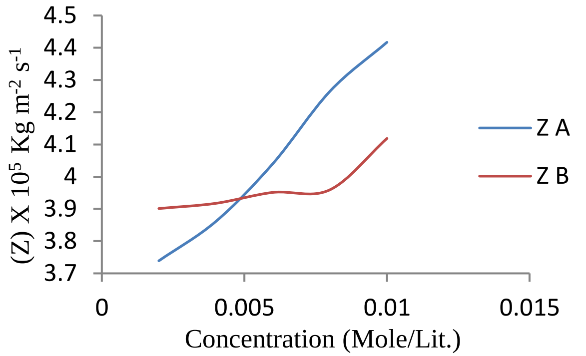


Fig. 9: Plot of Specific acoustic impendance

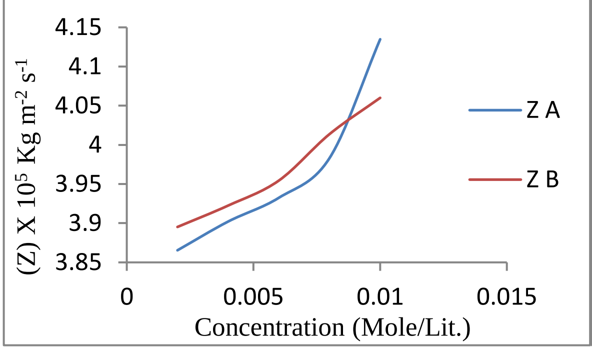


Fig. 10: Plot of Ultrasonic Velocity Us

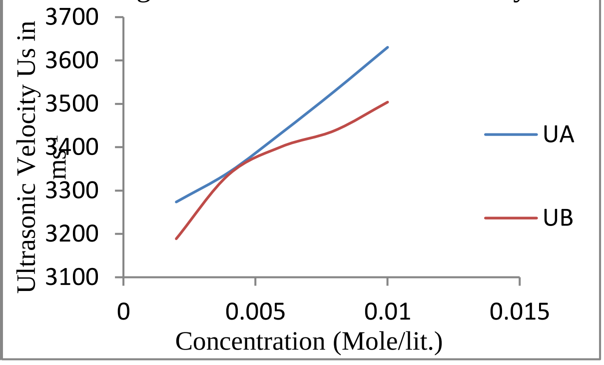


Fig.11: Plot of Ultrasonic Velocity Us in ms^{-1} Vs Concentration (Mole/lit.) in 80% DCM

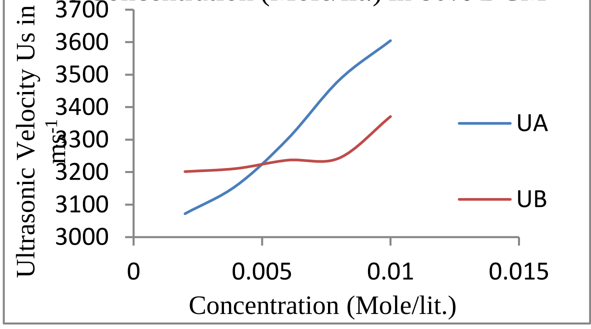
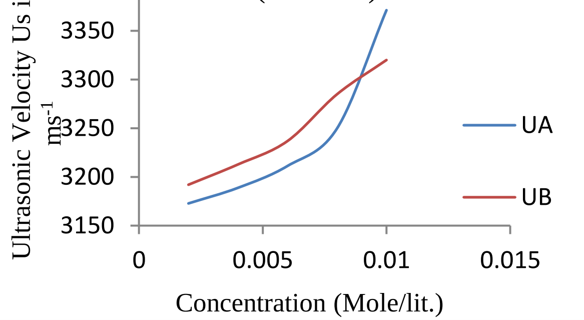


Fig. 12: Plot of Ultrasonic Velocity Us in ms^{-1} Vs Concentration (Mole/lit.) in 85% DCM



IV. RESULT AND DISCUSSION

In the present investigation, different acoustical parameters, such as ultrasonic velocity (U), adiabatic compressibility (βs), intermolecular free length (Lf), specific acoustic impedance (Z), of substituted chalconeimne in different percentage of DCM+water mixture at 303K have been studied. From table 1, it is found that ultrasonic velocity decreases with decrease in concentration for all systems. (Fig 10 to 12) This indicates that, there is significant interaction between ion and solvent molecules suggesting a structure promoting behavior of the added electrolyte. It was found that, intermolecular free length increases linearly on decreasing the concentration of substituted ketimines in different solution of DCM+water mixture (fig. 4 to 6). The intermolecular free length increase due to greater force of interaction between solute and solvent by forming hydrogen bonding. The value of specific acoustic impedance (Z) decreases with decrease in concentration for all substituted ketimines in different percent solutions of (DCM+water) mixture (fig.7 to 9). When concentration of electrolyte is decreased, the thickness of oppositely charged ionic atmosphere may increase due to decrease in ionic strength. The increase of adiabatic compressibility with decrease of concentration of solution may be due to the dispersion of solvent molecules around ions supporting weak ion-solvent interactions (fig. 1 to 3).

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Study of Complex Formation of Pyridoxine with Transition Metal ions in Aquaorganic Medium

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ABSTRACT

Complexes of vitamin Pyridoxine with transition metal ions V (II), Cr (II) and Fe (III) studied pH metrically in aqua-organic medium of methyl alcohol (Me-OH) and ethyl alcohol (Et-OH) at constant temperature 2980K and ionic strength 0.1M. The values of protein ligand and metal ligand stability constants were calculated and compared.

Keywords: Pyridoxine, Stability Constants, Binary Complexes, Transition Metals, Me-OH and Et-OH

I. INTRODUCTION

Water soluble vitamins are soluble in water due to their easy adsorption. They can not be retained by the body for long period of time. Pyridoxine is water soluble vitamins and it is known by vitamin B6.

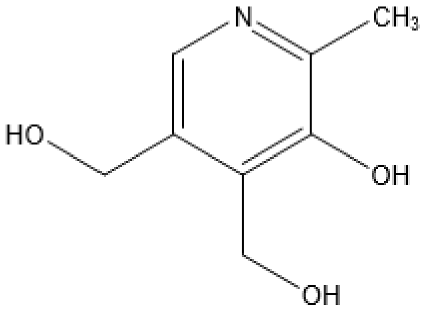
There are three different forms of Vitamin B6 namely Pyridoxine, Pyridoxamine and Pyridoxal. All these are phosphorylated and oxidized to functional pyridoxal 5-phosphate, which acts as a coenzyme in the metabolism of amino acid 1,2.

Deficiency of Vitamin B6 is uncommon because it usually occurs in association with a deficit in other B-complex3.

Vitamin B6 is useful in the treatment of balancing harmonal changes in woman during pregnancy.The source of this vitamin is yeast, leaver and cereals4,5.

Chemical formula of pyridoxine is $C_8H_{11}NO_3$ Its molecular wt.is 169.18 and its M.P. is 159 -1620C.

Pyridoxine



II. MATERIALS & METHODS

All the chemicals were used are A.R. Grade. Pyridoxine was obtained in pure form. The solvents ethyl alcohol and methyl alcohol are A.R. Grade and purified by distillation method. Metal ions were used in their nitrate from (S.D. fine chemicals). NaOH (0.01N) and NaClO4 (0.2N) solutions were prepared in double distilled water.

Table No. 1: The dissociation constant of Pyridoxine in 36% Me-OH water medium & 30% Et-OH water medium at 2980k and at μ = 0.1M NaClO4.

Pyridoxine	PK1	PK2
36% Me-OH	3.77	8.09
30% Et-OH	5.42	9.54

Table No. 2: The metal ligand stability constant of Pyridoxine with transition metal ions in 36% MeOH -Water medium at 2980k and at μ = 0.1M NaClO4.

Metal	log K1	log K2
V (II)	8.76	7.87
Cr (II)	5.5	4.79
Fe (III)	5.63	3.48

Table No. 3: The metal ligand stability constant of pyridoxine in 30% EtOH – water medium at 2980K and at μ = 0.1N NaClO4.

Metal	log K1	log K2
V (II)	9.34	7.89
Cr (II)	5.88	4.85
Fe (III)	7.14	3.5

The sodium hydroxide was standardized against oxalic acid solution and it was used for further pH metric titrations. The ionic strength was maintained at 0.1M by using NaClO4 (B.D.H) as supporting electrolyte. All solutions were prepared in CO2 free double distilled water. The concentration of metal ions solution was estimated by standard procedures6,7. The micro burette with graduation 0.02 ml was used and it is calibrated by the method given in Vogel 8. All glassware used in the experiments are of Borosil quality. An Elico model

L1-120 digital PH meter is connected with an Elico combined glass electrode consisting of glass and reference electrodes. The precautions were suggested by Bates 9. Albert and Sergent 10 were adopted for smooth handling of the electrode.

The experimental procedure for binary metal complexes involves following titrations.

1. Free HClO4
2. Free HClO4 + Pyridoxine
3. Free HClO4 + Pyridoxine + metal ion solution

This solution was titrated against standard solution of sodium hydroxide. The concentration of Pyridoxine and metal ions were 0.01M and concentration of HClO4 acid was 0.2N. The ionic strength of the solutions were maintained constant i.e. 0.1M by adding appropriate amount of 2M NaClO4. The titration was carried out at 2980K in an inert atmosphere by bubbling free nitrogen gas through an assembly containing electrode to expel out CO2 gas. The reading on pH meter in 36% (v/v) Me-OH-Water and 30% (v/v) Et-OH-Water medium were recorded at every addition of NaOH in order to evaluate dissociation constant and stability constants. The method of determination of the formation constant was describe by Irving Rossootti 11 and Hearon and Gilbert12 Calvin and Mechiar 13 and now known as Calvin Bjerrum titration technique.

III. RESULT & DISCUSSION

The proton ligand and metal ligand stability constants of Pyridoxine in 36% Methanol-Water and 30% Ethanol -Water medium at 2980K and at μ= 0.1M NaClO4 are depicted in table no. 1, 2 and 3.

In pyridoxine two pK values are obtained at temperature 2980K which are attributed to two – OH groups. The first pK value is due to dissociation of phenolic -OH (3) which is more acidic and second pK value is due to dissociation of alcoholic -OH (4) being para to ring nitrogen which is higher than first PK value. Pyridoxine can be corelated with Pyridine which has a pK value 5.2. The observed pK value is slightly less because negative value indicate effect of hydroxyl group present.

In case of Pyridoxin pK values are less in 36% (v/v) methanol -water than 30% (v/v) ethanol-water which indicates that in methanol more acidic complex is formed as compared to ethanol. The effect of solvent depends on its dielectric constant and its ability to solvate and stabilize ligand in acid base equilibria. Solvent having highest polarity or dielectric constant stabilized the ionized species, higher will be the pKa value and more stable will be in solution.

The metal ligand formation curve data for pyridoxine in 36% (v/v) methanol -water and
30% (v /v) ethanol -water medium with transition metal ions forms complexes 14 with Pyridoxine.

The order of metal ligand stability constants is as follows

36% (v/ v) Me-OH-Water medium

V (II) > Fe (III) > Cr (II)

30% (v / v) Et-OH -Water medium

V (II) > Fe (III) > Cr (II)

IV. CONCLUSION

In the present work PH metric study was performed to determine the stability constants and to assess binary species for pyridoxine with transition metals in 36% Me-OH -Water and 30% Et-OH -Water medium pH range 1.98 to 11.9. The following conclusions have been drawn.

1. Pyridoxine forms complexes with transition metal ions in the pH range 1.96 to 11.6
2. The pK values in 36% Me-OH-Water and 30% Et-OH -water medium are obtained.
3. The log K values in 36% Me-OH-Water and Et-OH -Water medium is evaluated.

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A Short Review on Synthesis and Biological Activity of Transition Metal Complexes

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ABSTRACT

The complexes of ML2 were synthesized where M= Co(II), Ni(II) and Cu(II) and L= 2-Butyl thioquinazoline 4 (3H)- semicarbazone (BTQS). The ligand have been synthesized by condensation of thioquinazoline-4(3H)-one with semicarbazide hydrochlande characterized by molar mass, elemental analysis, Infrared spectra, electronic spectra, magnetic susceptibility and molar conductance measurements.

AMR (Antimicrobial-resistant) pathogens like MRSA (Methicillin-Resistant Staphylococcus aureus) have develop prodigious peril to human health in the past few years with the failure of numerous antifungals & antibiotics in treating mild to chronic mycoses and septicemia. In the severe concern for threshing contagions, Azo-Schiff Bases with dual functionality and far-ranging pharmacological potential has been measured an excellent target for antimicrobial examinations. A diversity of homocyclic and heterocyclic organic precursors has been consumed for submitting innovation in the Azo-Schiff Base Ligands (ASBLs). Therefore, the present study encompasses the research undertaken throughout the last two decennia for the development and in vitro antimicrobial screening of these prospective drug agents.

I. INTRODUCTION

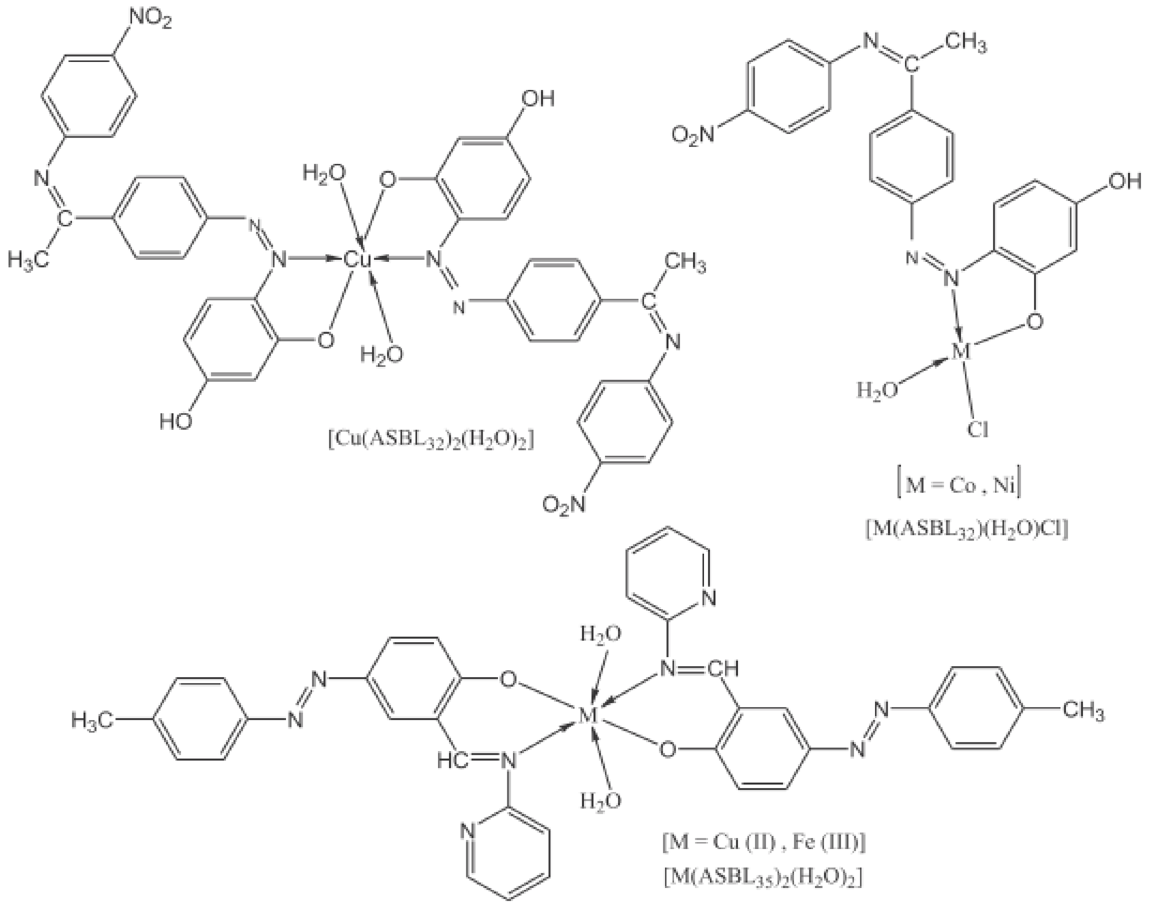
Transition metal complexes of Schiff base have been particularly investigated by Coordination chemists due to their interesting structural properties and their wide ranging applications.The coordination ability of Schiff bases with transition element, mostly with first row, give the study of the metals in such system. The first report on the catalytic activity of NHC–metal complexes had a great impact on improvement of NHC-ligated homogeneous catalysts for a plethora of organic reactions. The coordination chemistry has been a regulation of importance and engrossment for chemists and researchers as it comes up with pharmaco-therapeutic success in the field of remediation to severe diseases and improvements in a multiplicity of drugs.

II. PREPARATION OF THE COMPLEXES

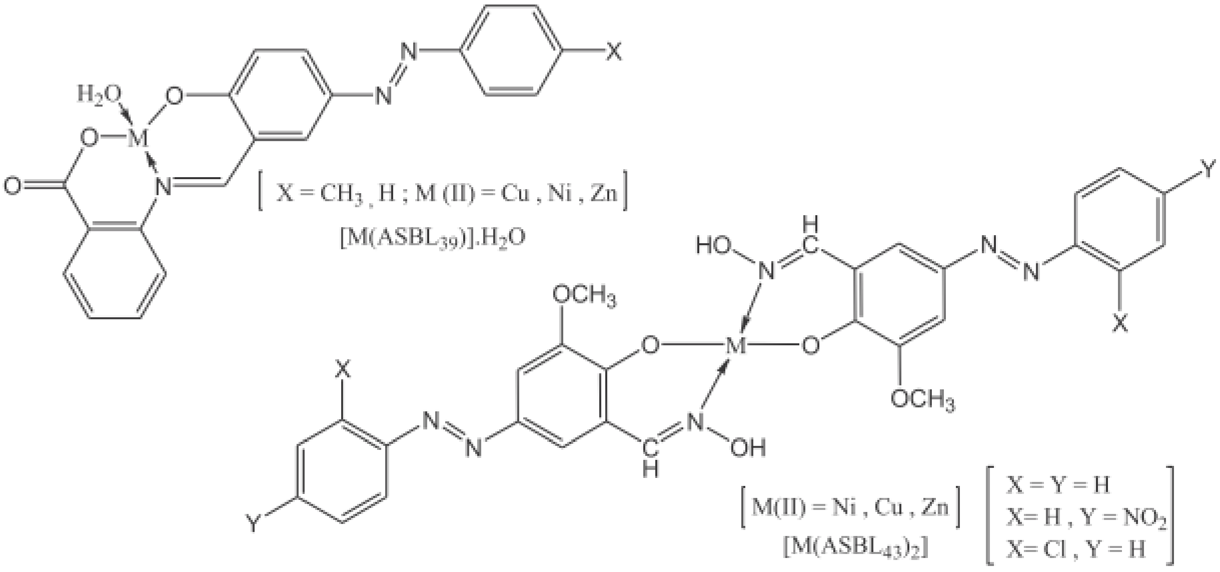
The complexes of Co(II) ,Cu(II), and Ni(II) have been synthesized by reacting solution of metal halides with solutions of the ligand BTQS in molar ratio 1:2. The solid coloured complexes which was separated on cooling were filtered, washed with ethanol, dried in oven. Yield in all cases 60-65% azomethine N in the bonding with metal ions.

The Azo-Schiff Bases, bearing numerous dentation, constitute a distinct class of organic ligands since they have been performed as a privileged scaffold in the coordination chemistry. The strategic synthesis of these ligands is largely reported in the literature by driving the fundamental diazotization-condensation scheme in two possible directions. The technique afforded excellent yield . The exceptionality of each ligand is based on the choice of different starting molecules with different substitutions. In one such example, Hankare, Petal.carried out the synthesis of ASBL1 by combining 2-hydroxy-5-thiazolylazo benzaldehyde and 4-chlorobenzenamine in ethyl alcohol. In the reaction, condensation of aldehydic carbonyl with amino-group of the aromatic amine is carried out. Bright coloured ligand was obtained with the help of combustion analysis., IR spectra, UV–Vis and XRD technique [1].

In one more novel study, the ethanolic mixture of 2-hydroxy-3 methoxy benzaldehyde was treated with two azo-derivatives of naphthalene disulfonic acid in the same way. The elimination of water molecule created the azo-methine connection between pre-cursor molecules. The ASBL2 (a-b) found with tridentate donor capacity were crystallized after 120’mins. The structure elucidation of ligands was done with the help of combustion analysis, IR, UV–Vis., MS and NMR studies [2].



The structures of some complexes



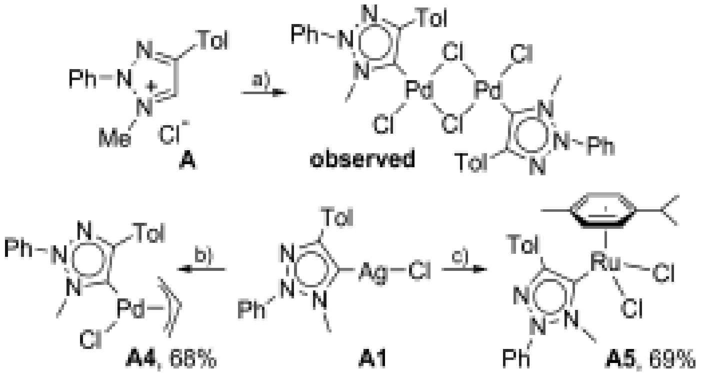
$[M(ASBL_{39})].H_2O$

$[M(ASBL_{43})_2]$

Synthesis of Ru and Pd Complexes Bearing 1,2,3-Triazolylidene Ligands:-

Since the cyclohexyl triazolylidene Ag complex B1 seems to show only restricted applicability in carbene transfer reactions, further examinations concentrated on methyl-substituted A1. As to date no examples for group 8 and group 10 complexes bound to normal 1,2,3-triazolylidene ligands are known and verified the carbene transfer reaction with A1 and common dimeric metal complexes [Pd(allyl)Cl]2 and [Ru(p-cymene)Cl2]2. Reactions with both precursors were directed at room temperature and allowed for facile isolation of triazolylidene-substituted Pd-allyl complex A4 and the correlated triazolylidene cymene Ru dichloride compound A5 in better yields (Scheme 4). Both compounds exhibit good constancy to air and moisture.

Scheme 4. Synthesis of New Pd and Ru Complexes with Methyl-Substituted Triazolylidene Ligands[a]



Applications of transition metal complexes:-

- The heterocyclic Azo-dyes have been engaged as indicators in classical analytical procedures and histological stains for anatomical studies.
- They have occupied a crucial existence as coloring factors in printings, edibles, cosmetics, woven fiber, paper, leather and other polymeric materials [3].
- The primary use of Azo-dyes is it act as a colorant and it provide in-numerable physiochemical, analytical, bioinorganic, pharmaceutics and catalytic utilities [4].

- The medicinal aspect of Azo-compounds was unveiled by the initiation of Prontosil, a sulphonamide coupled Azo-dye, used as a medicine against bacterial infections[5,6].
- Expeditiously revolving up biological features of Azo-compounds have made them center of sheer interest owing to their behaviour as potential bacteriostatic, fungicidal, anti-inflammatory, anti-oxidant, anti-diabetic, anti-viral (HIV), anti-cancer, anti-septic and genotoxic agents regarding drug innovation areas of research [11–12].
- Azo-compounds have been considered relevant materials for photoelectric conversions in solar cells [13–14].
- The Schiff-bases and their metal complexes bear no end of day-to-day applications as essential cost-effective synthetic substrates, excellent analytical tools and efficient catalytic, photochromic, thermochromic, stereo-chemical and anti-corrosive materials
- Some bivalent metal (cobalt, nickel, copper and palladium) complexes have been investigated for their ability to act as mesogens, industrial & biochemical catalysts and for their optical & magnetic behaviour pertaining to electronic media

III. CONCLUSION

The antimicrobial lineaments of ASBLs and their coordination complexes with a multiplicity of transition metals (Cr, Mn, Fe, Co, Ni,Cu, Zn, Pd, Pt, Cd, Pb and Hg) offer an significant potential for the formulation of novel drugs beside AMR pathogens. The ASBLs derived from heteroatomic organic molecules containing N,O and S possessed greater cytotoxicity beside microbial strains and their activity have still been nurtured drastically after metalation. The improved activity of complexes can reasonably be attributed to a cluster of factors such as the phenomenon of chelation, reduced polarity of metal ions, lipophilicity, availability of heteroatoms in ligands and geometry of the complexes. In the case of Pd-promoted Suzuki–Miyaura CC-coupling catalysis, stability issues prevent more successful catalytic application. Here, our examinations highlighted the drawbacks of the present N1-alkyl ligand design. It is highly likely that a triaryl substitution pattern will help to improve ligand stability of 'normal' 1,2,3-triazolylidenes as it was described for abnormal triazolylidenes in the literature.

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Nanotechnology for Green Innovation

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ABSTRACT

Now a days, nanotechnology is one of the fastest growing technology, which is used in every field of day today's life. Nanotechnology as defined by size is naturally very broad, including fields of science as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, micro fabrication, etc. Nanotechnology may be able to create many new materials and devices with a vast range of applications, such as in medicine, electronics, biomaterials and energy production. On the other hand, nanotechnology raises many of the same issues as any new technology, including concerns about the toxicity and environmental impact of nanomaterials, and their potential effects on global economics. Green nanotechnology refers to the use of nanotechnology to enhance the environmental sustainability of processes producing negative externalities. It also refers to the use of the products of nanotechnology to enhance sustainability. It includes making green nano-products and using nano-products in support of sustainability. Green nanotechnology brings significant potential gains at environmental, societal and economic levels, but there are also potential risks and costs.

Keywords: Cost, Green, Nanotechnology

I. INTRODUCTION

As green innovation is not yet clearly defined, there can be no clear definition of what nanotechnology for green innovation – green nanotechnology – should encompass. From published papers on the issue, one could describe green nanotechnology as a foundation for products and processes that are safe and have a low net environmental impact, being energy efficient, reducing waste, lessening greenhouse gas emissions and using renewable materials. Green nanotechnology can be seen as supporting the development of sustainable solutions to address global issues such as energy shortages and scarcity of clean water, and many other areas of environmental concern, and being present in environmentally-sustainable manufacturing processes. Green nanotechnology is linked to other concepts such as green chemistry and sustainable and green engineering and manufacturing. Green nanotechnology can have multiple roles and impacts across the whole value chain of a product and can be of an enabling nature, being used as a tool to further support technology or product development. Nanotechnology is increasingly being used for green applications in conjunction with other technologies and disciplines such as biology and life sciences, materials and environmental sciences and electronics and computing, leading to products that encompass multiple technological innovations. While green nanotechnology applications may save energy and reduce carbon emissions in the final product, there are concerns about the amount of energy that might be involved in the upstream production of component nanomaterial's [1].

With on-going research in the field, energy and manufacturing costs for nanomaterial production are likely to reduce over time as process technologies are improved and new materials emerge. Nonetheless, the energy, waste and resource extraction costs associated with the production of the materials used in green nanotechnology applications remain an important part of the equation in assuring the responsible development of green nanotechnology. As the overall field of nanotechnology raises concern about potential EHS risks, as well as ethical and social issues, this is no different for the green nanotechnology area. Concerns are, for example, linked to potential EHS risks through the use and disposal of nanostructures employed in green nanotechnology applications [2]. Many recent and current nanotechnology EHS studies contain calls for further research and monitoring, e.g. for research into more biocompatible alternatives. Many national and international initiatives are also being developed in order to better understand those risks and to reduce uncertainties in the field.

II. STRATEGIES FOR GREEN INNOVATION THROUGH NANOTECHNOLOGY

In many countries, supports for green nanotechnology have been mainstreamed within more general efforts to 'green' the trajectory of the economy. Green nanotechnology operates in a complex landscape of fiscal and legislative policies and allied measures for green growth and for science, technology and innovation more generally. Framing conditions - such as regulation and standards, and research, environmental and enterprise policy – strongly influence the development of green nanotechnology for use in processes or products. Policy to support green nanotechnology includes significant R&D efforts that are increasingly applications orientated and driven by grand challenges. Policy interventions to share and diminish the risks inherent in the development and commercialization of applications involving green nanotechnology are resulting in the creation of innovative public-private collaborations. Efforts to ensure that nanotechnology is developed in a responsible manner are being supported through investment and there is a growing number of initiatives (at the national and international level) looking at environmental health and safety (EHS) and ethical and social issues. There are also initiatives aiming to ensure the environmental and economic sustainability of manufacturing processes involving nanotechnology.

2.1 From basic research to technology applications

The potential to commercialize nanotechnology for green innovation has become a particular focus of interest in recent years as nanotechnology research is beginning to be used in multiple concrete applications. With the growing potential of the technology, and in the face of urgent environmental challenges, strategies and investment in nanotechnology have moved from being science-driven to being more application- and challenge-driven, focusing on how technologies, and nanotechnology in particular, could help to address some major national and global challenges. This challenge-driven tendency is apparent in both OECD countries and emerging economies [3]. The evolving policy landscape of most countries reflects a shift in focus from a concentration on funding basic research towards initiatives focused on improving the links between research and development for nanotechnology, for example stimulating technology transfer and demonstration projects. There is a direct link made between nanotechnology and its applications in the strategies of many governments, and, where significant levels of investments are being maintained, there is a tendency to move funding to more applied nanotechnology research.

2.2 Investment in environmental health and safety, ethical and social issues and sustainable manufacturing

Efforts to ensure the responsible development of nanotechnology are being made through a growing number of national and international initiatives looking at environmental health and safety (EHS) and ethical and social issues. While nanotechnology for green innovation is increasingly revealing its potential to enhance current technologies or create entirely new solutions, most of these innovations are still in the laboratory and very few products have reached the market to date. This is due to a number of factors, one being the economic costs which may be incurred in the use of nanotechnology for green innovation. For example, while the application of nanotechnology may save energy and reduce carbon emissions, significant amounts of energy may be involved in producing the component materials [4]. While energy and manufacturing costs are likely to reduce over time as process technologies using nanotechnology are improved and new materials emerge, it will be important to ensure that energy usage, gas emission and other environmental factors associated with the production of materials used in green nanotechnology applications are monitored. Some nanotechnology applications also raise EHS concerns related to the use and disposal of nanostructures which they employ. The environmental and safety costs of the technology are particularly important to look at when trying to develop and label commercial nanotechnology solutions as “green”. In response to these issues, governments are increasingly including the concept of responsible development in their nanotechnology policies and programmes. Such responsible development aims to stimulate the growth of nanotechnology applications in diverse sectors of the economy, while addressing the potential risks and the ethical and societal challenges the technology might raise. In 2012, the OECD Working Party on Nanotechnology launched a project to inventory activities in several OECD member and nonmember countries relating to the responsible development of nanotechnology. Preliminary results of that work show that some countries (e.g. Germany, Korea) have dedicated policies for the responsible development of nanotechnology. Most of the countries responding to the questionnaire fund activities and programmes in the areas of Environmental, Health and Safety (EHS) and Ethical, Legal and Social Implications (ELSI). It was also largely recognized by the participating countries that advances in analyzing the potential risks of using nanotechnology can help to reduce uncertainty, thereby encouraging the responsible application of nanotechnology-based innovation. Intergovernmental bodies, such as the OECD (in particular, the OECD Working Party on Manufactured Nanomaterials), the World Health Organization (WHO) and the Food and Agriculture Organization (FAO), are complementing these national and multi-national efforts with a number of programmes dedicated to the responsible development of nanotechnology. Organizations, such as the International Organization for Standardization (ISO), through its Technical Committee ISO TC229, are also contributing to the thinking around the development of frameworks for responsible development and to the development of standards in the area of nanotechnology.

There is also an increased focus on fostering greener manufacturing using nanomaterials, trying to strengthen the link between green nanotechnology, green chemistry and sustainable manufacturing. The United States EPA, for example, has a dedicated project looking at how energy consumption can be minimized and waste/pollution prevented in the manufacturing of nanomaterials and products. The OECD Working Party on Manufactured Nanomaterials also has a dedicated Steering Group on the Environmentally Sustainable Use of Manufactured Nanomaterials.

There are also networks of professionals and institutions engaged with issues such as green synthesis of nanomaterials and advanced manufacturing. The Sustainable Nanotechnology Organization (SNO) is a recently created non-profit, worldwide professional group of individuals and institutions. Its purpose is to provide a professional forum to advance knowledge of all aspects of sustainable nanotechnology, including both applications and implications. There are also numerous initiatives to address ethical, legal and social issues for nanotechnology development that base their work on the premise that societal buy-in and public awareness are key to the uptake of nanotechnology innovation. All these investments, programmes and initiatives aim to create a sufficient pool of knowledge to enable informed policy decisions on responsible and sustainable nanotechnology development, uptake and commercialization, balancing risks and societal, environmental and economic benefits.

2.3 Public-private collaborations: Fostering the transition of green nanotechnology from research to commercialization

For companies, investment in nanotechnology for green innovation can be costly and without guaranteed returns. Governments are seeking to mitigate these risks by fostering various types of public private collaborations to enhance the sharing of information, knowledge and resources to make the field advance more efficiently.

There is still a great hesitancy from the private sector to engage in green nanotechnology. This is due to a number of factors, such as the perception of the EHS and ELSI risks associated with the technology (also leading to issues of consumer acceptance), regulatory uncertainty, and the lack of maturity of the technology, potential economic costs, market uncertainty and strong competition with incumbent technologies. Nanotechnology often competes badly with existing technologies mainly for two reasons –cost competitiveness and familiarity. For example, Asian manufacturers produce large volumes of products at low cost and effectively out-price novel alternatives such as Nano based photovoltaic, the existing high-volume product being considered as "good enough". All of these factors lead to an environment of uncertainty and a perception of high investment risk. The possibilities that nanotechnology can offer for green innovation to address some of the major environmental and social challenges have triggered a response from governments that involves trying to reduce risks and uncertainty for companies, thereby aiming to facilitate and accelerate the transfer of nanotechnology innovation to the marketplace. Policies are being put in place to help bridge the gap between research and the market. This market-driven approach includes direct investment in SMEs, for example, but also creating partnerships between governments and public entities and the private sector in order to bring together the resources needed.

2.4 Beyond green nanotechnology: Convergence of green technologies

An increasing trend in science, technology and innovation strategies is to consider nanotechnology not only on its own but in convergence with other technologies. At the recent OECD/NNI Symposium on Assessing the Economic Impact of Nanotechnology, it was noted that it is from the integration of different key enabling technologies that it is most likely that their anticipated potential will be achieved [5]. One example of policies for the integration of nanotechnology with other technologies can be found in the third phase (20112020) of the Korean nanotechnology strategy. It highlights strategies for nanotechnology convergence in energy and environmental areas in Korea, especially the convergence of nanotechnology with information technology, energy technology and biotechnology.

III. THE IMPACT OF GREEN NANOTECHNOLOGY

There are significant potential markets for green nanotechnologies but very few products have been commercialized to date. It is expected that the contribution of nanotechnology will be significant but that one or two more decades might be needed to fully realize the market potential of green nanotechnology. In the process of producing and using green nanotechnology products, in addition to direct impacts, there are likely to be a series of indirect effects, including spillovers to third parties and other impacts on supply chains, impacts on the environment and energy usage. The costs associated with the application of green nanotechnologies need to be offset against their beneficial impacts, taking into account such factors as the timing and distribution of various benefits and costs, interest rates, opportunity costs, and the relative advantages of green nanotechnologies compared with conventional applications.

Not all of the benefits and costs will be easily measurable. As the technology is being developed, greater efforts are being made to find ways of assessing or tracking the impact of nanotechnology on specific policy objectives such as green growth. This is a very challenging task. Methodologies being considered for use in assessing the impact of green nanotechnology need to value the full range of potential impacts - economic, environmental and societal implications - which the technology might provide. The risks of using new green nanotechnologies need to be considered relative to the risks in using current technologies (which may be highly energy intensive, use toxic materials or have negative environmental impacts) and valued against the human and environmental costs of not effectively addressing key global challenges.

3.1. General Challenges in Assessing the Impact of Nanotechnology

Some of the numerous issues which make assessing the impact of nanotechnology difficult include the following:

1. There are no conventional definitions or classifications for nanotechnology, nor definitions of a nanotechnology product, a nanotechnology process or a nanotechnology company. It is in general not clear to what extent organizations, such as companies, universities and research institutions, are involved in exploiting and developing nanotechnology. Definitions are central to understanding the nature of the contribution of nanotechnology and to enable in data collection;
2. Measuring the impact of nanotechnology is made more complex by its multipurpose nature.
3. Nanotechnology can be fundamental to a product and give it its key functionality, or it can be ancillary to the value chain and constitute a small percentage of a final product; or it may not even be present in the final product, only affecting the process leading to its production. For a complete impact assessment it is necessary to look not only at the final product containing nanotechnology but also the potential impact of nanotechnology all along the value chain;
4. The sheer number of applications of nanotechnologies across all technology sectors, and their enabling nature, creates a complex and fractured landscape for analysis;
5. Gathering information from industry can be difficult because of sensitivity surrounding nanotechnology products.

3.2. Factors to be considered in Valuing Green Nanotechnology

Simple analyses of the economic contribution of green nanotechnologies would consider the net costs of technological development and market entry relative to the value of the outputs and outcomes achieved, taking into account considerations of time and perspective. The net costs include such inputs as public R&D investment, knowledge development costs and the costs of facilities, private industry

R&D costs and the cost of prototyping, testing, commercialization, production and marketing. The outputs from such expenditures can include contributions to scientific and other knowledge, development of generic or specific technologies, creation and use of intellectual property (including patents and licenses), the development of standards and the spin-off and start-up of new companies. These outputs can have intermediate economic value but the clearest economic impacts are through outcomes such as profitable sales from new products, increased productivity and other process improvements, cost savings, employment and wage generation, taxation and benefits to consumers and users [6]. These outcomes can lead to developmental and public benefits including contributions to national and regional gross domestic product, improved competitiveness and balance of trade and environmental and other societal benefits.

There can also be strategic benefits in the use of nanomaterials, for example to reduce reliance on rare metals and materials sourced from overseas locations. However, the relative weight of benefits and costs of a new technology may vary according to whether the perspective is that of a producer, competitor, customer, worker, industry, region, or country.

IV. FUTURE SCOPE

An increasing trend in science, technology and innovation strategies is to consider nanotechnology not only on its own but in convergence with other technologies wastewater treatment. At the recent, it was noted that it is from the integration of different key enabling technologies that it is most likely that their anticipated potential will be achieved.

V. CONCLUSION

In this way we can conclude that, green innovation is innovation which reduces environmental impacts: by increasing energy efficiency, by reducing waste or greenhouse gas emissions and/or by minimizing the consumption of non-renewable raw materials. The potential of nanotechnology to support green growth, focusing on two particular aspects: i) the potential for nanotechnology to contribute to green innovation; and ii) the potential and perceived risks and environmental costs of using the technology. The second of these may reduce the ability of nanotechnology to achieve its green goals, i.e. to meet its “Green vocation”

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P-XRD, Spectral and Antibacterial Studies of Mn[II], Cu[II] and Zn[II] Acetate Complexes of Schiff Base Ligand

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ABSTRACT

Transition metal complexes of O,N donor Schiff Base ligand (HEPP) of Mn[II], Cu[II] and Zn[II] have been synthesized and characterized by CHNS analysis, UV–visible, ^{1}H NMR, FTIR spectra, P-XRD, TGA and screened for antibacterial studies. From spectroscopic data, the stoichiometry of the metal complexes have been found to be 1:1 (M:L). The P-XRD data propose tetragonal crystal system for Mn(II) complex and orthorombhic crystal system for Cu(II) complex. The ligand (HEPP) and its metal complexes were screened for antibacterial studies against *S. aureus* and *E. coli.*

Keywords: Schiff base, FTIR, UV-Vis, TGA, P-XRD, Metal complexes.

I. INTRODUCTION

The coordination chemistry of Schiff bases having O, N donor atoms and their metal complexes have created much more interest in last decade due to its importance in medical, agricultural, analytical, biological and industrial field[1-3]. The Schiff bases having O, N donor atoms and their metal complexes have various applications in field of catalysis, agriculture, polymer and biological sciences as antimicrobial agent, in medicinal science as anticancer, in food and dyes industry, antiseptic and antiulcer agents [4-7].

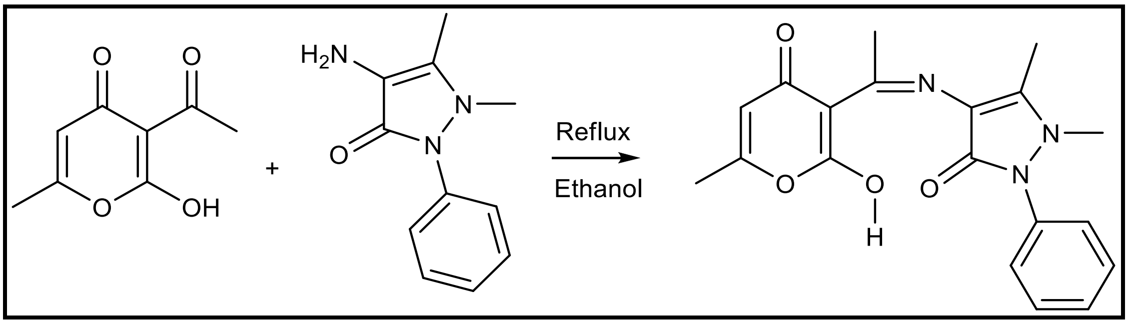
From above facts the reaction of the transition metal acetates and Schiff base ligand was carried out and structures of resulting complexes were investigated using spectroscopic data and P-XRD data. The results are discussed in this paper.

II. MATERIALS AND METHODS

All chemicals and solvents used for the synthesis of ligand and complexes were AR grade. The CHNS analysis was performed on Elementar-Vario EL-III analyzer. FTIR spectra was recorded on Spectrum RX-I spectrophotometer using KBr pellets. ^{1}H NMR spectra of ligand was measured in $CDCl_3$ +DMSO. A mass spectrum was recorded on Bruker Esquire 3000. The TG analysis was performed on Perkin Elmer TA/SDT-2960 and P-XRD were recorded on Philips 3701. UV–visible spectra of the complexes were recorded on JascoUV-530 spectrophotometer.

Preparation of Schiff Base (Z)-4-(1-(2-hydroxy-6-methyl-4-oxo-4H-pyran-3-yl)ethylidene amino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one **(HEPP).**

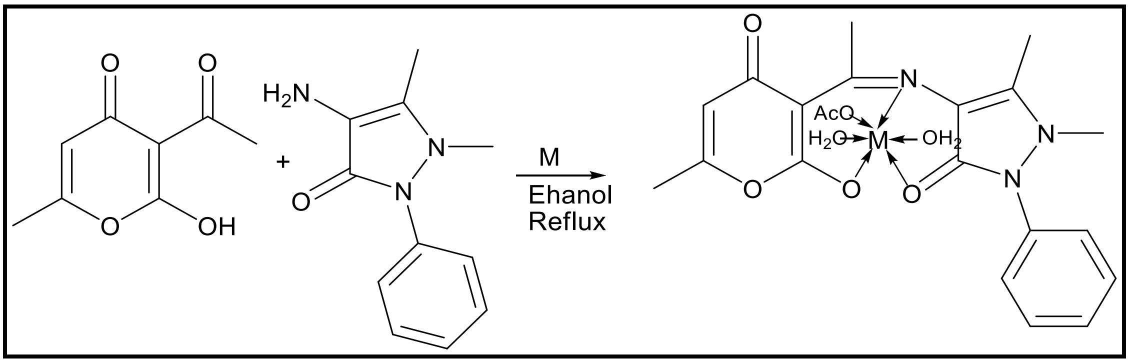
The alcoholic solution (25ml) of Dehydroacetic acid (0.005 mol) and alcoholic solution (25ml) of 4-aminoantipyrine (0.005 mol) was mixed slowly with stirring. The above reaction mixture was refluxed at 80-90ºC for 4–5 hrs. On cooling, the solid yellow ppt. was formed, which was filtered and washed thoroughly with ethanol and dried. (Yield: 72.27%).



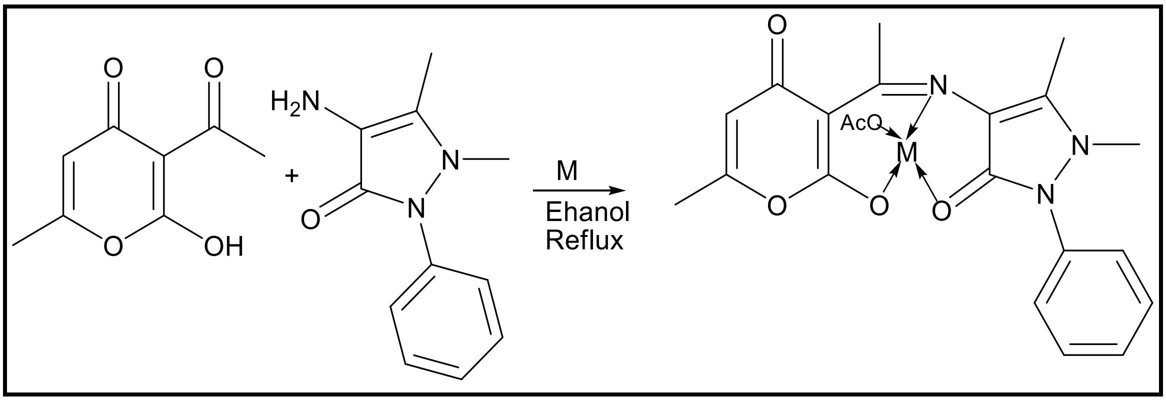
Scheme 1. Synthesis of Schiff base

Preparation of metal complexes

The alcoholic solution (25 ml) of the ligand (0.003 mol) and alcoholic solution (25 ml) of the respective metal acetate (0.003 mol) was mixed together with stirring. The pH of reaction mixture was maintained in between 7-8 by adding 10% solution of alcoholic ammonia. The reaction mixture refluxed for 2–3 hrs. (80-90ºC). On cooling colored ppt. was formed. It was filtered, washed thoroughly with ethanol and dried under vacuum [8].



Scheme 2. Synthesis of Mn(II) complex



Scheme 3. Synthesis of Cu(II) and Zn(II) complex

III. RESULTS AND DISCUSSION

All complexes having different colures, Insoluble in ethyl alcohol and methyl alcohol.

Table 1. Physical and analytical data of ligand HEPP and metal complexes

Sr. No.	Ligand/ Metal Complexes	Color	Yield (%)	M.P. °C	Elemental Analysis Found % [Calc.] %			
					C	H	N	M
01	HEPP	Yellow	72.27	208	64.63 [64.58]	5.38 [5.42]	11.83 [11.89]	-- --
02	[Mn(II) L(H_2O)$_2$(oAc)]	Grey	63.74	> 300	50.28 [50.19]	5.26 [5.17]	8.29 [8.36]	10.86 [10.94]
03	[Cu(II) L (oAc)]	Green	67.51	> 300	54.77 [54.90]	4.26 [4.15]	14.62 [14.55]	13.17 [13.21]
04	[Zn(II) L (oAc)]	Yellow	71.42	> 300	52.64 [52.92]	4.81 [4.62]	8.67 [8.82]	13.59 [13.65]

^{1}H NMR spectra of Schiff base

NMR spectra shows singlet for ^{1}H at δ=15.6 ppm due to Phenolic-OH and singlet for 3H of -NCH_3 at 3.6 δ ppm. Also singlet for 3H of first -CH_3 at 2.9 δ ppm, singlet for 3H of second -CH_3 at 2.5 δ ppm and singlet for 3H of third -CH_3 at 2.3 δ ppm. The signals of six aromatic protons observed in the range of 6.0-8.0 δ ppm.

Mass Spectrum of Schiff base

The mass spectrum of ligand HEPP shows a peak at m/z 354.14 (M+1 Peak) which confirms the formation of Schiff base (HEPP).

IR Spectra

The Infrared spectra of ligand HEPP and metal complexes were recorded and some selective bands are shown in Table No.2. The spectra of ligand HEPP and metal complexes were compared to know the changes during complex formation. The peak at 3441 cm^{-1} is due to υ [OH] of ligand and in metal complexes the peak at 3441 cm^{-1} is missing, it indicate that [-OH] is engaged in bonding with metal. The peaks at 1735 cm^{-1} and 1669 cm^{-1} are due to υ [C=O] and υ [C=N] in ligand and in metal complexes, their values are decreasing it indicates that [C=O] and [C=N] form bonds with metal. From above observations it is clear that Azo-methine nitrogen, carbonyl group and phenolic hydroxyl group take part in the coordination with metal ion [9-11].

Table 2. FTIR spectral data of the ligand (HEPP) and its Metal complexes (cm^{-1}).

Ligand / Metal complexes	υ (-OH)	υ (C=O)	υ (C=N)	υ (M-O)	υ (M-N)
HEPP	3441	1735	1669	--	--
[Mn(II) L(H_2O)$_2$(oAc)]	--	1706	1662	538	437
[Cu(II) L (oAc)]	--	1714	1647	540	423
[Zn(II) L (oAc)]	--	1706	1663	538	461

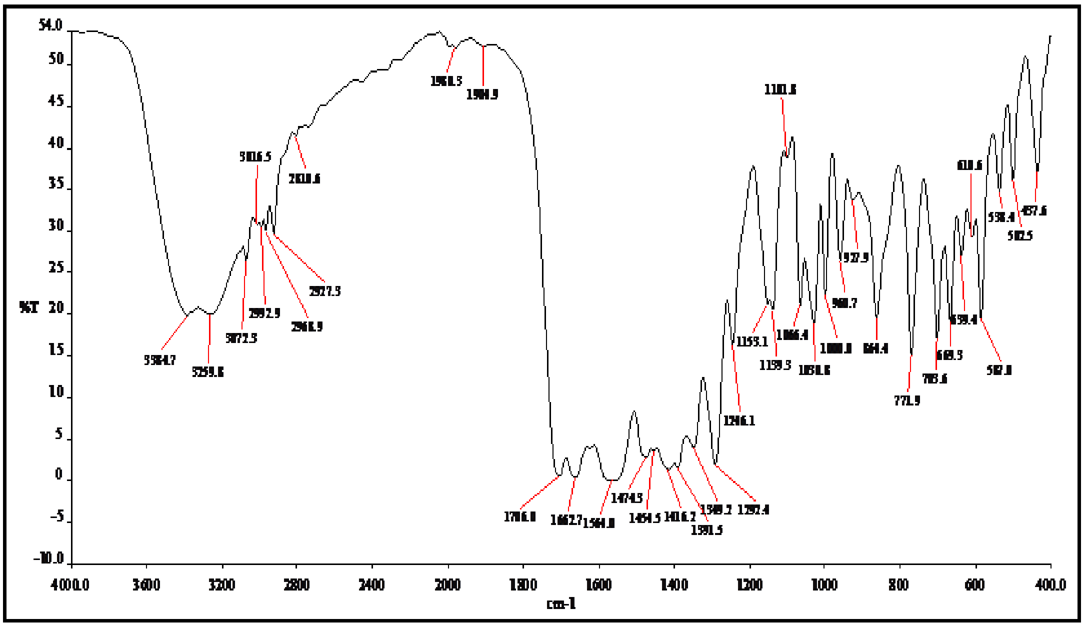


Fig.1. IR spectrum of Mn(II) complex.

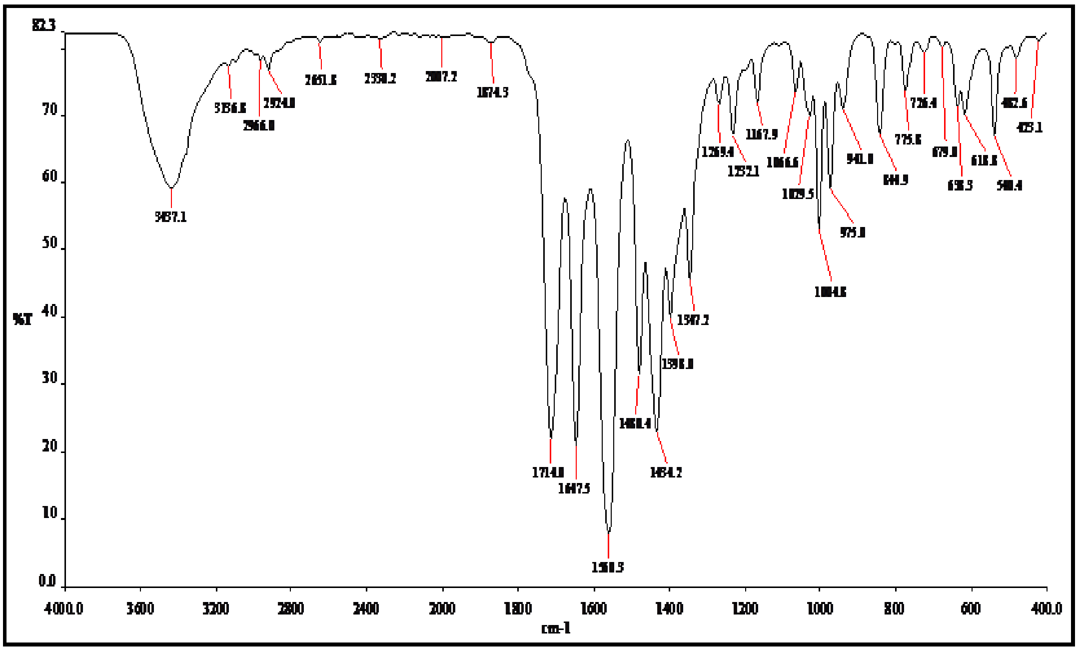


Fig.2. IR spectrum of Cu(II) complex.

Electronic spectral analysis

The electronic spectrum of ligand HEPP and metal complexes were taken in Dimethyl sulfoxide (≈5×10^{-4}) Molar in range of 50000 to 16666 cm^{-1}[12-16].

The ligand HEPP revealed two bands at 33333 and 25641 cm^{-1} due to $\pi\rightarrow\pi*$ and $n\rightarrow\pi*$ transition respectively.The Mn(II) complex shows two bands at 34482 and 25000 cm^{-1} assigned to charge transfer transition. The Cu(II) complex revealed three bands at 37037, 30303 and 23809 cm^{-1} assigned to charge transfer, charge transfer and $^2T_2g\rightarrow{}^2Eg$ transition respectively. The Zn(II) complex revealed two bands at 29411 and 24390 cm^{-1} assigned to charge transfer transition.

Electronic spectral data of the ligand HEPP and Metal complexes are given in table no.3.

Table 3. Electronic Spectral data of the ligand HEPP and its Metal complexes.

Ligand/ Metal Complexes	Absorption Maxima cm^{-1} (nm)	Proposed assignments
HEPP	33333	$\pi \rightarrow \pi*$
	25641	$n \rightarrow \pi*$
Mn(II) complex	34482	charge transfer
	25000	charge transfer
Cu(II) complex	37037	charge transfer
	30303	charge transfer
	23809	$^2T_2g \rightarrow ^2Eg$
Zn(II) complex	29411	charge transfer
	24390	charge transfer

Powder X-ray diffraction

The P-XRD of metal complexes were scanned in range $2\theta = 20\text{-}80^\circ$ at wave length 1.540Å. The P-XRD data is useful for the information of cell parameters; lattice parameters, crystal system etc. are given in table no.4. The diffraction pattern shows the crystalline nature of metal complexes [17].

The complex Cu(II) showed 23 reflections. The axis angle found are $\alpha = 90^0$, $\beta = 90^0$, $\gamma = 90^0$ and volume of unit cell, V = 2585.50 $Å^3$ belongs to orthorombic crystal system.

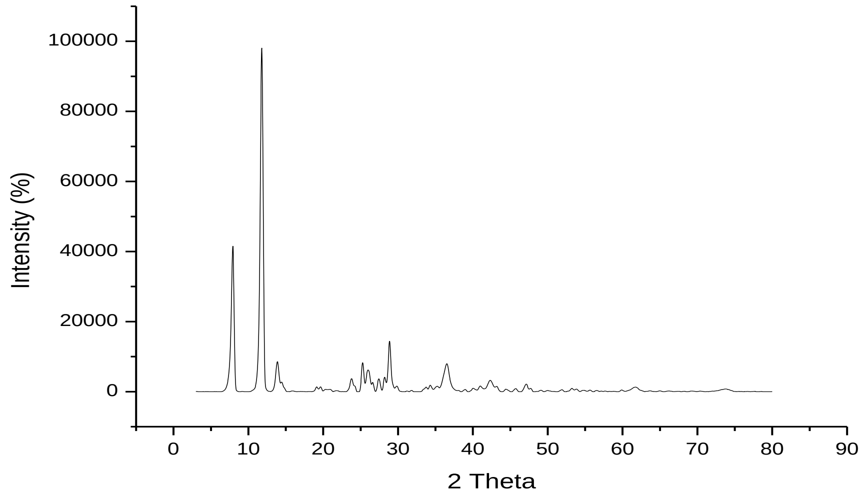


Fig.3. X-ray diffractogram of Cu(II) complex.

Antibacterial screening

The findings of in vitro bactericidal activity of the HEPP ligand and its metal complexes [Mn(II) $L(H_2O)_2(oAc)$], [Cu(II) L (oAc)], and [Zn(II) L (oAc)] are presented in Table No. 4. In this activity Ciprofloxacin used as positive standards and the solvent used was DMSO to dissolve metal complexes. The inhibition zone of ligand HEPP and metal complexes clearly indicates that metal complexes having more efficacy than free ligands.

Table 4. Antibacterial activity of Ligand HEPP and Metal complexes.

Ligand / Metal complexes	**Area of inhibition in (mm)**			
	Gram +ve		**Gram -ve**	
	S.aureus	**K. pneumoniae**	**E.coli**	**P. aerugenosa**
HEPP	17	16	19	20
Mn(II) Complex	19	22	20	22
Cu(II) Complex	19	18	22	21
Zn(II) Complex	18	20	21	19
Ciprofloxacin*	31	32	32	29
DMSO	7	6	6	7

IV. CONCLUSION

The Mn[II] complex shows coordination number six with octahedral geometry and Cu[II] and Zn[II] shows coordination number four with square planar geometry based on spectral and P-XRD data. Bacterial study of these complexes shows that some complexes show better activity than ligand. The FTIR data suggest that the ligand behaves as tridentate towards metal ion. The P-XRD data suggest that Cu(II) complex shows Orthorhombic crystal system.

V. ACKNOWLEDGMENTS

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Determination of pH and NPK of Soil in Majalgaon of Beed District

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ABSTRACT

Healthy soil produces healthy crops. Soil is the only source of nutrients for cultivating the crops. Health and fertility of any soil can be determined from the investigation its pH and the content of available NPK i.e., nitrogen (N), phosphorus (P) and potassium (K). Changes in pH of the soil changes the nutrient availability to large extent. Nitrogen is a macronutrient and it has major role in plant metabolism and growth. After nitrogen, phosphorus is the next required macronutrient for the plants and it makes greater than 1% of dry organic matter. It has remarkable effect on the growth of plants. It is available in plants in the soil in organic as well as inorganic form. Potassium is an important nutrient for plant growth. It is also needed in ample amount for plant growth. The role of potassium in plants is in opening and closing of their stomata. Lack of these elements has adverse effect on the plant growth and lowers the yield. For the systematic study soil samples from eleven villages were collected that are located in Majalgaon taluka of Beed district, Maharashtra, India. Results obtained by analysis suggests that pH is more than 7 which indicates that all the soil samples are slightly alkaline in nature, available nitrogen is in low to medium range, phosphorus is in low in range, potassium is in medium range. For the determination of pH and NPK, instruments used are pH meter, Micro-Kjeldahl digestion and distillation unit, UV-Visible spectrometer and Flame photometer, respectively. Study recommends the use of fertilizers to improve the fertility status of the selected locations.

Keywords: pH, NPK, soil, Majalgaon

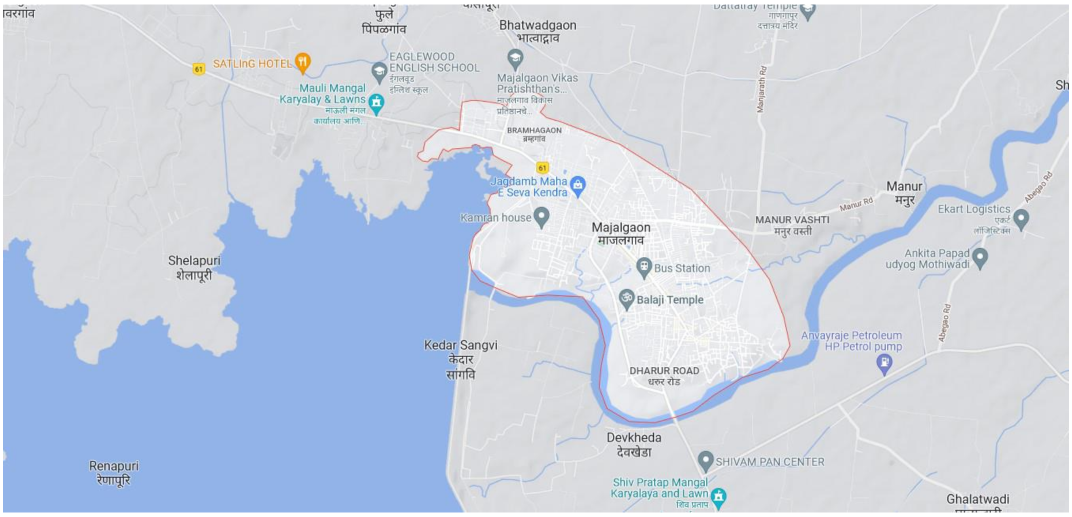
I. INTRODUCTION

Soil is essential for proper growth of plants. It should have all the required nutrients in ample quantity for proper growth and functioning in biological systems. If the soil is not healthy, plants grown on it will also lack those nutrients. If the soil has all the required nutrients then the crops grown are rich with nutrients. Thus, soil plays a crucial role in producing healthy crops and results in successful agriculture [1]. It is to be noted that production of crops also increases with soil rich in nutrients. To check health of soil it is important to check different constituents of soil by its analysis. What kind of fertilizer is to be used for a particular soil depends on the lack of nutrients in it. Different types of soil require different kind of fertilizers and in different amount.

Thus, type and amount of fertilizer to be used for a soil depends on the health of soil. Thus, by proper soil analysis one gets the idea about the nutrients present in soil. From this data, one can decide the type and amount of fertilizer to be used for the enrichment of soil. For different type of crops of soil different types of soil is needed. Thus, enrichment of soil with a particular nutrient relies on the type of crop to be produced in that soil [2]. This can be known from the analysis of soil.

This research is limited to the analysis of soil for pH, nitrogen, phosphorus and potassium. The fertility status of soil majorly depends on the pH and the said elements present in soil [1]. For this, eleven different village in Majalgaon taluka were selected. Therefore, analysis of soil in these regions is considered as the starting point for the determination of type and amount of fertilizer needed for the soil in these regions. Soil analysis provides the information about the type of soil and with this knowledge one can improve the fertility of soil by adding the fertilizers to yield the desire crops production. Determination of physico-chemical properties and available nutrient status of the soil of an area is vital for improving production of crops [3].

II. STUDY AREAS



The study area is eleven nearby villages of Majalgaon in Beed district. Beed district is under Maharashtra state in India. The eleven villages considered for soil analysis are Devkheda, Nagzari, Chinchagavan, Bramhgaon, Renapuri, Shelapuri, Punandgaon, Sawargaon, Mangrool, Laul and Limgaon. The selection of villages for soil analysis was determined from the amount of land used for crop productivity.

III. MATERIALS AND METHODS

Soil sampling

From each village three samples were collected from random areas. All together 33 samples were collected. After collection, soil samples were air dried and soil was made clean by removing roots, stones, pebbles etc. Soil samples were sieved and were collected in cloth bags with a tag of date and location from where the soil was collected. Total 4 parameters with respective methods as shown in table I were used to assess the physico-chemical properties of soil.

Table I: Showing the various parameters of soil sample analysis and methods. S. No	**Parameter**	**Method**
1	pH	pH metry
2	Available N	Micro-kjeldahl distillation unit
3	Available P	Spectrophotometry
4	Available K	Flame photometry

IV. RESULTS AND DISCUSSION

Soil pH: pH of soil strongly affect the nutrient availability and it is defined as the negative logarithm of hydrogen ion concentration (H^+). It is an notable property of soil as it greatly affects the microbial activity in the soil, physical properties of soil, and availability of nutrients to crops. pH affects all physical, chemical and biological properties of soil. Availability of N, P and K in general is low below 5 and above 7. pH values of different soil samples are shown in Table- II. It was found that the soil samples of all villages are slightly alkaline because their pH ranges between 6.9-8.5. Low alkaline characters may be due to less rain fall. Slightly alkaline pH of these soil samples may be due to the large quantity of calcium carbonate content in soil. The soil in these regions is basaltic organic which makes the soil rich in basic cations [4]. All these villages have a suitable pH for growing crops. There is no much pH difference between these eleven villages. The pH of the different sites is as shown in table II:

Available Nitrogen (N)

Nitrogen is a macronutrient and it is required in large quantity for plant metabolism and growth. Plant takes nitrogen in the form of NO_3^- ion, in an aerobic condition whereas in the form of NH_4^+ ion in anaerobic condition [5]. A Kjeldahl method was used for the determination of nitrogen content in the soil samples. The values of available Nitrogen of different soil samples are shown in table II. Nitrogen gives dark green colour to plants. Generally, nitrogen deficiency occurs in early growth and it results in delay in maturity in plants. It was observed that the soil sample of Shelapuri village has the highest nitrogen content with 485.40 kg/ha in the soil.

The lowest nitrogen content was found in Limgaon village with 210.65 kg/ha. It was found that the nitrogen content was low in some place and medium in some place. The nitrogen content in the soil low to medium as shown in table II.

Table II: Showing the value of pH and NPK content in soil samples

Sr. No.	Samples	pH	Nitrogen (kg/ha)	Remarks	Phosphorus kg/ha	Remarks	Potassium kg/ha	Remarks
1.	Devkheda	7.1	402.80	Medium	6.51	Low	217.322	Medium
2.	Nagzari	7.4	290.60	Medium	8.21	Low	275.421	High
3.	Chinchagavan	7.3	404.20	Medium	8.35	Low	268.641	High
4.	Bramhgaon	6.9	270.80	Low	7.23	Low	218.109	Medium
5.	Renapuri	8.4	365.50	Medium	7.41	Low	269.521	High
6.	Shelapuri	7.5	485.40	Medium	8.51	Low	250.468	High
7.	Punandgaon	8.2	365.21	Medium	10.29	Low	257.832	High
8.	Sawargaon	7.1	474.71	Medium	9.41	Low	252.322	High
9.	Mangrool	8.1	452.71	Medium	7.35	Low	274.324	High
10.	Laul	7.9	230.82	Low	8.41	Low	271.352	High
11.	Limgaon	7.7	210.65	Low	10.47	Low	220.720	Medium

Available Phosphorus (P)

Phosphorus is the next most essential macronutrient present in the biological systems, which makes more than 1% of dry organic matter [6]. It is also a major factor that affects plant growth. It is present in the soil in both organic and inorganic form. The values of available Phosphorus of different soil samples are shown in table-II. The primary role of phosphorus in a plant is to store and transfer the energy produced from the photosynthesis for growth and reproductive processes. Ample amount of phosphorus helps in root growth. Deficiency of P reduces the yield by delaying maturity, prevents growth, and restricts the use of energy by the plant. Phosphorus is a limiting nutrient for crops and forage for production. Soil samples of all villages selected shows that they are low in phosphorus content. The phosphorus content in the soils are found in the range of 6.51 kg/ha – 10.47 kg/ha which is quite low. Deficiency of P reduces the yield by delaying maturity, prevents growth, and restricts the use of energy by the plant. The details of phosphorus content in different soil samples is shown in table II

Available potassium (K)

Potassium is an essential nutrient for plant growth. It is a macronutrient since it is needed by plant in a major quantity [7]. Potassium helps the plant in opening and closing of their stomata. Lack of potassium reduces the plant growth and lowers the yield. The values of available potassium of different soil samples are shown in table- II. It was observed that soils of the villages have medium to high potassium content. It ranges from 217.322 kg/ha - 275.421 kg/ha.

V. CONCLUSION

Physico-chemical properties determination is needed to know the fertility status of soi. Form this data one can know the amount and type of fertilizer to be used to enhance the crop productivity. Soil fertility can be known from this data. Thus, it can be concluded that pH of soil is good for the type of crops taken in these regions. Low content of nitrogen and phosphorus suggests to use fertilizers rich in these nutrients. As the amount of NPK is different in these regions different amount of fertilizer is to be used. Fertility status can be improved by addition of inorganic fertilizers and organic manures. Results obtained by analysis suggests that pH is more than 7 which indicates that all the soil samples are slightly alkaline in nature, available nitrogen is in low to medium range, phosphorus is in low in range, potassium is in medium range. Present study will help the farmers to know the NPK content of the soil and use of different types of fertilizers to get the better quality of produce and conservation of soil and water.

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Analysis of Laminated Beam with Different Shear Deformation Theories

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ABSTRACT

The plan is based on the path of a beam as defined by a virtual work system rule and the thickness of a laminated beam. The virtual work standard is used to monitor beam differential conditions and point of confinement conditions. There are now explanations for transverse uprooting of beams and culpability in the case of shear deformation. The numerical data for the beam's various lengths and thickness extents was managed using MATLAB coding.

Keywords: Sinusoidal load, hyperbolic shear deformation theory, governingdifferential equations, MATLAB coding, thermal stress.

I. INTRODUCTION

A strong material called a composite, sometimes known as a composite, is created when at least two different substances, each with unique features, are mixed to create a new substance with properties that are better than the original parts in each application. Ozutok and Madenci [1] studied Considered mixed restricted part conditions that rely on a reasonable are acquired by employing Gateaux differential for overlay composite beams, and a higher order shear distortion hypothesis is offered, which includes nonlinear passage of shear stress across the thickness of layerwise beam. Layerwise composite plane beams have been investigated by Hasim [2] using the revised jumble hypothesis in an isogeometric static investigation.Another higher-order deformation based on migration is presented by Ali *et al.* [3]. Even for thick laminates and any combination of mechanical and thermal stacking, it has been shown that the idea, which is based on reasonable expulsion variances, is extremely accurate. For specific difficulties of flexure of composite laminates, Bhaskar *et al.* [4] proposed the action plans inside the construction of straight uncoupled thermoelasticity. In order to investigate the thermal response of orthotropic overlaying plates while taking into account the traditional rule of virtual evacuations, Carrera [5] compares as to deformations built out using the Reissner Mixed Variational Theory (RMVT).In Carrera's [6] study, methods for evaluating conventional and get over shear nerves in disorganised orthotropic plates were thoroughly reviewed. The progress of the principal designer's work on two-layered displays for thermal temperature testing of various composite plates is included in Carrera [7].

The beam under consideration

The beam under consideration as shown in Fig. 1.1 occupies in $0-x-y-z$ Cartesian coordinate system.

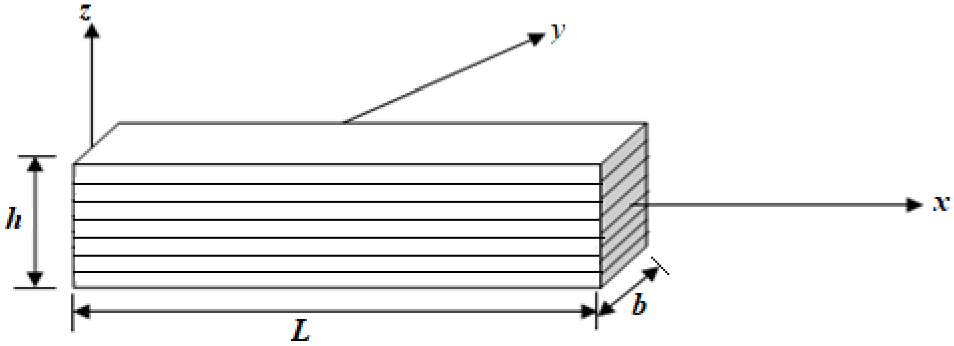

Fig. 1.1. configuration of a laminated composite beam

The Displacement Field

In light of the before referenced suppositions, the displacement field of the present composite laminated beam theory can be communicated as follows:

$$u(x,z) = u(x) - z\frac{dw}{dx} + \left[h \sinh\left(\frac{z}{h}\right) - \frac{4}{3}\frac{z^3}{h^2}\cosh\left(\frac{1}{2}\right) \right]\phi(x)$$

$$w(x,z) = w(x) \tag{1.1}$$

Where u is the displacement in the x direction and w is transverse displacement in the y direction of a point on the beam in mid plane.

Example 1: A simply supported beam with sinusoidally distributed load,

$q(x) = \sin(\pi x / L)$

The simply supported beam is having its origin at left support and is simply supported at *x=0 and x=L.* The beam is subjected to sinusoidally distributed load, $q(x) = \sin(\pi x / L)$

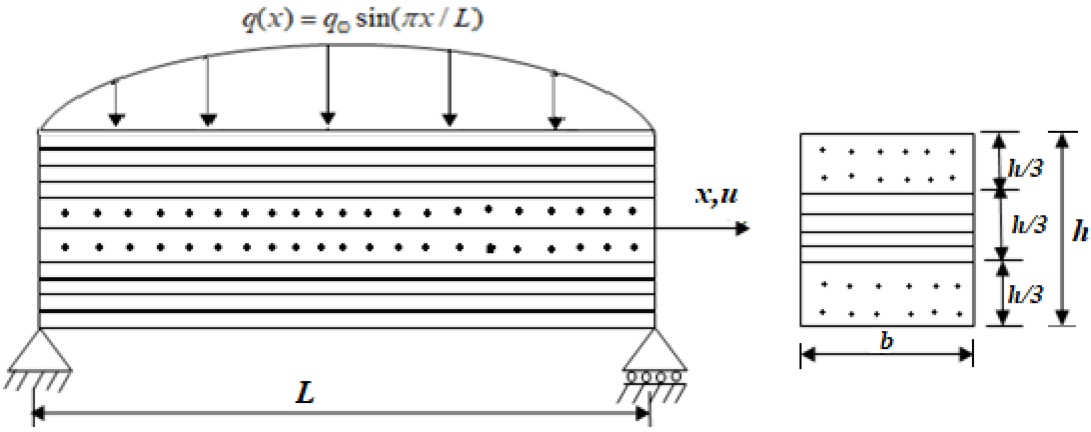

Fig. 1.2. Simply supported beam with sinusoidally distributed load of three-layer beam ($0^0/90^0/0^0$)

Non dimensional transverse displacement $\bar{w}$

For $0^0/90^0/0^0$

$$\bar{w}=\left[\frac{3.4071\times10^{5}6\alpha_L L^2Th^2\pi\left(6.2192\times10^{16}L^2+7.2006\times10^{18}h^2\pi^2\right)}{\left(1.1299\times10^{21}L^2h^3\pi^4+1.7980\times10^{20}h^5\pi^6\right)}\right]\left[\frac{h}{\alpha_L L^2T}\sin\frac{\pi x}{L}\right]$$

Table No: 1 Non-Dimensional Transverse Deflection ($\bar{w}$) at (*x = L, z = 0.0*) for Single Layer, Three Layers and Four Layersof Laminated Simply Supported Beam Subjected to Sinusoidally DistributedLoad $[\sin(\pi x/L)]$ for Aspect Ratio 2,4,10 and 20. (Example 1)

Theory	AS -2	AS- 4	AS-10	AS-20
Present HYSDT	9.951	3.468	0.965	0.562
TSDT [9]	9.045	3.022	0.869	0.540
HSDT [7]	10.562	3.533	0.960	0.563
FSDT [5]	0.462	0.437	0.430	0.429
ETB [3]	0.429	0.429	0.429	0.429

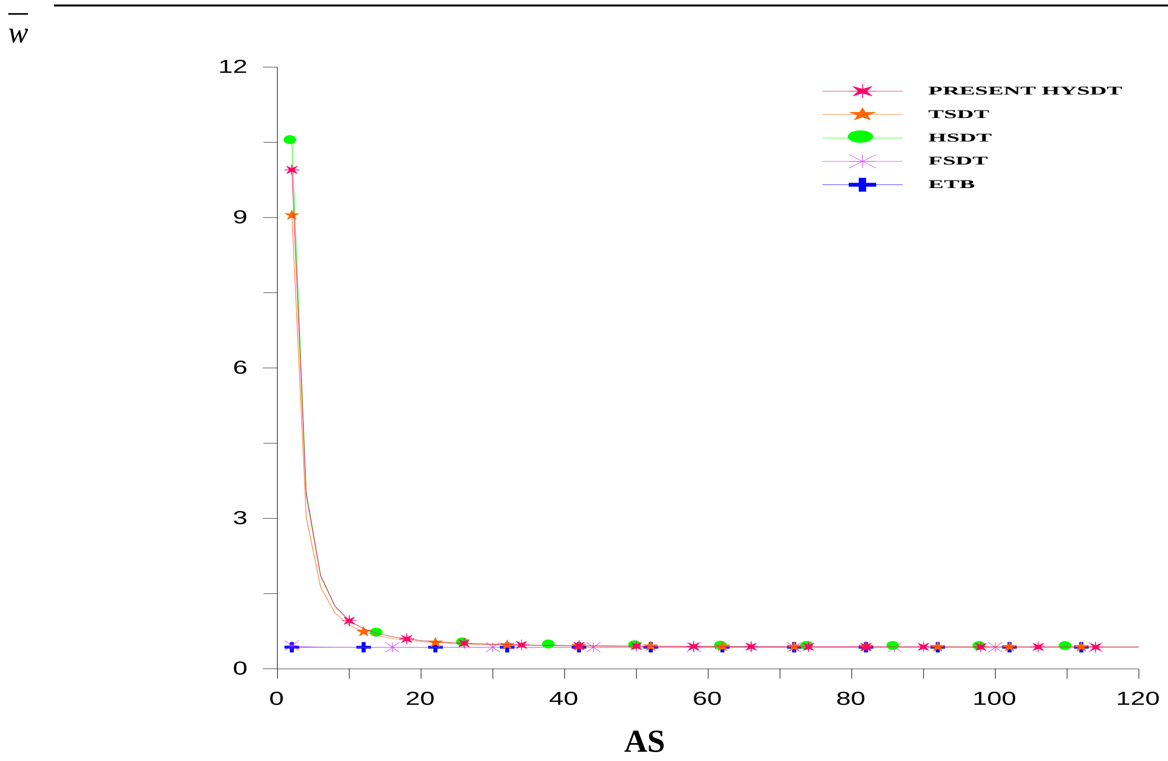

Figure 1.3: Variation of maximum transverse displacement ($\bar{w}$) at (*x = L, z = 0.0*) for single layer with ply angle ($0^0/90^0/0^0$) of laminated simply supported beam subjected to sinusoidally distributedload $[\sin(\pi x/L)]$ for aspect ratio AS. (Example 1)

II. CONCLUSIONS

1. The outcomes got by the current hypothesis are exact as seen from the correlation with othershear deformation theories.

2. The present hypothesis gives reasonable aftereffects of removal for the simply supported beam exposed to thermal stacking is in great concurrence with that of ETB, FSDT, HSDT and TSDT.

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Mathematical Aptitude in Marathwada Secondary School Students by using Tests

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ABSTRACT

Different Tests are common tools in evaluating learner's progresswhich plays an important role in teaching-learning situation. This descriptive study analyzed these tests of secondary mathematics in the Marathwada,Maharashtra, India, through thecollected first quarter test paper together with the table of specification and curriculum guide as framework of analysis.The grade 7 to grade 10 mathematicstests were examined to determine the types of test items used and the distribution of test items to each level of cognitive process dimensions of Anderson and Krathwohl Revised Bloom's Taxonomy. The respondents are the 56 public secondary mathematics teachers from the 14 schools (comprises of one purposively selected teacher respondent for each grade level). The result indicated that the most frequent type of test item under selected-response format is multiple-choice type while short answer type in constructed-response format. Multiple choice was also the type of test item common to the level of cognitive process dimensions considered by Mathematics teachers with Applying Level got the highest percentage (26%) followed by Understanding Level (25%). The teacher-made tests from grade 7 to grade 10 did not cover all the competencies for the quarter as supported by teachers' responses to interview. It is recommended that multiple-choice type of test item shall be formulated following the rules in making a good multiple-choice test question.

Keywords: Teacher-Made Test, Secondary Mathematics, Cognitive Process Dimensions, Selected-Response (SR), Constructed-Response (CR)

I. INTRODUCTION

Forming new test questions is not easy. On the part of the teachers, the person in-charge of constructing test questions, it entails ample time of planning and proper designing. This is to make sure that the test is parallel to the learning competencies, and content and performance-based standards as reflected in the curriculum. For seasoned teachers, constructing test maybe easy because of their experience in both instruction and assessment but not that easy for the rest. A competent teacher in terms of test is a teacher who inspires student to do better on test. This means students prepare for the test and show enthusiasm to learn more even after the test. D'Agostino (2007) revealed that for a learning to be meaningful, a teacher must be competent in the art and science of the tests.

Marathwada region Secondary Mathematics faces an alarming result of performance of high school students in Mathematics as reflected in their quarterly item analysis. The result revealed that in one school in grade 7 Math, 11 out of 40 test items were least mastered by the students, 4 items were too easy, and 7 items were too hard, and 9 out of 40 test items need to be improved due to misleading words and error on grammar. This revelation led to one of the causes of students' failure on the subject knowing that quarterly test takes twenty percent (20%) of student's grade. Therefore, developing test questions that comes after planning for assessment (Goh 2013) needs a degree of proficiency on the part of the teacher because the accuracy of test result is dependent upon the quality of assessment tool, hence, this investigation.

II. METHODS

Thisinvestigation utilized the descriptive method of research as a purposive process of gathering, analyzing, classifying, and tabulating data about prevailing condition, practices, beliefs, and processes and then making adequate and accurate interpretation about such data with or without the aid of statistical methods (Krathwohl 2009). The respondents were the 56 public secondary mathematics teachers from 14 schools of the Marathwada,Maharashtra, India,. The repondents comprised of one teacher per grade level with a total of four teachers per school who were on close coordination with the researcher.

The 40-item first quarter tests together with the corresponding table of specifications and mathematics curriculum guide were requested and gathered from each of the grades 7 to 10 mathematics teacher respondents. A cross examination of the content of the tests parallel to the curriculum guide was done first to identify the learning competencies coved by the test. Afterwhich was the analysis of the types of test items constructed by mathematics teachers in every grade level. This is to determine the type of test items along selected response format (SR) and constructed-response format (CR) frequently prepared. Further, the types of test items formulated along each level of cognitive process dimensions were determined and the percentage of test items per level to describe the teacher-made test.The data were encoded and analyzed and then treated using the descriptive statistics such as frequency count and percentage to answer the questions put forward in the study. To support the findings of the study, unstructured interview was done to the identified and selected teacher respondents.

III. RESULT AND DISCUSSION

This section presents the findings, the analysis and the interpretation of the data gathered. The presentation is in the following order: (1) the different types of test items frequently prepared by secondary mathematics teachers, (2) the types of tests formulated along the level of cognitive process dimensions,and (3) the percentage of the test items according to the level of cognitive process dimensions considered by the mathematics teachers in constructing test questions.

1. The different types of test items frequently prepared by secondary mathematics teachers in Marathwada, Maharashtra, India,

The types of test items used by mathematics teachers depend on the teacher's preferences. It may be a selected-response (SR) or a constructed-response (CR). The table below shows that on SR formats, the multiple choice (MC) was the most frequent type of test item prepared by mathematics teachers in Marathwada,Maharashtra, India, wherein 100% of them used it. One teacher shared: "Teachers prefer multiple choice because it is a standard test item. Periodic test measures the mastery level of the students over a grading period, we need to evaluate student's skills and knowledge on at least two units of learning. Thus, to cover a wide range of topic, MC is a go-to-type of questions. It gives students a chance to get the correct answer and at the same time make teachers check the test paper at ease".

Table 1. Types of Test Items Prepared by Secondary Mathematics Teachers in Marathwada,Maharashtra, India,

TYPE OF TEST ITEM	NUMBER OF TEACHERS PER GRADE LEVEL				TOTAL	PERCENTAGE
	Grade 7	Grade 8	Grade 9	Grade 10		
Selected-Response Formats						
Multiple Choice	14	14	14	14	56	100%
True or False	2	0	3	2	7	13%
Matching Type	2	0	0	0	2	4%
Constructed-Response Formats						
Short Answer (Problem Solving)	2	0	1	2	5	9%
Fill-in the Blank	0	0	2	0	2	4%

A multiple-choice (MC) type of test item strengthen the practice of one school in religious use of test bank quarterly after conducting an item analysis. This assures the teachers that the test items that were validated were kept for future use. Under this type, teachers can gauge the level of difficulties of questions. They can give basic skills of remembering to a more complex questions of evaluating using the multiple-choice type of test. This means secondary mathematics teachers of Marathwadawere able to categorize the test items on multiple choice type as easy, average, and difficult.

It is reflected on the table that grade 7, grade 9 and grade 10 teachers considered other types of test items aside from the multiple choice (MC). It was common to these three levels that the first part of the first quarter test is the multiple choice followed by either true or false, matching type, or fill-in the blanks. While short answer (problem solving) is usually placed at the last part. This usual practice was done to break the monotony of just choosing the answer among the given option on MC because students tend to just write the letter of their answers on their answer sheets and the 40-item test is done in just a matter of ten minutes.

On the other hand, grade 8 teachers only used multiple-choice type of test. In the interview conducted, they disclosed that students were oriented from the very start that their quarterly test is purely multiple-choice, hence they were expected to study better since it can cover a wide concept. They were also encouraged to use scratch paper in solving worded problems in which some teachers require them to submit together with their answer sheet. They emphasized that instead of giving a part for problem solving on the test, they choose to include it on the latter part of MC for easy checking.

Aside from MC, true or false was also considered by mathematics teachers. It can be noted that grade 10 teachers used a modified true or false instead of just merely true or false. Wherein, the students write true if the statement is correct but if false they have to change the underlined word/s to make a true statement. On the why's of choosing this type, one teacher disclosed: "Modified true or false to expose Grade 10 students to test item that trigger their critical thinking skills and good judgement. Writing true or false is easy as choosing the correct answer on the MC." While a grade 8 teacher stated that: "This matching type of test item is highly discriminatory. Those who are good will get a higher score while those who are not will tend to fail. The phrases on column A give hint to the possible correct answer on column B. For me it's a doll-out test". Short-answer type is also an option in constructing a math test as reflected on the table. This is done if a teacher needs to check the skill of the student to manipulate mathematical problem, though grade 8 teachers include this in MC type.

The data gathered shows that majority of secondary mathematics teachers in the Marathwada Division frequently prepared multiple-choice type of test items. The result was supported by the studies of Dibbatista and Kurzawa (2011) on "Examination of the Quality of Multiple-choice Items on Classroom Tests" and Tan and Cordova (2019) on "Development of Valid and Reliable Teacher-Made Test for Grade 10 Mathematics". They revealed that multiple choice type of test item was widely used because it is less expensive and the best test item that suits if the teachers handle a large class size. Less expensive because for them it is not time-consuming and can be checked by the machine or by the guide that can be made by the teacher for easy-checking. They also emphasize that the higher the number of class size, the bigger the responsibility of the teacher on assessing students that's why a cheaper tool can be considered.

The gathered data also reflects that many of the schools were not able to cover all the required competencies for quarter 1 as suggested on the Curriculum guide. In extreme case, one school only covers 4 out of 19 competencies for grade 8. This only supports the finding of Dio (2020) that the spiral design of the K to 12 Curriculum did not decongest the distribution of the content and the learning competencies which results to unrealistic implementation inside the classroom as revealed by the feedbacks and experiences of the mathematics teachers.

2. Types of Test Items formulated by Mathematics Teachers along the Level of Cognitive Process Dimensions

The level of cognitive process dimensions or also known as the Revised Bloom's Taxonomy (2001) came from the original Bloom's Taxonomy (1956). It is a multi-tiered model of classifying thinking according to six cognitive levels of complexity. The six levels of complexity are remembering, understanding, applying, analyzing, evaluating and creating. Each level provides a clear objective and set of skills appropriate for the level of comprehension, from basic skills of remembering to the higher order thinking skills of evaluating and creating.

Table 2. Types of Test Items formulated by Mathematics Teachers along the Level of Cognitive Process Dimensions

Cognitive Process Dimensions	Types of Test Items											
	Multiple Choice		True or False		Matching Type		Short Answer		Fill-in the Blank		Overall Total	Percentage
	Total	Percentage	Total	Percentage	Total	Percentage	Total	Percentage	Total	Percentage		
Remembering	341	16%	10	32%	0	0%	0	0%	0	0%	351	16%
Understanding	533	25%	11	35%	5	50%	0	0%	0	0%	549	25%
Applying	563	26%	0	0%	5	50%	8	21%	0	0%	576	26%
Analyzing	421	20%	0	0%	0	0%	22	58%	11	69%	454	20%
Evaluating	287	13%	10	32%	0	0%	8	21%	5	31%	310	14%
Creating	0	0%	0	0%	0	0%	0	0%	0	0%	0	0%
Total	2145	100%	31	100%	10	100%	38	100%	16	100%	2240	100%

Table 2 presents the types of test items formulated by mathematics teachers along the level of cognitive process dimensions. Each first quarter teacher-made test is composed of 40 items. This has been the practice of the Marathwadadivision secondary mathematics teachers, since the test is good for 1 hour and the students were given an average of 90 seconds to answer each item. This practice is in-line with the TIMMS guidelines (Mullis and Martin 2015) in making a test, where 2 minutes is given to a short answer type test and one minute for multiple-item test -an average of 90 seconds. This was discussed and agreed upon during the Division Learning Action Cell (LAC) for utilization.

The table shows that along the five cognitive process of remembering to evaluating, teachers formulated test items using the multiple-choice type of test. This validate the notion that multiple-choice type of test can be applied on all cognitive process dimensions. Remembering and understanding level comprises the questions that need simple recall like which of the following determines a well-defined set and what is the first step in factoring polynomial with greatest common monomial factor. These questions were constructed in line with the learning competencies “describes a well-defined set” and “factors different polynomial completely”. This implies that MC type of test item is an easy choice along these lower-order thinking skills level. Whereas, along applying, analyzing and evaluating, this type of test item is also a choice but not as easy as in the previous two levels. One grade 8 teacher shared: “Constructing average and difficult questions using the multiple-choice type needs a lot of time and focus because in MC every number corresponds a single point. And constructing three distractors is not easy.” This means, constructing questions along the higher levels using a MC type is advantageous on the part of the learners because they have options to choose from and solutions are not required. Though it will give ease on checking on the part of the teachers, constructing them is not an easy task.

The table also shows that multiple choice type of test is being used by secondary mathematics teachers as their main type of test for the first quarterly test, which has a total of 2,145 which represents 96% of the total number of items. This is because of the division city practice before when the periodic test is still for division wide use, where MC type of test is usually utilized for easy checking.

Another notable insight about Grade 7 level is that teachers formulated items under applying with the 3 different types of test, MC, short answer and fill-in the blanks. This is in-line with the school’s practice that Grade 7 teachers uses different approaches to deal with the adjustments of Grade 7 learners. Grade 7 is the transition stage of elementary and secondary mathematics.

Further analysis shows that Grade 8 teachers used a multiple-choice type of test only. Interviewed teachers emphasized that the reason behind this is because this level comprises the bulk competencies being discussed for the first quarter, competencies for factoring polynomials and rational algebraic expression. Both topics required prerequisite skills on integers and basic operations, which many students failed to achieved mastery during their previous year level. This dilemma added to the non-completion of all competencies required for the first quarter for Grade 8 mathematics. A teacher rants about it saying: “They could not master the basic operations on integers, how much more of fractions. At the end of the day, it will file-up to non-ending unmastered skills of the learners.” With this, almost half of the first quarter were allotted on mastering prerequisite skills before proceeding to the grade 8 topics.

This was also shown in the study of Capate and Lapinid (2015) about Assessing the Mathematics Performance of Grade 8 Students as Basis for Enhancing Instruction and Aligning with K to 12 Curriculum wherein they use Mathematics Achievement Test as instrument. They mentioned that their respondents, the grade 8 students, were in the Beginning level of achievement which means “the students struggle with understanding and prerequisite and fundamental knowledge and/or skills have not been acquired or developed adequately to aid understanding" (DepEd Order no. 31 s. 2012).

In addition, the different types of test were formulated by teachers because they fit on the skills necessary for each item. It is shown in the table that true or false, matching type, short answer and fill-in the blank were utilized by grades 7, 9 and 10 teachers. Often the skills to be tested were identified already on the curriculum guide, however teachers do the necessary adjustments to evaluate student's knowledge and skills based on their mastery level. A seasoned teacher emphasized the importance of formulating other types of test, aside from multiple choice: "We must prepare our students to the different national exams that will have in the future. We must expose them in different types of test so that they will be oriented and acquainted on the sets of instructions that each type of test have."

Unfortunately, there were no items falls under the level of creating. One reason could be attributed to its complexity and it requires longer time to be evaluated. Teachers disclosed that this level is used in performance-based tasks and even shared her view regarding the cognitive process of creating: "In us we arrived at the creating level once we give projects or performance task for the students. They need enough time to create tangible projects or product with their new set of skills."

3. The Percentage of the Test Items According to the Level of Cognitive Process Dimensions Considered by the Mathematics Teachers

The table 3 shows the distribution of the test items according to the level of cognitive process dimensions. It is presented by grade level so that emphasis on each level will be given. The data will give a clear picture of the level of cognitive process dimensions utilized by secondary mathematics teachers of Marathwada Division in constructing the First quarter Tests.

Table 3. The Percentage of the Test Items According to the Level of Cognitive Process Dimensions Considered by Mathematics Teachers

	GRADE LEVEL									
Cognitive Process Dimensions	Grade 7		Grade 8		Grade 9		Grade 10		Total	Percentage
Remembering	88	16%	62	11%	105	19%	96	17%	351	16%
Understanding	135	24%	112	20%	151	27%	151	27%	549	25%
Applying	118	21%	169	30%	129	23%	160	29%	576	26%
Analyzing	121	22%	131	23%	99	18%	103	18%	454	20%
Evaluating	98	18%	86	15%	76	14%	50	9%	310	14%
Creating	0	0%	0	0%	0	0%	0	0%	0	0%
Overall Total	560	100%	560	100%	560	100%	560	100%	2240	100%

It is noticeable in grade 7 that mathematics teachers constructed more of its test items along understanding, analyzing and applying. In the data gathered, the learning competencies (LC) with the highest number of items formulated in grade 7 were LC 6, 10 and 19. Getting close into it, LC number 6 states that: the learner performs fundamental operations on integers. Here, the mathematics teachers formulated test items under remembering, understanding, applying and evaluating. It can be noticed that this learning competency fall under applying yet the questions formulated do not just fall under it. One teacher reasoned that questions under remembering and understanding lead to applying level, in which the knowledge of students regarding the LC is essential to the next level. While LC number 10 states that the learner performs fundamental operations on rational numbers. In this particular LC, the teachers formulated questions along remembering, understanding, and applying. This means the test items constructed were appropriate to the target competency since it fall under applying level. One teacher shared: “Though the LC falls under applying, I choose to construct questions under remembering and understanding first to guide my grade 7 students. These questions are usually in order from remembering, understanding and applying.”

On the other hand, LC number 19 is on solving problems involving real numbers. This LC falls under evaluating, one of the highest levels. In here, the mathematics teachers formulated questions under understanding, applying, analyzing and evaluating. The questions constructed along this LC are leading to evaluating level. This practice of mathematics teachers is due to the nature of the concept being taught, a teacher disclosed: “I will not ask difficult questions that I know my students will not be able to get the correct answer or even will not make them think about it and just try their luck in choosing the correct one.”

The questions that fall under analyzing and evaluating on this LC will not just let the students decide whether the answer is correct or incorrect but also critic the solutions presented in a word problem. A secondary teacher shared: “Our goal for our learners is to be able to analyze and solve real-life problems. One way to test their knowledge on applying different concepts is through evaluating data. It could be easy as substituting values for the equation or as complex as making decisions based on the evaluated values.”

Looking into the test formulated by grade 8 teachers for the first quarter, the highest number of test items formulated fall under LC numbers 1 and 4. LC 1 is about factoring different types of polynomials completely while LC 4 is on simplifying rational algebraic expressions. Both competencies fall under higher-order thinking skills level but the test items formulated by the teachers were under remembering, understanding, applying, analyzing and evaluating. This implies that the grade 8 mathematics teachers in Marathwada region gradually assess the knowledge and skills of the students and not just focus entirely on one question on a direct level. Before giving questions under the higher level, they prepare first the students by giving easy type of questions that fall under remembering and understanding. A teacher said: “Even in quarterly test we made sure that the students are guided. Before giving them difficult questions, we give them first easy and average types.” Thompson (2008) interpreted the applying level as oftentimes falls both into Lower Order Thinking Skills (LOTS) and Higher Order Thinking Skills (HOTS). He emphasized that for the students to be at this level, they must know how to deal with a new situation. This practice means a lot to the students. One teacher shared: “I remember my student saying, “I know I will be answering difficult question on the latter part whenever I meet first an easy one, that is expected and it’s just fine at least I was guided by the previous question”.”

In grade 9, learning competency number 16 about solving problems involving quadratic functions was given the highest number of test items and therefore taught the longer period of time. This LC fall under applying level but in actual tests, more items fall under understanding level. The same practice in other grade level, grade 9 teachers make sure that topics were thoroughly mastered in the previous level first before going to the next level. Question like, solve for a, b, and c in $s^2+6s+24 = 0$ needs application of knowledge and skills learned in which understanding is necessary. This implies that the questions formulated in this level are still parallel to the learning competencies, thus the teachers comply to the set standards.

It is important to note that Grade 9 teachers put emphasis on Remembering as it composed 19% of its total number of items (1 out of 5). The basis for this practice is due to the nature of the topics for first quarter, they cover quadratic equations, inequalities, and functions. Since topics are new to the learners, grade 9 math teachers tend to give importance on testing basic knowledge and skills of their learners. A Grade 9 math teacher reveals their practice: “Back to basic. We want our learners to grasp the concept first before letting them explore to the different applications and extensions of quadratic equations.”

Applying level has been the focus of grade 10 teachers in constructing test questions which is preceded by understanding and analyzing levels. Considering competency number 3 which is on determining arithmetic means and nth term of an arithmetic sequence that fall under applying level, grade 10 teachers constructed question like what is the 14th term of the arithmetic sequence 5, 7, 9, 11, …? Here the student needs enough knowledge and skill about arithmetic means and arithmetic sequence necessary to find the 14th term. This means grade 10 teachers are particular in constructing test questions, if the competency falls under a particular level stipulated in the curriculum guide the question appropriate to it is constructed.

One practice of grade 10 teachers is that prior to applying concept, they make sure that learners must first understand the concept and principles of each topic. Understanding fully the concept behind every concept in mathematics makes it easier for students to comprehend and apply such skills into a new set of problems or situations. A grade 10 teacher shared: “We should holistically develop our learners. We train them so that they can handle both simple and complicated skills necessary for them to survive on real life world”.

Upon closer analysis of the data, the test items prepared by Grade 9 mathematics teachers lean towards under the easy categories. Among the four grade levels, Grade 10 observed properly the 60-30-10 rule in constructing test items along the cognitive process dimensions. Putting emphasis on Evaluating getting 9% (almost 10%) shared on the total number of items prepared for the first quarter test. The table reveals that the cognitive level of Applying got the highest percentage of 29% among the six level of skills. Considering that the covered competencies for the first quarter of Grade 10 mathematics are continuity of the lesson on Grade 9 and Grade 8 mathematics, teachers focused more on applying the concept of polynomials as reflected on their test construction and the submitted TOS. Under this level, learners are expected to apply and make use of their knowledge and skills in relating concept to real-life problem solving. Grade 10 learners are expected to realize the importance of every concept in mathematics by applying them on their daily activities. This is in consonance with the twin goals of Mathematics on the basic education Curriculum (K to 12 math Curriculum).

In general, each cognitive level received different percentage of distribution of test items per grade levels. But it is also noticeable that the top three cognitive levels of each grade levels are Applying, Understanding, and Analyzing. Further there are only few items falling under the Remembering level. This percentage shows that the teachers did not focus more on assessing simple recall of facts or concept. As one teacher shared: “There were few test questions on remembering level because this level is reflected on the higher level already. Students will not achieve the applying level without mastering the lower levels”. Remembering level is considered as the most basic yet represents an important foundation as it serves as a stepping stone to deeper learning (Persaud 2021). Basic because students simply recall information from a long-term memory. This can be observed to students who have good memorization skill and exhibit good comprehension.

And finally, the level with the least number of test items formulated is along Evaluating. Here, the students make educated judgement about the value of what they have just learned, applied, and analyzed in order to differentiate facts and opinions or inferences (Persaud 2021). This includes finding effective solution to a problem and justifying decisions using knowledge gained. Test questions at this level reflects that students are provoked with questions that can be answered only by critiquing its details and coming up with a sound judgement. Open-ended questions challenge the students to process the information and finally construct judgement and critique the result.

It is noticeable also that the last two levels, the evaluating and creating, gained the least number of test items. In the study of Husna, M., Johar, R., Hajidin, &Mailizar (2018) about the Development of algebra test questions based on Bloom's taxonomy, due to the exercises given in the Indonesian textbooks that usually covers the first four level – remembering, understanding, applying and analyzing, it is very rare that evaluating and creating level of questions are included on the test because the students are not particular of such level.

To sum it up, if the remembering and understanding levels will be categorized as easy, applying and analyzing levels as average and evaluating level as difficult, the result shows that they have percentage rate gets closer to the 60-30-10 design stipulated at DepEd order no. 79, series 2003.

Moreover, based on interviews conducted on selected teachers, the distribution of test items was greatly affected by the topic for the first quarter. This is evident for Grade 8 and Grade 10 mathematics as their content and choice of level of cognitive process dimension to assess was influenced by the topic they covered for the first quarter.

IV. CONCLUSIONS AND RECOMMENDATIONS

The analysis of the tests of secondary mathematics enabled the teachers to assess their instructions and practices of constructing test. The most frequent type of test item along the five levels of cognitive process dimensions prepared by secondary mathematics teachers is the multiple choice under the selected-response format (SR), and short answer under the constructed-response format (CR. There were no items based on the prepared first quarter test by the teacher respondents fall under creating level of the cognitive process dimensions. The level of cognitive process dimensions with the highest percentages considered by the mathematics teachers in constructing test questions are applying and understanding.

It is therefore recommended that the Multiple-choice type of test item must be formulated following the rules in making a good multiple-choice test question (Brame 2013). Mathematics teachers must use different types of test items with a 60-30-10 design of difficulty (easy-average-difficult) of test items stipulated in DepEd Order no. 79, s. 2003 and must be thoroughly followed to assess student's progress along the level of cognitive process dimensions. The mathematics teachers should establish the validity and reliability of the multiple-choice type of test item constructed in their respective schools. A capacity training in constructing a tests along with the five levels of cognitive process dimensions through the table of specifications is necessary to further improve the assessment practices of the mathematics teachers.

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Fredholm Integral Equations : Methods and Applications

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ABSTRACT

Integral equation has been one of the essential tools for various areas of applied mathematics. In this paper, we review different numerical methods for solvingFredholm integral equations. The goal is to categorize selected methods and assess their accuracy. Integral equation is one of the most significant branches of Mathematical analysis in many fields of mechanics, mathematical physics. In this research, we will address Fredholm integral equation, method of solutions and applications.

Keyword: Fredholm Integral Equations; Homogeneous; Linear; Nonlinear; First kind; Second kind

I. INTRODUCTION

Integral equations occur naturally in many fields of science and engineering [1-5]. A computational approach to solve integral equation is an essential work in scientific research. Integral equation is encountered in a variety of applications in many fields including continuum mechanics, potential theory, geophysics, electricity and magnetism, kinetic theory of gases, hereditary phenomena in physics and biology, renewal theory, quantum mechanics, radiation, optimization, optimal control systems, communication theory, mathematical economics, population genetics, queuing theory, medicine, mathematical problems of radiative equilibrium, the particle transport problems of astrophysics and reactor theory, acoustics, fluid mechanics, steady state heat conduction, fracture mechanics, and radiative heat transfer problems.

Fredholm integral equation is one of the most important integral equations. Integral equations can be viewed as equations which are results of transformation of points in a given vector spaces of integrable functions by the use of certain specific integral operators to points in the same space. If, in particular, one is concerned with function spaces spanned by polynomials for which the kernel of the corresponding transforming integral operator is separable being comprised of polynomial functions only, then several approximate methods of solution of integral equations can be developed. A computational approach to solving integral equation is an essential work in scientific research.

Most integral equations closely connected with differential equations are Fredholm Integral Equations [6]. Therefore, Fredholm Integral Equations are derived from boundary value problems for differential equations and then solved by many simplified methods. A strong motivation existed to discover this kind of equation by

Fredholm. The equations were renamed Fredholm Integral Equations after being discovered by Fredholm. It was the point of departure to resolve important obstacles which were impeding the development of mathematics [5]. Finally, we mention that Fredholm Integral Equations are also found in linear and non-linear forms, including the homogeneous and non-homogeneous variety [1, 3].

II. PRELIMINARIES

2.1 Fredholm Integral Equation

The general form of linear Fredholm integral equation is defined as follows:

$g\ (x)\ y\ (x) = f\ (x) + \lambda \int_a^b K(x,t) y\ (t)\ dt,$ (1)

Where,a and b are both constants.$g\ (x)$,$f\ (x)$and $(x,\ t)$ are known functions while $y(x)$ is unknown function. λ (nonzero parameter) is called eigenvalue of the integral equation. The function$(x,\ t)$ is known as kernel of the integral equation.

2.2 FredholmIntegral Equation of First Kind:

The linear integral equation is of form (by setting$g(x) = 0$ in (1))

$f\ (x) + \lambda \int_a^b K(x,t) y\ (t)\ dt = 0,$ (2)

Equation (2) is known as Fredholm integral equation of first kind.

2.3 Fredholm Integral Equation of Second Kind:

The linear integral equation is of form (by setting$g(x) = 1$ in (1))

$y\ (x) = f\ (x) + \lambda \int_a^b K(x,t) y\ (t)\ dt,$ (3)

Equation (3) is known as Fredholm integral equation of second kind.

2.4 Fredholm Integral Equation of Third Kind:

If(x) is neither 0 nor 1, then (1) is referred to as a Fredholm Integral Equation of the third kind .

2.4. Homogeneous and Non- homogeneous Fredholm integral equations :

Suppose that we have the Fredholm Integral Equation of the second kind as follows:

$y\ (x) = f\ (x) + \lambda \int_a^b K(x,t) y\ (t)\ dt$(4)This equation is called homogeneous if given function (x) is identically zero. Fredholm Integral Equation of the second kind called non-homogeneous if function$f\ (x)$ is nonzero.

2.5 Linear and non-linear integral equation:

An integral equation is called linear if only linear operators are performed in it upon the unknown function.On the other hand , an integral equation ,which is not linear is called as non-linear integralequation.

III. METHODS TO SOLVE FREDHOLM INTEGRAL EQUATIONS OF THE SECOND KIND

In this paper we will present some analytical and numerical method to solve fredholm integral equation of the nsecnd kind

3.1 The degenerate kernel method:

Consider Fredholm integral equation of second kind

$y\ (x) = f(x) + \int_a^b K(x,t) y\ (t)\ dt,$ (5)

Here we have assume that $K(x,t)$is separable, therefore we can take

$K(x,t) = \sum_{i=1}^{n} f_i(x) g_i(t)$ (6)Put this value of $K(x,t)$ in equation (5), we get

$y\ (x) = f(x) + \lambda \int_a^b [\sum_{i=1}^{n} h_i\ (x) g_i(t)\ ] y\ (t)\ dt$

$= f(x) + \sum_{i=1}^{n} \int_a^b h_i\,(x)\,g_i\,(\mathrm{t})y\,(t)\,\mathrm{dt}$

$= f(x) + \lambda\sum_{i=1}^{n} h_i\,(x)\int_a^b g_i\,(\mathrm{t})\,y\,(t)\,\mathrm{dt},$ (7)Assume that

$\int_a^b g_i\,(t)y(t)dt = C_i,$ (i = 1,2,3, … ,n), (8)

The equation (7) gives

$y\,(x) = f(x) + \lambda\sum_{i=1}^{n} C_i\, f_i(x),$ (9)

Now we want to evaluate the constants C_i.

Multiplying both sides of (9) successively by $g_1(x)$,$g_2(x)$,$g_3(x)$, ………, $g_n(x)$ and integrating over the range of [a,b], we get

$\int_a^b g_1\,(x)y\,(x)\,\mathrm{dx} = \int_a^b g_1(x)f(x)dx + \lambda\sum_{i=1}^{n} C_i \int_a^b g_1\,(x)h_i(x)dx,$ (10)

$\int_a^b g_2\,(x)y\,(x)\,\mathrm{dx} = \int_a^b g_2(x)f(x)dx + \lambda\sum_{i=1}^{n} C_i \int_a^b g_2\,(x)h_i(x)dx,$ (11)

….. ….. ….. ….. …..

$\int_a^b g_n\,(x)y\,(x)\,\mathrm{dx} = \int_a^b g_n(x)f(x)dx + \lambda\sum_{i=1}^{n} C_i \int_a^b g_n\,(x)h_i(x)dx,$ (12)

Let us define α

$\alpha_{ij} = \int_a^b g_j\,(x)h_i(x)dx\,,$ [i , j ϵ N] , (13)

$\beta_j = \int_a^b g_j\,(x)f(x)dx$ [j ϵ N], (14)

Using the value of $\alpha_{ij}$and $\beta_j$in (10) and using (9), we get

$C_1 = \beta_1 + \lambda\sum_{i=1}^{n} C_i\,\alpha_{1i},$

$= \beta_1 + \lambda\,(C_1\alpha_{11} + C_2\alpha_{12} + \cdots + C_n\alpha_{1n})$

$(1 - \lambda\alpha_{11})C_1 - \lambda\alpha_{12}C_2 - \cdots - \lambda\alpha_{1n}C_n = \beta_1$

Similarly, we can simplify (11), …….. (12). Then , we get a system of homogeneous linear equation to find the value of C_i

$(1 - \lambda\alpha_{11})C_1 - \lambda\alpha_{12}C_2 - \cdots - \lambda\alpha_{1n}C_n = \beta_1$ (15)

$-\lambda\alpha_{11}C_1 + (1 - \lambda\alpha_{12})C_2 - \cdots - \lambda\alpha_{1n}C_n = \beta_2$(16)

… … … … … … …

$-\lambda\alpha_{n1}C_1 - \lambda\alpha_{n2}C_2 - \cdots - (1 - \lambda\alpha_{nn})C_n = \beta_n$(17)

The determinant of (15)-----(17) , i.e. D(λ) , can be written as

$$D(\lambda) = \begin{vmatrix} (1-\lambda\alpha_{11}) & -\lambda\alpha_{12} & \cdots & -\lambda\alpha_{1n} \\ -\lambda\alpha_{11} & (1-\lambda\alpha_{12}) & \cdots & -\lambda\alpha_{1n} \\ \cdots & \cdots & \cdots & \cdots \\ -\lambda\alpha_{n1} & \lambda\alpha_{n2} & \cdots & (1-\lambda\alpha_{nn}) \end{vmatrix} \qquad (18)$$

Which is polynomial in λ of degree n.

Now there are following cases:

Case I: When at least one right member of the system (15)……..(17) is non-zero.

Here , we have following two situations:

(i) If D(λ)≠0 : In this case unique nonzero solution of the system (15)……..(17) exist and therefore (5) has unique non-zero solution given by (9).

(ii) If D(λ)=0 : Then the above equations have either no solution or they possess infinite solution and hence (5) has no solution or infinite solutions.

Case II : When $f(x) = 0$

Here, we have the following two situations:

(i) If D(λ)≠0 :In this case , unique zero solution $C_1 = C_2 = \cdots = C_n = 0$of the system (15)……..(17) exists and Therefore (5)has only unique zero solutions, i.e. $y(x)$=0.

(ii) If D(λ)=0 : In this case above system possess infinite non-zero solutions and therefore (5) hasinfinite non-zero solutions.

Case III : When $f(x) \neq 0$and $f(x)$is orthogonal to all $g_n(t)$.

In this case (14) gives $\beta_1 = 0, \beta_2 = 0 , \dots\dots, \beta_n = 0$ And therefore the equation (15)……..(17) reduce to system of homogeneous linear equations.

Now following situations may arise :

(i) If D(λ)≠0 : In this case , unique zero solution $C_1 = C_2 = \cdots = C_n = 0$ of the system (15)……..(17) exists and Therefore (5) has only unique solutions, i.e. $y(x)$ =$f(x)$.

(ii) If D(λ)=0 : In this case above system have infinite non-zero solutions and therefore (5) has infinite non-zero solutions.

3.2 Adomian decomposition method:

In this section, we use the technique of the Adomian Decomposition Method [4,7,8,9,10] . The Adomain Decomposition Method consists of decomposing the unknown function y (x) of any equation into a sum of an infinite number of components defined by the decomposition series

$y\,(x) = \sum_{n=0}^{\infty} y_n(x)$ (19)

Or equivalently

$y\,(x) = y_0(x) + y_1(x) + y_2(x)+y_3(x) + \cdots+y_n(x)$ (20)

Where the components y (x), $n \geq 0$ will be determined recurrently. The Adomain Decomposition Method concerns itself with finding the components $y_0(x)$, $y_1(x)$, $y_2(x)$, $y_3(x)$, ⋯individually. To establish the recurrence relation, we substitute (19) into the Fredholm integral equation (3) to obtain

$\sum_{n=0}^{\infty} y(x) = f\,(x) + \int_a^b K(x,)(\sum_{n=0}^{\infty} y_n(t))\, dt$(21)

Or equivalently

$y_0(x) + y_1(x) + y_2(x)+y_3(x) + \cdots = f(x) + \lambda\int_a^b K(x,t)\,[y_0(t) + y_1(t) + y_2(t)+y_3(t) + \cdots]\, dt$(22)

The zeroth component $y_0(x)$ is identified by all terms that are not included under the integral sign . (This means that the componentsy_n (x), $n \geq 0$ of the unknown function $y(x)$ are completely determined by setting the recurrence relation

$y_0(x) = f(x), y_{n+1}(x) = \lambda\int_a^b K(x,t)y_n(t)\, dt$, n≥0(23)

Orequivalently

$y_0(x) = f(x)$,

$y_1(x)=\lambda\int_a^b K(x,)\, y_0(t)\, dt$

$y_2(x) =\int_a^b K(x,)\, y_1(t)\, dt$

$y_3\,(x) =\lambda\int_a^b K(x,)\, y_2(t)\, dt$

$y_4(x) = \lambda \int_a^b K(x,) y_3(t)\, dt$(24)

And so on for other component's. In view of (24), the components

$y_0(x)$, $y_1(x)$, $y_2(x)$, $y_3(x)$, $\cdots$ are completely determined. As a result, the solution $y(x)$of the Fredholm integral equation (3) is readily obtained in a series form by using the series as assumption in (19)

3.3 The modified decomposition method [1,7]:

According to the above, the solutions from the Adomian decomposition method are an infinite series of components. Also, it is easy to compute the components y_j, $j \geq 0$ if the inhomogeneous term $f(x)$ in the Fredholm Integral Equation

$y(x) = f(x) + \lambda \int_a^b K(x,t) y(t)\, dt$,(25)

consists of a polynomial of one or two terms. In addition, if the function (x) consists of a combination of two or more of polynomials, trigonometric functions, hyperbolic functions, and others, the evaluation of the components y_j , $j \geq 0$ requires more work. It is worth mentioning that there is a reliable modification of the Adomian decomposition method that was developed by Wazwaz [1]. Where the amendment as presented before, the modified decomposition method depends mainly on splitting the function $f(x)$ into two parts, and as a result, this method cannot be used if the $f(x)$ consists of only one term. To illustrate more of this method, we remember that the standard Adomian decomposition method uses the recurrence relation

$y_0(x) = f(x)$, $y_{n+1}(x) = \lambda \int_a^b K(x,t)\, y_n(t)\, dt$, $n \geq 0$(26)

wherethe expression of the solution $y(x)$ by an infinite sum of components is defined by

$y(x) = \sum_{n=0}^{\infty} y_n(x)$,(27)

According to the (26), the components $y_n(x)$, $n \geq 0$ are easily obtained. The modified decomposition method offers a simple variation to the recurrence relation (26) to determine the components of (x) in the easiest and fastest style. For many cases, we can set

$f(x) = f_1(x) + f_2(x)$ (28)

where we put the function $f(x)$ as the sum of two partial functions, namely $f_1(x)$ and $f_2(x)$. By means of the modified decomposition method, the zeroth component $y_0(x)$ is delimited by one part of (x) ,namely $f_1(x) or f_2(x)$.The other part of $f(x)$ can be added to the component $f_1(x)$that exists in the standard recurrence relation. The modified decomposition method acknowledges the use of the modified recurrence relation

$y_0(x) = f_1(x)$,

$y_1(x) = f_2(x) + \lambda \int_a^b K(x,t) y_0(t) dt$,(29)

$y_{n+1} = \lambda \int_a^a K(x,t)\, y_k(t) dt$, $k \geq 1$.

In view of (26)and (29), we find that the difference between them rests only in the formation of the first two components $y_0(x)$ and $y_1(x)$. Moreover, we note that the remaining componentsy_j,$j \geq 0$ are still lingering in the two recurrence relations. In addition, we find that the slight difference between the formation of $y_0(x)$ and $y_1(x)$ is useful for accelerating the convergence of the solution and reducing the size of the calculations. Moreover, the effects of reducing the number of terms in $f_1(x)$ occur not only in the component $y_1(x)$ but also in the other components. As a result of the study of the modified decomposition method, we can make two remarks: if we make the proper choice of functions $f_1(x)$ and $f_2(x)$, the exact solution $y(x)$ may be obtained by using very few iterations, and sometimes by evaluating only two components. This means that the success of this method depends mainly on the proper choice of $f_1(x)$ and $f_2(x)$ [11], and this we can find by trials only. The modified decomposition method cannot be used if the case of $y(x)$ consists of one term only.

3.4 The noise terms phenomenon method [1]

Noise terms are defined as the identical terms, with opposite signs that may appear between components$y_0(x)$ and $y_1(x)$. Furthermore, they may appear between other components. These noise terms, if they appear, are very useful as they provide us with effective tools to find solutions quickly by using only two iterations. When the noise terms exist between the components $y_0(x)$ and $y_1(x)$, they provide the exact solution by using only the first two iterations. By means of canceling the noise terms between$y_0(x)$ and $y_1(x)$, even though $y_1(x)$ contains further terms, the remaining non-canceled terms of $y_0(x)$ may give the exact solution of the integral equation. Moreover, canceling the noise terms between $y_0(x)$ and $y_1(x)$ is not always sufficient to obtain the exact solution in spite of the appearance of these noise terms. Therefore, it is necessary to show that the non-canceled terms of $y_0(x)$ satisfy the given integral equation. The necessary condition for the appearance of the noise terms is required. In other words, the zeroth component $y_0(x)$ must contain the exact solution $y\ (x)$ among other terms. The following example clarifies this further:

3.5 The Variational iteration method[8,12]:

The general form of this integral equation is given by

$y\ (x) = f\ (x) + \int_a^b K(x,t)y\ (t)\ dt$, (30)

For solving equation (30) by variational iteration method, first we differentiate once from both sides of above equation with respect to x

$y'\ (x) = f'\ (x) + \int_a^b \frac{\partial}{\partial x} K(x,t)y\ (t)\ dt$, (31)

Now, we apply variational iteration method for above equation . According to this method correction functional can be written in the following form

$y_{n+1}(x) = y_n\,(x)+\int_0^x \lambda(s)\ (y_n'(\mathrm{s})-f'(\mathrm{s})-\int_a^b \frac{\partial}{\partial s} K(\mathrm{s},)\ (t)\ \mathrm{dt})\mathrm{ds}$, (32)

Where, λ(s)is a general Lagrange multiplier. To make the above correction functional stationary with respect to y_n, we have

$\delta y_{n+1}(x) = \delta y_n\,(x) +\delta \int_0^x \lambda(s)\ (y_n'\ (\mathrm{s})-f'\ (\mathrm{s})-\int_a^b \frac{\partial}{\partial s} K(\mathrm{s},)\ (t)\ \mathrm{dt})\mathrm{ds}$

$=\delta y_n\,(x) +\delta \int_0^x \lambda(s)\ \delta\ (y_n'\ (\mathrm{s}\ ))\mathrm{ds}$

$=\delta y_n\,(x) +\lambda(x)\delta y_n\,(x) +\int_0^x \lambda'(\mathrm{s})\delta y_n\,(\mathrm{s})\ \mathrm{ds}=0$, (33)

From the above relation for any δy_n , we obtain the Euler-Lagrange equation

$\lambda'(\mathrm{s})=0,$ (34)

With the following natural boundary condition

$\lambda(x)+1=0,$ (35)

By using equations (34) and (35), Lagrange multiplier can be identified optimally as follows

$\lambda(s)=-1,$ (36)

Substituting the identified Lagrange multiplier into equation (32), results in the following iterative formula

$y_{n+1}(x) = y_n\,(x) +\int_0^x \lambda(y_n'\ (\mathrm{s})-f'\ (\mathrm{s})-\int_a^b \frac{\partial}{\partial s} K(\mathrm{s},t)\ y_n(t)\ \mathrm{dt})\mathrm{ds},$ (37)

By starting from $y_0(x)$, we can obtain the exact solution or an approximate solution of the equation (30). In some Fredholm integral equations by differentiating from the integral equation, we obtain a differential equation and we can solve this differential equation by variational iterative method.

3.6 The successive approximations method [1,3,8] :

The method of successive approximations grants us a scheme that can be used for solving integral equations or initial value problems. Moreover, the technique of this method is finding successive approximations to the solution of issue by starting with an initial guess these are called the zeroth approximation. As a matter of fact, the zeroth approximation can be any real valued function $y_0(x)$ that will be used in a recurrence relation to determine the other approximations. Also, we can select any real-valued function for the zeroth approximation; the most frequently used values are 0, 1, or x. To illustrate more, let consider Fredholm Integral Equation of the second kind (3). We have put $y_0(x) = f(x)$, . It must be remembered that the zeroth approximation can be any selected real valued function $y_0(x)$, $a \leq x \leq b$. As a result, the first approximation y_1(x) of the solution of $y\ (x)$ is defined by

$y_1(x) = f\ (x) + \lambda\int_a^b K(x,t)\, y_0\ (t)\ dt$,(35)

We can get the second approximation $y_2(x)$of the solution $y\ (x)$ by replacing $y_0\ (x)$ in equation (35) by the previously obtained y_1(x);thus, we find

$y_2(x) = f\ (x) + \lambda\int_a^b K(x,t)\, y_1\ (t)\ dt$,(36)

These steps can be continued in the same technique above to get the n approximation. In other words, the successive approximations method can be summed up by $y_0(x)$= any selective real valued function

$$y_{n+1}(x) = f\ (x) + \int_a^b K\ (x,)\ (t)\ dt,\ n \geq 0 \quad (37)$$

we obtain the final solution by

$$y\ (x) = \lim_{n \to 0} y_n\ (x), \quad (38)$$

In other words, according to this method, we get a solution if it exists by (4.5). To illustrate this method we will study the following example.

3.7 Homotopy perturbation method (HPM) [1,13]

This method has been provided and developed by Ji-Huan He in [13]. In fact, the homotopy perturbation method was used recently in order to solve linear and nonlinear problems. Moreover, this method works to combine a perturbation technique and a homotopy technique of topology. Additionally, a homotopy with an embedding parameter p ∈ [0, 1] is constructed, which is considered to be a small parameter [9]. Furthermore, the limitations of the traditional perturbation technique have been eliminated due to the coupling between the perturbation method and the homotopy method. Finally, HPM can deal with the first kind and the second kind of Fredholm Integral Equation. However, in this section, we will discuss a special case of the Fredholm Integral Equation of the second kind according to what will be explained as follows:

First of all, let us consider the Fredholm Integral Equations of the Second Kind

$g(x) = f\ (x) + \lambda\int_a^b K(x,t)\ g(t)\ dt$,(39)

Second, we define the operator

$$L(y) = y\ (x) - f\ (x) - \int_a^b K(x,t) y\ (t) dt, \quad (40)$$

Where,$y(x) = g(x)$. Then we define the homotopy$H(y, p)$, $p \in [0, 1]$ via

$$H(y, 0) = F(y) \text{ and } H(y, 1) = L(y), \quad (41)$$

F(y) represents a functional operator. Now we establish a convex homotopy according to the following form:

$$H(y, p) = (1 - p)F(y) + p\,L(y) = 0, \quad (42)$$

This homotopy satisfies (41) for $p = 0$ and $p = 1$ respectively. By including the parameter p ,$y$increases monotonically from zero to one such as the trivial problem $L(y) = 0$. Additionally, the HPM admits the use of the following expansion

$y=\sum_{n=0}^{\infty} P^n y_n,$ (43)

Then,

$g = \lim_{p\to 1} \sum_{n=0}^{\infty} p^n y_n,$ (44)

When the solution exists, it leads to the series (44) , which converges to the exact solution. By substituting (43) in to (42) and using the formula $F(x) = y(x) - f(x)$ and using mathematical operations of equating conditions with like powers of the embedding parameter p, we obtain the following recurrence relation,

p^0: $y_0(x) = f(x)$,

p^{n+1}: $y_{n+1}(x) = \int_a^b K(x,t)\, y_n(t)\, dt$, $n \geq 0$, (45)

When we notice the recurrence relation above, we find that it is identical to the standard adomain decomposition method previously mentioned.

IV. METHODS TO SOLVE FREDHOLM INTEGRALEQUATION OF THE FIRST KIND [8,9]

we have defined the Fredholm Integral Equation of the first kind as the following form

$f(x) = \lambda \int_a^b K(x,t) y(t)$,(46)

The equation above (5)is determined by the occurrence of the unknown function$y(t)$only inside the integral sign and this causes special difficulties[2,13].Fredholm integral equation of the first kind is considered ill-posed problem , postulated the following three properties [2]:

1. Existence of a solution.
2. Uniqueness of a solution.
3. Continuous dependence of the solution on the data y (x).

This property means that small errors in the data y(x) should cause small errors. Now we will offer some of the methods which will be used to find a solution to the Fredholm Integral Equation of the first kind.

4.1 The method of regularization [1,9,10]:

Tikhonov and Phillips [2,12] established this method independently. This method transforms the linear Fredholm Integral Equation of the first kind.

$f(x) = \lambda \int_a^b K(x,t) y(t)\, dt$,(47)

To an approximation of a Fredholm Integral Equation of the second kind

$n y_n(x) = f(x) - \int_a^b K(x,t)\, y_n(t) dt$,(48)

where, nis a small positive parameter. It can be also noted that the Fredholm Integral Equation of the second kind (6) maybe expressed as follows

$y_n(x) = \frac{1}{n} f(x) - \frac{1}{n} \int_a^b K(x,t)\, y_n(t)\, dt$ (49)

Furthermore, it was proved that the solution $y_n(x)$ of the Fredholm Integral Equation of the second kind (8) converges to the solution y (x) of the linear Fredholm Integral Equation of the first kind (6) as$n\to 0$, which means that the exact solution y (x) may be obtained by

$y(x) = \lim_{n\to 0} y_n(x)$ (50)

4.2 The homotopy perturbation method (HPM) [1,10]:

As previously stated in this paper, we discussed this method and how to deal with the second type of Fredholm Integral Equation. In this section, we will discuss this method and how to deal with the first type of Fredholm Integral Equation. We first assume the following Fredholm integral equations of the first kind

$f\ (x) = \int_a^b K(x,t)y\ (t)dt$(50)

Second, we define the operator

L(y)=$f\ (x) - \int_a^b K(x,t)y\ (t)\ dt$ (51)

Now, we establish a convex homotopy according to the following form:

H(y, p) = (1− p)$y(x)$ + p L($y(x)$)= 0 (52)

To include the parameter p monotonically increasing from zero to one. The HPM admits the use of the following expansion:

$y = \sum_{n=0}^{\infty} P^n y_n,$ (53)

Therefore

g(x)=$\lim_{p \to 1} \sum_{n=0}^{\infty} p^n u_n,$ (54)

When a solution exists, it leads to that series and (14) converges to the exact solution. Substituting (53) into (52) and by re-applying the same previous steps, we obtain the recurrence relation

y_0 (x)=0, y_1 (x) = $f\ (x)$

y_{n+1} (x) = $y_n\ (x) - \int_a^b K(x,t)\, y_n$ (t) dt, n ≥ 1(55)

Then the following condition must be a justification for convergence when the kernel is separable:

$\left|1 - \int_a^b K(t,t)dt\right| < 1,$

V. APPLICATIONS OF INTEGRAL EQUATIONS

Due to the advancement of science has led to formulation of many physical problems which are governed by integral equations. The following are some of the areas where integral equations have been applied.

5.1 Seimic Response of Dams:

The dynamic behavior of dam with a full reservoir is known to be different from that of a dam with a empty reservoir.Thedeveloped hydrodynamic pressures affect the motion of the dam, , while the dam response influences in turn the dynamic response of the reservoir. This phenomenon is termed Dynamic Dam-Reservoir Interacction (DRI) it could be catastrophic in cases of resonance, that is when the two domains (dam and reservoir) are vibrating in two phases.

In order to analyze the safety and stability of an earth dam during an earthquake, we need to know the response of the dam to earthquake ground motion so that the inertia forces that will be generated in the dam by the earthquake can be derived.

Once the inertia forces are known, the safety and stability of the structure can be determined. Some approximations are made to create a mathematical model in the form of integral equations, that ist

$y = \int_0^{t} \ddot{a}(\tau)\ g[(t-\tau), z]\ dz$(56)

Where z is the level, y is the displacement, ä is the base acceleration and τ is the shear stress.

5.2 Flow of heat in metal bar:

Here , we consider a classical problem of heat flow in a metal bar to demonstrate the application of integral equations. The unsteady flow of heat in one-dimensional medium should be well defined. The ruling partial differential equation with its boundary are given as follows

$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} - qT$(567)

The boundary conditions are,

T(0, t) = T (l ,t), $\frac{\partial T}{\partial t}(0, t) = \frac{\partial T}{\partial t}$ (l ,t) (58)

And the initial condition is ,

T (x , 0)=$g(x)$(59)

Where T(x , t) is temperature at any time and at any position on the bar, α is the thermal diffusivity , q is the heat loss through the bar, $x = 0$ is the left hand side of the bar and $x = l$ is the right hand side of the bar, l is the length of the bar and t is the time.

VI. CONCLUSION

In this work, we have examined many solutions methods to solve Fredholm integral equations. Using these methods except variational iteration method, the Fredholm integral equations have been reduced to a system of algebraic equations and this system can be easily solved by any usual methods.Homotopy perturbation method (HPM)and Adomian decomposition method (ADM), etccan be also applied to approximate the solution of Fredholm integral equation.

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Static Flexural Analysis of Thick Isotropic Beams Using Higher Order Shear Deformation Theory

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ABSTRACT

For the static flexure analysis of thick isotropic beams, a higher order shear deformation theory is established in the current study. Axially displaced cantilever beam is examined. The theory's governing differential equation and boundary conditions are generated using the virtual work concept. The numerical findings were calculated for different length-to-thickness ratios of the beams, and the outcomes were compared with those of the Elementary, Timoshenko, trigonometric, and other hyperbolic shear deformation theories as well as with the solution that was published in the literature.

Keywords: Higher order shear deformation theory, Isotropic beam, virtual work, Shear deformation, thick beam, static flexure etc.

I. INTRODUCTION

When thick beams are subjected to transverse loads, shear deformation effects are more noticeable than they are when thin beams are subjected to the same loading. The consequences of shear deformation are more pronounced in thick beams. W. J. M. Rankine Bresse J. A. C. [1] The rotatory inertia and shear flexibility effects were the first dynamical effects in beam theory to be included by [2]. However, refers to this theory in the literature as the Timoshenko beam theory, Rebello C. A. et al. [3] and is known as first-order shear deformation theory. It is based on kinematics (FSDT).The rotatory inertia effect was incorporated by Rayleigh Lord [4], and Timoshenko S. P. later added the shear stiffness effect. Timoshenko demonstrated that shear has a significantly bigger impact on transverse vibration of prismatic beams than rotatory inertia does.

The Displacement Field

Based on the above mentioned assumptions, the displacement field of the present beam Theory can be expressed asfollows.

$$u(x,z) = -z\frac{dw}{dx}(x) + \left[\frac{z}{2}\left(\frac{h^2}{4} - \frac{z^2}{3}\right)\right]\phi(x)$$

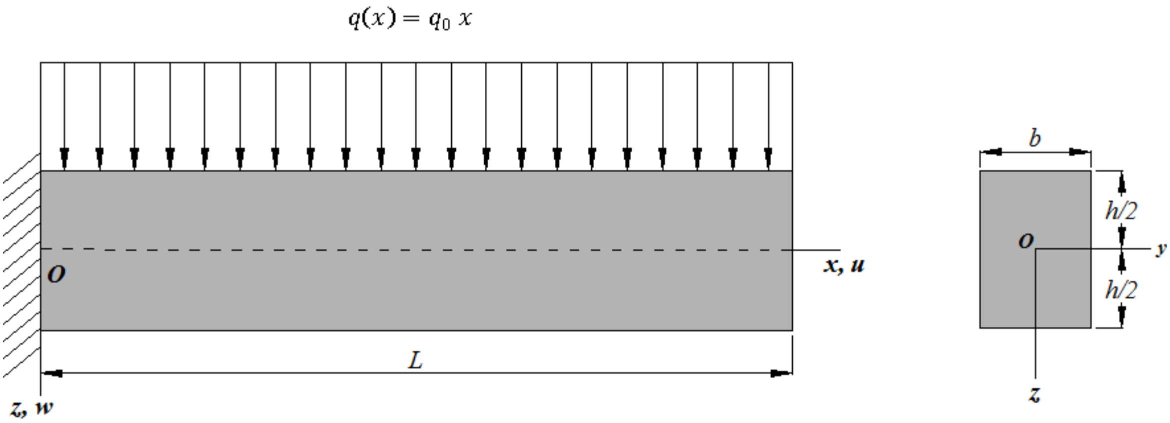
$$w(x,z) = w(x)$$

Where, u = Axial displacement in x direction which is function of x and z.
w = Transverse displacement in z direction which is function of x.
ϕ = Rotation of cross section of beam at neutral axis which is function of x.

Example-1: A Cantilever beam with uniformly distributed load
q□x□= q_0

The beam has its origin on left hand side fixed support at x = 0 and free at x = L. The beam is subjected to varying load, q(x) on surface z = +h/2 acting in downward z direction with minimum intensity of loadq_0

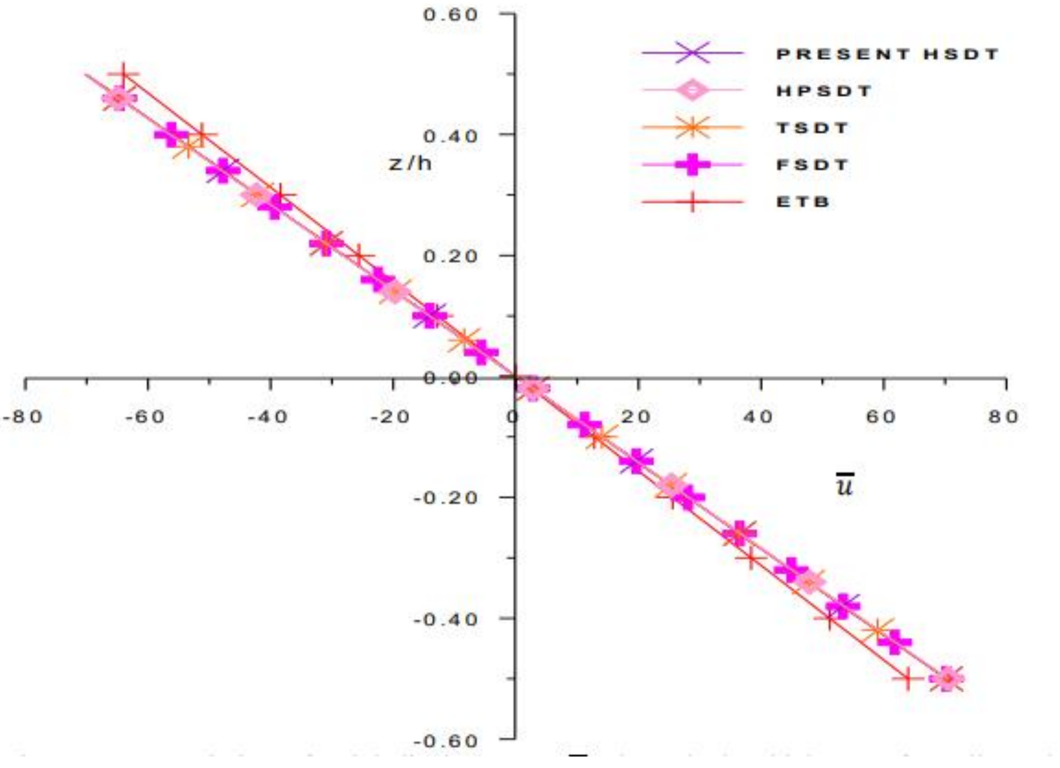
Cantilever beam with uniformly distributed load



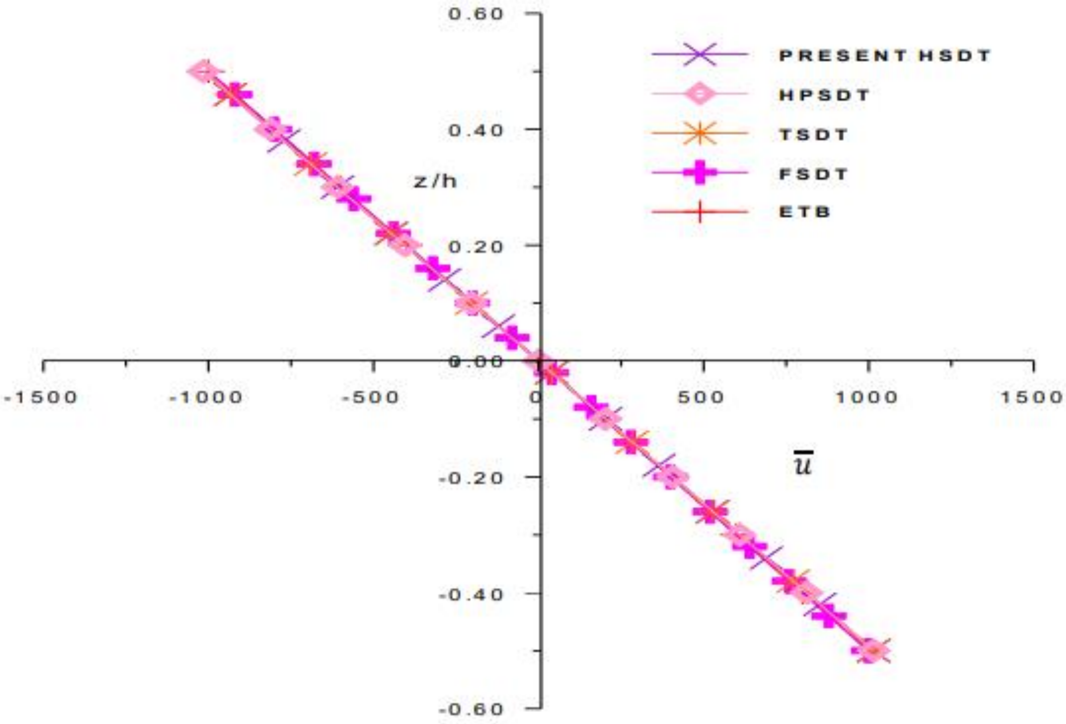
$$\bar{u} = -\frac{z}{h}\frac{L^3}{h^3}\left\{\left[\frac{2x^3}{L^3} - \frac{6x^2}{L^2} + \frac{6X}{L}\right] + \frac{E}{H}\frac{h^2}{L^2}\frac{A_0^2}{C_0}\sinh\lambda x - \cosh\lambda x + 1\right\} + \left[\frac{A_0}{C_0}\frac{E}{G}\frac{L}{h}\left(\frac{zh}{8} - \frac{z^3}{6h^3}\right)\left(\sinh\lambda x - \cosh\lambda x + 1 - \frac{x}{L}\right)\right]$$

Table No 1: Non-Dimensional Axial Displacement ($\bar{u}$) at (x = L, z = h/2), Cantilever Beam Subjected to Uniformly Distributed Load for Aspect Ratio 4 and 10.

Theory	AS -4	AS- 10
Present HSDT	70.24	1015.6
HPSDT	70.49	1016.22
TSDT	70.2	1015.57
FSDT	64	1000
ETB	64	1000



Variation of axial displacement ($\overline{u}$) through the thickness of cantilever beam at (x = L, z=0) when subjected uniformly distributed load for aspect ratio 4



Variation of axial displacement ($\overline{u}$) through the thickness of cantilever beam at (x = L, z=0) when subjected to uniformly distributed load for aspect ratio 10

II. CONCLUSIONS

1. It has been noted that the outcomes of the current hypothesis have a very good agreement with other hypotheses. However, compared to the values provided by other theories, ETB and FSDT produce lower values of this stress. This stress's through-thickness variation, as reported by ETB and FSDT, is linear throughout the thickness of the beam, which highlights the impact of shear deformation's neglect.
2. Due to significant stress concentration, current higher order and other refined theories explain the non-linear fluctuations of axial stress over the thickness at the built-in end. However, lower order theories like ETB and FSDT cannot account for this effect of local stress concentration.

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Fixed Point Theorems in Various Metric Spaces and Its Application

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ABSTRACT

In this paper we have discussed about the fixed point theory in detailed.Here, we have described fixed point theory from Banach fixed point theorem to its recent various forms in G-metric spaces, bg-metric space, generalization of metric spacesand about the differentcontraction mappings like commutative mapping, compatible mapping, weekly compatible mapping, R- contraction mapping in that metric spaces.In addition to this, we have also discussed about the application of fixed point theorem in game theory.

Keywords: Fixed Point Theorem; Contraction Mapping; Metric Space; Complete Metric Space; G-metric Space

I. INTRODUCTION

The notion of standard metric spaces is a fundamental tool in topology, functional analysis and nonlinear analysis. Banachintroduced the term of contraction maps in metric spaces and established the well-known Banach fixed point theorem. It has wide application in existence and uniqueness in ordinary and partial differential equations. Theory of fixed point is also used for existence for the solution of integro-differential equations, theory of games, economics, computer science etc. Banach fixed point theorem is generalized by many authors by the authors, Krasnoselskii , Edelstien , Rakotch, Seghal V. M., S. Reich [1], Geraghty M. A., Boyd D. W. and Wong J. S. W., Caristi J., L. B. Ciric , Zamfirescu , Kasahara, S., etc.

II. MAIN THEOREMS

- **Banach's contraction principle**

Let (X; d) be a complete metric space and **f : X →X** be a mapping such that,
for some $\sigma \in (0; 1]$,
$d(f(x); f(y)) \leq \sigma\, d(x; y)$
for all x; y ∈X. Then f has a unique fixed point in X.
Kannan proposed fixed point theorem for a self mapping on a complete metric space.
A mapping T on a metric space (X; d) is called Kannan mapping if there exists

$\alpha \epsilon$ [0; 1/2) such that

d(Tx; Ty) ≤ α(d(x; Tx) + d(y; Ty))

for all x; y ∈ X. In the year 1968, Kannan proved that if (X; d) is complete, then T has a unique fixedpoint in X. Kannan provided examples which show that Kannan's fixed point theorem is independentof the Banach contraction principle and Kannan mapping need not be continuous. Kannan's theorem is alsovery interesting because Subrahmanyam demonstrated that Kannan's theorem characterizes the metriccompleteness, that is a metric space (X; d) is complete if and only if every Kannan mapping on X has a fixed point. Several authors generalized Kannan's fixed point theorem. The fixed point theory of set-valued contractions which was initiated by Nadler[2] was developed in different directions by many authors, in particular, by Reich S.[1], Markin, J.T., Mizoguchi N. and Takahashi, W., Rhoades B. E. and B. Watson , noted fixed points for set-valued mappings on metric spaces. Rhoades B. E. explained a fixed point theorem for a multivalued non self mapping. Daffer, P.Z. and Kaneko, H. [3], Rus I. A. [4], Itoh, S. [5], Fixed points theorem for multi-valued mappings. Meir and Keeler [6] have given a different approach to Banach's contraction principle.

Jungck [7] coined the notion commuting mapping and established the first common fixed point in metric spaces. Das K. M., and Naik K. [8], propagated common fixed point theorems for commuting maps on a metric space. Later on, the concept of commuting map is generalize as follows: weakly commuting by Sessa [9], Compatible pair of maps by Jungck [10], weakly compatible maps by Jungck and Rhoades. property by Aamri M. and Moutawakil [11], $\varphi - \gamma$contraction by P. N. Dutta et. al. and developed the common fixed point theorems in metric spaces. Fisher B. and Sessa S. [12] introduced common fixed point theorems for weakly commuting mappings.

During the sixties, the notion of 2-metric space introduced by Gahler S. [13] as a generalization of usual notion of metric space[X, d] . Ha et al. [14] show that 2-metric need not be continuous function, further there is no easy relationship between results obtained in the two settings. In 1992, Dhage Bapure in his Ph.D. thesis introduce a new class of generalized metric space called D-metric spaces [15]. But Mustafa Z. and Brailey Sims [16], demonstrated that the most of the claims concerning the fundamental topological structure of D-metric space are incorrect and defined the new structure called the G-metric space.

- **Definition:** Let X be a non empty set and the mapping $G: X \times X \times X \to [0,\infty)$ The mapping G satisfies

(i) $G(x, y, z) = 0$ if and only if $x = y = z$ for all $x, y, z \in X$;

(ii) $0 < G(x, x, y)$ for all $x, y \in X$;

(iii) $G(x, x, y) \le G(x, y, z)$ for all $x, y, z \in X$ with $z \neq y$;

(iv) $G(x, y, z) = G(x, z, y) = G(y, z, x) = \cdots$ (symmetry in all three variables);

(v) $G(x, y, z) \le G(x, a, a) + G(a, y, z)$ for all $x, y, z, a \in X$ (rectangle inequality).

Then G is called a G-metric on X and the ordered pair (X,G) is called G-metric space.

They established the fixed point theorems for the basic contractive mappings. Many authors contributed fixed point results in this new setup detail see in [16]. The introduction of the notion of coupled fixed points by Bhaskar G. and Lakshmikantham [17] obtained interesting results related to differential equations with periodic boundary conditions by developing the mixed monotone property in the context of partially ordered metric spaces. As a continuation of this trend, many authors conducted research on the coupled fixed point theory and many results in this direction were published (see, for example, [18]). In this sequel Berinde and Borcut [19] introduced the concept of triple fixed point.

In 1996, Kada et al. [20] introduced the notion of w-distance and improved several classical results including Caristi's fixed point theorem. Suzuki and Takahashi [21] introduced single-valued and multi-valued weakly contractive maps with respect to w-distance and proved fixed point results for such maps. Generalizing the concept of w-distance, in 2001, Suzuki [22] introduced the notion of τ -distance on a metric space and improved several classical results including the corresponding results of Suzuki and Takahashi [21]. In 2001, Ume [23] introduced the new conceptof a distance called u-distance, which generalizes w-distance Tataru's distance and τ -distance. Then he proved a new minimization theorem and a new fixed point theorem by using u-distance on a complete metric space.

In recent years, several generalizations of standard metric spaces have appeared in literature. The concept of b-metric space was introduced by Bakhtin [24]. S. Czerwik [25] and Olatinwo, M.O. [26], investigated contraction mappings in b metric spaces. In [27],

- **Definition**: Let X be a non-empty set and mapping $d : X \times X \to [0;1)$ satisfies:

(i) $d(x; y) = 0$ if and only if $x = y$ for all $x; y \in X$,
(ii) $d(x; y) = d(y; x)$ for all $x; y \in X$,
(iii) There exists a real number $k \geq 1$ such that
$d(x; y) \leq k\,[d(x; z) + d(z; y)]$ for all $x; y; z \in X$.

Then d is called b-metric on X and (X; d) is called a b-metric space with coefficient k.

Matthews introduced the notion of a partial metric space. A lot of fixed point theorems were investigated in partial spaces (see, e.g., [28] and references therein). The notions of metric-like spaces [29] and b-metric spaces [30] were introduced in the literature, which are generalizations of metric spaces. Recently, the concept of b-metric-like spaces which is a generalization of metric-like spaces and b-metric spaces and partial metric spaces was introduced in [31]. Recently we are observing the development of fixed points in this setup. In 2000 Branciari [32] introduced a class of generalized metric spaces by replacing triangular inequality by similar ones which involve four or more points instead of three and improved Banach contraction mapping principle.

Modular metric spaces were introduced in [33]. The way we approached the concept of modular metric spaces is different. Indeed we look at these spaces as the nonlinear version of the classical modular spaces as introduced by Nakano [34] on vector spaces and modular function spaces introduced by Musielak [35] and Orlicz [36]. In [37] the authors have defined and investigated the fixed point property in the framework of modular metric space and introduced the analog of the Banach contraction principle theorem in modular metric space.

The notion of dislocated quasi-metric space has been introduced by Zeyada F.M.[38], and proved a version of Banach Contraction principle in such spaces

- **Definition:** Let X be a nonempty set and let $d : X \times X \to [0,\infty)$ be a

Function satisfying following conditions:

(i) $d(x, y) = d(y, x) = 0$, implies $x = y$,
(ii) $d(x, y) \leq d(x, z) + d(z, y)$, for all $x, y, z \in X$.

Then d is called a dislocated quasi-metric on X.

If d satisfies $d(x, x) = 0$, then

It is called a quasi-metric on X. If d satisfies $d(x, y) = d(y, x)$, then it is calledDislocate metric.

C.T. Aage and J. N. Salunke [39] proved dislocated quasi-metric version of Kannan mapping theorem. Then various types of fixed point theorems appear in theory of fixed point in dislocated quasi-metric spaces, [38,39].

The concept of cone metric space was introduced by Huan Long-Guang and Zhang Xian [40], where the set of real numbers is replaced by an ordered Banach space. They introduced the basic definitions and discuss some properties ofconvergence of sequences in cone metric spaces. They also obtained various fixed point theorems for contractive single-valued maps in such spaces. Subsequently, some other mathematicians have generalized the results of Guang and Zhang [40].

Recently Karapınar *et al.* [41] presented quasi-partial metric spaces and investigated the existence and uniqueness of certain operators in the context of quasi-partial metric spaces [12]. Very recently, Khojasteh *et al.* [42] introduced the notion of simulation function, which was later modified by Roldan-Lopez-de-Hierro et al. in a subtle way [43]. Now by Roldan-Lopez-de-Hierro et al. introduced the notion of R-contraction, which permits us to introduce such a large family of contractions that includes not only Meir-Keeler contractions, but Geraghty contractions, contractions depending on simulations functions and manageable functions, etc.

Mohamed Jleli and Samet introduced a new concept of generalized metric and extended some well-known fixed point results including Banach contraction principle Ciric's fixed point theorem a fixed point result due to Ran and Reurings and a fixed point result due to Nieto and Rodriguez-Lopez. This new concept of generalized metric spaces recover various topological spaces including standard metric spaces, b-metric spaces, dislocated metric spaces, and modular spaces.

Chakkrid Klin-eam and Suanoom established dislocated quasi-b-metric spaces and introduced the notions of Geraghty type dqb-cyclic-Banach contraction and dqb-cyclic-Kannan mapping and derived the existence of fixed point theorems for such spaces.

Most recently, Samet et al. [39] have defined$\alpha - \varphi$ contractive andα -admissible mapping and proved fixed point theorems for such mappings in complete metric spaces.

III. APPLICATION OF FIXED POINT THEOREMS IN GAME THEORY

We consider a game with n ≥2 players, under the assumption that the players do not cooperate among themselves. Each playerpursues a strategy, in dependence ofthe strategies of the other players. Denote the set of all possible strategies of the kth player by K_k, and

set $K = K_1 \times \cdots \times K_n$. An element $x \epsilon K$ is called a strategyprofile.

For each k, let $f_k : K \to \mathbf{R}$ be the loss function of the kth player.

If$\sum_{k=1}^{n} f_k(x) = 0$, for all $x \in K$ …(1)

The game is said to be of zero-sum. The aim of each player is to minimize his loss,
or, equivalently, to maximize his gain.

- **Definition**: A Nash equilibrium is a strategy profile with the property that noplayer can benefit by changing his strategy, while all other players keep theirstrategies unchanged. In formulas, it is an element $\bar{x}= (\bar{x}_1, \ldots ,\bar{x}_n) \in K$

suchthat

$fk(\bar{x}) \leq fk(\bar{x}_1, \ldots , \bar{x}_{k-1}, \bar{x}_k, \bar{x}_{k+1}, \ldots , \bar{x}_n)$, for all xk ∈ Kk …(2)

for every k = 1, . . . , n.

Strictly speaking, a Nash equilibrium suggests a convenient "cautious" strategyto be adopted by each player in the game. We said a strategy rather than thestrategy, since a Nash equilibrium (if it exists) might not be unique.

We need of course further hypotheses on the sets K_k and on the maps f_k. Itis reasonable to assume that, with all the other strategies fixed, the loss function f_k has a small variation in correspondence of a small variation of x_k. Also, looselyspeaking, it is assumed that the average of losses corresponding to two differentstrategies of the kth player is greater than the loss corresponding to the "average"strategy. Convexity can suitably translate this issue.The fundamental result of game theory is the following.

1.1Theorem [Nash]: For every $k = 1, \dots, n$, let K_k be a nonvoid, compactand convex subset of a locally convex space X_k. Assume that, for every k, the lossfunction fk is continuous on K. In addition, for every fixed $x_j \in K_j$ with $j \neq k$, themap

$f_k(x_1, \dots, x_{k-1}, \cdot, x_{k+1}, \dots, x_n) : K_k \to R$

is convex. Then there exists $\bar{x} \in K$ satisfying (2), i.e., there is a Nash equilibrium.

Proof: Define: $K \times K \to R$ as

$\varphi(x, y) = \sum_{k=1}^{n} [f_k(x) - f_k(x_1, \dots, x_{k-1}, y_k, x_{k+1}, \dots, x_n)]$

Then $\varphi$is continuous, and $\varphi(x, y)$ is concave for every fixed $x \in K$. From Theorem Ky Fan there exists $\bar{x} \in K$ such that

$$sup_{y \in K} \varphi(\bar{x}, y) \leq sup_{y \in K} \varphi(y, y) = 0$$

In particular, if we set $\bar{y} = (\bar{x}_1, \dots, \bar{x}_{k-1}, \bar{x}_k, \bar{x}_{k+1}, \dots, \bar{x}_n)$ for $x_k \in K_k$, we get$\varphi(\bar{x}, \bar{y}) \leq 0$, for all $x_k \in K_k$ which is nothing but (2)

The hypotheses can be weakened if we consider a two-player zero-sum game(sometimes called a duel). In this case, on account of (1), we have

$\gamma(x_1, x_2) := f_1(x_1, x_2) = -f_2(x_2, x_2)$.

Therefore, we can repeat the above proof taking γ to be convex and lower semi-continuousin the first variable, and concave and upper semi-continuous in the second.Now, γ is the loss function of the first player or, equivalently, the gain function ofthe second one.

1.2 Theorem [von Neumann]:

Let K_1 is subset of X_1 and K_2 is subset of X_2 be as in Theorem1.1

Let $\gamma : K_1 \times K_2 \to R$ be such that

(a) $\gamma(\cdot, x2)$ is lower semicontinuous and convex for all $x_2 \in K_2$;

(b) $\gamma(x1, \cdot)$ is upper semicontinuous and concave for all $x_1 \in K_1$.

Then there exists a Nash equilibrium $(\bar{x}_1, \bar{x}_2) \in K_1 \times K_2$.

Proof:

In this case $\varphi : (K_1 \times K_2.) \times (K_1 \times K_2.) \to \mathbf{R}$ has the form

$\varphi((x_1, x_2), (y_1, y_2)) = -\gamma(y_1, x_2) + \gamma(x_1, y_2)$

and the argument of the proof of Theorem 1.1 applies.

Theorem 1.2 is known in the literature as the minimax theorem. The reason is clear from the next corollary.

Corollary: In the hypotheses of Theorem 1.2, the equality

$inf_{x1 \in K1} sup_{x2 \in K2} \gamma(x_1, x_2) = \gamma(x_1, x_2) = sup_{x2 \in K2} inf_{x1 \in K1} \gamma(x_1, x_2)$

holds true.

Proof: Define $g(x_1) = sup_{x2 \in K2} \gamma(x_1, x_2)$ and $h(x_2) = inf_{x1 \in K1} \gamma(x_1, x_2)$ Then for all $x_1 \in K_2$ and $x_2 \in K_2$ we have

$h(x_2) \leq \gamma(x_1, x_2) \leq g(x_1)$

which entails

$sup_{x2 \in K2} h(x_2) \leq inf_{x1 \in K1} g(x_1)$

On the other hand, by Theorem 1.2,

$h(\bar{x}_2)=inf_{x1\in K1}\ \gamma(x_1, \bar{x}_2) = \gamma(\bar{x}_1, \bar{x}_2) = sup_{x2\in K2}\gamma(\bar{x}_1, x_2) = g(\bar{x}_1)$

Hence

$sup_{x2\in K2}\ h(x_2) \geq h(\bar{x}_2) = g(\bar{x}_1) \geq inf_{x1\in K1}\ g(x_1) \geq sup_{x2\in K2}\ h(x_2)$

So that all the above inequalities are in fact equalities.

We conclude the section considering a duel game where the sets K_1 and K_2 ofall possible strategies of each player are finite. We also assume that, for k = 1, 2,player k plays randomly the strategy $x_k \in K_k$ with probability $p_k(x_k)$. In this casetheplayers are said to adopt a mixed strategy. Denoting the loss function (of thefirst player) by γ, the average loss function is given by

$\gamma^p\ (p_1, p_2) = \sum_{x1\in F1}\sum_{x2\in F2} p1(x1)p2(x2)(x1, x2)$

defined on the set $K_1^P \times K_2^P$ where

$K_k^P = \{p_k :\ F_k \to [0,1] : \sum_{xk\in Fk} pk(x_k) = 1\}$

IV. CONCLUSION

In the above paper we conclude that the fixed point theorem is used in the game theory indicates that the strategy of the player in certain conditions of spaces, like convex and concave spaces, semi- continuous spaces. Fixed point theory is also used in discussing the solution of partial differential equation with boundary conditions. Theory of fixed point is also used for existence for the solution of integro-differential equations, theory of games, economics, computer science.

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Study of Two-dimensional Generalized Canonical Sine-Cosine Transform

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ABSTRACT

This paper is concerned with the definition of two-dimensional (2-D) generalized canonical SC- transform it is extended to the distribution of compact support by using kernel method. We have discussed inversion theorem for that transform. Lastly we have proved Uniqueness theorem for that transform.

Keywords: 2-D canonical transform, 2-D sine-cosine transform, 2-D sine-sine transform, 2-D cosine-cosine transform, 2-D fractional Fourier transform, generalized function.

I. INTRODUCTION

Now a days fractional Fourier transforms plays important role in information processing [5]. The fractional Fourier transform as an extension of the Fourier transform. It has been used many applications such as optical system analysis, filter design, solving differential equations. Phase retrieval and pattern recognition etc. [8] [3],In fact the fractional Fourier transform is special case of the canonical transform. The canonical transform is defined as

$$\{CT\,f(t)\}(s)=\frac{1}{\sqrt{2\pi ib}}\int_{-\infty}^{\infty}e^{-i\left(\frac{s}{b}\right)t}e^{\frac{i}{2}\left(\frac{a}{b}\right)t}f(t)\,dt\;\; b\neq 0 \qquad ....(1)$$

$$=\sqrt{d}\,e^{\frac{i}{2}\left(cds^{2}\right)f(d.s)}\qquad b=0$$

And the constraint that ad-bc=1 must be satisfied. The canonical transform defined above in (1) are all one-dimensional [1-D], in [1] [2], [10],[11],[12],[13],[14],[15], they have generalized them from one–dimensional into the (2-D) cases, [4] ,[06],[07].The two-dimensional canonical sine-cosine transform it is extended to the distribution of compact support by using kernel method [09] .
The two-dimensional canonical sine-cosine transform is defined as.

$$\{2DCSCT\;f(t,x)\}(s,w)=-i\frac{1}{\sqrt{2\pi ib}}\frac{1}{\sqrt{2\pi ib}}e^{\frac{i}{2}\left(\frac{d}{b}\right)s^{2}}e^{\frac{i}{2}\left(\frac{d}{b}\right)w^{2}}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\sin\left(\frac{s}{b}t\right)\cos\left(\frac{w}{b}x\right)e^{\frac{i}{2}\left(\frac{a}{b}\right)t^{2}}.e^{\frac{i}{2}\left(\frac{a}{b}\right)x^{2}}\;f(t,x)\,dxdt$$

When $b \neq 0$

Notation and terminology of this paper is as per [17], [18]. The paper is organized as follows. Section. 2 gives the definition of 2-D canonical sine-cosine transform on the space of generalized function in section. 3 inversion theorem is proved in section. 4 Uniqueness theorems proved lastly the conclusion is stated.

II. DEFINITION TWO DIMENSIONAL (2D) GENERALIZED CANONICAL SINE-COSINE TRANSFORM $[2DCSCT]$

Let $E^{l}(R\times R)$ denote the dual of $E(R\times R)$ therefore the generalized canonical sine-cosine transform of $f(t,x)\in E^{l}(R\times R)$ is defined as

$$\{2DCSCT\ f(t,x)\}(s,w)=\langle f(t,x),K_s(t,s)K_c(x,w)\rangle$$

$$\{2DCSCT\ f(t,x)\}(s,w)$$

$$=(-i)\frac{1}{\sqrt{2\pi ib}}\frac{1}{\sqrt{2\pi ib}}e^{\frac{i}{2}\left(\frac{d}{b}\right)s^2}e^{\frac{i}{2}\left(\frac{d}{b}\right)w^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\sin\left(\frac{s}{b}t\right)\cos\left(\frac{w}{b}x\right)e^{\frac{i}{2}\left(\frac{a}{b}\right)t^2}e^{\frac{i}{2}\left(\frac{a}{b}\right)x^2}f(t,x)\,dxdt$$

Where $K_s(t,s)=(-i)\frac{1}{\sqrt{2\pi ib}}e^{\frac{i}{2}\left(\frac{d}{b}\right)s^2}e^{\frac{i}{2}\left(\frac{a}{b}\right)t^2}\sin\left(\frac{s}{b}t\right)$ when $b\neq 0$

$$=\sqrt{d}\,e^{\frac{i}{2}(cds^2)}\delta(t-ds) \qquad \text{when } b=0$$

and $K_c(x,w)=\frac{1}{\sqrt{2\pi ib}}e^{\frac{i}{2}\left(\frac{d}{b}\right)w^2}e^{\frac{i}{2}\left(\frac{a}{b}\right)x^2}\cos\left(\frac{w}{b}x\right)$ when $b\neq 0$

$$=\sqrt{d}\,e^{\frac{i}{2}(cdw^2)}\delta(x-dw) \qquad \text{when } b=0$$

where $\gamma_{E,k}\{K_s(t,s)K_c(x,w)\}=\sup\limits_{\substack{-\infty<t<\infty\\ -\infty<x<\infty}}\left|D_t^k D_x^l K_s(t,s)K_c(x,w)\right|<\infty$

III. THEOREM :(INVERSION)

If $\{2DCSCT\ f(t,x)\}(s,w)$ is canonical sine- cosine transform of $f(t,x)$ then

$$f(t,x)=-ie^{\frac{-i}{2}\left(\frac{a}{b}\right)t^2}e^{\frac{-i}{2}\left(\frac{a}{b}\right)x^2}\sqrt{\frac{2\pi i}{b}}\sqrt{\frac{2\pi i}{b}}.$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{\frac{-i}{2}\left(\frac{d}{b}\right)s^2}e^{\frac{-i}{2}\left(\frac{d}{b}\right)w^2}\sin\left(\frac{s}{b}t\right)\cos\left(\frac{w}{b}x\right)\{2DCSCT\ \ f(t,x)\}(s,w)\,dsdw,$$

Proof: The two dimensional canonical sine- cosine transform if $f(t,x)$ is given by

$$\{2DCSCT\ f(t,x)\}(s,w)$$

$$=-i\frac{1}{\sqrt{2\pi ib}}\frac{1}{\sqrt{2\pi ib}}e^{\frac{i}{2}\left(\frac{d}{b}\right)s^2}e^{\frac{i}{2}\left(\frac{d}{b}\right)w^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\sin\left(\frac{s}{b}t\right)\cos\left(\frac{w}{b}x\right)e^{\frac{i}{2}\left(\frac{a}{b}\right)t^2}e^{\frac{i}{2}\left(\frac{a}{b}\right)x^2}f(t,x)dxdt$$

$$f(s,w)=\{2DCSCT\ f(t,x)\}(s,w)$$

$$\therefore f(s,w)$$

$$=-i\frac{1}{\sqrt{2\pi ib}}\frac{1}{\sqrt{2\pi ib}}e^{\frac{i}{2}\left(\frac{d}{b}\right)s^2}.e^{\frac{i}{2}\left(\frac{d}{b}\right)w^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\sin\left(\frac{s}{b}t\right)\cos\left(\frac{w}{b}t\right)e^{\frac{i}{2}\left(\frac{a}{b}\right)t^2}e^{\frac{i}{2}\left(\frac{a}{b}\right)x^2}f(t,x)dxdt$$

$$f(s,w).\sqrt{2\pi ib}\sqrt{2\pi ib}\ e^{-\frac{i}{2}\left(\frac{d}{b}\right)s^2}.e^{-\frac{i}{2}\left(\frac{d}{b}\right)w^2}$$

$$=-i\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\sin\left(\frac{s}{b}t\right)\cos\left(\frac{w}{b}x\right)e^{\frac{i}{2}\left(\frac{a}{b}\right)t^2}e^{\frac{i}{2}\left(\frac{a}{b}\right)x^2}f(t,x)dxdt$$

$$\therefore C_1(s,w)=f(s,w)\sqrt{2\pi ib}\sqrt{2\pi ib}\ e^{-\frac{i}{2}\left(\frac{d}{b}\right)s^2}e^{-\frac{i}{2}\left(\frac{d}{b}\right)w^2}$$

And $g(t,x)=e^{\frac{i}{2}\left(\frac{a}{b}\right)t^2}e^{\frac{i}{2}\left(\frac{a}{b}\right)x^2}f(t,x)$

$$C_1(s,w)=-i\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}g(t,x).\sin\left(\frac{s}{b}t\right).\cos\left(\frac{w}{b}x\right)dxdt$$

$$C_1(s,w)=\{2DCSCTg(t,x)\}\left(\frac{s}{b},\frac{w}{b}\right)$$

Where $\{2DCSCTg(t,x)\}\left(\frac{s}{b},\frac{w}{b}\right)$ is 2D Canonical sine-cosine transform of g(t,x).2D canonical sine -cosine transform g(t,x) with argument

$\therefore \frac{s}{b}=\eta$ and $\frac{w}{b}=\xi$ Therefore, $\frac{ds}{b}=d\eta$ and $\frac{dw}{b}=d\xi$

$$\therefore C_1(s,w)=\{2DCSCTg(t,x)\}(\eta,\xi)$$

By using inversion formula we get $\therefore g(t,x)=-i\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}C_1(s,w)\sin(\eta t)\cos(\xi x)d\eta d\xi$

$$g(t,x)=-i\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}F(s,w)\sqrt{2\pi ib}\sqrt{2\pi ib}\ e^{-\frac{i}{2}\left(\frac{d}{b}\right)s^2}e^{-\frac{i}{2}\left(\frac{d}{b}\right)w^2}\sin(\eta t)\cos(\xi x)d\eta d\xi$$

$$e^{\frac{i}{2}\left(\frac{a}{b}\right)t^2} e^{\frac{i}{2}\left(\frac{a}{b}\right)x^2} f(t,x) = -i\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} F(s,w)\sqrt{2\pi ib}\,\sqrt{2\pi ib}\; e^{-\frac{i}{2}\left(\frac{d}{b}\right)s^2} e^{-\frac{i}{2}\left(\frac{d}{b}\right)w^2} \sin\left(\frac{s}{b}t\right)\cos\left(\frac{w}{b}x\right)\frac{ds}{b}\frac{dw}{b}$$

$$e^{\frac{i}{2}\left(\frac{a}{b}\right)t^2} e^{\frac{i}{2}\left(\frac{a}{b}\right)x^2} f(t,x)$$

$$= -i\sqrt{2\pi ib}\,\sqrt{2\pi ib}\,\frac{1}{b}\frac{1}{b}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{\frac{-i}{2}\left(\frac{d}{b}\right)s^2} e^{\frac{-i}{2}\left(\frac{d}{b}\right)w^2} \sin\left(\frac{s}{b}t\right)\cos\left(\frac{w}{b}x\right) f(s,w)\,ds\,dw$$

$$f(t,x)$$

$$= -i\, e^{-\frac{i}{2}\left(\frac{a}{b}\right)t^2} e^{-\frac{i}{2}\left(\frac{a}{b}\right)x^2} \sqrt{\frac{2\pi i}{b}}\sqrt{\frac{2\pi i}{b}}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\frac{i}{2}\left(\frac{d}{b}\right)s^2} e^{-\frac{i}{2}\left(\frac{d}{b}\right)w^2} \sin\left(\frac{s}{b}t\right)\cos\left(\frac{w}{b}x\right)\left\{2DCSCT\ f(t,x)\right\}(s,w)\,ds\,dw$$

IV. THEOREM:(UNIQUENESS)

If $\left\{2DCSCT\ \ f(t,x)\right\}(s,w)$ and $\left\{2DCSCT\ g(t,x)\right\}(s,w)$ are 2D canonical sine-cosine transform and

$\sup pf \subset s_a$, and s_b and, $\sup p\,g \subset s_a, and\ \ s_b$

Where $s_a = \left\{t : t \in R^n,\ \ |t| \le a, a > 0\right\}$ and $s_b = \left\{x : x \in R^n,\ \ |x| \le b, b > 0\right\}$

If $\left\{2DCSCT\ \ f(t,x)\right\}(s,w) = \left\{2DCSCT\ g(t,x)\right\}(s,w)$

then, f = g in the sense of equality in $D'(I)$

Proof: By inversion theorem $f - g$

$$= \left(-ie^{\frac{-i}{2}\left(\frac{a}{b}\right)t^2} e^{\frac{-i}{2}\left(\frac{a}{b}\right)x^2}\sqrt{\frac{2\pi i}{b}}\sqrt{\frac{2\pi i}{b}}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{\frac{-i}{2}\left(\frac{d}{b}\right)s^2} e^{\frac{-i}{2}\left(\frac{d}{b}\right)w^2} \sin\left(\frac{s}{b}t\right)\cos\left(\frac{w}{b}x\right)\right.$$
$$\left.\left\{2DCSCT\ \ f(t,x)\right\}(s,w)\,ds\,dw\right)$$

$$-\left(-ie^{\frac{-i}{2}\left(\frac{a}{b}\right)t^2} e^{\frac{-i}{2}\left(\frac{a}{b}\right)x^2}\sqrt{\frac{2\pi i}{b}}\sqrt{\frac{2\pi i}{b}}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{\frac{-i}{2}\left(\frac{d}{b}\right)s^2} e^{\frac{-i}{2}\left(\frac{d}{b}\right)w^2} \sin\left(\frac{s}{b}t\right)\cos\left(\frac{w}{b}x\right)\right.$$
$$\left.\left\{2DCSCT\ \ g(t,x)\right\}(s,w)\,ds\,dw\right)$$

$$\therefore\ f - g = -i\sqrt{\frac{2\pi i}{b}}\sqrt{\frac{2\pi i}{b}}\, e^{-\frac{i}{2}\left(\frac{a}{b}\right)t^2} e^{-\frac{i}{2}\left(\frac{a}{b}\right)x^2}\int_{-\infty}^{\infty} e^{-\frac{i}{2}\left(\frac{d}{b}\right)s^2} e^{-\frac{i}{2}\left(\frac{d}{b}\right)s^2} \sin\left(\frac{s}{b}x\right)\cos\left(\frac{w}{b}x\right)$$
$$\left[\left\{2DCSCT\,f\left(t,x\right)\right\} - \left\{2DCSCT\,g\left(t,x\right)\right\}\right]ds\,dw$$

Thus f = g in $D'(I)$

V. CONCLUSION

In this paper two-dimensional canonical sine-cosine is Generalized in the form the distributional sense, we have inversion theorem for this transform is proved. Lastly uniqueness theorem is also proved.

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Different Versions of Vertex Degrees of the Molecular Graph and Topological Indices

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ABSTRACT

Research work in chemical graph theory is mainly focused on degree based and types of topological indices of molecular graphs. In the chemical graph theory, many degrees based topological indices have been introduced and studied which are given by the [1] general formula TI(G) $=\sum_{u\,v\in E(G)} F\left(\deg(u_i),\deg(v_j)\right)$.In this paper different versions of vertex degree and corresponding first Zagreb index, second Zagreb index and forgotten index are investigated for2-methylbutane.

Keywords: Degree,forgotten index, modified version of topological index, molecular graph, multiplication-degree,sum-degree, Zagreb index.

I. INTRODUCTION

Molecules and molecular compounds are often modelled by molecular graphs. A molecular graph is presentation of the structural formula of a chemical compound in terms of graph theory whose vertices correspond to the atoms of compound and edges correspond to chemical bonds. Degree based Zagreb indices and forgotten index are the basic degree basedtopological indices. There are different ways to define vertex degree and compute the topological indices by using the classical formulas or graph polynomials[2-14]. Let G(V,E) be a graph with n vertices and m edges.The degree of a vertex u∈V(G) is denoted by d_u and is the number of vertices adjacent to u. The edge connecting the vertices u and v is denoted by uv.The maximum and minimum degree of a vertex among vertices of G are denoted by $\Delta = \max\{d_v|v \in V(G)\}$, $\delta = \min\{d_v|v \in V(G)\}$respectively.The general formula for topological index is TI(G) $=\sum_{u\,v\in E(G)} F\left(deg(u_i),deg(v_j)\right)$,where F(x,y) is some function with property F(x,y) = F(y,x).

The R-degree first Zagreb index, R-degree second Zagreb index and R-degree forgotten index are defined as [15] $M_{R^1}(G)=\sum_{uv\in E(G)} [r(u)+r(v)]$,$M_{R^2}(G)=\sum_{uv\in E(G)} r(u)r(v)$ and

$F_R(G) = \sum_{uv\in E(G)}[r(u)^2 + r(v)^2]$,where R-degree of a vertex visr(v $= M_v + S_v$,S_v is sumdegree and M_v is multiplication-degree of v.

The revan-degree first Zagreb index, revan-degree second Zagreb index and revan-degree forgotten index are defined as[16]

$rM_1(G) = \sum_{uv\in E(G)}[r_G(u) + r_G(v)]$,$rM_2(G) = \sum_{uv\in E(G)} r_G(u)r_G(v)$ and
$rF(G) = \sum_{uv\in E(G)}[r_G(u)^2 + r_G(v)^2]$,where revan-degree of a vertex u is
$r_G(u) = \Delta(G)+\delta(G)-d_G(u)$.

The reverse-degree first Zagreb index, reverse-degree second Zagreb index and reverse-degree forgotten index are defined as

$cM_1(G) = \sum_{uv\in E(G)}(c_u + c_v)$,$cM_2(G) = \sum_{uv\in E(G)}(c_u c_v)$ and $cF(G) = \sum_{uv\in E(G)}(c_u^2 + c_v^2)$,wherethe reverse-degreeof a vertex v is $c_v = \Delta(G) - d_G(v) + 1$.

The S-degree first Zagreb index, S-degree second Zagreb index and S-degree forgotten index are defined as [17-18]

$M_{S^1}(G) = \sum_{uv\in E(G)} [S(u) + S(v)]$, $M_{S^2}(G) = \sum_{uv\in E(G)} S(u)S(v)$and
$F_S(G) = \sum_{uv\in E(G)} [S(u)^2 + S(v)^2]$, where S-degree of a vertex $S(v) = |M_v - S_v|$.

The modifiedleap degreefirst Zagreb index, leap degree second Zagreb index and leap degree forgotten index are defined as [19]

$LM_1^*(G) = \sum_{\boldsymbol{uv\in E(G)}} [d_2(u) + d_2(v)]$,$LM_2(G) = \sum_{\boldsymbol{uv\in V(G)}} d_2(u)d_2(v)$ and
$LF(G) = \sum_{uv\in V(G)}[(d_2^2(u) + d_2^2(v)]$.

The modifiedHDRfirst Zagreb index,HDR second Zagreb index and modified HDR forgotten index are defined as[20]

$HDRM_1^*(G) = \sum_{\boldsymbol{uv}\in E(G)}[d_{hr}(u) + d_{hr}(v)]$,$HDRM_2(G) = \sum_{uv\in E(G)}[d_{hr}(u)d_{hr}(v)]$ and
$HDRF^*(G) = \sum_{uv\in E(G)}[d_{hr}^2(u) + d_{hr}^2(v)]$,where $d_{hr}(u) = |\{u,v\in V(G)/d(u,v) = \frac{R}{2}\}|$,
d(u,v)is the distance between the vertices u and vin V(G) and R is radius of G.

The first Zagreb coindex and second Zagreb coindexand forgotten coindexare defined as [21-23]

$\overline{M_1}(G) = \sum_{uv\notin E(G)} (d_u + d_v)$, $\overline{M_2}(G) = \sum_{uv\notin E(G)} (d_u d_v)$ and $\bar{F}(G) = \sum_{\boldsymbol{uv\notin E(G)}} (d_u^2 + d_v^2)$.

The non-neighbor first Zagreb index and non-neighbor second Zagreb index and non-neighbor forgotten index are defined as [24]

$\overline{M_1(G)} = \sum_{uv\in E(G)} (\overline{d_G(u)} + \overline{d_G(v)})$,$\overline{M_2(G)} = \sum_{uv\in E(G)} \overline{d_G(u)}\overline{d_G(v)}$ and
$\overline{F(G)} = \sum_{\boldsymbol{uv\in E(G)}} [\overline{d_G(u)}^2 + \overline{d_G(v)}^2]$.

The downhillfirst Zagreb index,downhill second Zagreb index and downhill forgotten index are defined as[25-26]

$DWM_1(G) = \sum_{v\in \boldsymbol{V(G)}}(d_{dn}(v))^2$,$DWM_2(G) = \sum_{vu\in \boldsymbol{E(G)}} d_{dn}(v)d_{dn}(u)$ and $DWF(G) = \sum_{v\in \boldsymbol{V(G)}}(d_{dn}(v))^3$.

An uphillfirst Zagreb index, uphill second Zagreb index and uphill forgotten index are defined as [27]

$UPM_1(G) = \sum_{v\in \boldsymbol{V(G)}}(d_{up}(v))^2$,$UPM_2(G) = \sum_{v\in \boldsymbol{V(G)}} d_{up}(u)\, d_{up}(v)$ and $UPF(G) = \sum_{v\in \boldsymbol{V(G)}}(d_{up}(v))^3$.

The neighborhoodfirst Zagreb index,modified version of neighborhoodsecond Zagreb index and neighborhood forgotten index are defined as [28-29]

$M_{N1}(G) = \sum_{\boldsymbol{v\in V(G)}} [\delta_G(v)]^2$,$M_{N2}^*(G) = \sum_{\boldsymbol{uv\in E(G)}} [\delta_G(u)\delta_G(v)]$ and $F_N(G) = \sum_{v\in V(G)}[\delta_G(v)]^3$.

The ev-degree Randic index of the graph G is defined as [30-31]$R^{\beta}(G) = \sum_{e\in E(G)} c_e^{-\frac{1}{2}}$.

The ve-degree first Zagreb index, ev-degree modified second Zagreb index and ve-degree forgotten index are defined as

$M_1^{ve}(G) = \sum_{v\in V(G)} d_{ve}(v)^2$, $M_2^{*ev}(G) = \sum_{\boldsymbol{e\in E(G)}} \frac{\mathbf{1}}{\boldsymbol{d_{ev}(e)}}$ and $F^{ve}(G) = \sum_{v\in V(G)} d_{ve}(v)^3$.

In this paper R, revan, reverse,S, leap, HDR, coindex, non-neighbor, downhill, uphill,neighborhood degreesum and vedegrees based first Zagreb index, second Zagreb index and forgotten index of 2-methylbutane are investigated. All the symbols and notations used in this paper are standard and mainly taken from books of graph theory [32-34].

II. MATERIALS AND METHODS

A molecular graph G(V, E) is constructed by representing each atom of molecule by vertex and bonds between them by edges. Let V(G) be vertex set and E(G) be edge set.The chemical structure and molecular graph of 2-methylbutane are shown in figure 1. Let molecular graph of 2-methylbutane is denoted by G.The vertices 1,4 and 5 are pendent vertices with degree 1. The degree of vertex 2 is 3 and that of 3 is 2. The maximum,minimum degree among vertices of Gand different versions of vertex degree are observed for molecular graph G. In this paper R, revan, reverse, S, leap, HDR, coindex, non-neighbor, downhill, uphill, neighborhood degreesum and ve degrees based first Zagreb index, second Zagreb index and forgotten index of 2-methylbutane are computed by using definitions of these topological indices.

III. RESULTS AND DISCUSSION

The maximum degree among vertices of G is 3 and minimum degree is 1. Let molecular graph of 2-methylbutane is denoted by G.The basic definitions of first Zagreb index, second Zagreb index and forgotten index are used to compute topological indices (table 1).The edge partition of 2-methylbutane is the underlying point in the determination of different versions of vertex degree of a graph (table 2).

Theorem 1. R-degree firstZagreb index, R-degree second Zagreb index and R-degree forgotten index of 2-methylbutane are(i)M_{R^1} (G)= 49,(ii)M_{R^2} (G)= 149and (iii)F_R(G)= 307.

Proof. Byusingdefinitions and edge degree partition of molecular graph G, we get

(i)M_{R^1} (G) $=\sum_{uv\in E(G)}[r(u)+r(v)]$

$=\sum_{13\in \square(\square)}(6+6)+\sum_{12\in E(G)}(4+7)+\sum_{23\in E(G)}(7+7)$=2(6+6)+(4+7)+(7+7)= 49.

(ii)RM_2(G) $=\sum_{\boldsymbol{uv\in E(G)}} [r(u)r(v)]$

$=\sum_{13\in \square(\square)}(6*6)+\sum_{12\in \square(\square)}(4*7)+\sum_{23\in \square(\square)}(7*7)$=2(6*6)+(4*7)+(7*7)= 149.

(iii) F_R(G)= $\sum_{uv\in E(G)}[r(u)^2+r(v)^2]$

$=\sum_{13\in E(G)}(6^2+6^2)+\sum_{\square\square\in \square(\square)}(4^2+7^2)+\sum_{23\in E(G)}(7^2+7^2)$

$= 2(6^2+6^2)+(4^2+7^2)+(7^2+7^2)$= 307.

Theorem 2. Revan-degree firstZagreb index, revan-degree second Zagreb index and revan-degree forgotten index of 2-methylbutaneare(i)rM_1(G) = 16,(ii)rM_2(G) = 14and(iii)rF(G) = 38.

Proof. Byusingdefinitions and edge degree partition of molecular graph G, we get

(i)rM_1(G)$=\sum_{\boldsymbol{uv\in E(G)}} [r_G(u)+r_G(v)]$

$=\sum_{13\in \square(\square)}(3+1)+\sum_{12\in \square(\square)}(3+2)+\sum_{23\in \square(\square)}(2+1)$= 2(3+1)+(3+2)+(2+1)= 16.

(ii)rM_2(G)$=\sum_{\boldsymbol{uv\in E(G)}} [r_G(u)r_G(v)]$

$=\sum_{\square\square\in \square(\square)}(3*1)+\sum_{\square\square\in \square(\square)}(3*2)+\sum_{\square\square\in \square(\square)}(2*1)$= 2(3)+6+2= 14.

(iii)rF(G)$=\sum_{uv\in E(G)}[r_G(u)^2+r_G(v)^2]$

$= \sum_{\square\square\in\square(\square)} (3^2+1^2)+\sum_{\square\square\in\square(\square)} (3^2+2^2)+\sum_{\square\square\in\square(\square)} (2^2+1^2)= 2(10)+13+5= 38.$

Theorem 3. Reverse-degreefirstZagreb index, reverse-degree second Zagreb index and reverse-degree forgotten index of 2-methylbutane are

(i)$cM_1(G)= 16$,(ii)$cM_2(G)= 14$and (iii)$cF(G)= 38$.

Proof. Byusingdefinitions and edge degree partition of molecular graph G,we get

(i)$cM_1(G)=\sum_{uv\in E(G)}(c_u+c_v)$

$= \sum_{13\in\square(\square)}(3+1)+\sum_{12\in\square(\square)}(3+2)+\sum_{23\in\square(\square)}(2+1)= 2(4)+5+3= 16.$

(ii)$cM_2(G)=\sum_{uv\in E(G)}(c_uc_v)$

$= \sum_{13\in\square(\square)}(3*1)+\sum_{12\in\square(\square)}(3*2)+\sum_{23\in\square(\square)}(2*1)= 2(3)+6+2= 14.$

(iii)$cF(G)=\sum_{uv\in E(G)}(c_u^2+c_v^2)$

$= \sum_{13\in\square(\square)}(3^2+1^2)+\sum_{12\in\square(\square)}(3^2+2^2)+\sum_{23\in\square(\square)}(2^2+1^2)$

$= 2(3^2+1^2) + (3^2+2^2) + (2^2+1^2)= 38.$

Theorem 4.S-degree first Zagreb index, S-degree second Zagreb index and S-degree forgotten index of 2-methylbutane are(i)$M_{S^1}(G)= 8$,(ii)$M_{S^2}(G) = 2$and (iii)$F_S(G) = 18$.

Proof. Byusingdefinitions and edge degree partition of molecular graph G, we get

(i)$M_{S^1}(G)=\sum_{uv\in E(G)} [S(u)+S(v)]$

$= \sum_{13\in\square(\square)} (0+2) + \sum_{12\in\square(\square)} (0+1) + \sum_{23\in\square(\square)} (1+2)= 2(2)+1+3= 8.$

(ii)$M_{S^2}(G) =\sum_{uv\in E(G)} S(u)S(v)$

$= \sum_{13\in\square(\square)} (0*2) + \sum_{12\in\square(\square)} (0*1) + \sum_{23\in\square(\square)} (1*2)= 1*2= 2.$

(iii)$F_S(G) =\sum_{uv\in E(G)} [S(u)^2+S(v)^2]$

$= \sum_{13\in\square(\square)} (0+2^2) + \sum_{12\in\square(\square)} (0+1)^2+\sum_{23\in\square(\square)} (1^2+2^2)= 2(2)^2+1^2+3^2= 18.$

Theorem 5. Leapmodified first Zagreb index, leap second Zagreb index and leap forgotten index of2-methylbutane are(i)$LM_1^*(G) = 12$,(ii)$LM_2(G) = 8$and (iii)$LF(G) = 20$.

Proof. Byusingdefinitions and edge degree partition of molecular graph G, we get

(i)$LM_1^*(G)=\sum_{\boldsymbol{uv\in E(G)}} [d_2(u)+d_2(v)]$

$= \sum_{\square\square\in\square(\square)} (1+2) +\sum_{\square\square\in\square(\square)} (2+1)= 2(1+2)+2(2+1)= 12.$

(ii)$LM_2(G)=\sum_{\boldsymbol{uv\in V(G)}} d_2(u)d_2(v)$

$= \sum_{\square\square\in\square(\square)} (1*2)+\sum_{\square\square\in\square(\square)} (2*1)= 2(1*2)+2(2*1)= 8.$

(iii)$LF(G) =\sum_{uv\in V(G)}[d_2^2(u)+d_2^2(v)]$

$= \sum_{12\in\square(G)}(1^2+2^2) +\sum_{21\in\square(G)}(2^2+1^2)= 2(1^2+2^2)+2(2^2+1^2)= 20.$

Theorem 6.HDRmodifiedfirst Zagreb index, HDR second Zagreb index andHDR modified forgotten index of2-methylbutaneare

(i)$HDRM_1^*(G) = 16$,(ii)$HDRM_2(G) = 14$and (iii)$HDRF^*(G) = 38$.

Proof. Byusingdefinitions and edge degree partition of molecular graph G, we get

(i)$HDRM_1^*(G)=\sum_{\boldsymbol{uv}\in E(G)}[d_{hr}(u)+d_{hr}(v)]$

$= \sum_{\square\square\in\square(\square)}(1+3)+\sum_{\square\square\in\square(\square)}(3+2)+\sum_{34\in\square(\square)}(1+2)= 2(1+3) +1(3+2) +1(1+2)= 16.$

(ii)$HDRM_2(G) =\sum_{uv\in E(G)}[d_{hr}(u)d_{hr}(v)]$

$= \sum_{\square\square\in\square(\square)}(1*3)+\sum_{\square\square\in\square(\square)}(3*2)+\sum_{34\in\square(\square)}(1*2)= 2(1*3) +1(3*2) +1(1*2)= 14.$

(iii)$HDRF^*(G) =\sum_{uv\in E(G)}[d_{hr}^2(u)+d_{hr}^2(v)]$

$=\sum_{12\in E(G)}(1^2+3^2)+\sum_{23\in E(G)}(3^2+2^2)+\sum_{34\in E(G)}(1^2+2^2)$

$= 2(1^2+3^2) +1(3^2+2^2) +1(1^2+2^2)= 38.$

Theorem 7. FirstZagreb coindex, second Zagreb coindex and forgotten coindex of 2-methylbutaneare(i)$\overline{M_1}$(G) = 11,(ii)$\overline{M_2}$(G) = 7and (iii)$\overline{F}$(G) = 19.

Proof. Byusingdefinitions and edge degree partition of molecular graph G, we get

(i) $\overline{M_1}$(G)=$\sum_{uv\notin E(G)} (d_u + d_v)$

= $\sum_{51\notin E(G)} (1+1)$+$\sum_{53\notin E(G)} (1+2)$+$\sum_{24\notin E(G)} (3+1)$= 2(1+1) +1(1+2) +1(3+1)= 11.

(ii)$\overline{M_2}$(G) =$\sum_{uv\notin E(G)} (d_u d_v)$

= $\sum_{51\notin E(G)} (1*1)$+$\sum_{53\notin E(G)} (1*2)$+$\sum_{24\notin E(G)} (3*1)$= 2(1*1) +1(1*2) +1(3*1)= 7.

(iii)$\overline{F}$(G) =$\sum_{\boldsymbol{uv\notin E(G)}} (d_u^2 + d_v^2)$

= $\sum_{51\notin E(G)} (1^2+1^2)$+$\sum_{53\notin E(G)} (1^2+2^2)$+$\sum_{24\notin E(G)} (3^2+1^2)$

= 2(1^2+1^2) +1(1^2+2^2) +1(3^2+1^2)= 19.

Theorem 8. Non-neighborfirst Zagreb index, non-neighbor second Zagreb index and non-neighborforgotten index of 2-methylbutane are (i)$\overline{M_1(G)}$= 16,(ii) $\overline{M_2(G)}$= 14and (iii)$\overline{F(G)}$ = 38.

Proof. Byusingdefinitions and edge degree partition of molecular graph G,we get

(i)$\overline{M_1(G)}$ =$\sum_{uv\in E(G)} (\overline{d_G(u)} + \overline{d_G(v)})$

= $\sum_{\mathbf{12}\in E(G)}(3+1)$+$\sum_{\mathbf{23}\in E(G)}(2+1)$+$\sum_{34\in E(G)}(3+2)$= 2(3+1) +1(2+1) +1(3+2)= 16.

(ii)$\overline{M_2(G)}$ =$\sum_{uv\in E(G)} \overline{d_G(u) d_G(v)}$

= $\sum_{\mathbf{12}\in E(G)}(3*1)$+$\sum_{\mathbf{23}\in E(G)}(2*1)$+$\sum_{34\in E(G)}(3*2)$= 2(3*1) +1(2*1) +1(3*2)= 14.

(iii)$\overline{F(G)}$= $\sum_{uv\in E(G)}[\overline{d_G(u)}^{\,2} + \overline{d_G(v)}^{\,2}]$

= $\sum_{\mathbf{12}\in E(G)}(3^2+1^2)$+$\sum_{\mathbf{23}\in E(G)}(2^2+1^2)$+$\sum_{34\in E(G)}(3^2+2^2)$

= 2(3^2+1^2) +1(2^2+1^2) +1(3^2+2^2)= 38.

Theorem 9. Downhillfirst Zagreb index, downhill second Zagreb index and downhillforgotten index of 2-methylbutane are(i)DWM$_1$(G) = 48,(ii) DWM$_2$(G) =32and (iii) DWF(G) = 128.

Proof. Byusingdefinitions and edge degree partition of molecular graph G, we get

(i)DWM$_1$(G)=$\sum_{v\in \boldsymbol{V(G)}}(d_{dn}(v))^2$

= $\sum_{v\in \boldsymbol{V(G)}}(d_{dn}(n-1))^2$= (n-2)$(n-1)^2$= 48.

(ii) DWM$_2$(G)=$\sum_{vu\in \boldsymbol{E(G)}} d_{dn}(v)d_{dn}(u)$

= $\sum_{vu\in \boldsymbol{V(G)}} d_{dn}(n-1)d_{dn}(n-1)$+$\sum_{vu\in \boldsymbol{V(G)}} d_{dn}(n-1)d_{dn}(0)$= (n-3)(n-1)(n-1)= 32.

(iii)DWF(G) =$\sum_{v\in \boldsymbol{V(G)}}(d_{dn}(v))^3$

= $\sum_{v\in \boldsymbol{V(G)}}(d_{dn}(n-1))^3$= (n-3)$(n-1)^3$= 128.

Theorem 10. Uphillfirst Zagreb index, uphill second Zagreb index and uphill forgotten index of 2-methylbutane are(i)UPM$_1$(G) =39, (ii)UPM$_2$(G) = 26and (iii)UPF(G) = 105.

Proof. Byusingdefinitions and edge degree partition of molecular graph G, we get

(i)UPM$_1$(G) =$\sum_{v\in \boldsymbol{V(G)}}(d_{up}(v))^2$

= $\sum_{v\in \boldsymbol{V(G)}}(d_{up}(n-2))^2$+$\sum_{v\in \boldsymbol{V(G)}}(d_{up}(n-3))^2$= 3$(n-2)^2$+(n-2)$(n-3)^2$= 39.

(ii)UPM$_2$(G) =$\sum_{v\in \boldsymbol{V(G)}} d_{up}(v)\, d_{up}(u)$

$\sum_{v\in \boldsymbol{V(G)}}(n-2)(n-3)$+$\sum_{v\in \boldsymbol{V(G)}}(d_{up}(n-3)\ (n-3)$= 3[(n-2)(n-3)]+(n-3)[(n-3)(n-3)]= 26.

(iii)UPF(G) =$\sum_{v\in \boldsymbol{V(G)}}(d_{up}(v))^3$

= $\sum_{v\in \boldsymbol{V(G)}}(d_{up}(n-2))^3$+$\sum_{v\in \boldsymbol{V(G)}}(d_{up}(n-3))^3$= 3$(n-2)^3$+(n-2)$(n-3)^3$= 105.

Theorem 11. NeighborhoodfirstZagreb index, neighborhoodsecond Zagreb index and neighborhoodforgotten index of 2-methylbutane are

(i)M_{N1}(G)= 58,(ii) M_{N2}(G) = 53and (iii)F_N(G) = 213.

Proof. Byusingdefinitions and edge degree partition of molecular graph G, we get

(i) $M_{N1}(G) = \sum_{v\in V(G)} [\delta_G(v)]^2$

$= \sum_{1\in V(G)} 2^2 + \sum_{2\in V(G)} 5^2 + \sum_{5\in V(G)} 3^2 + \sum_{3\in V(G)} 4^2 = 2*2^2+5^2+3^2+4^2 = 58.$

(ii) $M_{N2}(G) = \sum_{uv\in E(G)} [\delta_G(u)\delta_G(v)]$

$= \sum_{12\in E(G)} (2*5) + \sum_{25\in E(G)} (5*3) + \sum_{23\in E(G)} (5*4) + \sum_{34\in E(G)} (4*2)$

$= 2*5+5*3+5*4+4*2 = 53.$

(iii)$F_N(G) = \sum_{v\in V(G)} [\delta_G(v)]^3$

$= \sum_{1\in V(G)} 2^3 + \sum_{2\in V(G)} 5^3 + \sum_{5\in V(G)} 2^3 + \sum_{3\in V(G)} 4^3 = 2* 2^3+5^3+2^3+4^3 = 213.$

Theorem 12. The ve-degree firstZagreb index, ev-degree modified second Zagreb index and ve-degree forgotten index of 2-methylbutane are

(i) $M_1^{ve}(G) = 54$,(ii) $M_2^{*ev}(G) = 1.033$and(iii) $F^{ve}(G) = 190$.

Proof. Byusingdefinitions and edge degree partition of molecular graph G,we get

(i)$M_1^{ve}(G) = \sum_{v\in V(G)} d_{ve}(v)^2$

$= \sum_{1\in V(G)} d_{ve}(3)^2 + \sum_{2\in V(G)} d_{ve}(4)^2 + \sum_{4\in V(G)} d_{ve}(2)^2 = 2*9+2*16+4 = 54.$

(ii)$M_2^{*ev}(G) = \sum_{e\in E(G)} \frac{1}{d_{ev}(e)}$

$= \sum_{12\in E(G)} \frac{1}{2} + \sum_{23\in E(G)} \frac{1}{5} + \sum_{34\in E(G)} \frac{1}{3} = 2*\frac{1}{4} + \frac{1}{5} + \frac{1}{3} = 1.033.$

(iii)$F^{ve}(G) = \sum_{v\in V(G)} d_{ve}(v)^3$

$= \sum_{1\in V(G)} d_{ve}(3)^3 + \sum_{2\in V(G)} d_{ve}(4)^3 + \sum_{4\in V(G)} d_{ve}(2)^3 = 2*27+2*64+8 = 190.$

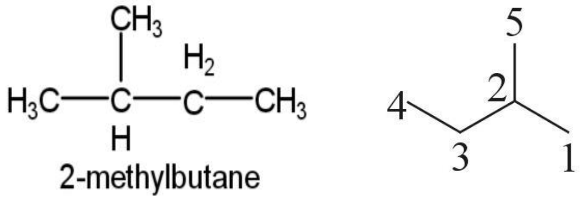

Figure 1. The chemical structure and molecular graph of 2-methylbutane.

Table 1. Basic formulas of topological indices.

Topological index	First Zagreb index	Second Zagreb index	Forgotten index
f(x,y)	x+y	xy	x^2+y^2

Table 2. Edge degree partition of 2-methylbutane.

(d_u, d_v)	(1,3)	(1,2)	(2,3)
Number of edges	2	1	1

IV. CONCLUSION

The revan, reverse, HDR and non-neighbor degrees-basedstudied topological indices have similar values for respective topological indices. From degree of vertices of a molecular graph: R, revan, reverse, S, leap, HDR, coindex, non-neighbor, downhill, uphill, neighborhood and ve degrees are observed for 2-methylbutane and then corresponding first Zagreb index, second Zagreb index and forgotten index are computed. This concept can be applied to any molecular graph to investigate corresponding degree based topological indices.

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Equations Dealing with Topological Indices : Zagreb Indices

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ABSTRACT

The main aim of study of chemical graph theory is to compute the distance and degree based topological indices and bounds in topological indices of molecular graphs. Topological equations comprise degree based topological indices, degree of a graph, degree of a complement graph and coindices. Some topological equations based on first, second, third, hyper Zagreb indices, forgotten index, Banhatti indicesand Sombor index are investigated for polycyclic aromatic hydrocarbons (PAHs).

KEYWORDS: Complement of graph, degree, line graph, molecular graph, polycyclic aromatic compound, topological equation, topological index.

I. INTRODUCTION

Let G be a simple,finite, connected graph with vertex set V(G) and edge set E(G). Family of descriptors that all have the general form D(G) = $\sum_{u=v} F(d_u, d_v)$,where summation goes all over all pairs of vertices u,v of the molecular graph G and d_u denotes the degree of vertex u was studied by I.Gutman[1].Topological indices of a simple graph are numerical descriptors that are derived from graph of chemical compounds. Conventional way of computing the topological indices of molecular graph is by using classical formulas, graph exponentials, M-polynomials and degree-distance polynomials[2-12].For a simple connected graph G, the first and second Zagreb indices are defined as [13]

$M_1(G) = \sum_{uv\in E(G)}(d_u + d_v)$and $M_2(G) = \sum_{uv\in E(G)} d_u\, d_v$.

The hyper Zagreb index is defined as [14]

$HZ(G) = \sum_{uv\in E(G)}(d_u + d_v)^2$.

The topological analysis of polycyclic aromatic hydrocarbonsusing irregularity indices was done by J.Konsalraj et al.in [15].The first and second Zagreb coindices and forgotten coindex are defined as [16-19]

$\overline{M_1}(G) =\sum_{uv\notin E(G)}(d_u + d_v)$,$\overline{M_2}(G)=\sum_{uv\notin E(G)} d_u\, d_v$and $\overline{F}(G)=\sum_{uv\notin E(G)}(d_u^2+ d_v^2)$.

The hyper Zagreb index is related to F(G) and $M_2(G)$[20] by,

$HZ(G) = F(G) + 2M_2(G)$. (1)

Let G is graph of order n and size m then the following equations relate first and second Zagreb indices as[21-22]
$\overline{M_2}(G) = 2m^2-\frac{1}{2}M_1(G)-M_2(G)$, (2)
$\overline{M_2}(\overline{G}) = m(n-1)^2-(n-1)M_1(G)+M_2(G)$, (3)
$M_1(\overline{G}) = M_1(G)+n(n-1)^2-4m(n-1)$, (4)
$M_1(L(G)) = 4m-2M_1(G)+2M_2(G)+F(G)$, (5)
$\overline{M_1}(\overline{G}) = 2m(n-1)-M_1(G)$, (6)
and $RM_2(G) = M_2(G) - M_1(G)+m$. (7)
The Banhatti indices are related to first Zagreb index and hyper Zagreb index by
$B_1(G) = 3M_1(G)-4m$ and $B_2(G) = HM_1(G) - 2M_1(G)$, (8)
where $B_1(G)$ and $B_2(G)$ are first and second Banhatti indices [23-24] and $HM_1(G)$ is hyper first Zagreb index.
The complement of a graph G, denoted by $\overline{G}$,is a simple graph on the same set of vertices u and v are connected by an edge uv, if and only if they are not adjacent in G. The degree of a vertex v in $\overline{G}$ is given by $d_{\overline{G}}(v) = |V(G)|-1-d_G(v)$, where $|V(G)| = n$.Let L(G) be the line graph of G then $d_G(e)= d_u+d_v-2$[25].The irregularity measure index is defined as

$IRM(G) = F(G)-2M_2(G)$, where $IRM(G) =\sum_{xy\in E(G)}[d(x)-d(y)]^2$ (9)
and the F-coindex is defined as $\bar{F}(G) = (n-1)M_1(G)-F(G)$. (10)
In complement form forgotten index is expressed as
$F(\overline{G})= n(n-1)^3-6m(n-1)^2+3(n-1)M_1(G)-F(G)$,
$\bar{F}(\overline{G})= 2m(n-1)^2 -2(n-1)M_1(G)+F(G)$
and $\overline{M_1}(\overline{G}) = \overline{M_1}(G)$ and $\bar{F}(\overline{G}) \neq \bar{F}(G)$. (11)
If G is any graph, then the Sombor index (with $p = \frac{1}{2}$) is [26]
$SO_{\frac{1}{2}}(G) = M_1(G)+2RR(G)$ (12)
where $SO_p(G) = \sum_{uv\in E(G)}(d_u{}^p + d_v{}^p)^{\frac{1}{p}}$,we call $SO_p(G)$ as the p-Sombor index, where $p \neq 0$ clearly,$SO_1$is the first Zagreb index and SO_2 original Sombor index and RR(G) is reciprocal Randic index given by $RR(G) = \sum_{uv\in E(G)}(d_ud_v)^{\frac{1}{2}}$.
The third Zagreb index is defined as
$M_3(G) = F(G)+2M_2(G)$. (13)
Polycyclic aromatic hydrocarbons (PAHs) are a class of chemicals that occur naturally in coal, crude oil, and gasoline. By calculation we obtain $|V(G)| = 6n^2+6n$ and $|E(G)| = 9n^2+3n$ for PAHs.From figure 1,it is observed that $PAH_1= C_6H_6$ and $PAH_2 = C_{24}H_{12}$. In PAHs there are two types of edges based on the degree of end vertices of each edge as [27-35] E_{13},E_{33},which are expressed by $E_{13}= \{uv\in E(G)|d_u=1, d_v=3\}$, $|E_{13}|= 6n$,$E_{33}= \{uv\in E(G)|d_u=3, d_v=3\}$, $|E_{33}|= 9n^2-3n$.Topological equations comprises degree based topological indices, degree of a graph, degree of a complement graph and coindices.Let G bethemoleculargraphofPolycyclicaromatichydrocarbons (PAHs) and G'be the line graph of the moleculargraph of first member of Polycyclic aromatic hydrocarbons (PAHs) n > 2. There are $9n^2+ 3n$ nodes and $18n^2$ linksinG'.Outof $9n^2+3n$ nodesinG',$9n^2-3n$ nodesareof degree 2 and 6n nodes of degree 4. Let us consider the edge partition of G'basedondegree,thefirstedgepartitionhas12nlinkswith $d_{L(G)}(u)= 2$, $d_{L(G)}(v)= 4$ andthesecondedgepartitionhas $18n^2-12n$ linkswith $d_{L(G)}(u)= d_{L(G)}(v) = 4$.Let $d_G(e)$denote the degree of an edge e in G, which is defined as $d_G(e) = d_u+d_v-2$,with e = uv.By calculation we get the first and second Zagreb indices as $M_1(G) = 54n^2+6n$ and $M_2(G) = 81n^2-9n$. The notations used in this paper are standard and mainly taken from standard books of chemical graph theory [36-38].In this paper topological equations based on first, second,

third, hyper Zagreb indices, forgotten indices, Banhatti indices, irregularitymeasure indexand Sombor index are investigated for polycyclic aromatic hydrocarbons (PAHs).

II. MATERIALS AND METHODS

A molecular graph G(V, E) is constructed by representing each atom of molecule by vertex and bonds between them by edges. Let V(G) be vertex set and E(G) be edge set. The molecular graph of first three members of polycyclic aromatic hydrocarbons and line graph of benzeneare shown in figure 1 and 2 respectively.Let the molecular graph of polycyclic aromatic hydrocarbons is denoted by G and line graph of PAHs by G'.The degree and edge degree of vertices of these molecular graphs are observed and used in the computation of $M_1(G)$, $M_2(G)$ and RR(G).In this paper Zagreb indices, forgotten indices, Banhatti indices, Sombor index and irregularity measure index of polycyclic aromatic hydrocarbons(PAHs) are computed by using topological equations (1-13).

III. RESULTS AND DISCUSSION

Let molecular graphs of PAHs is denoted by G and line graph of first member of PAHs by G'. The definitions of first Zagreb index, second Zagreb index and forgotten index are used to compute these topological indices by using edge partition. The edge partition for degree and edge of molecular graph PAHs graph is represented in table 1. In this section we compute the topological indices by using equations (1-13).By using formulas and edge partition from table 1,the first and second Zagreb indices are obtained as $M_1(G) = \sum_{uv\in E(G)} (d_u + d_v) = 6n(4)+(9n^2-3n)6=54n^2+6n$, $M_2(G) = \sum_{uv\in E(G)} (d_u d_v) = 6n(3)+(9n^2-3n)9=81n^2-9n$.

Theorem 1. The first Zagreb indices of polycyclic aromatic hydrocarbons are
(i)$M_1(\overline{G})=-n(35n^2-76n-19)$,(ii)$M_1(L(G)) = 12n(21n-1)$and (iii)$\overline{M_1}(\overline{G}) =6n(3n^2-11n-2)$.

Proof. Byusingtopological equations (4-6),figure (1-2) and edge degree partition of PAHs, we get
(i)$M_1(\overline{G}) = M_1(G)+n(n-1)^2-4m(n-1)$
$=54n^2+6n+n(n-1)^2-4(9n^2+3n)(n-1)= -n(35n^2-76n-19)$.
(ii)$M_1(L(G)) = 4m-2M_1(G)+2M_2(G)+F(G)$
$= 4(9n^2+3n)-2(54n^2+6n)+2(81n^2-9n)+162n^2+6n= 12n(21n-1)$.
(iii)$\overline{M_1}(\overline{G}) = 2m(n-1)-M_1(G)$
$= 2(9n^2+3n)(n-1)-(54n^2+6n)= 6n(3n^2-11n-2)$.

Theorem 2. $\overline{M_2}(G)$,$\overline{M_2}(\overline{G})$ and $RM_2(G)$ of polycyclic aromatic hydrocarbons are
(i)$\overline{M_2}(G)=-6n(15n-2)$,(ii)$\overline{M_2}(\overline{G}) = 3n^2(n-4)(3n-11)$ and (iii)$RM_2(G) = 12n(3n-1)$.

Proof. Byusing equations (2, 3 and 7) and edge degree partition of PAHs, we get
(i)$\overline{M_2}(G) = 2m^2-\frac{1}{2}M_1(G)-M_2(G)$
$= 2(9n^2+3n)^2-\frac{1}{2}(54n^2 + 6n) - (81n^2-9n)= -6n(15n-2)$.
(ii)$\overline{M_2}(\overline{G}) = m(n-1)^2-(n-1)M_1(G)+M_2(G)$
$= (9n^2+3n)(n-1)^2-(n-1)(54n^2+6n)+81n^2-9n= 3n^2(n-4)(3n-11)$.
(iii)$RM_2(G) = M_2(G) - M_1(G) + m$
$= 81n^2 - 9n - 54n^2 - 6n + 9n^2+3n= 12n(3n-1)$.

Theorem 3.$\overline{F}(G)$,$\overline{F}(\overline{G})$ and$F(\overline{G})$of polycyclic aromatic hydrocarbons are
(i)$\overline{F}(G) = 6n(9n^2-35n-2)$,(ii)$\overline{F}(\overline{G}) = 2n(9n^3-69n^2+59n+12)$and

(iii) $F(\overline{G})$= -n($53n^3$-$249n^2$+321n+43).

Proof. By using equations (10-11) and edge degree partition of PAHs, we get

(i) $\bar{F}(G)$= (n-1)$M_1(G)$-F(G)

F(G) = $\sum_{uv\in E(G)}(d_u-d_v)^2$+2$M_2$(G)=6n$(1-3)^2$ + 2($81n^2$-9n) = $162n^2$ + 6n.

$\bar{F}(G)$ = (n-1)($54n^2$+6n) – ($162n^2$+6n) = 6n($9n^2$-35n-2).

(ii) $\bar{F}(\bar{G})$= 2m$(n-1)^2$-2(n-1)M_1(G)+F(G)

= 2($9n^2$+3n)$(n-1)^2$-2(n-1)($54n^2$+6n)+$162n^2$+6n= 2n($9n^3$-$69n^2$+59n+12).

(iii) $F(\overline{G})$=n$(n-1)^3$-6m$(n-1)^2$+3(n-1)M_1(G)-F(G)

= n$(n-1)^3$-6($9n^2$+3n)$(n-1)^2$+3(n-1)($54n^2$+6n)-($162n^2$+6n)= -n($53n^3$-$249n^2$+321n+43).

Theorem 4. The hyper Zagreb index, Sombor index (with p = $\frac{1}{2}$), second and first Banhatti indicesof polycyclic aromatic hydrocarbons are(i)HZ(G) = $324n^2$-12n,(ii)$SO_{\frac{1}{2}}$(G) = $108n^2$+8.78n,(iii)B_2(G) = $216n^2$-24n and (iv)B_1(G) = 6n(21n+1).

Proof. Byusingequations (1,12 and 8) and edge degree partition of PAHs, we get

(i)HZ(G) = F(G)+2M_2(G)

= $162n^2$+6n+2($81n^2$-9n)= $324n^2$-12n.

(ii)$SO_{\frac{1}{2}}$(G) = M_1(G)+2RR(G)

RR(G) = $\sum_{uv\in E(G)}(d_u d_v)^{\frac{1}{2}}$= (6n)$3^{\frac{1}{2}}$+($9n^2$-3n)3 = $27n^2$+1.39n.

$SO_{\frac{1}{2}}$(G) = $54n^2$+6n+$54n^2$+2.78n= $108n^2$+8.78n.

(iii) B_2(G) = HM_1(G)-2M_1(G).

HM_1(G) = $\sum_{uv\in E(G)}(d_u+d_v)^2$= 6n$(1+3)^2$+($9n^2$-3n)$(3+3)^2$= $324n^2$-12n.

B_2(G) = $324n^2$-12n-2($54n^2$+6n)= $216n^2$-24n.

(iv) B_1(G) = 3M_1(G)-4m.

= 3($54n^2$+6n)-4($9n^2$+3n)= 6n(21n+1).

Theorem 5. The third Zagreb index and irregularity measure index of PAHsare

(i)M_3(G) = $324n^2$and (ii)IRM(G) = 24n.

Proof. Byusing equations (13, 9) and edge degree partition of PAHs, we get

(i)M_3(G) = F(G)+2M_2(G)

=($162n^2$+6n)+2($81n^2$-3n)= $324n^2$.

(ii)IRM(G) = F(G)-2M_2(G).

F(G) = $162n^2$+6n and M_2(G) = $81n^2$-9n.

IRM(G) = $162n^2$+6n-2 ($81n^2$-9n)= 24n.

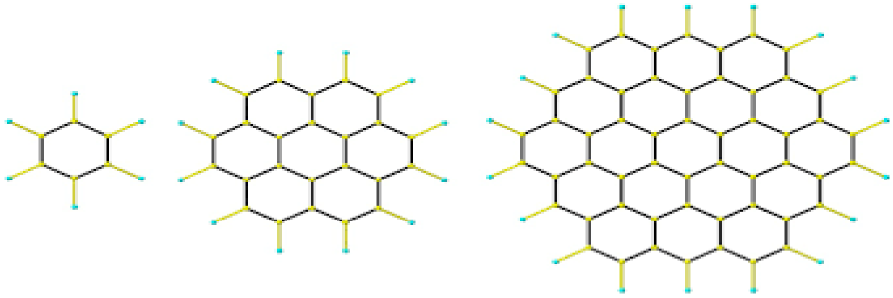

Figure 1:Molecular graphs of PAH_1, PAH_2 and PAH_3.

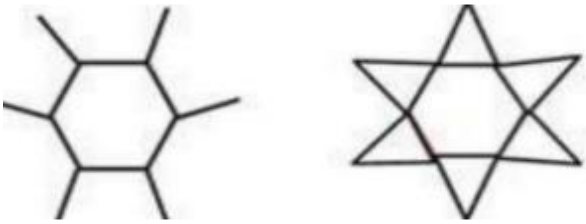

Figure 2:The molecular graphs of$PAH_1$and L(PAH_1).

Table 1. Edge degree partition of polycyclic aromatic compounds.

(d_u, d_v)	(1,3)	(3,3)
$d_G(e)$	2	4
Number of edges	6n	$9n^2$-3n

IV. CONCLUSION

The first, second,third Zagreb indices, forgotten indices, Sombor index, first,second Banhatti indices and irregularity measure index are computed by using topological equations for polycyclic aromatic hydrocarbons. The relations $\overline{M_1}(\overline{G}) = \overline{M_1}(G)$ and $\overline{F}(\overline{G}) \neq \overline{F}(G)$arevalid for PAHs.This is novel idea to compute the degree based topological indices by using topological equations of the molecular compounds.

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Analysis On Use of Nanotechnology in Computer Science

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ABSTRACT

Nanotechnology is an innovative developing tool having infinite uses in the existent Universe. This is a skill whose upcoming is a totally uncharted; that is both science and technology to planes we never imagined. It is an interdisciplinary field having its use and growth in various fields such as applied science, mechanical, electrical and numerous others. In fresh year's nanotechnology have brought development in current era of various application. In this paper we focus the part of nanotechnology in computers science and the current development, chances happened in recent years. This existence a review paper gives short-term info about the research taken place till this age.

Keywords: nanotechnology, quantum computing, computational nanotechnology

I. INTRODUCTION

Nanotechnology is the innovation in view of small things generally containing nanostructures, iotas and particles. Its size of estimation is nanometre scale, which is one billionth of a meter which is more modest than frequency of noticeable light or hundred thousand width of a human hair. It is the designing of utilitarian framework at sub-atomic scale. In its unique sense, 'nanotechnology' alludes to the extended capacity to build things from the base up, utilizing methods and apparatuses being grown today to make total, elite execution items. The possibility of nanotechnology was first proposed by a physicist named Richard Feynman in 1959. Feynman never in fact utilized the expression "nanotechnology" or "nanite" yet he gave a discourse called "There's A lot of Room At the Base" wherein he discussed how we would one day have the option to control particles and particles and really create them into anything we desired them to be. He then, at that point, talked about the chance of us, in the far off future, making minuscule machines that would act as little devices. This thought was before viewed as totally revolutionary; we currently consider nanotechnology to be an undeniable and possible innovation soon. Nanotechnology wasn't viewed as an extensive idea until the 1980s when Eric Drexler started doing examination into nanotechnology, including the perception of Feynman's discourse. Drexler went through innumerable years idealizing this idea and getting a wide range of researchers engaged with really delivering nanotechnology. It has influences in different fields, for example, Registering and Information stockpiling, Materials and Assembling, Wellbeing and medication, Energy, Transportation and so on. In Figuring and Information stockpiling field, it assists being developed of processors with high velocity, high toughness, less energy utilization and so on. Additionally helps in progress in show and quantum advances. In Materials and Assembling field, it helps underway of self-mending machines, Nano scale building blocks and different materials without help of machines. In Wellbeing and Medication field, it helps in creating Nano robots to battle disease cells, Nano sensors for early determination, and so on. In Transportation field, it helps in delivering light weight and low fuel consuming vehicles and furthermore warm and wear safe coatings. In energy field, it gives elective wellspring of energy which has the ability to supplant even sunlight based energy. The essential idea that joins nanotechnology to software engineering very much like numerous different applications is when materials are scaled to the nano level they foster different tenable and advantageous properties, for example, optical, electronic, mechanical, attractive which are generally missing in mass materials. Likewise suggested by Moore's regulation - which has seen that, over the historical backdrop of figuring equipment, the quantity of semiconductors in a thick coordinated circuit has multiplied roughly like clockwork - PC gadget parts are being downsized endlessly further as a result. Conventional bulk scale or miniature size silicon-based semiconductors couldn't stay aware of this downscaling of size, subsequently nanotechnology and nanomaterial came into the image. Software engineering has huge extent of utilization in connection with nanotechnology. This paper gives a survey on the job of nanotechnology in field of software engineering. The association of paper is in following way initial segment of paper is Presentation, it is trailed by advancement of nanotechnology and different cycle engaged with developing the Nano scale framework, third part remembers the ongoing improvement of utilization of nanotechnology for field of software engineering and ultimately the difficulties ,future extension ,finish of nanotechnology and software engineering.

II. DEVELOPMENT, TECHNOLOGY AND USE

A. Development of Nanotechnology

As indicated by Mihail Roco of the U.S. Public Nanotechnology Drive, the development of nanotechnology has been isolated into four ages in view of the items, Rocco said that the original of Nanotechnology started in 2000. Original items, otherwise called "uninvolved nanostructures," are intended to perform one undertaking like colloids and sprayers. The subsequent age, which happened in 2005, is designated "dynamic nanostructures." They have a performing multiple tasks capacity, and the models are actuators and sensors. The third era, or the period of frameworks of Nano frameworks, is supposed to start in 2010. These Nano frameworks will comprise of thousands of associating parts like 3D systems administration and new various levelled designs, mechanical technology, and directed gathering. The fourth era of Nanotechnology will start in around 2015 when the first coordinated Nano frameworks are supposed to be created

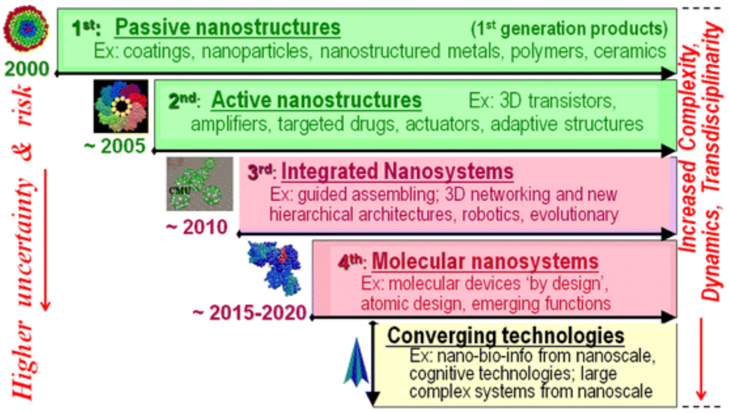

Figure 1: Four generation of Nanotechnology

B. Technology and Techniques

Innovation and Procedures

Nanotechnology utilizes the procedure of Nanofabrication which assists with controlling and coordinates at nuclear level and is especially interest for PC engineer since it makes the way for super-high-thickness microchips and memory chips. It is the plan and assembling of gadgets with aspects estimated in nanometres. One can extensively separate different nanofabrication strategies into two classes:

TOP-DOWN APPROACH:

Big picture perspective tries to make more modest gadgets by utilizing bigger ones to coordinate their gathering. The big picture perspective frequently involves the conventional miniature manufacture strategies wherein remotely controlled devices are utilized to cut, factory and shape materials into the ideal shape and request .The most well-known top down creation strategy is nano lithography. In this cycle required material is safeguarded by a cover and the uncovered material is carved away. Contingent fair and square of goal expected for highlights in the eventual outcome scratching of the base material should be possible artificially utilizing acids or precisely utilizing bright light, x-beams or electron radiates. This is the method applied to produce microchips.

BOTTOM-UP APPROACH:

It depends on sub-atomic acknowledgment and self-gathering to create nanostructures out of more modest structure blocks (particles, colloids, and groups). It has a more substance designing and material science flavour and depends on essentially various standards. A genuine illustration of this sort of approach is tracked down in nature; all cells use catalysts to create DNA by taking the part particles and restricting them together to make the last design. Substance union, self-gathering, and atomic manufacture are instances of base up procedures. Self-gathering happens when little control happens, yet parts precipitously meet up to frame requested Nano scale structures, for example in the arrangement of nanotubes and some monolayers.

III. CURRENT SITUATIONS OF NANOTECHNOLOGY AND COMPUTER SCIENCE

The effect of nanotechnology on PCs has a couple of exceptional turns; which are for the most part in the innovative work stages. This is instances of the way nanotechnology has changed PC and its different angle:

Carbon Nanotube Computer:

Carbon nanotubes (CNTs) are empty chambers made out of a solitary sheet of carbon particles. It has been seen that CNT has same property as Silicon semiconductor and accordingly they go about as semiconductor which makes them reasonable for being utilized as semiconductor in microprocessors. A group of Stanford engineers has fabricated an essential PC utilizing carbon nanotubes, which can possibly make another age of electronic gadgets that run quicker, and utilizes less energy, as contrasted and silicon chips [8]. This nanotube processor is comprised of 178 semiconductors, every one of which contains carbon nanotubes that are around 10 to 200 nanometre long. It has been accounted for by the they have made six renditions of carbon nanotube PCs, out of which one them can be associated with outside equipment, and a mathematical keypad that can be utilized to include numbers for addition[9].

Quantum Computing:

Quantum registering likely could be the eventual fate of most top of the line server farms. These future PCs are not in light of computerized 1's and 0's. Rather these future PCs depend on qubits (quantum bits). The force of attractive powers at a subatomic scale will release the outstanding force of future PCs. By controlling the pivot of molecules, information can be sent and put away at a phenomenal rate. Physicists have figured out how to broaden the quantum lifetime of electrons by more than 5,000 precent. Electrons show a property called 'twist' and work like small magnets which can face up, down or a quantum superposition of both. The condition of the twist can be utilized to store data thus by expanding their life the exploration gives a huge step towards building a usable quantum computer [13][14].

Computational Nanotechnology:

Nano scale frameworks, however tiny, are comprised of thousands, even many thousands, of iotas. In this manner, depicting their electronic designs and elements requires critical hypothetical expertise and much PC power. It is the strategy to study nanoparticles utilizing PC models to anticipate their way of behaving and illuminate genuine nanoparticle physical science and science. Computational nanotechnology is a useful asset for understanding nanoparticle material science and science. Subsequent to completing a reproduced try, hypothesis is created to make sense of the noticed outcomes, which is then approved by directing a lab explore. In the event that the anticipated outcomes and the hypothetical outcomes concur, the hypothesis is acknowledged. Surprising outcomes from lab work can likewise be inspected with hypothetical techniques, which frequently lead to the improvement of new hypothesis. One of the cases of Computational Nanotechnology is improvement of Nano Design; an exploration bunch at NASA has been fostering this product framework, for researching fullerene nanotechnology and planning sub-atomic machines. The product engineering of Nano Design is intended to help and empower their gathering to foster complex mimicked sub-atomic machines [2].

DNA Computing:

DNA calculation depends on the way that innovation permits us to 'grouping' (plan) single DNA strands which can be utilized as portrayals of pieces of parallel information. Innovation likewise permits us to greatly 'enhance' (repeat) individual strands until there are adequate numbers to tackle complex computational issues. DNA particle has a twofold helix structure made out of two sugar phosphate spines framed by the polymerization of deoxy-ribose sugar. Set between two spines are sets of nucleotides Adenine, Cytosine, Guanine and Thymine. DNA PCs utilize single strands of DNA to perform figuring tasks. DNA registering centers around the utilization of gigantic parallelism, or the designation of little parcels of a figuring undertaking to a wide range of handling components. The construction of the DNA permits the components of the issue to be addressed in a structure that is undifferentiated from the twofold code structure. Trillions of exceptional strands of DNA can address each of the potential answers for the issue. A few researchers foresee a future where our bodies are watched by little DNA PCs that screen our prosperity and delivery the right medications to fix harmed or undesirable tissue.[17]

Single Electron Transistor:

The single electron semiconductor is made of an island associated through two burrowing intersections to a channel and a source terminal, and through a capacitor to a door cathode. At the point when every one of the inclinations is zero, electrons need more energy to burrow through the intersection. Be that as it may, assuming that you increment the predisposition, however keep it not exactly the coulomb hole voltage, expanding the door predisposition over the mark of greatest slant on the coulomb flight of stairs prompts the state with one or no abundance electrons on the island to have a similar energy, bringing about the coulomb obstruction being eliminated and permitting electrons to burrow through the intersections and between the source and the channel. The Coulomb energy is given by Ec = e2/2C, Where e is the charge on an electron and C is the all-out capacitance of the source and channel intersections and the door capacitor. At the point when the predisposition between the source and channel is more prominent than e/C (e/2C across every intersection), called the Coulomb hole voltage, electrons effectively burrow across the intersections, bringing about an ongoing through the semiconductor free of the door inclination. Accordingly Single-electron semiconductors (SETs) hold extraordinary commitment for future Nano electronic circuits because of their little size, low power utilization, and capacity to perform quick and delicate charge measurement.[16]

Nanobots :

Nanobots will be the up and coming age of Nano machines. Progressed nanobots will actually want to detect and adjust to natural improvements like intensity, light, sounds, surface surfaces, and synthetic substances; perform complex estimations; move, impart, and cooperate; lead atomic gathering; and, somewhat, fix or even duplicate themselves. Nanotechnology is the science and utilization of making objects on a level more modest than 100 manometers. The outrageous idea of nanotechnology is the "base up" production of for all intents and purposes any material or item by collecting each molecule in turn. Despite the fact that nanotech processes happen at the size of manometers, the materials and articles that outcome from these cycles can be a lot bigger. Huge scope results happen when nanotechnology includes enormous parallelism in which numerous concurrent and synergistic Nano scale processes consolidate to deliver a huge scope result. Nano robots have possible applications in the get together and support of refined frameworks. Nano robots could work at the nuclear or sub-atomic level to construct gadgets, machines, or circuits, a cycle known as sub-atomic assembling. Nano robots could likewise deliver duplicates of themselves to supplant broken down units, a cycle called self-replication.

IV. CONCLUSION AND FUTURE SCOPE

- Nanotechnology will actually want to work on logical investigation by a long shot basically on the grounds that nanites are so little.
- The latest things and the future advancement will prompt immense commitment in the field of software engineering.
- Today nanotechnology being in the fourth era of advancement is probably going to show remarkable developments in not so distant future.
- This will increase the quality of life in our society.

V. ACKNOWLEDGMENT

We would extraordinary completely recognize Kenneth Buddha Pants for the graphical delineation in this paper meant as Figure 1 of Four Age of Nanotechnology and its helpfulness being developed of various item at nanoscle.

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Acetone Sensing Properties of Spray Deposited Nanocrystalline F: ZnO Thin Films

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ABSTRACT

Fluorine doped Zinc Oxide (F:ZnO) thin films were deposited on glass substrates by simple chemical spray pyrolysis technique. The effect of F doping (1 at% to 5 at%) on the Acetone gas sensing properties were studied. The Acetone gas response is higher at the operating temperature 300 OC of the film and it is lower on either side of operating temperature. The response and recovery times of the F: ZnO films were enhanced significantly compared to those reported for ZnO films. The response of 4% F doped ZnO film to Acetoneis certainly better than that others. For F doped ZnO film on exposure to 1000 ppm Acetone at 573 K, the response was increased to Acetone gas up to 4 at% while further increase in doping response was decreased.

Keywords: Spray pyrolysis; F-doped ZnO films; acetone sensing properties; response time.

I. INTRODUCTION

Zinc Oxide (ZnO) is one of the promising materials in the field of sensor which possesses many unique optical and electrical properties. It is a unique material that exhibits semiconducting, piezoelectric and pyroelectric multiple properties. ZnO has three key advantages: It is a semiconductor, with a direct wide band gap (3.3 eV) and a large excitation binding energy (60 meV). It is an important functional oxide, exhibiting near ultraviolet emission and high conductivity. Secondly ZnO shows piezoelectric effect, which is a key property in building electromechanical-coupled sensors and transducers.

In 1950's it was discovered that the electrical properties of some metal oxides are changed when they are exposed to reducing gases, especially at elevated temperatures [1, 2]. By applying this phenomenon, in 1962 Seiyama et al. proposed the idea of gas sensing using ZnO thin films [3]. The other commonly used sensor material, SnO_2, was proposed as a gas sensor in the same year by Taguchi [4], and since 1968 these sensors have been commercially available through Figaro Engineering [5]. The Taguchi Gas Sensor is a partially sintered SnO_2 bulk device whose resistance in air is very high and drops when exposed to reducing gases such as combustibles (H_2, CO_2 CH_4,) or volatile organic vapors and it has enjoyed a substantial popularity because of its ease of fabrication and stability relative to other competitive systems such as polymers and organic films. In addition to research on understanding the fundamentals of the sensing mechanism, the studies on SnO_2 sensors have been directed on enhancing the sensor performance through the addition of noble metals (Pt, Pd, etc.), synthesis of thick and thin film sensors, and doping with other semiconductors [6-18]. Other metal oxides such as Fe_2O_3, TiO_2, and WO_3 have also been used as gas sensors. Despite these broad studies in the semiconductor sensor area, problems such as insufficient gas selectivity, inability to detect very low gas concentrations, and degradation of the sensor performance by surface contamination still persist. Thus, there is a growing need for chemical sensors with novel properties.

II. EXPERIMENTAL DETAILS

The F-doped ZnO films were deposited onto amorphous glass substrates, chemically cleaned, using spray pyrolysis method at 450 ^{0}C substrate temperature. 0.5M solution of zinc acetate dehydrate [$Zn(CH_3COO)_2.2H2O$] diluted in methanol and deionized water (3:1) was used for all the films, and ammonium fluoride (NH_4F) was added to starting solution for fluorine-doping. Zinc acetate dehydrated and ammonium fluoride solutions were mixed together in different volume proportions ranging from 1 at% to 5 at% in steps of 1%. Air was used as the carrier gas, pressure at 0.2 bar. The ultrasonic nozzle to substrate distance was 28 cm and during deposition, solution flow rate was held constant at 3 ml/min.

The sensing study was made on sensor setup in the lab.

III. RESULTS AND DISCUSSIONS

Acetone sensing properties

(a) Effect of temperature and Acetone concentration

The operating temperature is an important factor for the gas sensing properties [19-20]. Here we did a series of experiments at different temperatures to obtain the optimal operating temperature for Acetone detection. Before exposing to the target gas, each sensor was stabilized for 30 min at the working temperature. The variation of Acetone response of F: ZnO film for different F at% to 1000 ppm Acetone at different temperatures is shown in Fig. 1. It is observed that as fluorine concentration increases in the film response increases and it is also observed that optimal temperature at 300^{0}C. Above 300^{0}C gas response decreased.

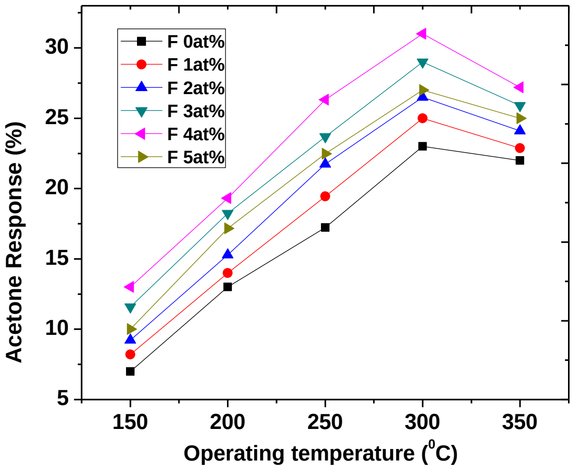

Figure 1: The variation of Acetone response of F: ZnO film for different F at%to 1000 ppm Acetone at different temperatures.

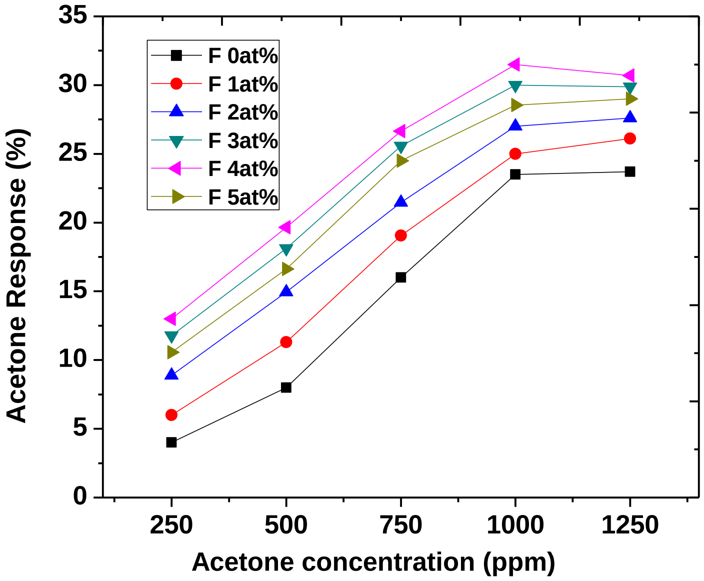

Figure 2: The variation of Acetone response of F :ZnO film to different Acetone concentrations

Fig2 shows the gas response as a function of Acetone concentration at 573 K. The figure reveals that the response increased with the Acetone concentration from 250 to 1000 ppm. However, at higher Acetone concentrations the increase in gas response value was gradual and almost constant.

(b) Dynamic gas response transients of F: ZnO film to Acetone

Fig. 3 shows the dynamic response transient of F:ZnO filmsensor upon exposure to 1000 ppm Acetone at 573 K. After the removal of Acetone, the recovery time is measured till the gas response dropped to the original value. Maximum response is found to F: ZnO films at 4 at%.

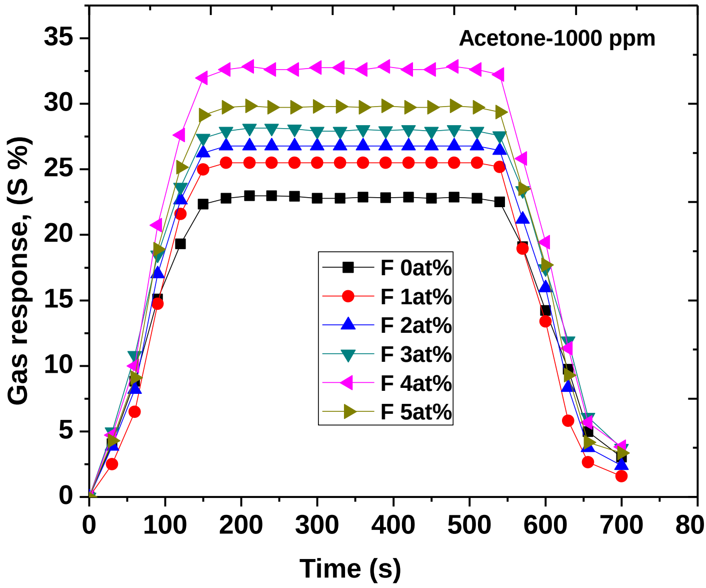

Figure 3: Dynamic Acetone transient response of ZnO films for different F at% exposed to 1000 ppm Acetone at an operating temperature of 573 K.

(c) Response and recovery time periods for Acetone

After introducing 1000 ppm acetone into the testchamber, allsensors samplesrespond immediately. The response time of 4 at% F-doped ZnO sensors is 140 and recovery time is155 s. Fig. 4, shows the response and recovery times for all The F doped ZnO thin films samples.

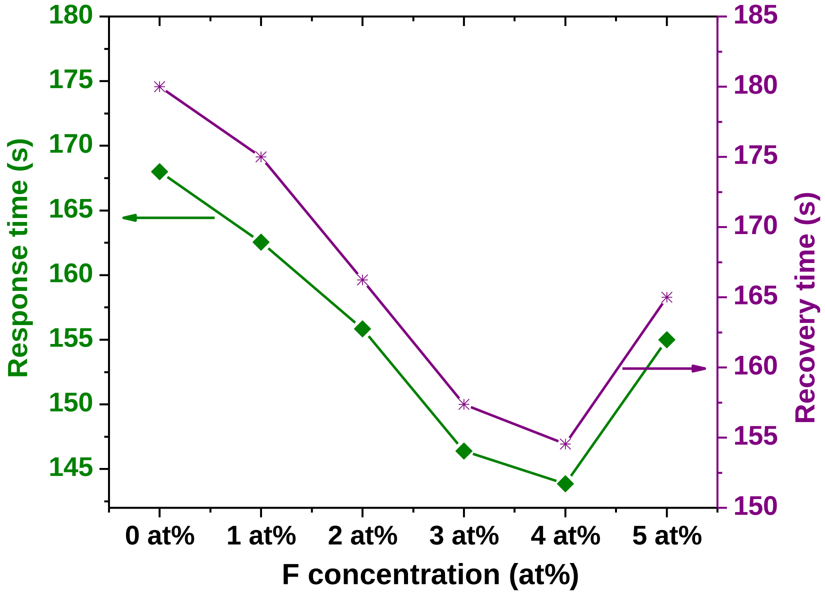

Figure 4: The variation of response and recovery time periods of ZnO films for different F at% upon exposure of 1000 ppm Acetone.

IV. CONCLUSION

The effect of F doping (1 at% to 5 at%) on the Acetone gas sensing properties were studied. The sensors response gradually increases up to the 1000 ppm Acetone concentration and then starts to saturate above 1000 ppm. The response and recovery times of the F: ZnO films were enhanced significantly compared to those reported for ZnO films. The response time of 140 s and corresponding recovery time is 155 s is observed for 4% F doped ZnO thin film.

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Dielectric Relaxation and Static Permittivity Theories

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ABSTRACT

The dielectric relaxation study for different binary mixtures has been carried out using Time Domain Reflectometry Technique. The dielectric parameters have been obtained from the complex permittivity spectra. The result obtained are used to interpret the nature and kind of solute – solvent interaction. Before this it is important to know dielectric relaxation and static permittivity theories.

KEYWORDS: Dielectric, Polarization, Relaxation, Permittivity, Displacement.

I. INTRODUCTION

DIELECTRICS:

Dielectrics are substance that does not conduct electric current. They do not have free electric charges. The not conducting means insulator [1]. Dielectric is polarizable, short range of moment of charges due to which electrostatic dipoles exist or form under the influence of an electric field [2].

The term dielectric was invented by Whewell [3] from the Greek "dia" meaning "through", since an electric field passes through the material but felt that "dielectric" was easier to pronounce. Electrical charges do not flow through the dielectric material when placed in an electric field but they can be polarized. Von Hippel, in his seminal book [4] takes this definition further. He states, "Dielectrics ... are not a narrow class of so-called insulators, but the broad expanse of nonmetals considered from the stand point of their interaction with electric, magnetic fields, of electromagnetic fields. Thus we are concerned with gases as well as with liquids and solids, and with the storage of electric and magnetic energy as well as its dissipation."

The study of dielectric materials describes how an electric field behaves inside a material.

II. DIELECTRIC THEORIES AND POLARIZATION

There are many dielectric theories, these theories depends on the applied field. In the development of these theories most contributions are due to Debye, Kirkwood, Frohlich, and Onsagar [5-8]. In this chapter only those dielectric theories are discussed which are needed to interpret the experimental results done in this work. When the electric field is applied to dielectric material, the molecular charges get displaced. The total charge passing through unit area within the dielectric, perpendicular to the direction of applied field is called polarization [9]. The polarization is of three types a) Electronic Polarization (Pe): Electronic polarization is due to the displacement of electrons with respect to the atomic nucleons. This polarization occurs in all atoms, and can be observed in all dielectrics. It takes very small interval of time to occur. It is of the order of 10^{-15} sec., which is comparable with time period of ultraviolet light.

b) Atomic Polarization (Pa): Atomic polarization is due to mutual displacement of atoms or group of atoms. It takes a short time of the order of 10^{-13} to 10^{-12} sec., which corresponds to period of infrared light.

These two polarizations together called as Distortion polarization (Pd), because it is caused by displacement of charges in atom with respect to each other in the direction of applied field. As there is redistribution of charges in response to applied field, it posses dipole moment called induced dipole moment. The magnitude of induced dipole moment depends on the field strength and polarizibility of the dielectric. The induced dipole moment, lasts so long as the electric field is present and does not depends on temperature of dielectric. The electrical energy required for distortion polarization is completely returned to the electric energy source after the removal of the voltage. For this reason it does not contribute to dielectric loss.

c) Orientation Polarization (Po): Orientation polarization is property of the polar molecules. It is due to rotation of permanent dipoles of dielectric medium. The molecular dipoles orient in the direction of the applied field. It is function of molecule size, viscosity, temperature, and frequency of applied field. Orientation polarization takes a time of the order of 10^{-12} to 10^{-10} sec., corresponding to period of microwave frequency region.

The total polarization is-

$$Pt = Pe + Pa + Po \qquad (1)$$

Thus the polar materials have greater permittivity than the non polar, because of additional polarization due to orientation.

III. DIELECTRIC RELAXATION

The theories of dielectric relaxation can be broadly divided into two parts as theories of static permittivity and theories of dynamic permittivity. In general, permittivity isn't a constant, as it can vary with the position in the medium, the frequency of the field applied, humidity, temperature, and other parameters. In a nonlinear medium, the permittivity can depend on the strength of the electric field. Permittivity as a function of frequency can take on real or complex values.

The polar dielectric materials having a permanent dipole moment, when placed steady electric field so that all types of polarization can maintain equilibrium with it, the permittivity of material under these conditions is called as static permittivity (ε_s). When dielectric material is placed in varying frequency electric field, then permittivity of the material changes with change in frequency of applied field. This is so because with increasing frequency molecular dipoles cannot orient faster to cope-up with applied field. Thus the permittivity of the material falls off with increasing frequency of applied field. The frequency dependent permittivity of material is called as dynamic permittivity. The different theories of static and dynamic permittivity are given in following sections.

IV. STATIC PERMITTIVITY

The dielectric constant may be expressed in terms of the force between two point charges q and q', separated by distance 'r' in a homogeneous dielectric as-$F = \frac{qq'}{\varepsilon r^2}$ (2)

where ε is the static dielectric constant, a characteristic of the medium between the two charges. It is also defined as the ratio of the field strength in vacuum to that in the material for the same distribution of charge. In MKS system the dielectric constant of free space is $8.854 * 10^{-12}$ farad/meter.

The capacitor, charged to q at potential V is said to have a capacity of-

$C = q/V$ (3)

If A is the area of each parallel plate with 'r' distance between them, filled by dielectric of 'ε', the capacity is given by

$C = \frac{\varepsilon A}{4\pi r}$ (4)

Where 'ε' is the ratio of the dielectric constant of the medium between the plates to that of free space. Often, it is referred as a measure of the ability of a fluid, (or solid) to decrease the force of attraction and repulsion between the charged particles. Also, ε is given by-

$\varepsilon = \frac{C}{C_0}$ (5)

where, C_0 is capacity with air of vacuum

The dielectric constant thus is dimensionless quantity.

The electric field between the plates of charged capacitor in vacuum is

$E_0 = 4\pi\sigma$ (6)

where, σ is the surface charge density. If the space between the plates is filled with a homogeneous dielectric material of dielectric constant ε, the field strength decreases to-

$E = \frac{4\pi\sigma}{\varepsilon}$ (7)

The decrease in field strength is

$E_0 - E = 4\pi\sigma\left(1 - \frac{1}{\varepsilon}\right) = 4\pi\sigma\left(\frac{\varepsilon-1}{\varepsilon}\right)$ (8)

The same decrease is possible by reducing the surface charge density from σ to $\sigma\left(\frac{\varepsilon-1}{\varepsilon}\right)$ by charging the surface of the dielectric opposite to each plates with a charge of opposite sign to that on the plate. Let this surface density be P.

$P=\sigma\left(\frac{\varepsilon-1}{\varepsilon}\right)$ (9)

It is produced by an induced charge shift through the dielectric. This is called polarization, which can be expressed as an electric moment per unit volume.

The dielectric displacement is defined as-

$D = 4\pi\sigma$ (10)

from eq.(7)

$D = \varepsilon E$ (11)

Using eq.(7), (9), (10), (11), we get-

$D = E + 4\pi P$

$\varepsilon E = E + 4\pi P$

$(\varepsilon-1) = \frac{1}{E} 4\pi P$ (12)

$\varepsilon = 1 + \frac{4\pi P}{E}$ (13)

This equation gives relation between applied electric field, polarization and permittivity.

The charge +PA on one surface of the dielectric material and -PA on the opposite surface, resulting from a displacement of charge throughout the dielectric, gives an electric moment (PA)(r), where 'r' being the thickness.

M = PA r

Let A r = V, volume of the slab,

M = P V (14)

Thus polarization P can be defined as electric moment per unit volume. The polarized slab behaves like an assembly of electric dipoles parallel to one another. And the total polarization is the sum of the polarization resulting from each mechanism. The polarization is time dependent in a time dependent applied field [7].

V. CONCLUSION

Dielectric relaxation is the momentary delay (or lag) in the dielectric constant of a material. This is usually caused by the delay in molecular polarization with respect to a changing electric field in a dielectric medium (e.g. inside capacitors or between two large conducting surfaces). Dielectric relaxation in changing electric fields could be considered analogous to hysteresis in changing magnetic fields (for inductors or transformers).

Dielectric relaxation refers to the relaxation response of a dielectric medium to an external electric field of microwave frequencies. This relaxation is often described in terms of permittivity as a function of frequency, which can, for ideal systems, be described by the Debye equation.

Dielectric relaxation occurs when a dielectric material is polarized by the externally applied alternating field. The decay in polarization is observed on removal of the field. The decay in polarization occurs due to orientation of electric dipoles in an electric field. This depends on the internal structure of a molecule and on molecular arrangement.

Several theories are available in the literature regarding the relaxation mechanism and its relation to the molecular structure. These may be broadly classified into two groups.

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Renewable Energy Technology and Sustainable Development

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ABSTRACT

Renewable energy sources (RES) provide 17 percent of the world's primary energy. Most renewable energy is provided by traditional biomass (9 percent) and large hydropower (6 percent). The so-called "new" renewable. An ever growing population means an ever growing requirement for energy. Nowadays, enormity of energy cannot be denied. It is essential in every walk of life. Energy sources can be broadly classified as renewable and non renewable. Knowing the dreadful fact that nonrenewable sources will eventually deplete, the importance of renewable sources cannot be underestimated. The most important aspect while utilizing them is their impact on the environment. This paper briefly presents the importance of renewable sources of energy owing to the backdrop of fossil fuel dilemma. Major emphasis is placed on the use of alternative energy technologies. Some applications of renewable sources and future of energy is also discussed.

Keywords: Energy, Renewable, Non renewable, Alternative energy technology, Sustainable Development

I. INTRODUCTION

Energy is that the fundamental input needed to sustain the economic process and for provision of basic necessities of life to the whole population. Energy can be a potent tool within the battle against abject poorness, particularly within the developing countries. It's the amount and pattern of consumption of energy from number of varied sources in any country which is a reflection of business development and living standards.

Man needs energy and utilized it at an expanding rate for his sustenance and prosperity as far back as a couple of million years ago. Primitive man required energy fundamentally for food. He derived this by eating plants or creatures which he chased. Later he found fire and his energy needs expanded as he made utilization of wood and different biomass to supply the energy requirements for cooking and additionally to keep him warm. With the progression of time, man began to develop land for farming. He added another dimension to the utilization of energy by taming and preparing creatures to work for him. With increasing demand for energy, man started to utilize the air for cruising ships and for driving windmills, and the power of falling water to turn waterwheels. Till this time, it would not be wrong to state that the sun was providing all the energy needs of man either directly or indirectly and that man was utilizing just sustainable wellsprings of energy.

The Industrial Revolution which began with the discovery of the steam engine (AD 1700) brought about a great many changes. For the first time, man began to use a new source of energy, viz. coal in large quantities. A little internal combustion engine was invented (AD 1870) and the other fossil fuels, oil and natural gas began to be used extensively. The fossil fuel era of using nonrenewable sources had begun and energy was now available in a concentrated form. The invention of heat engines and the use of fossil fuels made energy portable and introduced the much needed flexibility in man's movement. For the first time, man could get the power of a machine where he required it and was not restricted to a specific site like a fast-running stream for running a waterwheel or a windy hill for operating a windmill. This flexibility was enhanced with the discovery of electricity and the development 2 of central power generating stations using either fossil fuels or water power. A new source of energy—nuclear energy —came on the scene after the Second World War.

The first large nuclear power station was commissioned about 30 years ago, and already, nuclear energy is providing a small but significant amount of the energy requirements of many countries. The primary objective of the development discourse across the world has been to bring about an improvement in the quality of growth and correspondingly in the life of the masses. If one needs to measure the progress of any country, then it needs to look at factors like employment growth, life expectancy, agriculture development and along with it should also demonstrate decline in poverty, infant mortality rate etc. A combination of these factors leads to improvement in growth and quality of life of people. With the objective of increasing economic growth as well as human development, factors such education, transport, water, communication, availability of adequate energy infrastructure etc. play a critical role. Amongst these issues, availability of adequate energy and its management are most important for the faster development of a country’s economy. But, what is imperative to understand is that what sources of energy are most needed at the present time and are they sufficient to meet future demand? What is their environmental impact? In order to ensure energy for the future, it is extremely important to start preserving energy from now on, use various energy conservation measures and develop alternative sources of energy,

II. RENEWABLE ENERGY

Renewable sources of energy are increasingly becoming a larger part of the overall energy mix across the world, especially in the power sector and in countries where specific measures have been taken promote their usage. Growth rate in double digits have been observed in the past decade for some of renewable energy technologies and their growth is poised to move onto a higher trajectory provided necessary support in the form of favorable policy measures are put in place. Electricity generation from most sources of renewable energy are growing at a rapid pace while the use of renewable energy for heating purposes is comparatively growing slowly and still remains underexploited. After observing a period of rapid expansion, the use of biofuels has slowed down in recent years mainly on account of adverse weather conditions that have reduced harvests and increased the prices of livestock as well as the issue of sustainability. Investment in power generation through renewable sources has been rising consistently except in the year 2012. This is a reflection, partly, of the falling costs per unit along with the growing complexity of prospects of renewable. Europe has recently seen a swift growth of renewable power generation, especially solar and wind, which has been driven by the obligations under the European Union’s Renewable Energy Directive and targets set by various national governments. However, lower growth rates of demand of power as well as tough economic conditions raises uncertainty about future investment in renewable power and policymakers across the EU countries are slowly beginning to raise doubts about the issue of affordability of certain types of renewable power. These concerns mainly relate to higher than expected rates of photovoltaic systems. Some difficulties relating to integration of renewable sources in conventional electricity systems are also being faced by some countries in EU.

III. RESULTS AND DISCUSSION

Importance of Renewable Energy

The most significant feature of renewable energy is its plentiful supply. It is infinite. Renewable energy sources are hygienic sources of energy that have a much lesser negative environmental impact than conventional fossil energy technologies. Most renewable energy investments are spent on materials and personnel to build and maintain the facilities, rather than on costly energy imports. With technological advancements in mass communication, people have now become aware of the demerits of burning 17 fossil fuels. Renewable energy is the need of the hour. Its clean and sustainable nature has compelled the human beings to think seriously about it. Scientists and Engineers, around the world, are continuously working and researching in this domain. They are finding new ways to use these sources of energy effectively. Global warming is a huge hazard which is being caused by burning of coal, oil and natural gas. It is very harmful for the planet and the living beings on it. Moreover, fossil fuels are a cause of many unfortunate mishaps in the past as described before. To put an end to this apocalypse; we must resort to renewable sources. This is because they are cleaner and do not produce poisonous harmful gases. Moreover, fossil fuels are finite. They will certainly end one day. Therefore, before the crucial stage comes up, experts of energy sectors must maintain a positive attitude in this regard and should try their level best to replace fossils fuels with renewable energy sources as the main sources of generating electricity. Renewable energy is dependable and copious and will potentially be very cheap, once this technology and its present infrastructure are enhanced. The major sources of renewable energy include solar, wind, biomass, geothermal, hydropower and tidal energy. Non renewable energy, such as coal, natural gas and oil, require costly explorations and potentially dangerous mining and drilling, and they will become more expensive as supplies diminish and energy demand increases. Renewable energy produces only small levels of carbon emissions and therefore, helps battle climate change caused by fossil fuel burning.

Renewable energy sector is comparatively new in most countries and this sector can attract a lot of companies to invest in it. This can create a pool of new jobs for the unemployed. Therefore, renewable energy can play a very significant role in bringing the unemployment scale down in many countries, especially the developing ones. This, in turn, will make a substantial difference to their economies. Renewable energy can make the electricity prices stable. It is because their cost is dependent only on the initial invested capital and is free of the fluctuating costs of coal, oil and natural gas.

The Future of Energy

Proper use of energy is very vital in catering the need for energy demand. Experts all over the world are of the opinion to utilize renewable energy sources for power generation. Gone are the days when fuel prices were low and power companies resorted to fossil fuels for meeting energy demand. The sustainable nature of wind, hydropower, geothermal, solar and biomass highly encourage the energy supply companies to utilize them. Moreover, people can setup small solar panels over their homes to tackle their own load demands. These 18 sources of energy are not hazardous to the environment since they do not require any sort of mining and drilling and produce nearly no pollution. Most importantly, they are much more economical than fossil fuels and do not cause adverse mishaps. Conservation of energy and utilizing renewable sources is the ultimate destination of energy. Many vehicles run on gasoline (which is a fossil fuel). Gasoline will deplete one day and vehicle industry must resort to some new sort of energy such as hybrid systems to continue its business.

Energy can be conserved in many ways. Many a times, we take for granted the lights being switched on. When not in the room, the lights do not need to be switched on. This practice will certainly save lots of cash on electricity bill. Incandescent lamps can be replaced with Compact Fluorescent Lamps (CFLs). They consume very less power and give much more light using the same amount of current. This not only saves money, but it also conserves an energy source for others. Air conditioning and heating are responsible for a large percentage of electricity bills in various countries. Consider adjusting the thermostat of air conditioner and heater by a few degrees, but while still maintaining soothe. For example, if the heater is typically set to 71 degree Fahrenheit in the peak winter, set it to, for instance, 69 and if the air conditioner is at 73 in the peak summer, set it to, for instance, 75. Just a couple of degrees can make a considerable indentation in the amount of energy consumed while this also reduces the electricity bill.

Renewable energy sources as a factor of sustainable development

Energy stability and efficiency are crucial for successful functioning of modern economies. Renewable energy sources (solar energy, wind energy, water flow energy, biomass, etc.) are gaining in importance with a clear tendency to increase their share in total energy production and consumption. Solar energy is one of the most important renewable energy sources. Starting from the total annual needs for electricity at the level of the entire planet, the solar energy that reaches the Earth in one year is about 10,000 times higher than the total planetary energy needs. This fact clearly indicates the potential of solar energy and possibilities of satisfying the energy needs of humanity. Approximately 1kW/m2 of insolation can be obtained on the Earth's surface under optimal conditions. The values of insolation (the length of solar radiation during the day) depend on a number of factors: location, season, climate, etc. The duration of isolation and the inflow of solar energy are not proportional, because part of solar energy is lost through the passage of the sun's rays through the atmosphere and the absorption of oxygen, carbon dioxide and ozone. Also, radiation energy itself is dissipated by passing through the atmosphere. The use of solar energy, as an energy source, implies the use of solar energy when it reaches the Earth. This energy represents a huge energy potential. Namely, if we compare the energy of the Sun when it reaches the Earth with the total coal reserves in the world, it is about 170 times higher. Due to the great potential of solar energy, it is necessary to consider the techniques of its use. The use of solar energy implies the following direct principles of using solar energy passive techniques, solar collectors (conversion of solar energy into heat), photovoltaic cells (direct conversion of solar energy into electricity) and focusing solar energy (for use in large power plants).

Passive techniques are the simplest way to use solar energy. A common example is the use of solar energy to heat a greenhouse space. The passive technique of using solar energy means that the process of using solar energy is based on spontaneous natural processes. There is no electricity investment and this technology is 100% environmentally friendly. With such a passive technique, combined with active solar technology, heating systems ideal for residential areas can be constructed. Solar collectors absorb solar energy and convert solar energy into heat. These systems contribute to the preservation of the environment and achieve significant energy savings. The degree of conversion of solar energy into heat is extremely high (and ranges up to 70%). Extremely large economic savings can be achieved by combining water and air heating through solar collectors. The smallest collectors are about 2m2 in size. They are enough to heat water for the average household. It is common for solar energy absorbed in this way to be combined with some other energy source to ensure the availability of hot water throughout the year.

It could be noticed that one of the most economical ways of using solar energy for water heating is achieved through solar collectors, primarily in households. Photovoltaic (solar) cells enable the direct conversion of sunlight (energy) into electricity. These cells function on the principle of the photoelectric effect. Photovoltaic cells are very thin plates of silicon crystals with an admixture of arsenic. Exposed to sunlight, they act as a semiconductor junction. The solar cell industry is one of the fastest growing industries in the modern world. However, the disadvantage is the small degree of the use of solar energy, only about 15%. This industry was developed in Japan and then in other parts of the world. In order to achieve a significant percentage of the use of solar energy in the production of electricity, at least two more decades of technical and technological progress and the improvement of photovoltaic cells are necessary. Solar energy is focused with the help of a mirror or lens. Otherwise, it is used to drive large generators. This way of using solar energy requires a large space for the power plant. For that reason, they are most often built in deserts, where the sun's radiation is the largest and most pronounced

IV. CONCLUSION

Alternative energy sources are here to stay. They have become an integral part of the energy portfolio. The objective in using renewable energy sources is to reduce the pessimistic environmental effects associated with non renewable energy sources such as coal, oil and natural gas. Choosing to use a renewable energy source will not only translate into cost savings over the long-term, but will also help protect the environment from the risks of fossil fuel emissions. Energy conservation awareness campaigns must be initiated at government level to make people aware of the importance of conserving energy. Moreover, power companies should gradually resort to the use of renewable resources as they are profuse and will never deplete. Social media can play a key role in this by educating people about energy sources and their utilization. Colleges and universities should teach a compulsory subject on energy conservation and utilization. Given that these steps are followed accurately, the time is not far when the entire world will be reliant on renewable sources for power production because this is the definitive future of energy.

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Hot Interstellar Medium in Nearby Early Type Galaxy NGC 3585

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ABSTRACT

This paper presents the x-ray study of nearby early type galaxy NGC 3585. We present results based on the systematic analysis of Chandra archive data on the X-ray bright NCC 3585. Tricolour map, surface brightness profile were genrated to see distribution of hot gas among the galaxy. By fitting spectum to the diffuse component of hot gas and descrete point sources present in D25 region of this galaxy, we have finded x-ray luminosity of diffuse gas and luminosity of point sources.

Keyword: X-ray Analysis, NGC 3585.

I. INTRODUCTION

Early-type galaxies (ellipticals and lenticulars) had long been thought as the simplest stellar systems with considerable structural regularity with a deficient of ISM. Early Type Galaxies were simplest stellar systems with no trace of substructures, interstellar medium (gas as well as dust); and exhibiting characteristic surface brightness profiles of systematically decreasing luminosity from the bright nucleus till the infinite edge. X-ray emission in early-type galaxies partly originate from the hot interstellar medium (ISM) which is distributed throughout the galaxy, and partly from the population of point-like sources, known as low mass X-ray binaries (LMXBs) (Trienchieri & Fabbiano1985). The superb angular resolution of the Chandra X-ray telescope for the first time has made possible to spatially resolve the point sources in extragalactic environment. As hot gas distribution within a galaxy find gravitational potential of the baryonic particle, therefore, X-ray emission maps derived for external galaxies provides a powerful tool in investigating structure of the galaxy. Further, morphology and extent of the hot gas in early-type galaxies provide important input on the nature of the hot gas, metal enrichment history of the ISM of the target galaxy. In this paper we present morphology and spectral properties of hot gas and point-like sources in NGC 3585 early-type galaxy. We present results based on the systematic analysis of Chandra archive data on the X-ray bright galaxy with an objective to investigate x-ray properties. This is an elliptical galaxy located in the Hydra constellation, with apparent magnitude is 9.9. It is classified as a E6 galaxy [1].

Target Galaxy	NGC 3585
R. A.	11h13m17.1s
Dec	-26 d45m17s
Morphology	E6
Radial Velocity	1434 km/s
Redshift	0.0048
Major Angular Size	6.61 arcmin
Minor Angular Size	3.27 arcmin
Position Angle	1040

Table: Global Parameters of target galaxy

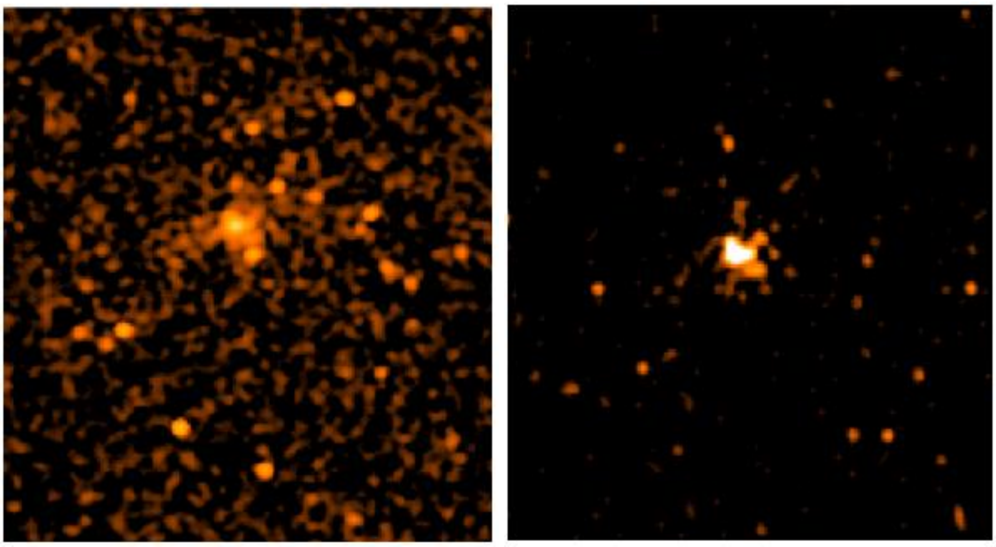

Figure 1: (a) 0.5-7.0 keV raw Chandra ACIS-S image of NGC 3585, overlaid on which are the 29 point sources detected within the chip S3. (b) ACIS-S3 exposure corrected, background subtracted 0.5-3.0 keV Chandra image of NGC 3585.

II. OBSERVATIONS AND DATA PREPARATION

X-ray Data Analysis:. NGC 3585 was observed with the back-illuminated Chandra ACIS-S3 detector on 12 March 2009 for a total exposure of 60 ks (ObsID 9506). We acquired the level-2 event file on this target from the archive of Chandra observatory. The data were reprocessed in a uniform manner using the standard tasks available within the Chandra Interactive Analysis of Observations (CIAO) v.4.6.1.1 and the corresponding calibration files CALBD v.4.6.1 provided by the Chandra X-ray Centre (CXC). Periods of high background were verified by plotting its 0.3-10 keV light curve extracted from the chip and were filtered out using the 3σ clipping. After removal of the background flares, the clean data had a net exposure of 59.41 ks. Background subtracted, exposure corrected, adaptively smoothed 0.3-7 keV Chandra emission map of NGC 3585 is shown in Fig:1. X-ray background component was adequately modeled using the “blank-sky” data sets. The point source detection was performed on CCD ID 7 using CIAO wavdetect task. This enabled us to detect a point sources within S3 chip . We generated exposure corrected, background subtracted 0.5 - 3.0 keV energy band image using dmmerge task available within CIAO 4.6.

Tricolour Map:

X-ray emission originating from different sources, we extracted X-ray photons in three different energy bands namely, soft (0.5 - 1.0 keV), medium (1.0 – 2.0 keV) and hard (2.0 - 7.0 keV) band. These counts in three different energy bands were then used to obtain the tri-color maps of target galaxies. Adaptively smoothed tricolor images representing diffuse X-ray emission thus derived after removal of point sources for target galaxies are shown in Figure 2. The color coding in these images is red color indicates soft component (0.5 - 1.0 keV) of X-ray emission, green color mid band (1.0 - 2.0 keV), while blue color represents the hard component (2.0 - 7.0 keV) of X-ray emission. A careful look this tricolour map reveals that the distribution of the X-ray emitting gas in this galaxy is not symmetric about centre of the galaxies but shows a wide range of morphological features like filaments, depressions in the surface brightness, etc.

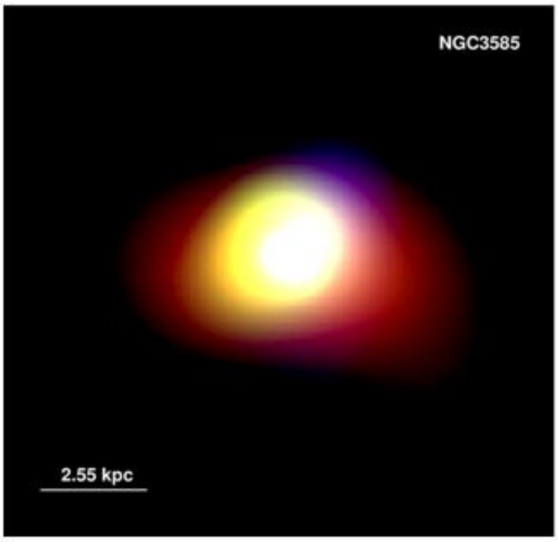

Figure 2: Tricolour image of the NGC 3585, , red color represents soft component (0.5 - 1.0 keV), green color represents the mid band (1.0 - 2.0 keV), while the blue color represents the harder component (2.0 - 7.0 keV) of the X-ray emission.

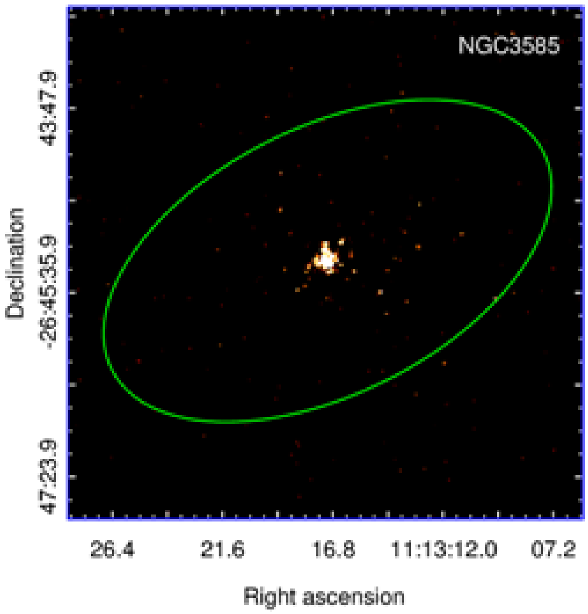

Figure 3: Csmoothed Chandra images in (0.5 - 3.0 keV) showing the morphology of diffuse hot gas distribution within NGC 3585, ellipse on images indicate optical D $_{25}$ region.

Azimuthally Averaged Surface Brightness Profile:

Azimuthally averaged surface brightness profile (red color 0–360°) of the extended emission from NGC 3585 in the energy range (0.3–3.0 keV) was derived by extracting counts from different concentric annuli up to a radius of 30 arcsec and is shown in Figure. After detecting the sources and finding their positions, we extracted X-ray counts from circular regions centered on individual sources along with their local backgrounds. 1-D beta model has been widely used in the literature to investigate surface brightness distribution of hot gas in galaxies[5]. This model was primarily developed for investigating hot gas properties in galaxy clusters, however, has also been used in literature for describing the hot gas properties in individual galaxies[6][7]. The azimuthally averaged surface brightness profile appears remarkably smooth and therefore the 1d-beta model was fitted to this profile[8]:

$$\Sigma(r) = \Sigma_0 \left[1 + \left(\frac{r}{r_c}\right)^2\right]^{-3\beta+0.5}$$

where r_c is the core radius and beta is slop parameter. The Best fitted parameters of the azimuthally average surface brightness profile are rc = 0.6300±0.099 arcsec and src.beta = 0.44±0.013. The resultant surface brightness profiles are shown in Figure 4 and show noticeable azimuthal variations.

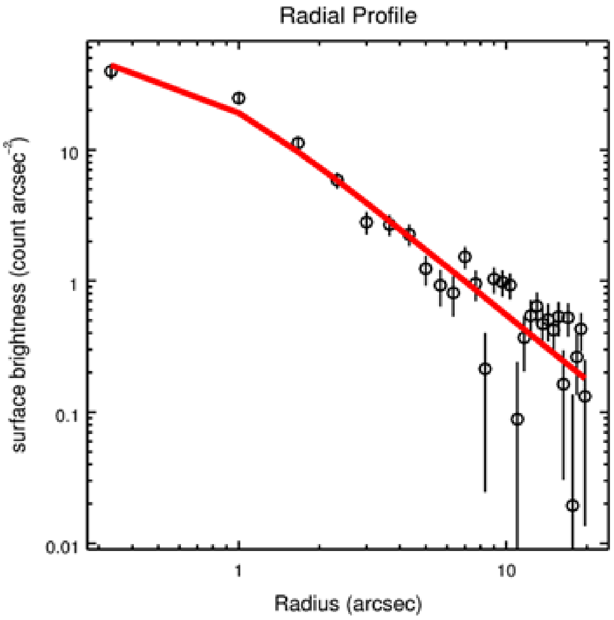

Figure 4: Azimuthally averaged, clean background subtracted 0.3–3.0 keV surface brightness profile of NGC 3585. The best-fitting β model is shown as a solid line.

Spectra of Diffuse Gas and Point Sources :

A significant amount of variation, particularly in the central region, was evident in the surface brightness distribution of the NGC 3585 (Fig. 4). With an objective to examine their relevance with temperature variation, we performed spectral analysis of the X-ray photons extracted from target galaxy. For this, 0.5-7.0 keV X-ray spectra were extracted from target galaxy using the CIAO task specextract and were grouped such as to get at least 20 counts in each bin. During this study we fixed the hydrogen column density at the Galactic value (NH= 2.46 × 1020cm−2) and the redshift at z = 0.0048. The metal abundance and temperature were allowed to vary during the fit. By fitting spectrum we have finded contribution of luminocity diffuse gas and descreate point sources within D_{25} region of the galaxy. Best fitted spectrum of diffuse hot gas and and point sources present in D25 region are as shown in Figure 5.

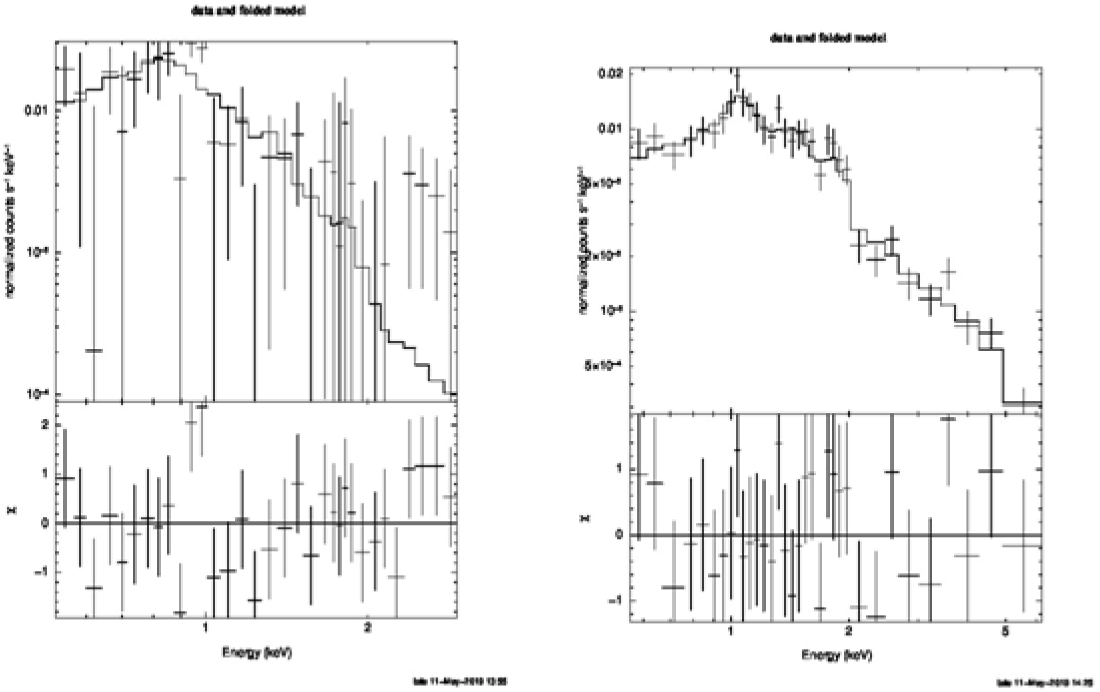

Figure 5: Spectra of diffuse gas (left) within D_{25} region and spectra of point sources detected in D_{25} region(right).

III. RESULT

We presented results obtained from the systematic analysis of a total of 59.41 ks of Chandra observations of a low-redshift (z= 0.0048) galaxy NGC 3585. X-ray analysis of this galaxy concludes that , X-ray Luminosity of diffuse gas in the D_{25} region of NGC3585 galaxy is found to be 2.70×10^{39} ergs/sec and is found to contribute about 29%, while the luminosity of point sources in D_{25} region is found to be 6.76×10^{39} ergs/sec with a contribution of 71%. Temperature of the diffuse gas is 0.26 ± 0.11 keV. We have detected 29 discrete point sources within D_{25} region of this1 galaxy, whose cumulative spectrum was well constrained by a power law component with photon index 1.35±0.15. Spatially resolved spectral analysis of the hot gas along outflows exhibit a gradient in the temperature. Similar gradient was also noticed in the measured values of metallicity, indicating that the gas in the halo is not yet enriched. The diffuse gas surface brightness profile of NGC 3585 was well fitted by the standard beta model with the core radius equal to 0.63 arcsec and the slope parameter equal to $\beta\sim0.44$.

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Metal-Oxide Nano Structures and Their Photo Electrochemical Applications - A Review

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ABSTRACT

The majority of modern commercial optoelectronics are built on the basis of traditional inorganic semiconductors. Over the last couple of decades, however a lots of progress has been made in producing devices based on electrochemical materials, which for many applications, may become less expensive alternatives to inorganic counterparts.

Various metal oxide compounds have shown to be of high interest and utility in electronic applications. The current development prospects of this materials are however mostly limited in their scope to relatively low performance areas. In this way the desirable properties can be synergistically exploited to overcome their limitations when used separately. More over, as an interesting facet, organic molecules can induce transparency to usually opaque in organic materials by reducing the aggregation between them. Various metal oxides nanoparticles prepared using solution process shows the high performance in electrochemical devices as like working or counter electrodes in photochemical cells, sensors for various oxidizing and reducing gases, electrochemical super capacitors and water splitting applications.

I. INTRODUCTION

The development of metal oxide nanostructures in nanotechnology has enabled exciting opportunities to designed materials with desired electronic, ionic, photonic and Mechanical properties. This development has also contributed to the advance in energy storage, sensing and photo catalytic applications. The electrochemical capacitor is sustainable high energy storage, environment friendly, inexpensive, long cycle life, high power and energy density and more reliable safety features. The explosive, toxic and hazardous gases are released in environment due to pollution by industrial development and population growth. Therefore gas sensors are the important part for environment and human being safety. Hydrogen production from water using catalyst and light energy sources is an ideal future fuel source and urgent subject for our daily life. Various materials are used for these applications but metal oxide nano structures plays important role. Metal oxide Nano structures having special properties such as available in many structures, variety in size high surface area, high conductivity,anti-flammable,high thermal stability, photo catalytic, transparent and long cycle life. Nano metal oxides are available in ultra high purity, transparent, coated and dispersed form.

II. SYNTHESIS METHODS

Micro emulsion method

Based on oil in water microemulsion method which is developed for the synthesis of inorganic nanoparticles at ambient conditions. This method involves organometallic precursors dissolved in manometer scale oil droplets of oil in water micro emulsion in which addition of oxidizing or reducing agents forms metal oxide nanoparticles.

Hydro thermal method

Hydro thermal synthesis involves synthesis of crystal metal oxide nanoparticles under high temperature and high pressure water conditions from substances which are insoluble at ordinary temperature and pressure. Hydrogen synthesis generally carried out below 300 degree Celsius because the critical temperature and pressure of water are 374 degree Celsius and 22.1 MPa.

Vapour evaporation method

Crystalline metal oxide nanostructures synthesized in high yields on the surface of SiO2/Si subtrate by vapour evaporation method. In this method, initially materials in a covered alumina crucible are thermally evaporated under high vacuum or a low pressure of ambient air.

Biosynthesis method

Biosynthesis method is reliable sustainable and eco friendly for synthesizing World range of metal oxide nano particles without any destructive effects associated with traditional methods. Nano particles are prepared from natural extracts contains biological components as phytochemicals.

Spray pyrolysis method

Spray pyrolysis consist of the chemical dissociation or evaporation of droplets containing a solute of the desired nanomaterials. The droplets gets carried and the particles forms inside the droplets which are in liquid phase. Solute containing droplets are injected into hot zone of furnace to obtain nanoparticles. The size of metal oxide nanoparticles can be controlled by regulating the vapour pressure of gases and temperature of furnace.

III. APPLICATIONS

Electrochemical sensors

A sensor is a device which produces a noticeable response to change in physical and chemical conditions and that receives signal or stimulates and responds and electric signal. Electrochemical sensor is advanced device due to its various applications such as environmental monitoring, medical diagnosis, public security, industrial emission monitoring etc.

Metal oxide nanostructures are useful in electrochemical sensors due to its unique properties like high sensitivity and selectivity, fast response and recovery time, lower operating temperature. Metal oxide nanostructures seems to be more advantageous due to their high surface area,surface energy, enhenced electron transfer and strong adsorption ability.

Electrochemical supercapacitors

Development of sustainable energy resource is essential for living species not only for completing basic needs but also for availing future needs. The growing energy crisis in recent decades due to the rising cost of fossil fuels, depletion of fossil fuels is serious and has adverse impact on issues like environmental pollution and global warming. Electrochemical super capacitors which acts as bridging function for the energy/power between batteries and fuel cells and high energy-power storage capacity. Use of metal oxide nano particles in electrochemical super capacitors having high energy storage capacity and long cycle life and proved their effectiveness.

Electrochemical water splitting

Hydrogen is considered as green fuel with a high density of energy. In nature hydrogen is not found in a free state and present in compound form for example water H2O.To Produce hydrogen from water water, it requires and efficient catalyst. Metal oxide Nano particle materials having high specific surface area, fast charge transport, rich catalytic sites and huge ion transport is found to be efficient electrochemical water splitting.

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Evaluation of Shielding Properties of Nickel Oxide (NiO_2) at Energy 122keV to 1330 KeV

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ABSTRACT

The most commonly employed significant parameters in the current study for explaining both the penetrating ability of various radiations and the penetration through particular objects or materials are half value layer, tenth value layer, and mean free path. The thickness of a shield or absorber that reduces the radiation level by a factor of one-half and one-tenth of the starting level, respectively, is determined by the half value layers (HVL) and tenth value layers (TVL). In shielding design, the ideas of HVL and TVL are frequently applied. For Nickel oxide in the energy range from 122 keV to 1330 keV, the values of the linear attenuation coefficient, mean free path (MfP), half value layer (HVL), and tenth value layer (TVL) were calculated in the current experiment.

I. INTRODUCTION

Recent years have seen a rise in the importance of studying how radiation interacts with various materials, particularly for medical uses the growing use of radioactive isotopes in a broad range of fields. Numerous scientific, agricultural, engineering, shielding, and medicinal applications can benefit greatly from information on the attenuation of gamma rays with materials (Singh et al., 2006). The extremely useful linear attenuation coefficient good for describing the spread and penetration of gamma rays in the medium they travel through. This depends mostly on the photon energy, the composition of the chosen material and medium density (Bashter, 1997).

Gamma radiation photon contact results input a variety of processes in the material, including coherent, incoherent, and photoelectric effects. It is based on the processes of pair creation and dispersion power of a photon (Berger and Hubbell, 1987). The partial photon interaction processes' linear attenuation coefficient values, such as those for the photoelectric effect and Compton scattering, pair production and all of these are offered in the form of Berger and Hubbell's software package XCOM (1987). It has been noted that the density and incident photon energy both influence the value of the linear attenuation coefficient practically in every field. From both theoretical and experimental standpoint, the study of how gamma radiation interacts with particular oxide samples is quite interesting. In the energy range of 122-1330 keV, the linear attenuation coefficient of the nickel oxide is computed. Since total radiation attenuation is not achievable, it is important to understand how radiation shields function.

Tenth-value layer, or half-value layer, For gamma-ray shielding, and mean free path (mfp) are crucial theoretical parameters that are measured (Gundogdu et al., 2016). The TVL denotes an absorber's thickness that will reduce gamma radiation to a tenth of its initial intensity, whereas the HVL represents an absorber's thickness that will reduce gamma radiation to half (Akkurt et al., 2010). For the energy range of 122 keV to 1330 keV, the HVL, TVL, and mfp values for oxides are computed in the current experiment. To understand how well certain radiations can penetrate a certain material, HVL and TVL values are highly helpful parameters.

II. THEORY

Mass attenuation coefficient:

We are researching here some theoretical parameters of some oxide that have been used to determine the mass attenuation coefficient μm in the present work and other similar parameters which are based on it. The relationship is generally referred to as the Beer-Lambert law as a parallel beam of the measured intensity I of the transmitted mono-energetic X-ray or photons passing through matter relevant to the incident intensity I_0.

$$I = I_0 e^{-\mu_m X} \qquad (1)$$

Where I_0 and I are incident and transmitted photon intensities respectively, γ-photons X is mass per unit area (g/cm^2), μ_m is mass attenuation coefficient (cm^2/g) given by the following equation for a compound or mixture of elements (Jackson D. F. and Hawkes D.J., 1981; Hubbell and Seltzer, 1995). By using the Eq. (1) we obtain the following equations for the linear attenuation coefficient;

$$\mu = 1/t \ln (I_0/I) \qquad (2)$$

The sample's mass attenuation coefficient is calculated by means of the following equation:

Half value layer (HVL) and Tenth value layer (TVL) :

The HVL and TVL thickness values are determined using Eq.11 and Eq.12, respectively. In the rapid determination of shielding parameters, the HVL and TVL are very significant factors.

$$HVL = X_h = \ln 2/\mu, \qquad (11)$$

$$TVL = X_t = \ln 10/\mu. \qquad (12)$$

Mean free path:

The mean free path is the mean distance at which a single particle moves before interacting with material through the medium of a given sample and is determined by thefollowing equation.

$$X_m = 1/\mu. \qquad (13)$$

III. EXPERIMENTAL

Radioactive sources having energies 122, 279, 320, 364, 637, 1115, 1408 keV were used for irradiation on nickel oxide. The gamma ray photons were detected using NaI (Tl) detector with resolution of 0.101785 at 662 keV. Signals from the detector were enlarged and analyzed with 8K MCA. The effectiveness of NaI (Tl) detector is higher at low source energy (Mohamed Abd-elzaher).

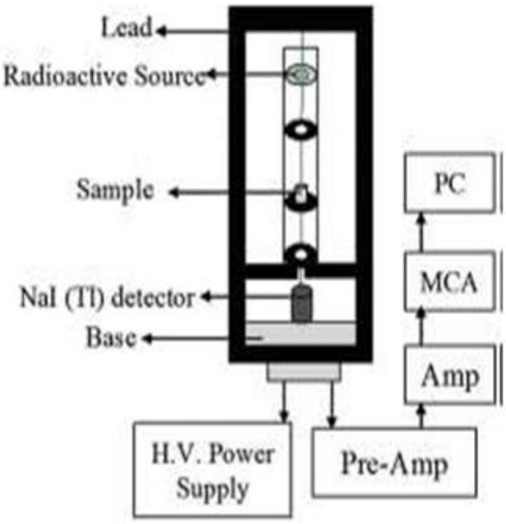

Figure 1: Narrow-beam Good Geometry Set-up

The uncertainty in determined experiment is found to be 1-4 % (Mustafa Racep Kacal). To use nickel oxide as radiation target we use KBr press machine to prepare pellets having same thickness (0.13 g/cm2) and then filled in a cylindrical plastic container having the same diameter as that of sample pellets. A travelling microscope is used to determine the thickness of the prepared pellets. We made some experiment with the empty sample container and found that attenuation of photons of the empty containers were negligible. The experimental part is discussed. In this we measured linear attenuation coefficient, half value layer, tenth value layer were calculated from formulas.

Sr. No.	Energy range keV	μ Expt.	μ Theo.	HVL Expt.	HVL Theo.	TVL Expt.	TVL Theo.	MfPExpt.	Mfp Theo.
1.	122	1.7875	1.8009	0.3877	0.3848	1.2882	1.2786	0.5594	0.5553
2.	356	0.7003	0.6870	0.9896	1.0087	3.2881	3.3517	1.4241	1.4556
3.	511	0.5536	0.5736	1.2518	1.2082	4.1593	4.0143	1.8064	1.7434
4.	662	0.5202	0.5069	1.3322	1.3671	4.4264	4.5425	1.9223	1.9728
5.	840	0.4238	0.4468	1.6352	1.5511	5.4332	5.1535	2.3596	2.2381
6.	1170	0.4135	0.4335	1.6759	1.5986	5.5686	5.3116	2.4154	2.3068
7.	1275	0.3935	0.3801	1.7611	1.8232	5.8516	6.0579	2.5413	2.6309
8.	1330	0.3401	0.3201	2.0376	2.1649	6.7704	7.1934	2.9404	3.1241

IV. RESULT AND DISCUSSION

In the present work, the values of linear attenuation coefficient μ of investigated nickel oxides. The variation between experimental and theoretical values of μ (cm^{-1}) for all sample studied at 122, 360, 511, 662, 840, 1170, 1275- and 1330-keV photon energies are shown in Table 1, and those for all oxide samples are plotted in Figure 2. It can be observed from the figure and table that m decreases with increasing photon energy. It is observed that he experimental values of m agree with the theoretical values calculated using the XCOM program. r The half-value layers, tenth-value layers and mean free paths of nickel oxide sample materials for different radiation energies levels from 122KeV to 1330KeV have been obtained and are presented in Table 1. The mean free path, half value layer and tenth value layer of oxide increases with increases in energy of photon.

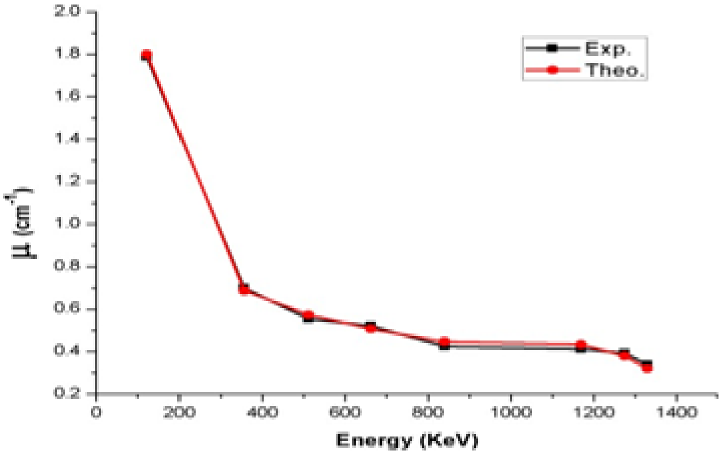

Fig.2 linear attenuation coefficient (μ)

V. CONCLUSION

The present experimental study was carried out to obtain information on linear attenuation coefficient, μ and related parameters such as half value layer (HVL), tenth value layer (TVL) and mean free path (mfp) for the selected nickel oxide samples. It has been found that μ is an extremely useful and sensitive physical quantity for the determination of these parameters for nickel oxide samples which is emitted by the radioisotopes 60Co, 57Co, 133Ba, 54Mn, 22Na, and 137Cs. For the interaction of photons with matter the values of that depend on the physical and chemical environments of the samples. It is found that from table and figure these values decrease with increasing photon energies. From the study it is clear that it depends totally on the number and nature of atoms. In the present work, it has been observed that the data on linear attenuation coefficient (μ) and other parameters are HVL, TVL and mfp are very useful in industrial, biological, technological, shielding and other applications, solar cell and recently in sensors field.

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Energy Storage Applications of Conducting Polymers and Its Nanocomposite : A Special Emphasis on Supercapacitor

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ABSTRACT

The implication of the conducting polymers (CPs) for various technological applications rapidly increased. Owing to the electrical conductivity approaching those of metallic conductors and other extra ordinary properties makes it distinguishable from the other synthesized materials. Herein, we discussed a broad overview of recent advances in the applications of CPs for the supercapacitor. We first focus the fundamentals of CPs, synthesis techniques and properties. We then highlight the potential supercapacitor applications of CPs, specifically polyaniline, polypyrrole and its nanocomposites with various other materials. Finally, we conclude present study by offering our perspectives on the current challenges and future opportunities for the CPs in supercapacitor applications.

Keywords: Energy Storage Devices, Supercapacitor, Polyaniline, Polypyrrole

I. INTRODUCTION

Recently, improved and advanced technologies have been changes the human life and make it lavish and comfortable. Worldwide, various scientific, academic and industrial groups are devoted their research work to develop new technologies.However, no advanced technology can work without the use of energies such as mechanical, chemical, electrical and thermal etc. As a result, more research into energy harvesting and storage is required for advancement in a variety of fields.Recently, the developed world has faced a number of serious global issues, including insufficient energy production, the availability of portable water, global warming, and so on. [1, 2]. The main cause of these serious issues is the rapidly increasing population and human standard of living. Electrical energy has become a part of everyday life. The production of electrical energy and its long-term reserves is a major and serious impediment to research. Solar energy, wind energy, tidal energy and biomass energy production are considered worrisome options. However, it has many flaws, including a large workforce, a large land business, accuracy, inefficiency, and high costs. As a result, scientists are looking for alternatives to traditional global energy sources such as super capacitors, batteries, fuel cells, and so on. [3, 4].

Recently, energy production from renewable energy sources has been increased rapidly. However, its contribution to global energy production is only low or less than 1%. The energy generated from the power plant is used for various applications such as direct lighting, cooling and communication devices [5]. Saving energy through storage devices in the absence of renewable sources requires a variety of applications. But nowadays there are insufficient efficient storage devices that can store a large number of charges and distribute them as needed. Thus, storage systems such as batteries and electrochemical capacitors (ECs) have taken more interest in saving the energy produced and have played an important role in storing maximum energy [6].

The improvement in the available storage devices with new designs and techniques are not helping to store the energy to the desired level. Therefore, utilizing new advanced technology and with new materials the properties of energy storage devices can be enhanced in desired performance. The selection of the novel materials and techniques can give us the user friendly, light weight, less hazardous, economically cheap and highly efficient energy storage devices. Concerned to the storage of energy in electrochemical form have many superior advantages such as direct energy conversion, portability, absence of moving parts and convenient for mass production. However still it has some critical issues in the developments of electrochemical energy storage devices such as environmental security, light weight, portability, efficiency and low cost etc. [7].

From the last decades the huge efforts are devoted by the many scientists and researchers to develop and enhanced the physical and chemical properties of electrochemical storage system. Electrochemical energy storage systems are broadly classified in three major types based on their properties i.e. (I) batteries, (II) fuel cells and (III) supercapacitors.

Super capacitor is an emerging and become the most promising energy storage device in recent years. Basically, the same principles are used in supercapacitors as conventional capacitors. Supercapacitors are distinguished with high surface area electrodes and thin dielectrics by conventional capacitors to obtain more capacitances. Super capacitors fall between the battery and the capacitor i.e., energy density greater than conventional capacitors and higher energy density than batteries [8].

Supercapacitors have better option for energy storage devices than batteries and fuel cells. However, it faces the challenges such as low energy density, high cost, high self-discharging rate and practical use. Thus, the researchers have scope to enhance the performance, modified electrode structure, achieved the desired thickness of the electrode layer, and porosity. Recently, carbon species (activated carbon, graphene, carbon nanotubes, etc.), metal compounds and conducting polymers are the three main types used as electrode materials for energy storage devices. As well as transition metal oxide (RuO_2, NiO, MnO_2, Co_3O_4, IrO_2 Mn_3O_4,) nanomaterials, carbon nanomaterials, binary, ternary nanocomposites, conducting polymers and conducting polymers nanocomposites and so on. Carbon species-based electrodes with high conductivity and stability usually have excellent cycling stability and high-power density as supercapacitor electrodes. However, carbon-based electrodes for supercapacitors are usually exhibits low energy density because of the limitation in energy storage mechanism. Metal compounds owing to high activity and good intrinsic electrochemical properties in supercapacitors still they have problems like low conductivity, high cost and limited natural abundance [9].

Conducting polymers (CPs), like Poly (3,4- ethylenedioxythiophene) (PEDOT), polypyrrole (Ppy) and polyaniline (PANi), have gained more attention as promising candidates for energy storage devices. CPs has the excellent and unique electronic, optoelectronic, and electrochemical features. As well as CPshave pseudocapacitive features, facile synthesis protocol, good environmental and chemical stability, tunable conductivity, low production cost, etc.Their simple components (C, H, N or S) also indicate the high affordability. CPs based devices show high specific capacitance compared with electrochemical double-layer supercapacitors, and has faster kinetics than most inorganic batteries, which can narrow the gap between inorganic batteries and carbon-based capacitors. The combination of conducting polymers and carbon materials, metal compounds is quite popular with excellent performance taking advantage of each component, shown superior performance in asymmetric supercapacitor [10, 11].

The superiority of supercapacitors decides by cyclic life which depends upon the stability of the electrode materials during charge/discharge cycles. Conducting polymers incorporated with nanomaterials attain higher stability of the electrode material in terms of cyclic life. Also, the decoration of polymer nanocomposites with nanomaterials enhances the electrochemical conductivity, thermal stability and optical and mechanical properties and large surface area to stored charges [12].

The recent development concern to the supercapacitors have been discussed in the following headings using the polyaniline and its nanocomposites as well as polypyrrole and its nanocomposites.

II. SUPERCAPACITOR APPLICATIONS OF CONDUCTING POLYMERS AND ITS NANOCOMPOSITE

Payami, E., et. al; developed ternary nanocomposite consisting of modified GO (GO-Fc), Mn_3O_4 nanoparticles, and polyaniline (PANI) via a simple physically mixing procedure. As synthesized ternary nanocomposite further used as a battery-type supercapacitor and obtained results reveals the promising ability via supercapacitor parameters high power density and cyclic stability [13].Röse, P. et.al; synthesized polyaniline (PANI) nanofibers via chemical oxidative synthesis route using sodium phytate as a plant derived dopant. Electrochemical properties of the synthesized PANI as electrode material for supercapacitors shows the high specific capacitance analyzed by galvanostatic charge/discharge (GCD) curves. The PANI electrode shows the capacitance retention of 67.6% of its initial value, low solution resistance (Rs) value of 281×10^{-1} Ohm and charge transfer resistance value (Rct) of 7.44 Ohm. As well as after 1000 charge discharge cycles retained 95.3% in coulombic efficiency without showing any significant degradation of the material [14].Deshmukh, P. R. et. al; prepared the polyaniline-ruthenium oxide (PANI-RuO_2) nanocomposite thin films by a chemical bath deposition (CBD) method. The PANI–RuO_2 exhibits specific capacitance of 830 Fg^{-1} with 216 $Whkg^{-1}$ and 4.16 $kWkg^{-1}$ specific energy and power respectively [15].Gui, D., et.al; synthesized three polyaniline (PANI)/grapheneoxide (GO) nanocomposite electrode materials by chemical polymerization with the mass ratio (mANI:mGO) 1000:1, 100:1, and 10:1 in ice water, respectively. The electrochemical behavior of the PANI/GO with the mass ratio (mANI:mGO)1000:1 possessed excellent capacitive behavior with a specific capacitance as high as 355.2 F g^{-1}at 0.5 A g^{-1} in 1 mol $L^{-1}H_2SO_4$electrolyte and after 1000 cycles, the specific capacitance of the composite still has 285.8 F g^{-1} [16].Mishra, A. K. et.al; synthesized graphene via hydrogen-induced exfoliation and functionalized to decorate with metal oxide (RuO_2, TiO_2, and Fe_3O_4) nanoparticles and polyaniline using the chemical route. Electrochemical performance of as-prepared nanocomposites is examined using cyclic voltammetry and galvanostatic charge discharge techniques for supercapacitor applications. A maximum specific capacitance of 80, 125, 265, 60, 180, and 375 F/g for HEG, f-HEG, RuO_2-f-HEG, TiO_2-f- HEG, Fe_3O_4-f-HEG, and PANI-f-HEG nanocomposites, respectively, is obtained with 1 M H2SO4 as the electrolyte at the voltage sweep rate of 10 mV/s. The specific capacitance for each nanocomposite sustains up to 85% even at higher voltage sweep rate of 100 mV/s [17].Khalid, M., et.al; using electrodeposition process synthesized composite thin films of polyaniline (PANI) nanofibers and graphene oxide (GO) nanoplatelets for electrochemical capacitors. An electrochemical property of thin films shows capacitance of 662 F g^{-1} at a low current density of 0.025 mA cm^2 with simultaneous high energy density (64.5 Wh kg^{-1}) and high-power density (1159 Wh kg^{-1}) [18].Viswanathan, A., et.al; synthesized reduced graphene oxide, copper oxide and polyaniline (GCP) nanocomposites by facile in-situ single step chemical method by varying the weight percentage of each of the constituent materials. The weight percentage of composites G12%: Cu_2O/CuO 40%: P48% (G12CP) exhibits the maximum specific capacitance of 684.93 Fg^{-1}, specific capacity of 821.91 Cg^{-1}, energy density of 136.98Wh kg^{-1}, and power density of 1315.76Wkg^{-1} at the current density of 0.25 Ag^{-1}. The composite shows the retention of 84% of its initial capacitance up to 5000 cycles at a scan rate of 700mVs^{-1} [19].Devadas, B., et al; Synthesized the polymer@Cdots composites by in situ chemical oxidative polymerization method and studied the specific capacitances. The specific capacitances of composites were 676 and 529 F/g for PPy@ Cdots and PANI@Cdots, respectively, at current density of 1 A/g [20].Ashokkumar, S. P., et al; reported the electrochemical performance of polyaniline (PANI)/copper oxide (CuO) nanocomposites (PCN) for energy storage device applications. The Cyclic Voltametry (CV) result shows the specific capacitance PANI is 294 F/g and 424 F/g for highest concentration PCN2 nanocomposites and GCD reveals the cyclic stability up to 4000 cycles [21].

III. CONCLUSION

In this review paper, we have discussed recent progress in the development of conducting polymers-based supercapacitor.Owing to the excellent properties of the conducting polymers it is employed for the supercapacitor applications. Worldwide various research groups devoted their research to improve the super capacitive performance of the conducting polymers. The mainly polyaniline and polypyrrole were highly studied due to some exceptional qualities compared to the other conducting polymers. We have thoroughly summaries the recent development in the fields of supercapacitor using polyaniline and polypyrrole. Finally, we conclude that the present work may be highly useful for the upcoming researcher.

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Review on Biomedicinal Applications of Ferrite Nanoparticles

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ABSTRACT

Ferrite Nanoparticles exhibit enormous promise in biological applications due to their capacity to accurately regulate the behaviour by an external magnetic field. Ferrite Nanoparticles are remarkable magnetic capabilities make them ideal nanoagents for a variety of applications such as targeted medication administration, MRI, biosensors, magnetic hyperthermia (MHT), magnetic separation and antibacterial agents. The issue is maintaining the high magnetism, which declines when size is reduced to the nanoscale.The manufacture of these ferrite nanoparticles is significant, with the selection of an optimum synthesis procedure playing an important role.As a result, characteristics like as shape, chemical and physical properties, and biocompatibility influence the effectiveness of ferrite nanoparticles in biomedical field. In this review article, we focuse the biological importance of Ferrite Nanoparticles.

Keywords: MRI; superparamagnetism; targeted drug delivery; magnetic hyperthermia; nanoferrites; toxicity.

I. INTRODUCTION

In past few years, nano-science, nanotechnology and nanostructurehave now become common words not only in science but also in daily life. Nano-materials depict, in principle, materials of which a single unit is sized (at least one dimension) between 1-100 nm (10 meter) can be accomplished by the assembly of the constituents of molecules or atoms of few angstroms or 10^{-10} m in size. Nano-materials study takes a materials science based approach to nanotechnology in materials measurement and synthesis which have been developed in support of micro-fabrication research. Materials with arrangement at the 'nanoscale' (1-100 nm) often have unique electronic, optical, mechanical properties, which are expected to be utilized in several different applications, including optical filters, sensors, low-threshold laser, biological detection and controlled drug delivery.

The research on synthesis, exploration and characterization of nanosized (1-100nm) materials were increased in the last few decades for the development of science. The term "nanoscale materials" refers to a group of substances with at least one dimension of fewer than 100 nanometers[1]. Some nanoparticles are found naturally, but artificial nanomaterials are of particular interest. Engineered nanomaterials are resources that have been developed at the molecular (nanometre) level to make use of their small size and unique features that aren't found in their bulk counterparts[2]. Increased relative surface area and novel quantum effects are the two main reasons why materials might have distinct properties at the nanoscale. Nanomaterials have a substantially higher surface area to volume ratio than traditional materials, which can increase chemical reactivity and weaken them[3]. Quantum effects can also play a greater role at the nanoscale in determining material properties and characteristics, resulting in unique optical, electrical, and magnetic features.

As a result, nanomaterials have important applications such as biosensors, medication delivery, energy storage, and so on. On the basis of dimensions, nanomaterials are classifieds into four different classes. The properties of nanomaterials depend on the synthesis procedure. Basically, nanomaterials are synthesized by using two different approaches, one is a top-to-down approach and the second is the bottom-up approach.

Ferrites have established their potential in several applications due to their remarkable electrical and magnetic properties and also in magnetic resonance imaging (MRI). Nanomaterials are interesting because they exhibit unique optical, magnetic, electrical, and other properties at such a small scale. These emergent features have the potential to have huge implications in sectors like electronics, medicine, and others. In comparison to bulk materials, nanoparticles exhibit significantly innovative and improved chemical, physical, magnetic, and other properties[4].

II. INTRODUCTION TO FERRITES

Ferrite exhibits ferrimagnetisms due to the super-exchange interaction between electrons of metal and oxygen ions. The opposite spins in ferrite results in the lowering of magnetization compared to ferromagnetic metals where the spins are parallel. Due to the intrinsic atomic level interaction between oxygen and metal ions, ferrite has higher resistivity compared to ferromagnetic metals. This enables the ferrite to find applications at higher frequencies and makes it technologically valuable. Ferrites are chemical compounds consisting of ceramic materials with iron oxide (Fe_2O_3) as their main component [5]. The chemical formula of ferrite is generally expressed as $MeFe_2O_4$, where 'Me' represents a divalent metal ion. (e.g. Fe^{2+}, Ni^{2+}, Mn^{2+} , Mg^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}etc). The crystal lattice of ferrite is spinel with cubic symmetry.

The crystal structure of spinel ferrite possesses two sub-lattices namely tetrahedral (A) and octahedral [B] sites. The cations can occupy either tetrahedral (A) or octahedral [B] or both sites partially. On the occupancy of cations at tetrahedral (A) and octahedral [B] sites, the spinel ferrites are known as normal, inverse and random spinel. Most important commercial spinel ferrites are cobalt ferrite and nickel ferrite have inverse spinel structureand they exhibit high electrical resistivity, high saturation magnetization, high permeability and high Curie temperature[6]. The high values of resistivity and magnetic properties are useful in making composites materials.

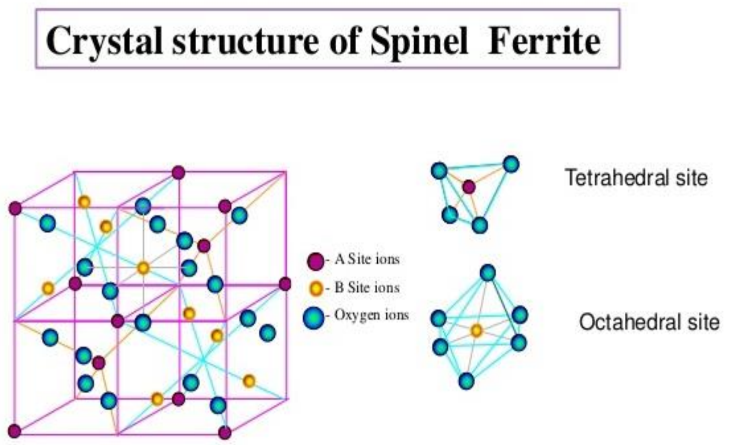

Figure 1: Crystal structure of spinal ferrite.

Among the magnetic ceramics, magnetic oxides are the most Important and rather the only relevant material from the point of view of their application .The number of mixed oxides such as ferrites, ferroelectrics, peroviskites etc, are being used in many technological applications. Ferrite are mixed metal oxide having iron oxide as their main constituent. Ferrite can be classified into three group's viz. spinal ferrite, garnet and magnetoplumbite according to their crystal structure. Spinal ferrite has the general formula MFe_2O_4, Where M is divalent metal ions like Co, Ni, Mg, Mn, Zn, Cd, Fe etc. Ferrites are the ferromagnetic oxides with combined electric and magnetic properties, which are useful in many applications such as antenna rod, transformer core, memory chips, sensors ,as catalyst, microwave devices like circulators, phase shifters, gyrator etc. Apart from their excellent elliptical and magnetic properties they have another advantage like chemical stability, easy preparation, low cost etc. They exhibit high electric resistivity, low eddy current and dielectric losses, high saturation magnetization, high curie temperature etc. These properties of ferrites are sensitive to method of preparation, cation distribution, type and nature of dopants also radiation dose, dose rate etc.

Types of ferrites

Types	Structure	General formula	Example
Spinal	Cubic	$M^{II}Fe_2O_4$	M^{II}=Cd,Co,Mg,Ni,Zn etc.
Garnet	Cubic	$Re^{II}Fe_2O_{12}$	Re^{II}=Y,Sm,Eu,Cd,Tb,Dy,etc.
Magnetoplumbite	Hexagonal	$Me^{II}Fe_2O_{19}$	(Er,Tm and Lu)

Ferrites are ferromagnetic in structure as originally proposed by Neel.It play an important part in the field of telecommunication, electronic, entertainment digital computer industries. Since the appearance of the first commercial ferrite product was in about 1945. The unique property of these ferrites is high magnetic permeability and high electrical resistivity. The required properties of ferrite may be classified as intrinsic and extrinsic. Number of applications depends on the extrinsic properties.

Nickel ferrite

Nickel Ferrite is a significant magnetic material with a wide range of applications, including ferrofluid fabrication, catalysis, and magnetic refrigeration. It is one of the most important soft ferrites, with low conductivity, low eddy current losses, and excellent chemical stability, mechanical hardness and electrochemical consistency[7]. Additionally, nickel ferrite's bulk phase is entirely made up of inverse spinel structures. The structure and morphology (form, size, and surface topology) of ferrite nanostructures may be precisely controlled by modifying the composition as well as the techniques of synthesis, according to the researchers. Various procedures for creating ferrite nanostructures have been developed over the years, including solid state, sol-gel, thermal decomposition, co-precipitation, hydrothermal, and mechanical milling. Despite several concerted attempts, a highly efficient and precise process for synthesis of ferrite nanostructures is still a long way off. Furthermore, no association has been discovered between the compositions, cationic distributions in the structure, electric and magnetic characteristics of ferrite nanostructures. This ferrite is an inverted spinel ferrite, with eight units of $NiFe_2O_4$ incorporated within the spinel structure's cell. Half of the ferric ions preferentially occupy tetrahedral sites, whereas the other half preferentially occupy octahedral sites. As a result, the compound is represented by the formula $(Fe^{3+})_A\ [Ni^{2+}Fe^{3+}]_BO_4^{2-}$.

The magnetic characteristics of nickel ferrite are comparable to those of magnetite and maghemite. Composition and microstructure, which are susceptible to the synthesis preparation technique, have an impact on the characteristics of synthesised materials. Furthermore, the magnetic properties of $NiFe_2O_4$ nanoparticles are very size-dependent. The creation of $NiFe_2O_4$ nanoparticles with the best magnetic characteristics is already generating a lot of attention. Numerous techniques have been devised to create nanocrystalline nickel ferrite, including sol-gel, organic gel-thermal decomposition, hydrothermal, co-precipitation, gel assisted hydrothermal routes, thermolysis, wet chemical co precipitation approach, microemulsion, and microwave synthesis [8]. Nickel ferrite nanoparticles are suitable for photocatalytic and waste water applications due to their large band gap and modern saturation magnetization. The performance of devices utilised in sensing and biological applications, such as contrast agents for magnetic resonance imaging and heat mediators for magnetic fluid hyperthermia, may be implemented due to the large tuning ability of nickel ferrite[9].

The following are the main applications of nickel iron oxide nanoparticles:

- Resistant suspension for levitated railway systems
- In the process of preparing nickel cermet for the anode layer of solid oxide fuel cells
- Magnetic recording medium with a high density
- Magnetic refrigeration
- As a catalyst, magnetic liquid, and microwave absorbers
- In lithium nickel iron oxide cathodes for lithium micro batteries
- In electrochromic coating, polymers, and fabrics.

III. LITERATURE REVIEW

The co-precipitation process was used to make nickel ferrite nanoparticles. To identify the structure of $NiFe_2O_4$ nanoparticles, an X-ray diffraction pattern was employed. FT-IR analysis revealed the existence of $NiFe_2O_4$ nanoparticles. Scanning Electron Microscopy was used to examine the surface morphology of $NiFe_2O_4$ nanoparticles. Transmission Electron Microscopy might be used to measure the particle size of nickel ferrites nanoparticles. The research sought to investigate the dielectric characteristics of nickel ferrite nanoparticles at various frequencies and temperatures, such as dielectric loss and dielectric constant. The magnetic characteristics of nickel ferrites were also investigated. XRD confirmed that $NiFe_2O_4$ nanoparticles corresponded to the cubic spinel structure. $NiFe_2O_4$ nanoparticles have an average particle size of 28nm. The dielectric investigations revealed that frequency had a detrimental influence on both the dielectric constant and the dielectric loss[10].

The $NiFe_2O_4$ nanoparticles were manufactured by the hydrothermal technique and the inhibition of surfactant on the particle growth is explored. It demonstrated that the products were pure $NiFe_2O_4$ and also nanoparticles develop with increasing the temperature, whereas surfactant hinders the particle growth under the same circumstances. The average particle size was evaluated by the TEM micrographs and found to be in the range of 50-60 nm that reduced up to 10-15 nm in the presence surfactant. Nano sized nickel ferrite particles were produced with or without surfactant aided hydrothermal techniques. The findings revealed that with rising in the temperature, the crystallinity of nanoparticles is enhanced. In the presence of surfactants, the crystallinity of $NiFe_2O_4$ nanoparticles reduced in comparison with surfactant - free produced samples. All of the nickel ferrite nanoparticles were superparamagnetic at normal temperature[11].

$NiFe_2O_4$ was synthesized by two methods – chemical sol gel method and the high frequency plasma chemical synthesis and magnetic properties, crystalline size, specific surface area of synthesized products was characterized. The average particle size of nano powders obtained by the sol-gel method self-combustion method is in the range of (25-40) nm and ferrites synthesized in plasma have wider particle size distribution range (10-100) nm with some particles of 200 nm. The magnetic properties of sample obtained by the sol gel self-combustion method differ from those of the plasma products. Dense material from the plasma nano powders forms at 1000 degree Celsius but from the sol gel self-combustion nano powders at 1200degree Celsius[12].

The citrate precursor technique was used to create $Ni_{0.5}M_{0.5}Fe_2O_4$ nanoparticles. At 400 degrees Celsius, the citrate precursor was annealed. An X-ray diffractometer was used to characterise the annealed powders. The observed XRD data was further investigated, revealing that particles annealed at temperatures up to 450 degrees Celsius had a cubic spinel structure, but particles produced at temperatures above 450 degrees Celsius have a tetragonal spinel structure. Sharp variations in particle size, lattice constant, magnetism, and retentivity were detected in the temperature range 450-500 degrees Celsius, indicating that growth differs at temperatures above and below a critical temperature in this range. The characteristics of nano size ferrite samples are highly dependent on the temperature of production[13].

$NiFe_2O_4$ nanoparticles were synthesized using co-precipitation method. The X-Ray diffraction was used to determine the structure of nickel ferrite nanoparticles. The fact that $NiFe_2O_4$ nanoparticles belonged to cubic spinal structure was established by XRD. The presence of nickel ferrite nanoparticles was confirmed by FT-IR spectrum. The details of surface morphology of $NiFe_2O_4$ nanoparticles were obtained by scanning electron microscopic analysis. SEM analysis showed that nanoparticles agglomerated to form spherical-shaped particles. The particle size was determined by Transmission electron microscopy. The average particle size of $NiFe_2O_4$ nanoparticles was found to be 28 nm. The work aimed at investigation of the dielectric properties such as dielectric loss and dielectric constant of $NiFe_2O_4$ nanoparticles at varied frequencies and temperature. From the dielectric studies it became evident that the frequency negatively impacted both the dielectric constant and the dielectric loss as decreased with increase in the frequency[14].

IV. SYNTHESIS METHODS

SOL-GEL TECHNIQUE

The sol-gel method of synthesizing nanomaterials is very popular and is widely employed to prepare ferrite materials[15-16]. The interest in this synthesis technique arises due to the possibility of synthesizing nano ferrite materials at very low temperatures; precursors are very simple chemical reagents, good stoichiometric control, special instruments are not needed, dopant ions can be quickly introduced into the resultant material and less agglomeration of grains in the product. The main advantage is one can get uniform nanoparticles with good quality by the sol-gel approach. The chemical reaction is carried out by dissolving the citric acid and metal nitrates in a minimum quantity of distilled water at room temperature. The citrate precursors are usually preferred due to their low solubility and low decomposition temperature. Generally, in order to achieve a complete reaction within the shortest time period and at the lowest possible temperatures, mixing of the component cations on an atomic scale is necessary. The mixture is heated in order to evaporate excess amount of water. Then the gel was dried at 150^0Cand as a result of which, the dry gel self-ignited to form intended ferrite powder. Throughout the auto-combustion process, exothermic redox chemical reaction along with fuel oxidation and decomposition of nitrates take place. The gasses like N_2 and CO_2 emerge, supporting the formation of nano ferrite powder.

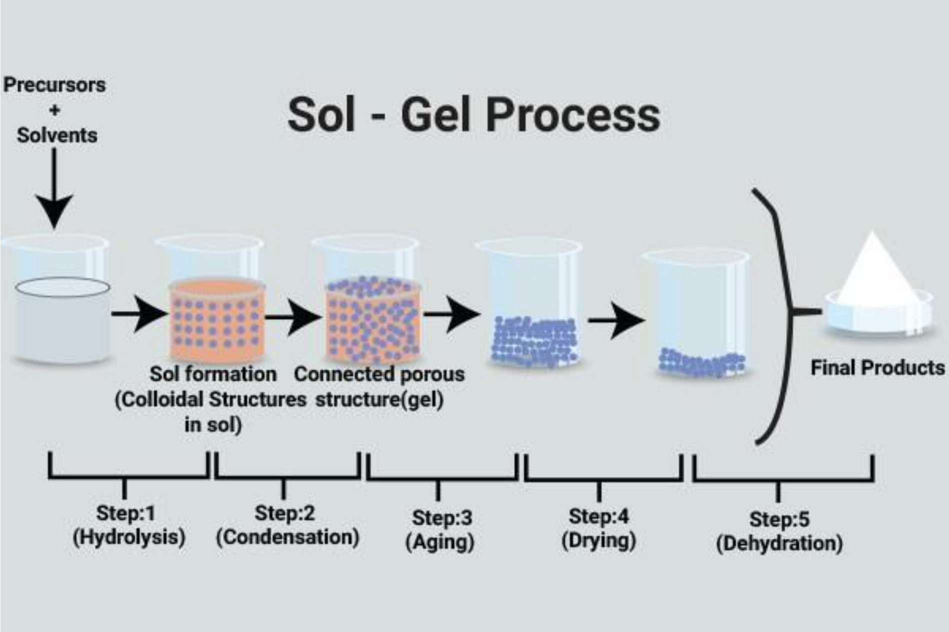

Figure 2. Sol-gel technique

The advantages of this technique are as elucidated below[17-18].

- The intimate mixing of the elements in gel form results in reaching the ingredients in a short period of time.
- Grinding procedure is not required to achieve homogeneous single phase ferrites, which avoids contamination (high product purity).
- The precise size control of the particles is also strength of a sol-gel processing.
- The possibility of controlling the porosity of the product material is highly attractive. (High crystalline ferrite nanoparticles)
- It is attributed to more uniform phase distribution in multicomponent systems like ferrites.

- Exothermic decomposition of precursor provides heat to the solid-state reaction, thus reducing the external temperature required for the ferrite formation in shorter time.
- Fine particle size and uniform particle size distribution
- Simple equipment and simple synthesis process
- It is a cost effective method.

Among the available chemical methods, sol-gel is a simple technique without much- complicated procedure and produce ferrite nanoparticles of high purity at minimum cost.

Solid-State Technique

The solid-state approach is extensively utilised for the production of single crystal and polycrystalline powders of transition metal phosphates and arsenates and monovalent cations[19]. This is a typical method for producing polycrystalline material from solid reagents. This approach use a chemical reaction to generate a new solid with a well-defined structure from solid starting ingredients. Fine grain metal compounds are mixed, pelletized, and heated at a given temperature for a certain amount of time. Extreme circumstances, such as high temperature and pressure, are required for some metal compounds, such as metal oxides or salts, to begin reactions in a molten flux or a rapidly condensing vapour phase. This method is also known as "shake and bake" or "heat and beat" chemistry. Characterizing the reaction rate in solid state synthesis is especially critical. Because approaches for purifying produced solids are extremely constrained, solid-state processes must be completed. The rate of the solid-state reaction is determined by the reaction circumstances, which include the structural qualities, shape, and surface areas of the reactants, the rate of diffusion, and the thermodynamic parameters of the process. The chemical precursors and preparation procedures determine the chemical and physical characteristics of the final products. Metal compound reactions are initiated by an energy source and propagated by the heat emitted during the synthesis of products and byproducts in this approach. The downsides of this approach are its slowness and high energy requirements. In reality, the reaction takes place at high temperatures (500-2000 degrees Celsius) for several hours and continues for several days. Heating at these temperatures may cause the target chemical to breakdown[19].

Hydrothermal technique

The hydrothermal technique is a novel approach for producing nanocrystalline inorganic materials. It is characterised as a homogeneous or heterogeneous reaction that occurs under high temperature and pressure in the presence of aqueous solvents, resulting in the development of solid compounds that are generally insoluble under normal circumstances. It is a low-cost and environmentally friendly approach. Temperature, water, pressure, and reaction time are therefore the three required physical parameters in hydrothermal processing. This synthesis method is also known as a solvothermal procedure, which indicates that additional solvents are employed in addition to water. In a typical experiment, the precursor material is dissolved in a suitable solvent and transported to an autoclave, which is a stainless-steel tank. In such experiments, water is frequently selected as the solvent. After the transfer is complete, the vessel is firmly sealed and exposed to heat treatments. For the synthesis of simple nanostructures, the temperature is set between 80 and 250 degrees Celsius. The supercritical solvent interacts with the precursor material at these extreme temperatures, resulting in the creation of products. Surfactants, in addition to precursor materials, are used in such reactions to create a nanostructure with the appropriate shape. Furthermore, the technique of simplicity and beauty is being forgotten[20]. The hydrothermal approach was used to create aluminium phosphate nanosheets[21].

Application of nanoferrites in biomedical sciences

Ferrite nanoparticles notably ferrites have attracted a lot of interest in recent years due to their uses in various sector and particularly in biomedical field where there improved magnetic characteristics enable diversity in imaging diagnosis and therapy. There are several varieties of ferrites that have been synthesized and presented for diverse uses but ferrite based on cobalt, nickel, and zinc has shown potential for biomedical applications due to strong magnetic biocompatibility and anisotropy[22]. With the objective of increasing the response in magnetic hyperthermia therapies and other biomedical applications, a nanoparticle system based on nickel ferrites has been studied.Monodispersed ferrites nanoparticles with varied proportions of Ni^{2+} ions and sizes have been created using an improved synthesis based on the thermal decomposition method and the seed-growth methodology. It has been demonstrated that structures with low Ni^{2+}cation percentages promote saturation magnetization levels and a decrease in the magnetic anisotropy constant[23]. Recently, magnetic nanoparticles (MNPs) have demonstrated significant promise in biological applications.

Among other uses, MNPs can be utilised as protein separators, contrast agents for magnetic resonance imaging (MRI), medication delivery systems, and heat generators. MNPs have a wide variety of uses and may be utilised for both treatment and diagnostic at the same time. To have a satisfactory performance for both purposes, the qualities and characteristics of the magnetic material should be adjusted (diagnosis and treatment). In the scientific literature, there are several publications on the use of MNPs as heat producers in magnetic fluid hyperthermia or contrast agents for MRI diagnosis or cancer therapy. Despite the fact that both uses are the consequence of magnetic fields interacting with one another[24].

Targeted drug delivery

The low toxicity and good biocompatibility of magnetic nanomaterials form them suitable materials for targeted drug delivery. Magnetic nanoparticles are widely used in targeted drug delivery applications. The direct intake of medicine affects non-targeted healthy organs to overcome these problems targeted drug delivery becomes a standard and promising technique nowadays. The other healthy tissues are not affected by any medicine in the case of targeted drug delivery application[25-26]. Magnetic nanoparticles have excellent magnetic properties which reveal the reduction of nanomagnets concentration in blood. The coating and doping of suitable components increase the effectiveness of magnetic nanoparticles in drug delivery applications.Spinel ferrites nanoparticles have received a lot of interest for their use as a drug delivery agent under the control of an external magnetic field because of their simplicity, effectiveness, ease of manufacture, and capacity to adjust their characteristics for specific biological applications[27–28]. German scientist Paul Ehrlich (1854–1915) introduced the idea of a "magic bullet" that would only kill sick tissue around a century ago[29]. The current history of drug delivery began to use microencapsulated drug particles in the 1950s[30]. The volume of papers in this biological field has significantly expanded since that time.

The literature now accessible contains several studies and research papers employing nanoparticles made of silica[31-32], gold, polymers, and other materials. It follows that since a variety of nanoparticles can be employed, magnetism isn't a need when building a drug delivery nano system. However, the application of magnetic nanoparticles in medication delivery has received significant interest recently[33]. The typical drug delivery approach from non-specific cell and tissue distributions with metabolic instability results in total body toxicity and decreased therapeutic effectiveness[34]. Spinel ferrite nanoparticles' capacity to enclose cytotoxic medicines within the polymer matrix and distribute them to cells is another noteworthy characteristic[35–36]. Spinel ferrite nanoparticles may transport medications without spilling and can quickly reach the target tumour location with the aid of an external magnetic field, helping to successfully treat cancer cells while avoiding normal cells[37]. Up till it reaches the sites of action, the medicine will be released and have therapeutic effects. Multifunctional nanoparticles, which contain semiconductors (for cell imaging), anticancer medicines, spinel ferrite nanoparticles, and biocompatible coating agents, are very useful for cancer therapy. It has been established that $CoFe_2O_4$ nanoparticles with lauric acid caps might be exploited as a potential drug delivery agent with pH-sensitive release[38]. Spinel ferrite nanoparticles may also be made more stable and have less hazardous effects on cells by being coated or capped with biocompatible materials. Spinel ferrite nanoparticles need to be completely demagnetized after being exposed to an external magnetic field in order to be employed for magnetically driven medication delivery.They can also maintain colloidal stability and avoid aggregation as a result, which enables them to be employed in biological applications[39]. One of the hypothesised causes of spinel ferrite nanoparticle aggregation is magnetic attraction between the particles[40].

Magnetic hyperthermia

Magnetic hyperthermia is one of the promising cancer treatments based on the heating ability of nanoparticles. Chemotherapy, radiotherapy, etc are some cancer treatments but these treatments have some drawbacks like these treatments affect normal tissues[41]. To overcome this problem, the use of magnetic hyperthermia is widely increased in the biomedical field. In this treatment, only cancer tissues of cells are killed with the help of an applied magnetic field and do not affect normal tissues or cells. The specific absorbance rate (*i.e.*SAR) value reveals the heating rate of nanoparticles[42]. Hyperthermia, a mild increase in temperature to 40-43 degree Celsius, can trigger the death of cancer cells and boost the effects of radiation and chemotherapy. However, the fulfilment of its full potential as a therapeutically relevant therapy approach was limited due to its inability to heat malignant cells efficiently and locally. This obstacle can be avoided by the intravenous introduction of magnetic nanoparticles focused at cancer cells that aggregate in the tumour, followed by the use of an alternating magnetic field to increase the temperature of nanoparticles situated in the tumour tissue. This tailored approach allows locally heating cancer cells, at the same time, without injuring surrounding normal tissue, which potentially boosts the effectiveness and safety of hyperthermia. The most common materials for magnetic hyperthermia are magnetite or maghemite nanoparticles.

Magnetic nanoparticles can be administered to the tumour by intra-tumoral, intra-arterial, intra-cavitary, intravenous injection. There oral delivery is not possible since most of the nanoparticles will be excreted from the body. Intra-tumoral and intra-cavitary injection localises magnetic particles in the tumour and can lead to efficient heating of primary tumours. Although the following routes of administration are well suited for certain circumstances, intravenous injection is the most adaptable delivery strategy for a wide spectrum of oncological disorders. When magnetic particles of iron oxide are given in this way, the accumulation of nanoparticles of tumour partially depends on the impact of increase permeability and retention[43]. This phenomenon refers to the tendency of nanoparticles to mainly collect in tumours due to the permeability of their vasculature and inadequate lymphatic drainage. Target ligands (antibodies and their fragments, ligands of particular receptors located on the surface of tumour cells, peptides, and aptamers) linked with the magnetic particles might improve the absorption of nanoparticles by malignant cells[44].

Their predominant concentration in malignantneoplasms leads to targeted local heating of tumours and the preservation of adjacent normal tissues under the influence of an alternating magnetic field. Despite the encouraging findings of preclinical trials of magnetic hyperthermia, there are several unanswered challenges in this area. This includes the establishment of optimal limits of magnetic field strength and frequency, their correlation with the duration of treatment, the toxicity of, magnetic nanoparticles (including the dependence of toxicity on the presence of specific ligands that improve the accumulation of magnetic particles in tumour cells), and determining their optimal concentration in the affected organ.

MRI and cancer diagnosis

There are several motivations for creating technology that can detect cancer in its earliest stages because early detection is linked to a favourable result with any sort of therapy[45]. Due to the availability of curative therapy, stage 1 cancer discovery is often linked with a 5-year survival rate higher than 90%[46,47]. Cancer may currently be found using a number of medical tests, including blood, urine, or imaging methods. When cancer is just a few millimetres (e.g., MRI) or centimetres (e.g., PET) in diameter, when it already contains more than a million cells, conventional imaging techniques often identify it. To address this drawback, molecular imaging has recently been proposed. Recent advancements in nanotechnology, molecular cell biology, and imaging technologies made it feasible to create this novel imaging modality. While magnetic resonance imaging (MRI), which offers the best spatial resolution when compared to other techniques and is noninvasive or at the very least minimally invasive, is of particular interest, molecular imaging imaging applies to a variety of imaging techniques such as Positron Emission Tomography (PET), computed tomography, or ultrasound.

Implementation of iron-based nanoparticles increased MRI sensitivity due to buildup of iron in the liver produced by selective action of the hepatobiliary system. Nanoparticles have been lately exploited by biologists, pharmacologists, physicists, doctors as well as pharmaceutical business. There are roughly 20 clinically approved nanomedicines utilized for the therapy. Some examples are Abraxane, an albumin-bound form of paclitaxel with cobalt of mean particle size of approximately 130nm that is used to treat breast cancer and Doxia, also based on Cobalt, is used for the treatment of refractory ovarian cancer and AIDS-related Kaposi’s sarcoma and it consist of nanoparticles with a polyethylene glycol coating. A fundamental aspect of nanoparticles delivery systems is their potential to boost transport systems is their ability to enhance the concentration of anticancer medicines in tumor cellssince certain nanoparticles passively accumulate in tumor's after their intravenous injection. Nanoparticles may pass via microscopic capillaries and are taken up by cells, which allow efficient drug accumulation at target locations and also sustained and regulated release of medications at target areas over a period of days and weak[45].

V. CONCLUSION

In this reviews article, the use of magnetic hyperthermia, targeted medication delivery, and nanoferrite in MRI was briefly discussed. Nanoferrites are a great choice for all of these biological applications due to their superb characteristics and adjustable magnetic behaviour. The main issues that need to be addressed when employing different nanoferrites for biomedical applications to increase effectiveness are stability and biocompatibility. Although there have been many in vitro research on nanoferrites, there haven't been many clinical trials on the substance.

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Hydrogen Storage Capacity on MO Doped Graphene: A DFT Study

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ABSTRACT

The hydrogen storage capacity of Molybdenum doped graphene investigated via first principles density functional calculations. Our reported simulation implies that the four hydrogenmolecules can easily able to bindsMolybdenumatom withpristine graphene sheet (PGrs). Thecalculated binding energy found in the range -0.534 to-0.626 eV/H2.The s and d orbitals ofH2 molecule with Molybdenum (Mo)atom at -0.3eV overlaps of main peaks indicates strong hybridizing with binding of s and d orbitals of H2 and Mo atom respectively.

Keywords: Molybdenum, DFT, Graphene, Hydrogen Storage, Binding energy

I. INTRODUCTION

The energy is need to every animate and inanimate bodies in this universe. It's demand in every sector show's we need more energy consumption at global level. To resolve an energy consumption,we have to find suitable solution on it. In our article we find alternative solution to replace oil consumption by using new energy sources. We can use molecular hydrogen as an alternative energy resource [1-2]. We are facing the major challenge for efficient and clear energy, hydrogen energy is one of the eco-friendly in nature as alternative energy source in future [3].

Pristine graphene sheet (PGrs) is having two–dimensional (2D) structure of carbon atoms which are densely packed by sp^2–bonding[4].

The theoretical work reported in terms of poor capacity of H_2 adsorption on monolayer graphene surface with Cs doping[5]. The evaluated binding energy of Gr-Cs complex system found in the range -0.502 to-0.606 eV/H_2.Thebiomolecule interactions (DNA base cytosine) with graphene by doping Molybdenum (Mo) found the adsorption energy for Gr-Mo is -188.62eV/H_2 and for complex system Gr-Mo-Cyto is -201.70 kJ/mole [6], However, adsorption energy of hydrogen on surface of graphene can be improve its uptake at room temperature [7]. Graphene and Molybdenum disulphide hydrides for energy applications and Hydrothermal synthesis of layered molybdenum sulfide /N-Doped graphene hybrid with enhanced supercapacitor performance implies the core role of Mo in graphene for utility of H_2 storage as well. [8,9].

The Fe Mo-Co-doped graphene for electrocatalytic N_2-to-NH_3 conversion reveals the Mo role in graphene [10], The effect of Mo additive on hydrogen absorption of rare-earth based hydrogen storage alloy signifies the Mo plays vital role for hydrogen storage capacity by means of adsorption[11] ,The Molybdenum carbide-derived carbon for hydrogen storage shows capacity of H_2 storage[12].The Enhanced hydrogen evolution on graphene coated Molybdenum Carbide Electrocatalysts signifies the enhanced capacity of H_2 for a complex system [13].

The article provides insight with its findings of possibility of hydrogen storage for a considered complex system,we adsorbed hydrogen atoms on the surface of Molybdenum doped Graphene sheet.TheMo atom doped PGs reasonably enhance the hydrogen storage capacity on the surface of the proposed complex system. The molybdenum able to increase the adsorption of dissociated hydrogen atoms.We suggested Molybdenum doping is one of the suitable and practical approach for application of hydrogen storage to manage our daily needs in terms of energy.

II. METHODS

We considered the model consisting of Carbon 48 (C-48)atoms [14] and further quantum chemical calculations were applied by using density functional theory. The Vienna ab initio simulation code (VASP) [15-16] within PAW method is used. The studied complex system PGrs-Mo-H_2 utilized the exchange and correlation within local density approximation. To interpret all the characteristics of molecular interactions no density functional theory describes it accurately, particularly Van der Waals (VdW) interactions [17-18]. The LDA method employed to study the physisorption energies of H_2 on CNT and graphene are in good agreement with experimental values [19-20].

However, the overestimate of the binding energy by LDA is compensated by the ignored van der Waals interactions [21-22]. The electron wave functions are expanded by plane waves with a kinetic energy cutoff of 450 eV to attain the required convergence. All of the self-consistent loops are iterated until the total energy difference of the systems between the adjacent iterating steps is less than 10^{-7} eV. The Brillouin zone is sampled by 5 × 5 × 1 mesh points in k-space based on Monkhorst-Pack scheme [22-23]. The effective range of the kinetic energy cutoff and the validity of the mesh density used in this calculation are determined by a convergence test using the theoretically estimated lattice constants of the pristine graphene, 2.46 Å. To avoid the interactions of adjacent slabs, the vacuum space of 20 Å is introduced for 4 × 4 supercell consists of48 carbonatoms.We also employed DFT method available in Gaussian 09 by applying WB97XD method with basis set LanL2MB [24-25].

III. RESULTS AND DISCUSSION

3.1 Model considered Pristine GrapheneSheet(PGS)

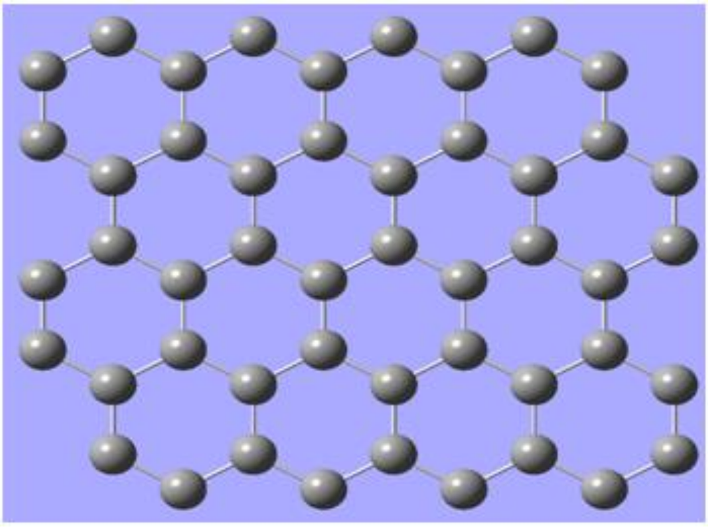


Figure 1. The optimized structures of Pristine Graphene sheet (PGs)with C-48 atoms

Figure 1 shows the pristine graphene sheet consisting ofCarbon 48(C-48) atoms.The proposed model utilized for H_2 storage system

3.2 Molybdenum (Mo)atom adsorption on Graphene surface

We considered the Mo atoms distributed uniformly on graphene sheet (Grs); the adsorption phenomenon of Mo studied on pristine graphene sheet (PGrs)determined extensively. The adsorption energy (E_{ad}) of Mo on graphene sheet (Grs) computedas:

$$E_{ad-Mo} = E_{Mo/Grs} - E_{Mo} \quad - E_{Grs} \qquad (1)$$

Where $E_{Mo/Gr}$, E_{Mo}, and E_{Gr} are evaluated total energies of the complex Mo-doped graphene sheet, isolated Moatom and pristine graphene sheet (PGrs).We reported the favorable adsorption site for molybdenum atom on surface of graphene sheet (Grs)has at the centre of a hexagonal ring.

The extracted value of the adsorption energy (E_{ad}) of Mo on graphene (E_{ad-Mo}) is -2.96 eV.

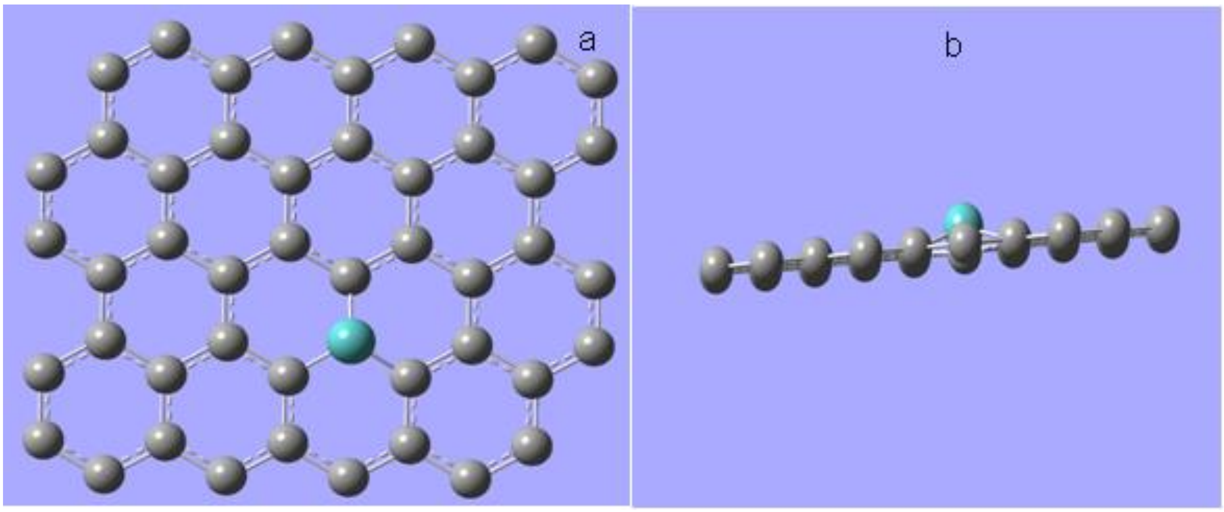


Figure 2. The optimized Mo doped Graphene sheet @ C-47 ,Mo-01 atoms for a complex system Top view (a) and side view (b) respectively.

The cohesive energy of complex system in solid phase of Molybdenumfound -3.82 eV/atom is greater than evaluated adsorption energy of Molybdenumatom on pristine graphene sheet. It reveals the Molybdenum atoms forms cluster as well.

Studied system is fully relaxed to achieve stable configuration .The Mo atom is at meta position the distance between meta to para (carbon atom)is 1.487 Å, it tends to stay top site near the carbon (C) atom as shown in figure 3. The distance between C-C 1.421Å whereas the distance between Mo and C atom(meta) is 1.473Å.

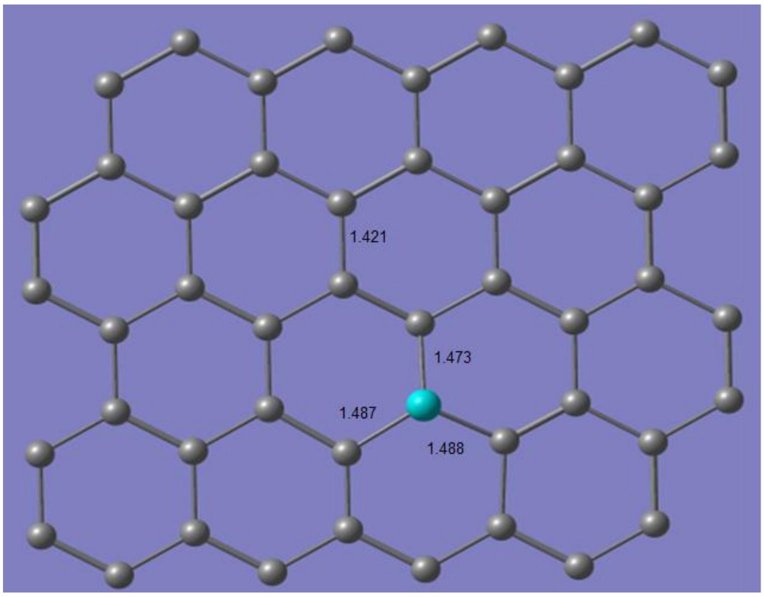


Figure3.The bond distance between Mo & C-C in Å

The investigated simulation result shows the adsorption energy of Mo doped atomGrs is -3.89 eV/atom is greater than bulk or complex solid phase molybdenum cohesive energy is -3.26 eV/atom.

We delineate the dipole moment of the complex system (Mo-C 47) in terms of its magnitude of charges and distance between the centers of positive and negative chargesevaluated value found 4.416893Debye. The values were calculated by using method B3LYP with 6-31G basis set within Gaussian 09 code [24].

3.3 Molybdenumdoped graphene by adsorption of hydrogen molecules

The reported complex system of Molybdenum doped graphene sheet (Mo-Grs-H_2)used as on board practical purpose itself.The phenomenon of adsorption mechanism of hydrogen (H_2) molecules on Molybdenum doped graphene sheet summarized in systematic path as described below.

We performed simulation with full relaxation optimized configurations of all H_2 molecules indicated in Figures 4 a-d (Top view).Figures 4a-d(side view) reveals the H_2 molecules prefers takes sites near to Mo atoms as well and vertical distance between first molecule and graphene sheet reported is 2.68 Å.However, the other molecules fellows same trends with the Grs as well.

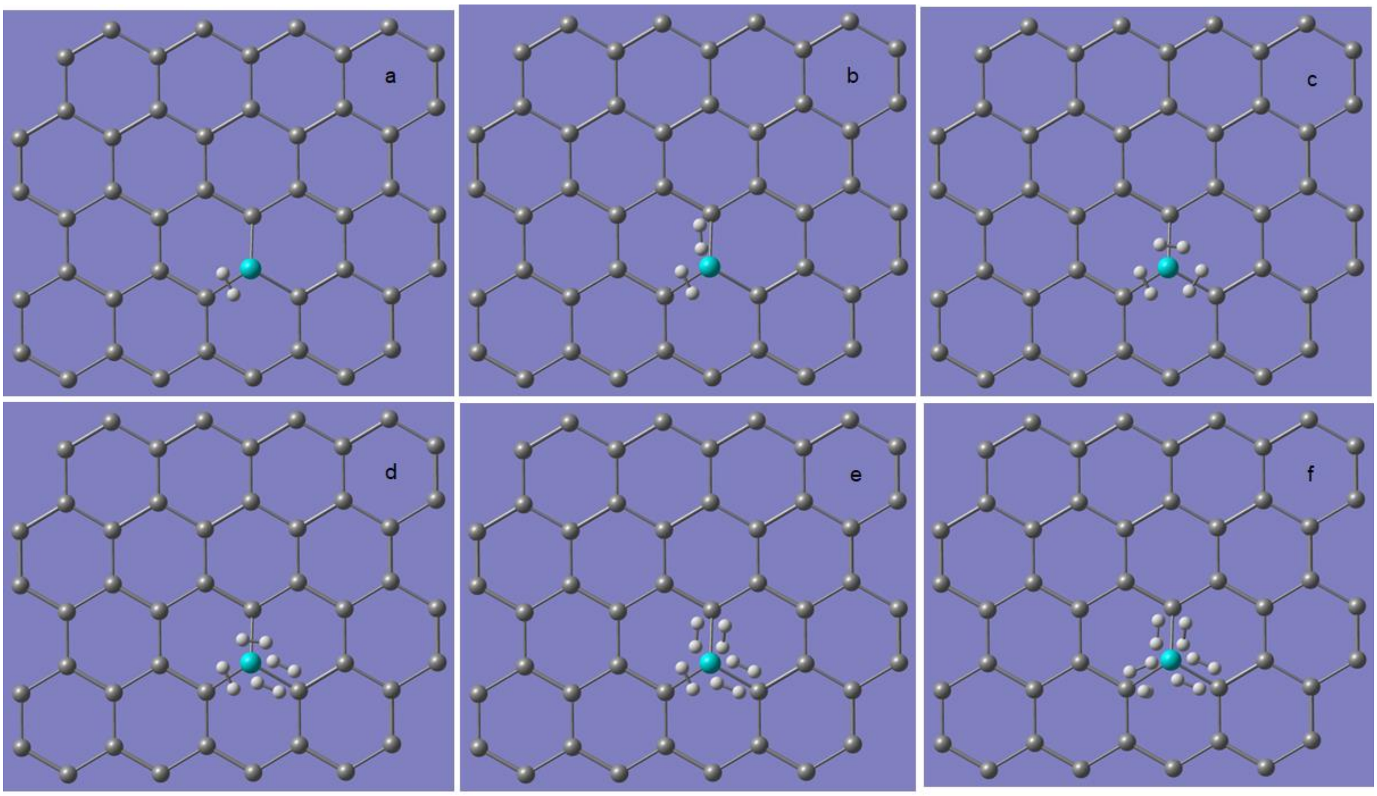


Fig.4 a-f. Molybdenum (Mo) doped Graphene sheet (Mo-Grs) optimized structuresadsorbedby H_2 molecules (top view).

The reported results manifest there is slightly distortions observed (Fig. a-f) in all configurations. Moreover, in plane distortion to the graphene sheet. The lattice distortion in graphene layer [11] by means of adsorption of 3d-trasition metals confirms the reported slight distortions in Graphene sheet (Grs).The stability of H_2 molecules adsorbed on modified graphene sheet; we calculated average adsorption energy of H_2 molecules using formula as written below

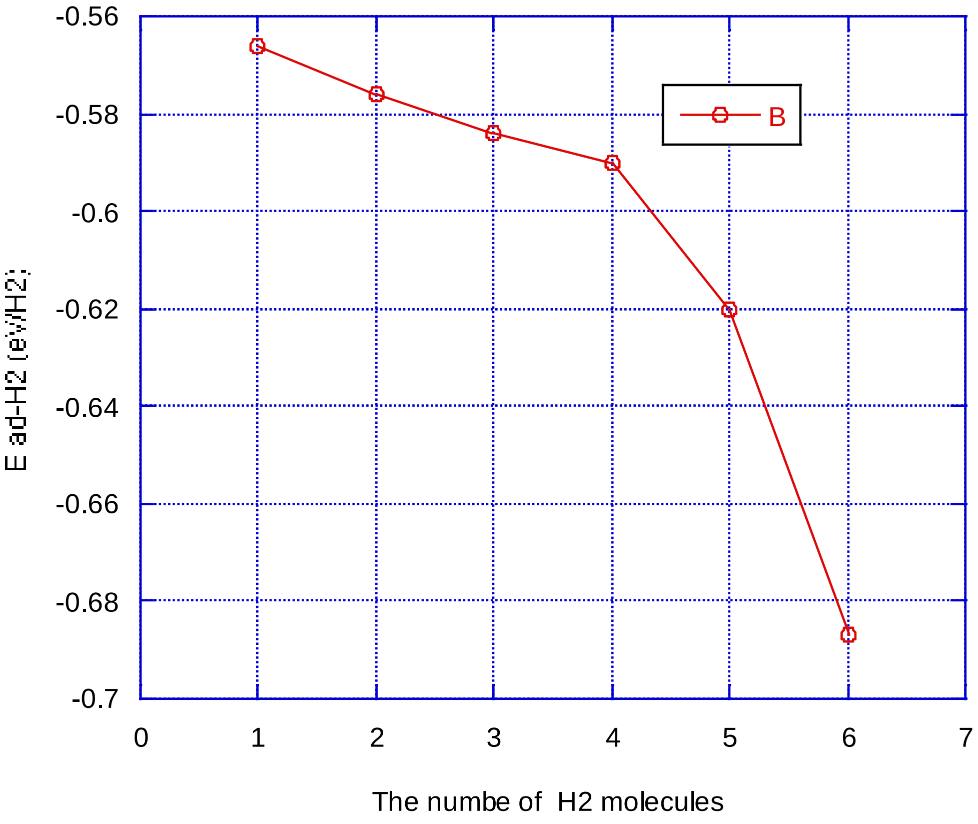
$$E_{ad-H2} = (E_{total} - E_{Mo/Grs} - nE_{H2})/n \qquad (3)$$

Serial Number	Number of H_2 molecules	Bond length of Mo/Grs in (Å)
1	$1H_2$	1.484
2	$2H_2$	1.997
3	$3H_2$	2.322
4	$4H_2$	3.165
5	$5H_2$	2.026
6	$6H_2$	2.374

Table 1 simulated bond lengths of the Mo doped graphene (Mo/Grs) sheet for one to six adsorbed hydrogen molecules per Mo atom.

The calculated values of bond lengths in Å of graphene sheet for one to six hydrogen molecules per Mo atom are shown in table 1.The The simulated data shows trends having continuous increase in bond length, when hydrogen molecules adsorbed on Modoped graphene sheet (Grs) upto three hydrogen molecules afterwards slightly smaller in the fourth configuration (3.165Å in $4H_2$) ,fifth configuration (2.026 Å in $5H_2$).We increased adsorbed number of hydrogen molecules on surface of Modoped Gr sheet, Moreover, slightly increase in bond length is observed at sixth configuration(2.374 Å in $6H_2$).

Figure 5 .The average adsorption energies of H2 molecule on graphene



The average adsorption energies of hydrogen molecules on graphene sheet shown in fig.5.

From the plot highest value of adsorption energies is observed at $4H_2$ molecules, due to the Van der Walls interaction between the H_2 molecules and surface of the graphene [24-25]. Experimentally the 72% of adsorbed hydrogen is chemisorbed due to adsorption of hydrogen atoms. Then, how hydrogen molecule dissociates the on the surface of Modoped graphene? To resolve the problem, we will be applyingthe NEB method to calculate the MEP of the hydrogen molecule dissociation on the surface of the Mo doped graphenein next article of complex system Grs-Mo-H_2.

Optimization process of complex system shows, we are able to evaluate the C-C bond lengths about1.423 Å, as well.The quantum chemically evaluated values were compared with experimental values for C-C bond lengths is 1.423 Å [25]to check its validity.

IV. CONCLUSIONS

We divulge the Molybdenum doped graphene by adsorption on Hydrogen molecules on its surface formed a cluster structure.Our simulation inferred that the four hydrogen molecules can easily able to binds

Molybdenum atom with pristine graphene sheet. The calculated binding energy found in the range -0.534 to-0.626 eV/H2. The s and d orbitals of H_2 molecule with Molybdenum (Mo) atom at -0.3eV overlaps of main peaks indicates strong hybridizing with binding of s and d orbitals of H_2 and Mo atom. Our reported scientific data of the adsorption energies of a complex system applicableto designing 2D Nanomaterial's for hydrogen storagewith exceptional potential.

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Methods of Preparation of Nanoparticles : A Review

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ABSTRACT

Nanotechnology attracts huge attention in recent research field. The development in technology in the preparation of nanomaterials gives extra interest in this research field. Many fields of research such as Physics, chemistry, material science, medical sector, pharma sector and many more carry out research in this field. Many scientists and researchers made significant development in the preparation of nanomaterials. The properties of materials in its bulk form are totally different than the properties in nano size. These nanoparticles show interesting properties. Due to quantization of electronic states the properties which depends upon size of the materials such as magnetic, optical shows apparent changes. Other properties such as thermal, electrical and mechanical properties change due to high surface to volume ratio of these nano sized materials.in this review different methods of preparation of nanomaterials are discussed.

KEWORDS: Nanoparticles, Electrolyte, Suspension, electro deposition.

I. INTRODUCTION

Nanoscience or nanotechnology is the science of very very small particles which are less than 100 nanometer size. Hence the nanomaterials are also very small in size. There are various techniques for the synthesis of nanomaterials. These methods are broadly synthesized into two types. Top-down approach and bottom-up approach. These methods are further divided into Physical methods, chemical method and biological methods. Synthesis of nanomaterials depends upon various factors such as Temperature, Pressure, Time, material size and shape, pH Value and environment. We will discuss some of the methods for the preparation of nanomaterials.

II. CHEMICAL VAPOR DEPOSITION

In this method of preparation, a solid material is deposited from a vapor by some chemical reaction occurs on the heated substrate material. This method nis primarily used in semiconductor industry in the preparation of thin films.in this method the chemical reaction taking place between some organometallic compound to be deposited on the substrate material.

By products are removed by carrier gas flow through the reaction chamber.to avoid desired chemical reaction the substrate surface temperature, pressure deposition time are carefully selected. The material obtained is high purity in nature. The decomposition can enhance with the plasma.[12]

III. ELECTRON BEAM LITHOGRAPHY

It is very expensive method. The rate of this reaction is very slow.as the material is subjected in a great stress in this method there occurs some surface defects.

IV. BALL MILLING

This is the physical method of synthesis of nanomaterial. The simple mechanism in this method is to grind and blend materials to form the desired nanomaterials. The hollow cylindrical shell which rotates about its own axis of rotation. This axis may be inclined or horizontal.it is partially filled with the ball which is made up of ceramics, stainless steel or rubber. These balls form the grinding media. The inner surface of the shell is coated with an abrasion resistant material. Generally, rubber is used as it causes less wear in mills. The key properties of grinding medial which are taken into consideration are size, density, Hardness and composition. There are mainly two types i.e., grate type and overall type. There are many advantages of this method. Some of them are lost cost, this is suitable for both batch and continuousoperation, material of any hardness can be grounded. This method is used in synthesis of metal oxide nanomaterials in the gas detection. Some chemicals, ceramics, raw materials can also be grinded by using this method.

V. SOL GEL PROCESS

It is a bottom-up approach of synthesis. A sol is a colloidal suspension in which solid particles are suspended in liquid solvent. A gel is a semi rigid mass that forms when the solvent form the sol begins to evaporates.it is a multi-stepped chemical reaction which is used in recently used in the field of material science and technology.[14]

The process generally starts with mixing of metal alkoxides in a suitable solvent at a high temperature. The metal oxide or metal chlorides are the precursors in this method. The hydrolysis reaction takes place in this method. Hence in this method metal oxo or metal hydroxy polymers are formed. A base is added in the reaction because it is very important to control the PH of the solution to avoid the co precipitation catalyst is used to start the reaction. Hydrolysis, condensation, growth of particles and collection of the particles are the steps in this method of preparation. The rate of the reaction depends on the temperature.it is a one of the cheap methods. High purity products are formed in this reaction.in powder synthesis smaller particle size and morphological control takes place. The cost of the raw materials i.e., chemicals may be high in this method. A very close monitoring is required in this method as this is a multi-step reaction.

This method has a wide applications.it can be used to produce powders and fibers.by using this method we can deposit thin films on different surfaces.it is used in drug delivery systems. we can make UV protection gels by using this method.it is suitable for producing lubricants and scratch free materials.

VI. ELECTRODEPOSITION

It is a liquid phase chemical method of synthesis of nanomaterials.it is a bottom-up approach.it is a most suitable method for depositing thin film from aqueous solution. The reaction is based on the discharge of metal ions which are present in the electrolyte ate cathode surface. The metal ions accept the electron from the electrically conducting material and there is a deposition of metal atoms. The thin films are formed by this method are strong and uniform. certain properties such as electrical resistivity, Hardness are strongly affected by the size of grains.

This method has a high utilization rate of the raw materials.it is a low energy consumption process.in this method we can precise the film thickness, morphology and doping. This method is used in the deposition of few atoms or up to large dimensions.

VII.LASER VAPORIZATION

In this method a pulse of high-power LASER beam is used to vaporize the given material. Thesetup assembly consist of anultra-highvacuum chamber with inert or reactive gas, laserbeam, atarget and a substrayte.by using this method the cluster of any material can be made. A powerful LASER beam evaporates the solid surface and the formation of cluster of atoms takes place. They condense on called substrate. This method is also known as LASER Ablation. The particle size depends upon the gas pressure.

VIII. SUMMARY

Nanomaterials are used in variety of applications in recent decades. This field of Nanotechnology is very dynamic in nature. There are various methods to preparation of particles. scientists and researchers find many methods to prepare nanoparticles and research is still going on.

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Distributional Natural Transform and Its Operational Calculus

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ABSTRACT

Purpose: To compare the methods of automated noise measurement at the polyester resin (PESR) phantom images and clinical abdominal images.

Method: The

Keywords: CT scan, noise, automated noise, IndoQCT, tube voltage

I. INTRODUCTION

The Natural transform is one of the new transform defined by Khan and Khan[1] by the integral equation

$$\mathbb{N}[f(t)] = R(s,u) = \int_0^\infty e^{-st} f(ut)dt \qquad (1)$$

where $Re(s) > 0, u \in (\tau_1, \tau_2)$,s and u are the transform variables. The Natural transform of functions $f(t) \quad t \geq 0$ are come to exists which are piecewise continuous and of exponential order defined over the set $A = [f(t)/\exists M, \tau_1, \tau_2 > 0, |f(t)| < Me^{\frac{|t|}{\tau_j}}, if t \in (-1)^j \times [0,\infty)]$
The above equation can be rearranged in another form

$$\mathbb{N}[f(t)] = R(s,u) = \frac{1}{u}\int_0^\infty e^{-\frac{st}{u}} f(t)dt \qquad (2)$$

The inverse Natural transform of function $R(s,u)$ is denoted by symbol $\mathbb{N}^{-1}[R(s,u)] = f(t)$ and is defined with Bromwich contour integral[2, 3]

$$\mathbb{N}^{-1}[R(s,u)] = f(t) = \lim_{T\to\infty} \frac{1}{2\Pi i}\int_{\gamma-iT}^{\gamma+iT} e^{\frac{st}{u}} R(s,u)ds \qquad (3)$$

If R(s,u) is the Natural transform,F(s) is the Laplace transform and G(u)is Sumudo transform of function f(t)∈A then we can have Natural-Laplace and Natural-Sumudo duality as

$$\mathbb{N}[f(t)] = R(s,u) = \int_0^\infty e^{-st} f(ut)dt = \frac{1}{u}F(\frac{s}{u}) \qquad (4)$$

and

$$\mathbb{N}[f(t)] = R(s,u) = \int_0^\infty e^{-st} f(ut)dt = \frac{1}{s}G(\frac{u}{s}) \qquad (5)$$

---

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The Natural transform plays as a source for other transform and also it is the theoretical dual of Laplace transform.Further study and applications of Natural transform can be seen in[3, 4, 5]. The aim of this paper is to extend the theory of Natural transform to the distributional space and to study the properties of Natural transform in this distributional space.[6, 7, 8, 9, 10]

2 Generalized Natural Transform

2.1 Testing function space $\mathfrak{D}_{a,b}$

let $\mathfrak{D}$ denotes the space of all complex valued infinitely smooth functions $\phi(t)$ on $-\infty < t < \infty$ such that

$$\underset{t\in K}{Sup}|D_t^k\phi(t)| < \infty \tag{6}$$

Where K is compact set and D_t^k is the k^{th} derivative with respect to t. A sequence of testing functions $(\phi_n(t))$ is said to converge in $\mathfrak{D}$ if $\phi_n(t)$ are in $\mathfrak{D}$, if for every fixed non-negative integer k, the sequence $(\phi_n^k(t))$ converges uniformly on every compact set K. With the terminologies used in [11, 12], $\mathfrak{D}$ is complete and hence a Frechet space.$\mathfrak{D}'$ denotes the dual of $\mathfrak{D}$ i.e. f is member of $\mathfrak{D}'$ iff it is continuous linear function on $\mathfrak{D}$. Thus $\mathfrak{D}'$ is a space of generalized functions.

Given a generalized Natural transformable generalized function f,the kernel $e^{\frac{-st}{u}}$ as a function of t is a member of $\mathfrak{D}'$. The generalized Natural transform of f as conventional function is defined by equation

$$R_f(s,u) \triangleq \mathbb{N}[f(t)] \triangleq < f(t), \frac{1}{u}e^{\frac{-st}{u}} > \tag{7}$$

Note that the properties like linearity and continuity of generalized Natural transform will follows from [**?**]

3 Operational Calculus Properties

In this section we will prove some operational properties of distributional Natural transform

Theorem(1): The distributional Natural transform is linear.

Proof: The proof of this theorem is very straightforward according to the definition.

Theorem(2): Let $f(t) \in \mathfrak{D}'$ and $R_f(s,u)$ be the distributional Natural transform of f(t) then

$$D_s^k R_f(s,u) =< f(t), D_s^k(\frac{e^{\frac{-st}{u}}}{u}) > \tag{8}$$

Where $D_s^k = \dfrac{d^k}{ds^k}$ be the k^{th} derivative with respect to s.

Proof: To prove the theorem we apply the method of induction on k. For k=0 the result is very obvious i.e.

$$R_f(s,u) =< f(t), \frac{e^{\frac{-st}{u}}}{u} >$$

Assume that the result is true for $(k-1)^{th}$ derivative i.e.

$$D_s^{k-1}R_f(s,u) =< f(t), D_s^{k-1}(\frac{e^{\frac{-st}{u}}}{u}) >$$

Let s,u be fixed and $\Delta S \neq 0$ then consider

$$\frac{D_s^{k-1}R_f(s+\Delta S,u) - D_s^{k-1}R_f(s,u)}{\Delta S} - < f(t), D_s^{k-1}\frac{1}{u}e^{\frac{-st}{u}} >=< f(t), \psi_{\Delta S}(t) > \tag{9}$$

Where $\psi_{\Delta S}(t) = \frac{1}{\Delta S}[D_s^{k-1}e^{\frac{-(s+\Delta S)t}{u}} - D_s^{k-1}e^{\frac{-st}{u}}] - D_s^k\frac{1}{u}e^{\frac{-st}{u}}$

Now to prove the result for k,it is enough to show that $|\Delta S| \to 0, \psi_{\Delta S}(t)$ converges to zero in $\mathfrak{K}_{a,b}$.

For the non-negative integer n,consider

$$\psi^{(n)}_{\Delta S}(t) = \frac{1}{\Delta S}\int_{s-t}^{s-t+\Delta S}\int_{s-t}^{y} D_{\zeta}^{n+k+1}(\frac{e^{\frac{-\zeta t}{u}}}{u})d\zeta dy \qquad (10)$$

Let $\Upsilon : [\zeta / s - t - \Delta S < \gamma < s - t + \Delta S]$

$$|\psi^{(n)}_{\Delta S}(t)| \leq \frac{\Delta S}{2}\underset{\zeta}{Sup.}|D_{\zeta}^{n+k+1}(\frac{e^{\frac{-\zeta t}{u}}}{u})|$$

$\therefore$ As $|\Delta S| \to 0, \psi_{\Delta S}(t)$ converges to zero in $\mathfrak{K}_{a,b}$.

Hence result is true for k i.e.

$$D_s^k R_f(s,u) = < f(t), D_s^k(\frac{e^{\frac{-st}{u}}}{u}) > \qquad (11)$$

Hence the proof.

Note that same proof can be made for another variable u i.e.

$$D_u^k R_f(s,u) = < f(t), D_u^k(\frac{e^{\frac{-st}{u}}}{u}) >$$

Theorem(3): Let $f(t) \in D'$ and $R_f(s,u)$ be the distributional Natural transform of f(t)Let $f(t) \in \mathfrak{D}^{'}$ and $R_f(s,u)$ be the distributional Natural transform of f(t) and

$$g(t) = \begin{cases} f(t-\lambda) & t \geq \lambda \\ 0 \quad t < \lambda \end{cases},$$

then

$$R_g(s,u) = e^{\frac{-s\lambda}{u}} R_f(s,u)$$

Where $R_g(s,u)$ is the distributional Natural transform of g(t).

Proof: From the definition of function g(t),we can say that $g(t) \in D'$ we have

$$\begin{aligned} R_g(s,u) &= < f(t-\lambda), \frac{e^{\frac{-st}{u}}}{u} > \\ &= < f(t), \frac{e^{\frac{-s(t+\lambda)}{u}}}{u} > \\ &= e^{\frac{-s\lambda}{u}} < f(t), \frac{e^{\frac{-st}{u}}}{u} > \\ &= e^{\frac{-s\lambda}{u}} R_f(s,u) \end{aligned}$$

Hence the proof.

Theorem(4): Let $f(t) \in \mathfrak{D}^{'}$ and $R_f(s,u)$ be the distributional Natural transform of f(t) then

$$R_f(t^n D_t^n f(t); s,u) = u^n D_u^n R_f(s,u)$$

Proof: Let $R_f(s,u)$ be the distributional Natural transform of f(t) then

$$\begin{aligned} D_u^n R_f(s,u) &= D_u^n < f(t), \frac{e^{\frac{-st}{u}}}{u} > \\ &= D_u^n < f(ut), e^{-st} > \\ &=< D_u^n f(ut), e^{-st} > \\ &=< t^n D_t^n f(ut), e^{-st} > \\ &= \frac{1}{u^n} < (ut)^n D_t^n f(ut), e^{-st} > \\ &= \frac{1}{u^n} R_f(t^n D_t^n f(t); s,u) \end{aligned}$$

Hence the proof.

Theorem(5): Let $f(t) \in \mathfrak{D}'$ and $R_f(s,u)$ be the distributional Natural transform of f(t) then

$$R_f(f(at);s,u) = \frac{1}{a} R_f(f(t); \frac{s}{a}, u)$$

Proof:

$$\begin{aligned} R_f(f(at);s,u) &=< f(at), \frac{e^{\frac{-st}{u}}}{u} > \\ &= \frac{1}{a} < f(t), \frac{e^{\frac{-\frac{s}{a}t}{u}}}{u} > \\ &= \frac{1}{a} R_f(f(t); \frac{s}{a}, u) \end{aligned}$$

Hence the proof.

Theorem(6): Let $f(t) \in \mathfrak{D}'$ and $R_f(s,u)$ be the distributional Natural transform of f(t) then

$$R_f(e^{at} f(t); s,u) = \frac{s}{s-au} R_f(\frac{su}{s-au})$$

Proof:

$$\begin{aligned} R_f(e^{at} f(t); s,u) &=< e^{at} f(t), \frac{e^{\frac{-st}{u}}}{u} > \\ &= \frac{1}{u} < f(t), e^{-(\frac{s}{u}-a)t} > \\ &= \frac{s}{s-au} < f(\frac{su}{s-au} t), e^{-st} > \\ &= \frac{s}{s-au} R_f(\frac{su}{s-au}) \end{aligned}$$

Hence the proof.

Theorem(7): Let $f(t) \in \mathfrak{D}'$ and $R_f(s,u)$ be the distributional Natural transform of f(t) then

$$R_f(tf(t);s,u) = \frac{u^2}{s} D_u^1 R_f(f(t);s,u) + \frac{u}{s} R_f(f(t);s,u) = \frac{u}{s} D_u^1 u . R_f(f(t);s,u)$$

We can generalize above result as

$$R_f(t^n f(t);s,u) = \frac{u^n}{s^n} D_u^1 u^n . R_f(f(t);s,u)$$

Proof: For $f(t) \in D'$ and using the property of differentiation we have

$$\begin{aligned} D_u^1 R_f(f(t); s, u) &=< f(t), D_u^1 \frac{e^{\frac{-st}{u}}}{u} > \\ &= \frac{s}{u^2} < tf(t), \frac{e^{\frac{-st}{u}}}{u} > - \frac{1}{u} < f(t), \frac{e^{\frac{-st}{u}}}{u} > \\ R_f(tf(t); s, u) &= \frac{u^2}{s} D_u^1 R_f(f(t); s, u) + \frac{u}{s} R_f(f(t); s, u) \end{aligned}$$

with the help of mathematical induction we can easily prove that result is true for t^n i.e.

$$R_f(t^n f(t); s, u) = \frac{u^n}{s^n} D_u^1 u^n . R_f(f(t); s, u)$$

Hence the proof.

4 Conclusion

In this paper the Natural transform is defined over distributional space of compact support.Also the operational calculus properties like differentiation,shifting etc.are proved.

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