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CONFERENCE PROCEEDINGS

National Conference on New Trends in Green Chemistry and Environmental Science

Organised by
Department of Chemistry
Navgan Shikshan Sanstha Rajuri's
Mrs. Kesharbai Sonajirao Kshirsagar alias Kaku Arts,
Science & Commerce College,
Beed. 431122, Maharashtra, India

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The Conference : An Overview

National Conference on 'New Trends in Green Chemistry & Environmental Science' (NTGCES- 2022). Green chemistry which are still in use today, that focus on the minimization or non-use of toxic solvents in chemical process and analyses as well as non-generation of wastes from these process. These principles propose environmentally favorable actions form planning of the product to its synthesis processing, analysis and its destination after use. It inculcates green approaches in chemical synthesis there by providing positive contribution towards environmental protection. The main objective is to minimize the environmental and occupational hazard inherent in industrial activities. The main idea behind organizing this conference is to expose academic students & researchers to the new trends in industries & provide necessary platform to interact & share essential ideas related green chemistry .environmental chemistry which will be beneficial for the development of clean & environmental benign process.

Webinar Background

Chemistry is everywhere, the impact of Chemistry on everyday life is increasing a day by day. The objective of the webinar is to confront how Chemistry meets the global challenges of clean air, safe water, healthy food, dependable medicines from plants and the latest outstanding development in the field of Chemistry.

6. Themes to be Pondered Sessions will include invitees' Lectures/ Research Papers/.

Following Topics to be covered

1. Green Chemistry.
2. Polymer chemistry.
3. Synthetic chemistry.
4. Material science.
5. Computational chemistry
6. Environmental chemistry.
7. Nano-technology.
8. Catalysis.
9. Spectroscopic methods in chemistry

About College

The college is one of the reputed institutions in Marathwada region run by Navgan Education Society Rajuri, Beed. The society was founded by former Member of Parliament, Late. Sou. Kesharbai Sonajirao Kshirsagar with the aim of imparting education to the rural strata of Marathwada region. Late. Sou. Kesharbai Kshirsagar was a woman of masses who donated all her mind and heart to the cause of education of the downtrodden, poor and ignorant that really forms the major bulk of society. The college is affiliated to Dr. Babasaheb Ambedkar Marathwada University, Aurangabad. The college is ISO-9001:2015 certified and Reaccredited by NAAC at 'A – Grade' with CGPA 3.18 in Nov. 2018 for its meritorious academic records and overall infrastructure development. The college is continuously pursuing the tradition of promoting education. Department of Chemistry is the integral part of college since its beginning. Dept have potential faculty members having SET/NET, JRF, Ph.D. qualifications.

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Green Channels for Synthesis Of 3,4-Dihydro-3-Substituted-2h-Naphtho[2,1-E][1,3]Oxazine Derivatives From Ammonium Metavanadate (H4no3v)

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ABSTRACT

An efficient and novel one-pot synthesis of various 3,4-dihydro-3-substituted-2H-naphtho[2,1-e][1,3]oxazine derivatives from 1-naphthol, various anilines and formalin at room temperature stirring is presented. The six-membered N,O-heterocyclic skeleton was constructed via ammonium metavanadate (H4NO3V) promoted Mannich type reaction.

Keywords: Mannich Type Reaction; 1,3-Oxazines; Ammonium Metavanadate (H4NO3V); Stirring; Multicomponent Reaction.

I. INTRODUCTION

There have several researches has accomplished for the synthesis of 1,3-oxazine compounds using solvent-free conditions for condensation of alchols with amine derivatives in acidic medium or its derivatives as a precursor [1]. This synthesis assists to analysis the products of reactions using phenol, aniline and formaldehyde [2]. Over the past decade, this condensation reactions has investigated in the presence of the various catalyst, such as cerium ammonium nitrate, ionic liquids, tin tetrachloride, silica perchloric acid and P2O5 supported on SiO2 [3,4]. This is Multicomponent reactions (MCRs), in which three or more different reactants react to give a desired product in a one-pot procedure, which has used as a vigorous tool to attain this aim. These approch let molecular complexity and diversity to be created by the schematic formation of various new covalent bonds in a one-pot transformation, As Multicomponent reactions (MCRs) associate two major principles of organic synthesis, convergence, and atom economy [5]. Multicomponent reactions are one of the most worthy practice for synthetic efficiency and reaction design [6]. Multicomponent reactions play a significant role in organic synthesis, medicinal chemistry, and material science [7].

The development of the environmentally benign and cost-efficient synthetic procedure has demanded from the viewpoints of green sustainable chemistry [8]. Oxazines are very important class of heterocyclic compounds, they are categorized into three isomeric forms like 1,2-oxazine, 1,3-oxazines, and 1,4- oxazines, They are an principal grade of heterocycles, which has enraptured much synthetic significance due to their

comprehensive array of biological activities [9]. In inclusion these action use only small organic molecules as catalysts consequently prove to be ideal green substitution for metal or non-metal Lewis acid catalysts [10].
1,3-oxazine is a six-membered heterocyclic ring it is the well-known core of the number of biodynamic natural and synthetic molecules [11]. It has describe to manifest a extensive range of biological and pharmacological activities [12]. Several methods have been reported for the synthesis of 1,3-oxazines owing to their biological importance [13,14]. The in-vitro anti-inflammatory and anti-oxidant activities reported in some of the researches. Isomeric oxazine derivatives synthesized from chalcone are known to possess various activities, like anti-hyperglycemic, antiulcer, anti-inflammatory [15], anti-microbial, anti- viral [16], anti-malarial, analgesic, anti-cancer, anti-tubercular [17], anti-oxidant, and anti-leishmanial [18], anti-coagulant activities [19]. Oxazine derivatives have played very important role in the improvement of heterocyclic chemistry and are ordinarily used in organic synthesis [20]. Oxazine derivatives have been reported to possess anti-fungal, anti-bacterial [21]. Amino acids have a unique bifunctional, structure that serves to conveniently from peptides, peptidomimetics, and proteins. Due to its numerous biological activities reported [22].

II. EXPERIMENTAL

1) General procedure for synthesis of 3,4-dihydro-3-substituted-2h-naphtho[2,1-e][1,3]oxazine derivatives (4a-i)

Take (5 mmol) α-naphthol in Round bottom flask (RBF) to it add (5 mmol) Ar-NH2 and (10 mmol) formaldehyde in it. Now stir the mixture for 5 to 10 min at room temperature. Now, to a stirred mixture of α-Naphthol, Formaldehyde & Ar-NH2, Like 1(a-i) add acid catalyst i,e. NH4VO3. Continue the stirring for around 42–54 min at room temperature. A thick paste product is obtained. The reaction is monitored by TLC. After completion of reaction, reaction mixture was extracted with methylene dichloride (3×50 mL), washed with water (2×10 mL) and brine (2×20 mL). Thus separated organic layer was dried over anhydrous Na2SO4. The solvent was removed under reduced pressure. The obtained crude product was purified by column chromatography on silica gel by hexane: ethyl acetate as an eluent.
IR spectra were recorded on JASCO FT-IR 4100, Japan using KBr discs. 1HNMR and 13C NMR spectra were recorded on Varian NMR spectrometer, Model Mercury Plus (400MHz)

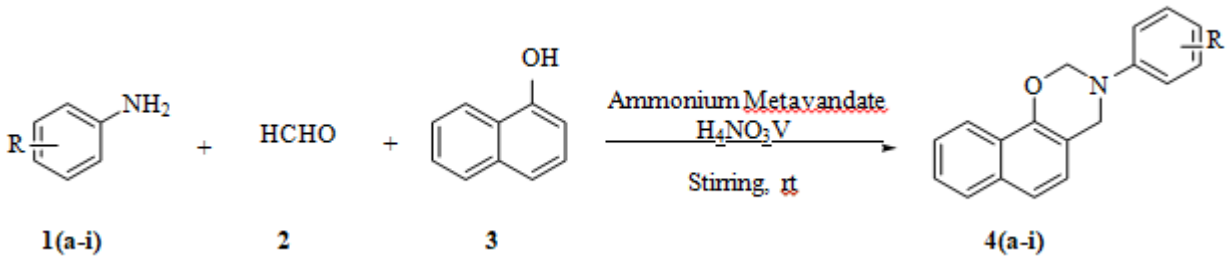
2) SPECTRAL ANALYSIS:

3-(4-fluorophenyl)-3,4-dihydro-2H-naphtho[2,1-e][1,3]oxazine (4g).

IR (KBr, vmax/cm-1): 1024 (sym.C-O-C), 1248 (asym. C-O-C);
1H NMR (DMSO-d6, 400 MHz, δppm): 4.88 (s, 2H, -Ar-CH2-N-),5.54 (s, 2H, -O-CH2-N-), 6.78-7.83 (m,10H, Ar-H);
13C NMR (DMSO-d6, 75 MHz, δ ppm): 48.2,79.5, 111.2, 115.4, 116.4, 117.4, 118.5, 122.8, 123.6, 125.4, 125.3, 126.3, 127.7, 128.6, 130.6, 150.5;

III. RESULTS AND DISCUSSION

We had performed the Multicomponent reaction of Aromatic amine, formaldehyde and α-naphthol, (1:2:1) in the presence of (10 mol%) various acid catalysts to synthesize 1,3 oxazine derivative at room temperature.
"Ammonium metavanadate" a catalyst that we used to synthesis 1,3oxazine derivative through which we obtained the maximum quantitative yield for the Synthesis of 3,4-dihydro-3-substituted-2H-naphtho[2,1-e][1,3]oxazine derivative i.e. 85 to 96% and in minimum time i.e. 42 to 54 min.
We have synthesis the model reaction with the Aniline and with various acid catalysts through which we obtained the best results with H4NO3V.
Further we have optimized the reaction by using different-different model reactions (Table 1) in presence of H4NO3V as a catalyst (Table 2).
The Synthesis has performed by using acetic acid and oxalic acid through which we obtained about 70 to 80% yield and in 60 to 90 min for obtaining the desired product.
By using boric acid and citric acid as a catalyst and we found that the product obtained is having a yield of about 58 to 65% and the time required for the reaction is about 90 to 120 min to obtain the product.
H4NO3V has used as an oxidizing agent for the condensation of 1,3oxazine derivative which is one of the most suitable and efficient acid catalysts to obtain a maximum yield of a product in a minimum time.



Scheme 1: Synthesis of 1,3-Oxazine derivatives catalyzed in H4NO3V

Mechanism: Synthesis of 1,3-Oxazine derivatives catalyzed in H4NO3V

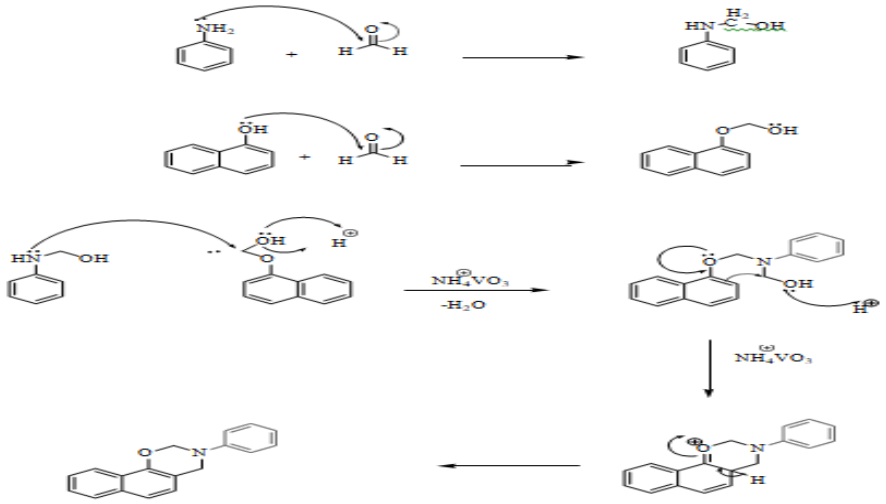


Table 1. Effect of catalyst loading on model reaction on Aniline (1a).

Entry	Catalyst	Time (min)	Yield (%)
1a	H4NO3V	42	91
1a	CH3COOH	78	80
1a	Oxalic Acid	76	76
1a	Citric Acid	112	58
1a	Boric Acid	98	65

Table 2. Synthesis of 1,3-Oxazine derivatives catalyzed in H4NO3V

Compound	**R**	**Time (min)**	**Yield (%)a**	**M. P. (°C)**
4a	H	42	91	60-62
4b	4-OMe	48	85	280 (d)
4c	4-OEt	50	87	78-80
4d	2,4,6-Tri Br	60	78	70-72
4e	4-Me	45	83	194-196
4f	2-OEt	44	90	188(d)
4g	4-F	50	96	120-122
4h	3-OMe	52	85	290(d)
4i	2-Me	54	88	88-90

aReaction Condition: Formalin (20 mmol), aniline (10 mmol), 1-naphthol (10 mmol), room temperature, stirring, H4NO3V (10 mol%). bIsolated yields.

IV. ACKNOWLEDGEMENTS

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V. CONCLUSION

In conclusion, H4NO3V a catalyst used to synthesis 1,3-oxazine has best results. The method is advantageous due to high conversion, short reaction time, clean reaction profile, simple experimental and workup procedures for the synthesis of (4a-i) compounds.

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Acoustical Parameters Study of Novel Benzothiazole Derivatives in Binary Solvent Mixtures at Different Frequencies

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ABSTRACT

Density and ultrasonic velocities of different concentrations of benzothiazolyl substituted derivatives with dioxane-water and acetone-water mixtures were measured at 30˚C by using ultrasonic interferometer at frequency 2 MHz and 4 MHz. The density, Concentration and ultrasonic velocity were used to calculate adiabatic compressibility (βs), intermolecular free length (Lf), relative association (RA) and specific acoustic impedance (Z). The results were used to discuss solute-solvent interactions.

Keywords: Ultrasonic velocity, Acoustic, interferometer, molecular interaction.

I. INTRODUCTION

In recent years the ultrasonic velocity measurement are widely used to understand the nature of molecular interactions existing between liquid mixtures[1]. From the solute-solvent interaction, structure making and breaking properties of liquids have been measured[2-4]. Ultrasonic velocity has been suitably employed in understanding the nature of molecular interaction in pure[5,6], binary[7,8] and tertiary mixtures[9]. The ultrasonic technology is employed in a wide range of applications in biology, agriculture, sonochemistry, industry, medicine, material science, oceanography etc. because of its non-destructive character

Ultrasonic waves have been useful in the preparation of protein microperes, biomaterials, in the modification of polymers and polymer surfaces etc[13-14]. A literature review show that scanty of work has been done on benzothiazole derivatives in binary liquid mixture with different frequency range. The synthesis of benzothiazole derivatives[15-17] was carried out by microwave technique which was then used for ultrasonic study to determine intermolecular free length L_f, adiabatic compressibility (β_s), specific acoustic impedance (Z), relative association R_A of mixture at different concentration.

II. EXPERIMENTAL

MATERIALS AND METHOD

Substituted benzothiazole derivatives (1-Benzothiazol-2-yl-[1,2]diazetidine-3-ylidene)-4(phenyl-thiazole-2-yl)-amine (1c) and (1-Benzothiazol-2-l-[1,2]diazetidine-3-ylidene)-phenyl-amine (1d) were synthesized by

using microwave assisted technique. These derivatives were recrystallised and were used for the ultrasonic study. All weighing were made by Wensar electronic balance (±0.001g). The accuracy measurement was within ± 1% Kgm^{-3}. Multi-frequency Ultrasonic interferometer from Mittal enterprises, Model M-83 with accuracy of ± 0.03% and frequency 2 MHz and 4 MHz was used for the measurement of ultrasonic velocities of different solutions.

In the present study some thermodynamics parameters such as adiabatic compressibility (β_S), intermolecular free length (L_f), relative association (R_A) and specific acoustic impedance (Z) have been calculated with the help of following equations-

$$u = \lambda x f$$

$$L_f = K\sqrt{\beta}$$

$$\beta = \frac{1}{\rho u^2}$$

$$R_A = \left(\frac{\rho}{\rho_o}\right)\left(\frac{u_o}{u}\right)^{1/3}$$

$$Z = \rho \; x \; u$$

III. RESULTS AND DISCUSSION

In the present work, different acoustical thermodynamic parameters were determined by using ultrasonic velocity and density. These parameters were calculated at different concentrations from 0.01M to 0.000625 M of 75% binary mixture (Acetone-water and Dioxane-water) at fixed temperature (30˚C) and at different frequency. All readings were taken at 2 MHz and 4 MHz frequency. Some acoustical thermodynamic parameter were determined, Ultrasound Velocity (U), Acoustic Impedence (Z), Adiabatic compressibility (β), Relative association (R_A), Intermolecular free length (L_f).

Table. 1 Acoustic Parameters in 75 % Acetone-Water mixture (Temperature: 30˚C; Ultrasonic frequency- 2 MHz and 4 MHz)

Conc. (M)	U/m.s^{-1}	β/x10^{-10}.m^2.N^{-1}	Lf/x10^{-11}.m	Z/Kg.m^{2}s^{-1}	R_A/m^3.mol^{-1}
Frequency- 2 MHz					
1c					
0.01	1406	4.4965	4.8215	1194791	0.962
0.005	1395	4.5636	4.8869	1201682	0.960
0.0025	1388	4.6306	4.9523	1202573	0.959
0.00125	1374	4.7377	4.9978	1203463	0.954
0.000625	1367	4.7747	5.0632	1222354	0.951
1d					
0.01	1416	4.6933	4.8676	1141109	0.946

0.005	1413	4.7449	4.9708	1149921	0.943
0.0025	1411	4.8445	4.9836	1067331	0.943
0.00125	1407	4.8605	4.9902	1075461	0.941
0.000625	1406	4.8997	4.9968	1176359	0.940
Frequency- 4 MHz					
1c					
0.01	1425	3.5291	4.3738	1192922	0.984
0.005	1420	3.8947	4.5483	1221043	0.982
0.0025	1413	3.9305	4.565	1266678	0.981
0.00125	1406	4.2445	4.7092	1270482	0.976
0.000625	1405	4.4609	4.8061	1323128	0.973
1d					
0.01	1438	3.7281	4.5221	1119181	0.972
0.005	1438	4.8467	5.0326	1129754	0.969
0.0025	1418	5.1522	5.1631	1133134	0.969
0.00125	1413	5.1692	5.1703	1161220	0.967
0.000625	1405	5.253	5.2054	1303336	0.966

Table. 2 Acoustic Parameters in 75 % Dioxane-Water mixture (Temperature: 30°C; Ultrasonic frequency- 2 MHz and 4 MHz)

Conc. (M)	U/m.s^{-1}	β/x10^{-10}.m^2.N^{-1}	Lf/x10^{-11}.m	Z/Kg.m^{2}s^{-1}	R$_A$/m^3.mol^{-1}
Frequency- 2 MHz					
1c					
0.01	1479	3.2782	4.2501	1420730	0.956
0.005	1474	3.3201	4.2710	1429563	0.954
0.0025	1468	3.3953	4.3082	1444434	0.951
0.00125	1465	3.4820	4.3509	1456051	0.949
0.000625	1457	3.5262	4.3724	1462208	0.946
1d					
0.01	1491	3.3264	4.2741	1437714	0.975
0.005	1488	3.3658	4.2937	1438067	0.973
0.0025	1485	3.4123	4.3166	1441502	0.970
0.00125	1483	3.4223	4.3216	1448786	0.969
0.000625	1479	3.4319	4.3263	1459719	0.966
Frequency - 4 MHz					
1c					
0.01	1499	3.0297	4.1238	1365820	0.999

0.005	1494	3.1757	4.1984	1420942	0.996
0.0025	1488	3.3116	4.2667	1459092	0.990
0.00125	1482	3.5256	4.3721	1482163	0.985
0.000625	1475	3.8705	4.5369	1511636	0.983
1d					
0.01	1511	3.0835	4.1515	1440643	0.990
0.005	1502	3.1242	4.1723	1476681	0.997
0.0025	1495	3.1964	4.2089	1483271	0.989
0.00125	1485	3.2142	4.2179	1492716	0.985
0.000625	1477	3.4148	4.3179	1499492	0.982

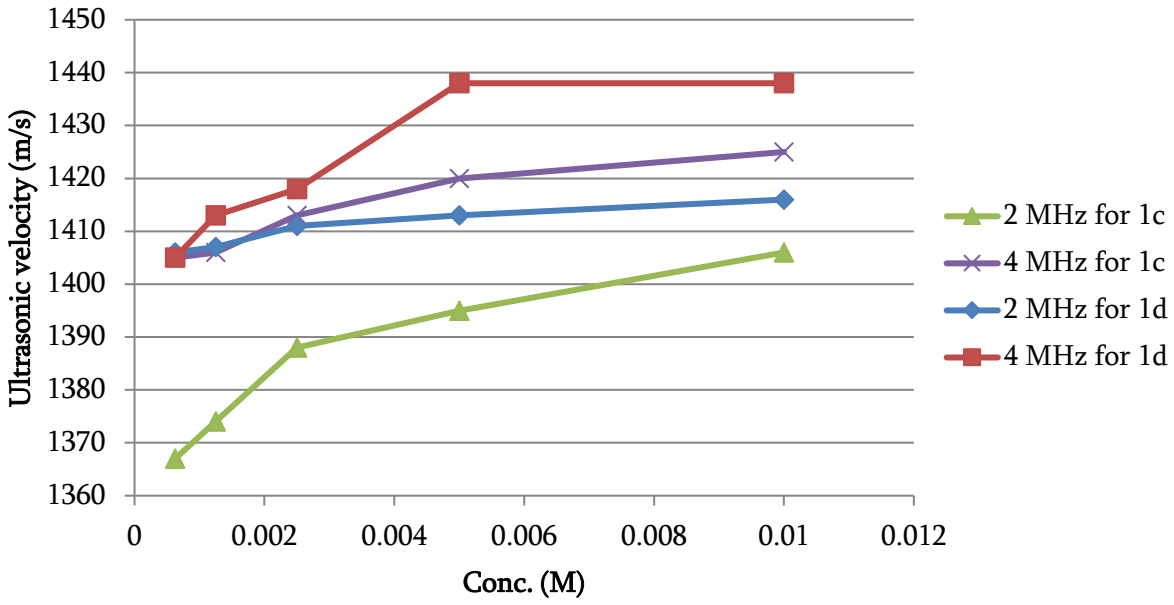

Fig.1. Utrasonic velocity Vs Concentration for compound 1c and 1d in 75% Acetone-water mixture at frequency 2 MHz and 4 MHz.

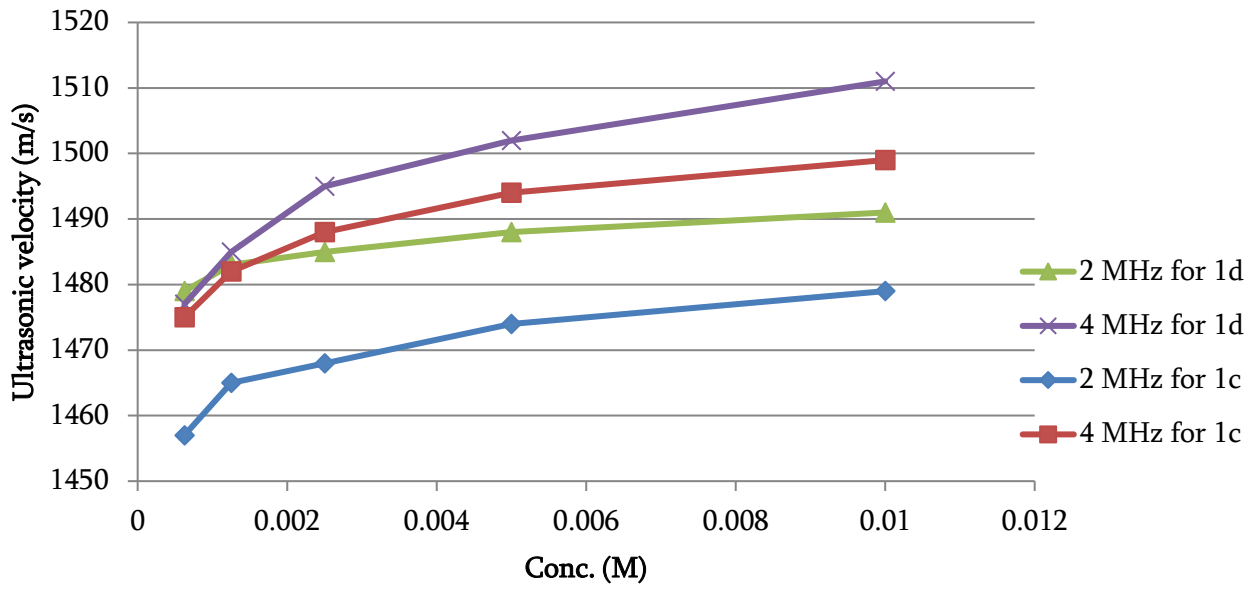

Fig.2. Utrasonic velocity Vs Concentration for compound 1c and 1d in 75% Dioxane-water mixture at frequency 2 MHz and 4 MHz.

The calculated values of some acoustic parameters are listed in Table 1 and table 2. The velocity of the solution increases as concentration increases (Fig. 1 and 2). The increase in velocity is directly proportional to the molecular weight of the solute. Hence lead to solute-solvent interaction. While increase in frequency 2 MHz to 4 MHz ultrasonic velocity also increases due to molecular interaction in binary liquid mixture.

The ultrasonic velocity (U) for both of the compounds was found to be the lowest at low concentration and the increase in ultrasonic velocity with increase in concentration. This linear increase suggests that there were maximum association among the molecules of mixture and strong solute-solvents interactions in the solution mixture. from the observation table its is reveals that the velocity values are higher in 75% Dioxane-water mixture than that of the 75% Acetone-water mixture which may be due to the greater solute-solvent interaction found in 75% Dioxane-water system. This is due to the structural differences in 75% Dioxane-water and 75% Acetone-water.

Adiabatic compressibility (β) values increase with decrease in concentration which may be due to aggregation of solvent molecules around the solute increase in solute-solvent interactions. The increase in intermolecular free length with decrease in concentration is a normal trend. The decrease in compressibility brings the molecules to a closer packing resulting into a decrease of intermolecular free length. As the ultrasonic velocity increase, intermolecular free length decrease and vice-versa. The values of acoustic impedance (Z) in 75% Dioxane-water are higher than in 75 % acetone-water system supporting the findings that solute-solvent interactions is stronger in 75% dioxane-water system. Relative association R_A decreases linearly with decrease in concentration. It is influenced by breaking of ions. The values R_A are found to be lower in acetone-water system as compared to dioxane-water system.

IV. CONCLUSION

It is observed that the compound (1-Benzothiazol-2-l-[1,2]diazetidine-3-ylidene)-phenyl-amine (1d) shows strong solute-solvent interaction with binary mixture solvent Acetone-water as well as Dioxane-water in two different frequencies at 30˚C.

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'Thiazolo Pyrimidinone' as a Versatile Nucleus in Pharmaceutical Field

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ABSTRACT

Bacterial and fungal infections represent one of the most prevalent health problems that cause functional disability, leading to lifestyle sacrifice and further complications. Upcoming needs for the clinical drugs candidates for the improvement signifies an exciting and challenging approach to improve the clinical efficacy of current drugs in the development of new therapeutic approaches. The synthesis of fused pyrimidinones and their evaluation against antibacterial and antifungal therapeutic area displayed decent antibacterial and antifungal profiles. The compounds of thiazolo pyrimidinones are considered as a promising class of bioactive heterocyclic compound having a wide range of biological activities such as anti-inflammatory, Anti- hypertensive, antibiofilm, antiviral, antioxidant, antitumor, anti-HIV, calcium channel blocking, antitubercular.

Keywords: Pyrimidinones, Therapeutic, Antibacterial, Bioactive, Antioxidant.

I. INTRODUCTION

Heterocyclic compounds containing nitrogen or sulphur as a heteroatom have been described for their biological activity against various micro-organisms. Indole unit is the key building block for a variety of compounds which have important roles in the functions of biologically significant molecules. Introduction of different groups to the modified indole structure can produce a series of compounds with numerous activities. Various 3-substituted indoles had been used as starting materials for the synthesis of a number of alkaloids, pharmaceuticals, agrochemicals and perfumes. Also 3-substituted indole derivatives possess various types of broad spectrum's biological activities such as anti-microbial, antitumor, analgesic, anti-inflammatory and antipyretic activities [1,2]. Moreover the substitution at the 3-position of the indole ring can take place by

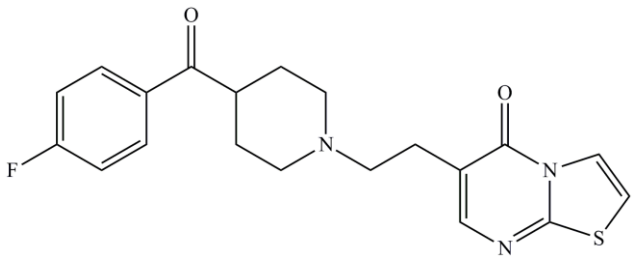
connecting an additional heterocyclic ring such as thiazolo pyrimidinone. For the rapid development of bacterial drug resistance is a very important global problem. Because of that, there is a urgent need to develop new antimicrobial drugs with potent activity in order to overcome the bacterial drug resistance. Electron-rich nitrogen and sulfur having compounds play a very important role in diverse biological activities. Thiazolo [3,2-*a*] pyrimidinone nucleus have been consistently regarded as structural similarities of biogenic purine bases and can be considered as potential purine antagonists [3].

These heterocyclic systems are the key chemical building blocks for numerous compounds that also play important roles in the functioning of biologically active molecules. As one type of those heterocyclic rings, 5*H*-thiazolo [3,2-*a*]pyrimidin-5-ones are considered a promising class of bioactive heterocyclic compounds having a wide range of biological activities such as anti-inflammatory[4,5], Anti- hypertensive [6], antifungal [7], antibiofilm [8]. These compounds also have antibacterial [9], antiviral [10], antioxidant [11], antitumor [12.13], calcium channel blocking [14], anti-HIV [15] antitubercular [16] activities. Apart from this our research group also newly synthesize earlier some potent biologically active compounds like antimicrobial [17] and anti-tubercular agents [18-20].

Bacterial and fungal infections represent one of the most common health problem that cause functional disability and other complications. Upcoming needs for the clinical drugs candidates for the improvement signifies an exciting and challenging approach to improve the clinical effectiveness of current drugs in the development of new therapeutic approaches. Current report reveals the synthesis of fused thiazolo Pyrimidinones and their evaluation against standard antibacterial and antifungal drugs.

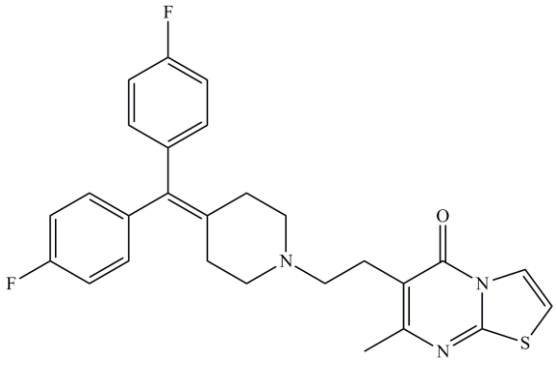
The literature on thiazolo [3,2-a] pyrimidines has been reviewed mainly due to the interesting biological and pharmaceutical activities associated with this ring system.

Meyer JH [21] and co-workers newly synthesized Setoperone (**1**) is a compound that is a ligand to the 5-HT2A receptor. It can be radio-labelled with the radioisotope fluorine-18 and used as a radio-ligand with positron emission tomography (PET). Several researcher studies have used the radiolabeled setoperone in neuroimaging for the studying different neuropsychiatric disorders, such as depression.



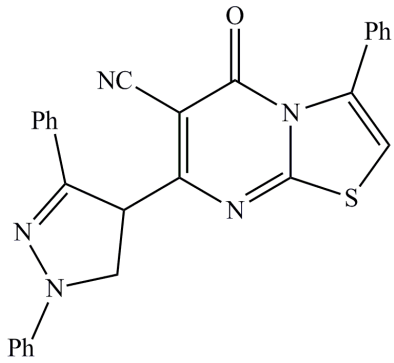
1

Nappi G [22] and co-workers newly synthesized a Ritanserin (**2**) is a serotonin antagonist with possibilities for the treatment of many neurological disorders. Ritanserin may also be effective in the prophylaxis of chronic migraine headaches.



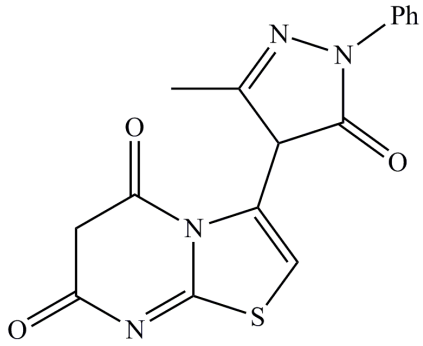
2

El-Emary T [23] and co-workers reported the synthesis and antimicrobial activities of some thiazolo [3,2-a] pyrimidine derivatives (**3**). The results revealed that all tested compounds exhibit moderate to strong activity against *E. coli* and were inactive against *B. cereus*.



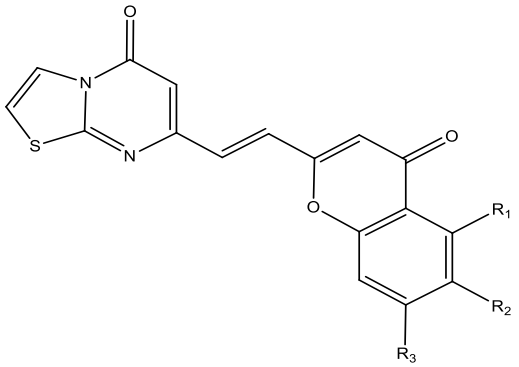
3

Youssef M [24] and co-workers have developed reactions of aminothiazole and synthesis of thiazolo [3,2-a]pyrimidine. Some of the prepared compounds were tested for their antimicrobial activity against six fungal and five bacterial species. Compound **4** showed a wide spectrum of antifungal action but a narrow spectrum of antibacterial effects with minimum inhibitory concentrations (MIC) ranging from 5 to 50 mg/cm^3.



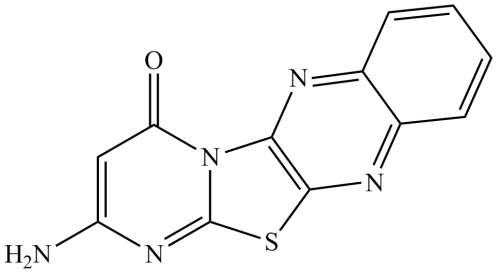
4

Babasaheb Z [25] and co-workers synthesized the hybrid molecules of fused thiazolo [3,2-a] pyrimidone-5-one with substituted chromone **5** and their subsequent evaluation as antibacterial and antifungal agent have been explained. The mono alkyl and halogen substitution on phenyl ring displayed decent antibacterial and antifungal profile when compare with standard reference.



5

Abu-Hashem A[26] and co-workers synthesized a variety of tetra and penta cyclic thiazolopyrimidine derivative and these were subjected to anti-inflammatory and analgesic activities. Compounds (**6**) and **(7)** showed similar and higher anti-inflammatory activity than diclofenac sodium. The result of analgesic activity revealed that all tested compounds exhibited significant activity.



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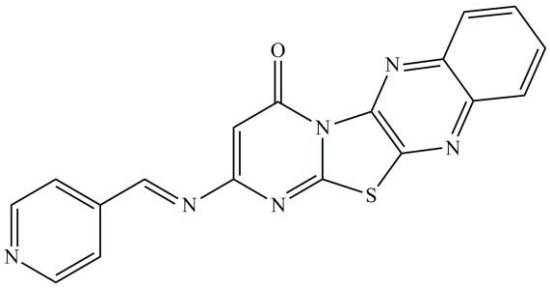
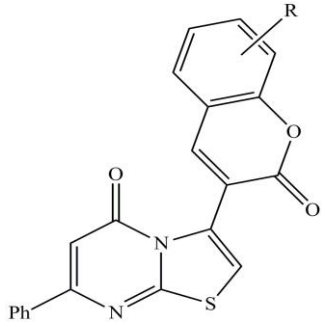


7

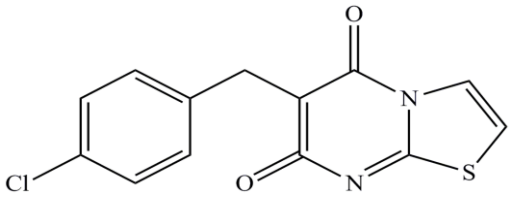
Yaragatti B[27] and co-workers synthesized a Coumariyl thiazolo-[3,2-a]-pyrimidines **8** from 3-bromoacetyl coumarin using azole and azine approaches and screened them for their antibacterial activities and have exhibited moderate to excellent growth inhibition.



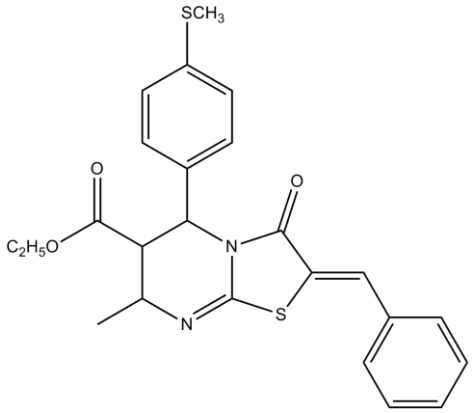
8

Zhao H [28] and co-workers synthesized a Thiazolopyrimidine **9** is used in the manufacture of a medicament for the therapy of hyperalgesic pain conditions and their symptoms.

9

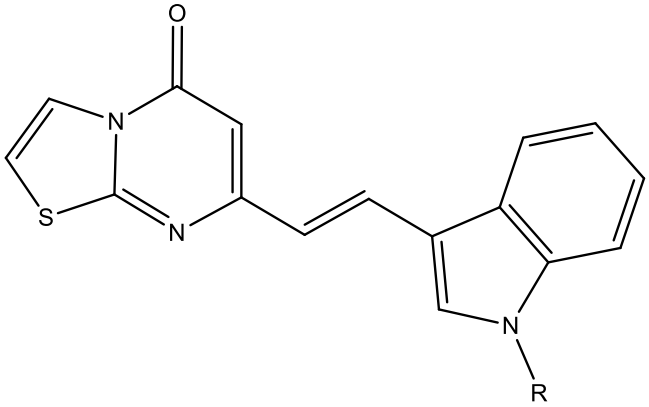


Ashok M [29] and co-workers have reported a new series of new 2-(arylidine)-5-(4-methylthiophenyl)-6-carboethoxy-7-methyl-5*H*-thiazolo[3,2-*a*]pyrimidine-3(1*H*)-ones. The newly synthesized compound **10** was screened for their antibacterial and antifungal activities and have exhibited moderate to excellent growth inhibition of bacteria and fungi.



10

Babasaheb Z [30] and co-workers synthesized series of novel thiopyrimidin-5-one **11** as antimicrobial and antifungal agents. The synthesized compounds after structural illustrations were subsequently subjected for their antimicrobial and antifungal studies. As results, all the synthesized compounds displayed almost comparable antifungal profile, moreover, some compounds were found to be superior in *Aspergillus niger* and *Candida albicans* when compared with flucanazole as standard reference. Similarly, in antibacterial evaluation, propenyl substituted was superior derivative exhibited good performance with excellent antibacterial properties when compared with ciprofloxacin as standard reference.



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II. CONCLUSION

Due to the presence of sulphur and nitrogen in the heteroaryl compounds skeleton, they show various biological activities. Pyrimidine and fused pyrimidine are the important heterocyclic compounds which show promising pharmacological activities i.e. anticancer, antioxidant, anti-tubercular, antimicrobial, antimalerial etc. Combination of thiazole nucleus with pyrimidine can be a potential therapy for the treatment of large

number of diseases because thiazole nucleus has been showing different biological activities such as antihypertensive, antibacterial, anti-inflammatory, hypnotic etc.

These applications have motivated researchers a continuous search for the synthesis of new compounds in this field and ready to the appearance of some new drugs in the market.

III. ACKNOWLEDGMENTS

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Binary Excess Molar Volumes (V^E) and Viscosity Deviations (Δ_η) of Benzaldehyde with N-Propanol at Temperatures- 298.15, 308.15 and 318.15 K

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ABSTRACT

Binary excess molar volumes and viscosity deviations of benzaldehyde with n-propanol are determined by measuring densities and viscosities over the range of all compositions at three temperatures 298.15, 308.15and 318.15 K. Other thermodynamic parameters like molar volumes Vm and excess free energies of activation of viscous flow ΔG*E of these binary mixtures are also estimated by using the experimental data. All estimated values of these properties are correlated using the Redlich-Kister polynomial equation to obtain their coefficients and standard deviations. It is that in all cases the experimental data obtained fitted with the values correlated by the corresponding model very well. The molecular interactions existing between the components are also discussed in this paper.

Keywords: Excess molar volume, Viscosity deviation and excess free energies of activation of viscous flow ΔG*E.

I. INTRODUCTION

Measured and estimated values are extremely useful in the processing and designing of equipment in chemical industries. Unusual behavior of binary mixtures of aldehydes and alcohols withdrawn considerable attention of many researchers. Aim of the present study is to produce the data on the density, viscosity, Viscosity deviations ($\Delta\eta$), molar volumes V_m, excess molar volumes V^E and excess free energies of activation of viscous flow ΔG^{*E} of given binary liquid mixtures. The volumetric studies of binary liquid mixtures and their analysis in terms of interpretative models constitute a very interesting subject. The characteristic study of these mixtures through their thermodynamic, volumetric and transport properties is important from the point of understanding mixing behavior of these mixtures [1-9]. Hence, the viscosities and some thermodynamic parameters of binary mixtures of benzaldehyde with n-propanol at three temperatures i.e. 298.15, 308.15 and 318.15 K are determined in the present paper. A detailed study of fluid properties of non-aqueous solutions is essential in many chemical and industrial applications. 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 [10-13]. 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 many industrial processes [14].

Density (ρ) and viscosity (ŋ) of binary mixtures of Benzaldehyde and n-propanol are measured at various temperatures 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}) are calculated from the experimentally measured former data. Estimated values of deviation in viscosity and excess functions were fitted to the Redlich-Kister polynomial equation and the results are analyzed and eventually molecular interactions are studied.

II. MATERIAL AND METHODS

Benzaldehyde and n-propanol used were of analytical grade and are obtained from SD fine chemicals India. The benzaldehyde and n-propanol were again purified for obtaining it in 99% purity, as reported in literature [3-4]. Binary mixtures of benzaldehyde and n-propanol at various compositions were prepared by mass using electronic digital balance with an accuracy of ± 0.0001 gm. The uncertainty in the mole fraction of the binary mixtures was estimated to be less than ± 0.0001. Density and viscosity measurements were carried out using a thermostatically controlled water bath (Kinematic Viscosity Bath) to maintain temperature constant. The binary liquid mixtures of different known compositions were prepared in stopper measuring flasks. The density and viscosity were measured as a function of composition of the binary liquid mixture at 298.15 K. The density was determined using a single-arm pycnometer with precision in density of $1x10^{-3}$ gm cm^{-3}. The weight of the sample was measured using electronic digital balance with an accuracy of ± 0.0001 gm. An Ubbelohde viscometer was used for the viscosity measurement. The flow time measurements were made using an electric stopwatch with a precision of ± 0.015. An average of 4 or 5 sets of flow times was taken for each liquid mixture [15-20].

III. RESULTS AND DISCUSSION

Experimentally measured values of density and viscosity are used to calculate excess molar volumes and viscosity deviations of the binary mixtures of benzaldehyde and n-propanol by using following 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 benzaldehyde and n-propanol respectively. ρ_m and η_m are the density and viscosity of the binary mixture.

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

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

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 benzaldehyde and n-propanol respectively.

V_m is obtained from equation 4 below.

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

Where η_1, η_2 and η_m are the viscosity of benzaldehyde and n-propanol respectively [21-27].

The densities and viscosities of given binary liquid mixtures of benzaldehyde and n-propanol over an entire range of composition at different temperatures i.e. 298.15, 308.15 and 318.15 K and calculated the data of deviation in viscosity ($\Delta\eta$), 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 (1,2,3)** as below.

Table-1: The density, viscosity, deviation in viscosity ($\Delta\eta$), excess molar volume (V^E) & excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) of benzaldehyde with n-propanol at **298.15 K.**

x_1	ρ	η	$\Delta\eta$	V_m	V^E	ΔG^{*E}
0	0.8051	1.9311	0	74.6429	0	2163.981
0.0785	0.8291	1.8707	-0.0125	76.85008	0.0860	2492.36
0.1608	0.8529	1.8094	-0.0236	79.14114	0.1521	2702.934
0.2473	0.8767	1.7485	-0.0317	81.5327	0.2074	2862.738
0.3382	0.9006	1.6876	-0.0372	84.01642	0.2344	2982.018
0.4340	0.9245	1.6269	-0.0395	86.61018	0.2421	3063.034
0.5349	0.9484	1.5649	-0.0399	89.32552	0.2409	3102.388
0.6414	0.9723	1.5022	-0.0367	92.17325	0.2114	3093.749
0.7541	0.9962	1.4447	-0.0265	95.1668	0.1605	3028.31
0.8734	1.0201	1.3838	-0.0146	98.31985	0.0906	2871.414
1	1.0442	1.3213	0	101.6582	0	2496.524

Table: 2: The density, viscosity, deviation in viscosity ($\Delta\eta$), excess molar volume (V^E) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) benzaldehyde with n-propanol at **308.15 K.**

x_1	ρ	η	$\Delta\eta$	V_m	V^E	ΔG^{*E}
0	0.7915	1.5444	0	75.6442	0	2381.981
0.0785	0.8158	1.5148	-0.0156	77.8513	0.117	2710.36
0.1608	0.8402	1.4862	-0.0267	80.1424	0.1831	2920.934

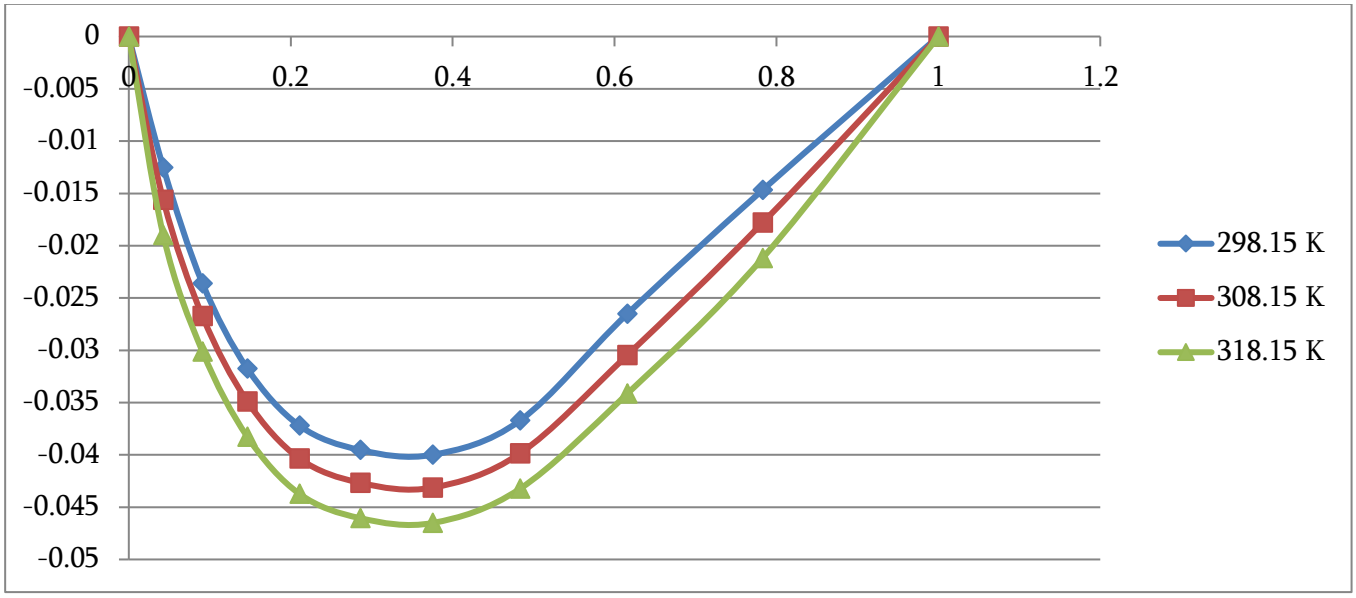
0.2473	0.86459	1.4577	-0.0349	82.534	0.2384	3080.738
0.3382	0.8889	1.4295	-0.0403	85.0177	0.2654	3200.018
0.4340	0.9133	1.4016	-0.0426	87.6114	0.2731	3281.034
0.5349	0.9376	1.3705	-0.0431	90.3268	0.2719	3320.388
0.6414	0.9620	1.3406	-0.0398	93.1745	0.2424	3311.749
0.7541	0.9863	1.3124	-0.0304	96.1681	0.1915	3246.31
0.8734	1.0107	1.2835	-0.0178	99.3211	0.1216	3089.414
1	1.0361	1.2452	0	102.6595	0	2714.524

Table: 3: The density, viscosity, deviation in viscosity ($\Delta\eta$), excess molar volume (V^E) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) benzaldehyde with n-propanol at **318.15 K**.

x_1	ρ	η	$\Delta\eta$	V_m	V^E	ΔG^{*E}
0	0.7733	1.1121	0	76.7645	0	2618.981
0.0785	0.8024	1.1171	-0.0191	78.9716	0.1622	2947.36
0.1608	0.8274	1.1217	-0.0301	81.2627	0.2283	3157.934
0.2473	0.8525	1.1265	-0.0382	83.6543	0.2836	3317.738
0.3382	0.8775	1.1312	-0.0437	86.1380	0.3106	3437.018
0.4340	0.9026	1.1358	-0.0460	88.7317	0.3183	3518.034
0.5349	0.9277	1.1406	-0.0465	91.4471	0.3171	3557.388
0.6414	0.9527	1.1456	-0.0432	94.2948	0.2898	3548.749
0.7541	0.9778	1.1502	-0.0341	97.2884	0.2489	3483.31
0.8734	1.0029	1.1546	-0.0211	100.4415	0.1668	3326.414
1	1.0279	1.1612	0	103.7798	0	2951.524

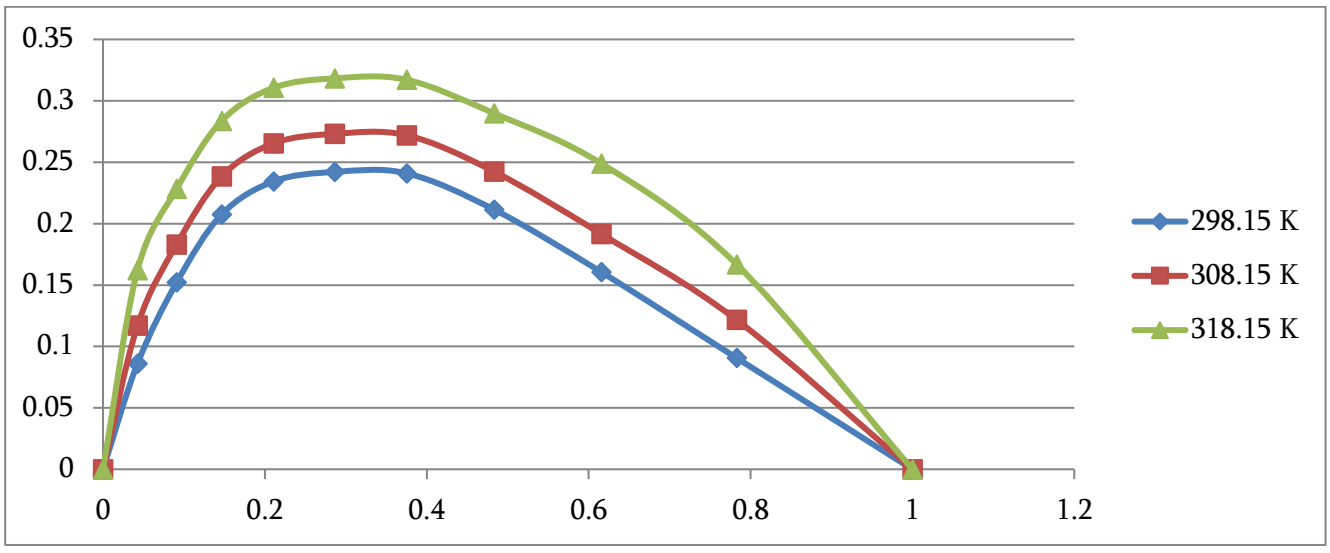
The plot of deviation in viscosity, excess molar volumes, excess Gibbs free energy of activation of viscous flow against mole fraction at 298.15, 308.15 and 318.15 K for binary mixtures of benzaldehyde with n-propanol are represented as below (**Figure-1,2,3).**

Figure-1: The plot of deviation in viscosity against mole fraction at 298.15, 308.15 and 318.15K for binary mixtures of **benzaldehyde with n-propanol.**



The plot of deviation in viscosity against mole fraction at 298.15, 308.15 and 318.15 K for binary mixtures of **benzaldehyde with n-propanol** reveals that deviation in viscosity increases with increase in temperature. Deviation of physical properties of liquid mixtures from the ideal behavior is the measure of the interaction between the molecules which is attributed to either adhesive or cohesive forces. The plot of deviation in viscosity against mole fraction for binary mixtures of benzaldehyde with n-propanol found to be negative at all temperatures. The negative values of the deviation in viscosity ($\Delta\eta$) suggest the existence of weak intermolecular interactions upon mixing in n-propanol. This leads to suggest that non-interactive forces are responsible for these negative interactions.

Figure-2: The plots of excess molar volumes against mole fraction for binary mixtures of **benzaldehyde with *n-propanol*** at 298.15, 308.15 and 318.15 K.



The variation of excess volumes with the mole fraction (X_1) of benzaldehyde and n-propanol at (303.15, 308.15 and 313.15) K are represented in figure-2. The excess molar volume values of the mixtures are positive and

increase when temperature increases. This shows that the excess molar volumes are always positive for all the studied temperatures. Roux and Desnoyers [19-20] suggested that V^E is the resultant contribution from several opposing effects.

IV. CONCLUSION

From the experimental values and graphs is observed that viscosity of all binary mixtures of benzaldehyde and n-propanol are found to be decreased with increase in temperature. The deviation in viscosity of the binary systems of benzaldehyde with n-propanol are observed negative and it decreases with increase in temperature while excess molar volumes are positive for all binary systems. As the temperature increases V^E also increases because of inconvenient interstitial accommodation due to thermal agitations among benzaldehyde and n-propanol. There is intermolecular interaction among the components of the binary mixtures leading to possible hydrogen bond formation between unlike molecules confirming intermolecular hydrogen bond formation between benzaldehyde and n-propanol mixtures. Excess molar volumes (V^E) and the viscosity deviations ($\Delta\eta$) were used to predict the intermolecular interactions in the mixtures. In case of all binary mixtures it was found that the experimental data obtained, matches with the McAllister model and Redlich-Kister equation with a certain degree of similarities.

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Synthesis, Characterization, Antibacterial and Antifungal Activities of Manganese (II) Complex of (E)-1-(2,6-dihydroxyphenyl)-3-(5-methylfuran-2-yl)prop-2-en-1-one Ligand

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ABSTRACT

TheManganese (II)metal complex has been synthesizedby using novel(E)-1-(2,6-dihydroxyphenyl)-3-(5-methylfuran-2-yl)prop-2-en-1-one ligand. The ligand was prepared by the Claisen-Schmidt condensation method of 2,6-dihydroxy acetophenone and 5-methylfurfural. The structure of the complex has been characterized by the analytical data such asElemental analysis, magnetic moment, conductivity measurement, UV-Vis spectrum, IR spectrum. Analytical data shows 1:2 stoichiometry and the magnetic moment, suggests thatMn(II) complexhasoctahedral geometry.The conductivity data revels that the complex is non electrolyte.Antibacterial and Antifungal activities of the complex with selected bacterial strain and fungal strain carried out and the results have been compared with commercial standards.The synthesized Mn(II) complex shows promising antibacterial and antifungal activity.

Keywords: Antibacterial and Antifungal activities, UV-Vis spectrum, IR spectrum,Physico-chemical property, Magnetic Susceptibility and Conductivity.

I. INTRODUCTION

Chalcones are constitute an important group of natural products, which has two aromatic rings joined by α, β unsaturated carbonyl system. Chalcones are open chain precursors for biosynthesis of flavonoids and isoflavonoids and occur mainly as polyphenolic compounds whose color changes from yellow to orange [1]. They exist as either Trans (E) or Cis (Z) isomers having two aromatic rings those are joined by a three carbon alpha beta unsaturated system. In case the E isomer is more stable from the perspective of thermodynamics, which makes it the predominant configuration among the chalcone. The configuration of the Z-isomer is unstable due to the strong steric effect between the carbonyl group and the A ring [2].

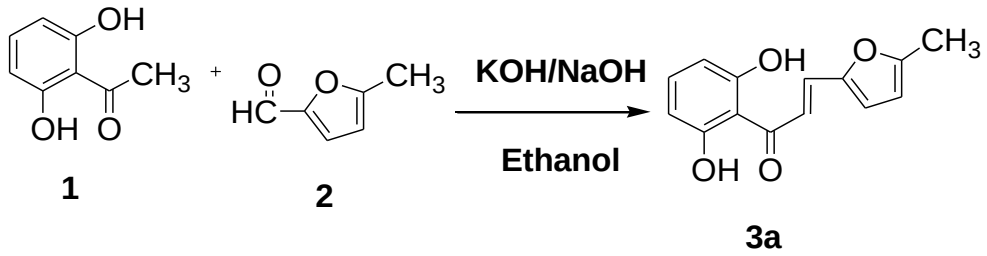
The electrophilic nature of the alpha-beta unsaturated carbonyl system, this moiety is capable of forming the irreversible bond with biological macromolecules, resulting in a number of toxic effects, such as allergenic reactions, carcinogenicity, and mutagenicity[3].

The metal complexes possess interesting biochemical properties, such as antioxidant, antimalerial,antitumor, anti-fungal and antimicrobial activities[4].

II. MATERIALS AND METHODS

2.1 Synthesis of (E)-1-(2,6-dihydroxyphenyl)-3-(5-methylfuran-2-yl)prop-2-en-1-one ligand (3a):

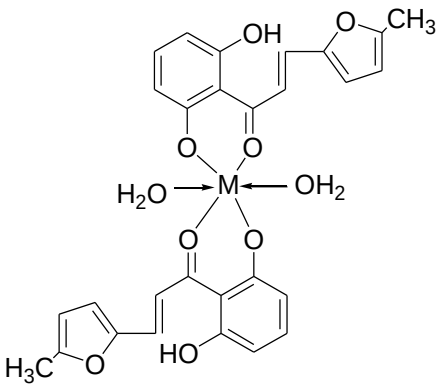
The reagents used for preparation of(E)-1-(2,6-dihydroxyphenyl)-3-(5-methylfuran-2-yl)prop-2-en-1-one (**3a**)are of A.R. grade. The mixture of 2,6-dihydroxy acetophenone (**1**) (0.01 mol) and 5-methyl-Furaldehyde (**2**) (0.01 mol) is dissolved in ethanol (20 mL) and then sodium hydroxide 10 mL (40%) was added to it. The mixture was stirred for overnight till brown color precipitation was observed. The progress of the reaction was monitored by Thin Layer Chromatography by using eluent Petroleum ether: Ethyl acetate (7:3), from thin layer chromatography the completion of the reaction is observed. After completion of the reaction, the contents were poured into ice cold water and then acidified by dil.HCl. The solid obtained was filtered and crude product (**3a**) was recrystallized from ethanol to give the chalcone [5]. (**Scheme-1**)



Scheme-1: Synthesis of (*E*)-1-(2,6-dihydroxyphenyl)-3-(5-methylfuran-2-yl)prop-2-en-1-one Ligand

2.2 Synthesis of Metal Complex:

The solution of 0.02 mole of (E)-1-(2,6-dihydroxyphenyl)-3-(5-methylfuran-2-yl)prop-2-en-1-one (**3a**) ligandwas taken in round bottom flask containing 30 ml of anhydrous methanolicsolution and boiled for 10 minutes. A hot solution of 0.01 mole, ofManganese acetate in 20 ml of methanol was added drop wise to the solution of the chalcone of 5-methylfurfural (**3a**)to this reaction mixture, 10% alcoholic ammonia was added up to slightly alkaline pH. The complex was precipitated atpH 8 range. The pH8-10range was definite for these complexes [6]. 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 synthesized metal complex (**4a**) was determined by Thiele's melting apparatus. The structure of Mn (II) complex is shown in **Figure-1**.



M= Mn (II)

(4a)

Figure-1: Structure of Mn (II) complex (4a)

III. RESULTS AND DISCUSSION

3.1 Physical parameters:

Metal complex of Manganese (II)with (E)-1-(2,6-dihydroxyphenyl)-3-(5-methylfuran-2-yl)prop-2-en-1-one (**3a**)was reddish brown in color. The complex was precipitated atpH 8 range, having Melting point 310^{0}C. The complex is insoluble in water and soluble in DMSO, DMF [7].

3.2 Magnetic susceptibility, solutionconductivity and electronic absorption spectral data

3.2.1: Magnetic susceptibility:

The magnetic moment of Mn(II) complexes 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) complexes by earlier workers [8].

Metal 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
Mn(II) Complex	4.37	5.86	24630(406)	29411(340)	33557(298)

3.2.2: Solutionconductivity and electronic absorption spectral data:

The solution conductivities of 10^{-3} M solution of metal complex in DMSO were measured on EQUIPTRONICSdigital 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) complexes in DMSO indicates their non-electrolytic nature.

Figure-2: Electronic absorption spectrum of synthesizedMn (II) complex

The electronic absorption spectra of Mn(II) complexes 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 [9-10]. (**Figure-2**).

3.3 CHO analysis of synthesized complex (4a):

The carbon, hydrogen, oxygen, Manganese metal percentage in Mn (II) complex 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: CHO analysis of synthesizedMn (II) complex

Metal complex	Chemical formula	Mol. Wt.	Elemental analysis :% found (calculated)			
			C	H	O	M
Manganese (II)	$[C_{28}H_{26}O_{10}Mn]$	577	58.23 (65.50)	4.53 (5.10)	27.70 (18.70)	9.51 (10.70)

3.4Infra-red spectrum:

The IR spectrum of α, β-unsaturated carbonyl group has characteristic bands of chalcone at prominent bands between 1625 to 1650 per cm [11-12]. The characteristic peaks in infra-red spectrum give the presenceof 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 metal complex of Manganese (II)with (E)-1-(2,6-dihydroxyphenyl)-3-(5-methylfuran-2-yl)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 metal complex of Manganese (II)with(E)-1-(2,6-dihydroxyphenyl)-3-(5-methylfuran-2-yl)prop-2-en-1-one is represented in table number (2) and the IR spectrum in **Figure-3.**

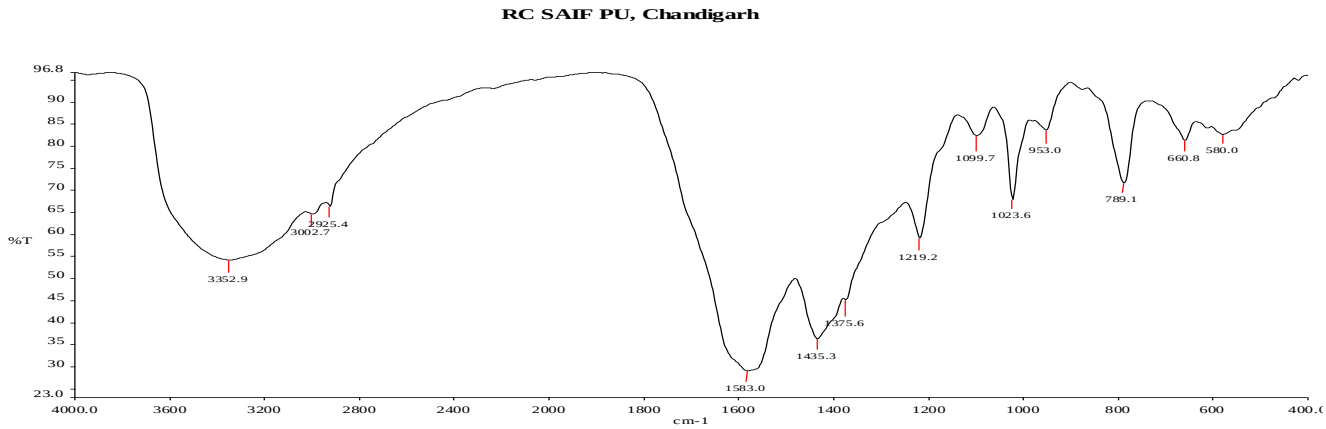


Figure-3: IR spectrum of metal complex of Mn (II)with(E)-1-(2,6-dihydroxyphenyl)-3-(5-methylfuran-2-yl)prop-2-en-1-one Ligand

Table-2: IR spectral data ofMn (II) complex with(E)-1-(2,6-dihydroxyphenyl)-3-(5-methylfuran-2-yl)prop-2-en-1-one Ligand:

Ligand/ Metal complexes	**υ (OH) cm^{-1}**	**υ (H_2O) cm^{-1}**	**υ (-CO-CH=CH-) cm^{-1}**	**υ (-C=O in pyron ring) cm^{-1}**	**υ (C-O-C) cm^{-1}**	**υ (C=C) cm^{-1}**	**Aromatic Ring (C=C) cm^{-1}**	**υ (M-O) cm^{-1}**
Chalcone	3420	-	1623	-	1095	1558	1439	-
[$Mn(A_2)_2$]	3003	3353	1583	-	1023	1435	1375	580

In chalcone ligand, there is a presence of phenolic -OH is confirmed by peak at 3420 cm^{-1} in the spectra of Mn(II) complexes, that is the complete disappearance of the peak at 3420 cm^{-1} suggests absence of phenolic group -OH indicates its coordination. (C-O-C) is shifted to a lower wave number compared with the free ligand. The new band is observed at 3352 cm^{-1} which is due to the -OH intense broad band of coordinated water molecules. In Mn(II) complexes new band is observed at 580 cm^{-1} due to the (M-O) bond. The band assigned to the carbonyl group (1623 cm^{-1}) is shifted to a lower wave number compared with that of free ligand, (1583cm^{-1}) proving its coordination. In the spectra of Mn(II) complexes, the strong bands appeared in the range of 1435-1490 cm^{-1} can be assigned to (C=C) stretching vibrational mode. These bands are found to remain unchanged in the complexes from their corresponding ligands, which indicate the non-involvement of (C=C) group in complex formation. The bands due to (C=C) aromatic ring vibrations may remain the same or shift their position as a result of change in the distribution of electrons and molecular environment due to introduction of a metal ion.

Omar-Al-Obaidi was assigned in flavone that, In the FT-IR spectra of ligands, the presence of phenolic –OH and the carbonyl group is confirmed by peaks at 3401 cm^{-1} and 1600 cm^{-1} however in the spectrum of the complexes that is the complete disappearance of the peak at 3401 cm^{-1} suggests absence of phenolic group –

OH which indicates its coordination. The band assigned to the carbonyl group is shifted to a lower wave number comparing with that of free ligand, proving its coordination[13].

3.7Antibacterial and Antifungal Activity:

3.7.1: Antibacterial Activity: The antibacterial activity of Mn (II) complex 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*, Shigellaboydii*ATCC 12034*, Enterobacteraerogenes*ATCC13048*, Pseudomonas aerogenosa*ATCC9027, *Salmonella abony* NCTC6017 were the Gram-negative pathogens used in this study.

3.7.2: Antifungal Activity: Antifungal activity was assayed by cup plate agar diffusion methodby measuring inhibition zones in mm. *In vitro*antifungal activity of synthesized compound and standard have been evaluated against strains of the fungal toxicity ofMn (II) complexwas studied *in vitro* against *Aspergillusniger*ATCC 16404*, Saccharomyces cerevisiae* ATCC 9763, *Candida albicans* ATCC10231 fungal pathogens at fixed 1% concentration.

From the result of antibacterial and antifungal activities of ligand 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

TheMn (II) complex was colored, soluble in most of the organic solvent. The stoichiometryratios of the metal complexwasobtained has been found to be 1:2.Solution conductivity of this metal complexshows non-electrolytic nature. The CHO analysis gives C, H, and O percentage in the metal complex. The magnetic moment, UV and IR spectral data suggests that Mn (II) has Octahedral geometry.From the antibacterial and antifungal activities of ligand and complex, it is clear that the complex shows enhanced antibacterial and antifungal activities than ligand.

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Role of Platinum Metal as an Anticancer Drug

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ABSTRACT

Metals are essential cellular components selected by nature to function in several indispensable biochemical processes for living organisms. Metals are endowed with unique characteristics that include redox activity, variable coordination modes, and reactivity towards organic substrates. Due to their reactivity, metals are tightly regulated under normal conditions and aberrant metal ion concentrations are associated with various pathological disorders, including cancer. For these reasons, coordination complexes, drugs become very attractive probes as potential anticancer agents. The use of metals and their salts for medicinal purposes, from iatrochemistry to modern day, has been present throughout human history. The discovery of cisplatin, cis-[PtII(NH3)2Cl2], was a defining moment which triggered the interest in platinum(II)- and other metal-containing complexes as potential novel anticancer drugs. Other interests in this field address concerns for uptake, toxicity, and resistance to metallodrugs. This review article highlights selected metals that have gained considerable interest in both the development and the treatment of cancer. For example, copper is enriched in various human cancer tissues and is a co-factor essential for tumour angiogenesis processes. However the use of copper-binding ligands to target tumour copper could provide a novel strategy for cancer selective treatment. The use of nonessential metals as probes to target molecular pathways as anticancer agents is also emphasized. Finally, based on the interface between molecular biology and bioinorganic chemistry the design of coordination complexes for cancer treatment is reviewed and design strategies and mechanisms of action are discussed.

I. INTRODUCTION

The medicinal uses and applications of metals and metal complexes are of increasing clinical and commercial importance. Monographs and major reviews, as well as dedicated volumes, testify to the growing importance of the discipline. Relevant reviews are to be found throughout annual series, for example Metal Ions in Biological Systems and Coordination Chemistry Reviews. The field of inorganic chemistry in medicine may usefully be divided into two main categories: firstly, ligands as drugs which target metal ions in some form, whether free or protein-bound; and secondly, metal-based drugs and imaging agents where the central metal

ion is usually the keyfeature of the mechanism of action.This latter class may also be conveniently expanded toinclude those radionuclide's used in radioimmunoimaging and radio immunotherapy. A reasonable estimate of the commercial importance is approaching US$5 billion annuallyfor the whole field. A list of clinically used chelating agents may be found in most pharmacopoeias,While new chelating agents continue to be sought. The use of chelating agents in the treatmentof Wilson's disease is a good example of how medical problems due to free metal ion (Cu-II)toxicity may be ameliorated by chelating agents. The extensive work on matrix metalloproteinase'slikewise represents a case study in design of small organic ligands as drugs to inactivate ametalloenzyme. Over expression of these zinc-containing enzymes is associated with severalDiseases including arthritis and cancer, so inhibition of the zinc active site is a reasonable drugdevelopment strategy. Indeed, enzymatic zinc is an attractive target because of the diversity of itsstructural and catalytic roles in enzymes.This chapter is restricted to the uses of well-definedinorganic compounds as drugs and chemotherapeutic agents. Current uses and prospective uses, aswell as those of essentially historical relevance, are covered. An important distinction to be made isbetween drugs as chemotherapeutic agents, whose function is to kill cells and drugs acting by apharmacodynamic mechanism—whose action must be essentially reversible and or short-lived.

Anticancer Platinum complex

Platinum (II) complexes has been used as anti cancer drugs since long, among them cisplatin has proven to be a highly effective chemotherapeutic agent for treating various types of cancers. This prototypical anticancer drug remains one of the most effective chemotherapeutic agents in clinical use. Cisplatin, (cis-[PtCl2 (NH3)2], also known as cis-DDP), (**Fig. 1**) is perhaps the best known example of a small molecule metal-containing drug. Cisplatin enters cells by passive diffusion and also, as recently discovered, by active transport mediated by the copper transporter in yeast and mammals. The cytotoxicity of cisplatin originates from its binding to DNA and the formation of covalent cross-links. Binding of cisplatin to DNA causes significant distortion of helical structure and results in inhibition of DNA replication and transcription. Inside the cell it interacts with a number of other negatively charged biomolecules besides DNA such as proteins, sulphur-containing compounds like metallothioneins and glutathione that sequester heavy metals like Pt and remove it from the cell.DNA damage and subsequent induction of apoptosis may be the primary cytotoxic mechanism of cisplatin and other DNA-binding antitumor drugs.Cisplatin is used for the treatment of testicular cancer, epithelial ovarian cancer, gestational trophoblastic tumours, and small cell lung cancer as well as for cervical, nasopharyngeal, oesophageal, and head and neck cancers. Despite this success, the clinical use of cisplatin against this and other malignancies is severely limited by dose-limiting side-effects such as n hepatic- and nephrotoxicity. In addition to the high systemic toxicity, inherent or acquired resistance is a second problem often associated with platinum-based drugs, which further limits their clinical use. In an effort to address these shortcomings, 2nd and 3rd generation platinum analogs, namely carboplatin and oxaliplatin (**Fig. 1**)have been designed and clinically approved to maintain a more manageable toxicity profile.

Carboplatin is second generation drug which have lesser side effect. Carboplatin is effective in the treatment of ovarian carcinoma, lung, and head and neck cancers, while oxaliplatin is clinically approved for the

treatment of colorectal cancer, which is resistant to cisplatin. Picoplatin (cis-PtCl2(NH3)(2-pic), previously AMD473; **Figure 1**) is a new generationSterically hindered platinum cytotoxic compound that provides a differentiated spectrum of activity against a wide range of human tumour cell lines and an improved safety profile. It is designed to overcome acquired resistance to cisplatin in vitro and in human tumour xenografts L-NDDP (Aroplatin; **Figure 1**) is a liposomal formulation of cis-bis-neodecanoato-trans R, R-1,2-diaminocyclohexane platinum (II), a structural analogue of oxaliplatin.

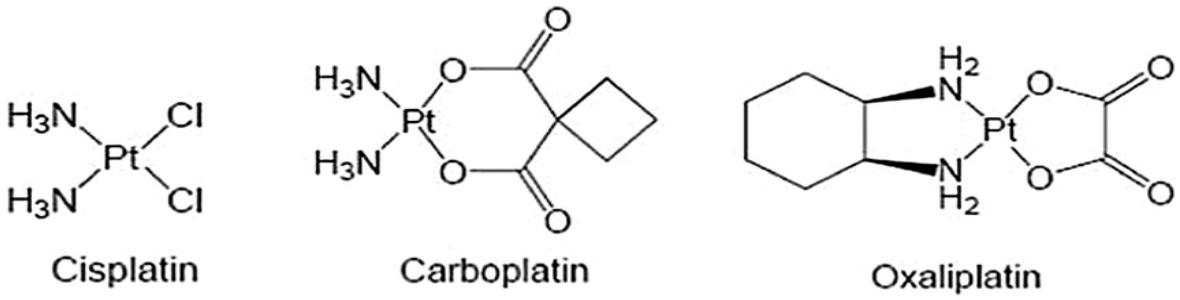

Figure 1: Platinum Containing Drug

Copper as an Anticancer drug.

One of the transition metal, whose complexes are extensively tested for antitumor application, is copper. Copper is a trace element essential for human life. It is a building element of several important enzymes (e.g. superoxide dismutase, cytochrome oxidase, tyrosine's) and it regulates the intracellular redox potential, while its complexes possess antibacterial, antifungal, antiviral, anti-inflammatory and anticancer properties. As potential anticancer Drugs, there are currently extensively studied mainly complexes of copper (II). There are only few complexes of copper (I) in the literature, whereas they also show a very strong cytotoxic activity against tumour cells in vitro.

Anticancer Activity of Copper

Anticancer activity of copper Over 95% of copper (both Cu(II) and Cu(I)) that is present in serum is bound to ceruloplasmin (peroxidise). However, it is not responsible for transporting copper inside the cell. Before they enter the cell, copper(II) ions are reduced to copper(I) by metalo-reducatases located on the cell's surface. Cu+ions are transported into the cell mainly by a specific copper transporter . The independent system of entering the cell, enables biologically active copper compounds to penetrate the cell surface without binding to other agents as opposite to coordination compounds of other metals. Anticancer activity of copper (I) compounds may be a result of different mechanisms. They are described in the following paragraphs of this review. Anticancer activity of copper complex compounds is related to their ability to produce reactive oxygen species (ROS). Copper(I) ions can reduce hydrogen peroxide to hydroxyl radical. Copper (II) ions may in turn be reduced to Cu(I) by superoxide anion(O2•-),or glutathione. Therefore, it can be concluded that the production of reactive oxygen species such as OH•are driven by the copper, regardless of the form in which it is initially introduced into the body – Cu+, or Cu2+[2, 5].Superoxide anion (O2•-) is the product of reduction of the molecular oxygen that occurs in many biological processes. It is converted into hydrogen peroxide

through dismutation. Both of these forms of ROS lead to the formation of another type of reactive oxygen species – the hydroxyl radical (OH•). It occurs in a reaction catalyzed by copper (or iron) ions. This radicals believed to be the main factor causing DNA damage in cells under oxidative stress Copper compounds are also thought to have nuclease activity. The ability of copper to cut a DNA helix has been proved in studies conducted with the use of Cu(I) complexes with two molecules of 1,10-phenanthroline (phen). [Cu(phen)2]+was initially noncovalently bound to DNA. In this form, it was oxidized to a copper (II) compound in the presence of hydrogen peroxide. The final result of those processes was cutting DNA or RNA strands into fragments. The postulated factor directly responsible for cutting the DNA was an adduct in which [Cu(phen)2]2+was coordinated with the hydroxyl radical OH•and linked by non-covalent interactions with DNA .Copper compounds coordinated to phenanthroline skeleton ligands (see Fig. 1), such as [Cu(dmp)2]+, are thought to have the ability of intercalation. Furthermore, it was indicated that the [Cu(dmp)2]+(dmp=2,9-dimethyl-1,10-phenanthroline) can be an inhibitor of the process of DNA transcription [9]. The [Cu(bcp)2]+(bcp=2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) is in turn believed to possess the ability of forming bridges between double-stranded fragment of DNA and another fragment of such a type

Mononuclear compounds

In 1987 Berners-Price and co-workers [11] presented copper(I) complexes with molecular formula [Cu(P-P)]Cl, where central Cu+ion was coordinated with two molecules of bidentate phosphine. The structures of these complexes are presented in Figure 1

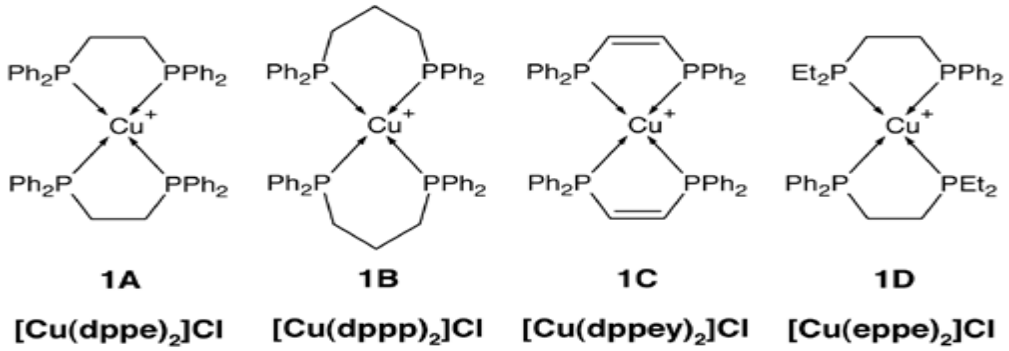

Fig. 1. The structures of copper(I) complexes with bidentate phosphine

II. CONCLUSION

Recent advances in medicinal inorganic chemistry gives significant prospects for the utilization of metal complexes in the development anticancer drugs. Platinum complexes cisplatin has proven to be a highly effective chemotherapeutic agent for treating various types of cancers. Besides the established use to treat arthritis, gold complexes exhibit anticancer property. Since higher concentrations of copper is a common trademark of many human tumours, targeting tumour cellular copper with copper chelating agents emerged as an exciting new approach in cancer therapy Antiproli-ferative activity for cervical cancer cells was proved

for copper complexes. Ruthenium complexes with antitumor activity are also emerging rapidly. Since metals are endowed with unique properties that are absent in conventional carbon-based drugs, the positive trend in anticancer drug discovery can be continued for the design of new metal based drugs.

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Role of Pincer Ligand in Organometallic Chemistry

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ABSTRACT

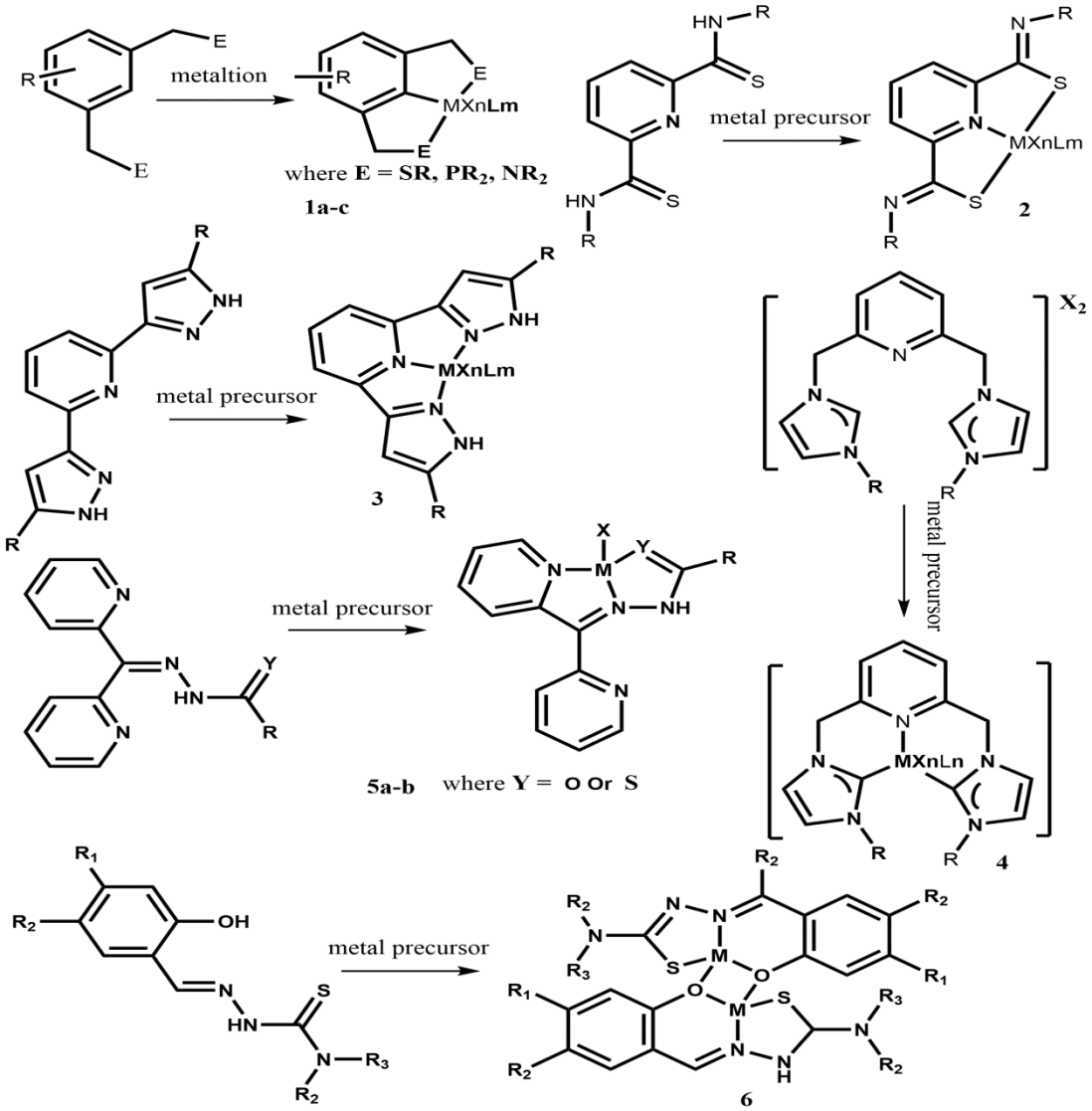
In this article we have studied the role of pincer ligand in organometallic chemistry. Pincer ligand is a type of chelating agent that bind tightly to three adjacent coplanar sites usually derived from tridentate six-electron donor on a transition metal in a meridian configuration transition metal complexes. The resulting pincer complexes enjoy a high thermal stability due to this tridentate coordination. Pincer ligands are of special interest and are the subject of this review. Over the years a plethora of these ligand systems have been synthesized and explored over the years, driven by promising results and potential scope for further development in the field. We also have been studied the application of palladacycles in bond formation reactions.

Keywords: organometallic; transition metal; cyclometalation; pincer ligands; chelating agent; palladacycles

I. INTRODUCTION

In chemistry pincer ligand is a type of chelating agent that bind tightly to three adjacent coplanar sites usually derived from tridentate six-electron donor on a transition metal in a meridian configuration transition metal complexes. Pincer ligands bind to the metal center via a central donar atom (traditionally an anionic carbon donar atom) along with two ortho pendant donar atoms (traditionally neutral nitrogen, phasphorous donar atom) [1]. The resulting pincer complexes enjoy a high thermal stability due to this tridentate coordination. Several categories of chelates have been reported, however, pincer ligands are of special interest and are the subject of this review. Over the years a plethora of these ligand systems have been synthesized and explored over the years, driven by promising results and potential scope for further development in the field. A modern definition of a pincer ligand is considerably accepted as a chelator that binds to three adjacents coplanar sites on the metal atom [2]. The combination of a metal to a terdentate pincer ligand usually form two five-membered metallocyclic rings (see Scheme 1), however, there are some examples of six-membered metallocyclic rings [3]. In synthetic chemistry ideally transition metal complexes are indefeasible tools and the metal-mediated processes should be selective, distinguishable and accomplished. There was some of the initial interest and subsequent development of pincer ligands for organometallic complexes, [4-7]. The mostly type of pincer ligand platforms was an aryl anion, capable of binding to the

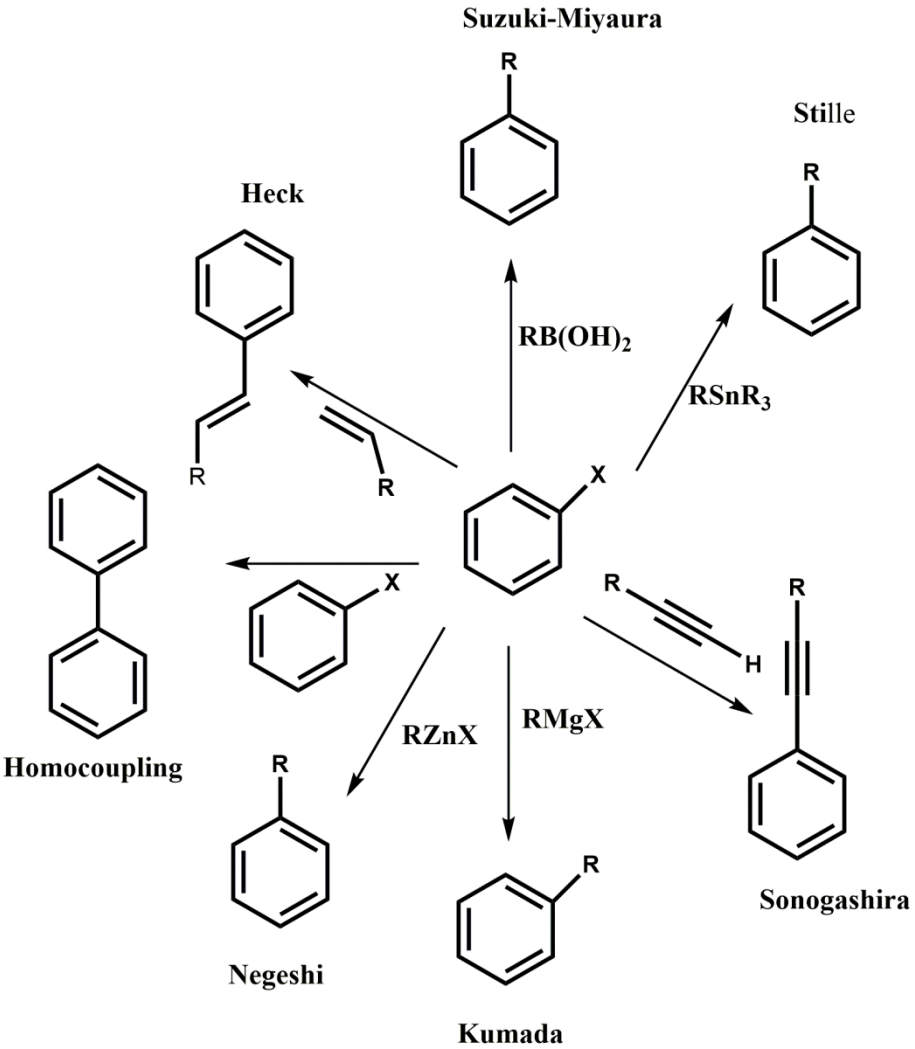
metal center only one metal–carbon □□bond and were based on a □3-"ECE" type design (**1a-c**). In these ECE type pincer ligands, E represents a neutral two electron donor such as NR2, or SR, PR2 leading to a NCN or SCS, PCP type system respectively, while C represents the anionic aryl carbon on a 2,6-disubstituted phenyl ring. In recent times, the coordinate modes have been extended beyond the "ECE" systems to include, but not limited to, ONS [8], CNS [9], CNC [10], NNO [11], NNN [12], PNP [13], SNS [14], NNS [15] and SeNSe [16]. These new generations of pincer systems (**2-6**) often do not employ metal– carbon □□bonds, but nonetheless, these ligands have been employed as chelators to several categories of metal centres. The pincer ligand offers considerable scope of be employed in coordinated state along with the free ligands in various applications. Pincer complexes have been synthesized since the early 1970s, and new designs continue to emerge. In this article, we have explore some aspects of pincer ligands and will focus on the various applications of the different categories of the pincer ligands.



Scheme 1: Some pincer ligands and corresponding pincer complexes; 1- ECE types, 2- SNS, 3 - NNN, 4 - SNO, 5 - NNO/S, 6 – CNC

II. APPLICATION OF PINCER COMPLEXES IN COUPLING REACTION

Pincer complexes have found application in a coupling reaction of C-C, C-N or C-X bond formation, C-H bond activation processes, to exploiting luminescence properties [17]. In 1995 Herrmann, Beller and co-workers first reported use of palladacycles in catalytic C-C bond coupling in the Suzuki-Miyaura [18] and Heck reactions,[19].Thier after application of palladacycles in other bond formation reactions have been studied. In addition to the many examples of application of palladacycles in the Suzuki-Miyaura coupling between organic halides and boronic acids [20,21–23] and the Heck coupling between organic halides and akene [24-28] examples include the coupling of organic halides in the Sonogashira coupling with terminal alkynes[28–29], the Stille coupling between organic halides with organotin reagents[30–31], the Kumada coupling between organic halides with Grignard reagents [30], the Negishi coupling between organic halides with organic zinc[32], and the homocoupling of organic halides[33]. A general summary of coupling reactions performed using a number of palladacycles. (**Scheme 2)**



Scheme 2 Performance of several cross coupling reactions by using palladacycles.

III. CONCLUSION

In summary, we report on a Pincer ligand bind to the metal center via a central donar atom (traditionally an anionic carbon donar atom) along with two ortho pendant donar atoms (N, P, O, S, Se donar atom). The combination of a metal to a terdentate pincer ligand usually form two five-membered metallocyclic rings, however, there are some examples of six-membered metallocyclic rings. The resulting pincer complexes enjoy a high thermal stability due to this tridentate coordination. The pincer ligand offers considerable scope of be employed in coordinated state along with the free ligands in various applications.

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Metal Doped Magnetic Cobalt Ferrite Nanoparticles and Their Nanocomposites Photocatalyst for Degradation of Organic Dye Pollutants: Mini Review

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ABSTRACT

Day by day the increasing pollution is a big threat for the entire environment. The two main pollutions Viz. Air and aqua pollution is more rapidly expanding due to fast urbanization around the world. Although the researchers are working very hard to defeat pollution related problems, but the pollution scenario is becoming very complex issue for all the mankind. Particularly, water pollution is quite serious issue for flora and fauna. There are many methods have been developed so far to treat the industrial, chemical, pharmaceutical, drug and dyes industries pollutant, which discharged through the water stream around the coastal region. The discharged effluent is the major contributing factor for inception of water pollution. The researchers are developing very cheap and effective material to be utilized as catalyst for discrimination of the various pollutants in the form of dyes present under water stream. Mainly metal oxide based semiconducting material have gain more attraction in the field of photocatalysis due to their inherent properties such as tunable band gap, enhanced surface area, excellent thermal stability and good redox mechanism ability. The metal oxide based semiconductors such as Fe3O4, ZnO, CuO, SnO2, TiO2, Fe2O3, ZrO2, NiO, LaFeO3, NiFe2O4, CoFe2O4 etc. are most common and suitable catalysts used in the field of photocatalysis.

The present review is correlated with the utilization of cobalt oxide nanoparticles and nanocomposites in the field of photocatalysis. The CoFe2O4 being magnetic in nature and excellent thermal stability it is extensively as photocatalyst for degradation of common and azo based dyes. The present review elaborates the detailed methods of fabrication of CoFe2O4, their common characterization techniques and extensive utilization of cobalt ferrite in the field of photocatalysis.

Keywords: Magnetic CoFe2O4, Photocatalysis, environmental remediation, Dye degradation.

I. INTRODUCTION

From last few years, the photocatalytic degradation of organic dyes have gained more attention for the treatment of wastewater.[1] Broadly there are three techniques to remove dyes from wastewater that are physical, chemical and biological techniques. Physical processes includes Membrane filteration, adsorption method, Coagulation-flocculation technique, ion-exchange technique, etc while, biological processes make use of aerobic, anaerobic micro-organisms depending on it there are three major type of biological techniques aerobic treatment, anerobic treatment and both aerobic-anaerobic treatment.[2] Organic dyes are relatively stable as they have aromatic system in there structure that provides extra stability so they are not completely mineralized by physical and biochemical method.[3] However, in case of chemical processes "advanced oxidation processes" (AOP) heterogeneous photocatalysis technique have ability to mineralize most of organic dyes completely.[4] Worldwide per year beyond 1,00,000 dyes are commercially made available.[5] Dyes are frequently used in textile, paper, rubber, plastic, food processing, pharmaceutical, leather, cosmetic, etc industries in order to make the products colorful and attractive.[6] These industries discharges effluents that primarily contains dye in fresh water leading it into a wastewater. Organic dyes such as azo dyes, nitro dyes, indigoid dyes, anthraquinone dyes, phthalein dyes, triphenyl methyl dye, nitrated dyes are harmful, toxic and some of them carcinogenic. So it is necessary destroy and clean the wastewater from such toxic dyes.[7] Metal ferrites especially, cobalt ferrite is used to treat wastewater as it have astonishing perperties such as high chemical stability, reasonable heterogeneous catalytic activity, magnetic nature that makes its separation from reaction medium more feasible, high magnetic crystalline anisotropy (~10^6 erg/cm^3), high coerecivity, it have good curie temperature 520℃, it have excellent mechanical hardness, low toxic.[8-11] $CoFe_2O_4$ nanoparticals are iron based semiconductors that are n-type and have reasonable band gap of 1.76 eV, but $CoFe_2O_4$ alone don't have ability to total mineralize the organic dyes.[12] Metal doped $CoFe_2O_4$ nanoparticles and their nanocomposites increased the heterogeneous photocatalytic activity drastically.[13] Photocatalytic degradation of rhodamine B (RhB) dye by $CoFe_2O_4$ is 73.0% while Mg doped $CoFe_2O_4$ have degradation efficiency around 99.5%. Band gap of Co-Cu nanoparticles band gap is 1.57eV while sm^{+3} substituted nanoferrites have lower band gap ~1.36eV that makes it more feasible towards degradation of organic dyes.[7]

II. EXPERIMENTAL

Cobalt ferrite, metal doped cobalt ferrite and their nanocomposites can be prepared by different methods such as Sol-gel method, Hydrothermal method, Co-precipitation method, Combustion method, etc. Every method have its own advantages. Preparation of cobalt ferrite and zinc doped cobalt ferrite by Co-precipitation method has been discussed below,

2.1. Materials:

99.9% pure form of reagents ordered from Merck brand chemicals that were used without any futher purification. $Zn(NO_3)_2 \cdot 6H_2O$ (Zinc nitrate hexahydrate), $Co(NO_3)_2 \cdot 6H_2O$ (Cobalt nitrate hexahydrate) and

$Fe(NO_3)_2 \cdot 9H_2O$ (Ferric (III) nitrate nonahydrate) were used as a precursor for zinc, cobalt and iron respectively. Sodium hydroxide pellets (NaOH), and double-distilled water are used as precipitating agent and solvent for the reaction respectively.[14]

2.2. Preparation:

Pure form of Zn doped CoFe2O4 nanoparticles were synthesized with the help of Co-precipitation technique. By taking the cobalt nitrate and ferric nitrate precursors as the ratio of 1:2 respectively. They were dissolved in 100 ml of distilled water and magnetic stirrer inserted into it so obtain homogeneity by constant and vigorous stirring. Drop by drop addition of (4 M) molarity, aqueous NaOH solution is done till the mixture turns into light brown color from colorless solution. Further, the mixture is allowed to stir vigorous for about 6hr. After the magnet stirrer is switch off and the mixture is kept as it for one night to settle down the precipitate in the bottom of the beaker. The precipitate than centrifused 3 times each 20 min. at 3000 rpm and washed by distilled water followed by ethanol till the pH becomes 7. The precipitate is dried on petri dish at temp 80°C using a hot air oven. At last the particles are calcined for 2 hr at 400°C in a muffule furnace. In same way Zn doped $CoFe_2O_4$ are synthesized by co-precipitation method here the only difference is cobalt nitrate wt% is reduced and corresponding wt% of zinc nitrate is added to the reaction medium.[14]

III. RESULTS AND DISCUSSION

Characterization and analysis of cobalt ferrite nanoparticles specially there doped form with metals and their nonacomposite is done by different techniques like X ray diffraction (XRD),[8] XPS,[9] EDAX,[20] FT-IR,[23] UV-Vis,[13] DRS,[16] SEM/TEM,vibrating sample magnetometer VSM,[19] high-resolution transmission electron microscopic (HRTEM),[20] electron paramagnetic resonance (EPR)[25] that indicates the presence of radicals that are useful for the photodegradation of organic dyes such as hydroxide radical ($OH^{\cdot}$) and superoxide radical ($O_2^{\cdot -}$). Among the discussed characterization techniques XRD technique is elaborated in detail below;

3.1 XRD analysis

XRD data was recorded to study the structural properties of syn- thesized MoO_3 nano-rods, $CoFe_2O_4$ Nps and their composite MoO_3/ $CoFe_2O_4$ by X-Ray diffractometer. The diffraction peaks MoO_3 appeared at two theta 25.85°, 29.2°, 35.4°, 41.8°, 43.11°, 45.3°, 46.6°, 48.8°, 50.13° , 51.9° , 53.2° , 56.1° , 57.9° , 61.6° , 67.06° and 68.9° belonging to reflections (210), (300), (310), (224), (320), (410), (404), (008), (500), (330), (420), (280), (334), (430), (610) and (524) respectively and corresponding to JCPDS No. 21–0569 as shown in Fig. 1 (a). The size of molybdenum trioXide was calculated to be 14.1 nm using well known Scherrer's formula given below:

$$\eta = \frac{0.9\lambda}{\beta \cos\theta} \quad - (1)$$

D is the crystallite size of nanomaterial, θ represents the Bragg's angle, λ is the wavelength of used X-rays (Cu Kα 1.5Å) and β is the full width at half maximum value.

The diffraction peaks of $CoFe_2O_4$ appeared at 31.04°, 36.50°, 44.47°, 48.46°, 55.6°, 64.9°, 71.02°, 75.1° and 77.36° with corresponding lattice planes (220), (222), (400), (331), (511), (531), (620), (622), and (444) in Fig. 1 (b). The peaks were matched with JCPDS card No. 22–1086. EXtra peaks of iron oXide were also examined by the XRD data which are 50.08°, 59.07° and 68.9° belonging to reflections (024), (018) and (208) respectively matched with the JCPDS card No. 33–0664. The formation of secondary phase of Fe_2O_3 was formed due to the favour- able heating conditions during the synthesis of cobalt ferrite. The size of the cobalt ferrite nano-particles was calculated to be 7.2 nm using the Scherrer formula.

The formation of the nanocomposite $MoO_3/CoFe_2O_4$ was confirmed by XRD analysis as presented in Fig. 1 (c). The synthesized composite possesses characteristic reflections at (300), (204), (310), (410) and (424) with 2θ values of 29.3°, 31.0°, 36.8°, 44.6° and 59.0° respectively, for MoO_3 and matched with the JCPDS No. 21–0569. The characteristic reflections of cobalt ferrite at (222), (331), (511), (531) and (422) corresponding to 2θ values at 38.0°, 47.9°, 55.5°, 65.03° and 53.0° were observed and matched with JCPDS No. 22–1086.[8-9]

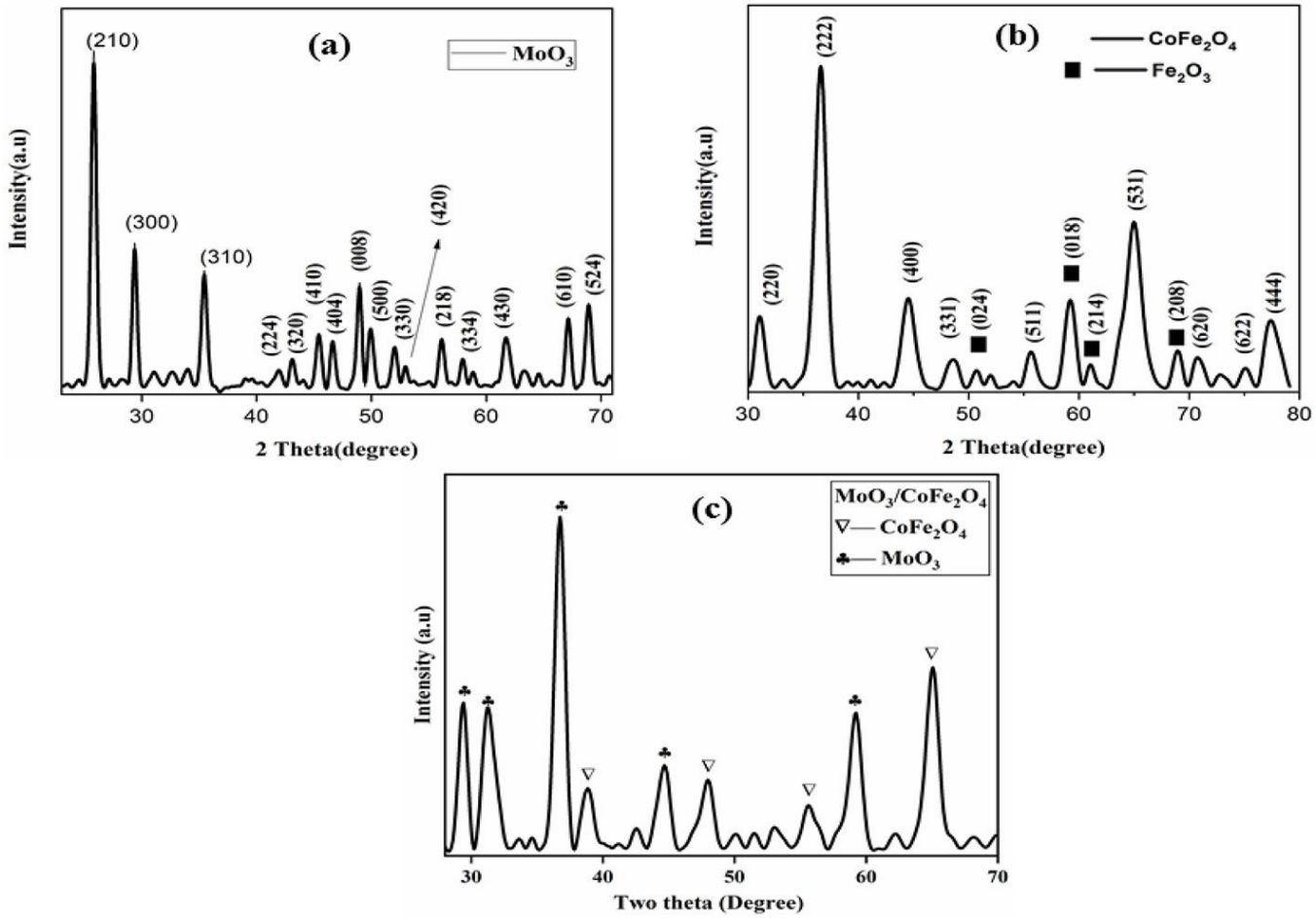

Fig. 1. XRD Diffractogram of (a) MoO_3 (b) $CoFe_2O_4$ and (c) MoO_3/ $CoFe_2O_4$ nanocomposites

Following table presents the list of Photocatalyst, Pollutant (Dye) Degradation efficiency in percentage Irradiation Source and Time;

Sr. No.	Photocatalyst	Pollutant	Effecienc y (%)	Irradiation Source and Time		Refer ences
1.	$CoFe_2O_4$:Ni (Co-precipitation route)	Methylene Blue	83.41	90min.	Sunlight	[15]
2.	$CoFe_2O_4$ (Modified solvothermal route)	Methylene Blue	80	140min	Tungsten halide lamp (UV-Visible light source)	[16]
3.	Ru doped $CoFe_2O_4$ (Sol-gel method)	Remazol Deep red	-	30min	150 W Xe lamp as visible light source	[17]
4.	Al doped $CoFe_2O_4$ (Sol-gel method)	Methylene blue	93	120min	200 W visible light	[18]
5.	Mg doped $CoFe_2O_4$ (Microwave combustion method)	Rhodamine B	99.5	-	150 W halide lamp (Visible light)	[19]
6.	Sm substituted copper doped $CoFe_2O_4$	Rhodamine B	94.36	270min	Sunlight	[20]
7.	Rh loaded $CoFe_2O_4$	Malachite Green	97	60min.	Xe lamp (400 W)	[21]
8.	$CoFe_2O_4$ (Modified Solvothermal process)	Methylene blue	80	140min	Visible light	[22]
9.	Dy doped $CoFe_2O_4$ (Co-precipitation)	Methyl orange	78.65	2.0 hr.	Visible light	[23]
10.	$CoFe_2O_4$/ZnO (Co-precipitation method)	Acid violet Acid brown	76 63	-	UV lamp (32 W)	[24]
11.	Bi_2O_3/ $CoFe_2O_4$ (Hydrothermal route)	Methyl orange	92	-	300 W Xe arc lamp	[25]
12.	SnO_2-Tio_2/ $CoFe_2O_4$ (Sol gel method)	Rhodamine B	100	90 min	Sunlight	[26]
13.	ZnS-WO_3- $CoFe_2O_4$	Methylene Blue	95.97	180 min	Visible light radiation	[27]
14.	Li-Cr substituted $CoFe_2O_4$	Crystal violet	90.4	60 min	Sunlight	[28]

15.	$CoFe_2O_4/BaTiO_3$ (Sol gel method)	Methylene Blue	99.3	5 hours	Ultraviolet light radiation	[29]
16.	$MoO_3/CoFe_2O_4$ (Co-precipitation method)	Methylene Blue	91	-	Visible light radiation	[30]
17.	$CoFe_2O_4/Fe_2O_3$ (Hydrothermal Process)	Methyl Orange	93	5 hours	Ultraviolet light radiation	[31]
19.	Zn doped cobalt ferrite (Co-precipitation method)	Methylene Blue Rhodamine B Crystal Violet	97 83 91	90 min.	Sunlight	[33]
20.	$CoFe_2O_4$-CeO_2 (Hydrothermal method)	Orange II	98.5	60 min.	Visible light	[34]
21.	Mn doped $CoFe_2O_4$ (Sol-gel auto combustion)	Orange II	85.4	2 hours	Visible light	[35]
22.	$CoFe_2O_4$ (Sol-gel auto combustion)	Reactive Red 195	74	2 hours	UV lamp	[36]
23.	ZrO_2-TiO_2/ $CoFe_2O_4$ (Sol-gel method)	Rhodamine B	99.7	60 min.	UV light	[37]

Degradation of Remazol deep red dye was carried out under 150 W Xe lamp as visible light source where 50 mg catalyst was placed in 100 ml of 60 mg/L dye solution having pH=2.5 using H_2SO_4 addition 0.1ml of 30% H_2O_2 done for 30 min.[15]

Al doped cobalt ferrite a black colored photocatalyst minerize the methylene blue dye in 120 minutes. In 100ml beaker different concentration of catalysts were taken and MB dye of 10 mg/L in same reaction medium pH=11 was maintained.[19]

Rhodium B degradation by Mg doped cobalt ferrite is a fenton type rection in which addition of 30% H_2O_2 is done to generate $OH^{\cdot}$ various volume of dye and catalyst were mixed at constant pH=2 and the catalytic activity initiated in visible source of light and analyzed using UV-Visible spectrometer.[18]

IV. CONCLUSION

In this review, specifically metal doped cobalt ferrites and their nanocomposites that are responsible for the degradation of toxic and hazardous dyes, there comparative study has been carried out Zn doped cobalt ferrite, $CoFe_2O_4/BaTiO_3$ mineralize Methylene blue (MB) most efficiently 97% and 99.3% respectively, whereas, SnO_2-Tio_2/ $CoFe_2O_4$ and ZrO_2-TiO_2/ $CoFe_2O_4$ degrades Rhodamine B (Rh B) in presence of sunlight

most efficiently. Orange II is phaotocatalytically destroyed by $CoFe_2O_4$-CeO_2 around 98.5%. There is requirement of a photocatalyst that will mineralize the mixture of dyes at a time with almost same efficiency and comparative less time.

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A Volumetric and Viscosity Study for the Binary Mixtures of Cinnamaldehyde with Methanol over the Entire Range of All Compositions at 298.15, 308.15 and 318.15 K

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ABSTRACT

Densities, viscosities and molar volume (Vm) of binary liquid mixtures containing cinnamaldehyde and methanol were determined at 298.15K, 308.15K and 318.15K. Excess molar volume (VE), deviation in viscosity (□□) excess Gibbs free energy of activation of viscous flow (□G*E) were determined from the experimental results obtained. Viscosity deviations, excess molar volumes and excess free energies of activation of viscous flow were correlated by Redlich-Kister polynomial equation.

Keywords: Density, Viscosity, Excess molar volume, cinnamaldehyde and methanol.

I. INTRODUCTION

Studies on viscosity have been performed on binary systems of cinnamaldehyde with methanol. However, there is a bit of information on the effect of temperature on the viscosity of binary mixtures cinnamaldehyde with methanol. 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 cinnamaldehyde with methanol is rarely reported. The main purpose of this work was to formulate the information and data on effect of temperature on viscosity of binary liquid mixtures. Furthermore, 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 aldehyde and alcohol 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 cinnamaldehyde and methanol are reported at various temperatures 298.15, 308.15 and 318.15 K. Deviation in viscosity (Δŋ), molar volume (Vm), excess molar volume (VE) and excess Gibbs free energy of activation of viscous flow (ΔG*E) have been calculated from the density ((ρ) , and viscosity (ŋ), data. Experimentally determined values of deviation in viscosity and other excess properties were fitted to the Redlich-Kister polynomial equation and the results analyzed in terms of molecular interactions.

II. MATERIAL AND METHODS

The purities of cinnamaldehyde and methanol were checked by density determination at 298.15, 308.15 and 318.15 K. The densities of pure liquids and their binary mixtures were determined by using a single-arm pycometer which was calibrated at 298.15, 308.15 and 318.15 K temperatures with double distilled water. The sensitivity of the pycnometer corresponded to a precision in density of 1x10–3 gm cm–3. The binary liquid mixtures of cinnamaldehyde and methanol of various known concentrations were prepared in stoppered 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

To interpret the molecular interactions between cinnamaldehyde and methanol, viscosity deviation, excess molar volumes and excess Gibbs free energy of activation of viscous flow have been evaluated from experimental values of density and viscosity using equations 1 and 2 respectively.

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_m} - (x_1 M_1/\rho_1 + x_2 M_2/\rho_2) \quad -- \quad (1)$$

$$\Delta_n = n_m - (x_1 n_1 + x_2 n_2) \quad -- (2)$$

where x1and x2are the mole fractions calculated from mass fractions;M1and M2are molar masses; ρ1and ρ2are densities; ŋ1and ŋ2are the viscosities of pure components 1 and 2 respectively and ρm is the density and ŋm is viscosity of the mixture.

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

ΔG*E = RT [lnnmVm – (x1lnn1V1 + x2lnn2V2)] -- (3)

where R is the universal constant of gases, T is the absolute temperature, V1and V2 are the molar volumes of component 1 and 2, x1 and x2 represent the mole fraction of component 1 and 2.
V mis obtained from equation 4:

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

where ŋ1,ŋ2and ŋm are the viscosity of component 1 and 2 and mixture respectively.

From the experimentally obtained data on density (ρ) and viscosity (ŋ) of binary mixtures of cinnamaldehyde with methanol at temperature 298.15, 308.15 and 318.15 K, deviation in viscosity (Δŋ), molar volume (Vm), excess molar volume (VE) and excess Gibbs free energy of activation of viscous flow (ΔG*E) have been determined as mentioned in table 1, 2, 3.

Experimental values of density (ρ), viscosity (ŋ), deviation in viscosity (Δŋ), molar volume (Vm), excess molar volume (VE) and excess Gibbs free energy of activation of viscous flow (ΔG*E) of binary mixture of Cinnamaldehyde with Methanol of various composition at 298.15 K (Table-1),
308.15 K (Table-2) and 318.15 K (Table-3).

The plots of deviation in viscosity against mole fraction at 298.15, 308.15 and 318.15 K for binary mixtures of cinnamaldehyde with methanol are presented in graph 1. Deviations in viscosity were found to be negative. The negative values of the deviation in viscosity (Δŋ) suggest the existence of weak intermolecular interactions upon mixing in methanol. This shows that the strength of the specific forces is not the factor influencing the viscosity deviation in the liquid mixture. This leads to suggestions that combinations of non-interactive force are responsible in these positive and negative interactions.11-15

Table 1: Experimental density (ρ) , viscosity (ŋ), deviation in viscosity (Δŋ), excess molar volumes (VE) and excess free energies of activation of viscous flow ΔG*E for binary mixtures of Cinnamaldehyde with methanol at 298.15 K.

x_1	ρ (g cm^{-3})	η (mPa.s)	Δŋ (mPa.s)	V_m cm^3mol^{-1}	V^E cm^3mol^{-1}	ΔG^{*E} $J.mol^{-1}$
0	0.7864	0.5549	0	78.3319	0	2365.011
0.0347	0.8128	0.848	-0.0826	80.5675	0.0811	2714.698
0.0749	0.8392	1.1411	-0.1133	82.9096	0.1384	2942.214
0.1219	0.8658	1.4342	-0.1377	85.3894	0.1946	3113.73
0.1776	0.8923	1.7273	-0.1532	87.9834	0.2521	3238.674
0.2446	0.9187	2.0204	-0.1608	90.7686	0.2754	3320.279
0.3270	0.9451	2.3135	-0.1599	93.7443	0.2671	3355.794
0.4304	0.9715	2.6066	-0.1482	96.9151	0.2373	3337.678
0.5644	0.9979	2.8997	-0.1257	100.2844	0.1976	3252.496
0.7446	1.0243	3.1928	-0.0918	103.8813	0.1364	3071.165
1	1.0509	3.4768	0	107.7487	0	2663.734

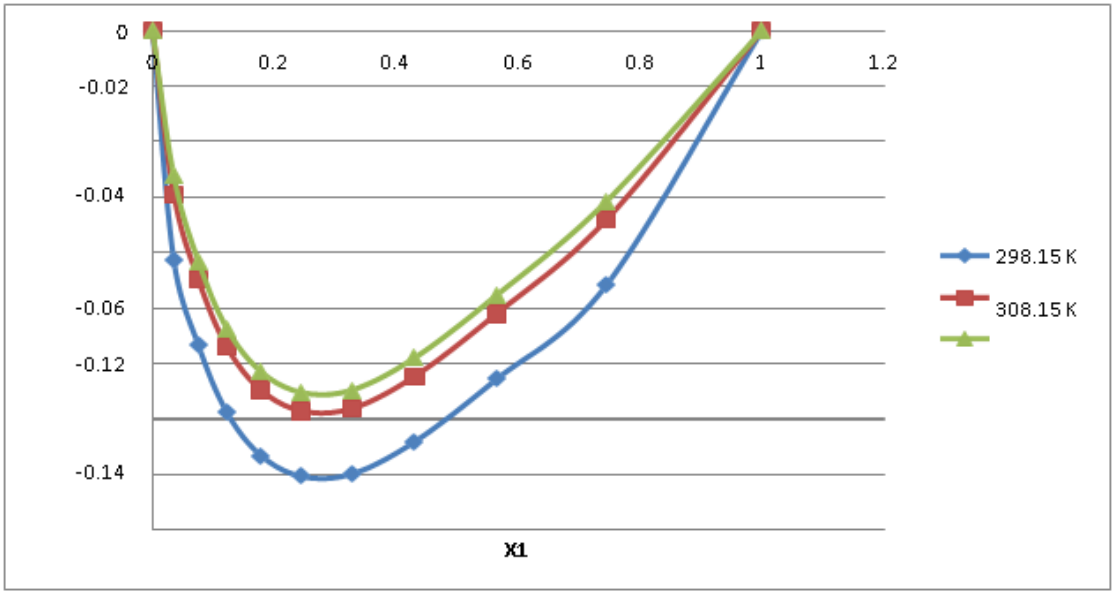
Table 2: Experimental density (ρ) , viscosity (ŋ), deviation in viscosity (Δŋ), excess molar volumes (VE) and excess free energies of activation of viscous flow ΔG*E for binary mixtures of Cinnamaldehyde with methanol at 308.15 K

x_1	ρ ($g\ cm^{-3}$)	η (mPa.s)	Δŋ (mPa.s)	V_m cm^3mol^{-1}	V^E cm^3mol^{-1}	ΔG^{*E} $J.mol^{-1}$
0	0.7764	0.4782	0	79.3182	0	2473.376
0.0347	0.8027	0.6973	-0.059	81.5538	0.0853	2823.063
0.0749	0.8290	0.9164	-0.0897	83.8959	0.1437	3050.579
0.1219	0.8553	1.1355	-0.1141	86.3757	0.1999	3222.095
0.1776	0.8816	1.3546	-0.1296	88.9697	0.2574	3347.039
0.2446	0.9080	1.5737	-0.1372	91.7549	0.2807	3428.644
0.3270	0.9343	1.7928	-0.1363	94.7306	0.2724	3464.159
0.4304	0.9606	2.0119	-0.1246	97.9013	0.2426	3446.043
0.5644	0.9869	2.231	-0.1021	101.2707	0.2029	3360.861
0.7446	1.0132	2.4501	-0.0682	104.8676	0.1417	3179.53
1	1.0398	2.6728	0	108.7351	0	2772.099

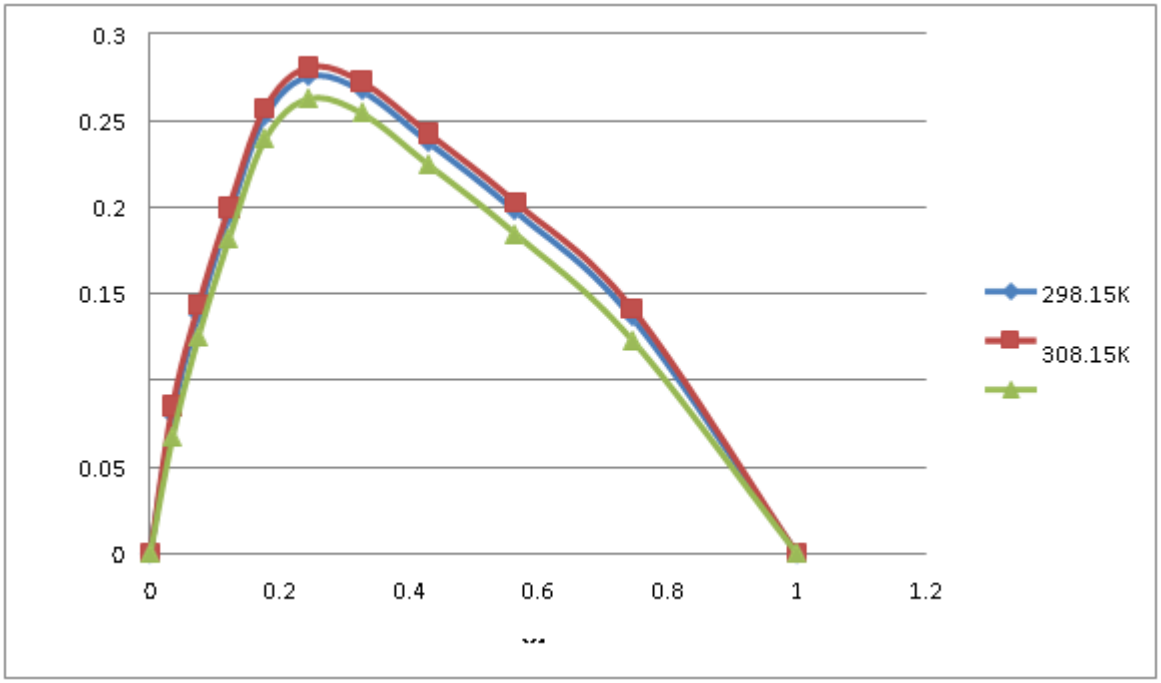
Table 3: Experimental density (ρ) , viscosity (ŋ), deviation in viscosity (Δŋ), excess molar volumes (VE) and excess free energies of activation of viscous flow ΔG*E for binary mixtures of Cinnamaldehyde with methanol at 318.15 K

x_1	ρ ($g\ cm^{-3}$)	η (mPa.s)	Δŋ (mPa.s)	V_m cm^3mol^{-1}	V^E cm^3mol^{-1}	ΔG^{*E} $J.mol^{-1}$
0	0.7711	0.4195	0	80.3207	0	2585.741
0.0347	0.7962	0.6051	-0.0524	82.5563	0.0671	2935.428
0.0749	0.8213	0.7907	-0.0831	84.8984	0.1255	3162.944
0.1219	0.8464	0.9763	-0.1075	87.3782	0.1817	3334.46
0.1776	0.8715	1.1619	-0.1231	89.9722	0.2392	3459.404
0.2446	0.8961	1.3475	-0.1306	92.7574	0.2625	3541.009
0.3270	0.9218	1.5331	-0.1297	95.7331	0.2542	3576.524
0.4304	0.9469	1.7187	-0.1181	98.9038	0.2244	3558.408
0.5644	0.9720	1.9043	-0.0955	102.2732	0.1847	3473.226
0.7446	0.9971	2.0899	-0.0616	105.8701	0.1235	3291.895
1	1.0222	2.2756	0	109.7375	0	2884.464

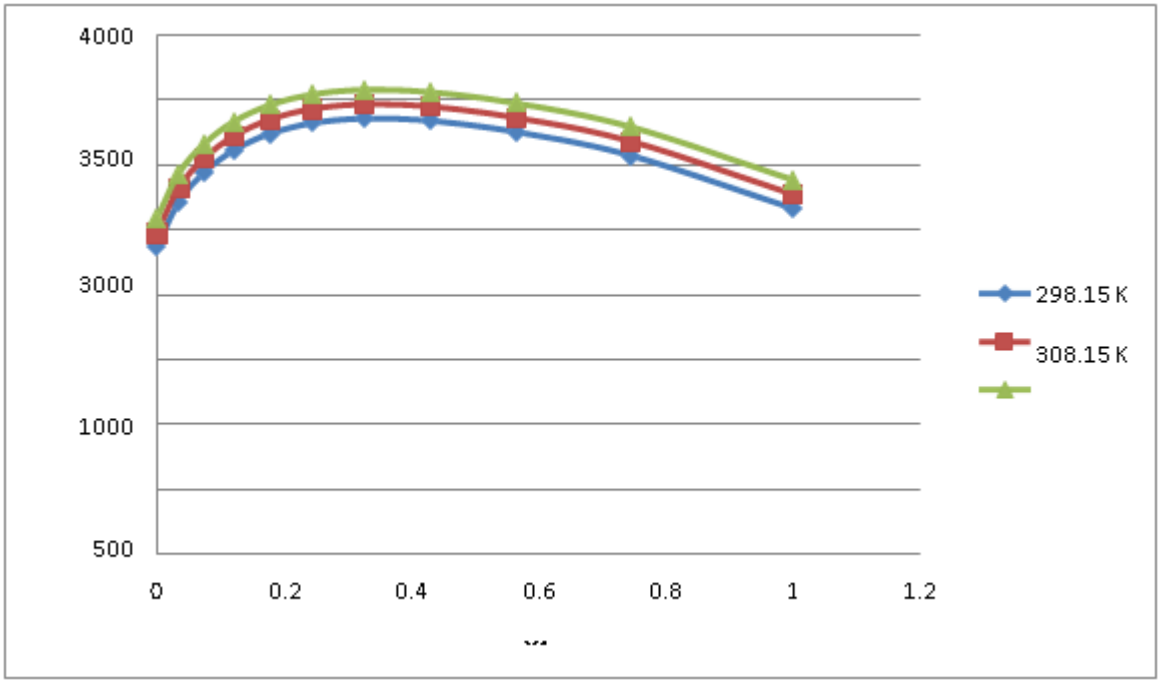
Figures 1: The plots of deviation in viscosity against mole fraction at 298.15, 308.15 and 318.15 K for binary mixtures of cinnamaldehyde with methanol.



Figures 2: The plots of excess molar volume against mole fraction at 298.15, 308.15 and 318.15 K for binary mixtures of cinnamaldehyde with methanol.



Figures 3: 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 cinnamaldehyde with methanol.



The experimental values of densities and viscosities of studied binary mixtures of cinnamaldehyde with methanol at 298.15 K, 308.15 K and 318.15 K over the entire composition range expressed by mole fraction x1 of cinnamaldehyde are listed in Tables 1-3. The densities and viscosities of the studied binary mixtures are found decreased with increasing temperature and increased with increasing of mole fraction of cinnamaldehyde. Analytical 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 cinnamaldehyde and alcohols in addition to intermolecular forces. Figure 1 shows the graphical variations of dη for binary mixtures of cinnamaldehyde with methanol at 298.15, 308.15 and 318.15 K. The values of dη are found negative for binary mixtures of cinnamaldehyde with methanol at all experimental temperatures. As temperature increased, dη values also found increased in all cases. 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 16-20.

Figure 2 shows graphical variation of VE for binary mixtures of cinnamaldehyde with methanol at 298.15, 308.15 and 318.15 K. In the investigation VE are found positive for all the binary mixtures of cinnamaldehyde with methanol at all experimental temperatures. When plotted x1 against VE, the curve with maxima is obtained at equimolar concentration for all binary mixtures.

Figure 3 exhibits variation of excess Gibb's free energy of activation of viscous flow ΔG*E with mole fraction and temperature. 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 cinnamaldehyde and alcohols and size effect of the mixing components21-22. Positive values of ΔG*E represents hydrogen bonding between cinnamaldehyde and alcohols is dominant over dispersion forces. ΔG*E values are found almost constant for methanol at all studied temperatures.

IV. CONCLUSION

The density, viscosity, deviation in viscosity, excess molar volume and excess Gibbs free energy of activation of viscous flow for the binary systems of Acetaldehyde with n-butanol at 298.15, 308.15 and 318.15 K has been reported. The deviations in viscosity of the binary systems of cinnamaldehyde with methanol are found to be negative and decreases 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 Ȏ---H-O between unlike molecules confirming intermolecular hydrogen bond formation between cinnamaldehyde and methanol mixtures. Excess molar volumes (VE) and the viscosity deviations (Δŋ) were used to predict the intermolecular interactions in the mixtures. The excess volume and viscosity deviation data were fitted by means of the Redlich-kister equation. It was found that in all cases the experimental data obtained, matches with Redlich-Kister equation with a high degree of precision.

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Synthesis, Characterization and Biological Activities of Schiff Base Ligand sand Their Co(II), Zn(II), Cu(II), Ni(II) Complexes

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ABSTRACT

Schiffbases and their complexes are versatile compounds that are synthesised by combining an amino acid with a carbonyl compound. They have a wide range of biological properties, including antibacterial, antifungal, antiviral, antimalarial, anti-proliferative, anti-inflammatory, anticancer, anti-HIV, antihelminthic, and antipyretic properties. In diverse processes and in the presence of moisture, manySchiffbase complexes display good catalytic activity. They're classified as a subclass of imines. The phrase is interchangeable with the term azomethine, which refers to secondary aldimines in particular. Primary ammines and carbonyl compounds condense to form these. Furfuraldehyde and its many derivatives are also used to make Schiffbases. With metals in the +2 oxidation state, Schiffbase produces a stable compound. Taking all of these factors into account, four novel complexes, Co(II), Zn(II), Cu(II), and Ni(II), have been synthesised and characterised with O- and N-donor Schiff bases generated from furfuraldehyde and ethylenediamine. The ligands of Schiffbase were produced by reacting furfuraldehyde with ethylenediamminein a 2:1 ratio in methanol in this chemical synthesis. The formulations are supported by the analytical data and the molecular weights of the substances. The colourful crystallineComplexes produced are soluble in acetone and DMF, but only sparingly.

Keywords: Azomethine; Characterization; Condensation; DMF; DMSO; Furfuraldehyde; Furfuraldehyde; Furfuraldehyde; Furfuraldehyde; Furfuraldehyde; Furfuraldehyde; Furfuraldehyde; Furfuralde

I. INTRODUCTION

Schiff bases and their complexes are versatile compounds that are synthesised by combining an amino acid with a carbonyl compound. They have a wide range of biological activities, including antibacterial, antifungal, antiviral, antimalarial, antiproliferative, anti-inflammatory, anticancer, anti-HIV, antihelminthic, and antipyretic properties[1]. ManySchiffbasecomplexesshowexcellentcatalyticactivityinvariousreactionsandinthepresenceofmoisture. Therehavebeenmanyreportsontheirapplicationsinhomogeneousandheterogeneouscatalysisinthepastfewyears.

ManySchiffbasecomplexes'highthermalandmoisturestabilitieswereusefulattributesfortheirapplicationascatalysts inhightemperaturereactions [2].

Because activity is frequently boosted by complexity, understanding the properties of both ligands and metals can lead to the creation of highly active molecules.

The impact of specific metals on these compounds' biological activity, as well as their inherent chemical interest as multidentate ligands, has motivated a significant increase in the research of their coordination behaviour [3].

Medical chemists are increasingly paying attention to the development of novel chemotherapeutic Schiff bases and their metal complexes.

The numerous synthesis processes and applications of Schiffbases and their metal complexes are summarised in this article.

Schiffbasesandtheirtransitionmetalcomplexes, which comprise nitrogen and oxygen donoratoms, are crucial in biological and inorganic research and have been extensively researched because of their unusual coordination and biological features [1,2].

TransitionmetalSchiffbasecomplexeshavefoundapplicationsinvariousfieldssuchasmedicine,agriculture,industriesetc.

The analytical reagent furfuraldehyde is well-known[4,5].

Itsvariousderivativesarealsouseful.

Cobalt produces relatively stable complexes with nitrogen donor ligands in both the di- and tri-valent states, and both are thought to be involved in vitamin catalysis. Zinc forms stable complexes in the variable +2oxidation state with ligands such as halides, CN, and those containing O,N, and S donor atoms.

The ligands of Schiffbase were produced in this chemical synthesis by reacting furfuraldehyde with ethylenediamminein2:1ratiorespectively in methanol.

Thereactionwasrefluxedonawaterbathfor3-4hours.

Theprecipitatestherebyobtainedwereseparatedandwashedwithmethanolandweredriedinavacuumdedicator.

Thecrystalsobtainedare Schiffbaseligand.

To make the complexes, a 1:1 ratio of ethanolic solution of Schiffbase and metal salts of Co(II), Zn(II), Cu(II), and Ni(II) chlorides was used. For 3-4 hours, the solutions were flushed. Theresultingprecipitatesdried. Because of the numerous uses of these compounds in various sectors, interest in the chemistryofSchiffbasesandtheirmetalcomplexeshasincreasedinrecentdecades [8].

Schiffbases have been demonstrated to have antifungal, anticancer, antibacterial, antimalarial, anti-inflammatory, antiviral, antipyretic, and herbicidal characteristics, among others.

However, it has been reported that chelating Schiffbases with transition metalions improves their biological potential; as a result, metalcomplexes of variousSchiffbases are known for their antibacterial, antifungal, anticancer, and antioxidant characteristics. Metal complexes of Schiffbase [Co(II), Zn(II), Cu(II), and Zn(II)ions] have played a key role in the development of co-ordination chemistry. TransitionmetalcomplexeshaveattractedcuriosityduetoDNAbindingandcleavagepropertiesunderphysiologicalconditions. Current research is focusing on the use of metal complexes as chemical nucleases [9]. Inorganic complexes as chemical nucleases have been proved to be the focus of current study. It has been established that organic compounds can be utilised as sequence-specific DNA binding agents in fingerprinting studies, as diagnostic agents in therapeutic applications, and for genomic research.

The remainder of the paper is structured as follows: Section I contains an introduction to Schiff base Complexes and their biological activities, Section II contains related work in the field of Schiff base Complexes pertaining to their preparation, identification, detection, and determination of biological activities, Section III contains the methodology of Schiff base preparation and also describes the preparation of Co(II), Zn(II), Cu(II), and Ni(II) complexes, and Section IV contains the results obtained from all of this experimental procedure.

II. METHODOLOGY

MethodofPreparation:

Allthechemicalsandsolventsusedwereofanalyticalgrade.ThemetalsaltsCoCl$_2$.6H2O,ZnCl2(Qualigens), CuCl2 and ZnCl2 available in pure state havebeen used as such. Furfuraldehyde obtained from Qualigensfinechemicalswasdistilledbeforeuse,whereasethylenediammineisusedasreceived.

Synthesisofligand (SchiffBase):

Theligandsweresynthesizedbythereactionoffurfuraldehyde with Ethylene in 1 : 1 or 2 : 1 molar ratiorespectivelyinMethanol.Thereactionmixturesworerefluxedfor 3-4 hrs. The precipitates thereby obtained wereseparatedandwashedwithmethanoland dried inoven.

SynthesisoftheCo(II)complex:

To the hot methanolic solution (25 mL) of the ligand wasadded the hot methanolic solution (15 mL) of CoCl2.6H2O(0.001 mol) and the reaction mixture was refluxedfor 4-5hrs.On cooling,theresulting colouredmetalcomplexesprecipitatedout.Theprecipitateswerewashedwithmethanol.

SynthesisoftheZn(II)complex:

ThehotethanolicsolutionsofZnCl2(0.001mol)andSchiff base (0.002 mol)were mixed and the mixture wasrefluxedfor 4-5 hrs. The precipitates of the resulting metalcomplexeswerefiltered,washedwithmethanol.

SynthesisofCu(II)Complex:

The hot ethanolic solutions of CuCl2 (0.001 mol) and Schiffbase (0.002 mol)were mixed and the mixture was refluxedfor4-5hrs.Theprecipitatesoftheresultingmetalcomplexes werefiltered,washedwith methanol.

SynthesisofNi(II)Complex:

The hot ethanolic solutions of NiCl2 (0.001 mol) and Schiffbase (0.002 mol)were mixed and the mixture was refluxedfor4-5hrs.Theprecipitatesoftheresultingmetalcomplexes werefiltered,washedwith methanol.

III. RESULTS AND DISCUSSIONPHYSICAL PROPERTIES

ThereactionsofcomplexeswithSchiffbaseshavebeencarriedoutinunimolarandbimolarratiosinethanol. Theanalyticalresultsandmolecularweightsofthecompoundssupporttheformulationsrepresentedinthetable-1. All of the complexes are coloured, crystalline powders that are soluble in acetone, DMF, and DMSO. The table below shows some of the physical properties of these complexes.

Table1:physicalCharacterization

Complex	Colour	M.P°C	F.wtg/mol	%yield
$[Co(SB)_2Cl_2]$	Dirtygreen	120	471.5	63.68
$[Cu(SB)_2Cl_2]$	Darkpurple	241	425.93	74.11
$[Zn(SB)_2Cl_2]$	Lemon yellow	243	409.75	72.75
$[Ni(SB)_2Cl_2]$	Reddish brown	240	242.17	65.94

Here (SB) is Schiff base.

IRSpectralstudies

The IRspectra of the ligandsshowed(Table 2) aband intherange 1647-1635 cm-1, which isduetoν(C=N).Thisband shifts to lower frequency1640-1620 cm-1in all theCo(II)andZn(II)complexespossiblyindicatingthecoordinationtometalionsthroughtheazomethinenitrogen9, 10.The C-O-Cband appeared at 1150 or1148cm-1in the spectra of SB1 or SB2,respectively, shifted to1140-

1120 cm-1in the spectra of the complexes. Such ashifting is probably due to the involvement of furfural ringoxygen in coordination11. Two distinct bands appeared inthe region 468-434 cm-1 and 592-548 cm-1 in the spectraof complexesare due to ν(M-N)and ν(M-O), respectivelyand these further provide evidence for the coordinated metalioninthe ligandframework.

Discussion:

TheSchiffbasewasformedbythereactionoffurfuraldehydeandethylenediammine.The colouroftheresultingcomplexeswaschangedfromthatoftheparentcompoundsthisindicatedthe formationofsomenewcompoundwhichwaslateronconfirmedmeasuringitssolubility.The resultingcompoundwasinsolubleinthesolventmethanolandwaspartiallysolubleintheinorganicsolvents. TheIRstudiesalsoprovidetheevidenceoftheformationof the Schiff base.Thepeaksof C=O whichshowspeaksat1500-1650cm-intheIRspectrumweredisappearedwhentheIRspectra oftheresultingcompoundwastakenagain.Newpeaksofcarbonnitrogendoubleat 1750cm-.thisshowsthattheresultingSchiffbasewasformed.ThereactionsofCoCl2.6H2Oor ZnCl2withthe Schiffbaseshavebeencarriedoutinunimolarandbimolarratiosinethanol.The analyticalresultsandmolecularweightsofthecompoundssupporttheformulationsrepresented inTable1.Allthecomplexesarecoloured,crystallinepowdersandaresolubleinacetone andDMFbutsparinglysolubleinDMSO.Differenttechniqueshavebeenusedtoconfirmthe formationoftheSchiffbaseandtheresulting metal complexeswhichhavewidespread antibacterialandbiologicalactivities.Allthetheoreticalandexperimentaldatasupportedtheformationof Schiffbase and itscomplexeswiththetransitionmetalshavingoxidationstateof+2.

ApplicationsofSchiffbaseIminecomplexes:

Theyhaveabroadrangeofbiologicalproperties:antitumor,antiviral, antifungal, and antibacterial [10].Theyarealsousedinthetreatmentfordiabetesand AIDS.Asbiological models,theyhelpinunderstandingthestructureofbiomoleculesandbiologicalprocessesoccurringinlivingorganisms.Theyparticipate,interalia,inphotosynthesisandoxygentransportinorganisms.Theyareinvolvedinthe treatment ofcancerdrugresistance,andoften testedasantimalarials.Italsocouldbeusedfortheimmobilization ofenzymes[11, 12].

BiologicalActivity:

Schiffbasesarecharacterizedbyaniminegroup–N=CH-,whichhelpstoclarifythemechanismoftransaminationandracemizationreactioninbiologicalsystem[1].Itexhibits antibacterialand antifungaleffectintheirbiologicalproperties[13,14].Metal-iminecomplexeshavebeenwidelyinvestigatedduetoantitumorandherbicidaluse.Theycanworkasmodelsforbiologicallyimportant species[13].

Antibacterialproperties:

Mortalityincreasecausedbyinfectiousdiseasesisdirectlyrelatedtothebacteriathathavemultipleresistancestoantibiotics.Thedevelopmentofnew antibacterialdrugsenrichedby innovatoryandmoreeffectivemechanismsofactionisclearlyanurgentmedicalneed[15]. Schiff bases are identified

as promisingantibacterialagents.Ex:N-(Salicylidene)-2-hydroxyanilineisactiveagainstMycobacteriumtuberculosis[4].

Antifungalproperties:

Fungalinfectionsusuallyarenotonlylimitedtothecontaminationofsurfacetissues.Recently, therewasaconsiderableincreaseintheincidenceof systemicfungalinfections,whichare potentiallylife threatening[17].Explorationanddevelopmentofmoreeffectiveantifungalagents isnecessity,andtheindividualSchiffbasesareconsideredtobepromisingantifungalmedicines[18].AntifungalpropertiesSomeof them,suchasiminederivativesofquinazolinonespossessantifungalpropertiesagainstCandidaalbicans,Trichophyton rubrum,T.mentagrophytes,AspergillusnigerandMicrosporumgypseum. Schiff bases andtheirmetalcomplexesformedbetweenfuranorfurylglycoxalwithvariousaminesexhibitantifungalactivityagainst Helminthosporiumgramineum–causingleafstripeinbarley,Syncephalostrumracemosus-contributingtofruitrotintomatoandColletotrichumcapsicumcausinganthracnoseinchillies[7]

Biocidalproperties:

Schiffbasesobtainedbythesynthesisofo-aminobenzoicacidandβ-ketoestershave foundbiocidaluseagainstS.epidermidis,E.coli,B.cinereaandA.Niger[2].Bycontrast,Schiffbases ofisatinderivativesareusedinthedestructionofprotozoaandparasites.

Metalcomplexinneurologicaldisorders:

Metalcomplexesalsoplayavitalroleinthetreatmentofvariousneurologicaldisorders.These complexesmaycuremanynervedisorderslikeHuntington'schorea,Parkinsonism,organicbraindisorder,epilepsyandparalysis.Transitionmetalssuchascopperandzincareinvolvedas atransmitterintheneuronalsignalingpathways.

Metalcomplexesindiabetes:

Somemetalcomplexesshowconsiderablereductionintheglucoselevelse.g.intakeofchromiummetalcomplex.InsulinomimeticZinccomplexwithdifferentcoordinationstructuresandwithabloodglucoseloweringeffectisreportedtotreattype2diabete.

AntitumorandCytotoxicActivities:

InteractionofDNAwithtransitionmetalcomplexes hasgainedconsiderablecurrentinterestduetoitsvariousapplicationsincancerresearchandnucleicacid chemistry.Tounderstandclearlythe bindingbehaviorofDNAwithSchiffbase metalcomplexes,abriefdescriptionaboutstructureofDNA,itsbindingmodesandcleavageis given below. 8) Antiviral propertiestheuseofvaccinesmayleadtotheeradicationofpathogensknownviruses,suchassmallpox,poliomyelitis(polio),whetherrubella.Although

therearemanytherapeuticwaystoworkagainstviralinfections,currentlyavailableantiviralagentsarenotfullyeffective,whichislikelyto causeahighrateofmutationofvirusesandthepossibilityofsideeffects.SalicylaldehydeSchiff basesderivedfrom1-amino-3-hydroxyguanidinetosylateareGoodmaterialforthedesignofnew antiviralagents[4].IsatinSchiffbaseligandsaremarkedbyantiviralactivity,andthisfactis veryusefulinthetreatmentofHIV.Inaddition,itwasalsofoundthatthesecompoundshaveanticonvulsantactivityan dmaybeincludedintheanti-epilepticdrugs.Gossypol derivativesalsopresenthighantiviralactivity.Increasingly, gossypol, oftenusedinmedical therapyisreplacedbyitsderivatives,becauseoftheirmuchlowertoxicity. Schiffbases haveobtainedacceptableresultsforCucumbermosaicvirus,whoseeffectivenesswasestimatedat74.7%[7].

Antimalarialproperties:

Malariaisadiseasewhichwhenisneglectedcausesseriushealthproblems.Humanmalariaislargelycausedbyfourspe ciesofthegenusPlasmodium(P.falciparum,P.vivax,P.ovateandP. malariae).Thesearchfornewdrugs,vaccinesandinsecticidesforthepreventionortreatmentof thisdiseaseisapriority.Schiffbasesareinterestingcompounds,whichcouldbepartof antimalarialdrugs.Forexample,thecompoundwithsucheffectisAncistrocladidine, whichisasecondarymetaboliteproducedbyplantsofthefamilyAncistroscladaceaeand Dioncophyllaceae,andpresentinganiminegroupinamolecularchain[4].

Applicationsinmoderntechnologies:

Photo andthermo chromicpropertiesofSchiffbasesaswellastheir biological activity make themapplicableinmoderntechnology.Amongothers,theyareusedinopticalcomputers,to measureandcontroltheintensityoftheradiation,inimagingsystems,aswellasinthemolecularmemorystorage,asorg anicmaterialsinreversibleopticalmemoriesandphoto detectorsinbiologicalsystems. Duetophotochromicproperties,Schiffcompoundscouldbehave asphoto stabilizers,dyesforsolarcollectors,solarfilters.Theyarealsoexertedinopticalsound recordingtechnology. Amongothers,worthyofinterestinthepropertiesassociatedwithSchiffrulesinclude:propertiesofliquid crystalchelatingabilitythermalstabilityoptical nonlinearityandtheabilitytocreatethestructureofanewtypeofmolecularconductorsusingelectricalproperties toprotontransfer. Becauseofitsthermalstability Schiffbasescanbeusedasstationeryphaseingas Chromatography.Theopticalnonlinearityofthesecompoundsallowsustousethemaselectronicmaterials,opto-electronic(inopticalswitches)andphotoniccomponent.Iminederivativescanbeexertedtoobtain conductivepolymers.Schiffbasesasanelectricalconductorpossessavarietyrangeofuses:ascatalystsinphoto electrochemicalprocesses,electrodematerialsandmicro-electronicequipment,organicbatteriesorelectro chromicdisplaydevice(graphicaloutputdevices)[7].Duetothe presenceoftheiminegroup,theelectroncloudofthearomaticringandelectronegativenitrogen, oxygenandsulfuratomsintheSchiffbasesmolecules,thesecompoundseffectivelyprevent corrosionofmildsteel,copper,aluminumandzincinacidicmedium.

IV. CONCLUSIONANDFUTURE SCOPE

Schiffbasesandtheircomplexesare flexiblecompoundssynthesizedfromthecondensationof anaminocompoundwithcarbonylcompoundsandextensively usedforindustrial purposes and alsoshow abroadrangeofbiologicalactivitiesincludingantibacterial,antifungal,antiviral,antimalarial,antiproliferative,anti-inflammatory,anticancer,anti-HIV,anthelminthicand antipyreticproperties.ManySchiffbasecomplexesshowexcellentcatalyticactivityinvarious reactionsandinthepresenceofmoisture.Wehavesynthesizedandcharacterizedfournew complexesofCo(II),Zn(II),Ni(II)andCu(II)withOandN donorSchiffbasesderivedfrom furfuraldehydeandethylenediammine.InthischemicalsynthesistheligandsofSchiffbasewas synthesizedbythereactionoffurfuraldehydewithethylenediamminein2:1ratiorespectivelyin methanol.Thereactionwasrefluxedonawaterbathfor3-4hours. Theprecipitatesthereby obtainedwereseparatedandwashedwithmethanolandfourcomplexesweremadefromthe resultingSchiffbaseligand.The ligandsandtheir metalcomplexeshave beencharacterizedon thebasisof IRstudies.Schiffbasesandtheir transition metal complexes, containing nitrogen andoxygendonoratoms,playanimportantroleinbiologicalandinorganicresearchandhavebeen studiedextensivelyduetotheiruniquecoordinationandbiologicalproperties1,2.Transition metalSchiffbasecomplexeshavefoundapplicationsinvarious fieldssuchasmedicine,agriculture,and industries3etc.furfuraldehydeiswellknownasananalyticalreagent4,5.Theirderivatives arealsousefulinvariousbiologicalandantibacterialactivities.

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Current Status and Future of Green Chemistry

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ABSTRACT

Since last decade, the researchers are more focusing on the concept of green chemistry, as it can protect human health and also economically beneficial manner. Various synthetic methods are being involved in key research areas such as design of safer chemicals, development of renewable feedstocks and environmentally being solvents. The future chemists are being indulged into design of products with an increased awareness for environmental impact. The sustainable society will depend on chemical products and processes that are designed following principles that make them conductive to life. The products, feedstocks and manufacturing processes will need to integrate the principles of green chemistry.

I. INTRODUCTION

Chemistry has brought about medical revolution in which drugs and antibiotics are being discovered. The worlds food supply also increased enormously due to discovery of hybrid varieties, improved methods of farming better seeds, use of insecticides, herbicides and fertilizers. The quality of life on earth became much better due to the discovery of dyes, plastics, cosmetics and other materials. The ill effects of chemistry also became pronounced, main among them being the pollution of land, water and atmosphere. This is caused mainly due to the effects of by-products of chemical industries.

II. DESIGNING OF GREEN SYNTHESIS

In any synthesis of target molecule, the starting materials that are made to react with a reagent under appropriate condition. The same product can also be obtained by modifying the conditions. The method of choice should not use toxic starting materials and should eliminate by-products and wastes.

III. CHOICE OF STARTING MATERIALS

It is very important to choose the appropriate starting materials. The synthetic pathway will depend on this. Till now most synthesis make use of petrochemicals which are non- renewable. Petroleum refining also requires considerable amount of energy. It is therefore important to reduce the use of petrochemicals by

using alternative starting materials, which may be of agricultural/biological origin. Some of the materials that have biological origin are butadiene, pentane, benzene, toluene, xylene, aldehydes, acrylic acids, methyl aryl ethers etc.

IV. CHOICE OF REAGENTS

The selection of the right reagent for a reaction is made on the basis of the efficiencies, availabilities and its effects on environment.

V. CHOICE OF CATALYSIS

Certain reactions proceed much faster and at a lower temperature with the use of catalysis. Heavy metal catalysis should be avoided as they cause environmental problems and are toxic in nature. Use of visible light to carry out the required chemical transformation should be explored.

VI. CHOICE OF SOLVENTS

Most of the common solvents generally used cause sever hazards. One of the commonly used solvents, benzene is now known to cause or promote cancer in humans and other animals. Toluene could cause brain damage or cause liver and kidney problems. Therefore it is ideal to carry out the reaction in aqueous phase if possible. The use of water as a solvent has distinct advantage.

VII. GREEN CHEMISTRY

Maximum incorporation of the reactants (starting materials and reagents) into the final product.

The percentage yield is calculated by

$$\%\text{yield} = \frac{\text{Actual yield of the product}}{\text{Theoretical yield of the product}} * 100$$

The chemists globally consider that if the yield of a reaction is about 90%, the reaction is good.
In other words, of one mole of starting material produces one mole of the product, the yield is 100%.
The reaction or the synthesis is considered to be green if there is maximum incorporation of the starting materials and reagents in the final products.

$$\%\text{atom utilization} = \frac{\text{Mw of desired product}}{\text{Mw of (desired product + waste products)}} * 100$$

$$\%\text{atom economy} = \frac{\text{Fw of atom utilized}}{\text{Fw of the reactant used in the reaction}} * 100$$

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Catalytic Acylation of P-Toluidine with Acetic Acid and Mercuration Reaction

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ABSTRACT
An easiest and environmentally friendly N-Acylation reaction is reported. In this reaction an effective N-C bond forming reaction takes place to give primary amides, in which primary amines was treated with acetic acid in presence of metal free catalyst benzophenone. The probable mechanism and mercuration reaction with acetamide was discussed.
Keywords: environment friendly; N-Acylation; amides; mercuration; metal free catalyst

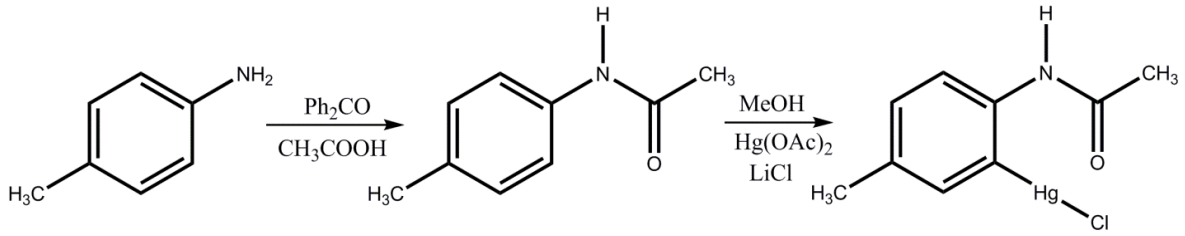
I. INTRODUCTION

Amide derivatives have attracted much attention of researchers due to their widespread applications in the pharmaceutical industry. Amide group are commonly employed as a protective group in synthetic methodology [1,2]. The amide bond generally can be developed through the treatment of primary amines with acyl halides [3], acid anhydrides [4], esters [5] and acids [6] in different conditions. In 2008 Wang and co-workers has reported a simple, convenient, and efficient synthetic method for amides using primary amine and acetic acid/benzoic acid under microwave irradiation in good to excellent yield [7]. Recently Sharley and Williams has developed a cheap and easiest method for acylation of a variety of amines. In this reaction acetic acid was used as catalyst and ethyl acetate/butyl acetate as the acyl source [8]. In 2009 Brahmachari et al. reported that the zinc acetate alone can act as a selective N-acetylation agent without any solvent under closed vessels microwave irradiation [9]. However all these procedure have several limitations. Hence, development of novel and environmental friendly methodologies using organic catalyst is still required for its usefulness in synthetic chemistry. On the basis of these backgrounds, we are reported here an easiest and environment friendly N-acylation reaction between *p*- toluidine and acetic acid is in presence of metal free catalyst benzophenone. Finally we also discussed its probable mechanism and mercuration reaction with N-(*p*-tolyl)acetamide.

II. RESULT AND DISCUSSION

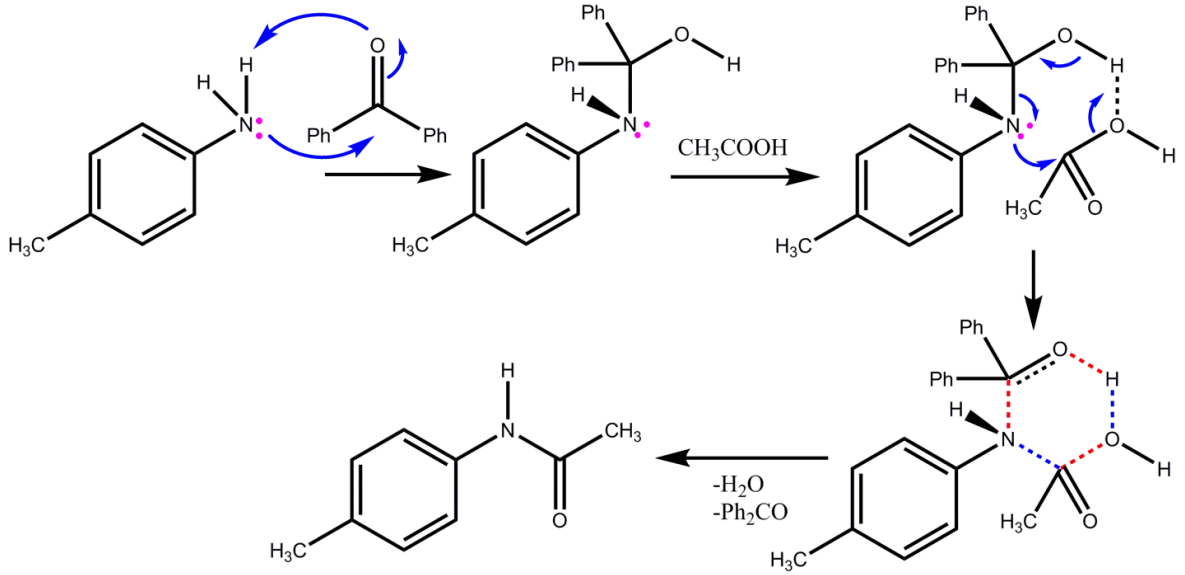
During the experiment *p*- toluidine was treated with acetic acid in presence of benzophenone at 80° C for 12 h. Reaction mixture after 12 h allow cooling to room temperature and poured in distilled water. The organic

phase was extracted with ether and dried over sodium sulphate. The ether solution was evaporate to give a off white colour crystalline solid of N-(*p*-tolyl)acetamide in excellent yield. The isolated solid was characterized with the help of melting point (149-150 °C) and ^{1}H NMR spectrum. (**Figure 1**) In proton NMR spectra of N-(*p*-tolyl)acetamide shows two sets of singlet at 2.12 and 2.29 ppm for *p*-methyl and acetyl group respectively. In aryl region we can see a two set of double-doublet of aryl proton at 7.10-7.07 & 7.35-7.38 ppm (for four aryl proton) with coupling constant 2.8 Hz. Along with theses a broad singlet was observed at 7.71 ppm for NH proton. In next reaction we treated N-(*p*-tolyl)acetamide with mercuric aceate followed by lithium chloride to give rise a white crystalline solid of (2-acetamido-5-methylphenyl)mercury(II) chloride in good yield. However this compound was less soluble in common organic solvent but good soluble in polar solvent like DMSO. It proton spectra was recorded in DMSO-d6 solvent. (**Figure 2**) In proton spectra again we observed here two sets of singlets at 2.00 and 2.21 ppm for *p*-methyl and acetyl group respectively. In aryl region we can see a two sets of double doublet at 7.06-7.09 and 7.51-7.54 ppm (for two aryl proton) with coupling constant 3 Hz along with these we also get two singlet at 7.18 ppm (for one aryl proton) and 9.66 ppm (for NH proton). These two singlet observed in aryl region confirmed that mercuration reaction takes place in tolyl ring. A probable mechanism was sketched in **Scheme 2** in which benzophenone was act as a catalyst.



Scheme 1 Catalytic acylation of *p*- toluidine and mercuration reaction with N-(*p*-tolyl)acetamide.

Mechanism



Scheme 2 Probable mechanism for catalytic acylation of *p*-toludine

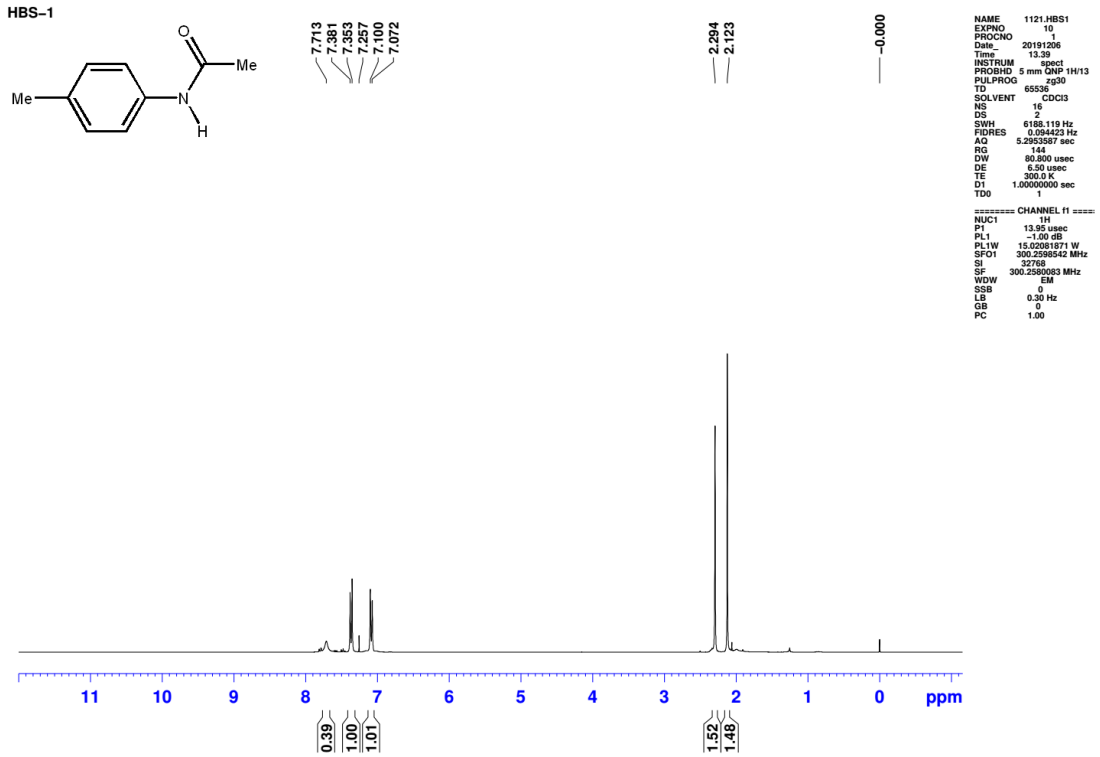


Figure1 ^{1}H-NMR spectrum of N-(*p*-tolyl)acetamide in $CDCl_3$ solvent.

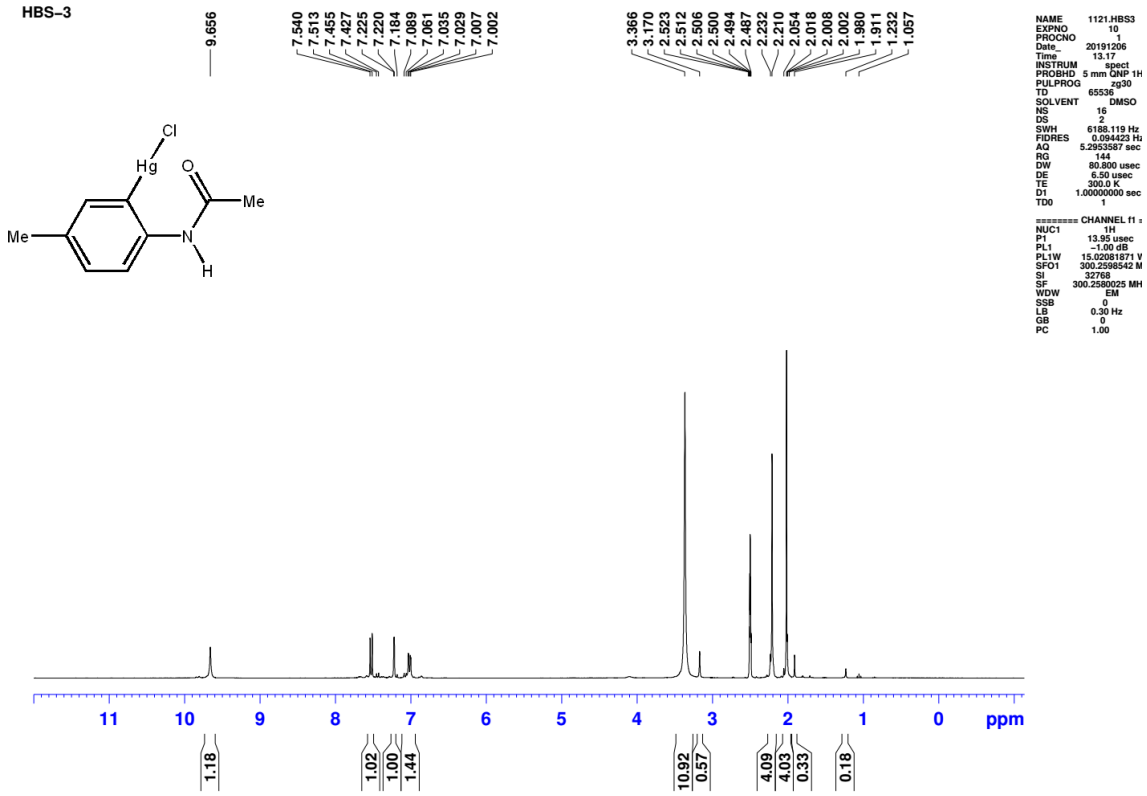


Figure 2 ^{1}H-NMR spectrum of (2-acetamido-5-methylphenyl)mercury(II) chloride in dmso-d_6 solvent.

III. EXPERIMENTAL

Melting points were determined with a micromelting-point apparatus. Proton NMR spectra were recorded on a Brucker AMX 300-MHz spectrometer, using $CDCl_3$ and DMSO-d_6 as solvent. Chemical shifts are reported in parts per million (d) relative to TMS as an internal standard. *p*- toluidine, benzophenone, Mercuric acetate, Lithium chloride, acetic acid and methanol were purchased from standard sources and purified using literature procedures.

Synthesis of N-(*p*-tolyl)acetamide:

A 50 mL round-bottomed flask was charged with *p*-toluidine (5.35 g, 50 mmol) in acetic acid (50 mL). Under vigorous stirring benzophenone (9.11 g. 50 mmol) was added. The mixture was stirred for 12 h at 80° C. The reaction mixture was allowed cooling to room temperature. For workup reaction mixture was poured in 100 ml distilled water. The organic phase was extracted with ether and dried over sodium sulphate. The ether solution was evaporate to give a off white colour crystalline solid of N-(*p*-tolyl)acetamide in excellent yield. Yield: 7.00 g (94%). Mp. 149-150 °C.

Mercuration recation of N-(*p*-tolyl)acetamide:

A 250 mL round-bottomed flask was charged with N-(*p*-tolyl)acetamide (1.49 g, 10 mmol) in methanol (100 mL). Under vigorous stirring mercuric acetate (3.18 g. 10 mmol) was added. The mixture was stirred for 24 h at 80° C. The reaction mixture was allowed cooling to room temperature and added 1 g lithium chloride in the reaction mixture to replace acetate ion with chloride ion afforded white precipitate. The precipitate was filtered and washed with dry methanol to give white powder solid of (2-acetamido-5-methylphenyl)mercury(II) chloride in good yield. Yield: 3.10 g (89%).

IV. CONCLUSION

In conclusion we have reported synthesis characterization of N-(*p*-tolyl)acetamide and (2-acetamido-5-methylphenyl)mercury(II) chloride in excellent yield. Both compounds were characterized with proton NMR spectrum.

V. ACKNOWLEDGMENT

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Environmental Balance and Remote Sensing

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ABSTRACT

Remote sensing provides a technique for mapping and monitoring broad areas. The information from remotely sensed images can be used in a number of ways for a number of purposes. Synthetic aperture radar (SAR) is a technique that allows us to remotely map the reflectivity of objects or environments with high spatial resolution through the emission and reception of electromagnetic (EM) signals. Satellite remote sensing is used for monitoring many environment related disciplines including environmental science, geology, agriculture climatology and oceanography. Natural environment is a general term for biological resources, climate resources, water resources and land resources which affects human beings survival and development. It is closely related to the sustainable development of society and economy. This paper provides a review of the progress in regard to the Satellite remote sensing technique and its applications in environmental sciences that can deal with environmental challenges. Satellite remote sensing is an excellent tool for environmental impact assessment. To keep the environmental balance of various sources of the earth, this modern approach will helpful.

Keywords: - Remote sensing; Environmental Monitoring

I. INTRODUCTION

The natural environment is essential for human survival and development since it provides water resources, land resources, biological resources and climate resources etc. The environmental degradation occurs frequently due to economically motivated activities. The advances in research and application of remote sensing from five aspects: ecological index retrieval, environmental monitoring in protected areas, rural areas, urban areas and mining areas. Due to the characteristics of large-scale and dynamic observation, remote sensing technology has been an indispensable approach for environmental monitoring. Global and regional environmental monitoring relies heavily on remote sensing satellite and sensors which are capable of quickly collecting spatial and spectral information of large-extent entities on the Earth's surface [1].

Remote Sensing has a growing consequence in the modern information society. Microwave remote sensing is the study of the interaction of matter and electromagnetic radiation in the microwave region of the

electromagnetic spectrum. The microwave SAR currently represents the best approach for obtaining spatially distributed geophysical parameter present on the Earth's surface or planetary bodies. Synthetic aperture radar (SAR) bounces a microwave radar signal off the Earth's surface to detect physical properties.

In the last 50 years, space information technology, especially satellite remote sensing technology, has provided advanced detection and research means for the investigation of the earth's resources, the monitoring of local and regional environmental changes, and even the study of global changes, with the advantages of being macro, comprehensive, fast, dynamic, and accurate. Remote sensing data are mainly used for environmental parameter monitoring based on physical models. Remote sensing satellite sensors feature a tradeoff among the spatial, temporal, and spectral resolutions [2].Satellite remote sensing is a powerful tool for acquisition of images over broad areas in short time and with great repetition. Satellite observations over land, oceans, and atmosphere and especially during the phenomena have become very important to protect the global environment, reducing disaster losses and ensuring sustainable development. From the remote sensing techniques, the DInSAR (Differential Interferometric Synthetic Aperture Radar) is cost effective and is the only one which can map the land surface deformation and it can assess the impact of mining on the environment. [3].

In recent years, the environment monitoring has turned into a smart environment monitoring (SEM) system, with the advances in the internet of things (IoT) and the development of modern sensors. Health and hygiene are key components of the sustainability of mankind and progress of any country, which comes from a clean, pollution free and hazardous free environment. Thus, its monitoring becomes essential so as to ensure that the citizens of any nation can lead a healthy life. Environment monitoring (EM) consists of proper planning and management of disasters, controlling different pollutions and effectively addressing the challenges that arise due to unhealthy external conditions. By focusing on agriculture, as a relevant issue for the growth of any nation, it is easy to underline how SEM can play a significant role by providing a "smart or green agriculture" that can deal with major challenges and factors involved in sustainable growth and enhancing productivity within the agriculture sector. In this case, the health of soil, moisture analysis, water contamination level, water quantity level and several other factors are very important in obtaining sustainable productivity in the agriculture sector [4].

Remote sensing is a popular technique that is using in the mapping and monitoring of earth features. Remote sensing works on electromagnetic radiation. Electromagnetic radiation consists of the electrical and magnetic field. Early remote sensing was predominantly passive, i.e. it depends upon the sun for energy. Over the time, significant innovations and improvements have been made in the active remote sensing which resulted in the form of sophisticated imaging techniques like Synthetic Aperture RADAR (SAR) and Light Detection And Ranging (LiDAR). SAR uses the microwave range for remote sensing. SAR can provide a quantitative estimation of ground changes and can be used in all weathers. [5].

Remote sensing provides spatial coverage by measurement of reflected and emitted electromagnetic radiation, across a wide range of wavebands, from the earth's surface and surrounding atmosphere. The microwave spectrum is divided up into bands depending on the wavelength of energy. Each of the bands has different uses and scientific applications.

Since SAR is an active sensor and uses the microwave band in the broad radio spectrum as in Figure 1, it has a day-and-night imaging capability, and an ability of penetrating could cover, and to some extent, rain. Further, L-band and P-band SAR has relatively long penetration depth into vegetation and soil, enabling to extract information on the interior of the targets. Because of these characteristics, SAR has been used in various fields of research.

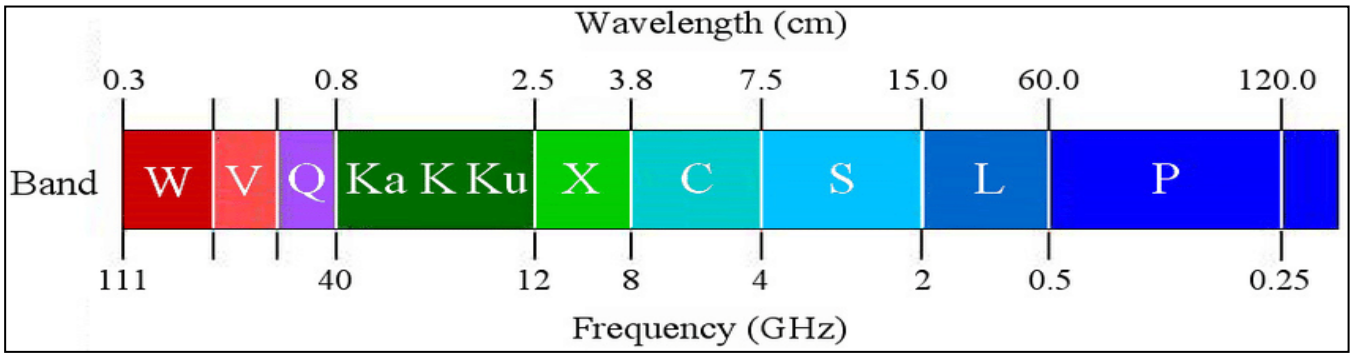

Figure 1. Band designation of microwave spectrum used for SAR.

Amplitude is the most basic parameter in SAR data, containing information on the electric and structural properties of scattering objects. Alongside with interferometry and polarimetry, utilization of amplitude data in single polarization and combination of different polarizations will be continued in various applications such as measurements of forest biomass and soil moisture, monitoring of agricultural crops, extraction of geological features, disaster monitoring and mitigation [6].

II. LITERATURE REVIEW

Vegetation parameters, such as LAI, biomass, fractional vegetation cover (FVC), vegetation height, vegetation water content (VWC), and chlorophyll, can be retrieved from remote sensing data owing to the relationships between vegetation characteristics and remote sensing observations, such as backscattering, bright temperature, and various vegetation indexes calculated by combining visible and near-infrared bands.

The sensitivity of different vegetation parameters to different remote sensing observations is distinct, and the auxiliary variables used for inversion are also diverse. Therefore, the selection of the most suitable auxiliary variables and models for inversion is an essential research topic [2].Unmanned aerial vehicle (UAV) based hyperspectral imaging is a relatively new remote sensing technology. The technology is increasingly being used to obtain fast and accurate information. Recently developed methods for data acquisition and pre-processing have mostly focused on agriculture and forestry applications. A pre processing workflow was developed to address the specific issues of monitoring the heterogenous distribution of the swamp vegetation and assess its condition. The workflow was used to produce reflectance products and vegetation indices. A clear understanding was obtained of the operational flexibilities and challenges in generating accurate spectroscopic products from UAV-hyperspectral systems to derive vegetative stress models in these environments. The research demonstrated how UAV-based near-earth monitoring tools can provide accurate

environmental monitoring in a remote and safe manner, which is important for monitoring sensitive environments. The data can also be used to identify health status at the species or community level [7].

Interferometric synthetic aperture radar (InSAR) is a rapidly evolving remote sensing technology that directly measures the phase change between two phase measurements of the same ground pixel of the Earth's surface. When two coherent single-look complex SAR images acquired by repeat satellite passes on different dates are co registered precisely and the difference of the phase values of individual pixels on the two SAR images are calculated pixel by pixel, an interferogram is formed. Repeat-pass interferometry allows the detection and mapping of the earth surface by using the temporal and spatial coherence characteristics, which can be successfully used for land cover classification, mapping of flooded areas, monitoring of geophysical parameters. The basic measurement of interferogram is the changes of spatial and/or dielectric properties using two images. The surface deformation and/or dielectric property change can be due to various forcing: earthquakes, landslides, lake or river surface water flow, oceanic water motion, movement of glaciers and ice sheet, accumulation of snow, forest canopy height, sand dune movement, dielectric constant change resulted from soil moisture change, freezing, or thawing, land subsidence due to ground water withdrawal, underground mining, hydrocarbon extraction, and permafrost melting, etc.[8].

The betterment of agriculture depends on various environmental parameters such as soil temperature, soil moisture, relative humidity, pH of soil, light intensity, fertilizing property of the soil, etc. Any small changes in any of these parameters can cause problems like diseases, improper growth of plant, etc. mainly resulting in lesser yield. There are number of techniques of doing the remote sensing for crop growth, vegetation growth and other related study for harvesting. The various methods have been used by On-field & Off-field sensors to estimate surface soil moisture information using remote sensing [9].

Remote sensed information of growth, vigor, and their dynamics from terrestrial vegetation can provide extremely useful insights for applications in environmental monitoring, biodiversity conservation, agriculture, forestry, urban green infrastructures, and other related fields. Specifically, these types of information applied to agriculture provide not only an objective basis (depending on resolution) for the macro and micro management of agricultural production but also in many occasions the necessary information for yield estimation of crops. Different environments have their own variable and complex characteristics, which needs to be accounted when using different Vegetation Indices (VIs) . Therefore, each VI has its specific expression of green vegetation, its own suitability for specific uses, and some limiting factors. Therefore, for practical applications, the choice of a specific VI needs to be made with caution by comprehensively considering and analyzing the advantages and limitations of existing VIs and then combine them to be applied in a specific environment [10].

The intensification of agricultural practices—under the auspices of the "Green Revolution" that includes better seeds, extensive fertilizer use, and irrigation—has dramatically altered the relationship between humans and environmental systems across the world. Satellite remote sensing offers tremendous potential for routine monitoring of irrigation due to the synoptic nature of the data and readily available archives of imagery [11].

Soil surface characteristics, namely the soil moisture content and roughness, play an important role in different applications such as hydrology, agronomy or meteorology. Floods, excess runoff, and soil erosion are, among others, key factors controlled and influenced by soil surface conditions [12-14].Indeed, soil moisture and surface roughness affect numerous processes on the soil surface such as infiltration capacity, temporary surface storage, deposition or detachment of particles, etc. RADARSAT-2 data and simulations using the Integral Equation Model (IEM) were analyzed to evaluate the polarimetric SAR parameters' sensitivities to the soil moisture and surface roughness.

The results showed that the polarimetric parameters in the C-band were not very relevant to the characterization of the soil surface over bare agricultural areas. Low dynamics were often observed between the polarimetric parameters and both the soil moisture content and the soil surface roughness. These low dynamics do not allow for the accurate estimation of the soil parameters, but they could augment the standard inversion approaches to improve the estimation of these soil parameters [15].

The IEM modelling is a one of the realistic method for measurement of geophysical parameter of the Earth surface using microwave SAR dataset. The modelling makes the process of estimating information beyond the real observation range for data interpretation. Most widely used modelling techniques for the microwave SAR dataset is an Integral Equation Model (IEM) which is implemented for above said geophysical parameters retrieval [16].

III. RESULT AND DISCUSSION

Remote sensing provides tools for regular monitoring and spatial assessment of earth surface and processes. To understand the consequences of natural phenomena and human actions on the environment there are needed data acquired in real-time that are the basis of modeling various environmental impacts.

Thus, from the remote sensing perspective, studies that attempt to map earth areas have been rare and scientific consensus on mapping methodologies is fragmented and evolving. It contributes to the building of a domain knowledge base which will be used further in the development of Remote sensing applications for environmental management. Suitable monitoring is necessary so that the world can achieve sustainable growth, by maintaining a healthy society.To maintain environmental safety it is very necessary strengthen the management and protection of the environment with remote sensing technology.

IV. CONCLUSION

A systematical review on the Environmental monitoring by remote sensing techniques is presented in this paper. Remote sensing is valuable for environmental investigations and possibly for preliminary warning. Satellite remote sensing is in securing and making correct decisions. The participation of environmental organizations, regulatory bodies and general awareness would strengthen smart environment monitoring efforts. The modern remote sensing practices have caused significant environmental change in many regions

at the regional as well as global scales. The advances suggested many opportunities and challenges for disasters for environment monitoring.

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Thermal Cracking of Used Engine Oil to Produce Diesel Range Fuel

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ABSTRACT

The lubricating oils used by automotive engines have to be replaced at least every 10000 km and 3000km for cars and motorcycles respectively as it becomes unfit for further use. This oil is labeled as used engine oil. Such used lubricating oil becomes unfit for further use due to accumulation of contaminants in the oil and chemical changes in the lubricating oil. Mismanagement of used engine oil has a serious environmental problem.Most of used oil is handled improperly, and some is dumped into sewers,some is dumped into the ground or is poured into dirty roads or is dumped in deserts, where it could contaminate surface and ground water.It is also used for heating purposes resulting in air pollution. All of such uses are adversely affecting the environment.Therefore recycling of used oil became the need of hour due to economic, environmental, health and legal reasons. Using used engine oil as a source of energy or feedstock for chemical industries is a good option for any country, importantly for India, as it would conserve both the valuable natural resources as well as foreign exchange. There are two options available, either recovering the heating value of used oils by converting it into fuel that can be used to power the IC engine or re-refining used oil to recover lube oil base stock to formulate the fresh lubricants. This study is focused on the thermal cracking of used engine oil to produce high value diesel range fuel.

Keyword: Used engine oil, re-refining, recycling, environment, thermal cracking.

I. INTRODUCTION

Thermal cracking, catalytic cracking and hydrocracking are well known refinery processes based on the principle of breaking larger hydrocarbon molecules into smaller ones and by doing so these processes increases the value of low value residual part of crude oil as thelighter hydrocarbons are more valuable than heavier ones.

Thermal cracking is a common refinery process which is used to crack heavier hydrocarbons from high boiling residue to lighter hydrocarbons. Thermal cracking reactions start at about 360^0C and it follows free radical mechanism.

Hydrocarbon molecules in lube oil are generally straight chain paraffinic hydrocarbons, aromatic, naphthenic or naphthenoaromatics. Straight chain molecules are termed paraffinic,these paraffinic hydrocarbon

molecules are the easiest hydrocarbon molecules to crack while polynuclear aromatics are the most difficult to crack. Paraffins are most desirable hydrocarbons in the lube oil because of their high Viscosity Index therefore used engine oil is ideal feedstock for a thermal cracking process.

Straight chain paraffinic hydrocarbons in the boiling range of diesel fuel have low self-ignition temperature which is most important characteristic of diesel fuel and therefore they are very much desirable in the diesel fuel.

Various hydrocarbons present in the feedstock responds to cracking conditions in different way depending on size and structure of that particular molecule. Therefore this process produces a wide range of hydrocarbon molecules of different boiling points and therefore process conditions needs to be controlled very closely to produce the desirable product with minimum undesirable components.

To achieve the objective of producing desirable hydrocarbons the temperature, pressure, and residence time in the thermal cracker needs to be controlled closely.

II. EXPERIMENTAL WORK

The used oil is first filtered to remove the particulate contaminants from it and then dehydrated to remove the lighter hydrocarbons and moisture from it. Used oil contains 6% to as high as 15% or more water in the emulsion form.

The used oil is subjected to cracking at 440^0C temperature; the feed flow rate is maintained so that the required conversion of the used oil to diesel range hydrocarbons is obtained. The cracked product contains non-condensable hydrocarbon gases, lighter hydrocarbons, diesel range hydrocarbons, heavy hydrocarbons as well as residual material. The temperature and feed flow rate is optimized so that maximum yield of the desired hydrocarbons are obtained and the yields of undesired components is decreased. This cooled liquid product is distilled to separate the diesel range hydrocarbons from lighter and heavier hydrocarbons as well as to separate the residual part from the cracked product.

The products

- Off-Gases: These are lighter non-condensable gases.
- Lighter liquid hydrocarbons: These are lighter hydrocarbons liquid falling in the boiling range of naphtha fraction.
- Gasoil: This is the main product of the thermal cracking and yields of about 80 per cent by weight of dried feed can be obtained.
- Heavy Residual Fuel: The bottoms from the cracked product.

III. CONCLUSION

The significant aspect of thermal cracking process is its ability to adjust process operating conditions to tailor the desired product, diesel range hydrocarbons. In this process operating parameters can be adjusted to vary

the boiling range of product, thus the process can also be manipulated to maintain a target product quality with feed variability.

The thermal cracking process is emerging as the technology of choice for progressive environmental services companies as they consider technology choices. Conversion of used oil to diesel range hydrocarbons is desirable from an environmental point of view since the product displaces the need to consume a virgin diesel range hydrocarbon fraction produced from crude oil.

Diesel range fraction has a value that is high relative to heavy distillate fuel oils or residual replacement fuels. Diesel fuel is cleaner burning and the markets for diesel fuel are very large and diesel fuel is marketable anywhere in the world. Thus the technology has potential application worldwide. This could be a significant benefit to the world environment in aiding to solve the used oil problem. There are various processes available to process the used engine oil so that valuable hydrocarbons from it can be claimed back, but the thermal cracking is the best process amongst these processes from the economic and environmental viewpoint.

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Environmental Studies of Sindphana Dam Tq. Shirur (k.), Dist. Beed

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ABSTRACT

The present study deals with the hydro biological properties of Sindphana Dam are located in Shirur Taluka in Beed district of Marathwada region. (M. S.)
The total elevation of the Sindphana River is 528m (1732 ft.). The height of the dam above lowest foundation is 19.05 m (62.5 ft.) while the length is 1,937 m (6,355 ft.). The construction of the dam is started in late 1950 and it was completed in 1963.
Sindphana Dam is constructed for Irrigation, Drinking, and Fish Culture purpose. It is constructed on the River which is named as Sindphana River near Shirur. The Sindphana Dam is also known by the name Hingewadi Dharan owned by Govt. of Maharashtra Determination of physic-chemical parameters (i.e. water temperature, turbidity, total dissolved solid, pH, free CO2) was carried out in time duration of 6 months (December 2019- May 2020). The ecological status of such reservoir is seen different in different regions.
Keywords: Total dissolved solids, Turbidity, pH and Water parameters.

I. INTRODUCTION

The water is a very interesting element of life chemically as well as physically. The environment of the water dams are directly affected by human activities like fishing, recreation. In this process not only the water quantity is lowered but the impact of human activities is also affect the biological, biotic, soil properties and physiochemical status. Even in the most unpolluted geographical areas.
The rainwater has dissolved O_2, CO_2, and N_2 may also carry the suspension dust or other particulars picked up from the atmosphere. Some of the important and recent contributions are eletta & Adekola 2005, Kiran 2010, Raut et.al 2011 and Naik et.al. 2012, who has been studied the physiochemical parameters of the various water bodies.

II. MATERIAL AND METHOD

In six month study of Sindphana dam (December 2019 to May 2020) water analysis were carried out as per the guidelines given in the chemical and biological method for water pollution studies Trivedi and Goel (1986).

Water temperature sample was recorded in the field itself with help of Centigrade thermometer.
These samples are collected in the comparative study between two stations i.e. Station A and Station B respectively in order to mention in observation table the Right Hand Side is station A and Left Hand Side is B.
Turbidity = the turbidity of the water was recorded in the laboratory with the help of the nephlo-turbiditymeter.
Total dissolved solid (TDS). 500ml of the filtered sample was taken in previously dried and the weighted beaker of 500ml of the filtered sample was taken in previously dried and weighted beaker and evaporated to dryness and weighted again.

$$\text{TDS mg/l} = \frac{\text{A-B x 1000 x 1000}}{\text{V}}$$

Where, A- Final weight of the dish 19 gm.
Where, B- initial weight of the dish in gm.
Where, C-Volume of sample taken in ml.

pH - pH of water sample were measured in the field with help of electronic pH Meter.
Free Carbon dioxide (CO_2) - Titrimetric
Take 100 ml of sample in conical flask and add a few drops of phenolphthalein indicator. If the color turns pink. Free CO_2 is absent and if the sample remains colorless, titrate it against 0.05N NaOH. At the end point Pink color appears.

Observation Table 1.1 Table showing Physico-chemical Parameters of Sindphana Dam

Month ↓	Water Temperature		Turbidity		TDS		pH		Free CO_2	
Station→	A	B	A	B	A	B	A	B	A	B
December	17.2°C	17°C	75	68	154	161	7.0	7.2	2.80	3.03
January	21.1°C	21.2°C	77	70	155	162	7.5	7.6	2.80	3.03
February	22°C	22.8°C	82	75	170	177	7.5	7.6	3.20	3.50
March	25.7°C	26°C	95	92	190	200	7.6	7.7	4.02	4.75
April	28.0°C	28.5°C	102	98	201	220	7.7	8.0	5.01	5.99
May	31°C	31.5°C	116	111	215	223	8.0	8.3	6.60	6.81

III. RESULTS AND DISCUSSION

1. Water temperature

Air and water temperature followed a common pattern it was higher in summer and relatively lower in monsoon and winter (Weltch.1935), (Laxminarayan. 1965). The maximum water temperature was recorded in the summer, while in the minimum was recorded in the winter season. Similar results were observed for Sonkhed Dam (Jadhav et.al. 2006). Temperature will depend up on season and time of sampling. In six

months investigation the range of water temperature was maximum in the month of May i.e. 31°C and 31.5°C Minimum temperature in the month of December i.e. 17.02°C and 17°C at station A and Station B. respectively at both station. Mohammad Abubaker Sithik et.al. (2009).

2. Turbidity

Turbidity interferes with disinfection and microbiological determination water with turbidity of less than 5 Nephlometer Turbidity Unit (NTU) B usually acceptable to consumer. In six months investigation the range of water turbidity was maximum in the month of May 116 and 111 NTU and Minimum turbidity in the month of December 75 and 68 NTU. At station A and at station B. respectively at both station. The turbidity of water showed seasonal and monthly variation, Ajmal and Razauddin (1988) have also reported this type of seasonal variation. Higher turbidity affects the life indirectly (Verma et.al. 1978) by lowering down the penetration of light utilized by aquatic plants for photosynthesis and there by depleting the rate of primary productivity and in turn affects fish and food.

3. Total dissolved solids (TDS)

Total dissolved solids (TDS) can have an important effect on the taste of drinking water. The palatability of water with TDS level of water is less than 600mg/l is generally considered to be good drinking water becomes increasing unpalatable at TDS level to greater than 200mg/l water with extremely low concentration of TDS may be unacceptable because platinsipsd taste. Arrnah Fredrick Ato et.al. (2010).

In six months investigation the range of water TDS was maximum in the month of May 215 and 223 and minimum TDS in the month of December 154 and 161 mg/l at Station A and Station B respectively

Mohammad A.F. Toufeek et.al. Reported that the TDS in the Lake Nasser water is ranged between 144 and 175mg/l indicate that the lake has high water quality for drinking, fisheries and irrigation.

Raj Narayan et.al. (2007) reported in his study period at texi temple pond the TDS of the pond was 120mg/l in summer which is the highest value and lowest values was noticed in winter.

4. pH

pH is the scale of intensity or acidity and alkalinity of water and the concentration of hydrogen ions. Most of the biological processes and biochemical reactions are pH dependent. (Adarsh Kumar et. al. 2006). In six month investigation the range of water pH was maximum in month of May 8.00 to 8.3 and minimum pH in the month of December 7.0 to 7.02 at station A and station B respectively at both station.

Khan and Siddiqui (1970) reported that fluctuation in pH values were mainly due to photosynthetic activity of phytoplankton and other higher aquatic plants.

5. Free CO_2

In an aquatic ecosystem source of carbon dioxide are community, respiration and decomposition, while it is consumed in the photosynthesis.

In six months investigation the range of water free CO_2 was maximum in the month of May 6.6 and 6.81 mg/l and minimum in the month of January 2.80 and 3.03 mg/l at station A and station B respectively at both station. Goldman and Harne (1993) the amount of free carbon dioxide funds on the decomposition of top soil and chemical nature underlying rock.

A Nargis et. al. (2008) noted the amount of free carbon dioxide was 24.7ppm in October 65.30ppm in April. The increased free carbon dioxide was possibly due to the accelerated O_2 bacterial decomposition.

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Impact of Nanomaterials on Everyday Life

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ABSTRACT

Nanotechnology is currently one of the top priority research areas in many countries because of its enormous potential and economic impact. Nanotechnology involves the research, development, production and processing of structures and materials on a nanometer scale in a variety of fields, including science, technology, healthcare, industry and agriculture. Identifying the potential benefits and unforeseen dangers of nanomaterials for the environment and human health is crucial to pursue their future development. This has been made clear by numerous publications in the field of nano-ecotoxicology which, although investigating the effects of many nanomaterials on many organisms, almost never accept clear statements about the potential dangers of these nanomaterials. This fact not only hinders the communication of all non-scientists but also complicates the transfer of the results obtained to other scientists.
Nanocomposites with nanomaterials and unique physical and chemical properties are increasingly being used by the construction industry to enable new applications. Yet, we face timely concerns about their potential effects on the environment and human health. To provide a risk perspective, the adverse biological and toxic effects associated with these nanomaterials are also reviewed along with their mode of action. Nanotechnology presents numerous opportunities to develop new and improved consumer products for the benefit of the community. However, as the industrial production and use of nanotechnology products expands rapidly, potential human health concerns and environmental protection measures for the environment need to be addressed.
Keywords: - Environmental impact, Nanocomposites, Nanotubes, Nanoparticals, Health and Social Impact.

I. INTRODUCTION

Nanomaterials are chemicals or substances that are rarely produced and used. Nanomaterials are developed to exhibit new properties compared to similar materials without nanoscale properties, such as increased strength, chemical reaction or conductivity. 'Material with any external dimension in nanoscale (size range approximately 1 - 100 nm) or material with internal structure or surface texture in nanoscale.
Nanotechnology is a general term for the design and construction of anything that is used depending on the specific structure of the nanoscale - generally considered to be 100 nanometers (100 millionths of a

millimeter or 100th of a meter) or less. This includes equipment or systems made by handling individual atoms or molecules, as well as materials that have very small structures. Nanomaterials are generally considered to be materials with an internal dimension of 100 nanometers or less or 100 nm or less internal structure. They can be in the form of particles, tubes, rods or fibers. Nanomaterials that have a similar composition to largely known substances may have different physico-chemical properties from the same material in bulk form and may behave differently if they enter the body. So they can create different potential dangers.

Nanomaterials can be defined as materials with an external dimension of at least 1-100nm. Nanomaterials can occur naturally, can be produced as a by-product of combustion reactions, or can be intentionally produced by engineering to perform a specific function. Nanomaterials are generally considered to be materials with an external dimension of at least 100 nanometers or less or an internal structure of 100 nm or less. They can be in the form of particles, tubes, rods or fibers. Nanotechnology can be used to design pharmaceuticals that target specific organs or cells in the body, such as cancer cells, and increase the effectiveness of therapy. Nanomaterials can also be added to cement, textiles and other materials to make them stronger and lighter. Through nanotechnology, nanoparticles can help make materials lighter, more durable and more reactive. Nanoparticles are applicable in a wide variety of industries and uses, including: electronics to make computers faster, memory chips smaller, and screens clearer and brighter [1-6].

II. HEALTH IMPACT

The health effects of nanotechnology are related to the effects of nanotechnological materials and equipment on human health. The impact of nanotechnology on health can be divided into two aspects: (a) the potential of medical applications to cure diseases in nanotechnological innovations and (b) the potential health risks posed by exposure to nanomaterials. The extremely small size of nanomaterials means that they are more easily absorbed by the human body than the corresponding large size particles. How these nanoparticles behave inside the body is an issue that needs to be addressed. A major concern is the accumulation of non-decomposable or slowly decomposing nanoparticles in organs. The behavior of nanoparticles is due to their shape, size and the function of the surface reactions of the surrounding tissues. Phagocytes, cells that consume and destroy foreign substances, can be overloaded by nanoparticles that trigger stress reactions that cause inflammation and weaken the body's defenses against other pathogens. Furthermore, nanoparticles that come in contact with tissues and fluids absorb some of the macromolecules found on their surface, which can affect the regulatory system of enzymes and other proteins. The human body has developed tolerance to most of the naturally occurring elements and molecules it comes in contact with. It does not have the natural immunity to new substances and is more likely to be toxic. Nanoparticles can enter the body through the skin, lungs, and digestive tract. It can help produce 'free radicals' which can cause cell damage. There is also concern that nanoparticles may cross the blood-brain barrier once they enter the bloodstream. Kirchner et al. After contact with living cells, three main causes of nanoparticle toxicity were identified: “(a) Chemical toxicity of the substances from which they are made. For example, Cd^{2+} cadmium is released from

nanoparticles of selenide. (b) Small size: Nanoparticles can stick to the cellular membrane and enter the cells. Attaching nanoparticles to the membrane and storing nanoparticles inside cells can impair cellular functions, even in the case of chemically inactive nanoparticles, which do not decompose and do not react with other matrix components. (c) Size. For example, carbon nanotubes can easily penetrate the cell membrane. " Nanotechnology has the potential to use molecular genomics and proteomics-based research to achieve this . Since 2003, a DNA chip based on a gene expression profile has been used to predict breast tumor growth, to determine which patients will receive complementary chemotherapy after surgical removal of the tumor. Similar chips are being developed to diagnose leukemia, mouth and throat tumors. Nanotechnology has played a role in the development of chips and their recognition to increase sensitivity and reliability. Many of the substances that can be used in theory, which are rarely soluble in medicine, are broken or inactivated before reaching their targets, have difficulty passing through specific biological barriers, and are uniquely distributed to all types of tissues and organs. These events make them ineffective, leading to high-dose treatments and ultimately unwanted side effects. Nanomedicine addresses the challenges of lack of specificity, toxicity of therapeutic compounds, poor bioavailability due to low solubility, and low efficacy due to large size content in regular drug delivery. Drugs or biomolecules can be trapped inside the nanoparticles or absorbed on their outer surface. As a drug delivery system, nanoparticles can penetrate the smallest capillary vessels; avoiding rapid clearance by phagocytes which greatly increases their stay in the bloodstream; Infiltration of cells and tissues to reach their target organs; improving the effectiveness of drugs and reducing toxic side effects. Drug delivery using nanocarriers / nanoparticles (liposomes, mycelium and polymeric nanoparticles) is of particular interest in overcoming the limitations of regular delivery systems as their biological properties can be handled and controlled to meet the desired requirements for pharmacological and therapeutic purposes. Although the use of nano-carrier systems is highly controversial in some research communities, there are empirical documents suggesting that nano-carriers penetrate tissues more efficiently and enhance tissue-specific action of drugs compared to regular drug administration routes. Research to improve the combination of uniqueness and carrier content to achieve the right rate of drug release; Conducts research on surface changes to increase the targeting capacity of nanoparticles; Research on optimization of nanoparticle preparations to increase drug delivery capacity, clinical usability and industrial production potential; Research on in vivo dynamic processes, targeting tissues and organs to uncover the interaction of nanoparticles with blood is all ongoing. Nanoparticles cannot simply act as drug delivery systems .They act as active substances under certain conditions. It has been reported that once metal-containing nanoparticles enter the tumor through the bloodstream, or when they are injected directly into the tumor, they can be heated using near-infrared radiation or using a fast magnetic field to destroy tumor cells [10].

III. POSITIVE IMPACT

Nanoparticles have many unique health benefits; Molecular imaging uses nanoparticles that help detect, quantify, and display molecular and cellular changes that occur in vitro and in vivo. Fluorescent biological

probes using biological dyes are traditionally used in biology because of their heavy properties and ability to communicate without losing sensitivity in various cellular reactions. In vivo, nanoparticles can be used as probes in conjunction with proteins, antibodies, and molecules of nucleic acids. These nanoparticles can then be used as tools to display and quantify molecular reactions in the body. They have high light stability, high levels of brightness and absorption coefficients in a wide spectral range. Site-specific-targeted drug delivery using nanoparticles is more effective and less costly for improved bioavailability, minimal side effects, reduced toxicity to other organs. Gold and silver nanoparticles have strong antifungal, antibacterial, and anti-inflammatory properties, and are used in anti-wrinkle creams, deodorants, and burn medications. An exciting potential use of nanoparticles in the treatment of cancer is the discovery of tumor-specific thermal scalpels to heat and burn tumors. Using a near infrared-absorbent polyethylene-coated gold 130 nm nanoshell, it can be used to prevent tumor growth [2].

IV. NEGATIVE IMPACT

The toxicity of nanoparticles depends on their surface properties, coating, composition, size and ability to assemble. If the solubility of nanoparticles is low, they can cause cancer. This is because nanoparticles have a higher surface area to volume ratio which enhances the chemical and biological reactions.[9]
Nanoparticles can enter the body in many ways; thermally, by inhalation, inhalation, injection or implantation. Nanoparticles penetrate the skin when contained in skin care products, hair products or lip balms with sunscreen and anti-wrinkle creams. Cosmetic products do not require clinical trials, but there are many products with nanoparticles. The nanoparticles in these products cause erythema, cobalt and chromium nanoparticles cross the skin barrier and damage fibroblasts. Several mechanisms have been proposed to explain the adverse effects that can result from cardiopulmonary abnormalities and death in populations exposed to nanoparticles.. The immune system begins to release cytokines, a chemical that is usually released when the body comes in contact with foreign substances [6].

V. ENVIRONMENTAL IMPACT

Nanotechnology is being used in many applications to improve the environment. These include clearing existing pollutants, improving production methods to reduce the production of new pollutants, and making alternative energy sources more efficient. Potential applications include: The use of silver nanoclusters as catalysts can significantly reduce the pollutant by-products produced in the process used to make propylene oxide. Electricity increasing the power generated by windmills. Epoxy is used to make windmill blades with carbon nanotubes. As a result, the blades are stronger and lighter, and therefore the power generation through each windmill is higher. To produce solar cells which electricity generates electricity at competitive cost. Researchers have shown that arrays of silicon nanowires embedded in polymers result in low-cost but high-efficiency solar cells. This can result in solar cells that generate electricity effectively at the cost of coal or oil. Nanotechnology has been declared a "revolution" in science for two reasons: first, because of the

radical approach to how chemicals and components, such as gold and silver, behave, compared to traditional scientific understanding of their properties. Second, the impact of these new discoveries, as applied to commerce, could transform the everyday life of consumer products, from sun tan lotions to cosmetics, food packaging, paints and coatings for cars, homes and fabrics, pharmaceuticals and thousands of industrial processes. Consumer-friendly use of nanotechnology, already in commercial flow, improves coating on inks and paints in everything from food packaging to car painting. Miraculous developments, for those who are eagerly awaiting these medical products, may seem science fiction, permanently shaping civil society with the emerging commercial impact of nanotechnology applications on consumer products. Thus, everyone under the jurisdiction of the Council of Europe is an end user of nanotechnology, regardless of how nanotechnology has touched everyday life [1].

VI. POSITIVE IMPACT

Nanotechnology enhances the strength of many materials and equipment, as well as enhances the efficiency of monitoring equipment, uses less energy, reduces material waste, prevents toxicity, measures environmental pollution, and produces renewable energy. These are considered to be the positive effects of nanotechnology. The use of nanomaterials and nanoparticles can lead to significant savings in resources and increase efficiency in manufacturing and energy related applications. Nanotechnology offers potential economic, social and environmental benefits. It has the potential to help reduce human footprint on the environment by providing solutions for energy consumption, pollution and greenhouse gas emissions. Nanotechnology promises to meet the global challenges of the 21st century in providing alternative energy, protecting the human right to clean water, ensuring wildlife conservation, cleaning up Brownfield's and reducing the burden of global diseases[8].

VII. NEGATIVE IMPACT

Nano materials vary in size and shape which are important factors in determining toxicity. Lack of information and methods of characterizing nanomaterials make current technology extremely difficult to detect nanoparticles in the air for environmental protection. Also, knowledge of the chemical composition is an important factor in determining how toxic a nanomaterial is, and minor changes in the chemical working group can radically change its properties. At all stages of nanotechnology it is necessary to assess the full risk of safety on human health and environmental impact. Risk assessment should include exposure risk and its likelihood, toxic analysis, transportation risk, survival risk, risk of change, and ability to recycle. Life cycle risk assessment is another factor that can be used to estimate environmental impacts. With the current nanoscale content getting smaller, it is more difficult to detect toxic nanoparticles from waste that can pollute the environment. There are ways in which nanoparticles or nanomaterials can become toxic and harm the surrounding environment [2].

VIII. SOCIAL IMPACT

It is the impact of technology on our quality and lifestyle is, in the end, often given a reason why we should embrace technological change, so it would be extremely annoying if we could not predict these things at all. Furthermore, if nanotechnology enthusiasts can articulate its benefits in terms of new consumer products, improved quality of life, and extended lifestyle possibilities, social critics need to consider how likely they are to become aware of these possibilities. Alternative, perhaps less attractive, situation. In fact, we can reasonably believe that nanotechnology will have a significant social impact on the balance of power between minimal-health and the medical sector, citizens and governments, and the balance of power between citizens and corporations. Furthermore, I believe that if you look beyond previous technology experience, you will have some idea of what this is likely to be [3].

As established in previous sections, nanotechnology has the potential to improve life through innovations in areas such as agriculture, water purification, healthcare, transportation and environmental biomedicine; and these capabilities come with the responsibility of the government, the private sector and the public. Throughout history, many technologies have been plagued by social controversy that has led to dislike of such applications. The social dislike of technology often has a negative effect on the commercialization of such technology [7]. For example, the literature showed that the introduction of genetically modified staple crops to the early generation market sparked widespread public debate, which was hostile to their support and, at least in some parts of the world, to commoditization. Moreover, there is a way to create fear in the minds of potential customers as unforeseen events and accidents have a negative impact on the public. Disputes about the occurrence and application of such unforeseen events have far-reaching effects on the level of rejection / acceptance of technology. As a result, it is important to be aware of the factors that determine the social acceptance of evolving technology.

Beyond the toxic risks to human health and the environment associated with first-generation nanomaterials, nanotechnology has broad social implications and broader social challenges. Social scientists have suggested that the social problems of nanotechnology should be understood and evaluated only as "downstream" risks or effects. Instead, challenges must be incorporated into "upstream" research and decision-making processes to ensure technological development that meet social goals. Many social scientists and civil society organizations suggest that the evaluation and governance of technology should include public participation. Stakeholder assessment is also an essential component for assessing the large-scale risks associated with nanotechnology and nano-related products [5].

Nanotechnology can provide new solutions for millions of people in developing countries who do not have access to basic services such as safe water, reliable energy, health care and education. The 2004 UN Task Force on Science, Technology and Innovation noted that some of the advantages of nanotechnology include low labor, land or maintenance, high productivity, low cost and reasonable use of materials and energy. However, there are frequent concerns that the claimed benefits of nanotechnology will not be evenly distributed and that any nanotechnology benefits (including technical and / or economic ones) will only reach rich nations. The long-term concern is whether the new technology will have a major impact on

society and whether it could lead to a post-scarcity economy or alternatively widen the wealth gap between developed and developing nations. The effects of nanotechnology on society as a whole, on human health and the environment, on trade, on security, on food, and even on the definition of "human" have not been described or politicized [4].

IX. CONCLUSIONS

The current work focuses on recent developments, particularly for periodontal management of nanoparticles and nanotubes, from hollow nanospheres, core shell structures, nanocomposites, nanomaterials to materials developed and nanomaterials. Once nanomechanics become available, the ultimate dream of every healer, physician andphysician in history will finally come true. Programmable and controllable microscale robots consisting of nanoscale components designed for nanometer accuracy will allow medical doctors to carry out therapeutic and reconstructive procedures in the human body at the cellular and molecular levels. 21st Century Nanomedical Physicians will still make good use of the body's natural healing powers and homeostatic system, because while all others are the same, they are the best at minimally invasive interventions.[6]

There is no doubt that nanotechnology will continue to evolve, benefit the society and improve the environment in various ways. Nanoscale materials will make products better in terms of efficiency, weight savings, lower energy consumption and cleaner environment. Shortcomings always exist when new uncertified technologies are released. Nanomaterials can help clean up some environmental waste, but can pollute the environment in other ways. Choosing the right nanoscale material for the future direction of nanotechnology is one of the key parameters. Engineering ethics needs to be defined before the commercial use of nanotechnology. Risk assessment on new nanomaterial based applications is important to assess the potential risk to our environment while the products are in use. The entire life cycle evaluation and analysis for all different applications should be conducted with constant attention [6].

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The Need of Green Chemistry in Today's Research

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ABSTRACT

In recently rapidly developed strategy in research is a branch of chemistry of green chemistry. It is need to reduce the wastes of raw materials in research and avoided environment damage by reuses of chemical in the reaction byproduct also man made materials like chemical component, un degradable chemical products that causes disorder, harm, instability to ecosystem. The increasing the pollution is risk to the live organisms and environment. The recycling the waste, minimizing waste, renewable biomass and bio refineries the utilizing green solvent to covers latest development in current research. It is necessary to restore ecological balance and to safeguard and sustenance of living kingdom, Green chemistry is the new and rapid enhancing emerging branch of chemistry.

Keywords: Green Chemistry, Pharmaceuticals, Hazardous chemicals, Environment Pollution and Sustainable chemistry.

I. INTRODUCTION

Green chemistry are root to develop research for recent processes and technologies which from thenewly methodare aimed to prevent low environmental pollution by reducing the wastes material and volume of chemical wastes also their toxicity or recently used green materials is as a starting materials are safer than those of harmful chemical materials. The today's science is faster growing towards to explosion and development. The green chemistry is new scheme or process to development and this process solve the problem of loss of environment for the future (1,2). The Heterogeneous catalysis, bio-catalysis, solvent-less synthesis, use of microwaves and ultrasound, etc. are part of green chemistry. However, many argue that green chemistry is not a new concept as it is made to believe, rather, it is the proverbial 'old wine in a new bottle (3).The Green approach towards thesustainability and development in research, in life style is also in every zones, various sector and daily routine.

The main source of green chemistry can be traced back to the Solvay process invented in 1811 for the manufacture of soda ash (NaCO3) from common salt and CaCO3. By 1873, the Solvay process came to the center stage replacing the polluting Le- Blanc process, based on CaCO3 and Na2SO4, which was practiced since 1787, wherein Na2SO4 was produced from NaCl and H2SO4. The irritating problems of disposal of

CaSO4 were never suitably solved, and enormous quantities of left-over calcium sulphate are still indisposed in Europe (4).

The number of organization has defined green chemistry in various ways.The International union of pure and applied chemistry (IUPAC) defined as“the design,invention and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances”; the EPA definition, “the use of chemistry for source reduction”;and the Organization for Economic Cooperation and Development (OECD) gives the definition, “sustainable chemistry”(5).

What is Green Chemistry? Green Chemistry is the chemical tool used to design a reaction, a process, or a new material benign to the environment. It is thechemistry applied in pollution prevention and waste minimization.In the design and development of new productsand processes, key environmental requirementsthat should be observed or are a priority in Green Chemistry are utilization of reusable or recyclable materials,thus avoiding consumption of nonrenewable natural, resources as material inputs, reduction and replacement of some of the traditionally, harmful reagents and solvents in industry, reduction in energy consumption, reduction in dissipative loss of waste materials,aiming for zero discharges, lessening of threats to the ecology and to humanhealth, lowering of safety risks (6). These all definition are different but expressed root is also differ but they forwarded towards the same goal and same target, the main objective of green chemistry are to environment free processes to design, manufacture, and use of efficient, more effective, safe chemical processes and it is lead to be controlling environment pollution.

A study on the emergence and twelve principles of green chemistry has been thoroughly discussed. Syntheses of polymers and nanoparticles with the aid of greener method have been elucidated. Phase transfer catalysis is found to play Key role in the synthesis of various multistep processes to one pot cascade reaction. Ionic liquids have emerged out as alternative green solvent in synthetic chemistry replacing traditional organic ones due to environmental and health concerns. Nonionic surfactants notably due to their characteristic temperature induced clouding phenomena and subsequent phase separation above cloud point have been found potential application in the field of pre concentration and extraction of various metal ions, organic and inorganic industrial pollutants and pesticides.

II. IMPORTANT METHODS OF GREEN CHEMISTRY

Green chemistry is a novel approach towards the sustainability, safety and decreases environment pollution and secures the future. There are number of methods in these like organic syntheses we can using green solvent such as water, bio solvents which are resultant from the agriculture crops and processing on it then Ethyl lactateis a one of them as a green solvent derived from treating corn. Ethyl lactate is a most usable solvent in paint industry for coating. It is more favorable due to 100% biodegradable and easy to recycle, noncorrosive, non-carcinogenic, and no ozone-depleting. It is mostly used to coating of metals, wood, polystyrene and also very effective for paint stripper and graffiti remover. Ethyl lactate has replacing many organic solvent such as acetone, toluene, and xylene.

Chemicals from glucose: Glucose is an origin of several organic solvent such as benzene, hydroquinone, catechol, and adipic acid.These all are the chemical compounds may be synthetic but glucose is alternative for it and these chemicals more demand in international market to production. Benzene is a starting material used for these materials, to the changing benzeneamid glucose can assist in lowering the usage of diverse reagentswith certain toxic. To the Synthesis of that chemical which takes region in instead of these bywater as areplacement for of natural solvents is more beneficial (7).

Polysaccharide Polymers: They are an essential group ofcompounds that include widespread packages. They have got theirdangerous consequences. The big range of compounds can be exploited. Polysaccharide because the feedstock have to be usedas beginning materials due to the fact that it's far extraenvironmentally feedstock. Those are organic and have the benefitof being renewable or viable, in place of petroleum feedstock. Onthe opposite side these don't have any chronic toxicity toenvironment and health of humans.

Green Dry Cleaning of Clothes: Perchloroethylene (PERC), Cl2C═CCl2 iscommonly being used as a solvent for drycleaning. It is now known that PERCcontaminates ground water and is a suspectedcarcinogen. A technology, known as Micelltechnology developed by Joseph De Simons,Timothy Romark, and James McClain made use of liquid CO2 and a surfactant for dry cleaningclothes, thereby replacing PERC. Dry cleaning machines have now been developed using thistechnique. Micell Technology8 has also evolved a metal cleaning system that uses CO2 and asurfactant thereby eliminating the need ofhalogenated solvents (9-10).

Avoid hazardous chemical uses: the reduce use of hazardous chemical during chemical production. The chemist have generally using conventional methodto synthesis today we are finding new way in production by using green solvent or green method and less hazardous reagent also in the synthesis method using less toxic to living organism, human health and to the environment.

Building with Green Technology: Green buildings use a variety of environmentally friendly techniques to reduce their impact on theenvironment. Reclaimed materials, passive solar design, natural ventilation and green roofing technology can allow builders to produce a structure with a considerably smaller carbon footprint than normal construction. These techniques not only benefit the environment, but they can produce economically attractive buildings that are healthier for the occupants as well. The chief benefit of building green is reducing a building's impact on the environment. Using green building techniques can also reduce the costs associated with construction and operation of a building. Green ventilation techniques involve open spaces and natural airflow, reducing the need for traditional air conditioning and preventing many of these problems (11).The more we know about how a chemical's structure causes a toxic effect, the more options are available to design asafer chemical (12).

Carbon Dioxide Capture: The high solubility of CO2 inILs in addition to its ability to form carbamates in the presenceof amine groups turned the attention of many researchers tothis type of solvent for CO2capture (13,14). One of the majorissues in the chemical capture of CO2 in aqueous amines bymeans of carbamate formation is water uptake in the gasstream. The loss of solvent may hinder the large scaleapplication of the process. Due to their negligible vapour pressure, ILs is viewed as a viable alternative for CO2 scavenging. Nevertheless, the high price of ILs still poses amajor drawback in the industrial application of theses

solvents.NADES can be viewed as a viable alternative. Like ILs, theyhave extremely lowvapour pressure,(15-16) but NADES are muchcheaper to produce.

Safer Solvent: Solvent is the major liquid compound which is required to dissolve the chemicals to form a solution. In a simple chemical process, sometimes it is required a large volume of solvent for reaction media and/or purification stage (17). Since the main role of the solvent is only for diluting the chemicals in the chemical reaction, it is quite possible to pre-vent the usage of flammable, toxic and environmentally damaging solvents such as benzene, carbon tetrachloride, formaldehyde, etc. (18).

III. BENEFITS OF GREEN CHEMISTRY

Economical, Energy efficient, Lowers cost of production and regulation, Less wastes,Fewer accidents, Safer products, Healthier workplaces and communities, Protects human health andthe environment,Competitive Advantage, Use of alternative feedstock's, Use of less hazardous reagents, Use of natural processes, like bio catalytic techniques, Use of alternative solvents, Design of safer chemicals and products, Developing alternative reaction conditions, Minimizing energy consumption.

IV. CONCLUSION

We are conclude that green chemistry is most valuable to as we design new chemical synthesis, decisions about whether hazardous substances will be used, whether toxic materials must be handled and so on. In recent in research green and sustainable chemistry are updating and development towards green method. Whether hazardous waste will require special disposal and the overall environmental issues associated with these processes must be seriously considered. The reduce chemical waste and recycling, develop renewable sources and sustainable materials also needs of uses of green solvent, green process, technologies and engineering, new business model life cycle assessment renewable energy storages. Important things is that we want to always keep in mind a Green approach in everywhere, every movement, all sectors and also in our live life it's more important to save environment, to reduce pollution and make better greener research

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Synthesis and Characterization of Substituted 2phenylimino-3-Amido-5-Aryl/Alkylimino1,3,4thiadiazolidine

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ABSTRACT

Several 2phenylimino-3-amido-5 aryl/alkylamino-1,3,4 thiadiazolidine(5a-g)have been synthesized by the interaction of 1-aryl -2 thio bis -urea(2a) and phenyliminocyanodichloride(1)in refluxing chloroform medium followed by basification of resulting compound(3a-g).The compound(2a-g) have been preparedbythe condensation of aryl/alkyl isothiocyanates and semicarbazide.The compound (5a-g)on acetylation afforded monoacetyl derivatives.Synthesis of these substituted heterocyclic compound were established on the basis of chemicaltransformationand structural interpretation by IR,1H-NMR and mass spectrum.

Keyword: Synthesis,1.3.4 thiadiazolidine, Heterocyclic chemistry

I. INTRODUCTION

Heterocyclic chemistry has been and continues to be one of the most active area of organic chemistry.As a result numerous heterocyclic compound such as thiazoles,thiadiazole,Oxadiazole and pyrroles have been successfully used as antibaterial,anticancer,antipyretic,antitubercular and anti-inflammatory agent.All large number of organosulphur compound occur in living and non-living object .Identification and application of these organosulphur compound lead to the fact that some of the compound are useful in scientific ,technical and industrial growth.Among the sulphur containing heterocyclic compound lot of research in the field of 1,3,4thiadiazolidene.Some salient features regarding structure,chemical reactivity and spectral studies.For the synthesis of 1,3,4-thiadiazolidine and cyclization and other routs have been employed earlier [1-6].Thiadiazoles are of vital importance as drugs, These compound posses diverse range of physiological activities[7-12].explore the new route for the synthesis of heterocyclic compound.In the present paper the synthesis and characterization of 2-phenyl-imino-3-amido-5-aryl/alkylamino-1,3,4thiadiazolidene have been reported.

II. MATERIAL AND METHOD:

Melting point of the synthesized compound were recorded using microcontroller based melting point apparatus were found corrected. purity of the compound was checked by thin layer chromatography using silica gel.The spot visualized by using uvchamber.The technique employed for the characterizationof the

synthesized compound were IR Spectra recorded on Perkin -Elmer spectrophotometer in nujol mull and KBr Pellets.PMR Spectra were recorded with TMS as internal standard using$CDCL_3$ and DMSO-d_6 as solvent.The chemical and reagent used in the present project were of AR grade.

Synthesis of 1-phenyl -2-thio-bis urea(2a):

Semicarbazide(0.01mol) phenyl isothiocyanate(0.01mol) was dissolved in 10mlchloroform.The resulting mixture was refluxed on a boiling water bath for 2 hr with occasional stirring.On distilling of chloroform a solid residue was obtained.It was with petroleum ether.It was recrystallized from ethanol to get a colourless crystalline solid (2a),The yield is 83% m.p was found to be 180°C.The above reaction was extended to synthesized compound (2b-g)crystallized fromethanol:**b**(85%),m.p110°C,**C(**74%,**)**m.p122°C,**d**(87%)m.p 160°C,**e**(78%),m.p174°C,**f**(81%)m.p170°C,**g** (69%) m,p,115°C.

Synthesis of 2-(4-Chlorophenylimino)-3-amido-5-aryl/alkylamino-1,3,4thiadiazolidine(5a)

1 Aryl-2-thio-bis urea(0.01mol) was suspended in 20ml chloroform to this solution phenylimino cyanodichloride(0.01 mol) in chloroform was added.The reaction mixture was then refluxed on a boiling waterbath for 3 hr.The evolution of hydrogen chloride gas was observed. After cooling the reaction mixture **,**the chloroform was distilled off when a sticky mass wasobtained.It was repeatedly washed with petroleum ether (60-80°C)followed byaddition of ethanol a colourless solid acidic to litmus was isolated.It was recrystallized from ethanol.m.p.141°C.On basification of 2-(4-chloro phenylimino)-3-amido-5-aryl/alkylamino-1,3,4thiadiazolidine hydrochloride with dilute ammonium hydroxide solution,a faint yellow coloured free base**(5a)** was obtained and crystallized from aqueous ethanol.

Synthesis of 2-(4-chloro phenylimino)-3-amido-4acetyl-5aryl/alkylimino-1,3,4-thiadiazolidine(6a)

A mixture of 2-(4-chloro phenylimino)-3amido-5aryl/alkylimino-1,3,4-thiadiazolidine(0.01mole),acetic anhydride (0.01mole) and glacial acetic acid(10ml).The resulting mixture was refluxed on a boiling water bath for 1hr.The reaction mixture was poured over a little in to a ice cold water.The granular solid was separated and recrystallized from ethanol.(81%),m.p193°C(Found:**C**,53.24;**H**,3.21;**N**,18.80;**S,**8.00;Calcd for $C_{17}H_{14}N_5O_2S$;**C**,53.58,**H**,3.61;**N**,18.00;**S,**8.25%)IR (KBr,cm^{-1});3390 and 3450v(-NH),1601 v(C=N),1308 v(C-N),1678 v(C=O),750 v(distributed benzene ring).This reaction was extended to other synthesize other acetyl derivatives**(6b-g)**

1 Aryl -2-thio-bis urea were prepared by the interaction of semicarbazide and aryl/alkyl isothiocynates while the phenylimino cyanodichloride was prepared by excessive chlorination of phenyl isothiocynates.The interaction of 1-aryl-2-thio bis urea and a phenylimino cyanodichloride in refluxing chloroform medium for 3hr proceeded with the evolution of hydrogen chloride gas .After completion of the reaction and distilling off the solvent the granular solid**(3a-g)**wereisolated.These were acidic to litmus and on determination of equivalent weights by titrimetric analysis were found to be monohydrochloride.The compound**(3a-g**) on basification with aqueous ammonia solution gave bases**(5a-g).**The compound**(5a-g)** on acetylation with acetic acid produced monoacetyl derivatives**(6a-g).**

III. RESULT AND DISCUSSION:

The title compound (5a-g) were subjected to various for their antimicrobial activities using cup-plate diffusion method[13].The bacterial organism used in the present investigation were isolated from human being with characterstic infection and diseases.The isolates were pathogenic.The pathogens used included bothgram positive and gram negative strains like E-coli,S.aureus, P.vulgaris,B-subtilis,shigella

Sensitivity plates were seeded with a bacterial inoculum of $1x10^6$(1µg/ml) and each well diameter(10mm) was loadedwith 0.1 mlof test compound solution(1000 µg/ml) in DMF ,so so that the concentration of each test compound was 100 µg/ml.The zones of inhibition were recordedafter incubation for 24 hr using vernier caliper.Inhibition zones of the compound clearly indicate that compound (4b) is having moderate to high activity.It is highly active against S.aureus.All the compound are having high activity against,S,aureus and most of them are inactive against B.subtilis.These compound showed moderate activity against E,coli and Shigella.

Table 1:Physicochemical properties of the synthesized compound

Compound name	Molecular formula	percentage yield(%)	M.P (°C)	Elemental analysis Calcd.(Found)			
				C	H	N	S
2(phenylimino)-3-amido-5-p-chlorophenylimino-1,3,4thiadiazolidine (5a)	$C_{15}H_{12}N_5OSCl$	83	140	52.01 (52.09)	2.91 (3.47)	21.0 (20.23)	9.00 (9.24)
----5-m-----chloro phenylimino— (5b)	$C_{15}H_{12}N_5OSCl$	70	90	52.34 (52.0)	3.60 (3.47)	2.32 (20.2)	9.20 (9.24)
2-(5-Diphenylimino)-3-(5c)	$C_{15}H_{13}N_5OS$	75	142	58.03 (57.87)	4.11 (4.18)	22.80 (22.56)	9.91 (10.28)
---5-O-tolylimino---(5d)	$C_{16}H_{15}N_5OS$	78	143	59.30 (59.25)	4.40 (4.62)	22.01 (21.60)	10.0 (9.87)
---5-m-tolylimino---(5e)	$C_{16}H_{15}N_5OS$	85	190	59.08 (59.25)	4.80 (4.62)	21.30 (21.60)	9.30 (9.87)
---5-p-tolylimino---(5f)	$C_{16}H_{15}N_5OS$	80	55	59.60 (59.25)	4.40 (4.62)	21.40 (21.60)	9,50 (9.87)
---5-t-butylimino---(5g)	$C_{13}H_{17}N_5OS$	75	98	54.00 (53.60)	5.32 (5.84)	23.92 (24.05)	9.95 (10.9)

Table 2: Interpretation of IR and NMR spectral values

Compound name	IR spectra values cm^{-1}	1H NMR Spectra value(ppm)
2(phenylimino)-3-amido-5-p-chlorophenylimino-1,3,4thiadiazolidine(5a)	3390,3450,NH-str.;1614 C=N str.;1538 Ar C=Cstr.;1334,C-N str.;750,C- S str,	6.0 1H,NH;9.6-10.0 2H,;CO-$NH_2$7.2-7.6 9H Ar-H;
------5-m-----chloro phenylimino— (5b)	1530ArC=Cstr,;3380NH str;A;750,C-Sstr.;1300,C-N str.;1614,C=Nstr.	4.12 1H,NH; 7.1-7.5 9H Ar-H;9.4-9.9 2H,C0-NH_2;Ar CH-str.5.07
2-(5-Diphenylimino)-3-- (5c)	1334,C-Nstr.;3086,Ar-CH;3327,NHstr.;721,C-Sstr,;1540Ar-C=Cstr,;1632 C=Nstr.	9.06 Ar-CH 2H,;8.13 NH-str,1H; 8.09,Ar-H,1H;4.06 2H,NH_2;4.15Ar-CHstr,1H;9.4-9.8 C0-NH_2,2H
---5-O-tolylimino--- (5d)	3100-3000Ar CHstr;1334ArC=Cstr,;1614C=Nstr,;3086,Ar-CH;750C-Sstr,;3363,NHstr;	6.0, 1H, NH,;9.6-10.0 2H, $CONH_2$,; 2.20, 3H, Ar-CH_3 ; 7.2-7.6, 9H, Ar-H
----5-m-tolylimino---(5e)	3390,3450NHstr,;1614 C=Nstr,;1550 ArC=Cstr,;1334,C-N str,;735,C-Sstr,;3086ArCH str,;	2.20, 3H. Ar-CH_3 ,; 9.6-10.00, 2H, CO-NH_2,; 8.0 2H, NH_2,; 6.0, 1H, NH,; 7.2-7.5, 9H Ar-H
---5-p-tolylimino-----(5f)	1550,C=C str,;750C-S str,;3086,Ar-CHstr,;3390NHstr,;1614,C=Nstr,;1308,C-Nstr.;	7.60 2H Ar-CH,; 2.2 3H, Ar-CH_3,; 6.0, 1H, NH,; 9.6-10.0 2H, $CONH_2$,; 7.2-7.6 9H Ar-H
---5-t-butylimino----(5g)	750C-Sstr,;3080,Ar-CHstr,;1601,C=Nstr,;1550,Ar-C=Cstr,;3390,3450,N-Hstr,;1308,C-Nstr,;	9.4-10.0 2H, $CONH_2$,; 6.0 1H, NH,; 2.14 6H Ar-CH_3; 7.2-7.6, 9H Ar-H,; 2.3, 6H Ar-CH_3

IV. CONCLUSION:

In this connection,a series of novel 1,3,4 thiadiazolidine derivatives were synthesized and the structure of the entire compound were confirmed by recording by their IR,1H NMR and Mass spectra. In conclusion, we fill that the preliminary in vitro activity results of this class of compound may possess potential for design of future molecules.All the synthesized compound showed moderate activity against bacteria. Therefore the ,the detailed literature surveyand screening studies have demonstrated that the newly synthesized compound exhibit promising antibacterialproperties,Hence it is concluded that there exists adequate scope for the medicinal chemist to further study in this class of compound.

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Influence of Air Pollution on Global Environment : A Short Review

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ABSTRACT

Impact of air pollution on climatic change as well as public and individual health due to increasing morbidity and mortality.
There are many pollutants that are major factors in diseases in human. Despite the fact that ozone in the stratosphere plays a protective role against ultraviolet radiations, it is harmful when in high concentration at ground level, also affecting the respiratory system.
The air pollutants which are very harmful to human beings such as carbon monoxide when breathed in at high levels causes direct poisoning.
Diseases occurring from the pollutants are mainly respiratory problems such as asthma, bronchitis, lung cancer & pulmonary diseases.
Environmental pollution affects climate change and geographical disturbances of many infectious diseases as do natural disasters.
The problem of environmental pollution is solved through public awareness with scientific experts, national and international organization must address the emergence of this threat and purpose sustainable solutions.
Key words: Pollutants, human beings, environment, diseases, public awareness, sustainable solutions.

I. INTRODUCTION

Pollution is defined as 'Into the environment introduction of harmful substances which are harmful to humans and other living organisms'. The pollutants are harmful solids, liquids, or gases produced in higher than the usual concentrations that reduce the quality of our environment.
Although the industrial revolution introduced the production of huge quantities of pollutants emitted into the air that is harmful to human health.
The urbanization and industrialization are reaching unprecedented and upsetting worldwide proportions. Air pollution is one of the biggest public health hazards given that it accounts for about 9 million deaths per year. (1) It is closely associated with climatic changes and affect multiple ecosystems causing problems such as food safety issues, ice and icebergs melting, animal extinction and damage to plants (2,3)

1. Major sources, area sources, mobile sources and natural sources.

periods. Air pollutants are dispersed particals, hydrocarbons, CO, CO2, NO2, SO3 etc. It also influence the quality of soil and water bodies by polluting precipitation falling into water and soil environments (4,5) soil may be amended due to acid precipitation by affecting plants, cultures and water quality (3,6)

Environmental pollution occurs when changes in the physical, chemical or biological constituents of the environment are produced. Pollutants have differences in physical and chemical properties explaining the discrepancy in their capacity for producing toxic effects. Gaseous compounds are eliminated more easily by our respiratory system which causes damage to lungs and enter the blood stream (7)

Climate and Pollution- Climate change and air pollution are closely related that reduces the quality of our earth (8). The earth temperature is increasing resulting in the melting of ice, icebergs and glaciers by the pollutants such as black carbon, methane, tropospheric ozone and aerosols affects the amount of incoming sunlight.

II. ENVIRONMENTAL IMPACT OF AIR POLLUTION

Air pollution is harmful not only to the environment but also harming to human health (9)

Acid rain is wet (rain, fog, snow) or dry (particulates and gas) which contain toxic amount of nitric and sulfuric acids. They are able to acidify the water and soil environment, damage trees and plantations and even damage buildings, outdoors sculptures, constructions and statues.

Haze is produced when fine partials are dispersed in the air and reduce the transparency of the atmosphere caused by emission in the air coming from industry, power plants, automobiles and trucks.

Stratospheric ozone is gradually damaged by ozone depleting substances. If this layer is thinned then UV radiation can reach our earth with harmful effects for human life (skin cancer) and crops.

In plants, ozone penetrates through the stomata, inducing them to close, which blocks CO2 transfer and induces a reduction in photosynthesis (10)

Global climatic change is known as the “greenhouse effect” is an important issue which keeps earths temperature stable.

Anthropogenic activities destroyed this protecting temperature effect by producing large amounts of greenhouse gases and global warming is mounting with harmful effects on human health, animals, forests, wildlife, agriculture and the water environment. A report states that global warming is adding to the health risk of poor people (11)

Wildlife is burdened by toxic pollutants coming from the air, soil or the water ecosystem and in this way animals can develop health problem when exposes to high levels of pollutants.

III. DISCUSSION

The first WHO global conference on air pollution and health in 2017 the WHO’s General Director, called air pollution a ‘Silent Public Health Emergency’ and ‘ he new Tobacco’ (12)

Air pollution has adverse effect on our lives in many different respects. Diseases not only caused economical impact but also a social impact due to absences from productive work.

Technologies to reduce air pollution at the source must be established and should be used in all industries and power plants.

To eradicate the environmental pollution, making a tight collaboration of authorities, bodies and governments should spread sufficient information and educate people and should involve professionals in these issues so as to control the emergence of the problem successfully.

International cooperation in terms of development research, administration policy, monitoring is a vital for effective pollution control.

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Green Synthetic Approach and Antimicrobial Activities of Some Novel Pyrimido[1,2-a]Quinoline Derivatives

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ABSTRACT

Novel phenolic and hetryl amino substituted derivatives of 3-(methylthio)-1-oxo-1H-pyrimido[1,2-a]quinoline-2,5-dicarbonitrile possessingpromising antimicrobial activities against S. aureus, B.Substilis, E.Coliwere prepared byfrom 2-aminoquinoline-3-carbonitrile (1) with ethyl 2-cyano-3,3-bis(thiomethyl)acrylate (2) in polyethylene glycol with catalytic amount of base cesium carbonate. All the synthesized compounds were characterized by spectral data like IR, Masss and NMR.

Keywords: Polyethylene Glycol (PEG), Cesium Carbonate, pyrimido[1,2-a]quinoline and ethyl 2-cyano-3,3-bis (thiomethyl)acrylate.

I. INTRODUCTION

Fused heterocyclic derivatives of Quinoline are always diverse pharmacological activity asacompound for new drug development. Quinoline ring system occurs in numerous natural products, especially in alkaloids and is often used for the design of many synthetic compounds with various pharmacological properties as anticancer[1-3], antimalarial[4-5], antitubercular[6],.The fused pyrido[3,2-g]quinoline derivatives show strong bonding with DNA[7].Accordingly and in continuation of our previous work on bioactive pyrimido quinoline[8-11], we intend to report here the synthesis of 3-(thiomethyl)-1-oxo-1H-pyrimido[1,2-a]quinoline-2,5-dicarbonitrile to investigate their antimicrobial activities.

II. EXPERIMENTAL SECTION

Progress of every reaction was monitored with TLC. Structures of newly synthesized compounds were confirmed on basis of spectral data. IR spectra of newly synthesized compounds were recorded (in KBr pallets) on Shimadzu Spectrophotometer. ^{1}H-NMR spectra of newly synthesized compounds were recorded (in

DMSO-d_6) on Avance-300 MHz spectrometer using TMS as an internal standard. The mass of compounds was recorded on EI-Shimadzu GC MSspectrometer.

1) 3-(methylthio)-1-oxo-1H-pyrimido[1,2-a]quinoline-2,5-dicarbonitrile(3)

A mixture of 2-anino-3-cyano-quinoline **1**(2.91g, 0.01 m mol) and ethyl 2-cyano-3,3-bis(thiomethyl)acrylate **2**(2.17 g, 0.01 m mol) was refluxed in the presence of PEGwith catalytic amount of cesium carbonatefor 5 hrs. The reaction mixture was cooled to room temperature and poured in to ice cold water. The separated solid was filtered, washed with water and recrystallized from N, N' –dimethyl formamide-ethanol mixture to afford compound **3**.

Spectral Data

Brown powder, (86% yield), Mp: 280°C; EI-MS (m/z-RA%) : 291 (M^+) ,IR (cm^{-1},KBr) : 1635 (CO), 2216(CN), ^{1}H NMR (DMSO-d_6, ppm) : 2.7 (s, 3H, SCH_3), 7.1-8.5 (m, 5H, Ar-H), ^{13}C NMR (300 MHz, DMSO-d_6, ppm)15,87,97,110,115,116,124,128,129,129,130,131,156,160,170

2) 2-Substituted derivatives of 3-(methylthio)-1-oxo-1H-pyrimido[1,2-a]quinoline-2,5-dicarbonitrile(4a-4d, 5a-5c)

A mixture of 3-(methylthio)-1-oxo-1H-pyrimido[1,2-a]quinoline-2,5-dicarbonitrile **(3)** (0.001 mol) and, independently react with hetryl amines, substituted phenols (0.001 mol) in PEG andcatalytic amount of cesium carbonate was refluxed for 5-6 hours. The reaction mixture was cooled to room temperature and poured into ice cold water. The separated solid product was filtered, washed with water and recrystallized from a N, N'- dimethyl formamide-ethanol mixture to give pure 2-Substituted derivatives of 3-(methylthio)-1-oxo-1H-pyrimido[1,2-a]quinoline-2,5-dicarbonitrile (**4a-d, 5a-c)**.

a) **4a:**Yellowish Brown powder, (85% yield), Mp: 272°C; EI-MS (m/z-RA%):417 (M^+),IR (cm^{-1},KBr): 1649 (CO), 2190(CN), ^{1}H NMR (DMSO-d_6, ppm): 7.2-8.7 (m, 9H, Ar-H)

b) **4b:** Brown powder, (80% yield), Mp: 263°C; EI-MS (m/z-RA%): 352 (M^+),IR (cm^{-1},KBr): 1642 (CO), 2216(CN), ^{1}H NMR (DMSO-d_6, ppm):3.8(s,3H, OCH_3), 7.1-8.8 (m, 9H, Ar-H)

c) **4c:** Brown powder, (92% yield), Mp: 278 °C; EI-MS (m/z-RA%): 372 (M^+),IR (cm^{-1},KBr): 1656 (CO), 2210(CN), ^{1}H NMR (DMSO-d_6, ppm): 7.1-8.9 (m, 9H, Ar-H)

d) **4d:** GreenishBrown powder, (80% yield), Mp: 294 °C; EI-MS (m/z-RA%): 372 (M^+), IR (cm^{-1},KBr): 1649 (CO), 2190(CN), ^{1}H NMR (DMSO-d_6, ppm): 7.1-8.8 (m, 9H, Ar-H)

e) **5a:** Brown powder, (75% yield), Mp: 288°C; EI-MS (m/z-RA%): 311 (M^+), IR (cm^{-1},KBr): 1678 (CO), 2219(CN), ^{1}H NMR (DMSO-d_6, ppm): 7.1-8.3 (m, 9H, Ar-H)

f) **5b:**Brown powder, (79% yield), Mp: Aobve 300 °C; EI-MS (m/z-RA%) : 330 (M^+), IR (cm^{-1},KBr) : 1656 (CO), 2210(CN), ^{1}H NMR (DMSO-d_6, ppm) : 1.9(s,1H,Ar-NH), 2.6-8.6 (m, 13H, Ar-H)

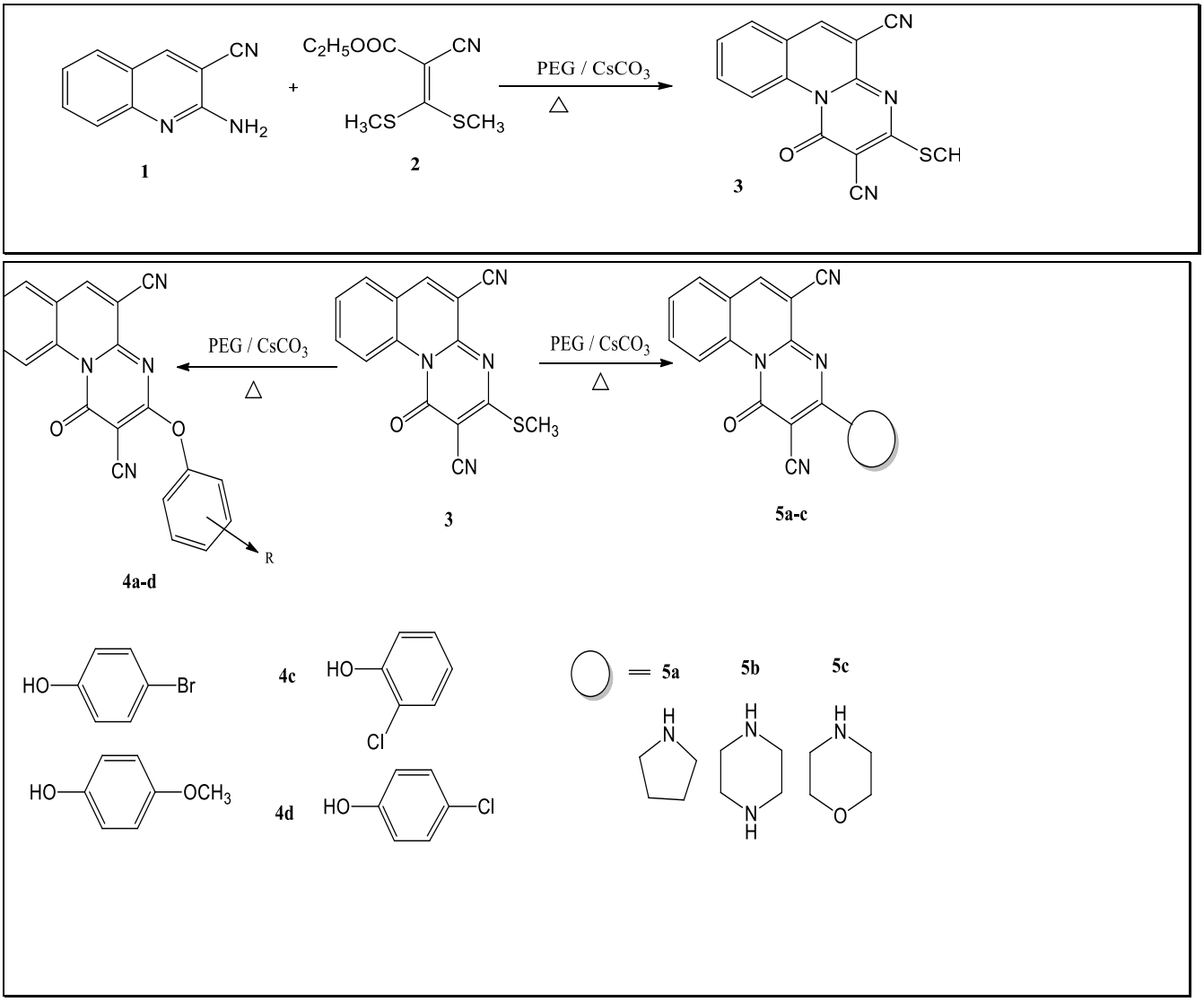
g) **5c:** Brown powder, (79% yield), Mp: Aobve 300 °C; EI-MS (m/z-RA%) : 311 (M^+), IR (cm^{-1},KBr) : 1666 (CO), 2220(CN), ^{1}H NMR (DMSO-d_6, ppm) : 1.9(s,1H,Ar-NH), 2.6-8.6 (m, 13H, Ar-H)

III. RESULT AND DISCUSSION

The compound 3,11-dicyano-4-imino-2-methylthio-*4H*-pyrimido[1,2-a]quinoline**(3)** obtained from 2-amino-3-cyano-quinoline **(1)** and ethyl 2-cyano-3,3-bis(thiomethyl)acrylate **(2)** in presence of PEGand catalytic amount of cesium carbonate.

The compound **(3)** possesses replaceable active thiomethyl group at 2- position which is activated by the ring 1-nitrogen atom and reactive 3-cyano group. Compound **(3)** was condensed with 2-amino substituted benzothiazole in presence of PEG and catalytic amount of cesium carbonate afforded the new heterocyclic compounds 4a-d and 5a-c 75-90 % yields.

The structure of these newly synthesized compounds was established on the basis of elemental analysis, IR, PMR and Mass Spectral data, spectral studies of all compounds shows that compounds are stable & do not exhibit any tautomerism.



IV. ANTIMICROBIAL ACTIVITY

All newly synthesized derivatives were tested for antifungal and antibacterial activity against species *Aspergillus flavus, Aspergillus niger, E. coli* and *B. Subtilis* by paper disc diffusion method. Control for fungal and bacterial species using Disc diffusion method, solvent DMSO was used, FungiCzapek's dox agar, Bacteria-Nutrient agar. Incubation period for fungi 4 days (24+/- 2 ^{0}C) and for bacteria 24 hrs (37 ^{0}C). The synthesized compounds exhibited zone of inhibition of 10-24 mm in diameter.

Sr. No.	**code**	**Zone of inhibition in mm**			
		Fungal species		**Bacterial species**	
		Af	***An***	***Bc***	***Bs***
1	4a	14	16	12	24
2	4b	10	--	14	17
3	4c	12	12	12	15
4	4d	14	15	13	18
5	5a	18	12	11	09
6	5b	12	14	16	18
7	5c	18	17	12	19
Positive control		**26**		**25**	
		Fluconazole		**Streptomycin**	

V. CONCLUSION

All the compounds were tested for their antimicrobial activity using disc diffusion technique against *S. aureus, B.Substilis,* the standard antibiotics showed zones of inhibition penicillin 20-24 mm , ampicillin 18-26 mm against bacterial strains.Compounds 4a,4c,5c show were highly active against *B.Substilis* and*E.Coli.* 4b, 5a,5b. display maximum activity against *S.aureus* and *S.Typhi.* respectively.

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Review Application of Biologically Active Derivative of Morpholine Based Schiff Base Ligand and Their Metal Complexes

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ABSTRACT

The heterocyclic Schiff base such as Morpholine based Schiff base ligand gives excellent application in many branches of chemistry like bioinorganic chemistry, coordination chemistry. The metal complexes of d-block and f-bock displays key role in pharmaceutical sciences for various biological and other activities.This reviewarticle focalized that the to make newSchiff base ligand from derivatives of morpholine and their transition/lanthanide metal complexes. They displayed manifest various types of biotic or pharmacological activities to be specific antioxidant activity, antimicrobial activity, anticancer activity, DNA binding ability etc.

Keywords: Morpholine, Schiff base, Biological activities, anticancer activity, transition metal complexes.

I. INTRODUCTION

The Schiff base reaction designed by noble prize winner, German scientist chemist Hugo Schiff from last 155 years ago,excellent and improved research work on Schiff base are constantly done from scientists and research students because of their wide range of applications in various fields. Structurally a Schiff base described as a nitrogen (N) analogue of an aldehyde (RCHO) or ketone (RCOR') in which the carbonyl group (CO) has been altered by an azomethine group (-CH=N-)orimine group(>C=N-). They fluently form a reactive as well as stable metal complex with transition / lanthanide metal ion. This is foremost discovered by Hugo Schiff. The majority of Schiff bases are artificial. They are extensively used for industrial purposes, medicinal use and in pharmaceutical fields and also exhibit a broad range of biological activities. By the donation of Nitrogen atom of Schiff base ligand to the transition metal atom and forms strong and stable metal complexes.Many literature reveals that the transition metal complexes of Schiff base ligands exhibit biological activities such as anticancer activity[1], antimicrobial activity [2], DNA binding [3], anti-inflammatory[4], analgesic[5], anticonvulsant[6], antitubercular[7].

Outside from the biological activities, Schiff base ligand used as polymer stabilizer, used as intermediate in organic reaction, used as catalyst [8].

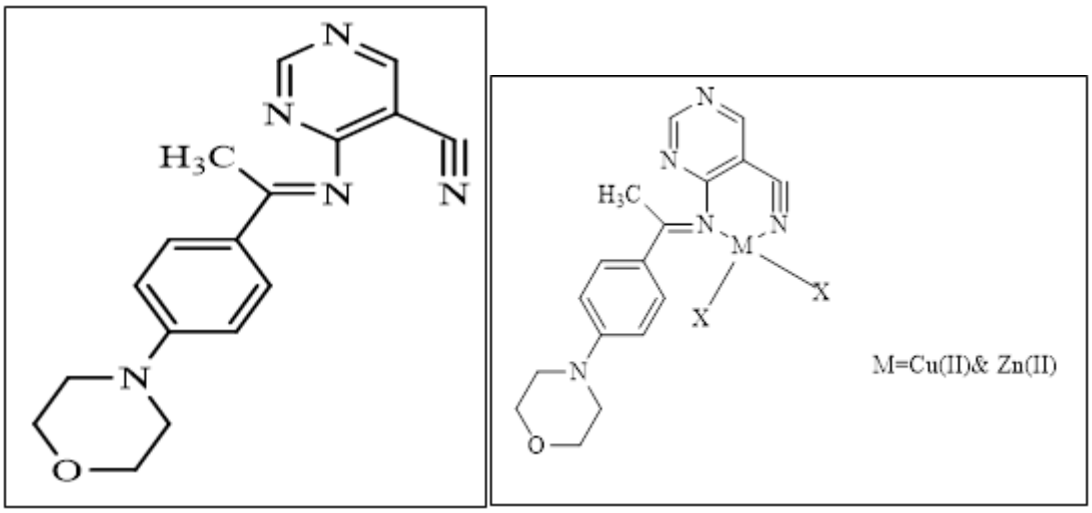
Currently,heterocyclic compounds containing Nitrogen and oxygen atomthat is morpholine are playing important role inmetabolism of living cell. And it is important for human life [9]. The derivatives of morpholine are widely used in to formation of Schiff base ligand. Derivative of morpholine based ligand synthesized by condensation of amine of morpholine with aldehyde or ketone.Structurally morpholine is six membered heteromonocycliccompound with functional group of amine (NH) and ether (-O-). This Nitrogen and Oxygen atom is essential for development of intermediate in organic synthesis/reaction [10] and also them essential for the medication of diverse kind of diseases. Derivative of morpholine shows analgesic, anti HIV, appetite suppressant, anti inflammatory local anesthetic, anti cancer, anti depressant agent, antimicrobial activity,antimalerial, anti spasmodic [11,16]

Consider the above facts in view; the need a review article for the various applicationsof derivative of morpholinebased Schiff base ligand and their metal complexes is essential.

Synthesisof transition metal complexes of derivatives of morpholine based Schiff base ligand and their diverse biological activities:

1. Synthesis of 4-(1-(4-morpholinophenyl) ethylideneamino) pyrimidine-5-carbonitrile) (L1)

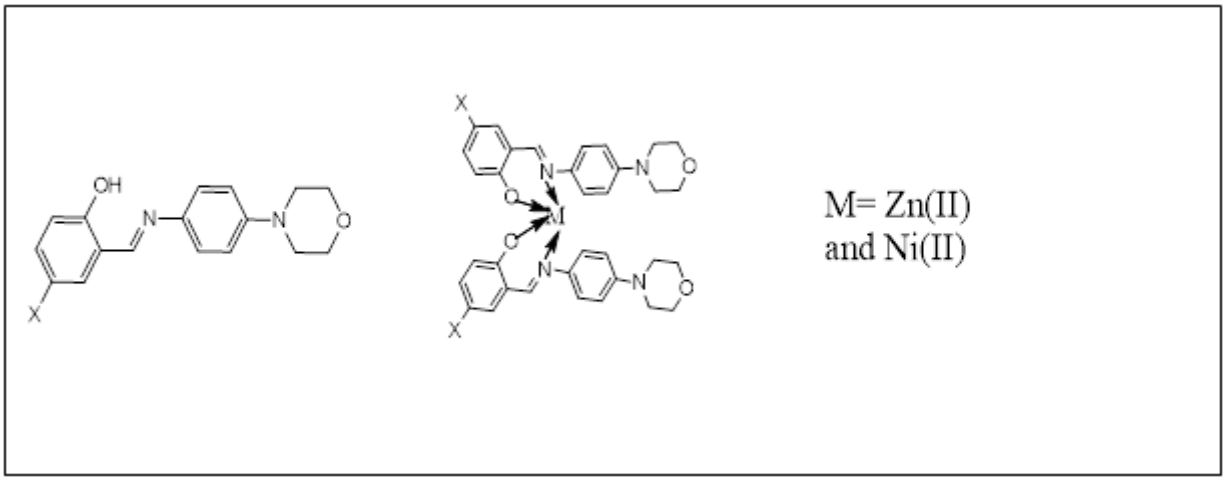
Synthesis of 4-(1-(4-morpholinophenyl) ethylideneamino) pyrimidine-5-carbonitrile) (L1) from Condensationof 4-morpholinoacetophenoneand 4-amino-5-pyrimidinecarbonitrile. Thederivatives of morpholine based Schiff base ligands (**L1**) and metal complexes of Cu (II) and Zn (II) showsantimicrobial activities versus C. *albicans* fungi and E. *coli* bacteria. According to electronic absorption, viscometric and cyclic voltammetric studies and competitive binding the binding of ligand and metal complexes with CT-DNA were confirmed. The anticancer activities shown that complexes have moderate cytotoxicity against cancer cell lines and low toxicity on normal cell line than Schiff base ligands [17].



2. Synthesis of 2-[(4 morpholinophenyl imino) methyl] 4-X-phenol (L2)

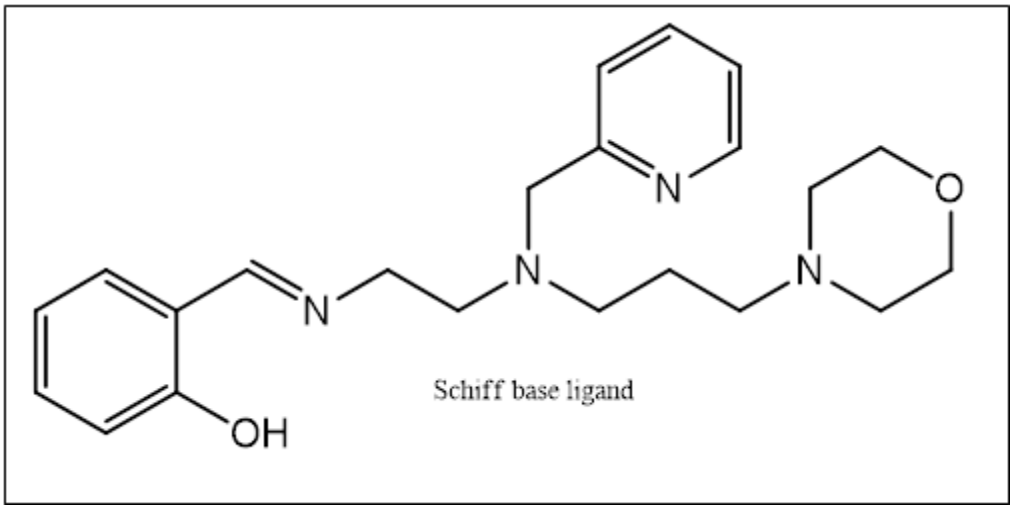
Auther discovered that 2-[(4 morpholinophenyl imino) methyl] 4-chlorophenol **(L2**)and2-[(4 morpholinophenyl imino) methyl] 4-bromophenol **(L3**). As reported by auther the morpholine based ligand

that is(**L2**),(**L3**)andmetal complexes of VO (IV), Zn (II), Cu (II), Co (II)) appear that the anticancer activity by human heptocarcinoma cell line (HepG2).According to the bioassay studyof derivative of morpholine based particularly metal complexof Zn (II) shows inhibitory activity against human gastric cancer cell lines[18]. The derivative of morpholine is 4-Phenyl-morpholineand4-(4-aminophenyl)-morpholine displayes antimicrobial properties, antiimmflametory activity [19-23]



3. 2-((2-(3-morpholinopropylamino)-N2-((pyridine-2-yl) methyl) ethylimino) methyl) phenol

Preparation of 2-((2-(3-morpholinopropylamino)-N2-((pyridine-2-yl) methyl) ethylimino) methyl) phenolfromcondensation of derivatives of morpholine such as morpholine containing branched amine with salicylaldehyde. The morpholine based Schiff base ligand **(L4)** and metal complexes of Zn (II) and Ni (II) shows anticancer activity vs (MDA-MB-23, MCF-71), (WI-38)and(PC-3)byutilizing[3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium Bromide] assay [24].

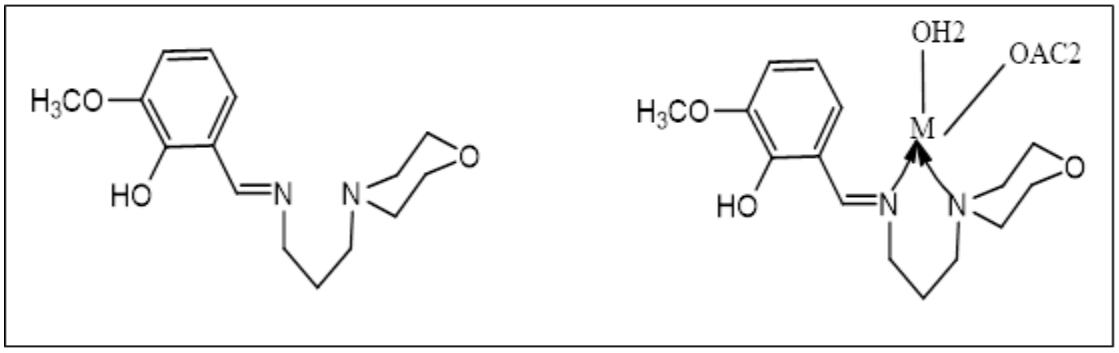


4. Synthesis of (E)-2-methoxy-6-(((3-morpholinopropyl) imino) methyl) phenol(L5)

Investigation of (E)-2-methoxy-6-(((3-morpholinopropyl)imino)methyl)phenol**(L5)**

From condensation of 2-hydroxy-3-methoxybenzaldehyde and 3-morpholinopropylamine. By using electronic absorption and viscometric methods the metal complexes of Cu (II) and Zn (II) exhibit DNA

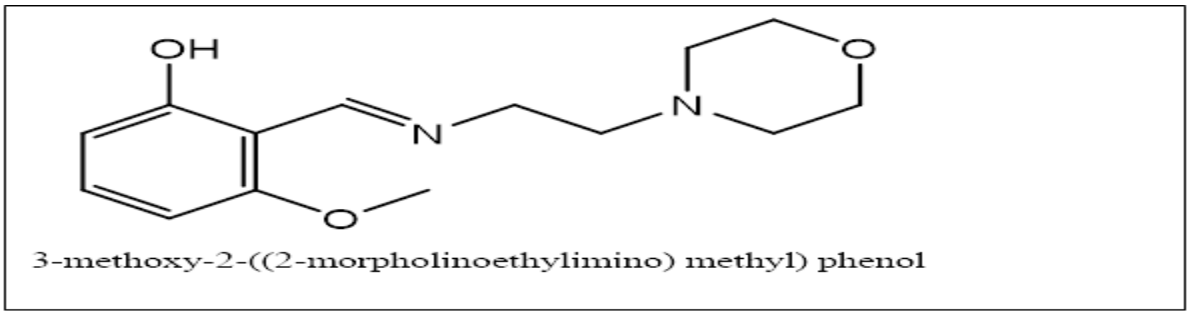
binding ability and they shows good radical scavenging activity vs 2,2-diphenyl-1-picrylhydrazyl radical. The derivative of morpholine based Schiff base ligand (**L5**) and Cu (II), Zn (II) metal complexes reveals the excellent antioxidant activity proposed by DPPH assay. The derivatives of morpholine based Schiff based ligand shows lower antimicrobial activity than morpholine based metal complexes of Cu (II), Zn (II) [25].



5.Synthesis of 3-methoxy-2-((2-morpholinoethylimino) methyl) phenol ligand (L6)

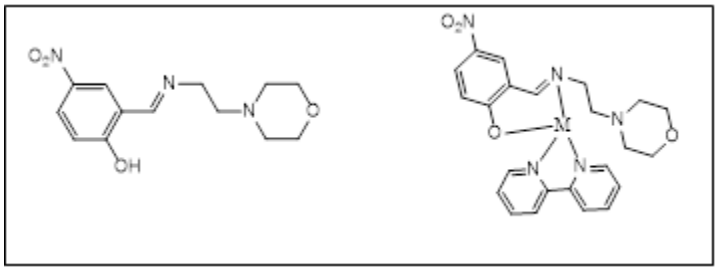
4-(2-aminoethyl) morpholine refluxed with 3-methoxy salicylaldehyde to gives 3-methoxy-2-(2-morpholinoethylimino) methyl phenols used as ligand for the formation of metal complexes.

By the study of colorimetric MTT [3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium Bromide] assayderivative of morpholine based Schiff base ligand(**L6)**and metal complexesof to be specific La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) revealed that theanticancer activity against breast cancer cell lines (MCF-7) [26]



6. Synthesis of (E)-2-(((2-morpholinoethyl) imino) methyl)-4-nitrophenol (L7)

(E)-2-(((2-morpholinoethyl) imino) methyl)-4-nitrophenol (**L7**) demonstratedby using reflux method 2-hydroxy-5-nitrobenzaldehyde with 4-(2-aminoethyl morpholine).Antifungal as well as antimicrobial activity ofmorpholine derivatives based metal complex shows vs selected bacteria.



II. CONCLUSION

Overall scrutiny proved that much more concentration focused on the chemistry of heterocyclic Schiff base ligand andtheir transition metal complexes and lanthanide complexes.They exhibit many more biological activities such as (**L1**) and their Cu (II) and Zn (II) metal complexes shows antimicrobial as well as anticancer activity and DNA binding ability. The anticancer activity of substituted(Chloro and Bromo)morpholine based ligand (**L2),** (**L3)** and metal complexes of Cu (II), Co (II)), Zn (II), or VO (IV) is done by MTT assay.And also theanticancer activity shown by **(L4)** with morpholine based metal complexes of Zn (II) and Ni (II).Morpholine derivative based ligand (**L5**) and Cu (II), Zn (II) metal complexes revealed antioxidant activity or free radical scavenging activity by using DPPH and antimicrobial activity against selected bacteria and fungi. Anticancer activity of (**L6)** with lanthanum metal complex. Only the metal complex of (**L7**) displays the antifungal as well as antimicrobial activity.

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A Review on Biological Significance of 4-Aminoantipyrine (An Antipyrine derivative)

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ABSTRACT

The derived from 4-Aminoantipyrine and its derivatives havelarge importance in medicinal, pharmaceutical as well as industrial field as is to be specificantiviral, antibacterial activity, antifungal activity, anticancer activity,antipyretic activity, antitumor activity, pestricides, as complexing agents etc.

Thenovelschiff basesbased on the 4-Aminoantipyrine and their d-block metal complexes are very much effective compounds. The biological superb importance of these metal complexes revealed that these molecules are also effective or productive against various strains of microorganisms. Schiff base complexes exhibitoutstanding catalytic activity in several types of reactions, their thermal stability is chief aspect for their applications as an activator or catalyst.

This article reported that thebriefsummary of biological significance of Schiff bases and metal complexes based on 4-Aminoantipyrine.

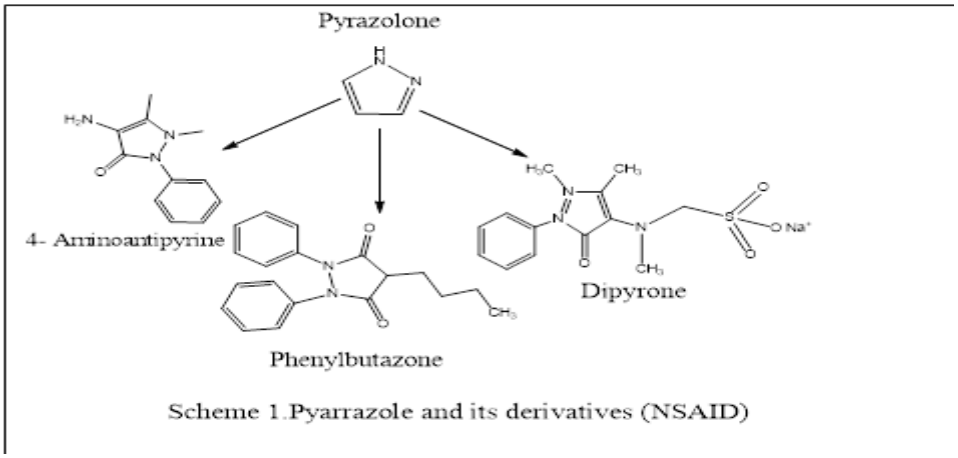
Keywords: 4-Aminoantipyrine, Pyrazole, NSAID, Schiff bases, metal complexes Anticancer, DNA.

I. INTRODUCTION

In recent day's heterocyclic compounds are attracting to the researcher towards them due to many reasons, among them mainly of their biological activities or pharmacological activities especially antifungal, antimicrobial, antidiabetics, anti HIV, anticancer, DNA binding, DNA cleavage etc. Because of these things scientist and research student are centralized on heterocyclic compounds (cyclic ring containing N, O or S atoms,). Many drugs are builts up by heterocyclic units. Some of the donor atoms such as nitrogen, oxygen, sulfur, azomethine nitrogen, amino-nitrogen and phenolic or alcoholic oxygen plays very important role in concerned with bioactivity.

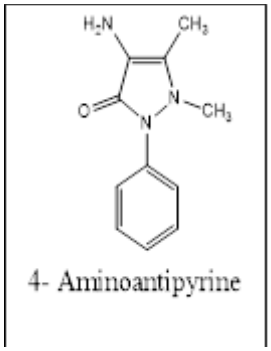
In the last few decades researcher have mainly focused on the Schiff bases derived from heterocyclic ring with carbonyl compounds, as its important special centre of attraction in many areas like medicinal, biological, analytical, clinical and pharmacological field [1-3]. Among them 4-aminoantipyrine based heterocyclic compounds have an extremely appreciated as it is originate in nature and have extensive biological or pharmacological activities [4],thederivative of pyrazolecalled as 4-Aminoantipyrine which is

actually temperature reducing agent [5]. It also utilizedfor the constitution of azo compounds (-N=N-) is usedas cytotoxic agents, as in printing industries [6]. Pyrazolone (N-heterocyclic compound) is an active moiety which evolves an important activity against arthritis, joint disorders as well as other musculo-skeletal disorders. Earlier work of many scientists revealed that some drugs exhibited increased much more activities when they areused as metal chelates by using Schiff base rather than as organic compounds.4-aminoantipyrine as coordination has been modified or reorganized into a flexible ligand (ductile) system with the help of condensation with a multiplicity of reagents such as aldehyde(RCHO), ketone(RCOR) etc. [7-11]. Pyrazolone is five-membered heterocyclic nitrogen containing compounds. The preparation of pyrazolines has been displayed [12-13] by the reaction of nucleophiles that isphenylhydrazineorhydrazine hydrate etc. Pyrazolines have been used as analgesic [14], antimicrobial agents and [15] antifungicidal [16]. Many medicines or drugs contain a pyrazole ring system. Derivatives of pyrazolineexhibit as insecticides and fungicidal agents. Pyrazolone sometimes referred as nonsteroidal anti-inflammatory agents. Derivatives of pyrazoloneis class ofNSAID (nonsteroidal anti-inflammatory drug) accommodate dipyrone, phenylbutazone, 4-Aminoantipyrine and oxyphenbutazone which are shown in scheme 1.They contain heteroatoms(nitrogen, oxygen or sulphur) in the ringthis heteroatom exhibit biological activities are to be specific nonsteroidal anti-inflammatory agents.4-aminoantipyrine is chief derivative. They have anelevatedpotency to attenuate or prevent the anti-platelet effects ofacetylsalicylic acid or namely as aspirin [17] and that is the reason that we have mainly focused on 4-Aminoantipyrine.



Scheme 1.Pyarrazole and its derivatives (NSAID)

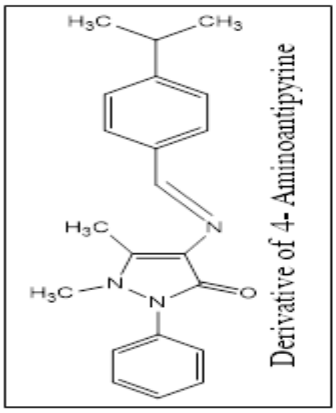
The antipyrine was firstly uncovered by the Knorr in 1884. He named the compound “Antipyrine” a derivative of pyrazole. The pyrazole derivatives displayed antipyretic activity i.e. temperature reducing agent in human body. Transition or d-block metal complexes derived from derivatives of pyrazolone are of appreciable interest of scientist, chemist and research student because of their significant biological or pharmacological activities, especiallyderivativesof pyrazolone based Schiff-base. Among the pyrazolone derivatives, 4-aminoantipyrine is capable to gives diverse types of Schiff bases with carbonyl compounds is to be specific Aldehydes or ketones, and they are considered to be higher ranking reagents in pharmacological, biological, clinical and analytical applications [13]. Antipyrine has been used as an antipyretic drugthat is for reduce the fever, swelling, immflamation and also it is analgesic drug to reduces the pain of particular body area.

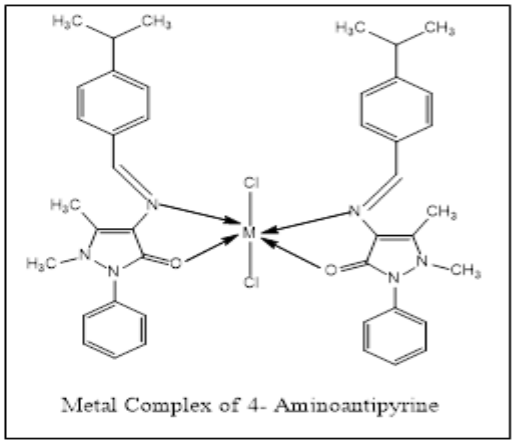


The 4-Aminoantipyrine also have been antiquated for the prophylactic of some diseases including cancer as well as the protection against oxidative stress, these are very important pathway in therapeutic applications [18]. Some of the derivatives of antipyrine were also used as antimicrobial [19], anticancer activity [20-22], analgesic [23], and anti-inflammatory [24]. The derivatives of 4-Aminoantipyrine are collectively introduced in travenously to invent liver infectious [25] in clinical medication.

Performance of 4-aminoantipyrine based Schiff base ligands and their metal complexesand study of antimicrobial activity:

In the company of pyrazole derivatives the metal complexes based on the 4-Aminoantipyrine are richer and more diverse in concerned with higher biological activities. 4-Aminoantipyrine based metal complexes displays multiplicity in bioactivities as antimicrobial, anti-malarial and anti-tumorous activities. Literature survey proved that Schiff bases synthesized from 4-Aminoantipyrine showed high inhibitory activities than ligands against S. aureus, K. pneumoniae, S. typhi, P. aeruginosa and Bacillus subtilis [26]. While observing the studies of 4-aminoantipyrine and its metal complexes; Cu (II) and Ni(II)complexes revealed that thehighly antimicrobial activity against K. pneumoniae, P. aeruginosa, S. aureus, Candida sp., E. coli and A. boumanii.[27]Also oxovanadil complexes derived from 4-Aminoantipyrine and its Schiff bases showed broad antimicrobial activities against Sarcinalutea, S. aphylococcus and B. subtilis (three gram +ve bacteria). P. aeruginosa, E. coli, S. typhi, K. pneumoniae, Proteus mirabilis, Serratiamarcescens and Shigellasonnie (seven gram -vebacteria). Candida albicans, Aspergillusflarus and Penicilliumchrysogenum (three fungal species)[28] From the observation it is clear that the inherent activities of metal-based pharmaceutical agents varies remarkably with a someexchanges in the Schiff base attached to the d-block metal ion [29].





DNA binding as well as DNA cleavage studies of 4-aminoantipyrine derived Schiff-base metal complexes:

Generally, because of the stacking interaction between aromatic chromophore of the complexes and the base pairs of DNA; the complexes binds to DNA with aromatic moieties by intercalation mainly results in bathochromism and hypochromism.4-Aminoantipyrine based ligands and their metal complexes have been showed interaction with DNA and capable to the breakage of DNA strands of cancer genes, due to this the replication property of cancer gene is demolished. It was observed that platinum based metal complexes showed the ability of breaking the DNA strands and due to this cis-platin is discovered. 4-Aminoantipyrine based ligands and their metal complexes also showed significant affinity towards DNA, specificity for the DNA base sequence recognition, tuning the redox potential [30-32].

Many researcher have been studied the metal complexes derived from 4-aminoantipyrine Schiff base ligands and electrophoretic behavior and cleavage activities against CT DNA of oxovanadiun metal complexes and reported that the metal complexes were able to convert super coiled DNA into open circular DNA[33-35].

Anticancer and Antioxidant aspects of 4-aminoantipyrine based ligands and their metal complexes:

Generally the Schiff bases of 4-Aminoantipyrine and its metal complexes shows large assortment of anticancer activities. Many researchers have observed that if cancer cells such as colon cancer (HCT-15) & Prostate cancer (PC-3) cells, breast cancer (MDA MB-231), cervical cancer (HeLa), and non-cancer cells like peripheral blood mononuclear cells (PBMCs) and human embryonic kidney cells (HEK-293) treated as per standard protocol the dose decreases up to 50% of the inhibition of the cells (IC50).

Recently the researcher has given the much more dedication on the anticancer activities of the ligand and metal complexes derived from 4-Aminoantiyrine Schiff bases. While studying they observed and reported that the cytotoxicity of the ligand and its metal complexes showed dose-dependent cytotoxicity in cancer cells. Among them, the nickel and copper complexes were more active at the lower dose levels in comparison with the ligand of other metal complexes. Remarkably, the cytotoxicity was more increased than their ligands and selective to the cancer cells. However, when this was compared with the standard reference of drug cisplatin, it was seen that nickel and copper complexes were more active. Similarly, theactiveand highly antioxidant activity of Ni (II) and Cu (II) complex was found [36-38].

II. CONCLUSION

Above all inclusive data the researcher opinion is thechemical study of heterocyclic Schiff base ligands and their transition metal complexes is flowering field that is being noticed. Recently more concentration focalized on Schiff bases and their metal complexes derived from 4-aminoantipyrine with derivative of aldehydes and ketones because they displayed wide ranging and number of applications. On the dissimilarity between Schiff base and metal complex; the metal complexes exhibit considerable biological as well as other activities than free organic ligands.

By the current scheme we can conclude that Schiff base ligands and their metal complexes have great capacity for future research in the synthesis of unique derivatives containing these types of moieties which

can be deeply explored for different types of biological activities. And there is a large scope in studies as well as selective biological studies of 4-Aminoantipyrine based Schiff base ligands and their metal complexes.

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Euglenoids of Manjara River and Its Reservoirs of Beed District in Maharashtra

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ABSTRACT

The Euglenoids are showing combine characters like plants and animals. According to Fritsch (1035) classify in signal orderEuglenales and family Euglenaceaewith five genera. To study diversity of Euglenoids ten sites of Manjra river ware selected for the collection samples.In present investigation Euglenoids were seen at all the ten sites in more or less numbers. Maximum number of Euglenoids was recorded at S3. This class was represented by species of Euglena06, Phacus04 and Trachelomonas03. During present study Euglenophyceae members were recorded in all seasons, maximum number of species was found in summer seasons.

Keywords – Euglenoids, Manjra River and Seasons.

I. INTRODUCTION

This is the protozoans – like organisms which sharply defined by unique and highly specialized feature. The derivation of euglenoids is obscure but there is some evidence that they evolved from marine ancestors. Most of the members are fresh water; few are sedentary, motile by one or two stoutflagella of complex structure. The euglenoids are showing combine characters like plants and animals. According to Fritsch (1035) classify in signal order euglenales and family euglenaceae with five genera. In the recent era great advances have been made in the investigation of fresh water algae in many parts of the world and particular attention has been paid to their biology and ecology. Survey of literature revels that, studies on euglenoidsdiversity in abroad and in India have been done extensively. In Maharashtra several workers have paid their attention on diversity of euglenoids. Marathwada is a one of the important geographical region of Maharashtra where large number of fresh water bodies is present. Review of literature reveals that the euglenoidsdiversity in Marathwada is still in infancy (Sarode and Kamat, 1979, 1980, 1981 and 1983; Ashtekar, 1980; Kamble, 2008 and Andhale, 2008). So far,Beed area has not been explored as its biotic diversity of euglenoids is concerned. Therefore to fulfil this lacuna, it has been decided to work oneuglenoidsdiversity of Manjarariver and its reservoir of Beed district in Maharashtra.

Considering the importance of fact, the present research work has been carried out by selecting different sites of ManjaraRiver during May 2007 – June 2009for euglenoidsdiversity study.

II. MAREIALS AND METHODES

Algal samples were collected at monthly intervals during May 2007 to June 2009 in Acid washed collection bottles. Floating, Planktonic and attached substratum algal samples were collected separately in collection bottles. After collection, algal samples were brought immediately to the Laboratory. The algal samples were preserved in 4% formalin for further taxonomic investigations. The fresh as well as preserved algal forms were observed under microscope and identified. Identification of algal taxa was performed by referring to the standard literature on algae (Prescott 1951).

III. RESULT AND DISCUSION

During present investigation Euglenoids were seen at all the ten sites in more or less numbers. Maximum number of Euglenoids was recorded at S_3(Table 2). The 13 euglenoids ware encountered belongs to 03 genera (Table 1). On the basis of number of texa*Euglena*dominant followed by*Phacus*and *Trachelomonas*.work has been conformed with the work of researchers Hosmani S.P. and Bharati, S.G. 1975hydrobiological studies in ponds and lakes of Dharwar III: Occurrence of two Eugleniods blooms,Kumawat and Jawale2004 researched the ecology of fish pond at Anjale, Jalgaon district with special emphasis on euglenoids and gener, Kumawat et. al .2007 Euglenineae form Jalgaon District, Maharashtra, Mahajan S.R. and S.N. Nandan 2007 contribution to the knowledge of Englonoids of Hartala lake of Jalgaon, Maharashtra, Munawar, M. 1972 ecological studies of Euglenineae in certain polluted and unpolluted environments.Waghodkekar V.H. et. al. 2001 Addition to Euglenoids of Maharashtra.During present study Euglenophyceae members were recorded in all seasons, maximum number of species was found in summer seasons. Similar kind of study was made bySingh and Swarup 1979 recorded a very thin population of Euglenoides in winter months. It reaches to peak in April of summer season.

Table.1 Euglenoids ofManjarariver and its reservoirs ofBeed district in of Maharashtra.

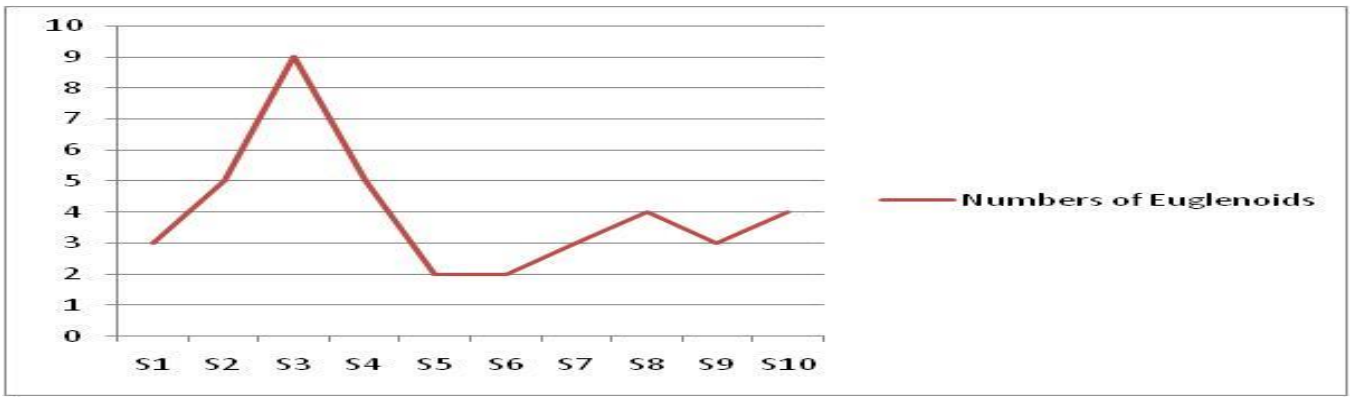
Sr. No.	Name of Algae	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
1	*Euglena acus*	-	-	-	+	+	+	+	-	+	+
2	*Euglena convolute*	+	+	+	-	-	-	+	+	-	-
3	*Euglena deses*	-	-	-	+	-	-	-	-	-	-
4	*Euglena elongata*	-	-	+	-	-	+	+	-	+	+
5	*Euglena gracillis*	-	+	+	+	+	-	-	+	-	-
6	*Euglena proxina*	-	-	-	+	-	-	-	-	-	-
7	*Phacusangulatus*	-	-	+	-	-	-	-	+	-	+
8	*Phacusbirgei*	+	-	+	+	-	-	-	-	-	-
9	*Phacus meson*	-	+	-	-	-	-	-	+	-	+
10	*Phacus* sp.	+	-	+	-	-	-	-	-	-	-
11	*Trachelomonasintermedia*	-	+	+	-	-	-	-	-	+	-
12	*Trachelomonasoblonga*	-	-	+	-	-	-	-	-	-	-

13	*Trachelomonasvolvocina*	-	+	+	-	-	-	-	-	-	-

Table.2 Site wise abundances of Euglenoids of Manjarariver and its reservoirs.

Sites	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
Numbers of Euglenoids	03	05	09	05	02	02	03	04	03	04

Graph.1 Site wise abundances of Euglenoids of Manjarariver and its reservoirs.



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Application of Nonmaterials in Agriculture

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ABSTRACT

Nanotechnology is considered as one of the possible solutions to problems in food and agriculture. Just like biotechnology, issues of safety on health, biodiversity, and environment along with appropriate regulation are raised on nanotechnology.

Nanotechnology in agriculture has gained momentum in the last decade with an abundance of public funding, but the pace of development is modest, even though many disciplines come under the umbrella of agriculture. Nanotechnologic intervention in farming has bright prospects for improving the efficiency of nutrient use through nanoformulations of fertilizers, breaking yield barriers through bionanotechnology, surveillance and control of pests and diseases, understanding mechanisms of host-parasite interactions at the molecular level, development of new-generation pesticides and their carriers, preservation and packaging of food and food additives, strengthening of natural fibers, removal of contaminants from soil and water, improving the shelf-life of vegetables and flowers, clay-based nanoresources for precision water management, reclamation of salt-affected soils, and stabilization of erosion-prone surfaces, to name a few.

Nanotechnology will play a vital role in the development of the agricultural sector, as it is capable of being used in agricultural products that protect plants and monitor plant growth and detect diseases. Scientists have been working towards exploring new applications of nanotechnology in agriculture and the food industry if these discoveries are applied sensibly, the environment, the agricultural sector and the food industry will indeed see tremendous changes for the better in the coming years.

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A Facile an Efficient Synthesis of Benz imidazole Using Reusable Phthalimide-N-Sulfonic Acid (PISA)

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ABSTRACT

A green and facile route has been developed for the synthesis of benzimidazole from condensation reactions of o-phenylenediamines with aromatic aldehyde in presence of phthalimide - N - sulfonic acid (PISA) as an efficient, cheap and reusable catalyst under mild reaction conditions.
Keywords: PISA, o-phenylenediamines, aromatic aldehyde, recyclable, Benzimidazole

I. INTRODUCTION

In medicinal Chemistry for a long time synthesis and biological study of heterocyclic compounds has been an interesting field. A number of heterocyclic derivatives containing nitrogen and sulphur atom serve as a unique and versatile scaffolds for experimental drug design [1]. The benzimidazole moieties are usually present in a large number of natural products in addition to pharmacologically active compounds [2]. It shows a wide range of biological and pharmacological properties such as antifungal [3], antimicrobial [4], anthelmintic [5, 6], antiviral [7, 8], topoisomerase inhibition [9] and anticancer activities [10]. A number of their derivatives are marketed as antifungal drug (Carbendazim) [11], anthelmintic drug (Mebendazole and Thiabendazole) [12], antipsychotic drug (Pimozide) [13] and antiulcer agent (Omeprazole) [14]. Due to their attractive pharmacological properties, huge attention has been paid to the synthesis of benzimidazoles.
Because of their wide range of synthetic, industrial and pharmacological application, many methods for the preparation of benzimidazole are reported in the literature. The most common method is direct condensation of 1,2-phenylenediamine and carboxylic acids [15, 16] or their derivatives [17], that require strong acidic conditions and sometimes need high temperature or the use of microwave [18]. In recent years, solvent-free synthesis of benzimidazoles under microwave irradiation using $Yb(OTf)_3$ [19], KSF clay[20], PPA[21], Na_2SO_4 [22], K-10 clay[23], have been reported.
However, a variety of catalysts have been reported for the synthesis of 2-aryl benzimidazole most of them suffer from disadvantages such as long reaction times, forceful conditions, low yields, low selectivity, tedious workup, and use of toxic or expensive reagents. Consequently, a new procedure that avoids these drawbacks

is desirable.We report herein an efficient, low cost and environmentally benign protocol for the synthesis of benzimidazole using reusable SuSA catalyst under mild reaction condition.

II. METHODS AND MATERIAL

All purchased chemicals were of analytical grade and used without further purification. Silica gel coated aluminum sheets (Merck made) were used for thin layer chromatography (TLC) to monitor progress of reactions. Melting points were determined in an open capillary tube and are uncorrected. ^{1}H NMR spectra were recorded using DMSO as solvent and TMS as internal standard at 300 MHz on Brucker Avance spectrophotometer. All the products were characterized by IR spectral data and comparison of their melting points with those reported in literature and found to be identical. Also, the some products were confirmed by ^{1}H NMR spectral data.

Preparation phthalimide-N-sulfonic acid:

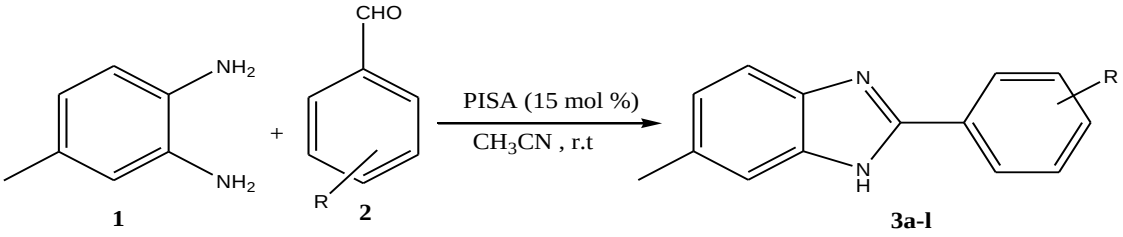
PISA was easily prepared by addition of an equivalent amount of cholorosulfonic acid to potassium phthalimide [24].

General procedure for the Synthesis of 2-aryl benzimidazole:

PISA (15 mol %) was added to a stirred solution of the aldehyde (1 mmol) and o-phenylenediamines (1 mmol) in acetonirile (3 ml), and the mixture was stirred at room temperature for appropriate time (Table 1). After completion of the reaction monitored by TLC, the solvent was removed under reduced pressure and ethyl acetate (5 ml) was added, and the catalyst was recovered by filtration and washed with ethyl acetate (5 ml). The filtrate was washed with water and then dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave the highly pure product obtained. Further recrystalization was done in ethyl alcohol.
Selected spectral data:

5-methyl-2-(4-nitrophenyl)-1H-benzimidazole (Table 2, entry 3c)

IR(KBr pallets): *V*max 3109, 1605, 1511, 1463, 1354, 1176, 739, 701 and 657 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-*d6*):δ 8.39 (s, 4H+1H, overlapped Ar-H and N-H), 7.54 (d, J = 8.0 Hz, 1H, Ar-H), 7.43 (s, 1H, Ar-H), 7.09 (d, J =8.3 Hz, 1H, Ar-H) and 2.44 (s, 3H, -CH_3); ^{13}C NMR (75 MHz, DMSO-*d6*):δ 159.0, 153.6, 143.2, 136.3, 131.0, 129.3, 127.9,119.4, 114.7, 114.6, 111.5 and 31.1. Mass (EI, m/z): 254 [M^{+}].



1 **2** **3a-l**

Scheme 1: Synthesis of benzimidazoles

III. RESULTS AND DISCUSSION

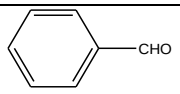
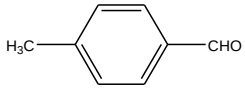
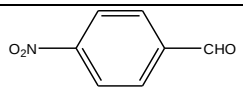
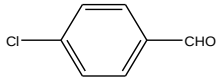
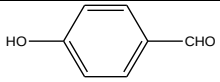
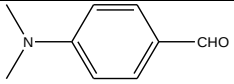
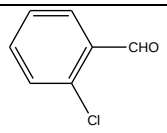
To explore the use of PISA as a catalyst for the reaction of benzaldehyde and o-phenylenediamines for the preparation of 2-arylbenzimidazole compound **3a** was considered as a standard model reaction (**Table 2**). Model reaction in the absence of catalyst did not led to desired product formation. It means interference of catalyst was must for initiation of the reaction. To determine exact requirement of catalyst for the reaction, we used model reaction at different concentrations of PISA (**Table 1**). During this study, we observed that, 15 mol% catalysts proved to be an efficient catalyst to carry out the reaction smoothly.

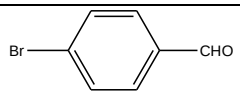
Encouraged by this result, in further set of experiments, in order to build the generality of the reaction, variety of aromatic aldehydes with either electron-donating or electron-withdrawing groups were converted to 2-arylbenzimidazoles derivatives in good to excellent yields. All the results are summarized in **Table 2.**

Table 1 Optimization of the catalyst

Entry	Catalyst (mol %)	Isolated Yield %
1	---	Trace
2	5	58
3	10	82
4	15	90
5	20	91

Table 2 Synthesis of 2-arylbenzimidazole [a]

Entry	**Aldehydes**	**Time (min.)**	**Yield[b] (%)**
3a		60	88
3b		62	88
3c		50	90
3d		52	90
3e		65	84
3f		65	87
3g		70	86

3h		65	88

[a] Reaction conditions: Aromatic aldehydes (1 mmol), o-phenylenediamines (1 mmol), PISA (15 mol%) at room temperature. [b] Isolated yield

IV. CONCLUSION

The Bronsted acid PISA is a catalyst that has high efficiency in the synthesis of benzimidazoles. The reaction of the condensation of aromatic aldehyde with o-diphenylamines in acetonitrile as a solvent at room temperature gave maximum yields. The present protocol has numerous advantages such as high reaction rates and excellent yield, ease of preparation and handling of catalyst, inexpensive with lower loading and a simple experimental procedure.

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Novel Synthesis, Characterization and Study of Biological Activity of 3-Arylazo-4- Hydroxy 2-H- Chromen-2-One Moiety

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ABSTRACT

(3-methylpyridin-2-yl)diazenyl)-4-hydroxy-2H-chromen-2-one, (4-methylpyridin-2-yl)diaze-nyl)-4-hydroxy-2H-chromen-2-one, (6-methylpyridin-2-yl) diazenyl)-4-hydroxy-2H-chromen -2-one and(antipyrine)diazenyl -4-hydroxy-2H-chromen-2-one weresynthesized by using coupling of 2-amino 3-methyl pyridine, 2-amino 4-methyl pyridine, 2-amino 6-methyl pyridine, 4-amino antipyrine with 4-hydroxy-2H-chromen-2-one. These azo compounds were characterized by IR, 1HNMR, 13CNMR and mass spectral analysis.In vitro biological screening effects of the synthesized compounds were tested for their antibacterial and antifungal activity. For antibacterial activity the bacterial species used were Bacillus subtilis, Escherichia coli, Salmonella typhi, andStaphylococcus aureus by Agar cup method whilefungal species usedAspergillusflavus, Penicilliumchrysogenum,Aspergillusniger and Fusariummoneliformed by the poison plate method.

Keyword: 4-hydroxychromen-2-one, amino pyridine, amino antipyrine, biological activity.

I. INTRODUCTION

4-Hydroxycoumarin is a structurally Benz[α]pyrone derivative which contains hydroxyl group in fourth position of coumarin. The various derivatives ofcoumarin moiety found in nature havingvaried biological importance1. Coumarin moiety contains a fused heterocyclic nucleus which shows variety of medicinal application. Several of these exhibit exceptional biological and pharmacological activities such as anti-inflammatory activity2, antioxidant3, anti-HIV4, anticoagulant5 and cytotoxic properties6. Its applications not only restricted to medicine but also found in food additives, perfumes, cosmetics, dyes and herbicides7.Like coumarin, azo dye functional group containing compound have importance because of its anti-microbial, and food coloring agentproperty8.

In the views of above facts, we arereporting the novelarylazo4-hydroxy coumarin compounds prepared by coupling 4-Hydoxy Chromen-2-onewith diazo-heteroaryl compounds. These diazoheteroaryl compounds were prepared by diazotization with 2-amino 3-methyl pyridine, 2-amino 4-methyl pyridine, 2-amino 6-

methyl pyridine and amino antipyrine. These synthesized compoundswere characterized by IR, 1HNMR, 13CNMR and mass spectral analysis.In vitro biological screening effect of the synthesized compounds were tested against the bacterial speciesBacillus subtilis, Escherichia coli, Salmonella typhi, andStaphylococcus aureusby Agar cup method while Fungal speciesused Aspergillusflavus, Penicilliumchrysogenum,Aspergillusnigerand Fusariummoneliforme were tested by the poison plate method.

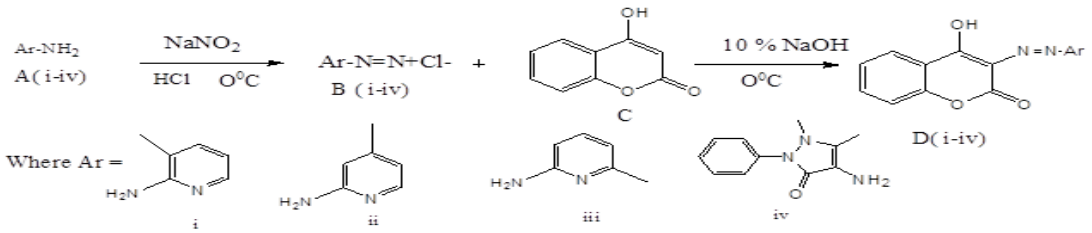
II. EXPERIMENTAL SECTION

The solvents and the reagents used in present study were of analytical grade and obtained from E-Merck and S. D. fine Ltd. Melting points were determined in an open capillary tube and are uncorrected. The purity of the compound has been checked by TLC. The C, H, N analysis of synthesized compounds were carried out by micro combustion method using CHNSO, EA1I08, Elemental analyzer model-CARLO-ERBA Instruments, at micro analysis division, National Chemical Laboratory, Pune. The samples weighing between 1-10 mg were used for the analysis. The molecular stoichiometry of each compound was established on the basis of elemental analysis. IR spectra were recorded in CHCl3 on a Shimadzu FTIR-8300 spectrophotometer. The 1H NMR (300 MHz) and 13C NMR (70 MHz) were run on a BrukerAvance DPX-250 spectrometer in CDCl3 using tetramethylsilane as an internal standard. Chemical shift values are given in δ scale. Mass spectra were recorded on Finnigan Mat LCQ Mass Spectrometer using methanol as mobile phase.The in vitro biological screenings of the investigated compounds were tested against the bacterial species by agar cup method and fungal species by the poison plate method.

Procedure:

Substituted 2-amino pyridine (5mmol) were dissolved in 8ml water and 5ml conc. HCl, mixture is heated until amine hydrochloride is completely dissolved. NaNO2 (5mmol) solution wasprepared by dissolving it in minimum quantity of water and kept both the reaction mixture in ice bath for cooling. When these mixtures attain 0-50C temperature then NaNO2solutionwas added to theSubstituted 2-amino pyridinesolution drop-wise with vigorous stirring. Near 00C temperature was maintained throughout the reaction. After the complete addition reaction mixture was kept in ice bath for 15 minutes with occasional stirring.

The diazotized reaction mixture was then poured in ice cooled solution of 4-hydroxy coumarin (5mmol) in 25 ml of 10% sodium hydroxide solution. This mixture was allowed to stand (0-50C) for 2hours and then filtered. The crude product thus obtained was dried and recrysallized from acetic acid to give the corresponding compounds.



Reaction Scheme

Antibacterial Activity

The antibacterial activity was measured by agar cup method9.The bacterial strains used as test organism were Escherichia coliand Salmonella typhi as a gram negative bacterial strains and Bacillus subtils and Staphylococcus aureu as gram positive bacterial strains. Nutrient agar (Himedia) was prepared and sterilized and kept for 15 minutes in the autoclave.All bacteria were cultured aerobically at 37°C in LB agar and LB broth medium. Before experimental use, cultures from agar medium were sub cultivated in liquid media, incubated for 12 h (37°C).The media plate were seeded with this both culture. Cups of 10mm diameter were made in the agar plate with sterile cork borer. 100 µl of compound solution prepared in ethanol (0.1%) was added in the cups under aseptic condition with the help of micropipette. 100µl of ethanol(0.1%) was placed in separate cups as blank (negative control). 100 µl of solution of Ciprofloxacinin ethanol (0.1%) was also placed on the seeded nutrient agar surface as standard reference antibiotic (positive control).The plates were allowed for diffusion of the compound from agar cup into the medium. Then the plates were incubated for 24 hours.Record the zone of inhibition of bacterial growth around the agar cup in millimeter (mm) using zone reader.

III. ANTIFUNGAL ACTIVITY

Procedure:

Antifungal activity was performed by Poison plate method10. A culture of Potato Dextrose Agar (PDA) medium for test of fungi wasused. The compound to be tested is added to the sterile medium in aseptic condition. A plate with ethanol was prepared as blank (negative control) similarly a plate with 1% Fluconazole was prepared as standard reference plate (positive control). For testing the fungal activity Aspergillusniger, Penicilliumchrysogenum, Fusariummoneliforme, Aspergillusflavuswere selected. They were allowed to grow on slant for 48 hours so as to get profuse sporulation. 5ml of 1:100 aqueous solution of Tween 80 was added to the slant and spores were scraped with the help of Nichrome wire loop to form suspension. The plates were incubated at room temperature for 48 hours.After incubation plates were observed for the growth of inoculated fungi. Results were recorded.

Table : 1Analytical data of newly synthesized azocoumarine analogues

Synthesised Azo compounds	IR (KBr, cm-1)	^{1}HNMR(CDCl3) (300 MHz)	^{13}CNMR(CDCl3) (300 MHz)	Mass Spectra

D(i) 3-(2-(3-methylpyridin-2-yl)diazenyl) -4-hydroxy-2H-chromen-2-one	3425(νO-H) stretch 3018 (νAr-H) stretch 1710(νC=O) of lactone 1610 (νC=C stretch coumarin 1557 (νN=N)Strech 1020 (νC-N) Strech	7.5-7.2m,4H,Ar-H of coumarin 2.64 S,3H(–CH3) 15.70 S,1H, (-O–H); 8.3-7.5m, 3H (Ph–H) of pyridine	164.9 for C_3 carbon, 158 for C_2 carbon & 117 to 154 for other carbon of coumarine moiety. 24.8 for CH_3 and 119 to 158 for carbon of pyridine moiety	[M+] = 280.06
D(ii) 3-(2-(4-methylpyridin-2-yl)diazenyl) -4-hydroxy-2H-chromen-2-one	3420(νO-H) stretch 3025 (νAr-H) stretch 1715(νC=O) of lactone 1620 (νC=C stretch coumarin) 1552 (νN=N)Strech 1025 (νC-N) Strech	7.4-7.2m,4H,Ar-H of coumarin 2.66 S,3H(–CH3) 15.75 S,1H, (-O–H); 8.3-7.5m, 3H (Ph–H) of pyridine	164.9 for C_3 carbon, 160 for C_2& 117 to 154 for other carbon of coumarine moiety. 15.3 for CH_3 and 121 to 151 for carbon of pyridine moiety	[M+] = 280
D(iii) 3-(2-(6-methylpyridin-2-yl)diazenyl)-4-hydroxy-2H-chromen-2-one	3428(νO-H) stretch 3022 (νAr-H) stretch 1722(νC=O) of lactone 1618 (νC=C stretch coumarin) 1555 (νN=N)Strech 1034 (νC-N) Strech	7.5-7.3m,4H,Ar-H of coumarin 2.665 S,3H(–CH3) 15.71 S,1H, (-O–H); 8.3-7.5m, 3H (Ph–H) of pyridine	164.9 for C_3 carbon, 159 for C_2& 117 to 154 for other carbon of coumarine moiety. 24.8 for CH_3 and 124 to 149 for carbon of pyridine moiety	[M+] = 280
D(iv) 4-(1,3-Dimethyl-2-phenyl-3-oxo pyrazolyl)-4-hydroxy-2H-chromen-2-one	3445(νO-H) stretch 3015 (νAr-H) stretch 1720(νC=O) of lactone 1620 (νC=C) stretch of coumarin) 1548 (νN=N) Stretch 1018 (νC-N) Stretch Pyrazolone Stretch 1660 (νC=O) stretch	7.5-7.4m,4H,Ar-H of Coumarine 2.63 S,3H(–CH3) 15.79 S,1H, (-O–H); 8.6-7.8m, 3H (Ph–H) of antipyrine	164.9 for C_3 carbon , 164 for C_2 & 117 to 154 for other carbon of coumarine moiety. 162.2 for C_3 carbon , 93 for C_4& 155 for C_5 carbon of antipyrine moiety	[M+] = 377

Table : 2 Physical data of newly synthesized azo compounds

Synthesised Azo compounds	Molecular Formula	Mol. Wt	Elemental analysis Found (Calculated)			Melting point	Colour	Yield (%)
			C	H	N			
D(i) 3-(2-(3-methylpyridin-2-yl)diazenyl) -4-hydroxy-2H-chromen-2-one	$C_{15}H_{11}N_3O_3$	281	62.92 (63)	3.39 (3.33)	15.72 (15.70)	185	Light Pink	80
D(ii) 3-(2-(4-methylpyridin-2-yl)diazenyl) -4-hydroxy-2H-chromen-2-one	$C_{15}H_{11}N_3O_3$	281	62.90 (62.85)	3.82 (3.54)	15.31 (15.20)	187	Brown	78
D(iii) 3-(2-(6-methylpyridin-2-yl)diazenyl)-4-hydroxy-2H-chromen-2-one	$C_{15}H_{11}N_3O_3$	281	62.30 (62.10)	3.72 (3.52)	15.53 (15.30)	185	Yellow	70
D(iv) 4-(1,3-Dimethyl-2-phenyl-3-oxo pyrazolyl)-4-hydroxy-2H-chromen-2-one	$C_{20}H_{16}N_4O_4$	378	62.82 (63.75)	4.28 (4.25)	14.89 (14.95)	182	Red	75

IV. RESULT AND DISCUSSION

The scheme of reaction approaching to the target aryl azo compounds is outlined above. In present investigation we report newly synthesized four aryl azo compounds. They were prepared by coupling 4-hydroxy-2H-chromen-2-one with diazotized aryl amines.The products formed were recrystallized in ethanol and purity was tested by TLC. Different aryl amines were firstly undergoing diazotization by the action of sodium nitrate at 0-5 0. This diazotised mixture produces N2+ as strong electrophile which triggers the coupling reaction with 4-hydroxy coumarine11. The synthesized compounds were summarized in table.

The Characterization of the synthesized compounds were done withIR, 1HNMR, 13CNMR techniques. The significant peaks observed in the spectra are summarized in the table-1.

The IR spectra of compound showed high intensity band observed at 1548-1557 cm-1 is assigned to ν(N=N) vibration suggesting the presence of N=N12while Broad weak band around 3420-3445 cm-1 is assigned to H bonded –OH in the compound. The band at 1567-1480 cm-1 is assigned to the combination of ν(C=C) of the aromatic ring. A high intensity band in the region 1018-1034 cm-1 is assigned to ν(C-N) vibration and 1722-1710 cm-1 for lactone carbonyl13.

The 1H NMR spectra ofcompoundrevealed singlet for H at 15.70-15.79 assigned to phenolic OH group14. Peaks between 7.5-7.0ppm are assigned to aromatic protons of 4-hydroxy coumarin while m(8.6-7.5) indicates aromatic proton from aryl amines15 . C13NMR showed peaks between 117 to 165 ppm for 4 hydroxy coumarinmoiety while between 124 to 140 ppm for aromatic carbon of pyridine group. Assignment given to other peaks observed in 1HNMR, 13CNMR spectra and also molecular ion peaks in mass spectra justifies the structures of compounds.

Table: 3 Anti-Bacterial Activity

Synthesised Azo compounds	Zone of Inhibition (diameter in mm)			
	B. subtilis	E. coli	S. typhi	S.aureus
Ciprofloxacin(Refernce)	18	24	25	25
D(i)3-(2-(3-methylpyridin-2-yl)diazenyl) -4-hydroxy-2H-chromen-2-one	20	16	20	24
D(ii)3-(2-(4-methylpyridin-2-yl)diazenyl) -4-hydroxy-2H-chromen-2-one	22	14	18	20
D(iii)3-(2-(6-methylpyridin-2-yl)diazenyl)-4-hydroxy-2H-chromen-2-one	23	15	19	21
D(iv)4-(1,3-Dimethyl-2-phenyl-3-oxo pyrazolyl)- 4-hydroxy-2H-chromen-2-one	24	18	21	28

Table: 4 Anti- fungal Activity

Synthesised Azo compounds	Growth of Fungi			
	A. flavus	P.chryso-genum	A. niger	F.mone-liforme
Fluconazole (Reference)(65µg/ml)	-	-	-	-
D(i)3-(2-(3-methylpyridin-2-yl)diazenyl) -4-hydroxy-2H-chromen-2-one(64µg/ml)	+	++	+	++
D(ii)3-(2-(4-methylpyridin-2-yl)diazenyl) -4-hydroxy-2H-chromen-2-one(64µg/ml)	-	+	-	+
D(iii)3-(2-(6-methylpyridin-2-yl)diazenyl)-4-hydroxy-2H-chromen-2-one(64µg/ml)	+	+	-	+
D(iv)4-(1,3-Dimethyl-2-phenyl-3-oxo pyrazolyl)- 4-hydroxy-2H-chromen-2-one(64µg/ml)	+	++	+	++

Moderate growth (++), Reduced growth (+) and No growth (-) of fungi

The aryl azo compounds synthesized were evaluated for anti-bacterial and anti-fungal activity with different strains of bacteria and fungi. Results are shown in Table-3 and Table-4. All azo compounds show good antimicrobial activity against B.subtilis compared to Ciprofloxacin as control. While D (iv) showed antimicrobial against S.typhi and S.aureus alongwith B.subtilis. All compounds showed encouraging antifungal activity against Aspergillus species as compared to P.crysogenum and F.moniliforme with D(ii) and D(iii) showing highly effective as compared to Fluconazole as control. The growth of the later was also reduced by these compounds.

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A Mini Review : Hydrogen as Promising Green Energy Source

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ABSTRACT

From fossil fuels are cheaper than renewable energy resources but on combustion produce large amount of CO2. Instead of traditional fuels, Hydrogen is a promising alternative renewable resources and environmental friendly. It has a number of good features.Therefore research community interested in potential usage of hydrogen as green energy source. In this review we have focused on hydrogen is an alternative green energy source. The objective is to understand the role of hydrogen in today and future scenario.

Keywords : Hydrogen, renewable, green energy, emission, energy

I. INTRODUCTION

World Bank data reveals that in the last 50 years, CO_2 emissions (metric tons per capita) have increased from 3.09 to 4.99 in the world[1]. Due to increasing industrialization increases large scale of CO_2 emission shown in figure 1.

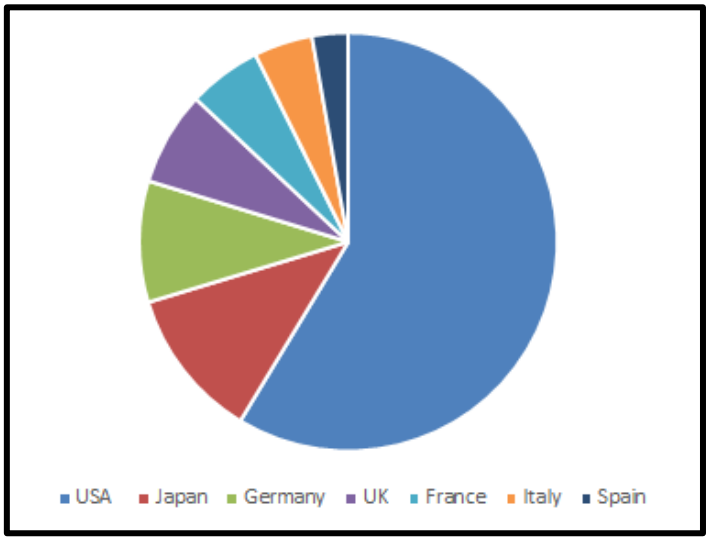

Fig 1.Emission of CO_2 by industries in the countries

According to report of India Energy Outlook 2021, due to an expanding economy, population, urbanization and industrialization, India has largest increase in energy demand than any other country. Italso thirdlargest energy consuming country in the world. Use of energy has doubled since 2000, with 80% of demand still being met by coal, oil and solid biomass. It has brought a serious impact on the environment.In this context,India's CO_2 emissions will be increases up to 50% in 2040[2, 3]. It already feeling their effects on air quality and health in some metro cities. Modern renewable sources of energy have started option for clean and efficient energy production[4].

II. HYDROGEN – PROMISING RENEWABLE SOURCE OF ENERGY

Hydrogen is one of the most abundant element on the earth, and it plays a vital role in the sustainability of lifecycle. The hydrogen atom is made up by a single proton and a single electron. As such, it is very abundant, but it doesn't really exist as a separate form of matter. Instead, it is usually combined with other elements. To separate hydrogen gas from its companion substances takes a lot of effort, but it produces a powerful, nearly clean source of energy. As a gas, it can be used in fuel cells to power engines[5].

Hydrogen gas is extracted from water by a technique known as electrolysis, which involves running a high electric current through water to separate hydrogen and oxygen atoms. The electrolysis process is quite expensive since it involves high energy expenditure[6].The energy used to generate electricity in the electrolysis process is harnessed from fossil fuels like natural gas, coal, or gasoline[7]. Their combustion produces Pollutant in large quantities such as SO2, NxOy, CO and CO2shown in table I& II. Renewable energy sources like hydropower, wind and solar to ensure there are no greenhouse gas emissions and help in reduction of CO2 emission[8].

TABLE I PERCENTAGE EMISSION OF POLLUTANT IN COMBUSTION OF FUEL (kg/kg OF FUEL)

Fuel	CO_2	SO_2	N_xO_y	H_2O
H	0	0	0.016	7
C	1.893	0.012	0.008	0.66
CH_4	2.75	0.03	0.007	2.15
C_8H_{18}	3.09	0.010	0.012	1.25

III. ROLE OF HYDROGEN IN NET ZERO EMISSIONS BY 2050

The key parameters of decarbonizing the global energy system are energy efficiency, renewables and hydrogenbased fuels.The important role of hydrogen in net zero emission conditions is evident from its increasing contribution to reducing total emissions. By increasing the demand for hydrogen and renewable energy technology for its production, hydrogen and hydrogen based fuels will be able to reduce 60 Gt CO_2 emissions in 2021 to 2050[9]. Green hydrogen arises as game changer in this filed.

TABLE II RELATIVE ANALYSIS OF MAIN POLLUTANT EMISSION BY THE INDUSTRIES

State	Sulphur dioxide	Nitrogen oxides	Carbon oxide	Carbon dioxide
USA	23,200	20,300	77,400	4,166,000
Japan	1314	1435	--	831,000
Germany	3200	3100	8650	666000
UK	4670	1812	8891	517000
France	3460	1847	5200	404000
Italy	3205	1506	5487	322000
Spain	3756	792	3780	198000

IV. OPPORTUNITIES IN GREEN HYDROGEN

Green Hydrogen is more expensive than grey. Gray hydrogen produced from natural gas but it has less environmental sustainability. Green hydrogen does not require fossil fuels, it is a good solution to decrease CO_2emission.

Among the potential energy alternative, hydrogen is a one of the clean fuel.It simply produces water as byproducts on combustion as shown in figure.as shown in figure 2.

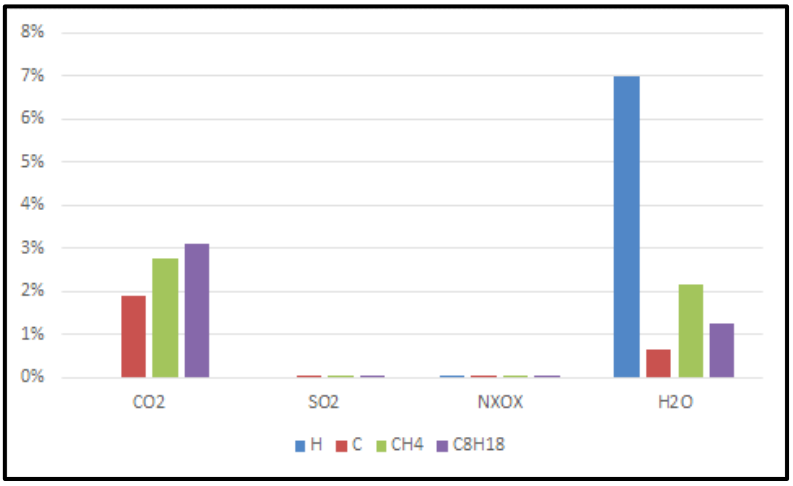

Fig. 2. Percentage emission of pollutant in combustion of fuel (kg/ kg of fuel)

V. METHODS OF PRODUCTION OF HYDROGEN BY USING GREEN CHEMISTRY

Molecular hydrogen is directly not available in nature, so it has produced by different ways.All methods of hydrogen production are not always green because some of the methods have CO_2 byproduct. On the basis of energy sources, hydrogen production is mainly divided into 4 categories such as electrical, thermal, biological and hybrid[10]. Production of hydrogen by electrolysis process, thermal decomposition process, photochemical water splitting[11], bio-photolysis[12]are green.

VI. IMPACT OF COVID-19 ON DEVELOPMENT IN ENERGY SECTOR

Pandemic of COVID-19 impact on every sector of word. The drop in demand in 2020 affect all fuels consistently. Energy demand across the world dropdown by 6% in 2020. Economies are expected to see rapid recoveries in energy demand, but now energy demand is remains below 3%.**Recently global hydrogen consumption is still less than 2% of global energy. But according to the Hydrogen Council, this consumption could reach 25% by 2050.**

Analysis by the International Energy Agency (IEA) finds that the cost of hydrogen production from renewable electricity mightdecrease 30% by 2030 as a result of declining costs of renewables and the scaling up of hydrogenproduction.

VII. CONCLUSION

Today's demand is that to identify abundant, reliable, affordable, green sources of energy for future. In context to increasing demand of energy,production of green hydrogenplay crucial role in long-term energy strategies of the nations. Day by day increases commercial demand for clean hydrogen anddevelopment in research,lower the production cost and attracting investors. It will help to reduce gap between supply and demand. In this way hydrogen energy will be able to solve the environmental problems that damages all the ecosystems on earth. Green hydrogen will be future ecofriendly, efficient, sustainable energy source.

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Synthesis of Ethyl 4,6-Dichloro 2-Methyl Nicotinate from 2,4,6-Trichlorophenol

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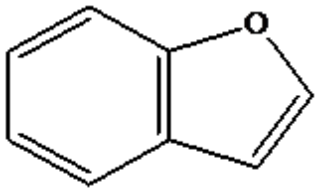
ABSTRACT

The present work on the preparation and trapping of Furo [3,4-c] pyridine inspired us to study the scope and limitations of this work. Beside this it was decided to work and study Tandem pummerer-Diels-Alder reaction on keto Sulphoxide. With these keto sulphoxides we turned our attention to the formation of some azalignans via the standard sequential pummerer Diels-alder reaction.The treatment of keto Sulphoxide with acetic unhydried.P-toluene sulphonic acid in presence of dimethyl maleate in refluxing toluenegave the bridged product.

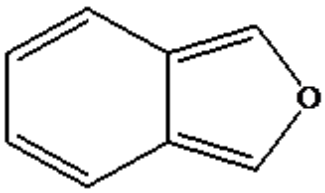
Keywords: Isobenzofuran ,Diels-Alder reaction.

I. INTRODUCTION

Isobenzofuran is a heterocyclic compound consisting of fused benzene and furan rings.Itis isomeric with benzofuran .



Benzofuran



Isobenzofuran

The IUPAC name of isobenzofuran is 2-benzofuran. Science these isobenzofurans and highly reactive and their ability to polymerizes rapidly. They can be prepared by thermolysis by using some suitable precursors and can be trapped at low temperature.Isobenzofurans represented by benzo[c] furan have for a long timeserved as an interesting ciass of reactive intermediates in organic synthesis.As a functional derivative of o-xylylenes. They take part in both inter and intramolecular Diels-Alder reactions leading to a veriety of polycyclic rings

systeams including natural products of biological significance(1).In contrast, heteroanalogues of isobenzofurans have received much less attention ,although this situation is changing in recent years(2,3).Unlike isobenzofurans,heteroisobenzofurans have not found as much as use in the synthesis of natural products.However,the limited work published in the literature is summerisedhere.One of the most interesting application of heteroisobenzofurans is found in a synthesis of the potent anticancer pyridocarbazole alkaloid ellipticine.

II. EXPERIMENTAL DETAILS

2, 4, 6 -Trichlorophenol

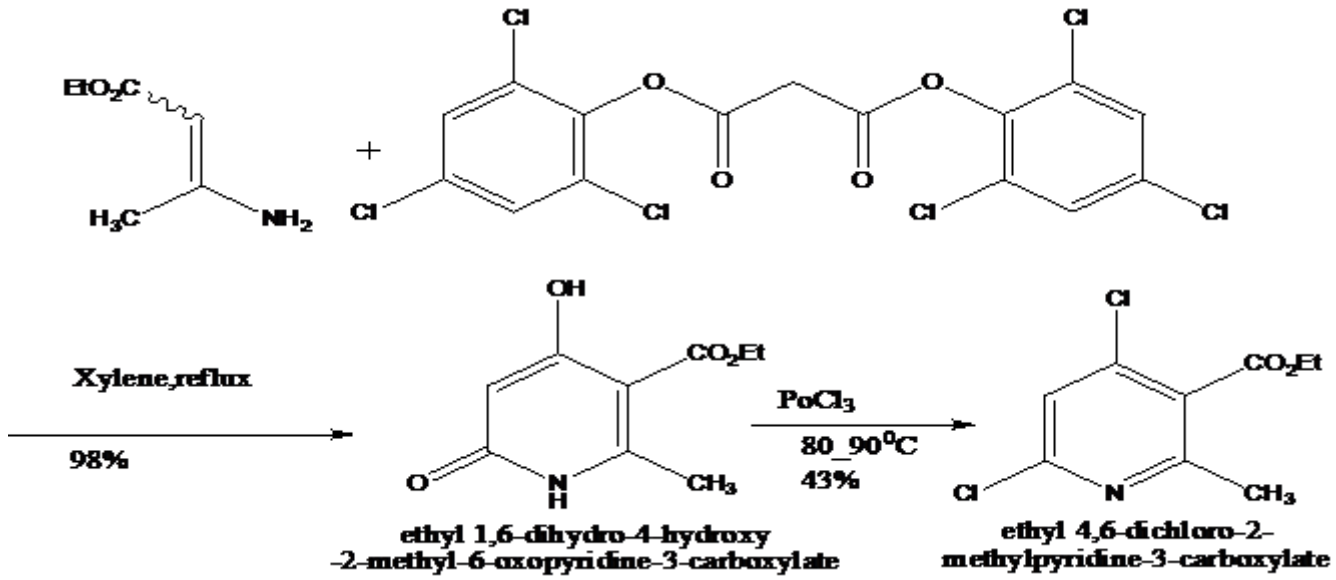
To a vigorously stirred solution of phenol (9.6 g,0.1 mol) in conc. HCl(150 ml) was addede 30% H_2O_2 (40 ml) dropwise at 0^0c over a period of 30 minute. The reaction mixture was heated at 60^0c for 4^{th} during which orange solid was formed. After filtration, washing and drying 19.8 g (98%) of titlecompound was obtained
MP 68^oc (lit[81]71^0c)

Bis 2,4,6-trichlorophenyl malonate[71]

To mixture of molanoic acid (3g.28.84 mmol),2,4, 6 – trichlorophenol (9.11 g 46.14 mmol) was added $POCl_3$ (10 ml) at 0^0c dropwise. Then the reaction mixture was allowed to come to room temperature and heated at 120-130^0c over a period of 6-7 hours. The resulting black solution was poured into ice-cold water slowly and stirred for 5 min. During which a brown precipitate was formed. The precipitate was filtered and repeatedly washed with water (5 times) and then dried in oven for 5h (keeping oven temperature below 800c) to give 8.5 g (63.6%) of the title compound. Bis2, 4, 6 -trichlorophenyl malonate.
M.P. 138-139^0 c

Ethyl 4, 6 – dichloro -2-methyl nicotinate

A stirred solution of 3- aminocrotonate(1.29 g,10 mmol) and bis -2, 4, 6 -trichloro phenyl malonate71 (4.63 g,10 mmol) in xylene (10 ml) was heated at reflux for 7-8 hours. Then the reaction mixture was cooled to room temperature and kept for overnight during which a brown precipitate was formed filtration and washing with benzene 3-4 time to remove any 2, 4, 6-trichlorophenol gave 1.93g of ethyl 4 – hydroxy-2-methyl-6-oxo- 1, 6-dihydropyridine-3- carboxylate,mp 225-228^0c (lit[72] 232^0c) in 98% yield, which was used for next step without further purification.
To the pyridone (1.9 g , 9.6 mmol) was added $POCl_3$(3.67 ml,40 mmol) at 0^0c and then heated on an oil bath keeping bath temperature fixed at 80-90^oc. After 70 hrat that temperature the resulting back solution was cooled to room temperature,pouredinto 50 ml of ice -cold water and extracted with CH_2Cl_2(3-4 times). The combined organic layer was washed with saturated aqueous $NaHCO_3$ solutiondried over anhydrous Na_2SO_4, concentratedand purified by column chromatography to give 980 mg (43% of the title compound. Ethyl 4, 6-dichloro-2-methylnicotinate, as a yellow liquid).



III. CONCLUSION

In conclusion, a synthesis of constrained nicotine analogues 84 a and 90 has been achieved.Furthermore,the importance of electron withdrawing group on the pyridine ring and of the phenylsulfanyl group in the pyridine sidearm has been demonstrated as in the earlier work reported from our laboratory. Although the structure of 84 a is evident from extensive NMR, HRMS dataand transition state analysis,further investigation may be needed to confirm its stereochemistry via preparation of a solid derivative and x-ray crystal structure determination of the latter.

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Synthesis of 5-Arylidene-2, 4-thiazolidinediones by Knoevenagel Condensation Using Tannic Acid as Catalyst

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ABSTRACT

The synthetic work has been carried out by simple Knoevenagel condensation reaction between various substituted aromatic aldehydes and active methylene compound (Thiazolidine-2,4-dione) using tannic acid as an efficient catalyst in ethanol solvent under reflux condition.

Keywords: Tannic Acid; Thiazolidine-2,4-diones; 5-Arylidene-2,4-Thiazolidinediones, Knoevenagel condensation

I. INTRODUCTION

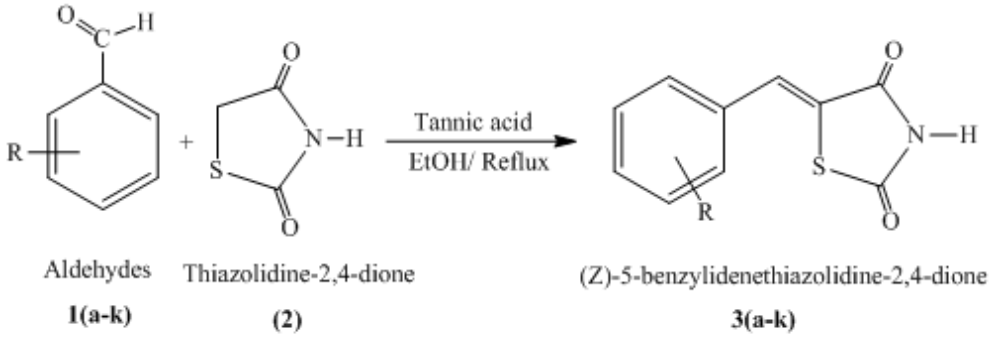
Tannic acid catalyzed Knoevenagel condensation of aromatic aldehydes and active methylene compounds (Thiazolidine-2,4-diones) has been performed. Knoevenagel condensation is multi-components reactions resulting in the formation of new C–C bonds. The reaction is applicable for the synthesis of substituted alkenes, α, β-unsaturated nitriles, esters, acids, dyes and polymers..[1-4]

The condensation of 2,4-thiazolidinediones with aldehydes has been a subject of considerable interest. The products 5-arylidene-2,4-thiazolidinediones are important structural elements in medicinal chemistry and are found to possess significant hypoglycemic,[5] anti-inflammatory,[6] antitumor,[7] antifungal, [8] antidiabetic, [9] and antimicrobial [10]activities.

There are several methods reported in the literature for the synthesis of benzylidenethiazolidine-2, 4-dione derivatives such as, baker's yeast,[11] piperidine in ethanol under reflux conditions [12], piperidinium acetate in DMF under microwave irradiation, [13] grinding with ammonium acetate in the absence of solvents, [14] sodium acetate in acetic acid under microwave irradiation [15] , KAl(SO4)2·12H2O in H2O at 90 C, [16] polyethylene glycol-300 at 100–120°C, [17] L-proline,[18] thiourea,[19] sodium acetate in acetic acid under reflux conditions [20] hydrochloric acid,[21] glycine/solvent free condition under microwave irradiation, [22] (DABCO) in aqueous media, [23] ethylenediamine diacetate, [24] catalyst free/water as green solvent under

microwave irradiation, [25] L-tyrosine/water [26] acidic ionic liquid,[27] calcium hydroxide, [28] tungstic acid, [29].

However, most of the reported methodologies still have certain limitations such as expensive catalysts, toxicity of solvents, restrictions for large scale applications, critical product isolation procedures, difficulty in recovery of high boiling solvents, excessive amounts of catalysts. Thus, the development of a simple and efficient method for the synthesis of 5-arylidene-2,4-thiazolidinediones derivatives would be highly desirable.



Scheme 1. Synthesis of substituted Benzylidenethiazolidine-2,4-dione derivatives.

Scheme 1: Synthesis of substituted Benzylidenethiazolidine-2,4-dione derivatives.

II. RESULTS AND DISCUSSION

During optimization of reaction conditions and solvent, it is obtained that reaction is not taking place at room temperature and not even at 50ºC while at 100ºC in ethanol reaction is faster and completed in less time as compared to other solvents such as water, DMF, DMSO, and mixture of ethanol : water.

Table1: Optimization of different solvents for the synthesis of 3c model product.

Entry	Solvent	Time (Hrs)	Yield (%)
1	EtOH	11	70
2	EtOH:H2O	30	60
3	Water	22	55
4	DMF	20	62
5	DMSO	19	62
6	Solvent less	25	64

Table 2: Tannic acid catalyzed synthesis of 5-arylidiene-2,4-thiazolidinediones derivatives in ethanol

Entry	Product	Aldehyde	Time (Hours)	Yield(%)	M.P (ºC)	M.P Lit. (ºC)
1	3a	C_6H_5-	32	76	237	240-241[26]
2	3b	2-(Cl)C_6H_4-	30	72	208	210-212[29]
3	3c	4-(Cl)C_6H_4-	27	70	110	109[23]
4	3d	3-(NO2)C6H4-	31	74	184	186-188[26]

5	3e	4-(NO2)C6H4-	33	70	180	182-183[26]
6	3f	3-(OH)C_6H_4-	28	68	116	118-120[23]
7	3g	4-(OH)C_6H_4-	20	59	114	111-113[23
8	3h	4-(OCH3)C6H4-	21	61	236	235-237[26]
9	3i	Furan-2-CHO	22	69	238	240-242[29]
10	3j	Thiophene-2-CHO	21	68	223	-
11	3k	Pyridine-3-CHO	25	71	216	-

III. EXPERIMENTAL

All the chemicals used were obtained from commercial suppliers and used without further purification. Progress of the reaction was monitored by thin layer chromatography in ethyl acetate and n-hexane (3:7) mobile phase. Melting points were recorded on open capillary method and were uncorrected.

3.1. General procedure for the synthesis of Benzylidenethiazolidine-2,4-dione derivatives:

A mixture of substituted aromatic aldehydes (1mmol), active methylene compound (Thiazolidine-2,4-dione) (1mmol) and ethanol (10 ml) was stirred at reflux temperature in the presence of tannic acid catalyst for a given specific time. The progress of reaction was monitored by TLC. After completion of reaction the reaction mixture was cooled to room temperature and ice cold water is added to it. The solid product was filtered, washed with cold water and recrystallized from ethanol to obtain pure Benzylidenethiazolidine2,4-dione derivatives.

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Stability Constant of Mixed Ligand Complexes of V(II) Metal with 8-Hydroxyquinoline and L-Amino Acids in 70% Methanol-Water Mixture

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ABSTRACT

The stability constant of vanadium mixed ligand complexes with 8-hydroxyquinoline (L1) and L-amino acids such as L-cystein (L2), L-phenylalanine (L3) etc. have been studied at 0.1 M ionic strength in 70% methanol-water medium. Experimental works have been done through digital pH meter and calculation parts have been done by Bjerrum method. It is observed that metal vanadium ion form a complexes with (L1) 8-hydroxyquinoline and (L2) L-amino acids in 1:1:1 proportion. The values of metal ligand stability constant (log k) during formation of complex were estimate and compare with literature data. The effects of various amino acids bonded to central metal vanadium were studied from estimated data.

Keywords: 8-hydroxyquinoline, L-amino acids, Vanadium, metal ligand stability constant (log k), pH-meter.

I. INTRODUCTION

The stability of complexes means in a most general sense, the complex exist under suitable conditions may be stored for a long period of time. How ever when the formation of complexes in solution is studied, they are having two types of stabilities, thermodynamic stability and kinetic stability [1,2].
Stability constant of mixed ligand alkaline earth metal complexes with metal ion was studied by Banarjee et al [3] many workers study the effect of transition metal on stability of complexes in pH metrically [4, 5] the studies of metal ligand complexes in solution having number of metal ions with ligands carboxylic acids, oximes, phenols etc. would be interesting which through a light on mode of storage and transport of metal ions in biological kingdom [6] metal complexation not only brings reacting molecules together to give activated complexes but also polarized electrons fro the ligands towards the metal [7] Naik et. al [8] carried out pH metric studies on formation constant of complexes of substituted pyrazoles with some lanthanide metal ions and the influence of ionic strength of on complex equilibria in 70% dioxane-water mixture. Altun et al [9] has reported the potentiometric studies on Ni (II), Co (II) and Zn (II) with Schiff base in 60% dioxane-water mixture. Nilesh et. al [10] reported pH metric studies on stability constant of bromophenyl amino and iodophenyl amino substituted isoxazole with lanthanide metal ions in 70% ethanol-water mixture.
In the language of thermodynamics the equilibrium constant of complex formation reaction are the measures of the heat released in the reaction and entropy change during complex formation reaction [11]. The greater

amount of heat evolved in the reaction most stable are the complexes. Secondly the increase in entropy during complex formation reaction, greater is the stability of product of complexes. Here we are mainly concerned with the thermodynamic stability of the complex compound [12-14].

In present article deals with stability constant study of 8-hydroxyquinoline (L_1) and L-amino acid (L_2) with V(II) metal ions in 70% methanol-water mixture.

II. MATERIALS AND METHODS

All chemicals used are of AR grade. The ligands (L_1) and (L_2 were) purchased from Babaji traders Parbhani recrystlise it before use. The stock solutions of the ligands and metal ions were prepared by dissolving required amount of compounds in 70% methanol-water mixture.

General Procedure:

Types of Titrations: (Total volume 25 ml)

i) Free acid $HClO_4$ (0.01M)

ii) Free acid $HClO_4$ (0.01M) + ligands (0.002M)

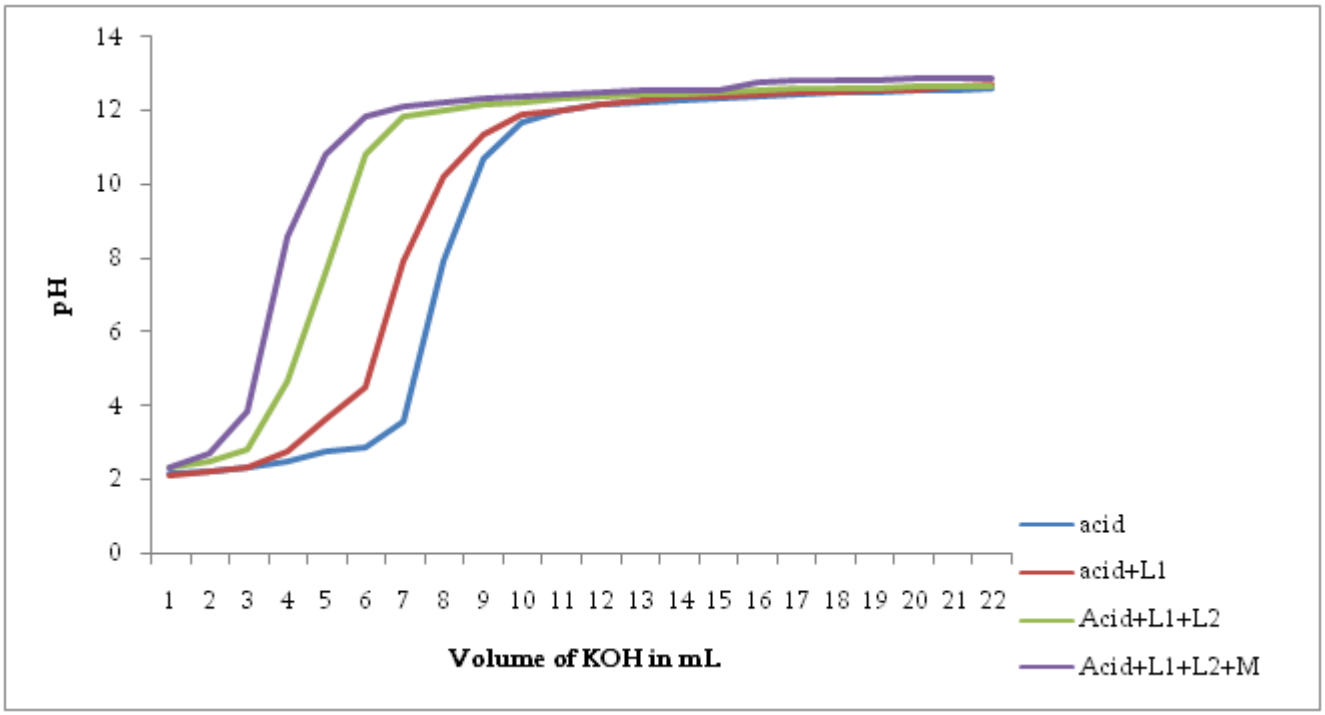
iii) Free acid $HClO_4$ (0.01M) + ligands (0.002M) + Metal ion (0.0004M) against standard 0.1N KOH solution. All the titrations were carried out in 70% metahnol-water mixture and readings were noted down for each 0.5ml addition of KOH. The graph of alkali added against pH values was plotted. The ligands involved in the present work may be considered as a monobasic acid having only one dissociable proton ion from acidic group of amino acids and it can therefore, be represented as HL. The dissociating equilibriua can be shown as.

III. RESULTS AND DISCUSSION

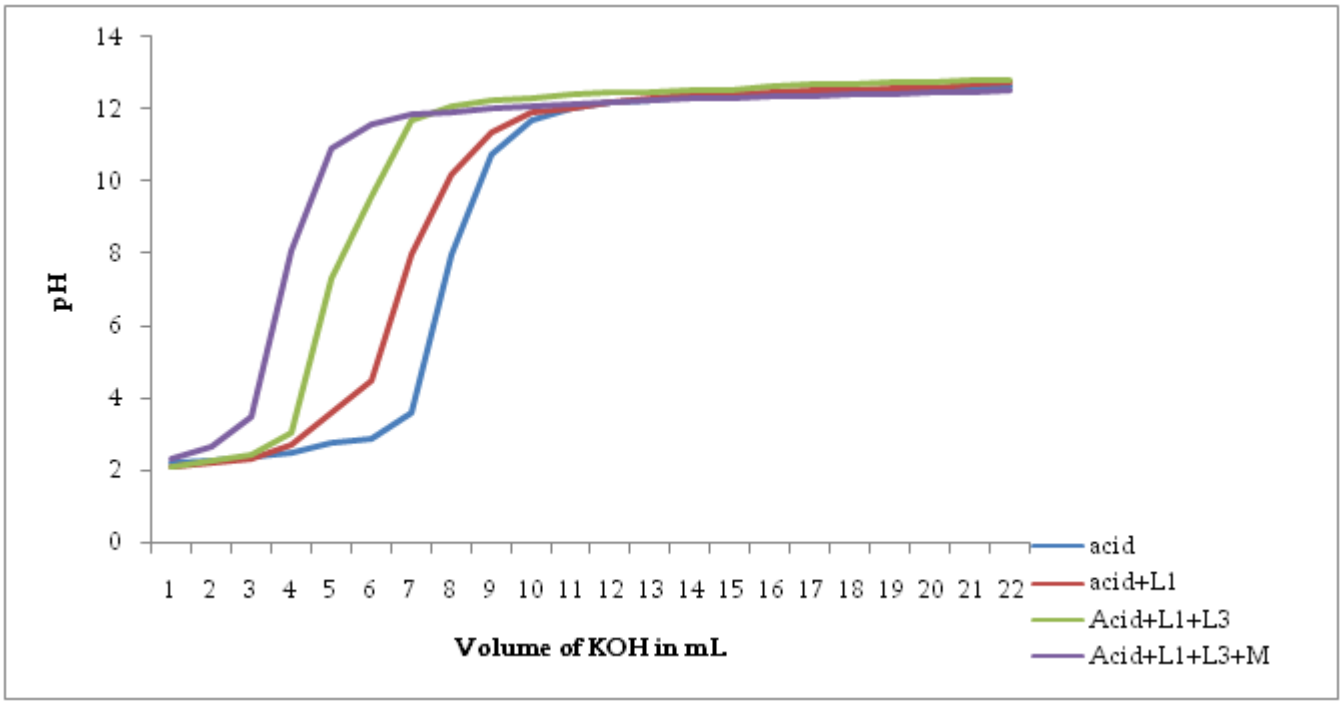
The graphs 1 and 2 indicates acid curve, acid with ligands 8-hydroxyquinoline (L_1) and L-Amino acids (L_2&L_3) curve and acid+ ligands+ metal curves between pH v_s volume of KOH added for L_2 and L_3 Ligands respectively. The titration curves indicate pH values of acid curve is lower than pH values of ligand curve and metal curves at the same volume of KOH added. This is due to the amino acids dose not form cation easily of free acid resulting in the decrease in the H^+ ion concentration. The ligand 8-hydroxyquinoline has only one dissociable proton from –OH group and also in L-amino acids have only one dissociable proton from –OH group of side chain. The proton dissociation constant for HL have been calculated by using following equation.

$HL \longrightarrow H^+ + L^-$ (1)

$$K = \frac{[H^+][L^-]}{[HL]} \quad (2)$$



Graph 1: Acid curve, acid with ligands 8-hydroxyquinoline (L1) and amino acid L-cystein (L2) curve and acid+ ligands (L_1+L_2) + metal curves



Graph 2: Acid curve, acid with ligands 8-hydroxyquinoline (L1) and amino acid L-phenylalanine (L3) curve and acid+ ligands (L1+L3) + metal curves

IV. PROTON-LIGAND STABILITY CONSTANT

The plots between volume of KOH and pH of the solution were used to determine the proton ligand stability constant (representing the replacement of H^+ ions from functional group of ligand with respect to pH value). The horizontal difference (V_2-V_1) was measured accurately between the titration curves of free acid and acid + ligand. It was used to calculate the formation number $\tilde{n}_A$ at various pH values[8].

$$\tilde{n}_A = \gamma - \frac{(V2-V1)\,(N+E^0)}{(V^0+V^1)TL^0} \quad (3)$$

Where, V^0 is the initial volume of the solution. E^0 and TL^0 are initial concentrations of the mineral acid and ligand respectively. V_1 and V_2 are the volumes of alkali of normality N during the acid and ligand titration at given pH. γ is the replaceable proton from the ligand. The data of $\tilde{n}_A$ obtained at various pH along with the horizontal difference for some representative systems are represented in Table 1.

Table-1: Proton ligand Stability constant

Ligand	**System**	pK	
		Half integral method	**Point Wise Method**
L2	L-cystein	2.015	2.136
L3	L-phenylalanine	2.098	3.009

The pK values of ligand was calculated by the algebraic method point wise calculation and also estimated from formation curves by noting pH values of titrations of ligands [12]. The values of L_2 (L-cystein) is lower than L_3 (L-phenylalanine). This difference of pK values is due to the more electronegative –SH group present in L_2 it is decreases the rate of proton displacement than ligand L_3.

V. METAL LIGAND STABILITY CONSTANT

Metal ligand stability constant were determined by the half integer method by plotting graph between ñ vs pH. The experimental values ñ are calculated by using following equation [12].

$$\tilde{N} = \frac{(E^o + N)\,(V3-V2)}{(V^o + V2)\,T^o_m} \quad (4)$$

Where E^o and T^o_m denotes concentration of free acid and concentration of metal ion in reaction mixture, V_2 is the volume of alkali added to reach the same pH reading, V_3 is volume of alkali added in the metal titration to attain the given pH reading, V^o is the initial volume of reaction mixture and N is the concentration of sodium hydroxide solution. The metal ligand stability constant is shown in Table-2 as follow.

Table-2: Metal ligand stability constant at room temp at 0.1 M ionic strength				
System	Metal ligand stability constant			
	Log K1	Log K2	Δ Log K	K1/K2
V(IV) + L_1	4.3205	2.5678	1.7648	1.5428
V (IV)+L_1+L_2	3.1615	2.0262	0.4236	1.0097
V (IV)+L_1+L_3	3.4263	2.2025	1.2758	1.2365

VI. CONCLUSION

The present work is observed that the pH metric curves of vanadium metal ion with 8-hydroxyquinoline (L_1), L-cystein (L_2) and L-phenylalanine (L_3). The curves (A+L_1), (A+L_1+L_2), (A+L_1+L_2+M) and (A+L_1+L_3+M) are started from the pH 1.92 to 2.16. The color of reaction mixture is change from colorless to dark balck in the pH range from 7.25 to 8.85 during titration it indicates complex formation between metal and ligand. The logK_1 and logK_2 values of L_1 And L_1+L_2 with vanadium metal is lower than L_1+L_3 due to in L-cyctein (L_2) has more electronegative -SH group which decrease the activity of ligand to form more stable complex also the difference between logK_1 and logK_2 is greater in (L_1+L_3) system than (L_1+L_2) but less than (L1) it indicates vanadium metal form stable complex with L-phenylalanine amino acid (L_1+L_3) system than L-cystein (L_1+L_2) ligands.

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Green Chemicals from Phyllanthus Emblica and Terminalia Chebula Seed Oils of Vidarbha Region

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ABSTRACT

In recent time, the world has been confronted with an energy crisis due to depletion fossil resources and increased environmental problems. Such situation has led to the increase of research for an alternative energy such as biofuels from sustainably biomass resources. Among various possible options, fuels derived from triglycerides present promising "greener" substitutes for Biofuels. Among biofuels, biodiesel exhibits fuel properties which compatible to those of petroleum-based diesel, and which can be used commercially. The present paper investigates, seed oils such as Awala (Phyllanthus emblica) and Hirda (Terminalia Chebula) found in Vidarbha region of Maharashtra as a potential source for green chemicals such as biodiesel. Biodiesel is an attractive alternative fuel because it is environmentally friendly and can be synthesized from edible and non-edible oils.The seeds had comparable oil contents in the range of 25 to 33 percent indicating good potential for commercial exploitation.Biodiesel has been prepared using a three-step method comprises with saponification of oil, acidification of the soap and esterification of FFA. The final step is esterification that produces fatty acid methyl ester (FAME). The effect of methanol to oil ratio and catalyst content has been investigated for esterification reaction. The biodiesel prepared from Awala and Hirda Seed oils have the properties comparable to the commercial diesel.

Keywords : Biofuel, Triglyceride, Saponification, , Esterification, Fatty Acid Methyl Ester (FAME).

I. INTRODUCTION

In recent times, the world has been confronted with an energy crisis due to depletion fossil resources and increased environmental problems. Such situation has led to the increase of research for an alternative energy such as biofuels from sustainably biomass resources. The scarce and rapidly depleting conventional petroleum resources have promoted research for alternative fuels for combustion engines. Among various possible options, fuels derived from triglycerides (vegetables/oils/animal fats) present promising "greener" substitutes for Biofuels Among biofuels, bio-diesel exhibits fuel properties which compatible to those of petroleum based diesel, and is commercialized for use in existing motor vehicles.

Vegetable oils are becoming a promising alternative to diesel fuel because they are renewable in nature and can be produced locally and environmental friendly as well. India which is abundant in natural resources

could utilize their natural oil resources to become raw material for biodiesel production. Biodiesel is an attractive alternative fuel because it is environmentally friendly and can be synthesized from edible and non-edible oils. Biofuels have become one of the fastest growing markets in the world at 15% growth a year. Many environmental NGO strongly support biofuels as one of many renewable technologies needed to reduce our dependence on hydrocarbons and to avert the worst of climate change. Importance of Biodiesel may be summarized as Environment friendly, clean burning renewable fuel, No engine modification, Increase in engine life, Biodegradable and non-toxic, Easy to handle and store.

The synthesis of biodiesel from edible oils like sunflower oil and from crude non-edible oils like Pongamia pinnata and Jatropha curcas have been studied. Physico-Chemical characteristics and fatty acid composition of Awala and Hirda seed oils have also been studied.This reports on the studies on biofuels from seed oils such as Awala and Hirda seed oils found in the Vidarbha region of Maharashtra.

II. MATERIAL AND METHODS

Seed material

Awala and Hirda seeds were collected from the Nagpur and Amravati region of Vidarbha. The seeds in good condition were cleaned, de-shelled and dried at high temperature of 100-105^{0}C for 35 min. Seeds were grounded using grinder prior to extraction.

Oil Extraction

The seed kernels were ground, using a mechanical grinder, and defatted in a soxhlet apparatus, using hexane (boiling point of 40-60^{0}C). The extracted oil was obtained by filtering the solvent oil contained to get rid of the solid from solvent before the hexane was removed using rotary evaporator apparatus at 40^{0}C. Extracted seed oil was stored in freezer at -2^{0}C for subsequent physico-chemical analysis.

III. ANALYSIS

The seed oils were analyzed for Oil content, Acid value, Iodine value, Saponification value and refractive index by standard methods.

Determination of Fatty Acid Compositions of the Oils

All the seed oils were converted to the respective methyl esters and fatty acid composition of seed oil fatty acids esters was determined using agilent 6890 series gas chromatography (GC) equipped with flame ionization detector and capillary column (30mx0.25mmx0.25mm). About 0.1 ml oil was converted to methyl ester using 1ml NaOMe (1 M) in 1 ml hexane before being injected into the GC. The detector temperature was programmed at 240^{0}C with flow rate 0.8 ml/min. The injector temperature was set at 240^{0}C. Hydrogen was used as the carrier gas. The identification of the peaks was achieved by retention times by means of comparing them with authentic standards analyzed under the same conditions.

IV. PREPARATION OF BIODIESEL FROM SEED OILS

Apparatus :

The apparatus used for transesterification consisted of oil bath, reaction flask with condenser and digital rpm controller mechanical stirrer. The volume of glass reactor capacity was 1 L and consisted of three necks, one for stirrer, and the other for condenser and inlet of reactant. A digital temperature indicator was used to measure the reaction temperature. The batch reactor had an opening value at the bottom for collection of the final product.

Preparation of Biodiesel from seed oils was carried out by the Transesterification process. The displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis except than an alcohol is used instead of water. The process in which an alcohol molecule brakes the triglyceride molecule to fatty acid alkyl esters and glycerol is called as Transesterification. The excess methanol was removed by vacuum distillation. The product was allowed to stand for 24 hrs. Upper (biodiesel) layer was separated from lower layer (glycerin). Biodiesel was washed with water, then heated from 15 min to remove moisture. Catalyst used was 1% KOH (w/v), Temperature 60^0c, Reaction time 3 hrs. and Yield was nearly 92%.

V. RESULTS

Table-1 Physico-Chemical characteristics and fatty acid composition of seed oils

Analysis of oil seeds

Physico-Chemical characteristics	**Awala Seed**	**Hirda Seed**
Oil content in seeds % by wt.	16.7	32.6
Specific Gravity :	0.9221	0.9132
Refractive Index :	1.4870	1.4700
Acid Value	2.3	4.9
Saponification Value:	192.8	201.3
Iodine Value	139.5	107.3
Fatty acid composition (by wt.%)		
Linolenic	8.8	1.1
Linoleic	44.0	23.3
Oleic	28.4	54.8
Stearic	2.1	9.6
Palmitic	3.0	1.4
Myristic	--	1.9

Table-2 Analysis of Biodiesel

Test	**Standard Biodiesel**	**Bio-diesel from AwalaOil**	**Bio-Diesel from HirdaOil**
Viscosity (30^0C)	3.6	4.1	5.6
Specific Gravity (15^0C)	0.85	0.92	0.91

Carbaon Residue (%)	0.15	0.11	0.23
Calorific Value	40-44	44-47	38-40

VI. CONCLUSION

The oil extracts exhibited good physicochemical properties and could be useful as biodiesel feedstock and industrial application. Feedstock costs account for a large percent of the direct biodiesel production costs, including capital cost and return. The way of reducing the biodiesel production costs is to use the less expensive feed stock containing fatty acids such as inedible oils, animal fats, waste food oil and by products of the refining vegetable oils. With no competing food uses, this characteristics turns attention to AWALA and HIRDA, which grows in tropical and subtropical climates across the developing world THEbio-diesel from AWALA oil (Table-2) gave comparable results. The results agreed well on work carried out on vegetable oils

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Opportunities and Challenges of Green Chemistry in Sustainable Development

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ABSTRACT

Chemistry is really very helpful to us as its applications are used worldwide for several purposes. We cannot really imagine a world without chemistry and its applications such as medicines. However, we should now concentrate on green chemistry or sustainable chemistry, which refers to reducing or stopping the damage done to the environment around us. Green chemistry is a philosophy and study of the design of products or substances that will not involve materials harmful to the environment. Hence, green chemistry could include anything from reducing waste to even disposing of waste in the correct manner. Another way to save the environment through sustainable chemistry is to make use of renewable food stocks. All chemical wastes should be disposed of in the best possible manner without causing any damage to the environment and living beings. Green chemistry therefore serves to promote the design and efficient use of environmentally benign chemicals and chemical processes.

Keywords: Green chemistry, designing safer chemicals, sustainable development.

I. INTRODUCTION

Sustainable development is one of the mostfrequently used terms in today's politicaldebate. Our current understanding ofsustainable development as a regulatoryidea was basically defined by the Agenda"Sustainable development is developmentthat meets the needs of the presentwithout compromising the ability of futuregenerations to meet their own needs." Asa consequence, all our individual andpolitical actions should be reflected inthe light of their societal, economicand ecological sustainability. This claimconcerns every field of society, amongthem particularly chemistry and chemistryeducation. Both fields should reflect onhow chemistry and chemistry educationcan contribute to more sustainability inour society, today and in future.

One of chemistry's contributions to meeting the challenge of more sustainability in the development of our society is the promotion of a sustainable chemistry, in research and industrial production. Under the name of green chemistry (or in Europe also sustainable chemistry) a lot of effort has been undertaken to make future chemistry less poisonous and less hazardous. Green chemistry aims at making chemistry more energy

efficient, at reducing waste disposal, and/or producing innovative products with less consumption of naturalresources. Alternative processes and reaction pathways are designed, new materials andproducts are developed contributing to meet our needs today, but with taking more care of the interests of future generations. Modern chemistry education is challenged by both the political aim of a sustainable development of our society in general as well from the call for green chemistry strategies in chemical research and industry in particular. School chemistry education should promote competencies of the young generation to become scientifically literate. This means chemistry education has to contribute to making students capable of actively participating in society. Competencies need to be promoted to allow students to understand and participate in societal debate about applications of chemistry and technology[1].

History of Green Chemistry

In 1990 the Pollution Prevention Act was passed in the United States. This act helped create a modus operandi for dealing with pollution in an original and innovative way. This paved the way to the green chemistry concept. Paul Anastas and John Warner coined the two letter word "green chemistry" and developed the twelve principles. In 2005 RyojiNoyori identified three key development in green chemistry: use of supercritical carbon dioxide as green solvent, aqueous hydrogen peroxide for clean oxidations and the use of hydrogen in asymmetric synthesis[2].

Opportunities for green and sustainable chemistry

Recent innovations in chemistry and advanced materials have created new opportunities throughout the value chain to advance sustainability. These include, for example: revolutionizing energy storage and battery development; creating sustainable building materials; improving the recyclability and biodegradability of a number of products; or turning carbon dioxide (CO_2) and wastes into chemical feedstock's and valuable products.Greener and more sustainable innovation at the interface of chemistry, biology and computer science is particularly promising (UNEP 2019). The SDGs provide a powerful reference and pave the way for advancing the green and sustainable chemistry agenda. A large number of SDGs stand to benefit from the direct contributions of green and sustainable chemistry, including: zero hunger, good health and well-being, clean water and sanitation, affordable and clean energy, sustainable consumption and production, and climate action. By reducing and/or eliminating chemical hazards, associated health and environmental impacts and pollution, green and sustainable chemistry will also contribute to other SDGs, such as decent working conditions, and economic growth, innovation and infrastructure, life below water, and life on land[2].

The challenges to chemists: Designing Safer Chemicals

Sustainable development is now accepted by governments, industry and the public as a necessary goal for achieving societal, economic and environmental objectives. Within this, chemistry has a key role to play in maintaining and improving our quality of life, the competitiveness of the chemical industry and the natural environment. This role for chemistry is not generally recognized by government or the public. In fact chemicals, chemistry and chemists are actually seen by many as causes of the problems. So chemists should be designedchemical products to preserve efficacy of the function while reducing toxicity. Chemists are molecular designers; they design new molecules and new materials. Green Chemists make sure that the things that we make not only do what they're supposed to do, but they do it safely[3].This means that it's not

only important howchemists make something, it's also important that *what* they make isn't harmful. In Chemistry: Function is NOT related to hazard. Making safe, non-toxic products is the goal.

Green Chemistry and Sustainable Development:

The UN defines sustainable development as 'meeting the needs of present without compromising the ability of future generation.' Green chemistry focuses on how to achieve sustainability through science and technology

- To better understand and solve the issue of environmental pollution, many approaches and models have beendeveloped for environmental impact assessments.
- Some of these approaches and models have been successful in predicting impacts for selected chemicals in selected environmental settings.
- These models have joined air and water quality aspects to point and nonpoint sources and have been very useful for the development of emission control and compliance strategies.
- However, some of the approaches and models were aimed primarily at evaluating the quantity of pollutants that could be discharged into the environment with acceptable impact, but failed to focus on pollution prevention.The concept of end-of-pipe approaches to waste managementdecreased, and strategies such as environmentally consciousmanufacturing, eco efficient production or pollutionprevention gained recognition[4].

The Twelve Principles of Green Chemistry

Green Chemistry is commonly presented as a set of twelve principles proposed by Anastas and Warner (1998)[1]. The principles comprise instructions for professional chemists to implement new chemical compound, and new synthesis and technological processes.

Prevention -It is better to prevent waste than to treat or clean up waste after it is formed;

Atom economy -Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product;

Less hazardous chemical syntheses -Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment;

Designing safer chemicals -Chemical products should be designed to preserve efficacy of function while reducing toxicity;

Safer Solvents and Auxiliaries -The use of auxiliarysubstances (e.g., solvents, separation agents, etc.) should bemade unnecessary wherever possible and innocuous whenused;

Design for energy efficiency -The use of auxiliary substances(e.g. solvents, separation agents, etc.) should be madeunnecessary wherever possible and, innocuous when used;

Use of renewable feedstock -Energy requirements should berecognized for their environmental and economic impacts andshould be minimized. Synthetic methods should be conductedat ambient temperature and pressure;

Reduce derivatives -A raw material or feedstock should berenewable rather than depleting wherever technically andeconomically practicable;

Catalysis -Reduce derivatives = Unnecessary derivatization(blocking group, protection/ de protection, temporarymodification) should be avoided whenever possible. Catalyticreagents (as selective as possible) are superior tostoichiometric reagents;

Design for degradation -Chemical products should bedesigned so that at the end of their function they do not persistin the environment and break down into innocuous degradationproducts;

Real time analysis for pollution prevention –Analyticalmethodologies need to be further developed to allow for real-time,in-process monitoring and control prior to the formationof hazardous substances and

Inherently safer chemistry for accident prevention -Substances and the form of a substance used in a chemicalprocess should be chosen to minimize potential for chemicalaccidents, including releases, explosions, and fires.

Progress in Green Chemistry

Over the past decade, green chemistry has convincinglydemonstrated how fundamental scientific methodologies canbe devised and applied to protect human health and theenvironment in an economically beneficial manner.Significant progress has been made in key research areas, such as atom economy, alternative synthetic route for feed stocks and starting materials, bio-catalysis, green solvent, bio sorption, designing safer chemicals, energy and waste management.

Atom Economy (Synthesis of Ibuprofen)

Atom economy is one of the fundamental principles of green chemistry. Atom economy looks at the number of atoms in the reactants that end up in the final product and by- product or waste.

% Atom economy = 100 x (FW of product /FW of reactants)

Alternative Synthetic Route for Feedstock & Starting Materials

Production of dimethyl carbonate (DMC) production DMC is a versatile and environmentally innocuous material for the chemical industry[5]. Owing to its high oxygen content and blending properties, it is used as a component of fuel. Traditional method for the production of DMC This method involves the use of phosgene (COCl2) and methanol (CH3OH) as shown below:

$COCl2 + 2CH3OH \rightarrow CH3OCOOCH3$ (DMC) + 2HCl

Alternative route for the production of DMC

This involves the use of copper chloride (CuCl), methanol (CH3OH), oxygen (O2) and carbon monoxide.

$2CuCl + 2CH3OH + 1/2O2 \rightarrow 2Cu(OCH3)Cl + H2O$

$2Cu(OCH3)Cl + CO \rightarrow 2CuCl + CH3OCOOCH3$

Bio-catalysis

Bioleaching is the extraction of specific metals from their ores through the use of microorganisms such as bacteria. This is much cleaner than the traditional heap leaching using cyanide in the case of gold extraction[6].

Extraction of gold

This can involve numerous ferrous and sulphur oxidizing bacteria, such as Acidithiobacillusferrooxidans andAcidithiobacillusthiooxidans (also referred to as Thiobacillus). For example, bacteria catalyse the breakdown ofthe mineral arsenopyrite (FeAsS) by oxidising the sulphur and metal (in this case arsenic ions)

to higher oxidation states whilst reducing dioxygen by H2 and Fe3+. This allows the soluble products to dissolve[7].

FeAsS(s) → Fe2+(aq) + As3+(aq) + S6+(aq)

This process occurs at the cell membrane of the bacteria. Theelectrons pass into the cells and are used in biochemicalprocesses to produce energy for the bacteria to reduce oxygenmolecules to water. In stage 2, bacteria oxidize Fe2+ to Fe3+(whilst reducing O2).

Fe2+ → Fe3++ e-

They then oxidize the metal to a higher positive oxidation state. With the electrons gained, they reduce Fe3+ to Fe2+ to continue the cycle. The gold is now separated from the ore and in solution[8,9].

Green Solvent

One of the green solvents is supercritical carbon dioxide (scCO2). Supercritical carbon dioxide refers to carbon dioxide that is in a fluid state while also being at or above both its critical temperature and pressure (Tc = 31.3 oC, Pc = 1071 psi (72.9 atm) yielding rather uncommon properties. Supercritical carbon dioxide has been used as a processing solvent in polymer applications such as polymer modification, formation of polymer composites, polymer blending, microcellular foaming, particle production, and polymerization[10].

Reaction of amines with CO2

RNH2 + CO2 RNHCOOH RNH3+ RNHCOORNH2

+ 2H2C (O) CH2RN (CH2CH2OH) 2

H2 C-O-CH2+ CO2 - [COO-CR-C-O-] (polycarbonates)

Bio sorption

Bio sorption is one such important phenomenon, which is based on one of the twelve principles of Green Chemistry, i.e., "Use of renewable resources." It has gathered a great deal of attention in recent years due to a rise in environmental awareness and the consequent severity of legislation regarding the removal of toxic metal ions from wastewaters. In recent years, a number of agricultural materials such as the following have been used to remove toxic metals from wastewater:

Energy

Fossil fuel is dogged with many environmental pollution problems. There is, therefore, a growing need for alternative energy sources to replace fossil fuels. Renewable energy resources that are currently receiving attention include, solar energy, wind energy, hydro energy[1]. Environmentally benign petrol can be obtained by the removal of Pb from petrol; by addition of ethanol produced from biomaterials to the petrol pool; by addition of methyl butyl ether (MTBE) to the petrol pool. MTBE has high octane and by use of electric vehicles powered by fuel cells[11].

II. CONCLUSION

The challenges in resource and environmental sustainability require more efficient and benign scientific technologies for chemical processes and manufacture of products. Green chemistry addresses such challenges by opening a wide and multifaceted research scope thus allowing the invention of novel reactions that can

maximize the desired products and minimize the waste and byproducts, as well as the design of new synthetic schemes that are inherently, environmentally, and ecologically benign. Therefore, combining the principlesof the sustainability concept as broadly promoted by the green chemistry principles with established cost and performance standards will be the continual endeavor for economies for the chemical industry. It is, therefore, essential to direct research and development efforts towards a goal that will constitute a powerful tool for fostering sustainable innovation. Green chemistry alone cannot solve the pressing environmental concerns and impacts to our modern era, but applying the twelve principles of green chemistry into practice will eventually help to pave the way to a world where the grass is greener.

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A Review on Biological Activities of Schiff bases and their Metal Complexes

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ABSTRACT

Metal complexes are plays crucial role in chemical sciences and widely used for industrial applications. They are also exhibit a broad range of biological activities including antifungal, antibacterial, anticancer and anti-inflammatory. Generally metal complexes are synthesized using ligands, here literature survey reveals that Schiff base is one of the bioactive key intermediates used for generation of metal complexes. Schiff bases were synthesized by condensation of amino compound with carbonyl compounds and have displayed several biological activities. Additionally Schiff bases are used for industrial application and exhibit several biological activity. In recent days efforts are directed towards the development of a new chemotherapeutic Schiff bases and their metal complexes.

Keywords: Complex, schiff base, metal, biological activites.

I. INTRODUCTION

The chemistry of the carbon-nitrogen double bond plays a vital role in the progresses of chemical science[1]. Azomethine group (-C=N-) containing compounds typically known as Schiff bases. Schiff bases form a significant class of compounds in medicinal and pharmaceutical chemistry with several biological applications that include antibacterial[2-6], antifungal[3-6], antitumor[7,8] , anticonvulsant[9], anti HIV[10] and anti-inflammatory[11] activities. Another important role of Schiff base structure is in transmination[12].

Conventionally Schiff bases have been prepared by refluxing mixture of the amines and the carbonyl compounds in organic solvent for example, ethanol or methanol[13]. The conventional method has been modified to obtain high yields of the Schiff bases by using aprotic non-polar solvents[14, 15], azotropic removal of water in a Dean-Stark apparatus, trace of acid[16] and or by adding suitable dehydrating agents[17,18].

Schiff bases is one of the bioactive key intermediate and have been studied extensively as a class of ligands[19-21] and are known to coordinate with metal ions through the azomethine nitrogen atom. Schiff base complexes related to synthetic and natural oxygen carriers[22]. Metal complexes make these compounds effective as stereo specific catalysts towards oxidation, reduction, hydrolysis, biological activity and other transformations of organic and inorganic chemistry[23]. Moreover, the incorporation of transition metal into Schiff bases enhances the biological activity of the ligand and decreases the cytotoxic effects of both the metal ion and ligand on the

host[24]. Literature reveals that Schiff bases continue to occupy an important position as ligands in metal coordination chemistry[25, 26] even almost a century since their discovery.

In view of the synthetic and therapeutic utilities of Schiff bases and their metal complexes, now days effort are directed towards the synthesis and biological activities of metal complexes using Schiff bases as ligand.

Biological Importance of Metal Complexes

A large number of metal complexes of Schiff bases have been displayed wide range of biological activities.
Four Platinum(II) Schiff bases complexes containing of salicylaldehyde and 2-furaldehyde with o- and p-phenylenediamineGaballa et al.[27] were reported as antibacterial against E. coli, Bacillus subtilis, P. aeruginosa, Staphylococcus aureus. The activity data show that Platinum(II) complex are more potent antimicrobials than the parent. El-Sherif and Eldebss[28], have been reported 2-Aminomethylthiophenyl-4-bromosalicylaldehyde Schiff base and its metal complexes have been screened for their antimicrobial activities using the disc diffusion method against bacteria, the results of antimicrobial activity show that the metal complexes exhibit antimicrobial properties and they show enhanced inhibitory activity compared to theparent ligand under experimental conditions.

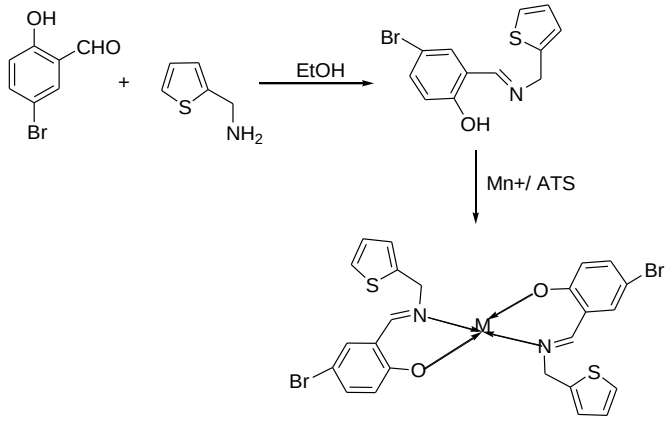

Fig:- 1

Raman et al.[29] Prashanthi et al.[30] have been studied the fungal activity of metal complexes of Cu(II), Ni(II) and Co(II) with Schiff bases of 3-(2-hydroxy-3-ethoxybenzylideneamino)-5-methyl isoxazole and 3-(2-hydroxy-5-nitroben-zylidene amino)-5- methyl isoxazole the compiexes gave better results against growth of fungi. platinum(II) complexes of reduced amino acid Schiff bases as potential anticancer agents and characterized them by 1H NMR, EA, MS, IR, and molar conductivity. These compounds were tested for their DNA interaction with salmon sperm DNA, and their in vitro anticancer activities have been validated against HL-60, KB, BGC-823, and Bel-7402 cell lines by the MTT assay. The cytotoxicity of one complex (5g) is better than that of cisplatin against BGC-823 and HL-60 cell lines, and show close cytotoxic effect against Bel-7402 cell line. Li et al.[31]

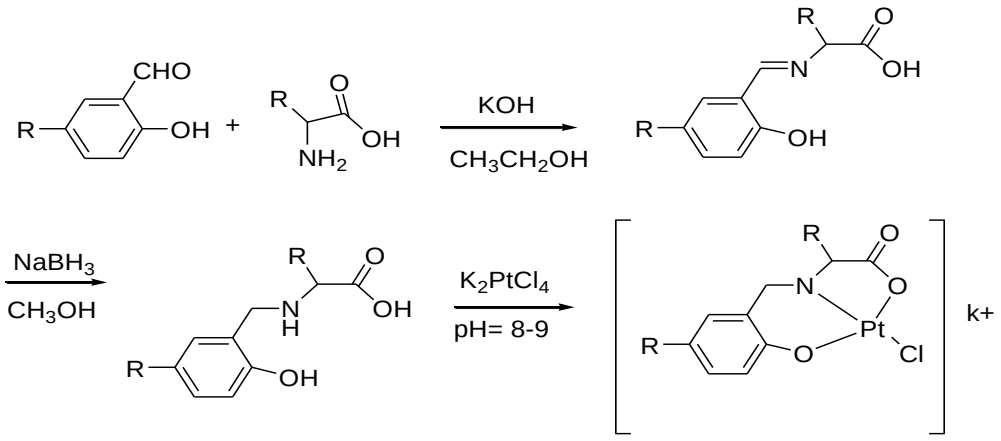

Fig:- 2. In 2014, Nura Suleiman et al.[32] were reported anticancer activities of morpholine Schiff bases and their metal complexes.

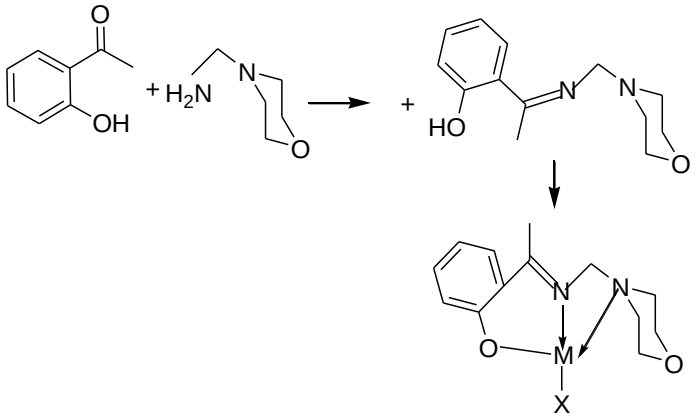

Fig:- 3

In 2010 Nirmal et al.[33] were synthesized A series of novel 3-(4-(benzylideneamino) phenylimino) 4-fluoroindolin-2-one derivatives The title compounds (N_1-N_{10}) were evaluated for analgesic, anti-inflammatory, and ulcerogenic index activities. Results displayed that compound N_3 exhibited significant analgesic activity. Among the title compounds studied, N_2, N_3, and N_8 exhibited significant anti-inflammatory activity comparable to reference standard.Antimicrobial studies of transition metal complexes of N-amino quinolone derivatives has been studied by Redha I. et al.[34]

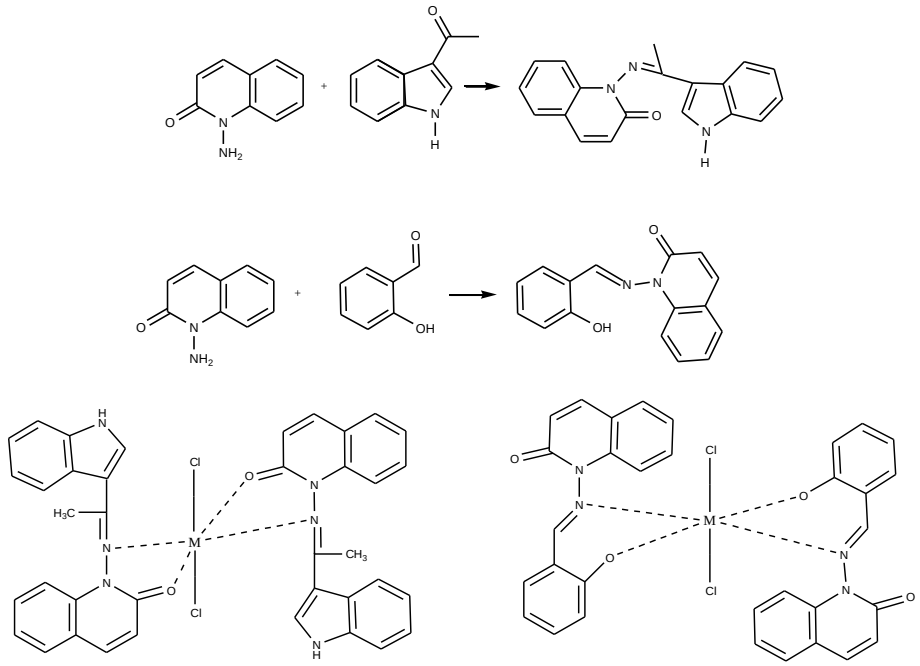

Fig:- 4

A.S. Thakar, H.B. Friedrich and K.T. Joshi[35] were reported novel Schiff bases derived from sulfadoxine and studied their antibacterial activity. The metal complexes had a higher antibacterial activity than the free ligand. Such increased activity of the metal complexes can be explained on the basis of the overtone concept[36] and chelation theory[37].

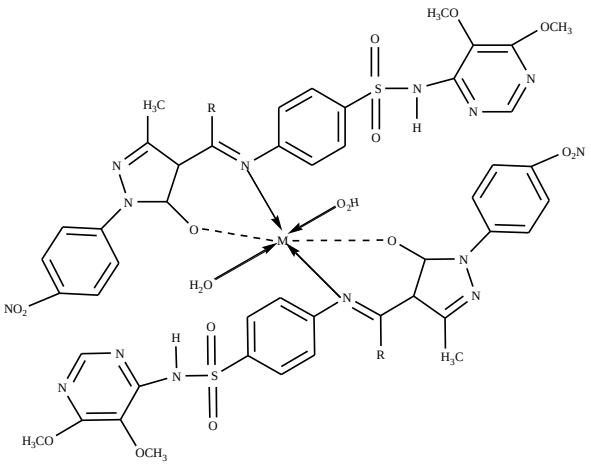

Fig:- 5

In 2014, Abhay Nanda Srivastava, Netra pal Singh and Chandra Kiran Shriwastaw[38] synthesized bioactive binuclear transition metal complexes of a Schiff bases ligand derived from 4-amino-1h-pyrimidine-2-one, diacetyl and glycine and some of the complexes displayed antibacterial and antifungal activities.

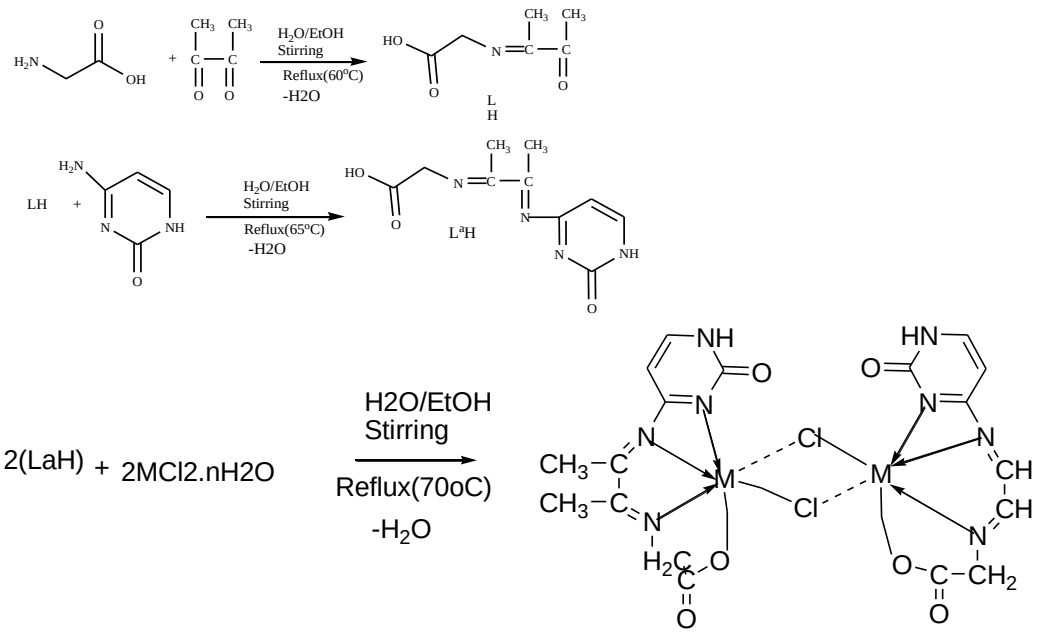

Fig:- 6

EmadYousif, MAhmed Majeed[39] and other co-researches reported metal complexes with antibacterial activity and ondicated that all the complexes obtained showed a moderate activity against the tested bacterial strains and slightly higher activity compared to the ligand.

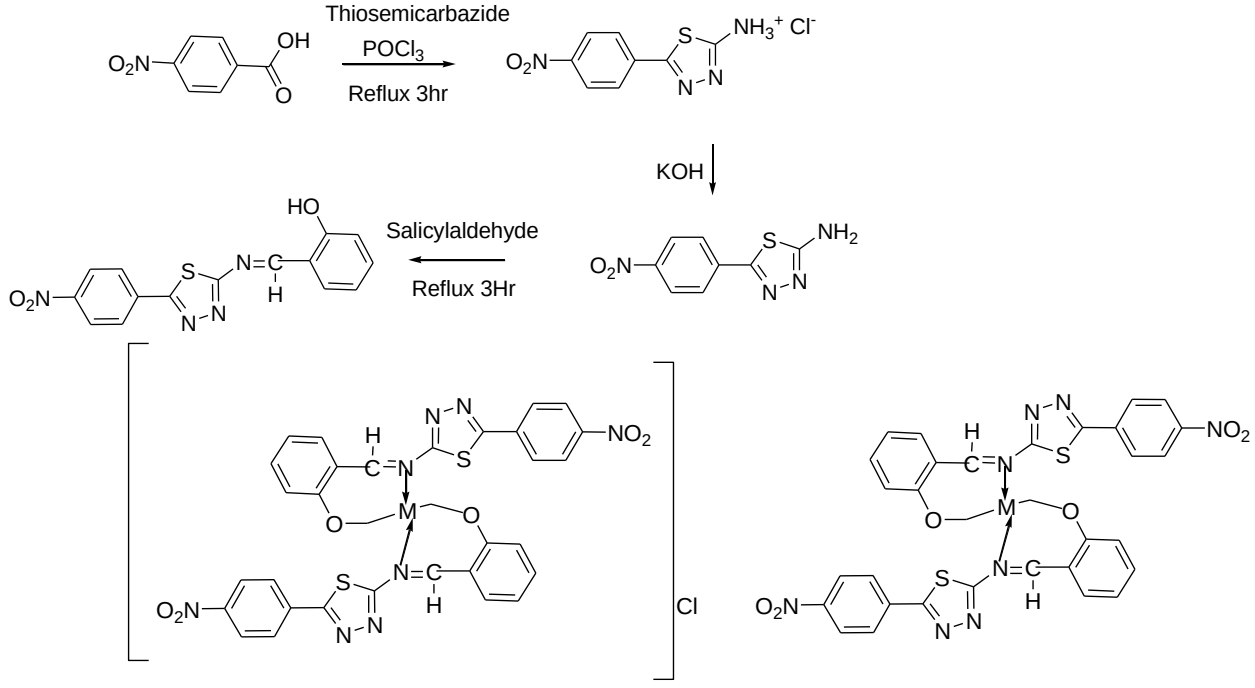

Fig:- 7

K. Babu and P. Amutha[40] reported the new Cu(II) and Ni(II) complexes of Schiff bases[49] showed good antibacterial activity.

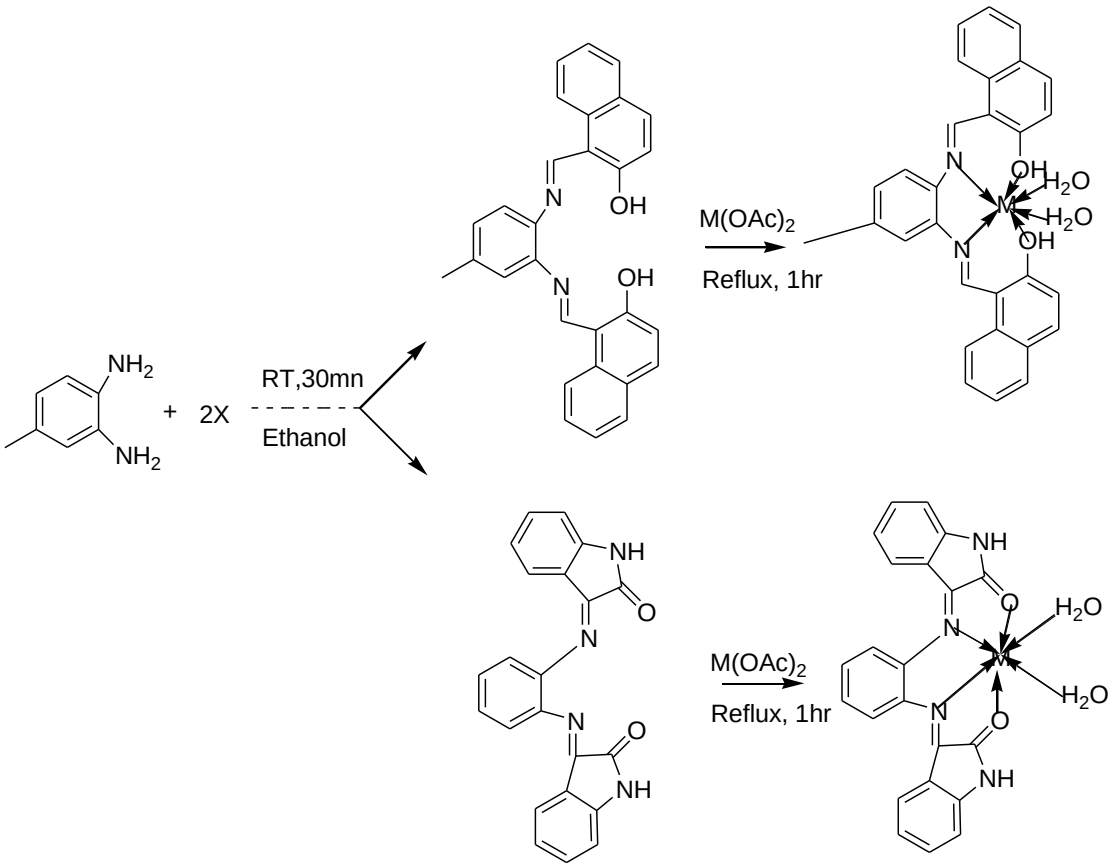

Fig:- 8

Conclusions:

The incorporation of transition metal into Schiff base have been studied extensively as a class of ligand, enhance the biological activities of the ligand and decreases the cytotoxic effects of both the metal ion and ligand on the host. Therefore recently more attention has been directed on the synthesis of metal complexes using bioactive Schiff base.

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Synthesis of 2,4,5-triarylimidazoles Catalyzed by Ni nps/ stilbite Zeolite

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ABSTRACT

Ni nps/stilbite shows promising results in various schemes of organic transformation. In the present research article, 2,4,5-triarylimidazoles are synthesized by refluxing benzil or benzoin, aromatic aldehyde, ammonium acetate and small amount of Ni nps/stilbite stilbite for appropriate time to get expected product. The reaction process was very simple. More yield and reusable catalyst are the benefit of present scheme.

Keywords: Green chemistry, designing safer chemicals, sustainable development.

I. INTRODUCTION

Nitrogen structured imidazole nucleus and there derivatives are found to possess a broad range of biological activities. They are well known as inhibitors of P38MAP kinase [1], fungicides, herbicides [2], anti-inflammatory [3], antithrombotic [4], growth regulators in plant [5] and as a therapeutic agents [6]. In addition, they are used as photosensitive compounds in photography [7]. Some substituted triarylimidazole are selective antagonists of the glucagons receptor [8] and inhibitors of IL-1 biosynthesis [9], also evaluated for cyclooxygenase-2(COX-2) inhibitory activity [10] and α-glocosidase inhibitory activity [11].

In 1882, First synthesis of the imidazole core starting from 1,2-dicarbonyl compounds, aldehydes and ammonia, to obtain 2,4,5-triphenylimidazole proposed by Radziszewski and Jaap [12]. Grimmett and et al proposed the synthesis of the imidazole using nitriles and esters [13]. Literature survey reveals several methods for the synthesis of many substituents for 2,4,5-triarylimidazoles using $ZrCl_4$ [14], zeolites HY/silica gel [15], $NaHSO_3$ [16], sulphanilic acid [17], SiO_2-$NaHSO_4$ [18], iodine [19], ceric ammonium nitrate [20], oxalic acid [21], ionic liquid [22] and also by microwave irradiation using acetic acid [23]. However, many of these procedures suffer from harsh reaction conditions, low yield, difficulties in work-up and relatively expensive reagents. Thus, a simple, general and efficient procedure is still in demand for the synthesis of 2,4,5-triarylimidazole derivatives via multi-component reaction. Moreover, there are relatively limited number of reports on the synthesis of 2,4,5-triarylimidazoles. Consequently, there is scope for work in preparing variations of the substituents in the product, mild conditions and better yields. Herein, we report a simple method for the synthesis of 2,4,5-triarylimidazoles using Ni nps/ stilbite zeolite [24] as a catalyst.

Experimental

All chemicals are purchased from Aldrich, Rankem and s.d. fine chemicals limited and used as received without purification. The melting points of the compounds were taken in an open capillary in a paraffin bath. IR spectra were recorded on a Jasco FTIR-4100 spectrophotometer. ^{1}H NMR spectra were recorded on an 80 MHz FT-NMR spectrometer in $CDCl_3$ as a solvent and chemical shift values are recorded in units δ (ppm) relative to tetramethylsilane (Me_4Si) as an internal standard.

General procedure for synthesis of 2,4,5-triarylimiazole derivatives

A mixture of benzil or benzoin (5 mmol), aromatic aldehyde (5 mmol), ammonium acetate (10 mmol) and Ni nps/ stilbite (1 wt% with respect to initial concentration of reactant) was refluxed in ethanol (15 mL) in a round bottom flask, for the time as mentioned in Table 2. The reaction was monitored by TLC using alumna foil. After completion of reaction, the reaction mixture was poured into crushed ice and the solid product is formed, was filtered and recrystallized from ethanol to obtain pure products.

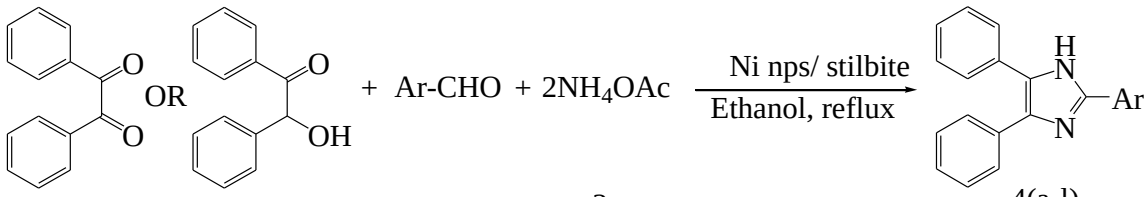
Spectroscopic data

2,4,5-Triphenyl-1*H*-imidazole **(4a).** IR (KBr, cm^{-1}): 3451 (N-H), 3053 (C-H), 1602 (C=C), 1575 (C=N). ^{1}H NMR ($CDCl_3$, 80 MHz,δ,ppm) : 7.16-8.00 (m, 15H, Ph), 9.21 (br s, NH).

EIMS (m/z, %): 297 (M+1).

2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-imidazole **(4c).** IR (KBr, cm^{-1}): 3451 (N-H), 1603 (C=C), 1583 (C=N). ^{1}H NMR ($CDCl_3$,80 MHz,δ,ppm):7.12-7.60 (m, 10H, Ph), 7.36 (d, 2H, J =10 Hz, Ar), 7.82 (d, 2H, J =10 Hz, Ar).

EIMS (m/z, %): 331 (M+1).



1 2(a-l) 3 4(a-l)

Scheme 1

Table 1. Optimization of reaction conditions and wt% of Ni nps/ stilbite for the synthesis of 2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-imidazole.

Solvent	Wt (%) of catalyst	Reaction time (min)	Yield(%)[a]
Water	0.5	30	54
Acetonitrile	0.5	30	72
Acetonirile-water (1:1)	0.5	30	66
Ethanol	0.5	30	93
Ethanol-water (1:1)	0.5	30	81
Ethanol	1	30	97
Ethanol	1.5	30	82

[a]All yield refers to isolated products

Table 2. Synthesis of 2,4,5-triaryl-1*H*-imidazole derivatives using benzil or benzoin, ammonium acetate, aromatic aldehydes, and 1 wt% Ni nps/ stilbite zeolite.

Entry	Ar	Time(min)		Yield (%)[a,b]		M.P. in °C
		Benzil	Benzoin	Benzil	Benzoin	Found
4a	C_6H_5	25	40	97	96	273-275
4b	2-ClC_6H_4	35	45	96	94	195-196
4c	4-ClC_6H_4	20	35	97	97	259-260
4d	4-MeC_6H_4	35	40	93	96	230-231
4e	4-$OMeC_6H_4$	35	35	93	95	228-229
4f	3,4-$(OMe)_2C_6H_3$	30	45	95	92	220-222
4g	4-$NO_2C_6H_4$	25	50	96	95	233-234
4h	4-$N(Me)_2C_6H_4$	20	40	97	95	250-261
4i	4-OHC_6H_4	25	45	95	91	266-267
4k	4-FC_6H_4	30	50	95	92	191-192
4l	2-Furyl	40	45	94	93	198-200

[a]All yield refers to isolated products. [b]-all compounds are known and spectral data matched with authentic data.

Table 3. Reusability of the catalyst for 4c (Table 2).

Entry	Cycle	Yield (%)[a]
1	Fresh	97
2	First	96
3	Second	95
4	Third	95

[a]Yield refers to isolated product.

Results and discussion

Initially, we studied the catalytic efficiency of Ni nps/ stilbite for synthesis of 2-(4-chlorophenyl)-4,5-diphenyl-1*H*-imidazole **(4c)** using 1: 1: 2 ratio of benzil, ammonium acetate and 4-chlorobenzaldehyde in different solvents and various wt% of Ni nps/ stilbite zeolite catalyst with respective to initial concentration of reactant (Scheme 1). The compound **4c** was isolated with 97% yield using optimized reaction condition (Table 1), in ethanol and 1 wt% Ni nps/ stilbite. Using the optimized reaction conditions, a range of 2,4,5-triarylimidazole derivatives were synthesized and results are summarized in Table 2.

The results of above synthetic route are inspiring. In a similar manner a variety of derivatives were synthesized using different substitute of aromatic aldehydes and in each case it is observed that the time period of synthesis was reduced considerably and the yield of the products changed to excellent yields. It is interesting to note that the nature of substituent (o-, m-, p-) on the aromatic ring does not affect on the yield of products. The reactions of various aromatic aldehydes substituent carrying electron-donating or electron-withdrawing groups were also successfully carried out with present method. The solvent play a vital role in the transformation, solvent free reaction is best, but if it needs solvent it should be water, which is universal solvent also, non-toxic, non-inflammable, inexpensive and abundantly available. But use of water in this reaction gave only moderate yield of product (54%). So we studied the effect of different solvents in the synthesis of 2-(4-Chlorophenyl)-4,5-diphenyl-1H-imidazole (4c) and results are summarized in Table 1. Among them ethanol was found to be the most efficient with respect to shorter reaction time and maximum yield of product (97%).

To determine the role of catalyst, the same reaction was carried out in the absence of catalyst, which resulted in very less product formation (36%), after 90 min. These results indicate that catalyst exhibit a high catalytic activity in this transformation due to its larger surface area. The reusability of the catalyst is important for all aspects to decrease the cost of material which is being prepared. Therefore the recovery and reusability of catalyst was examined. The catalyst was separated and reused after washing it with n-hexane and drying at 80^{o}C in the synthesis of 2-(4-chlorophenyl)-4,5-diphenyl-1H-imidazole (4c) and it was found that the catalyst shows good results with four successive reaction (Table 3).

This procedure has offers several advantages i.e. increased variations of substituents in the product with high yields, operational simplicity, minimum environmental effects and above all, the ease in purification of products simply by recrystallization.

Conclusion

In conclusion, we have developed a convenient and efficient protocol for one pot synthesis of 2,4,5-triarylimidazoles by three component coupling reactions of benzil or benzoin, aldehydes and ammonium acetate in the presence of Ni nps/ stilbite zeolite as a catalyst in ethanol solvent. The method is associated with several advantages such as simple experimental procedure, utilisation of heterogeneous catalyst, short reaction times, excellent yields and reusability of the catalyst. We feel the method will find important applications for the synthesis of 2,4,5-triarylimidazoles.

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Application and Synthesis of Nanoparticles use for Acid Based polymers in Polylactic Acid

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ABSTRACT

Social & economic development has driven considerable scientific development & utilization of polymers polylactic acid (PLA) is one of the most promising biopolymer as an important polymeric material for biochemical application its properties as biocompatibility, biodegradability, mechanical strength process ability. Lactic acid (LA) can be obtained by fermentation of sugar derived from renewable resources such as corn and sugarcane PLA is ecofriendly nontoxic polymer with features that permit use in the human body. As a degradable and environmentally friendly polymer, polylactic acid, also known as polylactide, is favored by researchers and has been used a commercial material in various studies. PLA based materials as well, where their use for the synthesis of nanocarriers for the targeted delivery of hydrophilic sugar emerged as new promising application. The purpose of the here presented it aims at providing PLA based materials & their properties, it offers a specific focus on their recent use in nanomedicine, highlighting opportunities & perspectives.

Keywords: Lactic acid, PLA

I. INTRODUCTION

Polylactic acid (PLA), classified as an aliphatic polyester of the ester bonds that connect the monomer units, has gained a key role in the biomedical field for a wide range of application. Suture threads, bone fixation screws, devices for drug delivery, just to scratch the surface. PLA merges several interesting properties that make it an ideal candidate for biomedical application. [1,2]

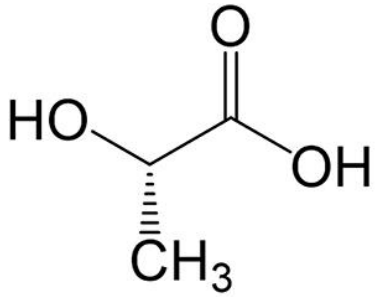
The main phenomena involved in the degradation mechanism and the most important factors that influence hydrolysis rate are currently well-established in scientific literature, consequently degradation kinetics and mechanical properties can be tailored by properly tuning few polymer properties, thus leading to the development of biomedical devices optimized for each specific application. Degradation products are recognized and metabolized by the body itself. This gives PLA an intrinsic biocompatibility that dampens the attainment of critical immune responses. [2,3]

Polylactic acid is a kind of lactic acid derivative produced from renewable resources such as wheat, straw, corn, and sorghum, and it is completely biodegradable [4,5]. It is environment friendly, and can be decomposed in to water and carbon dioxide by microbes, given the problem of global pollution focusing on improving the environment is a win-win situation, thus it is consider the most promising biodegradable polymer material on the market [6,7]. Although lactic acid, the monomer of PLA can be easily obtained in nature, it is traditionally produced by the fermentation of sugar & conversion into monomers after hydrolysis (8) polylactic acid is not easily affected by solvent swelling and dissolution during industrial processing. Temperature is generally 170-230^0 so it is also suitable for extrusion, spinning, biaxial stretching, and injection blow molding processing method. [9,10].

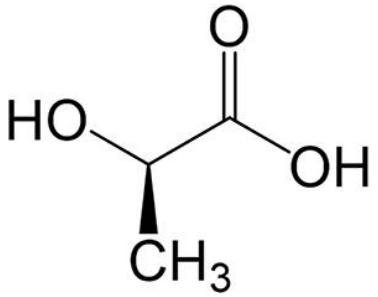
The synthesis of nanomaterials provides a good prospect for the development of nanomedicine. Nanopolymers can be used to encapsulate chemical drugs, proteins, and genetic drug to enhance the circulation of drugs in the human body while reducing the toxic side effects of drugs. Polylactic acid occupies an indispensable position in modern industrial technology. This article focuses on the synthesis & application of modified polylactic acid of the nanoparticles, from the synthetic routes of nano vectors to perspectives and opportunities.

Polylactic acid synthesis and properties

Polylactic acid is a monomer that comprises polylactic acid, and its existence is very common. It plays a vital role in the glycolytic energy cycle in organism, as well as beings an important substance for maintaining the growth and development of living organism. [11,20]. The simplest hydroxy acid, there is an asymmetric carbon atom in the molecule that is optically active, so there are two optical isomers. The L-lactic acid constitutes the main fraction of PLA, and it is produced from renewable source using L-lactic acid bacteria, PLA is highly versatile biodegradable polymer, which can be ideal for processing of different resins into a wide spectrum of products. The optically active L- and D- enantiomers, PLA can be crystallized in three forms (α, β, γ) an optically purity of the lactic acid is critical as small amount of other enantiomeric impurities can severely alter the PLA properties such asa crystallinity or biodegradability.



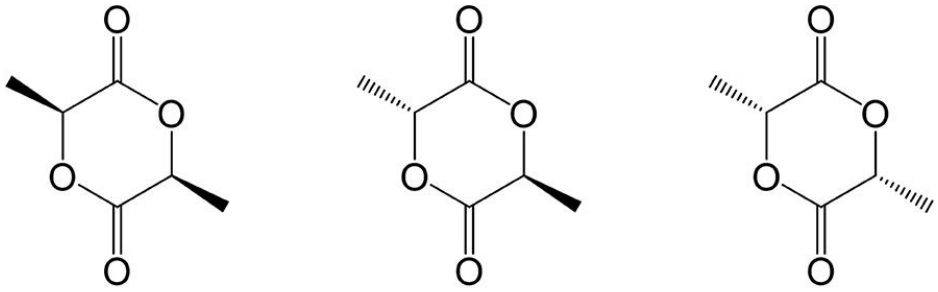
L-(+)-Lactic acid



D-(-)-Lactic acid

Chemical synthesis methods have also been applied for the industrial production of lactic acid these fall into roughly three types:

1. The lactonitrile method is hydrolyzed by sulfuric acid to obtain crude LA added to ethanol for esterification and refined lactic acid is distillation, concentration and decomposition.
2. The acrylonitrile method replacing lactonitrile, hydrolyzed with sulphuric acid. Then hydrolyzed products is reacted with methanol. The crude ester is sent to the distillation tower, and the refined ester is heated and vacuumed to product.
3. The propionic acid method as raw material, crude lactic acid is obtained chlorination and hydrolysis, then products is esterification rectification and hydrolysis only a few manufacturers use this method due to raw material. [12][27] chemical methods are able to achieve large-scale continuous production of LA and U.S. food and drug administration has approved the resulting product, the raw material are generally toxic.



L-lactide meso-lactide D-lactide

PLA Polmer

Since lactic acid is a chiral molecule with D-type and L-type isomers. Three forms of polylactic acid are formed poly-L-lactic acid (PLLA); poly-D-Lactic acid (PDLA) and poly-D, L-Lactic acid (PDLLA) these are optical activity. Three methods for the synthesis of polymer PLA (MW > 10000) 1. Direct condensation polymerization 2. Azeotropic dehydration condensation 3. Lactide ring-opening polymerization.

Direct condensation-polymerization method is low it can directly synthesis polymer PLA part of the cost corresponds to the coupling agent and esterification accelerator used in the synthesis process. The dehydration condensation if hydroxyl and carboxyl groups equimolar concentration on to produce low molecular weight polylactic acid. The azotropic dehydration condensation method avoids the use of adjuvants during the synthesis of PLA the disadvantage of this method is that dibasic acid and glycols are used as solvents in the reaction while the catalyst and diphenyl ether added to the reaction a molecule returned to the container for another 30-40 hour at polymer can then be separated precipitated for further purification.

The ring opening polymerization of lactide is one of the methods for industrial production of high molecular weight PLA lactide has three stereo- configuration L-lactide, mesolactide and D-lactide. It is purifying lactide involve steps such as condensing lactic acid at 115^0- 179^0 removing the condensed water, and removing the mesolactic acid and low molecular polymer through recrystallisation to obtain pure L- or D- lactide with high molecular weight after obtaining highly- purity lactide, depending on the catalyst, the

ring opening polymerization of lactide can adopt one of three mechanism. Cation, anion and coordination. Cationic initiators can generally be divided into protic acid, Lewis's acid and alkylating reagents.

Nanoparticle's synthesis

Polylactic acid-based materials experience a wide success in biomedical field for several reasons. Biocompatibility, low toxicity degradation through hydrolysis and tailored physical & chemical properties through the selection of molecular weight or through copolymerization blending or building more complex molecular architectures and processibility. The natural degradation of PLA based devices due to hydrolysis avoids the need of additional surgery for device removal improving patient core-nano medicine is an emerging field, focused on the development and application of engineered nanomaterials, whose size is 1 to 1000 nm is comparable to many molecules of biologist interest. Such as proteins and viruses like polymer nanoparticles by virtue of their small size, can be internalized by cells and this opens a wide range of new opportunities for the development.

E.g., New carriers for targeted delivery of drugs and vaccines or image contrast agents for diagnostic purpose because the interesting properties of PLA based polymers the most frequently used and promising methods to formulate nanosized particles can be divided into four categories.

Polylactic Based Nanoparticles

Toxicity of polylactic based nanoparticles behavior mainly depends on size, shape, morphology, and surface charge, this holds also for their unwanted side effects. Nanoparticles can provide cytotoxic effects, leading to the disruption of cell membranes or cytosolic components. Typical adverse effects are oxidative stress apoptosis, cytokine activation loss of mitochondrial and lysosomal stability they can also be source of genotoxic effects in addition nanoparticles may include hemolysis or blood coagulation PLA based nanoparticles may provide additional side effects through their degradation products.

There is an additional intrinsic risk of toxic responses when nanoparticles are used and injected in the blood stream. Nanoparticles interact with the components present in the environment through their surface. The driving force leading to the formation of this nano-bio interface are already known in scientific literature and are basically due to electrostatic and vender walls interaction as well as hydrophobic depletion effects.

Conclusion

The information on the properties and application of PLA as well as the different synthetic methods that are currently employed for its production, PLA would be one of the promising candidates for various industrial application. Biodegradable and bio-absorbable polymer synthesized from renewable resource for biomedical device application have attracted much attention of researchers and industry. The excellent biocompatibility, low cost and good material properties of PLA would open many avenues for its use in the medical field while commercial PLA blends have found a packaging industry ad are beings use in the

biomedical industry. The industrial prominence for the production can be produced by fermentation of sucrose sugarcane molasses by product of sugar manufacture and from sugarcane bagasse that is waste available in abundance in India. The use of PLA as cost effective alternative to petrochemical based plastics.

Nanoparticles showed a great potential as nanocarriers to deliver poorly soluble drugs, proteins and genes targeting the tumor and releasing the active compound at the desired rate enhancing in the therapeutic effect. The new perspective introduced by nanoparticles also brings new sources of toxicity connected with cytotoxicity and hemolysis also protein can provide undesired side effects that are not easily predictable the focused on the synthesis and the modification of PLA and remarkable progress has been achieved the last two decades. However vast opportunities as well as challenges remain interns of explaining the characteristics of PLA based materials and expanding their domains of application.

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