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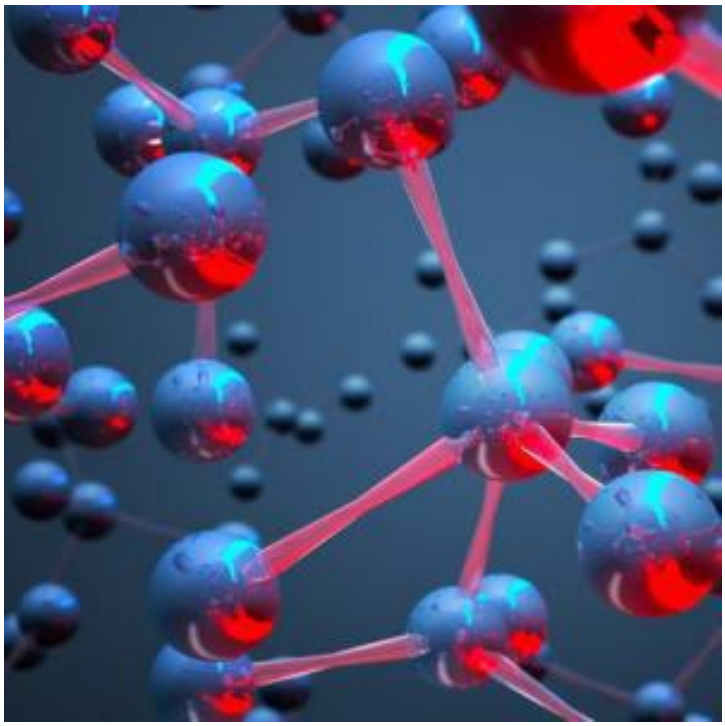
One day International e-Seminar 'Advances in Material Science and Nanotechnology'

(7th January, 2021)



Special Issue - 21 January - 2021

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One day International e- Seminar on 'Advances in Material Science and Nanotechnology'

Special Issue - 21

7th January, 2021

The Managing Editor:

Dr. Chirag M. Patel

(Research Culture Society & Publication)

Jointly Organized By

Department of Physics & Department of Chemistry,
Sir Sayyed College Of Arts, Commerce & Science
Aurangabad (MS) India.

and

Research Culture Society

One day International e- Seminar on 'Advances in Material Science and Nanotechnology'

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College Profile

Sir Sayyed College of Arts, Commerce & Science which runs under the aegis of Rehber Educational, Cultural & Welfare Society is one of the minority institutions in Aurangabad city established in 1990. It is one of the leading institutions engaged in imparting quality education in the stream of Arts, Commerce & Science since three decades. Prof. Mohd. Tilawat Ali is the Founder of Sir Sayed College. The ongoing century is being the century of youth, the college is marching ahead under the able guidance of the dynamic President, RECWS, Dr. Shamama Parveen. She has been leading the institution from the front and we are quite sure that she would take the institution to the appreciable heights. With the modest beginning in 1990, Sir Sayyed College has now evolved as a full-fledged college with many courses.

The college has been constantly striving to add new courses in an endeavor to offer quality education and prepare students to face new challenges of 21st century. The college offer Arts, Commerce & Science at junior and undergraduate level. Postgraduate courses in Arabic, Urdu, English, and Commerce & Organic Chemistry are also available. To meet the changing economic challenges, the college offer three years professional degree courses such as B.B.A & B.C.S.

The college has a long-standing academic tradition and boasts of a team of 34 experienced, well-qualified and dedicated faculty with 13 research guides in English, Commerce, History, Chemistry, Botany and Zoology. 28 teachers are doctorates and 11 teachers have qualified SET / NET Examinations so far. 38 students have stood in the merit list of Dr. BAMU, Aurangabad. Three students received GOLD medals in Arts and Science stream.

About the e-Seminar : Scope and Objectives

Chemical and physical sciences enjoy unique positions in sciences. Chemistry has strong bonding with other disciplines of science such as Physics, Biology, medicine, engineering etc. The progress of research in Physical and chemical sciences has been phenomenal leading to the emergence of many sub disciplines such as material science, solid state physics, surface science, chemical biology and nanotechnology. The seminar is being organized by the dept. of Physics & Chemistry. It aims to bring together the students, academicians, researchers and the scholars in the domain of interest from around the world. It would be an ideal platform for the researchers to present the latest research findings as the seminar focusses on the advances in material science and the nanotechnology.

The seminar covers the following areas:

- Crystal growth and characterization
- Organic synthesis
- Advanced Material processing
- Semiconductor Physics & Devices
- Material synthesis & Processing
- Nanomaterial & Nano bio application
- Analytical Chemistry
- Organometallics
- Environmental Science
- Applied Physical Chemistry

Editorial Committee

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Estimation of Emtricitabine and Tenofovir by HPTLC Method

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ABSTRACT:-

The HPTLC procedure was optimized for simultaneous determination of Emtricitabine and Tenofovir. The mobile phase Methanol: Toluene: Ethyl acetate: Ammonia (1.5:5.5:1.5:0.1 v/v/v/v) resulted in good resolution, and sharp and symmetrical peaks were obtained. It was observed that prewashing of HPTLC plates with methanol (followed by drying and activation) and pre saturation of HPTLC chamber with mobile phase for 20 min (optimum chamber saturation time) ensured good reproducibility and peak shape of three drugs.

KEY WORDS: *Mobile phase, environment-friendly solvents.*

1. INTRODUCTION:

High Performance Thin Layer Chromatography (HPTLC) is a powerful method equally suitable for qualitative and quantitative analytical tasks HPTLC has been reported to provide excellent separation, qualitative and quantitative analysis of a wide range of compounds, such as herbal and botanical dietary supplements, nutraceuticals, traditional western medicines, traditional Chinese medicines and Ayurvedic (Indian) medicines and determination of radio labeled substances in chemical, biochemical, biological, pharmaceutical, and medicinal samples. It includes the ability to analyze crude samples containing multi-components, application of large number of sample and a series of standards using the spray-on technique, choice of solvents for the HPTLC development is wide as the mobile phases are fully evaporated before the detection step, processing of standards and samples identically on the same plate leading to better accuracy and precision of quantification, different and universal selective detection methods, and in situ spectra recording in sequence to obtain positive identification of fractions, storage of total sample on layer without time constrains[1-3].

HPTLC is the most advanced form of modern TLC. It uses HPTLC plates featuring small particles with a narrow size distribution which results in homogenous layers with a smooth surface to be obtained. HPTLC uses smaller plates (10 × 10 or 10 × 20 cm). HPTLC plates provide improved resolution, higher detection sensitivity, and improved *in-situ* quantification and are used for industrial pharmaceutical densitometry quantitative analysis. Normal phase adsorption TLC on silica gel with a less polar mobile phase, such as chloroform– methanol, has been used for more than 90% of reported analysis of pharmaceuticals and drugs[4].Simple and precise HPTLC methods were developed for the simultaneous estimation of two anti-inflammatory drugs (curcuminand galangin). The method was tailored to analyze both drugs in their commercial dosage form (capsules) with no interference from ingredients. Chromatographic separation was performed over precoated TLC plates (60 F254, 20 cm× 10 cm, 250µm thickness, Merck, Darmstadt, Germany) via a linear ascending technique using n-hexane, ethyl acetate, acetic acid, and methanol as the mobile phase. Detection and quantification was achieved at 404 nm through spectrodensitometricanalysis[5].

The selection of mobile phase is based on adsorbent material used as stationary phase and physical and chemical properties of analyte. The mobile-phase systems are used based on their diverse selectivity properties are diethyl ether, methylene chloride, and chloroform combined individually or together with hexane as the strength adjusting solvent for normal-phase TLC and methanol, acetonitrile, and tetrahydrofuran mixed with water for strength adjustment in reversed-phase TLC. Separations byion pairing on C-18 layers are done with a mobile phase such as methanol–0.1 M acetate buffer (pH 3.5) containing 25 mM sodium pentanesulfonate (15.5:4.5).

A new high-performance thin-layer chromatographic (HPTLC) method has been established for determination of minocycline in human plasma. Chromatography was performed on aluminium plates coated with silica gel 60F254; the mobile phase was methanol: acetonitrile : isopropanol: water 5:4:0.5:0.5 (v/v)[6.]

2. RESULT AND DISCUSSION:

Emtricitabine is 4-amino-5-fluoro-1-[(2R,5S)-2-(hydroxymethyl)-1,3-oxathiolan-5-yl]-2-(1*H*)-pyrimidon (Figure I)[7-8]. Emtricitabine is a nucleoside reverse transcriptase inhibitor (NRTI) for the treatment of HIV infection in adults. Emtricitabine is structurally related with Lamivudine. The drug works by inhibiting reverse transcriptase, the enzyme that copies HIV RNA into new viral DNA. Tenofovir is [{(1R)-2-(6-amino-9H-purin-9-yl) -1-methylethoxy}methyl] phosphonic acid (Figure II)[9]. Tenofovirbelongs to a class of antiretroviral drugs known as nucleotide analogue reverse transcriptase inhibitors (nRTIs), which block reversetranscriptase, an enzyme crucial to viral production in HIV-infected people. Literature review revealed that UV[10-14],HPLC[15-23]and HPTLC[19-22]methods have

been reported for analysis of Emtricitabine and Tenofovir as a single form and in combination with other drugs. To date there have been no published reports on simultaneous quantitation of Emtricitabine and Tenofovir by HPTLC in bulk drug and in tablet dosage form. This present study reports for the first time the simultaneous quantitation of Emtricitabine and Tenofovir by HPTLC in bulk drug and in tablet dosage form. The proposed method is validated as per ICH Guidelines[23].

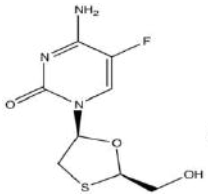

Figure I: Structure of Emtricitabine

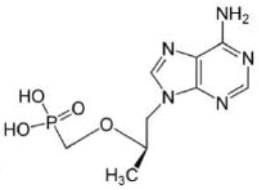

Figure II: Structure of Tenofovir

3. METHOD DEVELOPMENT:

The HPTLC procedure was optimized for simultaneous determination of Emtricitabine and Tenofovir. The mobile phase Methanol: Toluene: Ethyl acetate: Ammonia (1.5:5.5:1.5:0.1 v/v/v/v) resulted in good resolution, and sharp and symmetrical peaks were obtained at Rf 0.29 ± 0.02, 0.41 ± 0.02 for Emtricitabine and Tenofovir respectively. It was observed that prewashing of HPTLC plates with methanol (followed by drying and activation) and pre saturation of HPTLC chamber with mobile phase for 20 min (optimum chamber saturation time) ensured good reproducibility and peak shape of these drugs.

VALIDATION OF THE METHOD:-

LINEARITY-

Linear regression data for the calibration plots revealed good linear relationships between response and concentration over the ranges 320-1120 ng per spot Emtricitabine and 480-1680 ng per spot Tenofovir. Each concentration was applied in triplicate on the HPTLC plate (Table I).

Parameter	Emtricitabine	Tenofovir
Linearity range	320-1120 ng/spot	480-1680 ng/spot
correlation coefficient (r^2)	0.998	0.999
Slope	8.02	2.52
Intercept	178.8	50.14

Table I: Linear regression data for drugs

LOD AND LOQ: -

The LOD & LOQ were determined from slope of the lowest part of the calibration plot.LOD and LOQ of respected drug shown in table (II).

Parameter	Emtricitabine	Tenofovir
LOD	30.24	51.90
LOQ	91.64	157.29

Table II: LOD &LOQ for drugs

PRECISION:

The precision of the method was expressed as relative standard deviation (RSD, %). The results listed in Table (III)reveal the high precision of the method.

Drug	Conc.(ng/band)	Intra day			Inter day		
		*%mean	*SD	*%RSD	*%mean	*SD	*%RSD
Emtricitabine	800	99.90	0.73	0.73	99.96	0.90	0.90
Tenofovir	1200	99.98	0.72	0.72	99.73	0.82	0.82

Table III: Statistical evaluation of precision of developed method (n=3)

*Mean of three determinations, SD: Standard Deviation, R.S.D: Relative Standard Deviation

RECOVERY STUDIES:

When the method was used for extraction and subsequent analysis of these drugs from the pharmaceutical dosage forms and the extract was over applied with 100 and 120% of additional drug. As shown in the Table (IV) good recoveries of the Emtricitabine and Tenofovir in the range from 98.00 to 102.00 % were obtained at various added concentrations. The average recoveries of three levels (nine determinations) were 99.16±0.40 and 99.71±0.20 % for Emtricitabine and Tenofovir respectively.

Drug	Level of % recovery	%mean	*S.D.	*%R.S.D.
Emtricitabine	80%	99.59	0.13	0.13
	100%	99.23	0.32	0.32
	120%	98.68	0.65	0.65
Tenofovir	80%	98.59	0.60	0.60
	100%	99.93	0.24	0.24
	120%	100.63	1.64	1.64

Table IV: Recovery study Data

*Mean of three determinations, SD: Standard Deviation, R.S.D: Relative Standard Deviation

ROBUSTNESS:

The standard deviations of peak areas were calculated for the aforementioned four parameters (variation in composition of the mobile phase, amount of mobile phase, Time from spotting to chromatography, Time from chromatography to scanning) and coefficients of variation were found to be less than 2% in all cases as shown in Table (V).

Parameters	**% RSD for Emtricitabine***	**% RSD for Tenofovir***
Mobile phase composition (± 0.1 ml)	99.05	98.95
Amount of mobile phase (± 1.0 %)	99.08	98.55
Time from spotting to chromatography (5 min)	98.86	99.14
Time from chromatography to scanning(10 min)	98.94	98.90

Table V: Results of Robustness

*Mean of three determinations, R.S.D: Relative Standard Deviation

FORCED DEGRADATION STUDIES:

HPTLC studies of the samples obtained during the stress testing of Emtricitabine and Tenofovir under different conditions. Different degradations peak as shown in figures 2-10.The mass balance is a process of adding together the assay value and the levels of degradation products to see how closely these add up to 100% of initial value with due consideration of the margin of analytical error. The amount of drug recovered after degradation studies and the Rf of the degradation products are given in table (VI).

a) ACID INDUCED DEGRADATION: The drugs were degraded in the acidic condition and shows different degradation products at Rf 0.15, 0.24 for Emtricitabine and 0.14, 0.29, 0.79 for Tenofovir as shows in the fig. III-IV.

b) BASE INDUCED DEGRADATION: The drugs were degraded in the alkaline condition and shows different degradation products at Rf 0.25 for Emtricitabine and 0.02 for Tenofovir as shows in the fig. V-VI.

c) HYDROGEN PEROXIDE INDUCED DEGRADATION: The drugs were degraded in hydrogen peroxide (3%) at room temperature shows different degradation products at Rf 0.57, 0.37 for Emtricitabine and 0.58 for Tenofovir as shows in the fig.VII-VIII.

Stress condition	Drug	Mass balance (%assay of recovered + %impurities + % degradents)	Rf values of degradation Products
Acid hydrolysis (0.1N HCl)	Emtricitabine	99.99	0.15,0.24
	Tenofovir	99.12	0.14,0.29,0.79
Alkali hydrolysis (0.1N NaOH)	Emtricitabine	100.10	0.25
	Tenofovir	98.96	0.02

Oxidation ($3\%H_2O_2$)	Emtricitabine	99.96	0.57
	Tenofovir	100.02	0.37,0.58

Table VI: Results of Forced Degradation studies

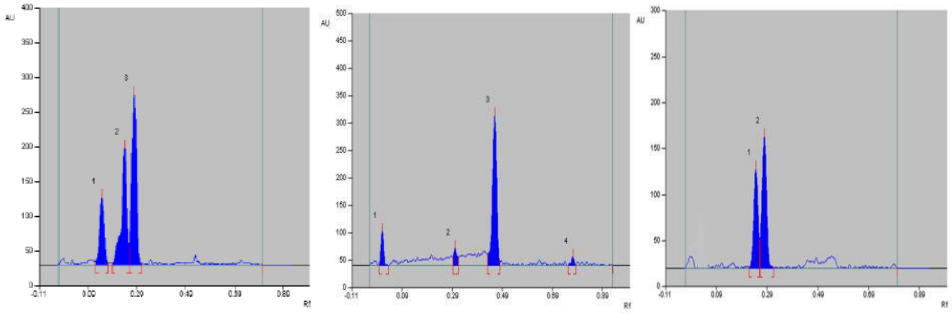

Fig. III: Densitogram of acid hydrolysisFig. IV: Densitogram of acid Fig. V: Densitogram of alkali
Of Emtricitabine hydrolysis of Tenofovirhydrolysis ofEmtricitabine

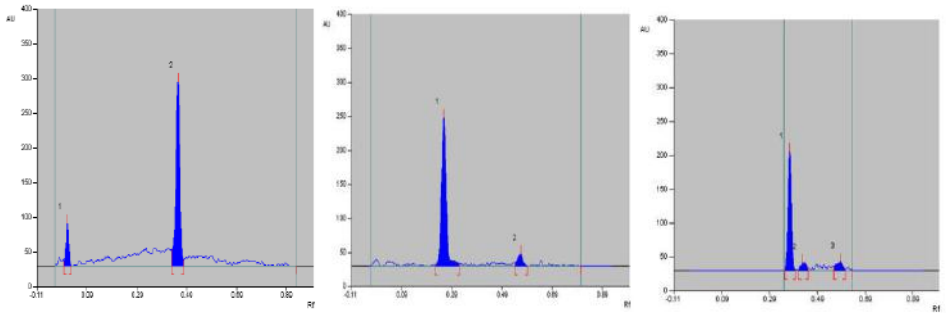

Fig. VI: Densitogram of alkaliFig. VII: Densitogram of oxidative Fig. VIII: Densitogram of oxidative
HydrolysisofTenofovirdegradation of Emtricitabinedegradation of Tenofovir

4. CONCLUSION:-

The proposed method based on the HPTLC was developed and validated as per ICH guidelines. The standard deviation and % RSD calculated for the proposed method is low, indicating high degree of precision of the method. The results of the recovery studies performed show the high degree of accuracy for the proposed method. Hence, it can be concluded that the developed chromatographic method is accurate, precise and selective and can be employed successfully for the estimation of Emtricitabine and Tenofovir in bulk and formulation.

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Microwave Assisted Synthesis of *β*-Amino-ketones in Ionic Liquid

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ABSTRACT:

Microwave irradiation has been used to synthesize β-aminoketones smoothly with low priced and eco-friendly heterogeneous catalyst in solvent free ambient condition Polymer supported ionic liquid medium. A range ofβ-amino-ketones have been obtained in three component tandem reaction between acetophenone or cyclohexanone, Aldehyde, and aniline with a better efficiency (up to 96% yield) within 5 min.

KEYWORDS: *Amino-ketones, Ionic liquid, Mannich, Microwave.*

1. INTRODUCTION:

One of the ultimate goals and challenges in chemistry is to develop the practical synthetic methods for the creation of functionalized molecules and in the journey of this pursuit, development of reusable novel heterogeneous catalysts also has an equally significant to match green chemistry principles in organic synthesis[1, 2].*β*-amino carbonyl compounds from simple and easily available starting materials is one of the such functionalized molecules which unceasingly fascinated to the organic chemists. The Mannich[3-14] type reaction is a classic method for the preparation of *β*-amino carbonyl compounds and therefore a very important carbon-carbon bond-forming reaction in organic synthesis. The versatility and potential to create both functional and structural diversity using this reaction have long stimulated the creativity of chemists[15-17].It has been employed numerous times successfully as a key step in natural product synthesis as well as in medicinal chemistry[18-21].The products of Mannich reaction, *β*-amino carbonyl compound, are synthetic intermediates of huge value. It is widely employed in the organic synthesis of natural compounds, medicine and biologically active compounds[22-26]. Today, it has shown broad applicability in other areas such as pesticides, explosives, dyes and paints. In case of catalyst several perspectives like reusability, sustainability, easy separations are endlessly adding the values in the organic synthesis of natural compounds and to get more and more biologically active products[22, 27] as well. Most Mannich reactions are catalyzed by Lewis acid or Brønsted acid[28-31]. In recent years, the researchers continued to study new synthetic methods and new catalysts including TMG[32], $Sm(OTf)_3$[33], $Fe(HSO_4)_3/SiO_2$[34], triphenylphosphine[35], nano-$Mn(HSO_4)_2$[36], Zeolite[37] were reported. Variety of asymmetric versions of Mannich reaction have been reported[38-43].

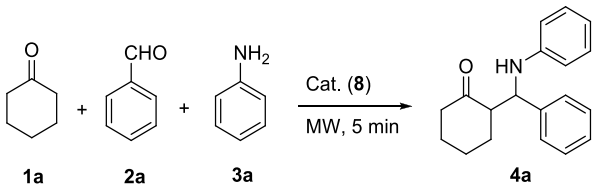
Various amino compounds such as amino ketones, amino aldehydes, amino acids and esters etc. can be obtained in a single step using the three component Mannich reaction. *β*-amino carbonyl compounds exhibit a wide range of biological activities. Particularly *anti*-tubercular[44], *anti*-HIV[45], *anti*-cancer[46], *anti*-fungal[47], *anti*-malarial[48] etc. Also, *β*-amino-ketones are the immediate precursors to the 1, 3-aminoalcohols. Although there are many excellent methods for the preparation of *β*-amino-ketones, most of them suffer from the common drawbacks use of strong acids, metal catalysts, long reaction hours, low diastereoselctivity, non-reusable solvents, poor yields etc. Encouraged by the all this researched literature along with pyridinium supported ionic liquid reagents and catalysts[49-52] and as a part of our continual endeavour to develop new heterogeneous catalyst, our team worked to synthesize metal free polymer supported ionic liquid an outstanding heterogeneous catalyst for the synthesis of *β*-amino carbonyl compounds from simple and easily available starting materials. In this manuscript, we have described an environment friendly, microwave assisted, multicomponent method for the synthesis of *β*-amino-ketones in an ionic liquid medium, as a better alternative.

2. RESULT AND DISCUSSION:

Initially we stirred the cyclohexanone **1a**, benzaldehyde **2a** and the aniline **3a** in ionic liquid (prepared from the polymer supported pyridine, 1,2-oxathiane 2,2-dioxide and the triflic acid) (Scheme 1) at 25 °C, over 10 hours, however, we got 30 % conversion to the corresponding *β*-aminoketone **4a**. Carrying out the same reaction at 50 °C for just 90 min. resulted in the formation of the *β*-aminoketone **4a** in 65% yield. Continuation of the same reaction for next 4 hours could not improve the yield further. The elevation in the reaction temperature from 50 °C to 70 °C could reduce the reaction time from 90 min. to 60 min. but could not improve the yield considerably 68%. Increasing the temperature up to 100 °C resulted in 65% of the product yield. Based upon the obtained results It was concluded that the elevation in temperature could offer the yield up to 68% and reduce the reaction time to from 10 h to 1 h (table 1)

Therefore, we thought to try the same reaction under microwave irradiation. Accordingly when the cyclohexanone 1a, benzaldehyde 2a and aniline 3a were subjected under the microwave irradiation (Samsung microwave 470 W) in the prepared ionic liquid, the reaction was complete within 5 min. (monitored using thin layer

chromatography) and offered 97% of the *β*-aminoketone 4a. Inspired with this result, different ketones (1a-1p) and benzaldehydes (2a-2p) were treated with aniline (3a-3p) to offer the corresponding *β*-aminoketones (4a-4p) in excellent yields (Scheme 2). The results are summarised in table 1.

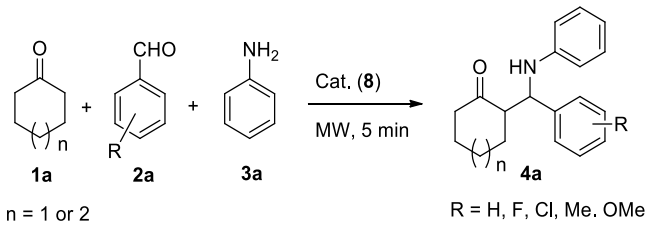


Scheme 1: Screening reaction to optimize reaction conditions.

Table 1. Optimization of the reaction condition under atmospheric heating

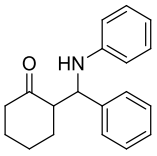
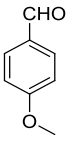
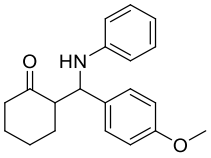
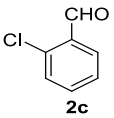
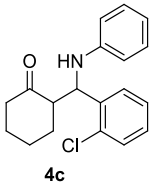
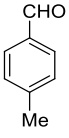
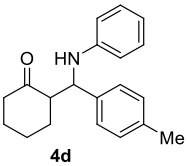
Entry	Temperature °C	Time (h)	Yield[a] (%)
1	25	10	30
2	50	1.5	65
3	70	1	68
4	100	1	65

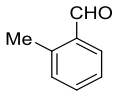
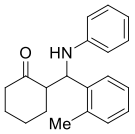
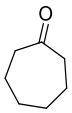
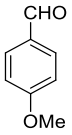
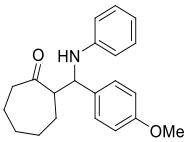
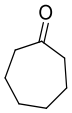
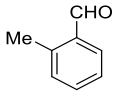
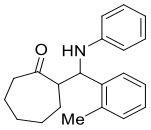
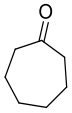
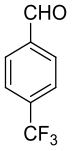
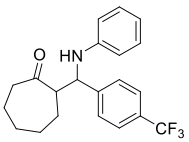
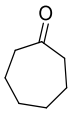
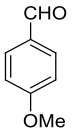
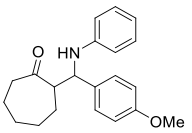
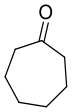
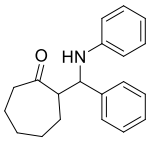
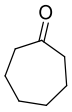
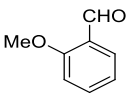
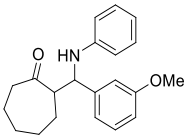
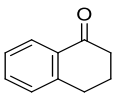
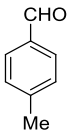
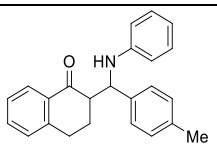
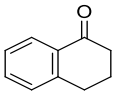
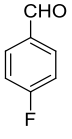
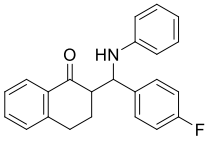
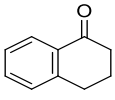
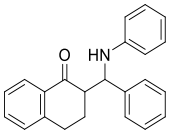
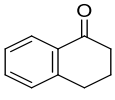
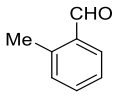
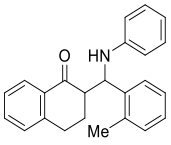
[a]All the products were purified using column chromatography and confirmed with melting point m.p. 118–120[53] °C

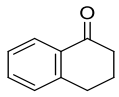
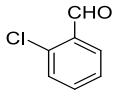
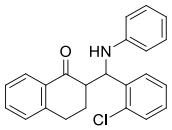


Scheme 2: Polymer supported ionic liquid medium catalysed three-component Mannich-type reactions with different ketones and aldehydes

Table 2. Synthesis of wide-ranging β-amino-ketones

Entry	Reactant 1	Reactant 2	Product	Yield[a] (%)
1	 1a	 2a	 4a	92%
2	 1a	 2b	 4b	96%
3	 1a	 2c	 4c	78%
4	 1a	 2d	 4d	83%

5	 1a	 2e	 4e	77%
6	 1b	 2b	 4f	86%
7	 1b	 2e	 4g	79%
8	 1b	 2f	 4h	88%
9	 1b	 2b	 4i	82%
10	 1b	 2a	 4j	85%
11	 1b	 2g	 4k	79%
12	 1c	 2d	 4l	80%
13	 1c	 2h	 4m	85%
14	 1c	 2a	 4n	82%
15	 1c	 2e	 4o	75%

16	 1c	 2c	 4p	78%

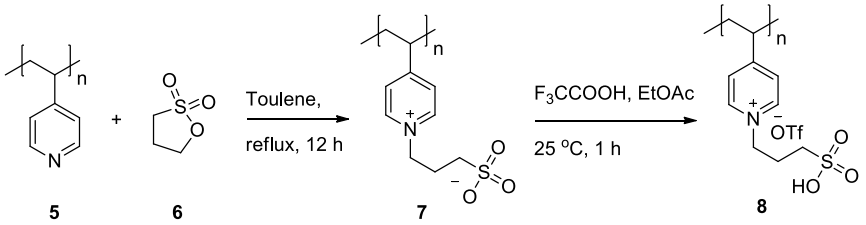
[a]Yields refer to isolated products

Yields obtained in case of use of cyclohexanones (1a-1e) were comparatively better than cycloheptanones (4f-4k) and dihydronaphthanones (4l-4p). All the products with ortho-substituted benzaldehydes resulted in considerable low yields due to the steric and electronic reasons. Whereas in case of benzaldehydes bearing strongly electron withdrawing group offered the best yields up to 96%.

3. EXPERIMENTAL:

All the A. R. grade chemicals used were purchased from sd Fine and Alfa Aesar companies and used without further purification Merck, pre-coated silica gel 60 F254 (Aluminium sheets) plates were used for analytical TLC. Compounds were confirmed by by melting point ^{1}H NMR spectra. Melting points were determined on electrothermal model 9100 apparatus and are uncorrected. ^{1}H NMR spectra were recorded (in $CDCl_3$) on Varian Mercury 300 MHz spectrometer using TMS as an internal standard.

The ionic liquid was prepared in two subsequent steps, (i) refluxing the polymer supported pyridine and 1,2-oxathiolane 2,2-dioxide in toluene for 12 h to obtain the *N*-alkylated intermediate (**7**) (ii) Stirring the obtained intermediate with trifluoroacetic acid in ethylacetate at 25 °C for 1 h.



Scheme 1. *Synthesis of Ionic liquid*

4. CONCLUSION:

A microwave assisted simple and efficient synthetic method has been testified for a variety of *β*-aminoketones by using a non-volatile, non-corrosive, and convenient ionic liquid containing sulfonic acid group as a reaction medium has been reported. This protocol is appropriate to structurally divergent arylaldehydes with ketones to afford corresponding *β*-aminoketones. Use of microwave irradiation offers a tremendous reduction in the reaction time required and increase in the product yield up to 96%

Spectral characterizations of selected synthesized derivatives

^{1}H NMR of (2-((4-methoxyphenylamino)methyl)cyclohexanone) (4b)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ(ppm) = 1.60-1.89 (m, 8h), 2.32-2.41(q, 1H, *j* = 20Hz), 3.76(s, 3H), 4.57-4.60(d, 1H, *j* = 12Hz), 6.50-7.30 (m, 9H).

^{1}H NMR of (2-((phenylamino)(P-Tolyl)methyl)cyclohexanone) (4d):-

^{1}H-NMR ($CDCl_3$, 400 MHz): δ(ppm) = 1.24-1.33 (m, 3H), 1.77-1.92 (m, 5H) 2.31(m, 1H), 2.47(s, 3H) 2.92-2.97(m, 1H, j = 8Hz), 4.47-4.59(d, 1H, j = 8Hz), 5.52(S, 1H), 6.30-7.97(m, 9H)

^{1}H NMR of (2-((4-methoxyphenylamino)methyl)cycloheptanone) (4f):-

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 1.28-1.84 (m, 8H), 2.35-2.84 (m, 3H), 3.76(s, 3H), 4.41-4.45(d, 1H, j = 16Hz), 4.87(s, 1H), 6.50-7.26(m, 9H)

^{1}H NMR of (2-furan-2-yl (phenylamino) methyl) cycloheptanone) (4g):-

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 1.29 -1.90 (m, 8H), 2.42-2.47 (m, 2H), 3.18-3.20 (m, 1H), 4.80-4.83 (d, 1H, *j* = 12Hz), 6.14-7.31(m, 8H)

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) = 24.11, 27.99, 28.41, 28.98, 43.29, 54.05, 55.19, 106.93, 110.19, 113.58, 117.87, 129.09, 141.41, 146.78, 154.20, 214.86.

^{1}H NMR of 2-((phenylamino)(4-trifluoromethyl)Phenyl)methyl)cycloheptanone (4h):-

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 1.26-2.47(m, 10H), 2.93-2.98(t, 1H, *j* = *8Hz*), 4.55-4.58(d, 1H, *j* = 12Hz), 4.69(s, 1H), 6.47-7.57(m, 9H)

^{1}H NMR of (2-(Phenyl(Phenylamino)methyl)cycloheptanone (4j):-

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 1.26-2.49(m,10H), 3.47-3.57(m, 1H), 5.26-5.31(d, 1H, j = 20Hz), 6.45-7.53(m, 2H) 7.00-7.61(m, 8H).

^{1}H NMR of 2-((2-chlorophenyl) (Phenylamino)methyl)cycloheptanone (4m):-

^{1}H-NMR ($CDCl_3$, 400 MHz): δ(ppm) = 1.59-2.42 (m,10H), 3.25-3.32(t, 1H, *j* = 8Hz), 5.86-5.91(d, 1H, j = 20Hz), 6.47-6.56 (m, 2H), 7.03-7.50 (m, 7H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ(ppm) = 24.75, 28.06, 32.63, 42.77, 55.35, 113.29, 117.50, 127.01, 128.18, 128.93, 129.12, 133.27, 139.12, 146.87, 213.14.

^{1}H NMR of 2-((4-Phenoxyphenyl (Phenylamino)methyl)cycloheptanone (4o):-

^{1}H-NMR ($CDCl_3$, 400 MHz): δ(ppm) = 1.26-1.89 (m, 10H), 2.36-2.93 (q, 1H, j = 20.4 Hz), 4.45-4.49(d, 1H, j = 16Hz), 4.80 (s, 1H), 6.53-7.30 (m, 14H)

^{13}C-NMR ($CDCl_3$,100 MHz): δ (ppm) = 24.83, 27.83, 29.03, 42.59, 58.28, 59.96, 113.50, 113.63, 117.44, 117.65, 117.84, 118.56, 122.10, 123.12, 129.02, 129.25, 129.68, 129.83, 143.71, 146.81, 157.16, 215.40

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Study of Ultrasonic Compressibility, Acoustic impedance and Physicochemical Properties of Binary Liquid Mixtures

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ABSTRACT:
Density and ultrasonic study for the binary mixtures of acrylonitrile and 1-4 Dioxane over the entire concentration range were measured at temperatures 303 K. The experimental data then used to calculate the compressibility, and acoustic impedance, molecular free length, Inverse relaxation time and Excess Parameters. The values of excess properties further fitted with Redlich–Kister polynomial equation to estimate the binary coefficients. The resulting excess functions were interpreted in terms of the interactions between the molecules in the binary mixtures. Results confirm that dipole-dipole bonded intermolecular interaction takes place between acrylonitrile and 1-4 Dioxane
KEYWORDS: *Compressibility, Acoustic Impedance Binary mixtures, Ultrasonic velocity, Excess parameters.*

1. INTRODUCTION:

Ultrasonic Study and its analysis for aprotic binary liquid mixtures containing polar- polar components is having significant importance in understanding intermolecular interaction and strength between the component molecules as they finds application in various industrial and technological processes [1]. Ultrasonic velocity and its derived acoustical parameters like adiabatic compressibility, free length, relaxation time, acoustic impedance with their excess parameters, gives important information about the molecular interactions and their strengths[1-10]. In the present paper, variation of various parameters of binary mixtures containing 1-4 Dioxane and acrylonitrile at 2MHz frequency have been studied for entire range of concentration (0-100%). 1-4 Dioxane is a polar molecule of heterocyclic ether family different than that of vinyl group family of acrylonitrile. When it is mixed with acrylonitrile, the dipole-dipole bonded interaction dominates. acrylonitrile is having big size and its double bonded linear aliphatic configuration is the important factor which mainly contributes to the volume expansion of the mixture[11]. 1-4 Dioxane is relatively a complex heterocyclic molecule.. It is highly reactive even if at low temperature. acrylonitrile being polar protic solvent is quite expected to be involved in any Weak interaction with the other components of the mixture [11-26].

2. EXPERIMENTAL:

Chemicals: In the present system of 1-4 Dioxane+ acrylonitrile binary mixture 1-4 Dioxane is used of Analytical Reagent grade and is obtained from MERCK (99.99) and acrylonitrile is of HPLC grade. Both the liquids are used without further purification.

Density Measurement The Density measurements were carried out by portable Digital Density meter (DMA-35, Anton Paar) for pure liquids and binary mixture. This Digital Density meter uses the vibrating U-tube principle to calculate the Density of the sample. The required quantity of sample is approximately 2ml. Accuracy of the instrument used is =0.0001 g/cm^3.

Ultrasonic Velocity Measurements: The ultrasonic Velocity measurements are studied using Ultrasonic Interferometer (Model F-05, Mittal Enterprises, New Delhi).It is single crystal interferometer operating at 2MHz fixed frequency. The sample cell of the instrument is made up of steel and is double walled; the required amount of the sample is approximately 10cc.

3. THEORY:-

The specific acoustic impedance[11] is given by ,

$$Z = U.\rho$$

Where 'U is the ultrasonic velocity (of the mixture) and 'ρ' is the density of the mixture.
The adiabatic compressibility[11] is given by,

$$\beta = 1/(U^2.\rho)$$

Where, 'U' and 'ρ' are the velocity and density of liquid mixture.
The general formula for calculating the excess parameters [1-3] is given below

$$A^E = A_m - (x_1M_1 + (1 - x_1)M_2)$$

Where, A^E is the excess parameter such as excess density x_1 mole fraction.
And the excess parameters are fitted to the Redlich-Kister polynomial equation [8] of third order and this equation is given by

$$A^E = x_1 x_2 \sum_{i=0}^{n} A_i (1 - 2x_2)^i$$

Where x_i is the mole fraction of pure component 1 and 2.

4. RESULT AND DISCUSSION:

Volume fraction of acrylonitrile		0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
Density (g/cm^3)		1.023	1.003	0.983	0.939	0.917	0.89	0.87	0.846	0.828	0.805	0.796
Viscosity (cP)		0.44	0.434	0.418	0.405	0.397	0.389	0.383	0.375	0.369	0.368	0.36
Velocity	(m/s)	1286	1298	1312	1327	1342	1359	1374	1391	1409	1427	1454

Table-1 Density , ultrasonic velocity of acrylonitrile+1-4 Dioxane at 303K

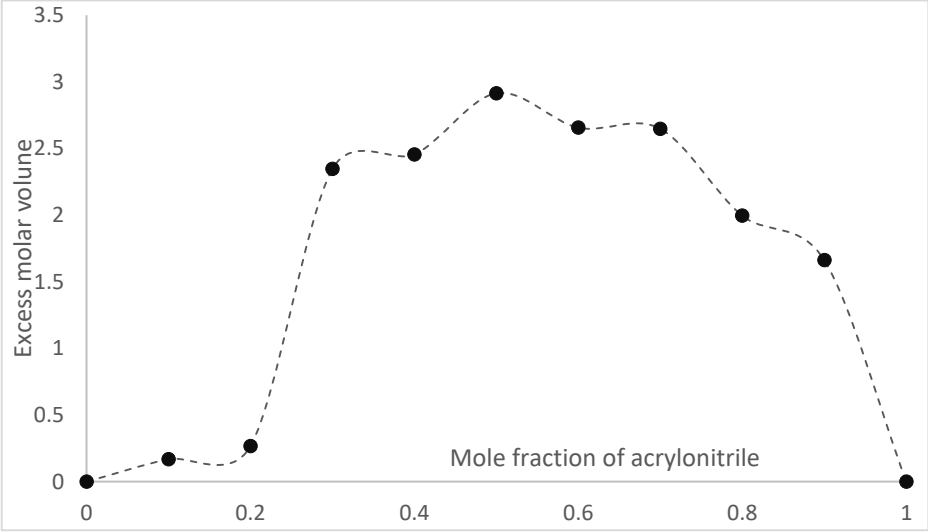

Fig 1- Excess Molar volume of acrylonitrile+1-4 Dioxane

Fig 1 gives excess molar volume of acrylonitrile+1-4 Dioxane. As concentration of acrylonitrile increases excess molar volume becomes positive. Positive values indicate that volume expansion takes place upon mixing due to cross association between dissimilar molecules. Positive values also attributed to weak dipole-dipole bonded interaction between unlike molecules.

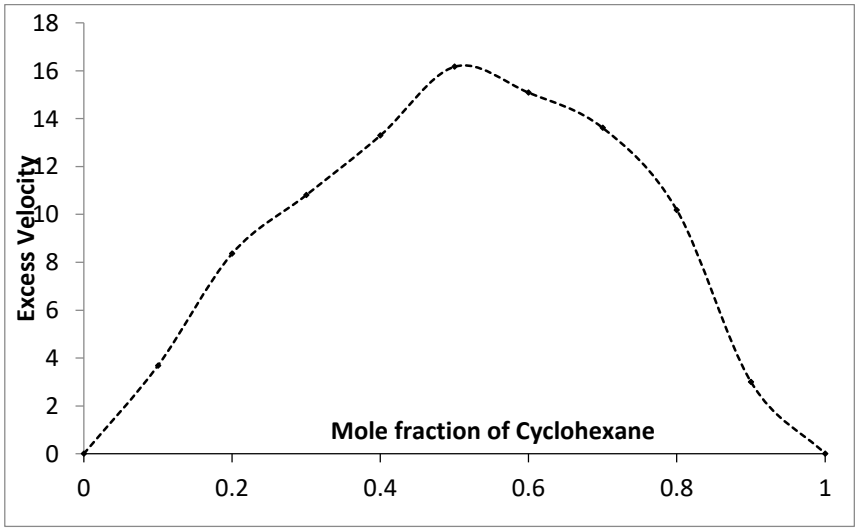

Fig 2- Excess Velocity of acrylonitrile+1-4 Dioxane

As shown in Fig 2 Excess Velocity becomes positive as concentration of acrylonitrile increases. Positive deviation and non linear dependence suggests the presence of Weak interaction between the components of the mixture Positive excess velocity can be concluded as the formation of the structure. Weak interaction arise among the components of the mixture leading to the formation of molecular aggregates and less compact structure then sound will travel faster through the mixture by means of longitudinal waves and hence speed of sound with respect to linear behavior will be positive

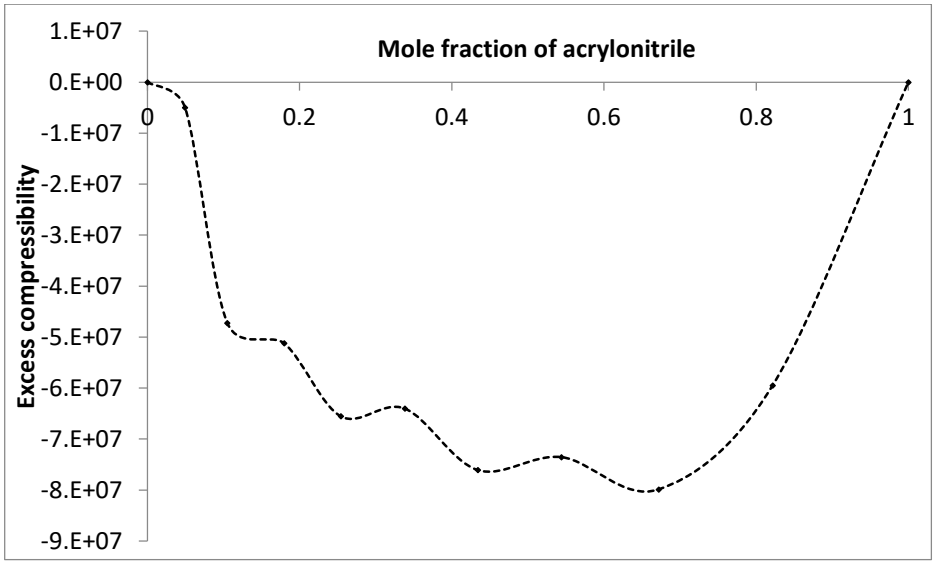

Fig 3- Excess compressibility of acrylonitrile+1-4 Dioxane

Fig 3 indicates Excess compressibility of acrylonitrile+1-4 Dioxane**.** Negative excess compressibility of values are due to less closed packed molecules ,which accounts for the existence of Weak molecular interaction between unlike molecules Sign of compressibility plays vital role in assessing the compactness due to molecular interaction in liquid mixture through dipole-dipole bonded interactions, leading to less compact structure making negative excess compressibility.

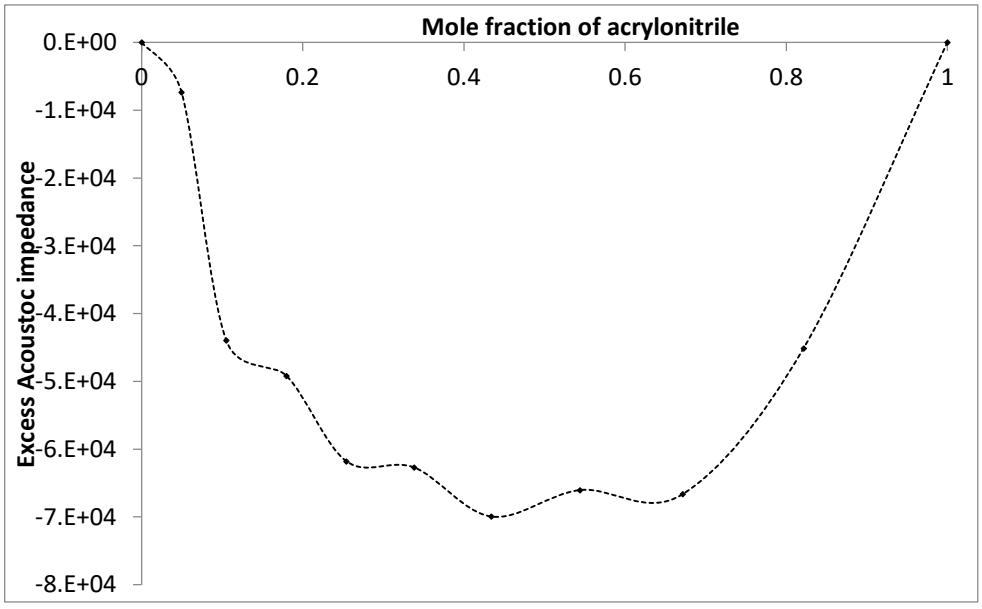

Fig 4- Excess acoustic impedance of acrylonitrile+1-4 Dioxane

Negative values of acoustic impudence as shown in fig 4 hint to the possibility of presence of Weak attractive forces between the reacting components of the mixture. Negative deviation also suggests that acrylonitrile molecules does not cooperate with 1-4 Dioxane molecules hence Weak intermolecular interactions occurs between them.

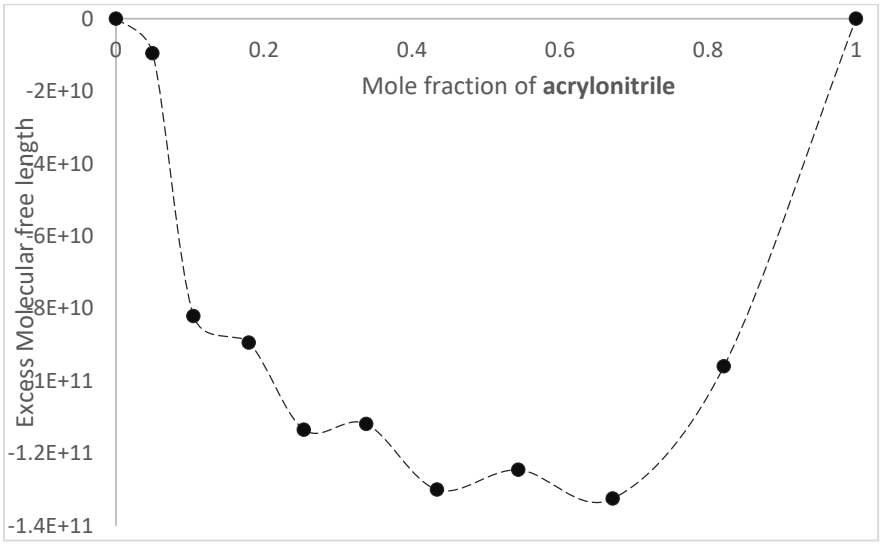

Fig 5- Excess molecular free length of acrylonitrile+1-4 Dioxane

Neagative values exhibit Weak interaction. Increase in values of free length with concentration can be concluded, as there is significant interaction between two liquids. Negative values also suggests that As acrylonitrile molecules are mixed with 1-4 Dioxane molecules their intermolecular distance increases and gives rise to dipole-dipole bonded interaction between them.

5. CONCLUSION:-

In this work, the measurement of density, ultrasonic velocity and other acoustical parameters of acrylonitrile in 1-4 Dioxane solution was studied in different concentrations at 303 K. Postive excess molar volume V_m^E values indicate the presence of Weak dipole-dipole bonded interactions. It has been observed that the excess velocity values become more positive with rise in concentration of acrylonitrile. The experimental ultrasonic velocity data and other acoustical parameters contain valuable information regarding the solute-solvent interactions in the measurements, it can be concluded that the concentration of the acrylonitrile affects and gives rise to Weak dipole-dipole bonded interaction. Our volumetric and ultrasonic study suggest that acrylonitrile acts as structure breaker Increase in concentration of acrylonitrile plays an important role in forming dipole-dipole bonded interactions in the solutions.

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Application of Nanoparticles in Water Treatment as Adsorbent for Effective Removal of Heavy Metal from Aqueous Solution

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ABSTRACT:

Developments in nano science inspires resolving several current problems associated with water quality using nanoparticles as adsorbents from subsequent growth of nanotechnology. The nanotechnology helps to decrease the concentration of harmful toxic compounds to tolerable level. The current work involves study of removal of Cd ions from aqueous solutions using Copper oxide nanoparticles as adsorbent. Removal of Cd ions were carried using different concentrations of adsorbent. Spectrophotometric method was used for removal of Cd ions on surfaces. Batch adsorption studies were performed as a function of contact time, initial heavy metal concentration and pH. The Cd metal ion sorption well fitted to Langmuir isotherm model.

KEYWORDS: *Copper oxide nanoparticles, adsorption, water.*

1. INTRODUCTION:

Water is the most vital compound for any living organism. In 21st century, clean and sufficient water supply is the major challenge. From many years, the development of industrial growth demands water. Contamination of water resources via hazardous materials such as heavy metals and pesticides represents a seriousglobal threat to the surrounding environment affecting allliving creatures[1]. Water pollution is extremely important in recent years due to the release of wastewater having organic and inorganic pollutants.

Water pollution is severe concern among all environmental issues since water is the key of life and enormously vital for the existence of all living organisms[2]. Different pollutants are released to wastewater with the rapid industrialization of human society, including heavy metal ions, organics, bacteria, viruses, and so on, which are serious harmful to human health[3]. Heavy metals are one of the prominent hazardous contaminants generate harmful health effects on all human beings. The various industrial activities enforced to discharge heavy metals into the environment. Heavy metals removal from water resources is very substantial and critical task for clean environment. Major concern is the effective removal of heavy metals from water worldwide today[4].

Numerous traditional methods like precipitation, ultra-filtration, electrode-depo-sition, reverse osmosis, electrochemical treatments, mem-brane filtration, evaporation, flotation, oxidation–reduction, and biosorption for elimination of heavy metal from aqueous solution[5]. These methods are generally insufficient because of cost and less effectiveness for minimum concentrations of heavy metals.However, these methods require high consumption of reagents with low selectivity and generation of secondarypollutants[6]. Adsorption is most commonly method used for heavy metals removal from water[7].

Adsorption is proficient, conventional, and cheap method for the removal, recovery, and being reprocess of harmful heavy metals from any wastewater. Therefore, the adsorption is considered as one of the most appropriate technique for elimination of heavy metals from any wastewater or water sources[8].

Recently, the innovative development of nanoscience and nanotechnology has shown significant potential for the remediation of environmental concerns[9]. The high surface area to mass ratio, high surface reactivity and unique catalytic activity are the most important. Unique surface properties of a nanomaterial led to increased efficiency as an adsorbent compare to macro sized of the material [10].

The nano-sized metal oxides like titanium oxides, ferric oxides, aluminium oxides, magnesium oxides, zinc oxide, and copper oxides[11] are favourable nanoadsorbents for elimination of heavy metals from any aqueous system. The most important factors are the shape and size of metal oxides nanoadsorbents with respect to their efficiency in adsorption. In current work, systematic study of removal of Cd ions from aqueous system were carried out by adsorption process with help of copper oxide nanoparticles sized 80 nm.

2. EXPERIMENTAL:

Materials:

The 99.9% pure form of copper oxide nanoparticles (CON) of desired size (80 nm) available directly from the manufacturer company MK Nano Sales of MK Impex Corp. Canada. This nano adsorbent used during the experimental work. The Cd metal ion solution like a model pollutant from industries was prepared in doubly distilled water using cadmium sulphate. The prepared solutions were standardized as per literature [12].

Method:

The batch adsorption experiments studied for Cd metal for different parameters like pH, initial concentration of metal ions, amount of adsorbent dose, contact time and temperature. Fixed amount of adsorbent and adsorbate was taken in 250 ml beaker and mixed by mechanical shaker at 150 rpm at pre-set time intervals. Using Whatman No.42 filter paper theseparation and decantation of adsorbate was done andthe supernatant solution was used for analysing Ni metal cations concentration spectrophotometrically (shimatzu-1211) at its respective wavelength i.e. λmax (420 nm). The adsorption capacity of CON in the experiments were analysed for different experimental parameters.

3. RESULT AND DISCUSSION:

Effect of pH:

The adsorption of Cd onto CON suggeststhe electrostatic attraction particularly at a relatively low pH. As the pH value increases from 3 to 11decrease in adsorption was observed as in figure (1). This may because of the competition of hydroxyl ions for the adsorbent sites and change in surface charge of the nano adsorbent that leads to electrostatic repulsion between CON nano adsorbent and metal ions and release of already adsorbed ions[13].

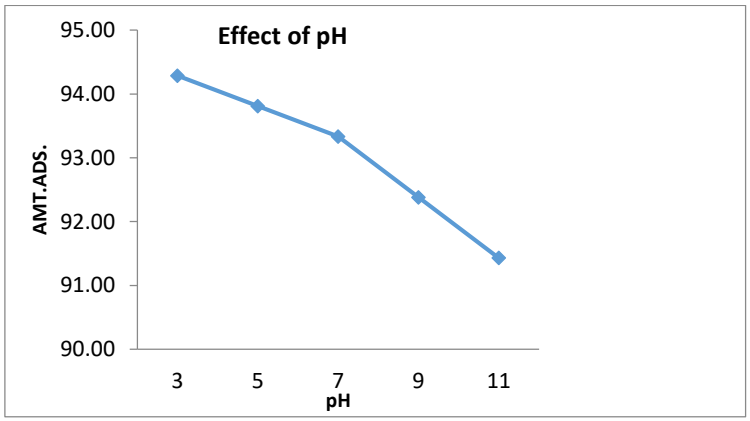

Figure (1): Effect of pH

Effect of initial concentration of metal ions:

With the increase in the initial metal ion concentration, the percentage removal of Cd metal ions decreases as shown in figure (2). When initial concentration of metal ion solution was low, comparatively high surface area adsorption, sites were available and the Cd metal ions were easily adsorbed.

At higher initial concentration of Cd metal ion, the total empty adsorption sites are limited; therefore decrease in percentage removal of Cd metal ions observed. The reason was repulsive forces present between bulk phase solute and adsorbed molecules of solute on the surface which makes difficult to occupy Cd metal ions with remaining vacant sites[14].

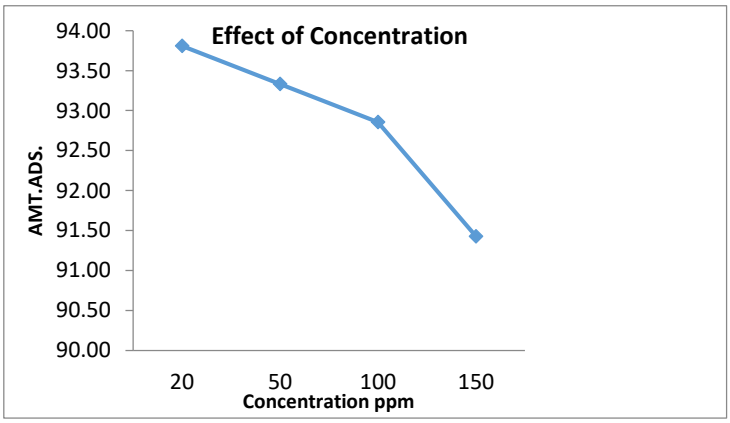

Figure (2): Effect of concentration of metal ion

Effect of adsorbent dose:

With the increase in adsorbent dose, the decrease in removal of Cd metal ion as in figure (3). Increase in dose of adsorbent the adsorption sites remainsunsaturated which decreases unit adsorption during the adsorption process [15].

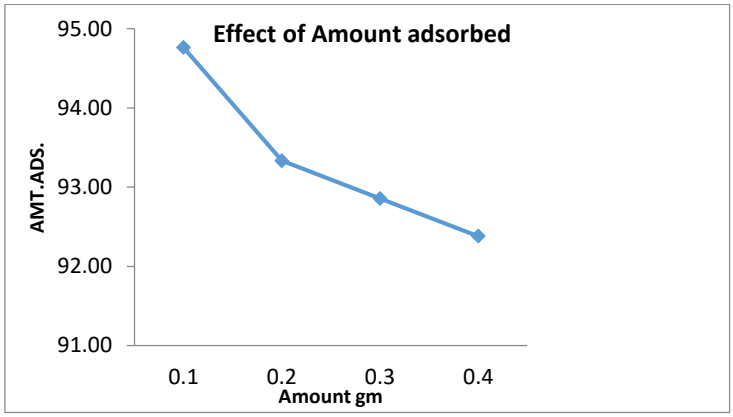

Figure (3): Effect of amount of adsorbent

Effect of time:

As shown in figure (4) initially adsorption of Cd gently increases because initially large number of available sites were occupied by the metal ions eventually decreases removal efficiency of adsorbent to attain equilibrium after gradual decrease in adsorption.

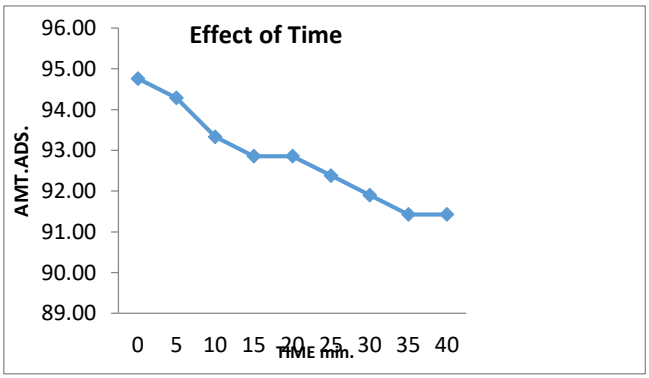

Figure (4): Effect of time

Effect of temperature:

As seen in the figure (5), the amount of Cd adsorbed increases as the temperature increased. This increase suggests that the adsorption was endothermic process. The steady increase in the Cd metal ions adsorption with rise in temperature may because of increase in mobile movement of metal ions, which subsequently increases the number of ions interacting with active sites of the surface of nano adsorbent. Such type of trend also found by other researchers.[16]

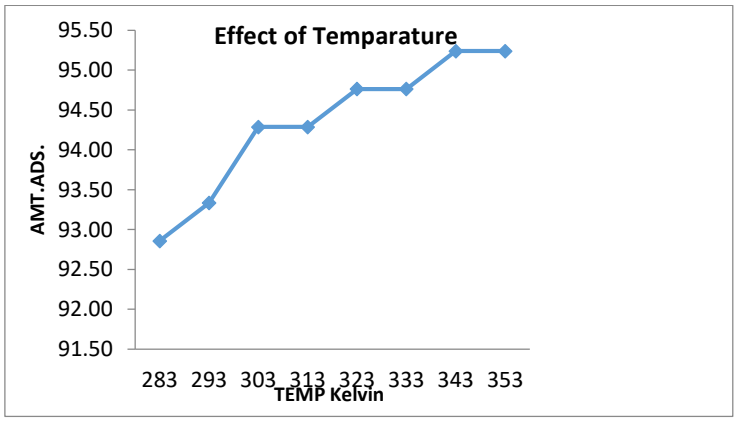

Figure (5): Effect of temperature

Isotherm Studies:

The information about how adsorbent and adsorbate interact with each other and their importance in improving the use of nano adsorbent is explained by adsorption isotherm. Langmuir and Freundlich isotherm are best fitted models for Cd metal ions adsorption onto copper oxide nanosorbent.

The Langmuir isotherm[17] is generally most appropriate to monolayer adsorption where all metal binding sites are of equal energy and there are no interactions between adsorbed molecules. There is no migration of adsorbate molecules in the plane of the surface area [22]asin figure (6)

The Langmuir isotherm is stated in terms ofimportant characteristic dimensionless constant separation factor or equilibrium factor R_L as suggested by the nature of the isotherm is below

R_L Value	Types of Isotherm
$R_L>1$	Unfavorable
$R_L = 1$	Linear
$O < R_L<1$	Favorable
$R_L = O$	Irreversible

For non-ideal adsorption, the Freundlich isotherm may be used involving heterogeneous sorption [18]. Freundlich theory consider that the ratio of the amount of solute adsorbed onto a given quantity of adsorbent to the concentration of the solute in the solutions are not constant during different concentration of solution as infigure (7).

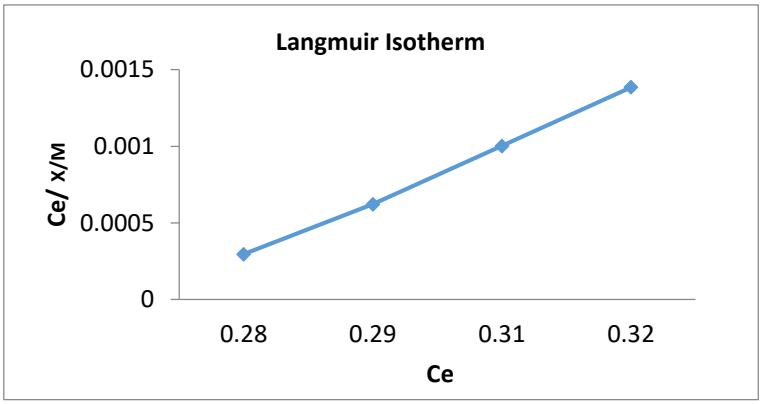

Figure (6): Langmuir isotherm

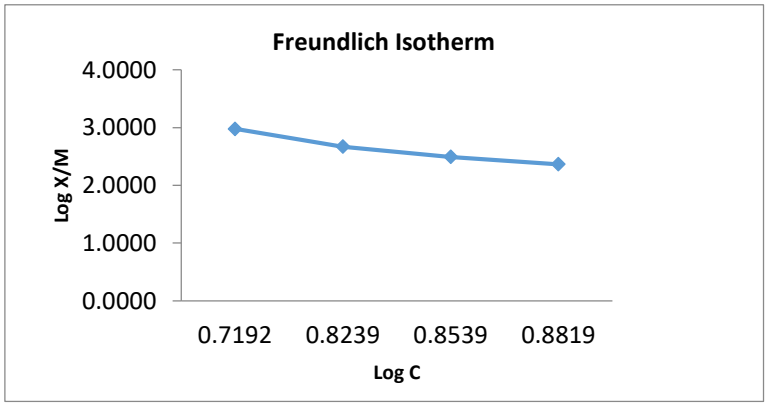

Figure (7): Freundlich Isotherm

4. CONCLUSION:

Investigational results show that the use of copperoxide nanoparticles for the removal of Cd heavy metal ion is quite feasible, environmentally friendly, and economically smart for the treatment of wastewater. As compare to traditional separation methods the adsorption separation method has the advantages like simple, fast and efficient. Adsorption capacity of CON depends mainly on the agitation time, pH of aqueous solution, temperature, initial contact concentration and dose of adsorbent. The correlation coefficient (R^2) which is nearly equal to one. This shows that the pseudo-second order model can show the adsorption of Cd metal ions. Copperoxide nanoparticles can be used as suitable nano adsorbent for removing Cd ions from aqueous systems.

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Comparative studies of dc resistance, Curie temperature and variation of log ρ due to the impact of gamma radiation on the Co-Zn ferrite system

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ABSTRACT:
Resistance of the Co,Zn,Fe204 samples is measured after irradiation with Co60 γ-radiation and compared with that prior to irradiation. The aim of the present work is to shed light on the effect of γ -radiation on the physical properties of Co-Zn ferrite, including resistance. The resistivity plots were plotted and the Curie temperature had been determined. In the present work, we report on a systematic investigation

KEYWORDS*: curie temperature, gamma radiation.*

1. INTRODUCTION:

Polycrystalline spinel ferrite is a well-known magnetic material and is very useful in microwave applications, high quality filters, antenna rods, transformer cores, etc. [1-3]. Due to their high-frequency applications, Nickel-Zinc ferrites have a high technological importance. Their properties largely depend on their composition and microstructure, which, in turn, is sensitive to the processing method, used to synthesis them. The selection of an appropriate process is therefore crucial in order to ensure better quality ferrites [4]. The twin features of the magnetic conductor and electrical insulator have made them useful in a wide range of applications. Properties like structural, electrical and magnetic known to be sensitive to chemical composition, microstructure, type and amount of doping. [5,6,7] etc

2. EXPERIMENTAL:

Sample preparation

Samples of the system Col.,ZnxFe204 (x = 0.0,0.2) were prepared by using the usual ceramic technique [8]. The ferrites were prepared by the conventional double-stage sintering process. The very pure COO, ZnO, $Fe_2$03(99.9%) were mixed intimately in stoichiometric proportions according to their molecular weights and preheated in air. The resulting powder was ground to a very fine powder by using an agate mortar. The powder was then sintered at 900oC for 12 hrs. The sintered powder is again ground and palletized. These pellets are finely sintered to 11000C for 24 hrs and then cooled to room temperature for 24 hrs. Finally the samples were polished to obtain disc with two uniform parallel surfaces.

Gamma radiation exposure

Co-Zn ferrite tablets were exposed to Co^{60} γ –rays. The source used in the present study is a commercially available laboratory source provided by Nucleonix systems (P) Ltd. Hyderabad. All measurements were performed before and after the absorbed gamma radiation dose, as well as after removal of the specimens from the radiation field.

3. ANALYSIS:

The d.c. electrical resistivity of all the samples before and after irradiation was measured using the two probe technique and in the temperature range 300 K to 800 K. The relation between the log value (logρ) of resistivity and the reciprocal temperature (1/T) is shown in figure 1(a) and (b). The plots represented in these figures two types of straight lines could be seen. Breaks in the slopes of resistivity versus temperature plots are in the vicinity of Curie temperature of the respective sample.

The resistivity plots indicate that resistivity decreases with temperature and obeys the relation given by

$$\rho = \rho_0 \exp [-E_g/kT] \quad (1)$$

where,

E_g is activation energy in eV,

ρ_0 is temperature dependent factor,

k is Boltzmann constant

T is absolute temperature.

4. FINDINGS:

It can also be seen from figure 1(a) and (b) that resistivity decreases after irradiation. The activation energy for all the samples before and after irradiation has been calculated using resistivity plots and equation (1). It is observed that activation in energy slightly decreases for irradiated sample for all the composition 'x'. The results on electrical measurements of the presently investigation samples is in good agreement with those reported in literature [9,10].

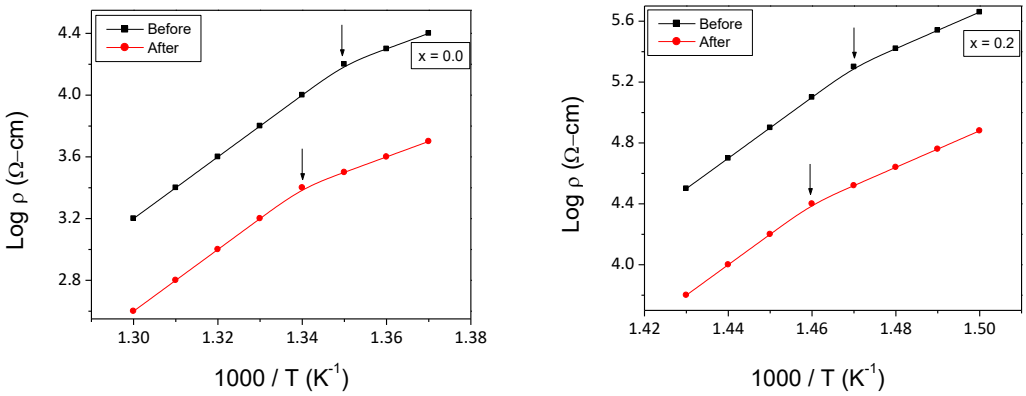

Fig. 1(a) and (b): Variation of log ρ with 1000/T of $Co_{1-x}Zn_xFe_2O_4$ for x = 0.0 and x = 0.2

5. RESULT:

The decrease in activation energy gamma irradiated samples is related to the increase in Fe^{2+} ions at octahedral B sites. When gamma radiation interacts with the samples, a Fe^{3+} ion gets converted in to Fe^{2+} ions as follows,

$$Fe^{3+} \leftrightarrow Fe^{2+} + e^{-}$$

The increase in Fe^{2+} ions increases the ratio Fe^{2+}/ Fe^{3+} which is responsible for decrease in activation energy of irradiated samples. The conduction mechanism in spinel ferrite is due to the hopping of electrons between Fe^{2+} ions and Fe^{3+} ions. As Fe^{2+} ions increases after irradiation the conductivity increases and hence resistivity decreases.

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Structural and Electrical Properties of Ti^{4+} Substituted Ni-ferrite Synthesized by Solid State Reaction Method

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ABSTRACT:

Tetravalent Ti-doped Ni-ferrite with generic formula $Ni_{1+X}Ti_XFe_{2-2x}O_4$ (x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7) series of samples were prepared by standard solid state reaction method using high purity oxide. X-ray diffraction technique has been employed to confirm the single phase nature of $Ni_{1+X}Ti_XFe_{2-2x}O_4$ samples. The X-ray diffraction pattern showed the presence of all planes which are belongs to cubic spinel structure. The analysis of XRD pattern revealed the formation of single phase cubic spinel structure of the samples. No extra peak has been observed in the XRD pattern. The XRD data was used to determine lattice constant 'a' of the system with an accuracy ± 0.002A.U. The lattice constant of ferrite system $Ni_{1+X}Ti_XFe_{2-2x}O_4$ decreases with Ti^{4+} substation. X-ray density decreases with Ti^{4+} substitution. The d. c. electrical resistivity measurements were carried out in the temperature 300K to 800K using two probe technique and results are presented in the paper. It is observed that d. c. electrical resistivity decreases with increase in temperature indicting semiconducting nature of the samples. The observed decreasing nature of d. c. electrical resistivity may be attributed to decrease in the electron hoping due to substitution of Ti^{4+} ions in the system. That activation energy calculated from resistivity plots is greater in paramagnetic region whereas it is found to be less in ferrimagnetic region.

KEYWORDS: *Lattice constant, ferrite material, electrical resistivity, activtion energy.*

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1. INTRODUCTION:

Today ferrite material is one of the part of material science. Ferrites are magnetic ceramics of great importance in the production of electronic and other components. The high electrical resistivity, low eddy current loses and good magnetic properties of the ferrite are responsible for its various application. They have wide range of applications from a small permanent magnet to sophisticated devices for the electronic industry. Some interesting applications are in computer peripherals, telecommunication equipment, permanent magnet, electronic and microwave devices etc. The important electrical and magnetic properties of ferrite depend on the processing condition, sintering temperature and time, chemical composition, type and amount of the dopant [1].

Nickel ferrite is a magnetic material of great scientific and technological interest because of their high electrical resistivity, moderate saturation magnetization, high Curie temperature, excellent chemical stability etc. Nickel ferrite is an inverse spinel ferrite in which Ni ions occupies octahedral B-site and Fe^{3+} ions are equally distributed at tetrahedral (A) and octahedral [B] site. Nickel ferrite and substituted nickel ferrite has been the subject of many workers [2-5].It has been reported that the addition of tetravalent ions in nickel ferrite influences the electrical and magnetic properties. The high electrical resistivity, low eddy current and dielectric losses makes nickel ferrite useful in many electronic devices at high frequency. Hence, the study of electrical and dielectric properties is very much important for possible use of nickel ferrite in microwave and other applications.

2. EXPERIMENTAL TECHNIQUES:

The polycrystalline samples of $Ni_{1+x}Ti_xFe_{2-2x}O_4$ were prepared by using a ceramic technique [6]. The A.R. grade oxides (SD fine) of corresponding ions (NiO, TiO_2 and Fe_2O_3) were mixed in stoichiometry proportion. Grinding using agate mortar for 4 hours was carried out for each sample. The samples were pre-sintered in a muffle furnace at 900^0C for 12 hours. After that the powder was reground and compressed into a pellet form using a hydraulic press with a pressure of 6 ton. The pellets were sintered at 1200^0 C in air for 24 hours. The samples were then furnace cooled to room temperature. X-ray diffraction patterns were taken at room temperature to confirm the single phase cubic spinel structure. The XRD patterns were recorded in the 2θ range 20^0 to 80^0. D.C. electrical resistivity measurements were carried out using two probe techniques in the temperature range 300 K to 800 K. A silver paste was applied on both the surfaces of the pellet to ensure good electrical contact.

3. RESULTS AND DISCUSSION:

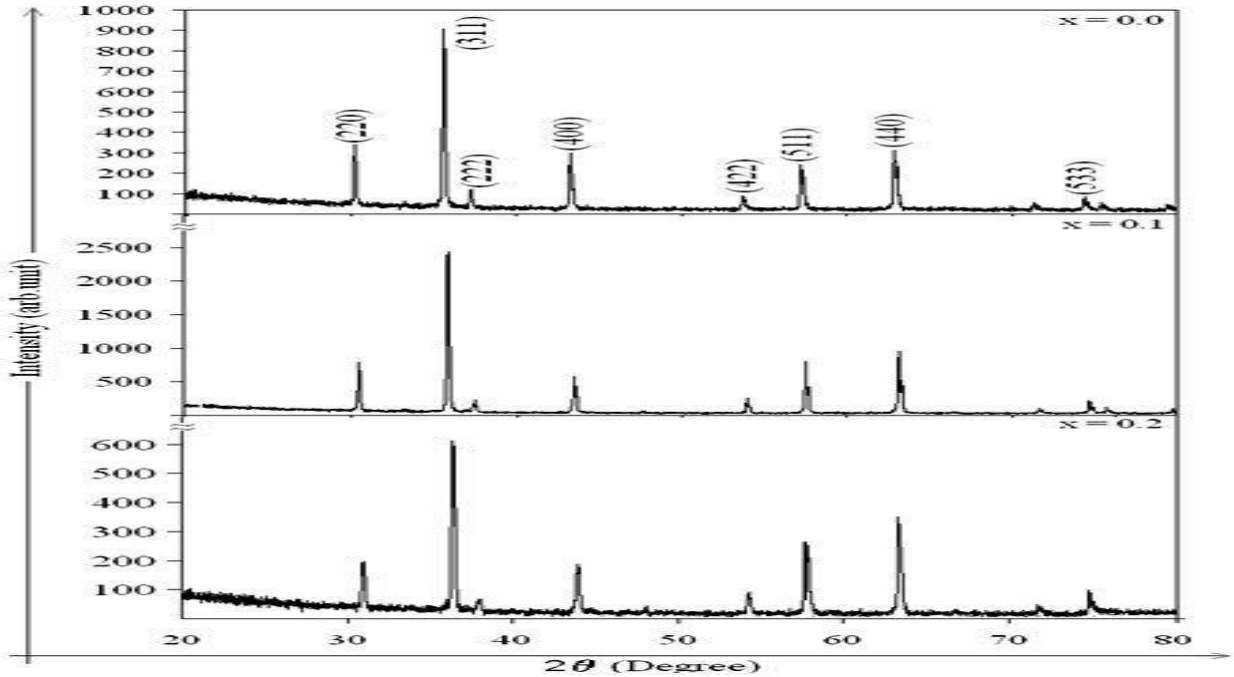

Fig.1 XRD pattern of Ti content x (= 0.0, 0.1 and 0.2) of $Ni_{1+x}Ti_xFe_{2-2x}O_4$ system

X-ray powder diffraction (XRD) patterns of $Ni_{1+x}Ti_xFe_{2-2x}O_4$ with typical sample x = 0.0, 0.1 and 0.2 are shown in Fig 1. XRD pattern shows the reflections (220), (311), (222), (400), (422), (511), (440), (533). These reflections are the indication of the presence of a cubic spinel structure. The diffraction line corresponding to a cubic spinel type and crystalline phase provide clear evidence of the single phase formation of a $Ni_{1+x}Ti_xFe_{2-2x}O_4$ spinel ferrite.

The lattice constant obtained from XRD data for all the samples are presented in Table 1. The value of the lattice parameter for nickel ferrite (a = 8.331Å) agree close to the reported data [7]. It can be seen from table 1 that the lattice parameter decreases slowly with the Ti concentration x. In the present series of $Ni_{1+x}Ti_xFe_{2-2x}O_4$, two Fe^{3+} ions are replaced by combination of divalent Ni^{2+} ions and tetravalent Ti^{4+} ions. The change in the lattice constant is related with the ionic radii of the constituent ions. The ionic radii of Ni^{2+} (0.72Å) and Ti^{4+} (0.64Å) are less than the ionic radii of $2Fe^{3+}$ ions hence we observe decrease in lattice parameter [8].

Table.1Values of lattice constant (a), Particle size, X-Ray density and percentage Porosity of $Ni_{1+x}Ti_xFe_{2-2x}O_4$ ($x=0.0 \leq x \leq 0.7$) system

Ti content	x	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
Lattice constant 'a' (Å)		8.332	8.325	8.32	8.316	8.313	8.311	8.308	8.306
Particle Size (Å)		453.9	480.3	454.2	416.2	416.3	499.8	454.1	356.8
X-Ray density	(gm/cm^3)	4.041	4.043	4.041	4.037	4.032	4.0271	4.022	4.017
Bulk density	(gm/cm^3)	3.729	3.806	3.828	3.779	3.684	3.647	3.522	3.508
Porosity	%	7.72	5.86	5.29	6.41	8.64	9.44	12.43	12.66

Using the lattice parameter values and molecular weight, the X-ray density of all the composition x was determined and the values are presented in table 1. The X–ray density decreases very slowly with respect to Ti content x. The bulk density was also determined for all the values of x using mass and volume of the samples. The values of bulk density are presented in table 1. It is observed from table 1 that bulk density increases with Ti concentration x. The X-ray density and bulk density values are used to obtain porosity of each sample. The porosity values are given in table 1. It is interesting to note that the porosity increases with Ti concentration x. The low values of porosity indicate the material is very dense and can be useful in high frequency application [9].

3.1. Electrical Properties

The variation of logarithm of resistivity versus reciprocal of temperature is depicted in Fig 2. The plot exhibits two regions (ferrimagnetic and paramagnetic) with change in slope. These regions are namely ferrimagnetic and paramagnetic region. The temperature at which slope changes may corresponds to Curie temperature (T_c) of the samples. The resistivity plots obeys the exponential relation given by,

$$\rho_{dc} = \rho_o \exp\left(\frac{\Delta E}{kT}\right)$$

where, ΔE is the activation energy in electron volt (eV), need to release an electron from one ion to the neighboring ions giving rise to the electrical conductivity. k-is the Boltzmann constant and T is absolute temperature.

Using the above relation and the values of the slope from resistivity plots (Fig. 2.), the activation energy corresponding to ferrimagnetic region and paramagnetic region was calculated. The values of activation energy for paramagnetic and ferrimagnetic region is given in the table 2.

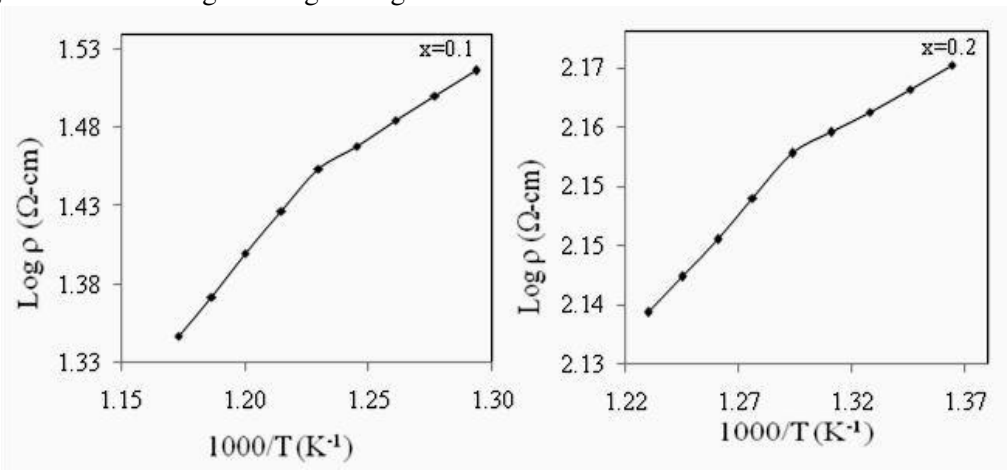

Fig.2 Resistivity plios of Ti content x (=0.1 and 0.2) of $Ni_{1+x}Ti_xFe_{2-2x}O_4$ system

Table.2 Values of variation of activation energy in Ferrimagnetic and paramagnetic region of $Ni_{1+x}Ti_xFe_{2-2x}O_4$ ($x=0.0 \leq x \leq 0.7$) system

Ti content	x	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
Activation energy (eV)	E_F	0.305	0.203	0.259	0.296	0.283	0.234	0.151	0.188
	E_P	0.699	0.385	0.325	0.359	0.709	0.411	0.34	0.581
ΔE	(eV)	0.394	0.183	0.066	0.063	0.426	0.177	0.189	0.393

The table 2 indicates the higher values of activation energy for paramagnetic region compared to that of ferrimagnetic region. The activation energy in the present case is below 0.2 eV this suggest that the conduction mechanism in the present case is due to the hopping of electrons ($Fe^{3+} \rightleftharpoons Fe^{2+}$, Ni^{2+} $Fe^{3+} \rightleftharpoons Fe^{2+}$, Ni^{3+}) [10]. During sintering process some of Fe^{2+} ions have been transformed to Fe^{3+} ions and generated electrons which take part in conduction mechanism. The presence of Fe^{2+} and Fe^{3+} on equivalent lattice site (octahedral B-site) may cause the low surface resistivity

4. CONCLUSIONS:

The structural, electrical properties of nickel ferrite system are very much influenced by non magnetic Ti substitution. X-ray diffraction analysis showed the formation of single phase cubic spinel structure. The lattice constant is decreases with increase in Ti concentration x. The d. c. electrical resistivity decreases with temperature showing semi conductive nature of the samples. The activation energy in paramagnetic region is greater than that in ferrimagnetic region.

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Synthesis, Characterization and Comparative Study of Drug-likeness Properties of Cinnamamide Containing Heterocyclic Moiety

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ABSTRACT:

In the present research work synthesis and characterization of (E)-3-Substituted phenyl-1-piperidino-2-propen-1-one and (2E)-1-(piperazine-1-yl)-3-subtituted phenyl prop-2-en-1-one Cinnamamides containing Piperidine, Piperazine heterocyclic moieties and screening of antimicrobial activities were carried out. The synthesized Cinnamamides prepared were firstly employed for studying their drug-likeness properties by using data visualization and analysis tool before carrying out antimicrobial activities. The comparative study of the various physico-chemical properties like clogP, solubility, druglikeness and drug score and also toxic related risks as tumorogenicity, mutagenicity, irritation, and reproductive effectivity were calculated of synthesized compounds by the methodology developed by Osiris. The results of this study of drug-likeness properties of synthesized compounds were found to be encouraging.

KEY WORDS:- *Synthesis, Drug-likeness, OSIRIS property calculator, Heterocyclic moiety, Cinnamamide.*

1. INTRODUCTION:

The concepts of drug likeness is an important characteristic for any molecule widely integrated into initial stage of lead and drug discovery. The different structural and molecular properties like hydrophobicity, hydrogen bond character, molecular size etc. are evaluated in order to determine whether the predicted compound is similar to the known drugs or not. Drug-likeness deduce as a tender balance in molecular properties affecting pharmacodynamics, pharmacokinetic of molecules which ultimately affects their absorption, distribution metabolism, excretion and toxic for human body such as drug[1]. The molecular properties involved molecular weight, hydrophobicity, electronic distribution, hydrogen bond acceptors and donors, solubility, and other concerned properties[2].

Actually the strategy of chemists in their drug research is to discover new chemical compounds which highly resemble drugs with respect to the key physicochemical and biological properties, with the information that find for drug like properties may help to achieve decent phamacodynamics and pharmacokinetic properties. In other word the motto of medicinal chemists is to design and discover structure that can be improve to leads, leads that can be optimized to candidates and candidates that will become valuable drugs[3].

Now generally the Lipinski's rule of Five (RO5) is used to determine the drug likeness of the evaluated drug molecules[4]. The complete chemical information remains preserved from studies of molecular properties because the molecular properties have to be logically and quantitatively represented as molecular descriptors. From the suitable molecular descriptors used for correctly predicating the drug likeness of a molecule is important for the screening the drug like molecules.

Methods for dug likeness predication involves from simple counting schemes like Lipinski's "rule of five" to machine learning approaches like artificial neural network and support vector machines. Lipinski's "rule of five" is a finding approach for predicting drug likeness starting that molecules having molecular weight greater than five hundred, logP greater than five, hydrogen bond doors greater than five and hydrogen bond acceptors greater than ten have poor absorption or permeation. This rule describes only the molecular properties related with pharmacokinetic of molecule which refers to the absorption, distribution metabolism, excretion and toxic (ADMET) properties of bioactive compounds in a higher organism[5]. There is no consideration for phamacodynamics aspect of molecules which deal with drug action on the body or on microorganisms and other parasites within or on the body. Moreover there are many demerits of this rule among existing drugs and vice versa, and therefore, fulfillment the rule of five does not offers that a molecule is drug-like. Drug likeness was a broad term used to define absorption, distribution metabolism, excretion and toxic (ADMET) properties of a drug molecule[6-11].

Heterocyclic compounds it may be natural or synthetic have been immensely explored for their profound applicability in the field of industrial, agricultural and medicinal chemistry. Cinnamamide containing heterocyclic moiety with a various of biological properties[7], like central nervous system depressant, anticonvulsant, muscle relaxant, anti-allergic, antineoplastic, antitumor, anesthetic, analgesic and anti-infective activities and anti-infective activities[12-15], etc. In agrochemical field, insecticidal, their avian repellent, herbicidal activities, and several excellent cinnamamide

are fungicides[16-18]. Inspire of wide range of their applications and very less attention is paid towards the synthesis of Cinnamamide derivatives containing heterocyclic moiety.

Drug-likeness of compounds was studied by using Data warrior software of Osiris property explorer. The toxicity concerned risks as tumorogenicity, mutagenicity, irritation, and reproduction effects and various physio-chemical properties like C-logP, solubility, drug likeness and drug score were calculated by the methodology developed by Osiris.

2. METHOD AND MATERIAL:

Reagents and chemicals were procured of high quality and were of analytical grade. Drug-likeness property of molecules was studied by using Data warrior software of Osiris property explorer. The Toxicity related risks as tumorigenic, mutagenic, irritation, and reproduction effectivity and various physio-chemical properties like C-logP, solubility, drug-likeness and drug score calculated by the methodology developed by Data warrior software of Osiris property explorer.

The (E)-3-Substituted phenyl- 1-piperidino-2-propen-1-one Cinnamamide and (2E)-1-(piperazine-1-yl)-3-subtituted phenyl prop-2-en-1-one cinnamamides containing Piperidine, Piperazine heterocyclic moieties were synthesized from Wittig reagents and substituted various benzaldehyde by more convent well known Wittig reaction using dry benzene as a solvent. Before the screening for antimicrobial activities the synthesized Cinnamamides prepared were firstly employed for studying their drug-likeness properties by using data visualization and analysis tool Data warrior software of Osiris property explorer.

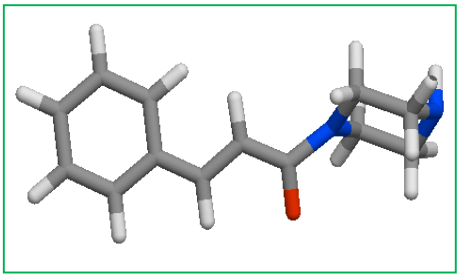


Fig.1- Structure of (E)-3-Phenyl-1-(1-piperazinyl)-2-propen-1-one Cinnamamide

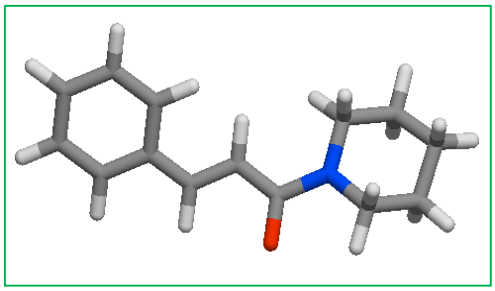


Fig.2- Structure of (E)-3-phenyl-1-Piperidino-2-Propen-1-one Cinnamamide.

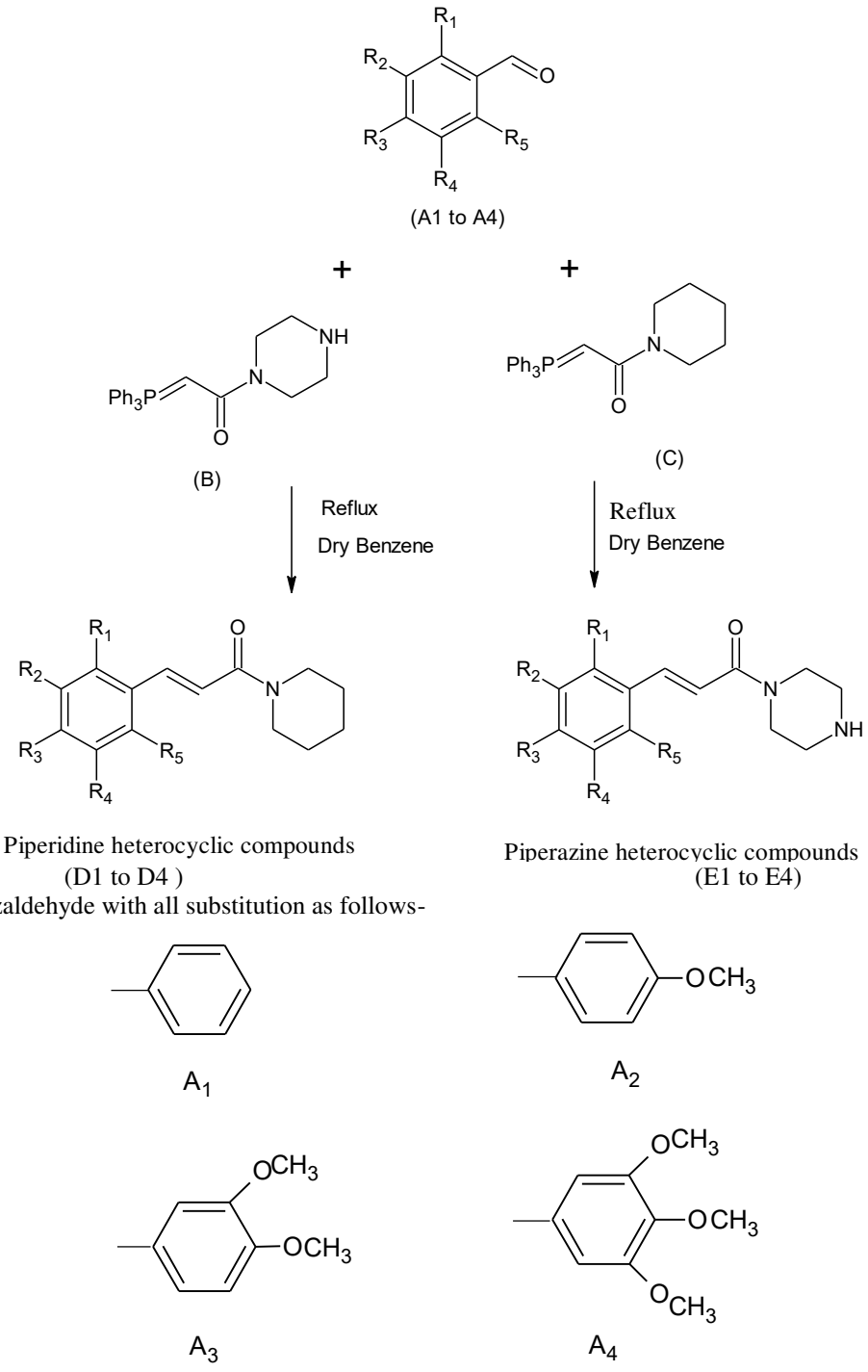
OSIRIS PROPERTY CALCULATIONS

The toxicity related risks like tumorogenic, mutagenicity, irritation, and reproduction effects and various physico-chemical properties such as clogP, solubility, drug-likeness and drug score can be calculated by the methodology developed by Osiris. The toxicity risk predictor locates fragments within a molecule, which indicate a potential toxicity risk. Properties calculated by OSIRIS Property Explorer are summarized in Table. The calculated octanol-water distribution coefficient value, aqueous solubility and molecular weight of analogue synthesized compound are under the acceptable criteria. The drug score combines druglikeness, cLogP, topological polar surface area, molecular weight and toxicity risks in one hand value than may be used to explain the compound's overall potential to qualify for a drug. This value is calculated by multiplying contributions of the individual properties with the first equation:

$$ds = \prod \left(\frac{1}{2} + \frac{1}{2} s_i\right) \cdot \prod t_i$$

$$s = \frac{1}{1 + e^{ap+b}}$$

Where, ds is the drug score, si are the contributions calculated directly from of cLogP, logS, molecular weight and drug-likeness. Parameters **a** and **b** are (1, -5), (0.012, -6) and (1, 0) for cLogP, molecular weight and druglikeness, respectively. ti are the contributions taken from the 4 toxicity risk types. The ti values are 1.0, 0.8 and 0.6 for no risk, medium risk and high risk, respectively.



- A1to A4 Benzaldehyde with all substitution as follows-

3. RESULTS AND DISCUSSION:

All synthesized novel cinnamamides compounds contained heterocyclic moiety as Piperidine and Piperazine. The Wittig reaction was convenient and green reaction pathway as well as important method for the synthesis of alkenes. By using this method novel (E)-3-Substituted phenyl- 1-piperidino-2-propen-1-one Cinnamamides and (2E)-1-(piperazine-1-yl)-3-subtituted phenyl prop-2-en-1-one cinnamamides containing Piperidine, Piperazine heterocyclic moieties were synthesized from substituted benzaldehydes and Wittig reagent having good yields. The yields of synthesized compounds were ranging from 62 to 84%. Now the total synthesized compounds were characterized on the basis of melting point, elemental analysis, IR spectra, ^{1}HNMR, and mass spectral analysis.

The molecular properties of the selected compounds were calculated using Data warrior (OSIRIS) of organic portal and the values were given in Table 3**.** The values of clogP (octanol-water distribution coefficient), molecular weight, drug likeness and the drug score were compared.

Molecular weights ranges of Piperdino cinnamamides 305 to 215 and in Piperazine cinnamamides range 306 to 216. The magnitude of drug-likeness and drug score same in both compounds series ranges from -0.93 to 3.43 and drug score 0.35 to 0.86. Toxicity risk of synthesized molecules based on Data warrior software of Osiris property explorer as only D2 and E2 molecules have high risk in case of irritation and reproduction effectivity while all other synthesized compounds are have no risk.

Table-1:- Characteristics data for synthesized Cinnamamides

Sr. No.	Entries	Mol. Formula	Mol. Weight	Yield in %	M.P. in ^{0}C
1	**D1**	$C_{14}H_{17}ON$	215	62	162
2	**D2**	$C_{15}H_{19}O_2N$	245	64	174
3	**D3**	$C_{16}H_{21}O_3N$	275	70	186
4	**D4**	$C_{17}H_{23}O_4N$	305	64	202
5	**E1**	$C_{13}H_{16}N_2O$	216	72	90
6	**E2**	$C_{14}H_{18}N_2O_2$	246	84	136
7	**E3**	$C_{15}H_{20}N_2O_3$	276	82	181
8	**E4**	$C_{16}H_{22}N_2O_4$	306	74	229

Table-2:-Elemental analysis of synthesized compounds (calculated % of element).

Sr. No.	Entries	Molecular Formula	Mol. Wt.	% C	% H	% O	% N
1	**D1**	$C_{14}H_{17}ON$	215	78.10 (78.14)	7.96 (7.91)	7.43 (7.44)	6.51 (6.51)
2	**D2**	$C_{15}H_{19}O_2N$	245	73.44 (73.47)	7.81 (7.76)	13.04 (13.06)	5.71 (5.71)
3	**D3**	$C_{16}H_{21}O_3N$	275	69.79 (69.82)	7.69 (7.64)	17.43 (17.45)	5.09 (5.09)
4	**D4**	$C_{17}H_{23}O_4N$	305	66.86 (66.89)	7.59 (7.54)	20.96 (20.98)	4.59 (4.59)
5	**E1**	$C_{13}H_{16}N_2O$	216	72.19 (72.22)	7.46 (7.40)	7.40 (7.40)	12.95 (12.96)
6	**E2**	$C_{14}H_{18}N_2O_2$	246	68.27 (68.29)	7.37 (7.32)	12.99 (13.00)	11.37 (11.38)
7	**E3**	$C_{15}H_{20}N_2O_3$	276	65.27 (65.22)	7.30 (7.25)	17.37 (17.39)	10.14 (10.14)
8	**E4**	$C_{16}H_{22}N_2O_4$	306	62.73 (62.75)	7.24 (7.19)	20.89 (20.92)	9.14 (9.15)

Table-3:- Drug likeness properties of piperidino/ piperazine cinnamamides:

Entry	Molecular Formula	Mol. Wt.	cLogp	Solubility	TPSA	Drug-likeliness Value	Drug Score
D1	$C_{14}H_{17}ON$	215	2.83	-2.58	20.31	-0.93	0.57
D2	$C_{15}H_{19}O_2N$	245	2.48	-2.29	40.54	0.57	0.75
D3	$C_{16}H_{21}O_3N$	275	2.69	-2.62	38.77	2.26	0.84
D4	$C_{17}H_{23}O_4N$	305	2.62	-2.64	48.00	3.43	0.86
E1	$C_{13}H_{16}N_2O$	216	1.52	-1.56	32.34	-0.93	0.57
E2	$C_{14}H_{18}N_2O_2$	246	1.54	-1.58	41.57	0.53	0.35
E3	$C_{15}H_{20}N_2O_3$	276	1.38	-1.60	50.8	2.26	0.85
E4	$C_{16}H_{22}N_2O_4$	306	1.31	-161	60.03	3.43	0.86

Table-4:- Toxicity risk of synthesized molecules based on Data warrior software of Osiris property explorer.

Sr. No.	Entry	Mutagenic	Tumorogenic	Irritation	Reproduction effect
1	**D1**	None	None	None	None
2	**D2**	None	None	High	High
3	**D3**	None	None	None	None

4	**D4**	None	None	None	None
5	**E1**	None	None	None	None
6	**E2**	None	None	High	High
7	**E3**	None	None	None	None
8	**E4**	None	None	None	None

THE SPECTROSCOPIC DATA:

The Spectroscopic data as IR, 1H NMR and Mass spectra of representative compounds (D1, D2 and E1, E2) of piperidino / piperazine cinnamamides series were recorded as follows-

➢**D1**=(E)-3-phenyl-1-piperidino-2-propen-1-one cinnamamides-

^{1}HNMR-(400 MHz, $CDCl_3$, δ ppm)- 1.2(m), (2H), CH_2; 1.4(m), (4H) CH_2; 3.4(t), (4H), $2CH_2$-N; 6.8 (d), (1H), (CH=CHCO), J=15.94 HZ; 7.2(d), (1H), (CH=CH-Ar) J=15.94 HZ; 7.2-7.5(m), (5H), (ArH).

IR spectra: (KBr) (cm^{-1})1607cm^{-1}(-C=C-), 1595; **Mass:** m/z (%): 215.13 (100) (M)+, 216.0 (15.50).

➢**D2** =(E)-3-(p-methoxyphenyl)-1-piperidino-2-propen-1-one cinnamamides-

^{1}HNMR-(400 MHz, $CDCl_3$, δ ppm))- 1.2(m),(2H), CH_2; 1.4(m), (4H) CH_2; 3.4(t), (4H), $2CH_2$-N; 6.8 (d), (1H), (CH=CHCO), J=15.94 HZ; 7.0 (d), (1H), (CH=CH-Ar) J=15.94 HZ; 7.2-7.5(m), (4H), (Ar-H); 3.2 (s), (3H), (-O-CH_3).

IR spectra: (KBr, cm^{-1}) 1685, 1600; **Mass:** m/z (%): 245.15 (100) (M)+, 246.14 (16.59).

➢**E1**=(2E)-1-(peperazin-1-yl)-3- phenylprop-2-en-1-one Cinnamamides

^{1}HNMR (400 MHz, $CDCl_3$) δ: 3.62-3.84 (m), (8H), 6.68 (d) (*J*= 15.2 Hz) (1H), 6.92d (*J*=15.2 Hz) (1H), 7.36-7.56 (m) (6H).

IR (KBr, cm^{-1}): 3040, 1690, 1610; **Mass:** m/z (%): 216.13(M+).

➢**E2**=(E)-3-(*p*-Methoxyphenyl)-1-(1-piperazinyl)-2-propen-1-one Cinnamamide

^{1}HNMR(400 MHz, $CDCl_3$)δ: 3.81(s), (3H); 6.9 (d), (2H); 7.4 (d), (2H); 6.7(d), (1H), (CH=CHCO), J=15.8HZ; 7.6 (d), (1H), (CH=CHC_6H_5) J=15.8HZ; 7.2(d), (2H); 7.4(d), (2H).

IR (KBr, cm^{-1}): 3070, 2925, 1475; **Mass:** m/z (%):246.14 (M+).

4. CONCLUSION:

The present research work was carried out with the intention to synthesize, characterization of cinnamamide containing piperadine and piperazine heterocyclic moiety and along with predicting their physic-chemical properties and druglikeness score. The eight compounds were tested for their molecular properties as molecular weight, clogp, Topological polar surface area, solubility, drug-likeness and drug score. One of the most important aspect of this study was consideration of credibility of the synthesized compounds were tested for their toxicity risk like tumorogenicity, mutagenicity, irritation, and reproduction effectivity using data warrior software of Osiris property explorer.

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Dielectric Estimation of Loss Factor and Field Strength Using TDR

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***ABSTRACT*:-**

A dielectric analysis has been done for the pure and binary mixture of 1-pentanol and ethanol at room temperature in the frequency interim of 10 MHz-50 GHz using TDR to study the cole-cole plot and also to estimate the values of dielectric loss tangent and dielectric field strength which depends on the values of dielectric constant.

1. INTRODUCTION:

Dielectric relaxation spectroscopy have allured much attentiveness of many researchers due to its ability to yield an information regarding intermolecular and intra-molecular interactions both in pure embodiment and binary mixture of liquids [1].Among the dielectric measurement techniques TDR is proved to be a powerful technique to scrutinize the molecular dynamics due to its higher frequency range [2].Molecules can be categorized in to hydrogen bonded and non-hydrogen bonded. The regular alignment of dipoles in hydrogen bonded molecules discriminate it from non-hydrogen bonded molecules [3]. Alcohols is an organic compound which do not only find its way towards applications in industry and science as reagents, solvents, fuels, and as fruitful solvents in green automation but also it's capacity towards intermolecular and intra-molecular self association makes its function crucial in abundant chemical reactions[4]. The short size of chain length of small chain alcohols causes the small chain alcohol molecules to act in dissimilar mode than the long chain alcohol molecules as the small chain alcohols has the rapid relaxation than the long chain alcohol molecules[5].Alcohols can be categorized as monohydric ,dihydric and trihydric depending on the number of hydroxyl groups attached to it and ethanol and 1-pentanol are monohydric alcohols because both are having one hydroxyl group and both are hydrogen bonded organic liquids.

The dielectric loss tangent of a material denotes the dissipation of electrical energy due to different physical processes such as electrical conduction, dielectric relaxation, dielectric resonance and loss from nonlinear processes and it is denoted as tan δ.

The complex aggregate which has two parts namely [6]

1) The real part which designate dielectric permittivity of material (ε')

2) The imaginary part which designate dielectric loss of material (ε'')

can be originated by the interaction of electromagnetic radiation with the dielectric material.

The study of cole - cole plot have been reported [7, 8]

The present study aims at to estimate the values of dielectric loss tangent tanδ and dielectric field strength Δε by using the equations (2) and (3) given below and also to report the Debye relaxation.

2. EXPERIMENTAL DETAILS:

Materials: -

The chemicals utilized for the present investigation was obtained from EMD llipore Corporation Germany grade having 99% purity and used without further purification.

Methodology:-

Samples were prepared by mixing the volume fractions of 1-pentanol in ethanol ranging from 0.0 (pure), 0.1 (10% 1-Pentanol+90% ethanol), 0.2 (20% 1-Pentanol+80% ethanol), and vice versa. Measurements were taken by placing the sample in electronically temperature controller bath with an accuracy of ± 0.1 °C.

The Tektronix DSA8300 sampling main frame oscilloscope sampling with the dual channel sampling module 80E10B has been used for time domain reflectometry. The sampling module provides 12 ps incident and 15 ps reflected rise time pulse. The coaxial cable used to feed pulse has 50 ohm impedance, inner diameter of 0.28 mm and outer diameter of 1.19 mm. Sampling oscilloscope monitors changes in pulse after reflection from the end of line. Reflected

pulse without sample R1 (t) and with sample Rx(t) were recorded in time window of 5 ns and digitized in 2000 points. The addition [q (t) = R1(t) + Rx(t)] and subtraction [p(t) = R1(t) - Rx(t)] of these pulses are done in oscilloscope memory. These subtracted and added pulses are transferred to PC for further analysis. The Fourier transformations of the pulse and data analysis were done earlier to determine complex permittivity spectra ε*(ω) using non linear least square fit method [9,10].

Frequency dependent complex permittivity spectra for 1-pentanol-ethanol mixture obtained in the frequency region 10 MHz -50 GHz at room temperature are shown in Fig 1. The values of ε' and ε'' for all the studied solvents were observed to be decreased with decreasing PI Polarity Index towards high frequency. Complex permittivity spectra are described by Havriliak-Negami equation [11] given as:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[1 + (j\omega\tau)^{1-\alpha}]^\beta} \qquad (1)$$

Where, ε_0 is static permittivity, ε_∞ is permittivity at high frequency, τ is relaxation time, α and β are the empirical parameters for the distribution of relaxation time between 0 and 1. The Havriliak-Negami function includes the Cole-Cole [12] (β=1), Cole-Davidson [13] (α=0) and Debye [14] (α=0, β=1) relaxation spectral function in limiting form. The complex permittivity spectra have been fitted in Debye type model using nonlinear least squares fit method to determine the dielectric relaxation parameters.

Whereas the dielectric loss tangent tanδ has been calculated by making use of[15]

$$\text{Tan}\delta = \frac{\varepsilon''}{\varepsilon'} \qquad (2)$$

$$\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty \qquad (3)$$

3. RESULTS AND DISCUSSION:-

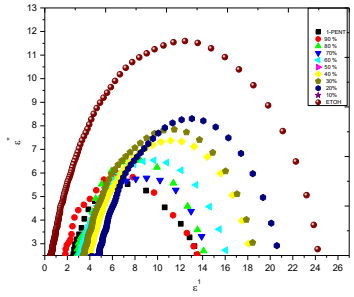

Figure 1

The cole-cole plot (ε' vs ε″ plot) for ETOH-1-PENT binary mixture at 25 ^{0}C

Fig 1 depicts the semicircular arcs which in turn depicts the Debye type behavior for cole-cole plot which means single relaxation time. Workers have perceived Debye model for lower concentrations of ethylene glycol [16].

Fig 2 depicts the nonlinear variations of tanδ according to varying concentrations of 1-pentanol in ethanol. Several workers have reported [17] that tanδ is the angle between polarization and the field which in turn yields the loss factor. At concentration 0.5 of 1-pentanol tan δ is highest this manifest angle between the polarization and the field is greater at concentration 0.5which in turn designates electromagnetic energy absorption is maximum at 0.5 volume fraction of 1-pentanol [18] and it is lowest at concentration 0.1 which designates the low dielectric loss and the non linear variations in tan δ values can be ascribable to the interactions [19]. Which takes place between two types of molecules.

Dielectric strength which relies on the structure of molecule is the interior electric field before breakdown and which gives an affirmation of extent of polarization of dielectric material [20].

Fig 3 demonstrates the sudden drop in dielectric field strength values at concentration 0.1,and thereafter it decreases gradually up to concentration 0.7.also fig 3 makes it clear that the values of dielectric field strength decreases with an increase in 1-pentanol composition this may be due to decrease in polarization of dielectric material.

In addition to this the non linear variations can be ascribed to the molecular association that takes place.

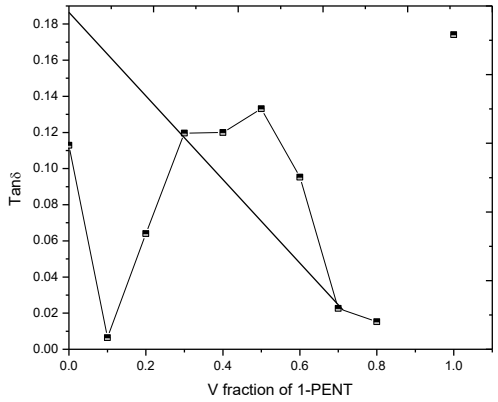

Figure 2
Variations of tan δ with volume fraction of 1-pentanol

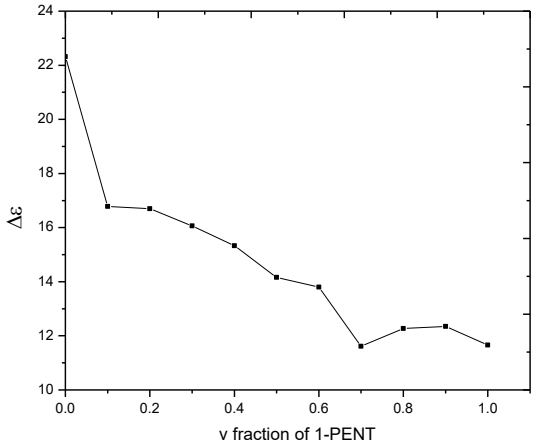

Figure 3
.Variations of Δε with volume fraction of 1-pentanol

4. CONCLUSIONS:

The cole-cole plot for ethanol-1-pentanol binary mixture exhibits Debye behavior. The study of tanδ reveals the nonlinear variations in the values of the same are due to the intermolecular interactions amid the two different systems. The dielectric field strength demonstrates the drop in values of the same due to increase in number of carbon atoms with an increase in composition of 1-pentanol in ethanol.

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Nessecity of Simulation

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ABSTRACT:

This paper addresses why simulation is necessary and various types of circuit analysis. Traditionally electronic circuit design was verified by building prototypes, subjecting the circuits to various stimuli and measuring its response using appropriate laboratory equipment's. It is time consuming, instead of this if we use various SPICE software's, we can perform the number of analysis of the same circuit virtually. Virtual results are very close to the actually build circuits. It gives new ideas that could lead to improve the circuit performance

KEY WORDS: *SPICE, Circuit Analysis, Virtual Components*

1. INTRODUCTION:

SPICE is a great tool to learn a lot in a short time. Also, busy lives and limited budgets can make experimenting with real parts and expensive equipment nearly impossible. What may take you an hour to wire up in the lab to get a minor concept could be covered in a few minutes with SPICE. For example, how does an amplifier's gain vary with bandwidth? Before the circuit parts were even collected, you can get hands on experience with the gain-bandwidth trade off. While text and equations tell you the story, a simulation can clarify the concept and drive it home.

It's true getting a circuit to work as you envisioned can be fun and satisfying. Trying one more RC combination can be addicting as you optimize a circuit. Simulation gives you an open-ended sense of play, a set of circuit blocks ready to be combined in some interesting or useful way. There's a challenge in creating a SPICE model for an electrical or non-electrical component in your system. It's easy to get lost in a circuit adventure. What better way to learn the art and develop a passion for circuit design?

Measuring some circuit voltages and currents can appear like a mission impossible. Here are some difficulties simulation can avoid. Some measuring equipment may load your circuit producing misleading results. Other measurements may require special test equipment you don't have or can't afford. Still others may be dangerous (high voltage or current measurements) or may inadvertently destroy the real circuit. [1, 2, 3, 4, 5]

2. ANALYSIS:

Types of Analysis:

DC Analysis: The dc analysis portion of SPICE determines the dc operating point of the circuit with inductors shorted and capacitors opened. The dc analysis options are specified on the .DC, .TF, and .OP control lines. A dc analysis is automatically performed prior to a transient analysis to determine the transient initial conditions, and prior to an ac small-signal analysis to determine the linearized, small-signal models for nonlinear devices. If requested, the dc small-signal value of a transfer function, input resistance, and output resistance is also computed as a part of the dc solution. The dc analysis can also be used to generate dc transfer curves: a specified independent voltage or current source is stepped over a user-specified range and the dc output variables are stored for each sequential source value.

AC Small-Signal Analysis: The ac small-signal portion of SPICE computes the ac output variables as a function of frequency. The program first computes the dc operating point of the circuit and determines linearized, small-signal models for all of the nonlinear devices in the circuit. The resultant linear circuit is then analyzed over a user-specified range of frequencies. The desired output of an ac small- signal analysis is usually a transfer function. If the circuit has only one ac input, it is convenient to set that input to unity and zero phase, so that output variables have the same value as the transfer function of the output variable with respect to the input.

Transient Analysis: The transient analysis portion of SPICE computes the transient output variables as a function of time over a user-specified time interval. The initial conditions are automatically determined by a dc analysis. All sources which are not time dependent (for example, power supplies) are set to their dc value. The transient time interval is specified on a .TRAN control line.

Pole-Zero Analysis: The pole-zero analysis portion of SPICE computes the poles and/or zeros in the small-signal ac transfer function. The program first computes the dc operating point and then determines the linearized, small-signal

models for all the nonlinear devices in the circuit. This circuit is then used to find the poles and zeros of the transfer function.

Two types of transfer functions are allowed: one of the form (output voltage) / (input voltage) and the other of the form (output voltage) / (input current). These two types of transfer functions cover all the cases and one can find the poles / zeros of functions like input / output impedance and voltage gain. The input and output ports are specified as two pairs of nodes. The pole-zero analysis works with resistors, capacitors, inductors, linear-controlled sources, independent sources, BJTs, MOSFETs, JFETs and diodes. Transmission lines are not supported. The method used in the analysis is a sub-optimal numerical search.

Small-Signal Distortion Analysis: The distortion analysis portion of SPICE computes steady-state harmonic and intermodulation products for small input signal magnitudes. If signals of a single frequency are specified as the input to the circuit, the complex values of the second and third harmonics are determined at every point in the circuit. If there are signals of two frequencies input to the circuit, the analysis finds out the complex values of the circuit variables at the sum and difference of the input frequencies, and at the difference of the smaller frequency from the second harmonic of the larger frequency.

Distortion analysis is supported for the following nonlinear devices: diodes (DIO), BJT, JFET, MOSFETs (levels 1, 2, 3, 4/BSIM1, 5/BSIM2, and 6) and MESFETS. All linear devices are automatically supported by distortion analysis. If there are switches present in the circuit, the analysis continues to be accurate provided the switches do not change state under the small excitations used for distortion calculations.

Sensitivity Analysis: Spice will calculate either the DC operating-point sensitivity or the AC small-signal sensitivity of an output variable with respect to all circuit variables, including model parameters. Spice calculates the difference in an output variable by perturbing each parameter of each device independently. Since the method is a numerical approximation, the results may demonstrate second order affects in highly sensitive parameters, or may fail to show very low but non-zero sensitivity. Further, since each variable is perturb by a small fraction of its value, zero-valued parameters are not analyzed.

Noise Analysis: The noise analysis portion of SPICE does analysis device-generated noise for the given circuit. When provided with an input source and an output port, the analysis calculates the noise contributions of each device (and each noise generator within the device) to the output port voltage. It also calculates the input noise to the circuit, equivalent to the output noise referred to the specified input source. This is done for every frequency point in a specified range. The calculated value of the noise corresponds to the spectral density of the circuit variable viewed as a stationary Gaussian stochastic process.

After calculating the spectral densities, noise analysis integrates these values over the specified frequency range to arrive at the total noise voltage / current (over this frequency range). This calculated value corresponds to the variance of the circuit variable viewed as a stationary Gaussian process. [6, 7, 8, 9, 10, 11]

3. CONCLUSION:

The sky is the limit with electronic devices and topologies. You can start with some high-level functional blocks. As the design takes shape, fill in the details with components until Presto. Your creative synthesis has given birth to a circuit ready for actual prototype and further verification.

Note: Now a day due to Covid -19 Pandemic condition education field is totally affected in comparison with other fields. So simulation is necessary for to give the realistic experience to the students. For this teachers should be techno friendly and sufficient technical infrastructure should be available.

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Synthesis, In Vitro Antimicrobial Activities Evaluation of Some Novel 3-Hydroxy-4*H*-Chromen-4-One Derivatives

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ABSTRACT:

In the present research work, a series of some novel substituted 3-hydroxy-4H-chromen-4- one derivatives ***(4a-j)*** *have been synthesized by oxidative cyclization of substituted 2-hydroxychalcone derivatives* ***(3a-j)*** *with 30 % H_2O_2 using methanol as solvent in the presence of 20 % NaOH in ice cold condition (0-5 ^{0}C) with moderate to good yield of substituted 3-hydroxy-4H-chromen-4-one (85%). The products were tested for purity by TLC and structures of newly synthesized compounds were confirmed by IR, ^{1}H NMR and Mass spectral analysis. All the newly synthesized compounds were tested for their in vitro antibacterial activity against Escherichia coli, Salmonella typhi, Staphylococcus aureus, Bacillus subtilis and in vitro antifungal activity against Aspergillus niger, Penicillium chrysogenum, Fusarium moneliforme and Aspergillus flavus, using Peniciline and Greseofulvin as the standard drugs by agar cup method and Poison plate method, respectively*

KEYWORDS: *2-hydroxychalcone, 3-hydroxy -4H-chromen-4-one, antimicrobial activities.*

1. INTRODUCTION:

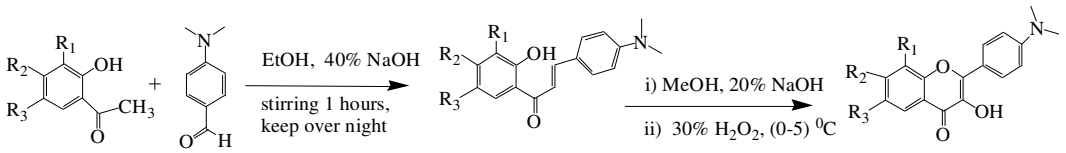
Flavonoids are well known group of naturally occurring aromatic oxygen containing heterocyclic compounds. They broadly distributed in higher plants kingdom and are found in many fruits, vegetables, tea and in red wines. They constitute most of yellow, red, blue colour flowers and fruits. Flavonoids are yellow colour pigments; some of the flavonoids show great medicinal value [1-2]the flavonoids family includes, flavones, flavanols (3-hydroxyflavone), isoflavones, flavanones. Many of the flavonoid compounds have been synthesized and studied their antimicrobial activities.[3-4] Synthesized flavonoids are display an important biological and pharmacological properties such as anti-viral,[5] antioxidant[,6-7] anti-inflammatory,[8-9] anticancer,[10-11] cytotoxicity,[12-13] anti-HIV,[14] and antidepressant[15] activities. Therefore, flavonoids are important class of potentially useful pharmacologically active compounds, and their synthesis has found wide spread application in organic chemistry.[16-17] Having these exciting biological activities, many flavonoid compounds have been synthesized and studied their antibacterial and antifungal activities.[18-19] In view of these observations, in this research work we report herein, the synthesis of novel substituted-2-(4′-dimethylamino-phenyl)-3-hydroxy-4*H*-chromen-4-one **(4a-j)** having substituted halogens, dimethylamino and methyl groups with an aim to find new most active *in vitro* antibacterial and antifungal agents.

2. MATERIAL AND METHOD:

All the solvents and reagents were obtained from commercial sources and were used without further purification. The melting points were determined by Open Capillary method and are uncorrected. The mass spectra were obtained with a Shimadzu GC-MS spectrophotometer. The IR spectra in KBr were recorded on Shimadzu Spectrophotometer and ^{1}H-NMR spectra were recorded in DMSO on Avance 300 MHz Spectrometer using TMS as internal standard. The chemical shift values are expressed in part per million (ppm) downfield from the internal standard and signals are quoted as, *s* (singlet), *d* (doublet), *t* (triplet) and *m* (multiplet). Thin-layer chromatography (TLC) was used to monitor the progress of all reactions and to check the purity of compounds by using ethyl acetate and petroleum ether as an eluent in the ratio of (3:7 v/v). All the newly synthesized substituted 3-hydroxy-4*H*-chromen-4-one compounds were tested for their antimicrobial activities by agar cup method and Poison plate method, respectively.

General procedure for the preparation of substituted 3-hydroxy-4*H*-chromen-4-one derivatives:

To a mixture of substituted 2-hydroxychalcone (0.001 mol) (**3a-j**) in 20 ml methanol was added 20% aqueous NaOH (10 ml), cooled at 0-5 ^{0}C, then added 30% H_2O_2 (10 ml) drop wise over one hour with constant vigorously stirring. The reaction mixture was further stirred for 3-4 hours at room temperature resulting light yellow reaction mixture was poured on crushed ice and neutralized with dilute cold 5N 80 ml HCl. The light yellow solid thus obtained was filtered, washed with cold water and dried. The solid product was recrystallized with ethanol to afford corresponding pure substituted 3-hydroxy-4*H*-chromen-4-one derivatives.



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

Table – 1: Physical data of substituted 3-hydroxy-4*H*-chromen-4-one derivatives (4a-j)

Sr. No.	Entry	R_1	R_2	R_3	Molecular Formula	Molecular weight	Yield in (%)	Melting point ^{0}C
1	4a	I	H	I	$C_{17}H_{13}O_3I_2N$	533	78	221
2	4b	I	H	CH_3	$C_{18}H_{16}O_3IN$	421	80	230
3	4c	Cl	H	Cl	$C_{17}H_{13}O_3Cl_2N$	349	75	225
4	4d	I	H	Cl	$C_{17}H_{13}O_3ICln$	441	80	227
5	4e	Br	H	CH_3	$C_{18}H_{16}O_3BrN$	374	75	220
6	4f	Br	H	Cl	$C_{17}H_{13}O_3BrClN$	394	82	198
7	4g	Br	H	Br	$C_{17}H_{13}O_3Br_2N$	439	76	202
8	4h	I	H	Br	$C_{17}H_{13}O_3BrIN$	486	75	222
9	4i	H	CH_3	Cl	$C_{18}H_{16}O_3ClN$	329	82	195
10	4j	H	H	Br	$C_{17}H_{13}O_3BrN$	359	74	217

ANTIMICROBIAL ACTIVITY:

In vitro antibacterial activity:

The synthesized substituted 3-hydroxy-4*H*-chromen-4-one compounds were screened for their antibacterial activity by using agar cup method[20] against four different bacterial strains such as *Escherichia coli, Salmonella typhi, Staphylococcus aureus and Bacillus subtilis.* Nutrient agar was used for bacterial culture. The culture strains of bacteria were maintained on nutrient agar slant at 37ºC for 24 hrs. The penicillin is the standard drug used for antibacterial comparison purpose. The corresponding pure substituted 3-hydroxy-4*H*-chromen-4-one compounds were tested at a concentration 100 µg/ml in DMSO (Dimethyl sulphoxide). The diameter of zone of inhibition was measured in mm. 25 ml of sterile nutrient agar media for bacteria was poured into sterile petri dishes and allowed to solidify. The media was seeded with the organism by spread plate method using sterile roads. To make holes of 8 mm diameter carefully using a sterile cork borer and these were completely filled with the test solutions. The bacterial petri plates were kept in incubator at 37ºC for 24 hrs, and then the zones of inhibition were recorded.

In vitro antifungal activity:

The antifungal activity of substituted 3-hydroxy-4*H*-chromen-4-one compounds (**4a-j)** were screened against four plant pathogenic and mold fungi, such as *Aspergillus niger, penicillium chrysogenum, Fusarium moneliforme and Aspergillus flavus.* The antifungal activities of the synthesized 3-hydroxy-4*H*-chromen-4-one compounds were assessed by poisoned plate method.21 Griseofulvin (100µg/disc) was used as standard drug for the antifungal test. Potato Dextrose Agar (PDA) was used as basal medium for test fungi. The compound 100 µg were mixed with sterilized potato dextrose agar (PDA) medium at 40^{0}C of the rate 100 mg/mL PDA. The medium was poured in sterilized petri-plates and allowed solidified PDA media and then incubated at 30^{0}C for 72 hours. The growth of fungal area was measured in mm after 4 days of incubation at 30^{0}C. A control set was maintained using only PDA with DMSO as growth medium. Results were measured as the growth of fungi (does not show antifungal activity), reduced growth of fungi (to observed moderate antifungal activity), and no growth of fungi (antifungal activity observed in the area).

3. RESULTS AND DISCUSSION:

In this research work we have synthesized the novel substituted 3-hydroxy-4*H*-chromen-4-one derivatives (**4a-j**) were synthesized by oxidative cyclization of corresponding 2-hydroxychalcones (**3a-j**), and 30% hydrogen peroxide in basic medium. All these substituted 3-hydroxy-4*H*-chromen-4-one derivatives didn't give violet coloration with $FeCl_3$ solution and pink coloration with concentrated H_2SO_4. The structures of newly synthesized compounds have been confirmed by spectral data. The IR spectra of substituted 3-hydroxy-4*H*-chromen-4-one derivatives, showed present of 3-hydroxy (-OH) group in the broad peak at regions 3250-3295 cm^{-1}, 1615 cm^{-1} (>C=O pyrone ring)**.** The ^{1}H NMR spectra showed singlet proton Ar-OH in the region δ 9.3 ppm but absence of singlet in the region δ 12.10-14.10 due to proton of *ortho*-hydroxyl group in the phenyl ring of chalcone which clearly indicates the formation of substituted 3-hydroxy-4*H*-chromen-4-one. These observations are in agreement with the spectral data as reported.22-23

In vitro antibacterial activity:

The synthesized substituted 3-hydroxy-4*H*-chromen-4-one compounds were screened for their in vitro antibacterial activity measured and comparison with standard (penicillin) drug using the agar cup method against four different selected pathogens such as *Escherichia coli, Salmonella typhi, Staphylococcus aureus* and *Bacillus subtilis.* The antibacterial activity data as presented in **Table 2.** Among all these synthesized compounds 6,8-dichloro-2-(4'-dimethylamine-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4c**) and 8-bromo-6-chloro-2-(4'-dimethylamino-phenyl)-3-hydroxy -4*H*-chromene-4-one (**4f**) recorded 15mm,15mm, 22mm 17mm and 13mm, 14mm, 22mm, 17mm respectively, shows potent antibacterial activity against all the four strains of bacteria. The compounds 8-iodo-6-methyl-2-2(4'-dimethylamine-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4b**), 8-iodo-6-bromo-2-(4'-dimethylamino-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4h**) and compounds 8-bromo-2-(4'-dimethylamino-phenyl)-3-hydroxy -4*H*-chromene-4-one (**4j**) does not showed activity against *E. coli* while compounds 8-iodo-6-chloro-2-(4'-dimethylamino-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4d**), 8-iodo-6-bromo-2-(4'-dimethylamini-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4h**) and compound 8-bromo-2-(4'-dimethylamino-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4j**) exhibited significant antibacterial activity against *Salmonella typhi* as compared to standard penicillin drug with a zone of inhibition of 20 mm. The compounds 6, 8-dichloro-2-(4'-dimethylamino-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4c**), 8-bromo-6-methyl-2-(4'-dimethyamino-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4e**), 8-bromo-6chloro-2-(4'dimethylamino-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4f**) and 8-iodo-6-bromo-2-(4'-dimethylamino-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4h**) showed maximum antibacterial activity against *Bacillus subtilis* as compared with standard drug with zone of inhibition 17mm, 18mm 17mm and 18mm respectively as compare to zone of inhibition 22mm. The compounds 6, 8-dichloro-2-(4'-dimethylamino-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4c),** 8-bromo-6chloro-2-(4'dimethylamino-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4f**), 6, 8-dichloro-2-(4'-dimethylamino-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4g**) and 8-iodo-6-bromo-2-(4'-dimethylamino-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4h**) showed good activity against *Staphylococcus aureus* as compared with standard zone inhibition 34mm. The rest of the derivatives of 3-hydroxy-4*H*-chromene-4-one showed moderate activity against *S. aureus.* Thus the main structural feature responsible for antibacterial activity is the presence of different halogen and dimethylamino groups substituted in phenyl ring and also 4-oxo groups. The presence of halogens, dimethylamino and 4-oxo groups resulted in an increase of antibacterial activity of synthesized 3-hydroxy chromone compounds as compare to standard drug.

In vitro antifungal activity:

The newly synthesized 3-hydroxy-4*H*-chromene-4-one compounds were evaluated for their *in vitro* antifungal activity and comparison with (Greseofulvin) standard drugs by the Poison plate method against four different pathogens such as *Aspergillus niger, penicillium chrysogenun, Fusarium moneliforme* and *Aspergillus flavus.* The antifungal activity data showed in **Table No. 3.** The study revealed that the newly synthesized 3-hydroxy-4*H*-chromene-4-one compounds exhibited good antifungal activity as comparison with (Greseofulvin) standard drugs against four different pathogens.

Among these, the compounds 6, 8-dichloro-2-(4'-dimethylamino-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4c**), 8-Iodo-6-chloro-2-(4'-dimethylamino-phenyl)-3-hydroxy-4*H*-chromene-4-one (**4d**) and 8-bromo-2-(4'-dimethylamino-phenyl)-3-hydroxy-4*H*-chromene-4-one (4j) exhibited significant reduction in growth in four fungal strains. Thus the presence of halogens, dimethylamino, methyl and 4-oxo groups is responsible for antifungal activity of the 3-hydroxy-4*H*-chromene-4-one compounds.

8-Iodo-6-methyl-2-(4′-(dimethylamino-phenyl)-3-hydroxy-4*H*-chromen-4-one (4b):-

Yield 80 %, melting point 230^{0}C**, IR (KBr):** 3295 cm^{-1} (Ar-OH str), 3066 cm^{-1} (>C-H str), 1587 cm^{-1} (>C=C< str), 1291 cm^{-1} (>C-O str), 1622 cm^{-1} (>C=O pyrone ring), **^{1}H NMR (DMSO)**; δ 3.0 - 3.1 ppm (s, 6H, N-$(CH_3)_2$), δ 9.1 - 9.3 ppm (s, 1H, -OH at C-3 in pyrone ring), δ 6.6 - 8.2 ppm (m, 6H, Ar-H), **MS (m/z):** (M+1)=421

6, 8-dichloro-2-(4′-(dimethylamino-phenyl)-3-hydroxy-4*H*-chromen-4-one (4c):-

Yield 75 %, Melting Point: 225^{0}C**, IR (KBr):** 3294 cm^{-1} (Ar-OH str), 3062 cm^{-1} (C-H str.), 1582 cm^{-1} (>C=C< str), 1293 cm^{-1} (>C-O str), 1615 cm^{-1} (>C=O pyrone ring), **^{1}H NMR (DMSO)**: δ 3.0 - 3.2 ppm (s, 6H, N-$(CH_3)_2$), δ 9.2 - 9.4 ppm (s, 1H, -OH at C-3 in pyrone ring), δ 6.7 - 8.12 ppm (m, 6H, Ar-H), **MS (m/z):** (M+1) =349

6-bromo-8-methyl-2-(4′-dimethylamino-phenyl)-3-hydroxy-4*H*-chromen-4-one (4e):-

Yield 75 %, Melting Point: 220^{0}C **IR (KBr):** 3292 cm^{-1} (Ar-OH), 3057 cm^{-1} (C-H str.), 1587 cm^{-1} (>C=C< str), 1292 cm^{-1} (>C-O str.), 1612 cm^{-1} (>C=O pyrone ring) , **^{1}H NMR (DMSO);** δ 2.1-2.3 (s, 3H, CH_3), δ 2.9-3.2 (s, 6H, N-$(CH_3)_2$, δ 9.2-9.3 (s, 1H, -OH at C-3 in pyrone ring), δ 6.6-8.12 (m, 6H, Ar-H) ppm, **MS (m/z);** (M+1): =374

8-Bromo-6-Chloro-2-(4′-dimethylamino-phenyl)-3-hydroxy-4*H*-chromen-4-one (4f):-

Yield 82%, Melting Point: 98^{0}C **IR (KBr):** 3296 cm^{-1} (Ar-OH), 3063 cm^{-1} (>C-H str.), 1588 cm^{-1} (>C=C< str), 1294 cm^{-1} (>C-O str.), 1621 cm^{-1} (>C=O pyrone ring), **^{1}H NMR (DMSO):** δ 2.0 - 2.3 (s, 3H, CH_3), δ 2.8 - 3.2 (s, 6H, N-$(CH_3)_2$, δ 9.2-9.3 (s, 1H, -OH at C-3 in pyrone ring), δ 6.5-8.2 (m, 6H, Ar-H) ppm, **MS (m/z):** (M+1) =394

6-chloro-7-methyl-2-(4′-(dimethylamino-phenyl)-3-hydroxy-4*H*-chromen-4-one (4i):-

Yield 82%, Melting point: 195^{0}C, **IR (KBr**): 3291 cm^{-1} (Ar-OH), 3058 cm^{-1} (>C-H str.), 1586 cm^{-1} (>C=C< str.), 1294 cm^{-1} (>C-O str), 1612 cm^{-1} (>C=O pyrone ring), **^{1}H NMR (DMSO):** δ 2.2 - 2.4 ppm (s, 3H, CH_3), δ 3.0 - 3.2 ppm (s, 6H, N-$(CH_3)_2$), δ 9.3 - 9.4 ppm (s,1H, -OH at C-3 in pyrone ring), δ 6.7 - 8.15 ppm (m, 6H, Ar-H), **MS (m/z)**: (M+1) =329.

8-bromo-2-(4′-dimethylamino-phenyl)-3-hydroxy-4*H*-chromen-4-one (4j):-

Yield 74%, Melting Point: 217^{0}C. IR (KBr): 3292 cm^{-1} (Ar-OH), 3062 (cm^{-1}C-H str.), 1587 cm^{-1} (>C=C< str.), 1290 cm^{-1} (>C-O str), 1614 cm^{-1} (>C=O pyrone ring), **^{1}H NMR (DMSO):** δ 3.0-3.2 ppm (s, 6H, N-$(CH_3)_2$), δ 9.2-9.4 ppm (s, 1H, -OH at C-3 in pyrone ring), δ 6.9-8.20 ppm (m, 6H, Ar-H), **MS (m/z):** m+1=359.

Table – 2 : Antibacterial activity of 3-hydroxy-4*H*-chromen-4-one derivatives (4a-j)

Sr. No.	**Entry**	**molecular formula**	**Antibacterial activity (Zone of Inhibition in mm)**			
			Escherichia coli	*Salmonella typhi*	*Staphylococcus aureus*	*Bacillus subtilis*
1	4a	$C_{17}H_{13}O_3I_2N$	14	--	14	12
2	4b	$C_{18}H_{16}O_3IN$	--	13	13	13
3	4c	$C_{17}H_{13}O_3Cl_2N$	15	15	22	17
4	4d	$C_{17}H_{13}O_3ICln$	14	17	--	--
5	4e	$C_{18}H_{16}O_3BrN$	17	--	19	18
6	4f	$C_{17}H_{13}O_3BrClN$	13	14	22	17
7	4g	$C_{17}H_{13}O_3Br_2N$	16	--	26	12
8	4h	$C_{17}H_{13}O_3BrIN$	--	17	21	18
9	4i	$C_{18}H_{16}O_3ClN$	15	12	--	--
10	4j	$C_{17}H_{13}O_3BrN$	--	16	17	13
+ve Control DMSO			**-ve**	**-ve**	**-ve**	**-ve**
Penicilline			**12**	**20**	**34**	**22**

(-- = No Antibacterial activity)

Table – 3 : Antifungal activity of 3-hydroxy-4*H*-chromen-4-one derivatives (4a-j)

Sr. No.	**Entry**	**molecular formula**	**Antifungal activity (Zone of Inhibition in mm)**			
			Aspergillus niger	*penicillium chrysogenum*	*Fusarium moneliforme*	*Aspergillus flavus*
1	**4a**	$C_{17}H_{13}O_3I_2N$	-ve	-ve	RG	-ve
2	**4b**	$C_{18}H_{16}O_3IN$	-ve	RG	RG	RG
3	**4c**	$C_{17}H_{13}O_3Cl_2N$	-ve	-ve	Ve	-ve
4	**4d**	$C_{17}H_{13}O_3ICln$	-ve	-ve	-ve	-ve
5	**4e**	$C_{18}H_{16}O_3BrN$	RG	RG	-ve	RG
6	**4f**	$C_{17}H_{13}O_3BrClN$	RG	-ve	RG	RG
7	**4g**	$C_{17}H_{13}O_3Br_2N$	RG	RG	-ve	-ve
8	**4h**	$C_{17}H_{13}O_3BrIN$	-ve	-ve	RG	RG
9	**4i**	$C_{18}H_{16}O_3ClN$	-ve	RG	-ve	-ve
10	**4j**	$C_{17}H_{13}O_3BrN$	-ve	-ve	-ve	-ve
+ve Control DMSO			**+ve**	**+ve**	**+ve**	**+ve**
-ve Control (Griseofulvin)			**-ve**	**-ve**	**-ve**	**-ve**

[+ve = No growth (Antifungal activity absent), RG = Reduced growth (more than 50 % but less than 90 % i. e. Moderate activity), -ve = No Growth (Antifungal activity observed 90 %)]

4. CONCLUSION:

In this work, we have demonstrated the synthesis of 3-hydroxy-4*H*-chromen-4-one compounds using simple experimental procedure with high yields, relatively short reaction time, easy work up and low cost. Considering the results of antibacterial and antifungal activities, it can be concluded that the 3-hydroxy-4*H*-chromen-4-one compounds and the ring system, presence of halogens, dimethylamino, methyl and 4-oxo groups are responsible for the antibacterial and antifungal effects. The results obtained in all these assays during the study will certainly useful for further research in synthesis and designing antimicrobial of drugs.

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Conflict of interest:

The authors declare no conflict of interest.

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Removal of Indigo dye from wastewater using novel reactive absorptive material

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ABSTRACT:

Treatment of industrial wastewater, including the textile wastewater, is an important environmental issue. One of the pollutants of this industry is the Indigo dye. In this study, adsorption of Indigo dye by chitosan-bentonite-TiO_2 adsorbent was investigated experimentally. The adsorption process of this dye from the effluent, and its COD was examined under optimal conditions (contaminant concentration=100ppm, pH=1-10 and time=30min). This new adsorbent was characterized by using scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA) and X Ray Diffraction (XRD).

KEYWORDS**:** *Chitosan . Bentonite . Indigo . Wastewater . Dye.*

1. INTRODUCTION:

Over the past few years, more stringent environmental laws have been introduced, along with increased restrictions on wastewater discharging in most countries. These new laws pose new challenges for industries all around the world. The environmental organizations have set standards for the discharging of effluents after industrial processes. In general, the ultimate goal of wastewater treatment is to reduce wastewater contamination to acceptable levels for later use [1]. With the growth and advancement of technology, the volume of production of industrial wastewaters has increased, and during various processes, large volumes of organic and mineral pollution are entering wastewater [2].

Various industries have different types of contaminants depending on their products and activities. pH in wastewater is usually in alkaline range and COD and BOD are relatively high in production effluents. The presence of high levels of organic dye material in the textile industry is one of the means of differentiating it with chemical and food industries [3]. An estimated annual amount of 280,000 tons of wastewater containing various industrial dyes is introduced into the environment. The treatment of dye effluents using effective methods is one of the most important challenges facing environmental engineers [4]. Most of the constituents of textile wastewater are dyes, organic compounds, persistent organic compounds, toxic substances, surfactants, AOXs (Adsorbable organic halogens) and heavy metals. Dyes as one of the important groups of pollutants are the colors that once entered the water, cannot be well purified and sometimes refined due to their artificial origin and their complex molecular structure. Therefore dyes are hard to decompose and hard to treat [5].

The adsorption process is considered as one of the most efficient and most widely used water and wastewater treatment technologies in the world. So far, valuable efforts have been made to develop low-cost absorbents using agricultural, industrial and urban waste. The use of agricultural wastes as low-cost absorbents is appropriate in terms of reducing their costs for waste disposal and helping to protect the environment [6].

Chitosan is a naturally occurring amino-polysaccharide that results from the deacidification of chitin in alkaline conditions. Chitosan is used by researchers as a natural biodegradable polymer to remove anionic dye from color solutions. Its increasing use as a biochemical agent is due to two main reasons: its low cost and abundance in nature. It has excellent oxidation behavior, and therefore it can absorb many metals. The macromolecular structure of chitosan and its unique cationic character have led to a variety of properties and applications in various sciences such as biotechnology, water purification, pharmaceuticals, cosmetics, food industry and more [7].

In this study for the first time a novel Chitosan-Bentonite-TiO_2 compound has been synthesized and its properties have been characterized by SEM, FTIR, TGA and XRD. Its ability to absorb and remove Indigo dye with the associated COD has been investigated.

2. EXPERIMENTAL:

Materials and methods

Chitosan, Bentonite, ethylene glycol dimethylacrylate, 4,4-Azobis (4-cyanovaleric Acid) (ACV) and acetic acid are used for the synthesis of this novel adsorbent. Except for TiO_2, all of the materials are research grade from Sigma Aldrich. Industrial grade TiO_2, with purity: $\geq$ 99.9 wt%, APS: 20nm, SSA: > m^2/g, Density: 3.9 g/cm^3, Volume density: 0.25 g/cm^3, Appearance: spherical, Crystal form: Anatase, Color: white is used. Industrial grade Indigo is also used without further purification.

First, 0.1 g of chitosan is mixed with 20 ml of acetic acid and added to TiO_2. ACV is dissolved in 3 ml of de-ionized water and added to the solution and stirred for 10 minutes at 60°C. Then bentonite is mixed in 5 ml of de-ionized water and added to the solution with EGDMA and stirred for 6 hours at 60 minutes. After that, the neutralization process is performed with NaOH and rinsed with methanol. At the end, at an oven 50°C, the drying process is performed. We found the optimum ratio of the material as Chitosan = 0.1 gr, TiO_2 = 0.1 gr, Bentonite = 0.1 gr and ACV = 0.03gr.

Characterization and Performance

XRD and FTIR are used to detect the phase of the substance and to determine the changes in the chemical bond. SEM and TGA are also used to check the morphology and thermal stability of the resulting polymer.

COD was measured according to the EPA standard method 5220 In short, a 2.5 cc sample was treated with 1.5 cc of digestion solution and 3.5 cc of sulfuric acid. The resulting solution was exposed to 150 C temperature for 20s hours, and the COD number was read using a UV spectrophotometer [8].

3. RESULTS AND DISCUSSION :

Optimization of Bentonite Concentration

In this part of the study, the amount of all ingredients except for bentonite have been kept constant as follows: EGDMA = 0.5 ml, Chitosan = 0.1 gr, ACV = 0.02 gr, TiO_2 = 0.1 gr.

Table. 1 Variable amounts of Bentonite and the final product after synthesis.

Bentonite(gr)	(gr) Final Product	%Removal COD (100ppm Indigo dye)
0.02	0.094	34.17
0.05	0.134	41.72
0.07	0.178	47.34
0.10	0.199	64.36
0.12	0.201	62.68
0.15	0.202	61.25
0.17	0.202	58.83
0.20	0.205	54.15

The optimum amount of bentonite for effective removal of COD is 0.1 grams according to the data.

Optimization of ACV Concentration

All quantities of consumables except ACV have been kept constant. The amount of consumables EGDMA = 0.5 ml, Chitosan = 0.1gr, TiO_2 = 0.1gr, Bentonite = 0.1gr.

Table. 2 Variable amounts of ACV and the final product after synthesis.

ACV(gr)	(gr) Final Product	%Removal COD (200ppm Indigo dye)
0.01	0.187	52.43
0.02	0.199	64.36
0.03	0.207	73.21
0.04	0.209	58.87
0.05	0.210	44.64

The optimum amount of ACV for effective removal of COD is 0.3 grams according to the data.

Optimization of EGDMA Concentration

All amounts of consumables other than EGDMA have been fixed. The amount of consumables is Chitosan = 0.1gr, TiO_2 = 0.1gr, Bentonite = 0.1gr, ACV = 0.03gr.

Table. 3 Variable amounts of EGDMA and the final product after synthesis

ACV(gr)	(gr) Final Product	%Removal COD (200ppm Indigo dye)
0.25	0.171	65.76
0.50	0.207	73.21
0.75	0.261	82.30
0.10	0.224	66.19
1.25	0.189	61.97

The optimal EGDMA value is 0.75 ml according to the Table 3.

Analysis of TiO_2

The TiO_2 used in these experiments were analyzed by TEM and XRD and the results are shown in Figure 1

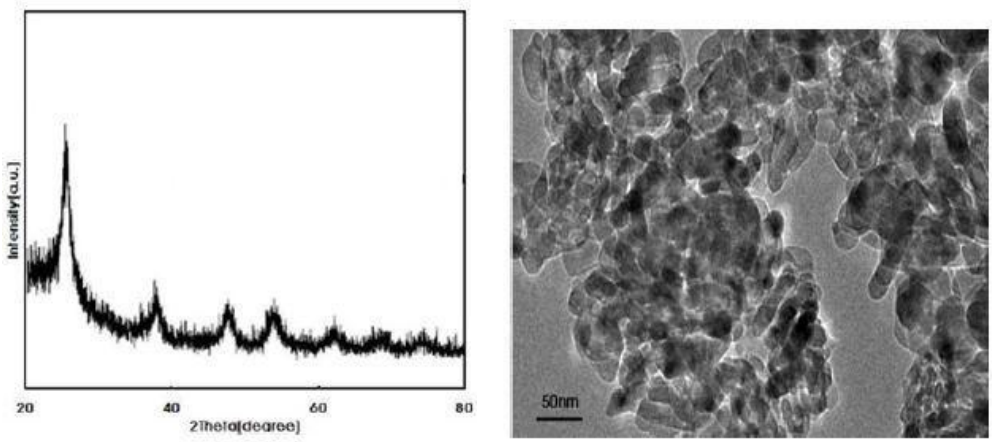

Fig. 1 Picture of TEM electronic microscope and XRD diffraction pattern from sample of TiO_2

Scanning electron microscopy (SEM)

Figure 1 shows the TEM image and XRD of TiO_2 and Fig. 2 illustrates the SEM images of chitosan-bentonite-TiO_2 under various resolutions. The particles on the synthetic polymer structure in a and b illustrate that TiO_2 is physically positioned on the polymer structure. Also, comparing image c and d with the SEM sample of chitosan [9], it can be seen that the resulting adsorbent has a rough surface, creating a much higher surface area, compared to pure chitosan.

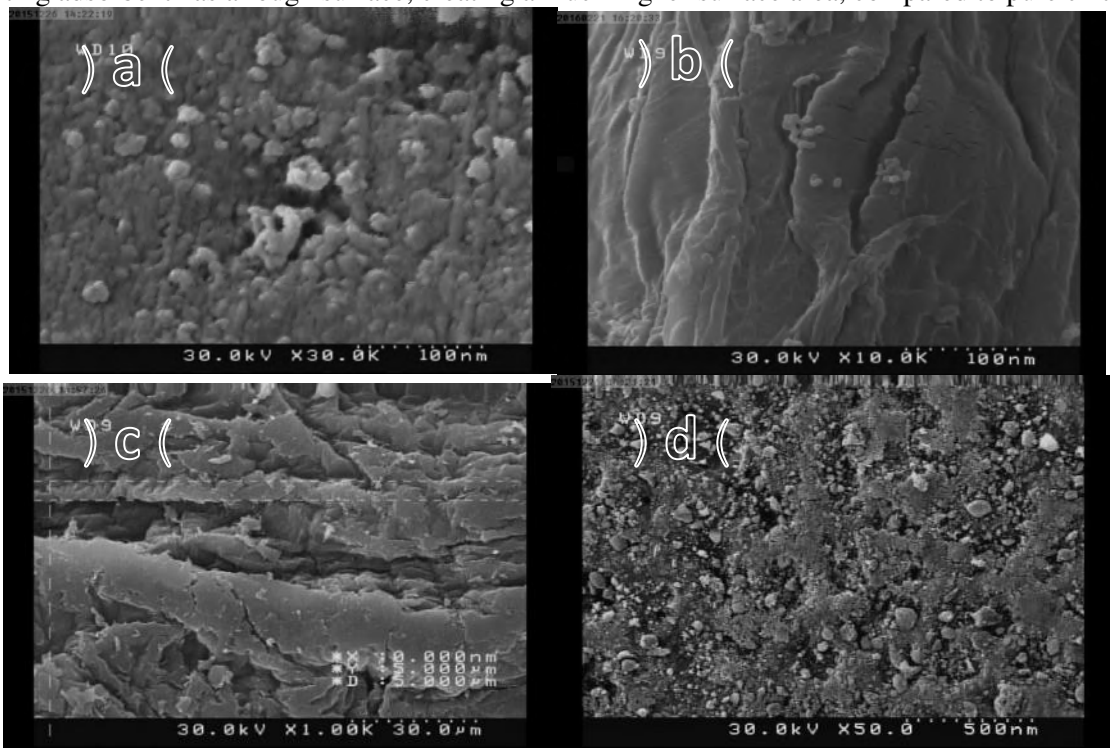

Fig. 2 SEM images of Chitosan-Bentonite-TiO_2 with different resolution

Fourier-transform infrared spectroscopy (FTIR)

According to the Chitosan FTIR diagram [9] and its comparison with the FTIR taken from the chitosan-bentonite-TiO_2 sample shown in Fig. 3, a spectral difference between the two chitosan spectra and Chitosan-bentonite-TiO_2 can be observed that can be described as follows:

The tensile vibration of NH and OH from 3436.27 cm^{-1} to 3417.21 cm^{-1}, the stretching of the symmetric CH_3 from 2879.02 cm^{-1} to 2853.96 cm^{-1}, the tensile vibration of C = O from 1605.68 cm^{-1} to 1637.82 cm^{-1}, the tensile vibration of CN from 1423.00 cm^{-1} to 1453.38 cm^{-1}, the curved vibration of CH_3 from 1379.60 cm^{-1} to 1379.22 cm^{-1}, the tensile vibration of NH_2 from 1255.43 cm^{-1} to 1295.84 cm^{-1}, the bending vibration of the COC from 1154.11 cm^{-1} to 1154.94 cm^{-1}, the tensile vibration of C-OH from 1089.91 cm^{-1} to 1048.23 cm^{-1} have been found. A number of additional peaks are observed after synthesis of binding to primary chitosan, which include: 13106.16 cm-1 with a bond of OH and Ti-O, in 2959.08 cm^{-1} with CH bond, in 2928.59 $cm^{-1}$with a CH bond, in 2020.99 cm^{-1} with a CC bond, in 1891.86 cm^{-1}

with a C = O bond, in 1723.29 cm^{-1} with a bond of C = O, in 1405.57 cm^{-1} with NC bond, in 1321.85 cm^{-1} with Al-O bond, in 1245.58 cm^{-1} with a bond of O = Si, in 885.61 cm^{-1} with Ti-O-Ti is observed, which adds to the presence of bentonite and TiO_2 in the synthesized material.

a

b

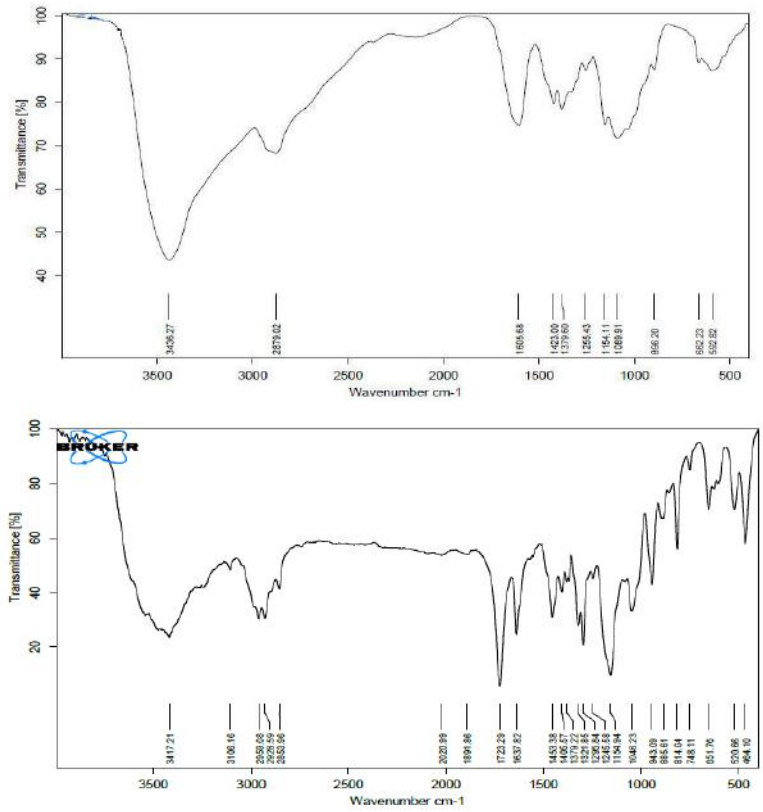

Fig. 3 FTIR diagram of Chitosan (a) [9] and Chitosan-Bentonite-TiO_2 (b)

Thermogravimetric analysis (TGA)

Fig. 4 shows the results of TGA-DSC analysis of the synthesized adsorbent. As compared to pure chitosan [9], this chitosan-bentonite-TiO_2 is thermally less stable, showing degradation at 220 ºC with an associated large exotherm and again at around 330 ºC. The lower thermal stability is expected due to newly formed bonds. However for the purpose of water decontamination, stability upto 220 ºC is quite sufficient.

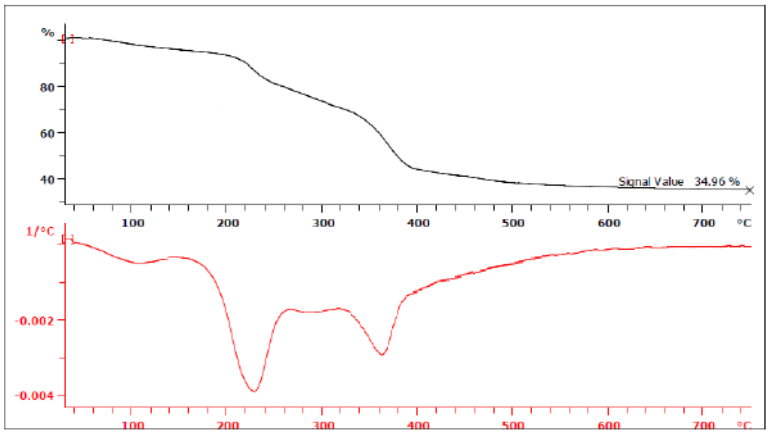

Fig. 4 Thermogravimetric analysis diagram of Chitosan-Bentonite-TiO_2

X Ray Diffraction (XRD)

The structure of the product was compared with pure chitosan using XRD. The XRD pattern of chitosan has been shown in articles [9] in two peaks of 2θ= 10, 20° and revealing high crystallinity. The crystalline structure of chitosan is a result of high levels of intramolecular bonds between hydroxyl and amino groups [10-11]. In addition, the chitosan structure has a special order. As a result, chitosan can easily form crystalline parts.

The characteristic peaks of grafted chitosan at 2θ = 10° and 20° disappeared, and a very weak and broad peak appeared at 2θ = 20°. This could be attributed to the deformation of the strong hydrogen bond in original chitosan due to the substitution of acid functional group and amid groups, which efficiently destroyed the regularity of the packing of the

original chitosan chains (Figure 5). Other characteristic peaks are 2θ =25-38-48-55-63-75-82 which conform to the Anatase phase JCPDS standard.

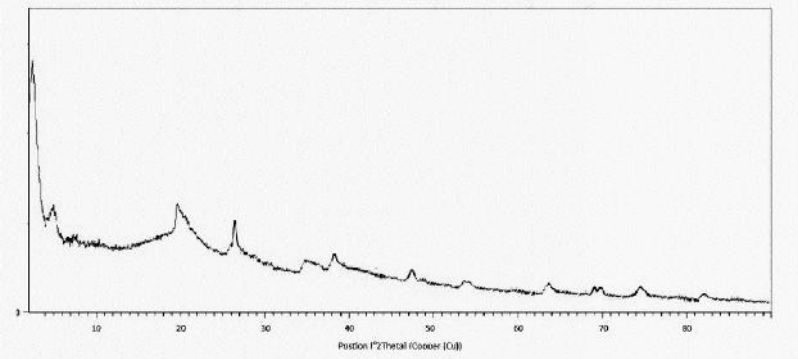

Fig. 5 X Ray Diffraction pattern

Capacity to remove COD

Fig. 6 shows the capacity of 0.01 gr of each of absorbents for removal COD from 10 cc of an indigo-tapwater solution with an initial COD of 285 mg/L. The novel adsorbent, chitosan-bentonite-TiO_2, is effective in removing up to a 100 ppm concentration of COD from the indigo solution and falls off in higher concentrations, and is consdierably more effective than pure chitosan and pure bentonite. the synthesized material of Chitosan-Bentonite-TiO_2 has been removed better than Chitosan and Bentonite.

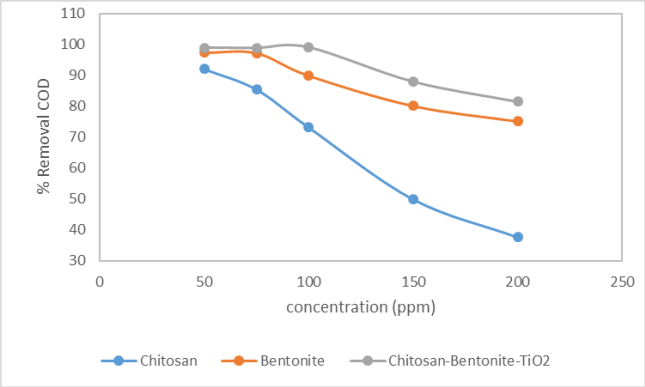

Fig. 6 Effect of Indigo concentration on COD reduction by the three different adsorbents

Effect of Solution pH

According to the Fig. 7, the synthesized absorbent shows a broad range of effectiveness, more than 95%, for removal of COD, which makes it useful for treatment of industrial wastewater without a need for expensive pH adjustment. It shows better performance than pure chitosan and pure bentonite in the entire pH range. The optimum pH for COD removal by Chitosan is about 8 and for Bentonite is 4.

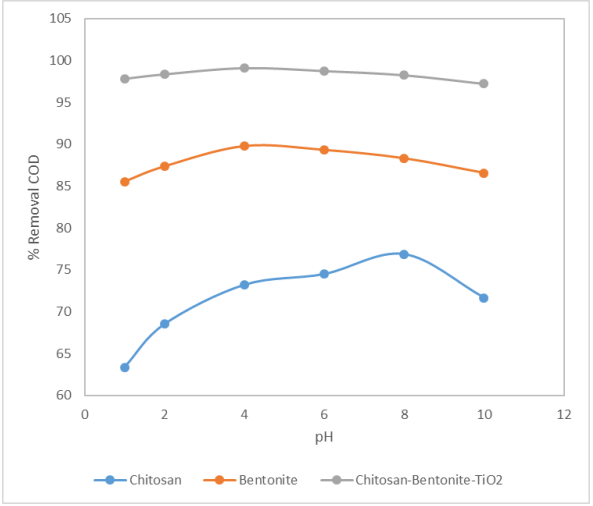

Fig. 7 Effect of solution pH on COD reduction by the three different adsorbents

Effect of time of absorption

Figure 8 shows that the synthesized absorbent is faster than bentonite or chitosan alone. Almost 100% COD removal is achieved after 30 minutes, whereas bentonite and chitosan require more than 60 minutes to reach equilibrium. The final COD achieved using chitosan as a adsorbent is 114 mg/L, for bentonite is 19 mg/L, and for chitosan-bentonite-TiO_2 is 3 mg/L.

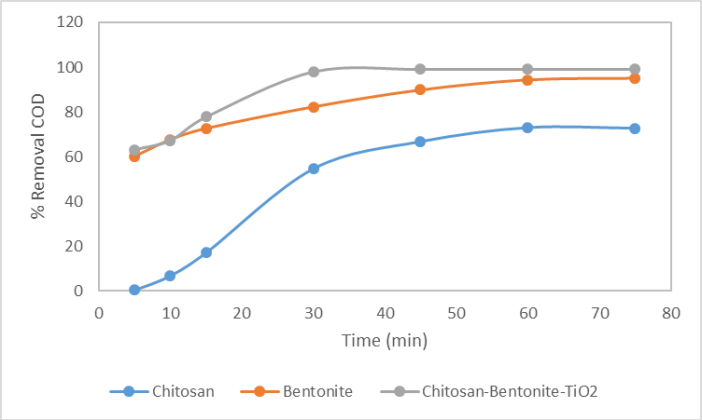

Fig. 8. Effect of time of absorption on COD reduction by the three different adsorbents

4. CONCLUSIONS:

Chitosan-Bentonite-TiO_2 was synthesized and the properties are investigated with SEM, FTIR, TGA and XRD. The optimal ratio of reactants is found to be: Bentonite = 0.1 gr, ACV = 0.03 gr and EGDMA=0.75 ml. SEM analysis shows that the morphology of Chitosan-Bentonite-TiO_2 is rough with a porous surface compared to pure Chitosan which is smooth and dense surface. FTIR spectra of grafted chitosan displays various new peaks showing newly formed bonds during the synthesis including Al-O, O = Si and Ti-O. Thermogravimetric analysis (TGA) shows that the newly formed polymer composite has a lower thermal stability as significant weight loss is observed at 230°C and 270°C. X-ray Diffraction Analysis (XRD) shows that the characteristic peaks of grafted chitosan at $2\theta = 10°$ and 20° disappeares, and a very weak and broad peak appeares at $2\theta = 20°$. Other characteristic peaks are 2θ=25-38-48-55-63-75-82 for TiO_2 in the Anatase phase, which is consistent with its JCPDS.The synthesized material shows promising results in removal of COD from indigo solutions compared to pure chitosan and bentonite over a very broad range of pH 1 to 10 with faster kinetics, achieving nearly 100% removal of COD in about 30 minutes.

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Detection of Adulterants Using Available Chemicals and Simple Techniques

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ABSTRACT:

Food is one of the basic needs for very living beings and is very important aspect of life. Health of human being depends on quality of food that they consume. Now a days foods are affected by different adulterants. Food is declared to be adulterated when some prohibited or cheaper substance is added / removed partially or wholly. Some food is completely imitated or artificial in other chemicals (like colour, flavour, processing) are added to improve its appearance and taste. In a country like India main cause of adulteration is to gain profit, increase weight of commodity and to lower the cost so as to compete with the market. Food prepared, packed or stored in unhygienic condition is also one of major cause of adulteration. Food adulteration is punishable act and many rules have been imposed by FSSAI but still adulteration is reported on daily basis. Awareness and knowledge of detecting common adulterant by simple methods can prove to be a one of weapon to fight against adulteration. Day to day food can be screened with little basic knowledge that is discussed in this paper so that safe food can be a goal for all citizen.

KEYWORDS : *Adulterant, appearance, profit, FSSAI and safe food.*

1. INTRODUCTION :

The healthy well being of mankind depends on the quality food they consume (Sunita and Sangita, 2019). Food adulteration is the process in which the quality of food is lowered either by the addition of inferior quality material or by extraction of the valuable ingredient (Sasi and Milcah, 2018). Food should be without or only with acceptable and safe levels of adulterants, contaminants or any other substances that may make food hazardous to health (Gahukar, 2014). Also, such food can deprive development (Majumdar, 2010). Therefore, health hazards related to foods and food products are considered to be a major problem particularly in developing and less developed countries (FAO, 2010; WHO, 2007). Adulterants are those substances which are used for human consumption (foodsafetyhelpline.com). Adulteration not only includes the intentional addition or substitution of materials but also the incidental contamination during the process of preparation, storage and transportation (Pradeep *et al.* 2016)

There are three types of adulteration -

i. Intentional adulterants: are sand, marble chips, stone, mud, chalk powder, water, mineral oil and coal tar dyes. This adulteration cause harmful effects on the body.
ii. Metallic contamination : include arsenic from pesticides, lead from water and mercury from effluents of chemical industries, tin from cans etc.
iii. Incidental adulterants: are pesticide residues, tin from can droppings of rodents, larvae in foods. Metallic contamination can also occur incidentally. Pests such as rodents and insects entered into food at high degree and produce filth in the form of excreta. The most common incidental adulterants are pesticides D.D.T. and marathon residues present on plant product. The maximum permissible residue allowed for D.D.T., Marathon is 3 ppm. D.D.T. is absorbed by the small intestine when ingested. The toxins usually pile up in the fatty tissues of such vital organs as the thyroid, heart, kidney, liver, mammary gland, and damage these organs. They can be transferred from the umbilical cord / blood to the growing foetus and through breast milk in children. Health hazards of food adulterants are depicted in Table 1.

Table 1. Health hazards of adulteration

Sr. No.	Adulterant	Food articles	Effect on health
1.	Argemone oil	Oils and fats	Epidemic dropsy, glaucoma, blindness, cardiac arrest.
2.	Pesticide residue	All types of foods	Acute or chronic poisoning with damage to nerves and vital organs.
3.	Mineral oil (used motor oil)	Oils and black pepper	Diarrhoea, Vomitting, cancer
4.	Methyl / alcohol	Alcoholic liquors	Blurred vision, blindness, death
5.	Lead chromate	Turmeric and powder mixed spices	Anemia, brain damage

6.	Metanil yellow	Turmeric, mixed spices, saffron, dehusked pulses, rice, golden beverages	Tumours, cancer, testicular degeneration in males.
7.	Lead	Tap water, some processing foods	Lead poisoning, causing foot drop, anemia, brain damage
8.	Kesari Dal	Pulses and besan	Paralysis of legs
9.	Dung	Coriander powder	Tetanus
10.	Iron filling	Suji, tea leaves	possibility of tetanus

Source: YOJANA April 16, 1980, Page 16, Government of India.

Food fraud is economically motivated. Food defense is considered to be food fraud and the motivation includes the intention to inflict public harm or threaten consumer. The harm associated with food fraud on public health is generally negligible, however sometimes mistakes and unintended health consequences occur (Johnson, 2014). Table 2 outlines the public health risk associated with various food risk types.

This is the simple contribution that deals with knowledge and awareness of common people about food adulteration. It also aims to measure the adulteration in food products through standard lab testing procedures by using available chemicals at home.

Table 2. Food protection Risk: Examples, Cause and effects

Risk Type	**Example**	**Cause and Motivation**	**Effect**	**Public health risk type**	**Secondary Effect**
Food Quality	Bruising of fruits accidentally	Mishandling	Possible additional contamination	None, or possible food safety	Brand equality or food safety incident
Food Fraud	Adulteration of milk with melamine intentionally	Increased profit margins	Toxic poisoning	Food safety	Public fear and possible lower prices industry wise
Food Safety	Contamination of raw vegetables unintentionally with *E.coli*	Protection and control during harvesting and processing is limited	Illness and / or death	Food safety	Damaged industry, recall expense, and public fear
Food Defense	Contamination of ground beef with nicotine intentionally	Revenge against the manager	Nonlethal poisoning	Food defense	Adulterated product, damaged industry, recall expense, public fear

Source: Spink *et al.* (2011)

2. Measures of Government to control adulteration:

The food safety and standards authority of India is an agency of the ministry of health and family welfare, government of India. (Manual of methods, 2012). To control adulteration the FSSAI has been established under food safety and standards Act, 2006. It consolidates various acts and orders that have hitherto handled food related issues in various Ministries and Departments. FSSAI has been created for laying down science based standards for articles of food and to regulate their manufacture, storage, distribution, sale and import to ensure availability of safe and wholesome food for human consumption. Along with the regulations in farming, production, packaging, transportation etc, FSSAI performing following important programmes.

i. Creating an information network across the country so that the public, consumers, panchayats etc., receive rapid, reliable and objective information about food safety and issues of concern.
ii. Provide training programmes for persons who are involved or intend to get involved in food business.
iii. Contribute to the development of international technical standards for food, sanitary and phytosanitary standards.
iv. Promote general awareness about food safety and food standards.

Government authorities with great efforts have succeeded in reducing the recurrent occurrences of adulteration. However, increased demand during festival season leads to rampant adulteration. Paneer, Khoa, Milk, Oils, Ghee etc. are the most targeted items. Milk and milk products are generally adulterated with starch which is used to give a thick, rich texture to these products. Urea, washing soda, alkali, etc., are the ingredients which are used to prepare synthetic

milk. Mustard seeds and mustard oil is generally adulterated by argemone seeds. Also, 'Palm Stearin', a non-edible by product of crude palm oil, is used as an adulterant is Vanaspati glsee. Artificial colours and dyes are used in the sweets to improve appearance and aroma.

3. Impact of Adulterants:

Now a days, it is very common to hear or read news about the food items being adulterated and such products are being openly sold out and are consumed by people, which cause various health hazards (Sharma, *et al.,* 2017). Human health is highly sensitive to food adulteration and sometimes shows immediate side effects like diarrhoea, dysentery and vomiting. For example, coffee powder substituted with date seed power or tamarind can cause diarrhoea (Lakshmi, 2012). News has shown how milk and milk products are being adulterated with urea, soap and other hazardous chemicals (Karla *et al.,* 1999; Venkateshwar, 2001). Also vegetables are beings injected to make them grow overnight. In chickens, steroids were being injected to make them into a hen in a very short period of time. Bacteriological profile of street foods in Mangalore was also done whose results were in accord. (Bhaskar, *et al.,* 2004). Adulteration of food leads to several health issues in humans (Nageswararao *et al.,* 1989; Bhatia *et al.,* 1999). Few health hazards include stomachache, bodyache, anemia, paralysis and increase within the incidence of tumors, pathological lesions in very important organs, abnormalities of skin and eyes (Shah *et al.,* 1999). Thus food adulteration ought to be very important because of its impact within the health significance of the public (Beniwal and Khetarpaul, 1999). The individuals are laid low with heart disease, kidney failure, skin diseases, asthma attack and alternative chronic diseases. The individuals are unfortunate victims of this adulteration trade running in full swing and uncurbed.

4. Test of Adulterants in various food items :

The following some food groups can be tested for the various adulterants at home with little effort using household and other chemicals.

1) Spices and condiments
2) Pulses
3) Milk and milk products
4) Fats and oils
5) Green vegetables and fruits

Table 3. Test for spices and condiments

Items	Adulterants	Interface	Reason for Adulteration	Health effects
Chilli powder	Brick Powder	1. Brick powder settles fast and chilli powder settles slowly when added into glass of water. Further rubbing the sediments will give the feel of grittiness. 2. To a little powder of chilli, add small amount of toilet cleaner and mix to the consistency of paste, dip the rear end of a match stick into the paste and hold over the flame, brick red flame colour due to the presence of calcium salts in the brick powder.	To increase the quantity	Stomach disorder
	Colour impurity	Water soluble colour can be detected by sprinkling a small quantity of powder on full glass of water. The water soluble colour will start descending in colour streak.	To improve the texture and feel of spices	Can cause cancer
	Starch	To test for starch, add few drops of tincture Iodine solution to the powdered spice. The appearance of bluish colour change, it shows the presence of starch.	To improve the bulk	Stomach disorder

Turmeric powder	Any powder (Starch, wheat flour, etc.) coloured with Metanil yellow)	Add few drops of toilet cleaner to the sample. Instant pink / voilet colour, which disappears on dissolution with water, indicates pure turmeric. If colour persists hence metanil yellow is present	To increase the quantity and texture of powder.	Stomach Disorder, Neurotoxic, (Nagraja and Desiraja, 1993), hepatotoxic (Saxena and Sharma, 2015)
	Chalk powder	Also, if the mixture releases small bubbles, it indicates the presence of chalk powder.		Not very toxic but may causes stomach disorder, kidney stone.
	Lead chromate	1. Mix a teaspoon of turmeric powder in a glass of water. If adulterated, it will immediately leak streaks of water-soluble colour. 2. Shake 1/2 taspoon with 5 ml of water and add a few drops of toilet cleaner. Pink colour indicates the presence of lead chromate.		Can damage all of the body system, including the heart, intestines, bones, kidneys, teeth, reproductive organs and the nervous and immune systems (Newman, 2018)
Asafoetida (hing)	Soapstone, other earthy matter	Shake a small quantity of powdered sample with water. Soapstone or other earthy matter will settle down at the bottom. If starch is added into it on dissolution in water a solution will turn turbid and retained after some time while pure hing solution will again turn into colourless solution	To increase the quantity	
Black pepper	Papaya seeds, light berries, etc.	1. Shake a small quantity of sample with water. Papaya seeds will float in water and black pepper will settle down. The results can be further improved if it is used spirit or nail polish remover instead of water. 2. Visually black pepper are black in colour and papaya seeds are brownish black and shrunken and oval in shape	To increase the quantity and making more profit.	Dhanya *et al.* 2009
Cumin seeds (*Jeera*)	Grass seeds coloured with charcoal dust	Rub cumin seeds on palm turns black	To increase the bulk	
Dhaniya powder	Horse dung	1. Soak little dhaniya powder in water. Horse dung will float and give foul smell. Natural smell of dhaniya powder will not be there. 2. Keep most dhaniya powder for 1-2 days, colonies of bacteria will grow if dung is present in it, it will give foul smell.	To increase the quantity	

Saffron	Coloured dried tendrils of maize cob	Genuine Saffron will not break easily but arificial saffron breaks. Artificial saffron lose colour before lasting whereas real saffron continues to give colour till end	To increase the quantity	
Clove	Magnesium, salt, sand, earth	Exhausted cloves can be identified by its small size and shrunken appearance. The characteristic pungent taste of genuine clove is less pronounced in exhausted cloves.	To increase profit	Philip *et al.,* 2001
Cinnamon Bark	Cassia Bark	Cinnamon bark is very thin and can be rolled around a pencil or pen. It also has a distinct smell. Cassia bark is very thick and stiff and cannot be rolled. Carsia bark comprises of several layers in between the rough outer and inner most, smooth layers. On examination of bark closely, a clear distinction can be made.		

Table 4. Test for Rulses

Items	**Adulterants**	**Interface**	**Reason for Adulteration**	**Remark**
Arhar	Kesari dal	1. Visual test- It is slant on one side and square in appearance in contrast to other dal. 2. Add 3-4 drops of toilet cleaner to small amount of dal in water and keep on simmering water for about 45 min. The pink colour indicates the presence of Kesari dal.	To increase quantity	
	Metanil yellow	Add toilet cleaner to small quantity of pulse. Keep on simmering water for about 15 min. The pink colouration indicates the presence of metanil yellow.	To enhance texture of yellow dal	Stomach Disorder Neurotoric[7], hepatotoxic[8]
All yellow pulses (Chana, Arhar, Dhuli, Moong, etc.)	Lead Chromate	Shake 5 gm of pulse with 5 ml of water and add a few drops of toilet cleaner. Pink colour indicates the presence of lead chromate		Can damage all of the body systems, including heart, intestines, bones, teeth, kidneys and reproductive organs, nervous and immune system (Newman, 2018)

Table 5. Tests for milk and milk products

Items	**Adulterants**	**Interface**	**Reason for Adulteration**	**Remark**
Milk	Water	Put a drop of milk on a polished vertical surface (provided some other thickening material is not added into it). The drop of pure milk flows slowly	To increase the quantity of milk	

		leaving a white trail behind it whereas the drop of milk adulterated with water will flow immediately without leaving any mark.		
Synthetic milk (mixture of water, area, soap, or detergent, stabilizer, sodium hydroxide, vegetable oil and salt)	Urea / detergent or soap / sodium hydroxide	Take small amount. Add 1/2 teaspoon of soybean or arhar dal powder. Mix up the contents thoroughly. After 5 min. add 1/4 spoon of turmeric powder in it. A change in colour from yellow to red indicates the presence of urea / washing powder in the milk.	To make profit / money.	
Khoa, Paneer and other milk products	Starch	Take a small sample of product, add 20 ml of water and bring it to boil. Cool to room temp. and add 1-2 drops of tincture iodine solution. If the solution turns blue then it indicates the presence of starch.	To give thick and rich texture	Stomach disorder
Ghee	Mashed potato, Sweet potato etc.	Boil 5 ml of sample, cool it and add a drop of tincture iodine solution. Blue colour indicates the presence of mashed potatoes.	To increase quantity and thickness	
	Vanaspati Margarine	Melt a small quantity of ghee and then add equal quantity of toilet cleaner, shake it well for one minute. Crimson red colour appears if Vanaspati or margarine is added	To make profit	Cardiovascular disease (Liu, 2017)

Table 6. Tests for oil, fats and others

Food Items	**Adulterants**	**Interface**	**Reason for Adulteration**	**Remark**
Mustard oil and Coconut oil	Argemone oil	Heat the mixture of oil with little amount of toilet cleaner for 2-3 min. Red colour appears	To increase the quantity and consistency	Epidemic dropsy, Carcinogenic (Babu *et al.,* 2007)
Coconut oil	Cheap oils	Freeze the oil in refrigerator for 1-2 hr, some oil remains in liquid form	To increase the quantity	
Honey	Sugar syrup, Glucose solution or starch	1. Refrigerate honey bottle, if it is pure will not solidify. 2. Take a cotton wick soak it with honey now burn. If sugar syrup is added, it burn with pop up sound.	To increase the quantity	Harmful for diabetic patients
Bura Sugar	Washing, Chalk Powder	1. Effervescence with toilet cleaner. 2. To the solution of bura powder in water add 1/4 tea spoon of haldi, will turn red.	To increase quantity and its consistency	May cause kidney stone
Jaggery	Metanil yellow	Dissolve jaggery in water then add toilet cleaner to it, colour changes to Magenta	To enhance the texture	Stomach disorder, Neurotoxic[7], hepatotoxic[8]
Tea and Coffee	Iron Filling	Move a magnet over tea or coffee, iron filling will click to it.	To increase quantity and weight	

	Tea coloured leaves	Rub leaves on white paper, artificial colour comes out on paper	To increase quantity and profit	
	Used tea	Tea leaves sprinkled on wet fitter paper. Pink or red spots on paper show colour	To earn more profit	
Coffee	Chicory, Tamarind seeds powder and date seed powder	1. Gently sprinkle the coffee powder sample on the surface of water in a glass. The coffee floats over the water but chicary begins to sink down within a few seconds. The falling chicary powder particles leave behind them a trail of colour, due to large amount of caramel. 2. Sprinkle the suspected coffee powder on white filter / blotting paper and spray 1% sodium carbonate solution on it. Tamarind and date seed powder will, if present, stain blotting paper / fitter paper red.	To earn more profit	Patrizia *et al.*, 2010 Downey *et al.*, 1997

Table 7. Tests for vegetables and fruits

Food Items	**Adulterants**	**Interface**	**Reason for Adulteration**	**Remark**
Green vegetables (Beans, Spinach, Parmal, Capsicum, Lady finger, Tori, Frozen matar, Bitter guard Kakora etc.)	Sprinkled or dipped in solution of malachite	Take a cotton piece soaked in liquid paraffin / vegetable oil and rub the outer green surface of a small part of green vegetable. If the cotton turns green, it can say that the vegetable is adulterated with malachite green.	To give attractive and fresh look	Cause carcinogenesis, mutagenesis, chromosomal fractures, teratogenecity and respiratory toxicity (Mani and Bharagava, 2016)
Apple	Coated with wax	Scratch the surface of apple with the help of knife, if some semisolid mass comes out, it is coated with wax	To prevent weight loss	
Black berries (*Jamun*)	Dipped in solution of crystal violet	Dip Jamuns in lukewarm water for 5 min. purple colour appears in water	Improve the brightness	Cause mitotic poison, potent careinogen and clastogene promoting tumor growth (Mani and Bharagava, 2016)

List of chemicals used (Available at home)

i. Toilet cleaner : Dil/con. HCI (Hydrochloric acid)
ii. Nail paint remover : Acetone
iii. Washing Soda : Sodium carbonate (Na_2CO_3)
iv. Edible Soda : Sodium bicarbonate ($NaHCO_3$)
v. Vinegar : 5% acetic and (CH_3COOH)
vi. Lemon juice : Citric acid
vii. Turmeric powder : Indicator
viii. Tincture Iodine : Iodine (I_2)
ix. Wax

Spices, condiments and Pulses

Consumers are not often aware of adulteration particularly in the pre-packaged food and the food that is categorized as loose. (e.g without any branding or packaging). This has relevance to the illiterate consumers who get often confused to the illiterate consumers who get often confused about the quality norms of permitted additives and become victim of irregularities or malpractices in the market.

In wholesome species, condiments and pulses dirt, dust, pebbles, stone, straw, damaged seeds, animal or bird excreta, dead insects may be present. Such adulterants can be easily recognized by naked eye examination. These can easily be separated just by hand picking. Problems, in this regards, will arise when that cannot be recognized visually and they are added into it intentionally and smartly to increase sale and earn more money from the items. The split grains or flour of pigeon pea or chick pea are adulterated with grass pea *(Lathyrus sativus)* while preparing snacks or meals. Sudarshan *et al.* (2009) reported metanil yellow in parboiled rice turmeric powder and split pulse grains. Some of the food items that are frequently found to be adulterated are depicted in table 3 and 4 along with the chemical test which can be easily performed at home using household chemicals.

Milk and Milk Products

Milk is considered to be the ideal food because of its abundant nutrients required by all (young and old). Everyone wants to consume milk and its products in sufficient amount. Unfortunately milk is being very easily adulterated throughout the world and in India. This is because, India is the largest country in milk production and consumption according to WSPA (World Society for the Protection of Animals) and the National Dairy Development Board, India. In Brazil, the fifth largest milk producer in the world and has 4.3% of global consumption (Hardings, 1999), until recently, liquid milk used to be the major target of food frauds (Kartheek, *et al.,* 2011). Milk can be adulterated with water, neutralizers to mask acidity, salt or sugar to mask extra water or high solid contents, cheese whey, among others (Fertig, *et al.,* 2004). Adulterants in milk and its product cannot be seen by naked eye, but it can be tested easily even in home by adopting simple tests on given in Table 5.

Oil, fats and miscellaneous

Vegetable oils and fats have a big contribution in our diet as cooking or frying oil, salad oil or in food products formulation. These are so expensive, hence there is temptation to adulterate them with other lower price vegetable oils and fats to achieve more profit, as given in Table 6. From the point of nutrition, the mixing of rancid oil in edible oils destroys vitamins A and E (Majumdar, 2010). Admixture of oleomargarine (a product of beef fat) in butter and gelatin, and formaldehyde in milk are common adulterants (Jaiswal, 2011).

Vegetables and fruits

A systemic fungicide (benomyl) in applied to vegetables to inhibit the growth of microorganisms and to avoid spoilage (Gahulcar, 2014). Vegetables and fruits are coloured (Majumdar, 2010) with the dye and waxed to enhance their colour and texture. The wax (containing morphiline as a solvent and emulsifier) is spread on fruits to retain moisture, prevent bursting and physical damage, enhances appearance and to extend storage period / shelf life. However,

the wax content in the market samples is below the Acceptable Daily Intake (ADL) of 2.0-3.6 μg/kg body weight / day (Bhat *et al.* 1997) Unripe fruits are artificially ripened with ethylene to retain firmness and to give ripening appearance (Siddiqui, *et al.,* 2010) Powder of calcium carbonate containing traces of arsenic and phosphorus is applied to fruits; fruits and vegetables are plumped up with injection of hormone 'Oxytocin' to retain freshness, and coloured water is injected into water melon to impart redness to pulp (Siddiqui, *et al.,* 2010) Simple tests of adulteration of fruits and vegetables are elaborated in table 6.

5. CONCLUSION

Food adulteration is worse in developing and under developing countries due to the absence of adequate monitoring and lack of proper law enforcement. It can be concluded that there is a lot of adulteration being done in different food products and when these food products are consumed, they are causing a lot of health issues to consumers. Most of the studies reviewed showed that consumers were moderately aware of the adulteration but were unable to detect them at their household level and also are unaware of the health issues caused by the adulterated food. Therefore, consumers have to be alert and check the adulteration by their own time to time using simple and easy experiments discussed above to keep themselves healthy.

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Corrosion inhibition studies of Al 5052 alloy by using 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol from electrochemical methods

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ABSTRACT:

Al 5052 is a metal which is commonly used in industries and manufacturing of equipment for most industries round the world. It is cheaper in cost compared with the other metals and its durable, hard and easy to wear physical properties make it a major choice in the manufacture of equipment parts. The main problem through the uses of Al 5052 in industry is its resistance against corrosion, especially in acidic solutions. This case lead to raise the cost of maintenance of equipment that used Al 5052 and as a result increased costs for the company. Organic corrosive inhibitors that also act as green chemicals, 4- hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol have been synthesized. This inhibitor is tested as corrosion inhibitor on a Al 5052 sample in 1M hydrochloric acid solution (HCl) using electrochemical measurements test includes PD (Potentiodynamic), EIS (Electrochemical Impedance Spectroscopy), OCP (Open Circuit Potential). The obtained results indicate that 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol acts as a good corrosion inhibitor for AL 5052 sample in HCl solution with efficiency above 90%. Changes in the impedance parameters postulated adsorption on the AL 5052 specimens' surfaces of, which it going to the formation of protective coating layer. It also shows that 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol corrosion inhibitors are effective in helping to reduce and slow down the corrosion process that occurs on Al 5052 surface in hydrochloric acid solution. Increase of corrosion inhibitor concentration provides a protective layer of Al 5052. However, this protective layer becomes weak when the temperature of the solution increases.

Keywords*; Corrosion, Polarization, EIS, 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol, SEM.*

1. INTRODUCTION:

Al 5052 is the aluminium that is used widely in the oil industries.Al 5052 is an Aluminium alloy that has a low quantity of Si in the range of 0.5–0.26% [1].The main problem is the use of Al 5052 industry is when dissolution in acidic media solution.Nature of very weak resistance to corrosion makes Al 5052 is easily to corrode.Among the areas that use al 5052 are cleaning industrial, oil field, petrochemical processing, heat exchangers, tanks and other.The metallic structure, chemical composition and its matter often go under damaged due to the aggressive corrosion behaviour of acidic environment and with present of hydrochloric acid which it has high aggressive rate to corrosion process which lead to issues serious consequences to industrial unity processing on cost and product aspect [2].Corrosion may be subdivided into two kinds of dry and/or wet corrosion. Dry one occurs when direct clash of atmospheric gases such as oxygen gas with metals. This clash led to the formation of the metal oxide layer called 'Theory of Wagner' [3]. For wet corrosion, it occurs when the liquid medium involved. In this process, one part will act as the anode and undergo a process of oxidation, while the other one acts as a cathode and undergo a process of reduction. In wet corrosion, the liquid medium involved acting as an electrolyte, which serves as an electron transfer medium using ion [4]. Industrial equipment exposed to corrode through using materials to clean them such as hydrochloric acid and sulphuric acid which are using in wide rang to clean and remove rust on metal surface after end of processes and in, this case protection form corrosion should apply to protect metal from corrode [5]. The incorporation effective of inhibitor has been among the present and give hopeful techniques to reduce the rate and impacts of corrosion process in past few years [6]. Mechanism and the rate of the corrosion process are depending on various factors (type of material, acidic or basic conditions). The Al 5052 surface corrosion in corrosive environment proceeds regarding to the overall reaction: $M+ 2H \rightarrow M2+H2$. This reaction consists of ion transferring the anode and/or cathode side. Electrochemical reaction in Al 5052 involving process of oxidation/reduction reactions [7]. The anode has oxidation reaction: $M \rightarrow {}^{M}2+2e-$ while the cathode has reduction: $2H+2e- \rightarrow H2$. Bubbles of hydrogen gas will be released as product of corrosion. In general, the corrosion inhibitors can be divided to, organic inhibitors and inorganic inhibitors, this division done according to chemical constituents of inhibitors [8]. In literature found that some selected inorganic inhibitors like phosphate and dichromate's in addition to arsenates and these inorganic inhibitors were usually avoided due to cost, toxicity and degradation behaviors. Moreover, it is too critical to maintain the pH of a solution and the concentration of inorganic inhibitors [7]. Therefore, using non- toxic organic corrosion inhibitors was the good decision to get significant strategy for corrosion prevention process on Al 5052 and includes instead of inorganic ones [9]. From the literature reports we found and indicated that most

organic molecules having double bonds, heteroatoms, which can donate single pair electrons to the metal surface and can prevent the corrosion form initiation [10]. In particular, heterocyclic molecules having nitrogen atoms performance demonstrates potential of inhibition toward corrosion process on surface of metals in corrosive environment [11]. The efficiency of inhibition having the sequence oxygen < nitrogen < sulfur < phosphorous [12], and these atoms if found in organic molecules having, especially nitrogen atom will lead to reduce corrosion attack on steel, studied in some detail has been done [13]. The organic inhibitors effectiveness depends on the rate of adsorption on the surface of the metal and covering abilities on metal surfaces. The adsorption on the surface of metal depend on the structures of the organic inhibitors molecules and the charge of the metal [14]. Adsorbed inhibitors on the surface of metal in aqueous solutions replace water molecules. Electrostatic interactions of organic inhibitor compounds and alloys are clear in corrosion process during this inhibition action [15]. Adsorption of inhibitors on alloy surface depends on, inhibitor group physicochemical properties, such as density of the electron at the donor atom, orbital character and electronic structure of the molecule [16]. Thiadiazole ring systems have been reported and so far a diversity of anti-cancer properties has been investigated for huge number of similar compounds. 1,3,4-thiadiazoles were synthesized starting from the precursors, utilized for the prepared of several derived and large varieties of impacts such as anti-inflammatory, antituberculosis, anticonvulsant, and antibacterial were proved [17]. The resonance structure of the 2-amino-1,3,4-thiadiazole ring systems assumes biological impacts. The studied compound 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol as inhibitor has hetroaromatic ring, aromatic benzene ring, azomethane group and heteroatoms, N, O, and S that have higher electron density and were act as protected layer on the surface of alloy by forming a coordination bonds between the inhibitor and the surface of iron. The inhibition performance of this inhibitor versus the corrosion of alloy in acidic solution could be demonstrate regarding to adsorption sites number, charge density and the performance to form a coordination bonds. The selection of our inhibitor was regarding to molecular structure. The inhibitor 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3, 4-thiadiazol is synthesized, and its chemical structure was cleared and confirmed by using spectroscopic techniques. The corrosion inhibitor effectiveness of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol on the corrosion process on Al 5052 sample in 1.0 M HCl was investigated by using electrochemical measurements.

2. MATERIALS AND METHODS:

The studied inhibitor prepared by condensation of 2-amino-5- ethyl-1,3,4-thiadiazol (0.004 mol) with 4-hydroxybenzaldehyde (0.004 mol) in methanol (25 mL) and the mixture was refluxed for six hours with stirring. The progress of reaction was monitored by TLC. The reaction mixture was concentrating, and solid was recrystallized from ethanol, yield 58%. The purity of inhibitor molecules was approved through Thin Layer Chromatography as in Fig. 1. Thin Layer Chromatography sheets have been coated by silica gel on aluminum 60F–254. IR: 3396.4 cm^{-1} (OH), 3077.8 cm^{-1} (aromatic group) and (C@N) 1611.2 cm^{-1}. ^1H NMR (DMSO-d_6); d: 1.54 (t, 3H for CH_3), 3.01 (m, 2H for CH_2), 5.83 (s, 1H for OH),

6.87–7.17 (m, 4H, Aromatic).

ELECTROCHEMICAL MEASUREMENTS

Al 5052 tested as metal sample immersed in acidic solution contain 1 M hydrochloric acid (HCL) with different concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol as corrosion inhibitor. Electrochemical measurements used in this study were carried out on CH Instrument and CH soft- ware where they designed with three electrode cell kit used for electrochemical corrosion tests. The Cell designed to hold cylindrical samples of metal, it consists of working electrode, counter electrode and reference electrode. Water bath connected to the three-electrode cell to control the temperature during running the test. CH instrument designed to perform potential of corrosion process, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PD). PD curve was varied from —0.2 to 0.2

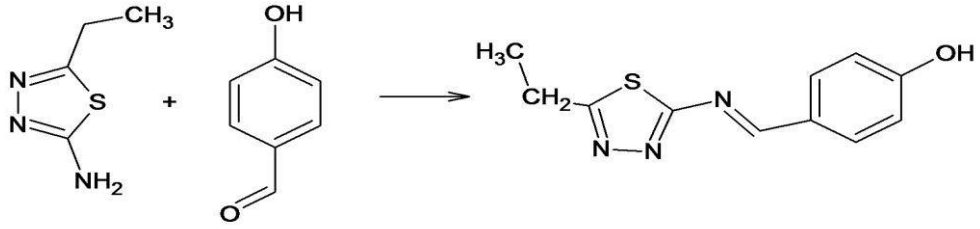

Fig.1 The chemical formation of 4-hydroxybensylideneaminomethyl-5-ethyl -1,3,4 - thiadiazol

V_{SCE} through scanning rate range of 0,5 mV/s. Electrochemical impedance spectroscopy carried out by using AC signal with 5 mV multitude of peak-peak at corrosion potential with range of frequency 100 * 10^3 to 0.1 Hz. By using

CH Echem analyst, all data of EFM impedance were fitted to appropriate equivalent circuit (EC). The data of electrochemical measurements started and began to be gathered after 30 min from immersing the working electrode in the acidic solution that's time is to allow steady state potential to stabilize.

Electrochemical polarization methods are classified as a method to control the potential (potentio-static, potentio-dynamic) and to control current (*I*), (Galvano static) approaches. Studies and works were done on potentio-static and potentio-dynamic methods and were used for measurement and corrosion rate control. For Potentiostat method is automatically adjusts the applied polarizing potential between the reference electrode (RE) and the working electrode (WE) at any prescribed value to measure the density of the current on the counter electrode (CE). The curve that associated with a potentiodynamic method is polarization curve.

Electrochemical impedance spectroscopy (EIS), this analysis will be conducted to test the effectiveness of corrosion inhibitors to protect the surface of Al 5052 in acidic solutions. It will be done at 30 °C with different concentrations of corrosion inhibitor that is 0.05 M, 0.1 M, 0.2 M 0.4 M, 0.5 M after that all data is obtained, a comparison will be made with the blank sample (no corrosion inhibitors used in the solution). After the decision spectroscopy electrochemical impedance (EIS) is measured, constant phase element CPE is used for matching circuit. It consists of a solution resistance R_s, charge transfer resistance R_{ct} and constant phase element CPE.

3. RESULTS AND DISCUSSION:

Synthesis

To synthesize 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3, 4-thiadiazol as a corrosion inhibitor, the reaction sequence out- lined in Fig. 2 was followed, starting from commercially available 5-ethyl-1,3,4-thiadiazol-2-amine. The synthesis was carried out by refluxing 2-amino-5-ethyl-1,3,4-thiadiazol in methanol with 4-hydroxybenzaldehyde. The molecular weight of the synthesized corrosion inhibitor is 233.06, which is calculated based on the molecular formula ($C_{11}H_{11}N_3OS$) and supported via mass spectrometry. 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol can be dissolved in acetone, dichloromethane, dimethyl formamide, dimethylsulfoxide, ethanol or methanol solutions. The FT- IR spectrum of this compound shows absorption bands at 3396.4 cm^{-1} for hydroxyl group. The band at 3077.8 cm^{-1} for aromatic ring, In addition the band at 1611.2 cm^{-1} was for azomethane group. H-NMR spectrum exhibits a triplet at 1.54 ppm and m at 3.01 ppm for due to the methyl and methylene protons respectively.

Electrochemical measurements- Electrochemical impedance spectroscopy (EIS)

These tests involve Al 5052 corrosion process (sample) in a solution of acidic media in the presence the compound of 4-hydroxy benzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol as corrosion inhibitors at different concentrations. Acid solution used is 1 M hydrochloric acid. The electrochemical measurement is a method used to measure the corrosion rate prevailing on Al 5052 sample in 1M hydrochloric acid with and without corrosion inhibitor. with corrosion inhibitor. Table 1 and Fig. 3 show the effective of increasing the concentration through fix temperature respectively. Using CH Analyst software, EIS experimental data can be analysed that data matching CPE for Al 5052/sample, calculating solution resistance R_s and constant phase element CPE, calculate the charge transfer resistance R_{ct} and charge double layer [19]. These data will prove that the corrosion inhibitor molecules have to absorb the Al 5052 sample surface thus form a protective layer on the Al 5052. Large charge transfer resistance corresponding to a corrosive system slowly [20]. With the increase in the value R_{ct}, the efficiency and capacity of inhibition (IE) will increased up to 90.86% at a concentration of 0.5 mm. The large transfer charge resistance corresponds to a slowly corrosive system [21]. Next in Table 2 and Fig. 4 show the experiment using the same concentration of corrosion inhibitors that is 0.5mM but at different temperatures at temperatures of 30, 40, 50 and 60 °C. Based on Fig. 4 it can be seen that the semi-circular graph at 60 °C is the smallest and at 30 °C is the largest. This shows that the diameter of the semi-circle is narrowing with temperature rise. In other words, the higher the temperature, the smaller the semicircle diameter. This result shows that the rate of corrosion inhibition is decreasing with increasing temperature. The increase in the temperature of the solution will lead to accelerate the corrosion process rate which is caused by the change of operating mechanism of corrosion [22].

Potential dynamic polarization

Measurements was done to obtain the potential curve of a Al 5052 in a 1 M hydrochloric acid solution at a different concentration of corrosion inhibitors at 30°C, Fig.5. The parameters obtained from the extrapolation of the Tafel line are the gradients of the anonical ba and cathodic bc Tafels, the density of corrosion current (i_{corr}), the potential of corrosion (E_{corr}) and the rate of corrosion. The data for this parameter is shown in Table 3. Inhibition efficiency (IE) can be calculated using the formula:

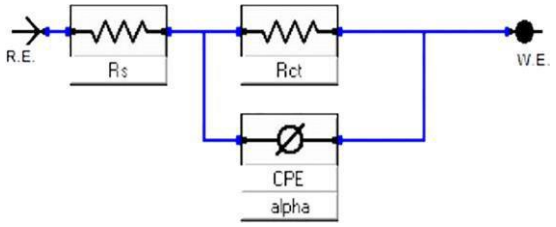

Fig.2 equilent circuit

Table 1 CPE matching data for Al 5052 sample in 1.0 M HCl with the concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol at 30 °C.

Concentration (mM)	R_s (ohm cm^2)	R_{ct} (ohmcm^2)	CPE_{dl}		C_{dl} ($mFcm^{-2}$)	IE (%)
Blank	0.4512	0.0778	924.6	0.914	338.7	0
0.05	0.4251	0.7607	5050	0.706	375.1	89.77
0.10	0.3251	0.7694	3812	0.728	820.9	89.89
0.20	0.3672	0.7808	2065	0.773	954.7	90.04
0.40	0.3935	0.7796	1690	0.806	365.9	90.02
0.50	0.5417	0.8509	435.4	0.854	266.2	90.86

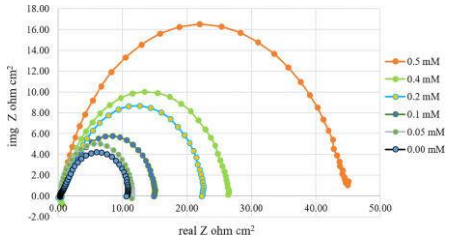

Fig. 3. Nyquist plots for Al 5052 in different concentration hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol in 30 °C.

Table 2CPE matching data for Al 5052 in 1.0 M HCl with 0.5 mM concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol at different temperatures.

Temp. (°C)	Concentration (mM)	R_s (ohm cm^2)	R_{ct} (ohm cm^2)	CPE_{dl}		C_{dl} ($mFcm^{-2}$)	IE (%)
30	Blank	0.2540	0.0779	924.6	0.914	338.7	0.00
	0.5	0.5509	0.8480	435.4	0.854	266.2	90.86
40	Blank	0.2481	0.2205	4526	0.928	502.0	0.00
	0.5	0.2299	0.3519	500.2	0.831	398.5	72.96
50	Blank	0.2315	0.1511	1634.01	0.731	835.9	0.00
	0.5	0.2127	0.3380	507.5	0.832	266.1	56.67
60	Blank	0.1840	0.1103	2172.87	0.840	920.8	0.00
	0.5	0.1699	0.2501	451.4	0.869	554.5	52.21

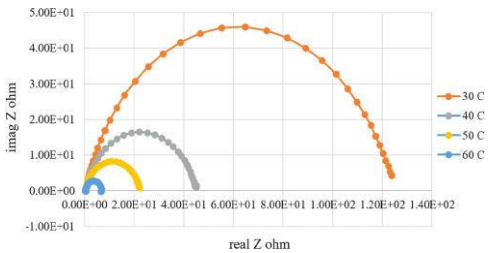

Fig. 4. Plot Nyquist for Al 5052 at a concentration of 0.5 mM of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol as corrosion inhibitor at different temperatures.

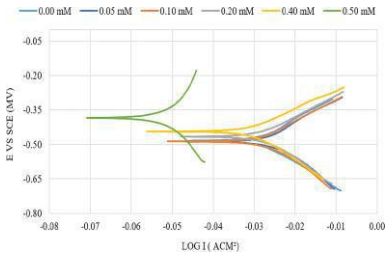

Fig. 5. The potentio-dynamic polarization curve for Al 5052 in 1.0 M HCl with different concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol.

Concentration (mM)		Blank	0.05	0.1	0.2	0.4	0.5
Potential Dynamic Polarization Parameters	b_a (V dec^{-1})	0.136	0.1291	0.1139	0.1021	0.0887	0.6012
	b_c (V dec^{-1})	0.1298	0.1286	0.1209	0.1179	0.114	0.4029
	I_{corr} ($mAcm^{-2}$)	659	601	408	339	180	44.59
	—E_{corr} (mV vs SCE)	489	478	468	456	449	390
	Corrosion rate (mpy)	7.601	7.004	4.836	4.015	2.038	0.0529
	IE (%)	0	10.53	40.01	48.6	74.39	93.21

Table 3 The polarization parameters for Al 5052 in 1.0 M HCl with different concentrations of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol

Based on Fig. 5, E_{corr} value change to more negative can be detected with increased corrosion inhibitory concentrations. This suggests that a layer of protection on a Al 5052 sample was produced due to the absorption of corrosion inhibitor molecules on the surface of the metal sample [23]. Along with this, it also proves that the reduced density of anodic and cathodic current causes the absorption of molecules over the surface of the Al 5052 sample more easily and rapidly [24].

Based on Table 3 and Fig. 5 above, it is seen that the decreasing current density (I_{corr}) value decreases as the concentration of corrosion inhibitors increases and thus increases the efficiency (IE) of corrosion inhibitors as well. In addition, the anonical (ba) and cathodic tafels (bc) gradients change with increasing concentration of corrosion inhibitors. This shows that the concentration of corrosion inhibitors concentration affects the anodic and cathodic action and reaction [25]. The inhibition efficiencies increased with increasing of inhibitor concentration and this could have explained on the basis of amount of adsorption with surfactant coverage molecules, increases with increasing concentrations. The inhibition performance increased parallel regarding to concentration inhibitor increased, that suggests the retardation of surface of Al 5052 corrosion in inhibited solution compared to uninhibited environment. Next part of this experiment is using the same concentration of corrosion inhibitors i.e, 0.5 Mm but at different temperatures at temperatures of 30, 40, 50 and 60 °C. Based on Table 4 and Fig. 6, E_{corr} to more negative values can be detected from 376 to 464 mV with a value change of 285 mV. From literature found that if E_{corr} value exceeds 85 mV, it can be categorized as anodic or cathodic corrosion inhibitor [26]. This proves that the protective layer produced by the corrosion inhibitor molecule is weakening when the temperature of the solution increases. High temperatures result in corrosion inhibiting of corrosion inhibitor molecules on the surface of Al 5052 samples [27]. The CH Analyst software provides data as shown in Table 4 below. Corrosion resistance (i_{corr}) and corrosion rate are higher when the temperature of the solution

Table 4Parameters of polarization for Al 5052 in 1.0 M HCl with 0.5 mM concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol at different temperatures.

Temp. (°C)	Concentration (mM)	Potential Dynamic Parameter (PD)					
		b_a ($Vdec^{-1}$)	b_c ($Vdec^{-1}$)	I_{corr} ($mAcm^{-2}$)	—E_{corr} (mV vsSCE)	Corrosion rate(mpy)	IE (%)
30	Blank	0.1360	0.1298	667.00	487.00	7.6010	0.00
	0.5	0.5994	0.3990	45.020	376.00	0.4987	93.21

40	Blank	0.7021	0.6695	550.00	660.00	76.7000	0.00
	0.5	0.0711	0.1063	134.00	540.00	13.7200	76.05
50	Blank	0.9692	0.7201	819.00	669.00	114.7980	0.00
	0.5	0.1301	0.1300	420.00	479.00	419.1000	50.21
60	Blank	4.0200	2.0296	1559.00	680.00	630.4000	0.00
	0.5	0.1389	0.1430	0998.00	464.00	1015.9000	35.93

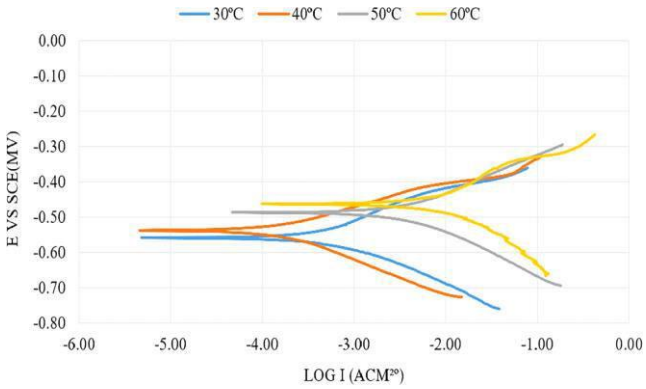

Fig. 6. The potentio-dynamic polarization curve for Al 5052 in 1.0 M HCl with 0.5 mM concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol at different temperatures.

Increases while the inhibition efficiency (IE) is decreasing as the corrosion inhibitor molecules on the surface of the Al 5052 sample are weakening and allowing the corrosion process to occur more quickly.

Surface Morpholgy

SEM technique was employed to further prove the corrosion resistance ability of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol, and the surface observation images of Al 5052 after a 2 h exposure in a HCl solution without and with inhibitors are shown in Figure.7. Before immersion, the naked aluminum plate appears very smooth. In contrast, in the absence of inhibitor, the Al 5052 presented a very rough surface covered with a huge amount of deep cracks and large holes, which suggests strong damage and a severe dissolution of alloy in contact with aggressive solution. Nevertheless, in Figure.7.c,d, the dissolution rate of alloy was substantially inhibited by 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol, exhibiting a comparative smooth surface with a few small pits. Therefore, it is concluded that the regular distribution of the 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol molecules adsorbed on Al 5052 surface generates consistent protective layers, which effectively prevent HCl molecules from penetrating into the aluminum surface.

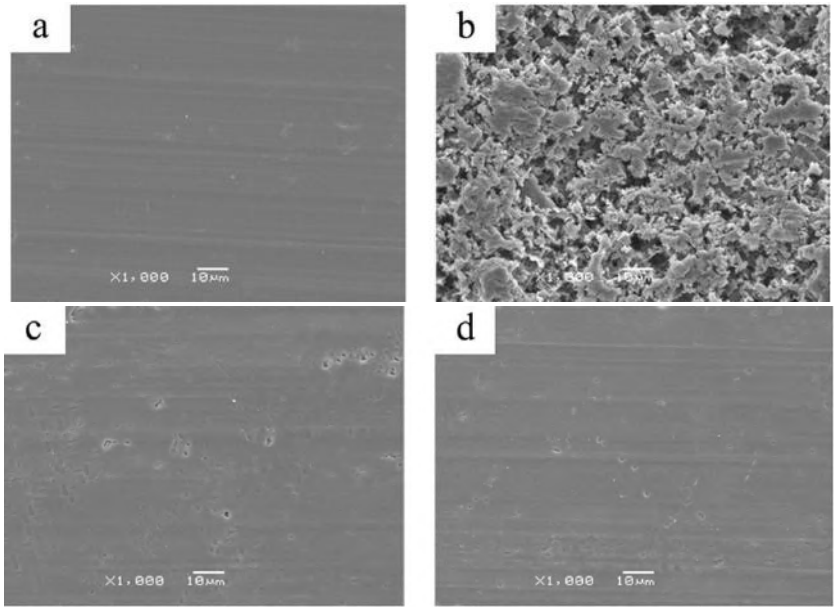

Figure-7.SEM images of a) Polished surface of Al 5052, b) After exposure to 2hour in HCl solution, c) After exposure to 2hour in HCl solution containing 4-hydroxy benzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol inhibitor solution

4. CONCLUSIONS:

The results of electrochemical impedance spectroscopy (EIS), Potentio-dynamic Polarization show that the corrosion-resistant of 4-hydroxy benzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol was able to reduce and slow down the corrosion process on Al 5052 caused by hydrochloric acid solution (HCl). For experiments using different concentrations at the same temperature, the results showed that the highest inhibitory efficiency was at 0.5 mM concentration with 90.86% for EIS, 93.21% for potentio-dynamic polarization and 99.65% for EFM. While for experiments using the same concentration at different temperatures, giving the opposite result where the highest inhibitor efficiency is at the lowest temperature at 30 °C where 90.86% for EIS, 93.21% for potentio-dynamic polarization. Based on the data received from the CH Analyst software, it is obvious that the increased concentration of 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol provides a protective layer that helps to prevent or slow down the corrosion process of Al 5052 while the increase in temperature of the solution causes a weakness in the corrosion prevention layer of corrosion inhibitor protection further more allowing and accelerating the process of corrosion on the Al 5052.

The mechanism of inhibition

The inhibition performance of this inhibitor versus the corrosion of alloy in acidic solution could be demonstrate regarding to adsorption sites number, charge density and the performance to form a coordination bonds. The selection of our inhibitor was regarding to molecular structure. The molecular structure was in Fig. 1. The inhibition effectiveness of this 4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol have consist fundamentally on nature and structure of the adsorb layers on the surface of alloy. Our inhibitor has heteroaromatic ring, aromatic benzene ring, azomethane group and heteroatoms, N, O, and S that have higher electron density and were act as protected layer on the surface of alloy by forming a coordination bonds between the inhibitor and the surface of Aluminium.

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Green Protocol for Synthesis of Hydrazones: A Bioactive Molecule

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ABSTRACT:

Substituted aryl hydrazones have been synthesis efficiently in short reaction time (2-5min) under solvents free condition in isolated yields(90-95%) by the grinding of aryl hydrazine's with carbonyl compounds in the absence of any added catalyst (green protocol). The short reaction time, cleaner reaction, and easy workup make this protocol practical and economically attractive. Hydrazones are present in many of the bioactive heterocyclic compounds and shows various biological and clinical applications.

KEYWORDS: *Aryl hydrazine: phenyl hydrazine: carbonyl compound, aromatic carbonyl compound, Grinding, room temperature, hydrazones etc*

1. INTRODUCTION:

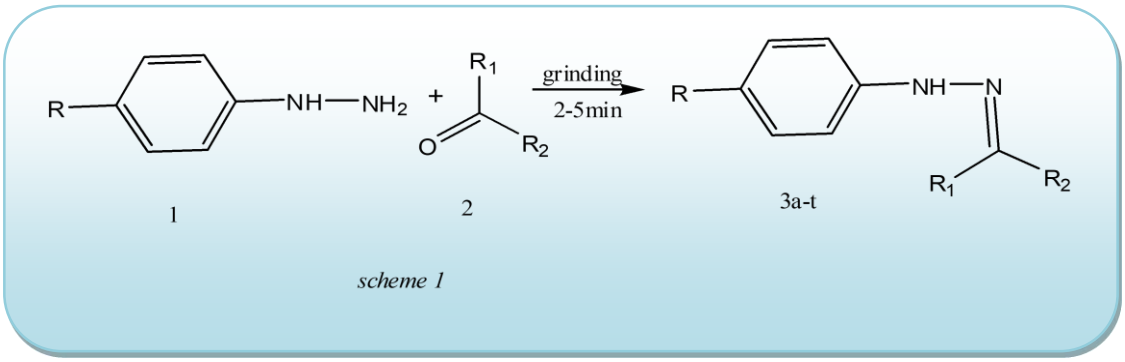
The synthesis and the importance of hydrazides were studied by many researchers shows various biological, medical and industrial activities. Hydrazones have been demonstrated to possess, among other, antimicrobial, antimycobacterial, antidepressant, anticonvulsant, anticancer, antimalarial, vasodilator activity, etc. The ease of preparation, increased hydrolytic stability relative to imines, and tendency toward crystallinity are all desirable characteristics of hydrazones. Due to these positive traits, hydrazones have been under study for a long time. The synthesis and the importance of hydrazides were studied by many researchers shows various biological, medical and industrial activities. Hydrazones have been demonstrated to possess, among other, antimicrobial, antimycobacterial, antidepressant, anticonvulsant, anticancer, antimalarial, vasodilator activity, etc. The ease of preparation, increased hydrolytic stability relative to imines, and tendency toward crystallinity are all desirable characteristics of hydrazones. Due to these positive traits, hydrazones have been under study for a long time. The present work put forth a brief account on efficient synthesis and biological activities of hydrazones derivatives. To design and conduct chemical reactions with "green" experimental protocol is an enormous challenge that chemists have to confront to improve the quality of the environment for present and future generations. Target areas for achieving this goal are the exploration of alternative reaction conditions and reaction media to accomplish the desired chemical transformations with minimized by-products or waste, and elimination of the use of conventional organic solvents, wherever possible. Traditional chemical syntheses or transformations generally require volatile and often hazardous organic solvents as reaction media to facilitate mass and heat transfer, and to isolate and purify desired product from reaction mixtures. In recent years, solid-state organic reactions have caused great interest. They have many advantages such as high efficiency and selectivity, easy separation and purification, and mild reaction conditions and benefit industry as well as the environment **[1].** Many articles about solid-state reactions with grinding have been reported, such as such as the Grignard reaction **[2],** aldol condensations**[3],**and other reactions**[4].**

Hydrazones are used not only to characterize aldehydes and ketones by derivatization with appropriate hydrazines**[5],** but they have also emerged as important synthons for several organic transformations **[6]** the most remarkable is the Fischer indole synthesis**[7].** Hydrazones are of interest also because of their importance in analytical chemistry, medicine and industry. Especially, isonicotinhydrazide and its N-isopropyl acylhydrazone have been used as effective drugs in curing human tuberculosis in the past few years **[8].** They have been studied as chelating ligands for spectroscopic and fluorometric determination of trace elements **[9].** The chelation of several classes of aryl and hetaryl hydrazones with metals, especially iron**[10],** has lead to their study as antiproliferative active agents against tumor cells**[11].** Recently some hydrazones have been found useful in treating sexual dysfunction **[12].** Hydrazones derivatives possessing anti-inflammatory **[13],** analgesic **[14]** antipyretic**[15]** and antibacterial**[16]** activities are also reported in the literature.Carbazole-based hydrazones have been investigated for their optoelectronic and high hole mobilities **[17].** Several substituted aryl hydrazones have been tested for their nonlinear optical properties **[18].**

Hydrazones synthesis from various precursors is well documented**[6].** Recently, some hydrazones have been prepared from carbonyl compounds and hydrazine hydrate in ethylene glycol**[19]** and toluene**[20]** by the application of MW irradiation. Some examples on supported reactions using silica gel/sodium hydroxide**[21]** and solvent-free synthesis of heterocyclic hydrazones under microwave irradiation conditions**[22]** and room temperature ionic liquid known**[23].** Very recently Verma *et al.* reported aqueous protocol for the synthesis of cyclic, bi-cyclic, and heterocyclic hydrazones using polystyrene sulfonic acid (PSSA) as a catalyst**[24**].

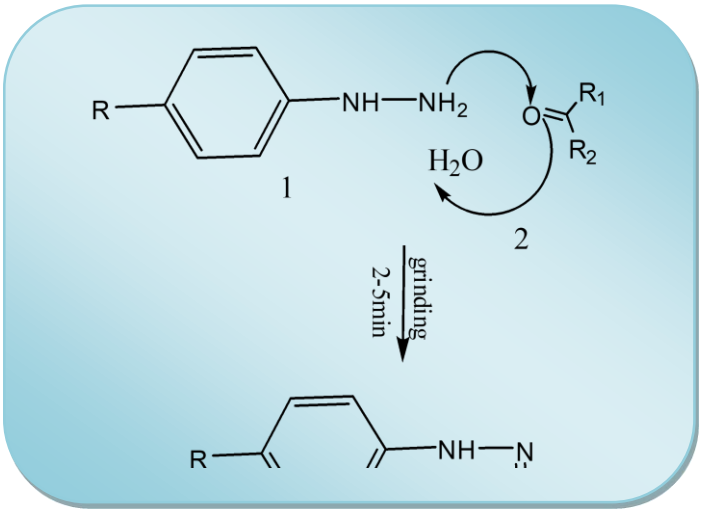
3. RESULT AND DISCUSSION:

We are increasingly aware of the environmental impact of human activity, and consequently of the need to develop cleaner and more energy-efficient technologies. It has long been recognized that the large-scale use of volatile organic solvents has important implications for environmental contamination **[25].** Approaches to the problems presented by organic solvents include the use of more benign solvents (especially water and supercritical CO2), or solvents with negligible vapour pressures (ionic liquids). It has also been said that 'the best solvent is no solvent **[26],** Despite the power of this statement, our use and understanding of solvent-free synthesis, especially where solid starting materials are concerned, has remained undeveloped in comparison to solvent based methods use of grinding to promote reactions between solid reactants is known as mechanochemistry and while its useful appearance have been recognized for a long time it has become neglected in comparison to solvent based methods.



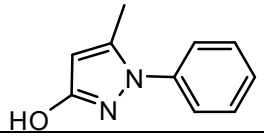
scheme 1

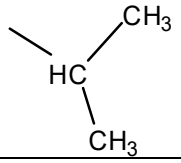
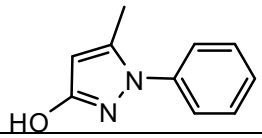
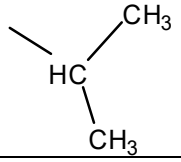
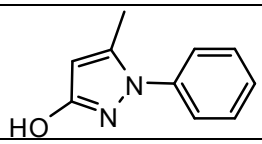
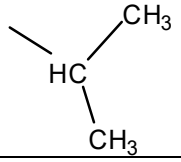
In continuation of our work on the mechanochemistry here we decided to synthesize the hydrazone under solvent free conditions. The methodology tolerates both electron withdrawing and electron donating substituents on the phenyl hydrazines. The reactions wherein both 1 and 2 are liquids (Entries 2–4 Table-1) when carried out neat required 2-5min for complete conversion under similar conditions.



Scheme-2 Possible mechanism of (3) hydrazone

Table 1:- Synthesis of Arylhydrazone(3)

Entry	Hydrazone 3	R	R_1	R_2	Time(min)	Yield[a] (%)
1	3a	H	H	n-C_5H_{11}	3	90
2	3b	H	H		5	92
3	3c	H	CH3	Ph	5	91

4	3d	H	CH3		4	94
5	3e	H	H	Ph	3	95
6	3f	NO_2	H	n-C_5H_{11}	5	91
7	3g	NO_2	H		5	93
8	3h	NO_2	CH3	Ph	6	94
9	3i	NO_2	CH3		4	91
10	3j	Cl	H	n-C_5H_{11}	3	92
11	3k	Cl	H		5	91
12	3l	Cl	CH3	Ph	3	93
13	3m	Cl	CH3		5	92

a:Melting points of compounds are uncorrected and compared with reported compounds.

4. BIOLOGICAL IMPORTANCE:-

Hydrazonone nucleus exhibited immense pharmacological activities. Hydrazones are present in many of the bioactive heterocyclic compounds that are of very important use because of their various biological and clinical applications. Hydrazone-based coupling methods are used in medical biotechnology to couple drugs to targeted antibodies, e.g. antibodies against a certain type of cancer cell. The hydrazone-based bond is stable at neutral pH (in the blood), but is rapidly destroyed in the acidic environment of lysosomes of the cell. The drug is thereby released in the cell, where it exerts its function**[27].**Hydrazides also have been used as chelating agents**[28]** . Various effective compounds for example iproniazide just like isoniazide is used as antitubercular drug**[29]** . Nifuroxazide is an oral nitrofuran antibiotic, used in anti-dehydration and colitis treatment, "neutralises microbacterials" in diarrhoea, and has a spectrum which covers most enteropathogenic microbacterials, Shigella, Escherichia coli, Salmonella, Staphylococci, Klebsiella, Yersinia.

4.1 Antioxidant activity:-

Anjoo Kamboj et. al. **[30]** synthesized new hydrazone derivatives from thiophene chalcone and evaluated for their antioxidant activity. It has been found that the presence of nitro and methoxy group enhanced the antioxidant activity of the synthesized hydrazones.

4.2 Antiviral Activity :-

Most of the antiviral drugs now available are designed to help deal with HIV, herpes viruses, the hepatitis B and C viruses and influenza A and B viruses. Designing safe and effective antiviral drugs is difficult, because viruses use the host's cells to replicate. This makes it difficult to find targets for the drug that would interfere with the virus without also harming the host organism's cells. Moreover, the major difficulty in developing vaccines and anti-viral

drugs is due to viral variation. ElSabbagh and Rady**[31]** evaluated acyclic hydrazone derivatives which showed a higher in vitro cytotoxic activity against hepatoma cell line (HepG2).

4.3 Antimicrobial Activity:-

N. G. Kandile and co-workers **[32]** synthesized hydrazones from 1-[4-(2-methoxybenzyl)-6-aryl pyridazin-3(2H)- ylidene]hydrazines and diacetyl. The synthesized products were screened for antimicrobial activity against Staphylococcus aureus and Streptococcus faecalis, Escherichia coli and Pseudomonas aeruginosa. The hydrazone derivative (1-[4-(2-methoxybenzyl)-6- methylphenylpyridazin-3(2H)-ylidene]hydrazine showed the highest biological activity.

4.4 Antimycobacterial Activity:-

Antimycobacterial drugs are used in the treatment of diseases caused by members of the Mycobacteriumgenus, including tuberculosis (TB) and leprosy, which have affected man since antiquity, and the nontuberculous mycobacterioses (NTM) that are increasingly recognized. Mycobacteria are unusual; they are slow growing with a thick waxy cell wall made of lipid rich material which makes penetration by drugs problematic. A large number of new agents with novel mechanisms of action are being trialed to assess their efficacy in treating mycobacterial disease. Maria Grazia Mamolo et.al**[33]** synthesized [5- (pyridin-2yl)-1,3,4-thiadiazole-2-ylthio]acetic acid arylidene-hydrazide derivatives (9) and evaluated their activity against Mycobacterium tuberculosis and Mycobacterium avium. Compounds exhibited moderate in-vitro antimycobacterial activity against the tested strain of Mycobacterium tuberculosis and Mycobacterium avium.

5. RESULT AND CONCLUSION:-

In summary we have demonstrated an efficient and green protocol for the dehydrative cyclization of carbonyl compounds to with phenyl hydrazines to hydrazones by grinding. Shorter reaction time, simple reaction conditions and higher yield render this grinding method superior. The method is clean and simple, which can be used as an alternative to the existing methods. In absence of organic solvent and any acid or base catalyst makes this an environment friendly methodology amenable for scale up. The present study also highlights the biological activities of hydrazone derivatives, such as antioxidant, antiviral, antimycobacterial, antimicrobial, activities. Therefore, these observations have been guiding for the development of hydrazones, which can be a lead nucleus for future developments to get safer and effective compounds

6. EXPERIMENTAL:-

All reported yield are isolated yield. Melting points are uncorrected and were recorded by open capillary. Infra red spectra were recorded with ATI MATT-SON RS-1 FTIR spectrometer in (KBr).^{1}H NMR spectra were recorded on a Bruker AC-200 (MHz) spectrometerin $CDCl_3$/ DMSO-d6 with TMS as an internal standard.

Phenyl hydrazine or substituted phenyl hydrazine's(1) were grind with a variety of carbonyl compounds (2) (alkyl, aryl and heteroaryl) at room temperature in solvent free condition (scheme 1). All the reactions proceed to completion in just 2-5 min. at room temperature without any organic solvent or any added catalyst. The respective hydrazones could be isolated in excellent yields in all the cases (Table 1). The hydrazones 3a–m are known compounds and were well characterized by melting point, IR, 1HNMR and mass spectra.[21]

SPECTRAL DATA:-

1-hexylidene-2-phenyl hydrazine (3a):

IR (cm $^{-1}$) 3418.70,3329.95,2859,1680.90,1599.86,1352,1121.24,667.68 **`HNMR($CDCl_3$),** δ 6.81(1H, d), 7.20 (1H, d), 7.35(1H, d), 11.12(1H, s), 7.50(1H, t), 1.3(2H, q), 1.29 (4H, six), 1.31 (2H, six), 0.90 (3H, t)

Mass 199(M^+) ,182,173,157,143,130,115,103,89,77.**$C_{13}H_{21}N_2$** Anal.Calcd C 76.10,H 10.40,N 13.70 Found C 76.05,H 10.31,N 13.64

3-Methyl-1-phenyl-1H-pyrazol-5-(4*H*)-1-ethylidene-2-phenylhydrazine(3b):

IR (cm $^{-1}$) 3223.23,1665.99,1498.96,1215.74, 669.02

'HNMR($CDCl_3$), δ 6.81(1H,d), 7.20 (1H, d), 7.35(1H, d), 11.12(1H, s), 7.50(1H, t), 2.3 (1H,d), 1.94 (1H,d),7.94(2H,d), 7.34 (2H,d) 7.19(1H,d)**Mass** 292(M^+), 275,201,185,171,155,133,118,105,93,77,65. **$C_{17}H_{18}N_4O$** Anal.Calcd C 69.70,H 7.20,N 18.10,O 5.20 Found C 69.65,H 7.14,N 18.05 ,O 5.15

1-phenyl-2-(1-phenylethylidene)hydrazine (3c):

IR (cm $^{-1}$) 3420.69,3019.04,1682.61,1600.1493.98,1267.73,1215.81,700.54,668.95

'HNMR($CDCl_3$), δ 6.81(1H,d), 7.20 (1H, d), 7.35(1H, d), 11.12(1H, s),2.43 (1H,s), 7.94(1H,d), 7.52 (1H,dd)**Mass** 210(M^+), 196,. 188,181,165,152,139,126,120,115,105,98,93,87,77,63 **$C_{14}H_{14}N_2$** Anal.Calcd C 79.99,H 6.80,N 13.40 Found C 79.97,H 6.71,N 13.32

1-(3-methylbutan-2-ylidene)-2-phenylhydrazine (3d):
IR (cm $^{-1}$) 3451.16, 3000, 1714.36, 1601.45.1215.74, 762.92, 669.16,
'HNMR($CDCl_3$), δ 6.81(1H,d), 7.20 (1H, d), 7.35(1H, d), 11.12(1H, s),1.94 (1H,s),
1.8(1H,m), 0.86 (1H,q)**Mass** 176(M^+),167,144,119,105,91,77. **$C_{11}H_{16}N_2$** Anal.Calcd C 74.99,H 9.20,N 15.15 Found C 74.96,H 9.15,N 15.09
1-benzylidene-2-phenyl hydrazine (3e):
IR (cm $^{-1}$) 3400.16,3020,,1623.25.1215,700.660.16,
'HNMR($CDCl_3$), δ 6.81(1H,d), 7.20 (1H, d), 7.35(1H, d), 11.37(1H, s),8.04 (1H,s), 7.52(1H,d).**Mass** 173(M^+),163,141,116,102,87,74 **$C_{13}H_{12}N_2$** Anal.Calcd C 79.65,H 6.23,N 14.33 Found C 79.56,H 6.16,N 14.27

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Molecular interaction of acetonitrile - 1, 2 Dichloroethane mixtures at 15^0C temperature using TDR

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ABSTRACT:

The dielectric permittivity spectra of acetonitrile(ACN) with 1,2 Dichloroethane(DCE) mixture has been studied at temperature 15^0C in the frequency range of 10 MHz to 20 GHz using time domain reflectometry (TDR) for 11 different concentrations of the system. The Kirkwood correlation factor of the mixtures has been determined. The static dielectric constants for the mixtures have been fitted with the modified Bruggeman model. The investigation shows that there is systematic change in dielectric parameters of the system with change in concentration. The interaction between the acetonitrile and dichloroethane is stronger.

KEYWORDS*: Relaxation, Kirkwood parameters, Bruggeman parameters, Time Domain Reflectometer.*

1. INTRODUCTION:

The information about formation of monomers and multimers as well as interaction between the molecules of the mixture get by the dielectric relaxation study of solute-solvent mixture at microwave frequencies [1-2]. Acetonitrile (ACN) is non-associative liquids and 1, 2 Dichloroethane (DCE) is associative liquid. ACN is C≡N group and DCE is of chlorine group. It is interesting to see the effect of nitrile group with chlorine-group. The objective of the present paper is to report the molecular interaction of acetonitrile and 1, 2 Dichloroethane mixture at 15^0C temperature using TDR.

EXPERIMENTAL

MATERIAL

A spectrograde acetonitrile and AR grade 1, 2 Dichloroethane (E-Merck) were used without further purification. The solutions were prepared at 11 different volume percentages of ACN in DE from 0 % to 100 % just before the measurements. The density and molecular weight of the liquids are as follows:

Acetonitrile-density - 0.7857gm cm^{-3}; mol. wt. - 41.05

1, 2 Dichloroethane -density: 1.256 gm cm^{-3}; mol.wt.-98.96

2. APPARATUS:

The complex permittivity spectra were studied using the time domain reflectometry [3, 4] method. The Hewlett Packard HP 54750 sampling oscilloscope with HP 54754A TDR plug in module has been used. A fast rising step voltage pulse of about 39 ps rise time generated by a pulse generator was propagated through a coaxial line system of characteristic impedance 50 Ohm. Transmission line system under test was placed at the end of coaxial line in the standard military applications (SMA) coaxial connector with 3.5 mm outer diameter and 1.35 mm effective pin length. All measurements were carried out under open load conditions. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In the experiment, time window of 5 ns was used. The reflected pulse without sample $R_l(t)$ and with sample $R_x(t)$ were digitized in 1024 points in the memory of the oscilloscope and transferred to a PC through 1.44 MB floppy diskette drive.

The temperature controller system with water bath and a thermostat has been used to maintain the constant temperature within the accuracy limit of ±1°C.

3. DATA ANALYSIS:

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range from 10 MHz to 20 GHz using Fourier transformation [5, 6] as

$$\rho^*(\omega)=(c/j\omega d)[p(\omega)/q(\omega)] \quad (1)$$

Where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $[R_1(t)-R_x(t)]$ and $[R_1(t)+R_x(t)]$ respectively, c is the velocity of light, ω is angular frequency, d is the effective pin length and $j=\sqrt{-1}$.

The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying bilinear calibration method [3].

The experimental values of ε* are fitted with the Debye equation [7]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1 + j\omega\tau} \quad (2)$$

With ε_0, ε_∞ and τ as fitting parameters. A nonlinear least-squares fit method [8] was used to determine the values of dielectric parameters. In Eq.(2), ε0 is the static dielectric constant, ε∞ is the limiting high-frequency dielectric constant and τ is the relaxation time

4. RESULTS AND DISCUSSION:

. The Kirkwood correlation factor g_f [9] is also a parameter for getting information regarding orientation of electric dipoles in polar liquids. The g_f for pure liquid may be obtained by the expression

$$\frac{4\Pi N\mu^2\rho}{9kTM} g_f = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} \quad (3)$$

Where is dipole moment in gas phase, is density at temperature T, M is molecular weight, k is Boltzman constant, and N is Avogadro's number. The dipole moments for ACN and DCE in gas phase are taken as 3.95D and 2.06 D [10] respectively.

For the mixture of two polar liquids 1, 2 Eq. (3) is modified by ref.[11] with the following assumptions:

1. Assume that g for the binary mixture is expressed by an effective averaged correlation factor g^{eff} such that the Kirkwood equation for the mixture can be expressed by

$$\frac{4\Pi N}{9kT}\left(\frac{\mu_1^2\rho_1}{M_1}\phi_1 + \frac{\mu_2^2\rho_2}{M_2}\phi_2\right) g^{eff} = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2} \quad (4)$$

With ϕ_1 and ϕ_2 as volume fractions of liquids 1 and 2 respectively.

2. Assume that the correlation factors for molecules 1 and 2 in the mixture contribute to the effective g proportionality to their pure-liquid values g_1, g_2. Under this assumption the Kirkwood equation for the mixture can be written

$$\frac{4\Pi N}{9kT}\left(\frac{\mu_1^2\rho_1 g_1}{M_1}\phi_1 + \frac{\mu_2^2\rho_2 g_2}{M_2}\phi_2\right) g_f = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2} \quad (5)$$

Where g^{eff} is the effective Kirkwood correlation factor for a binary mixture, with ϕ_1 and ϕ_2 as volume fractions of liquids 1 and 2 respectively.

In equation (4), the values of g^{eff} will change from g_1 to g_2 as concentration of molecule 2 will decrease from 100% to 0%. The Kirkwood correlation factor (g_f) which gives angular correlation between the molecules of the studied system. The values of g^{eff} are less than one; it shows that there is an antiparallel alignment of dipoles. The values of g_f are deviated less and are near to unity. It shows the weaker molecular interaction between the constituent molecules of the system.

The values of g^{eff} and g_f are calculated from equation (4) and (5) for the mixtures of the system. Temperature dependent g^{eff} and g_f for the system are shown in figure 1.

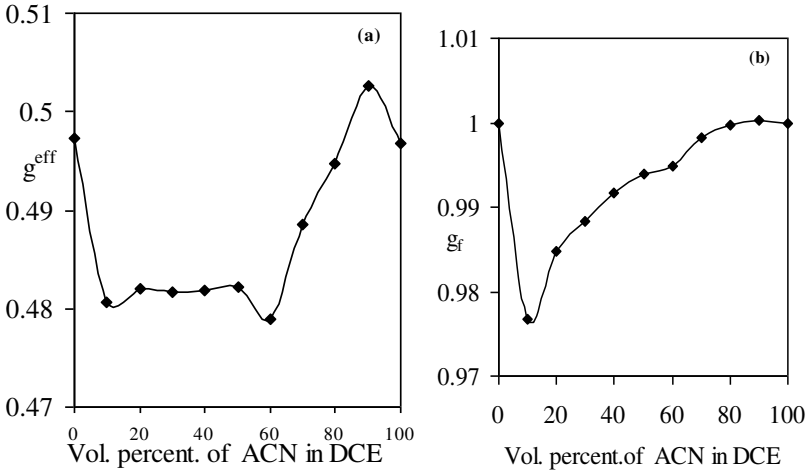

Figure 1. (a) The Kirkwood effective correlation factor g^{eff} and **(b)** the correlation factor g_f versus volume percentage of ACN in DCE.

The modified Bruggeman equation [12] is another parameter, which may be used an indicator of liquid 1 and 2 interaction. The Bruggeman factor f_B is given by,

$$f_B = \left(\frac{\varepsilon_{0m}-\varepsilon_{02}}{\varepsilon_{01}-\varepsilon_{02}}\right)\left(\frac{\varepsilon_{01}}{\varepsilon_{0m}}\right)^{1/3} = (1-\phi_2) \qquad (6)$$

According to equation (6), a linear relationship is expected which will give a straight line when plotted f_B against ϕ_2. However, here the experimental values of f_B were found to deviate

From the linear relationship. The Bruggeman dielectric factor f_B versus volume fraction ϕ_2 of ACN at 15°C is given in Figure 2.

To fit the experimental data, Eq. (6) has been modified [13]

$$f_B = 1-[a-(a-1)\phi_2]\phi_2 \qquad (7)$$

Where 'a' is numerical fitting parameter.

The parameters ‘a’ has been determined by the least squares fit method and it is found to be 0.784. The value of ‘a’ = 1 corresponds to the ideal Bruggeman mixture formula. The deviation from 1 relates to interaction between corresponding liquids 1 and 2. The large deviation of “a” suggest that stronger interaction between ACN and DCE.

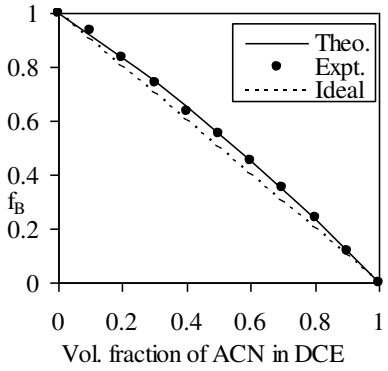

Figure 2.The Bruggeman plot for ACN-DCE mixture at 15°C. Dashed line denote original model (equation 6).Continuous line is the theoretical curve obtained from equation (7). Experimental points are shown by the symbol•.

5. CONCLUSION:

The Kirkwood correlation factors have been reported for ACN-DCE mixtures at 15°C temperature for 11 different concentrations. The interaction of the chlorine group with the nitrile group liquids is discussed. One observes significant deviation from the various models. The values of Kirkwood parameter g_f are deviated less from unity and it shows that the weaker interaction between the constituent molecules. The deviation of Bruggeman parameter ‘a’ from unity is small and it indicates that weaker interaction between the molecules of the ACN-DCE mixture.

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Study of cellulose degrading microorganisms isolated from agriculture land of Aurangabad region

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ABSTRACT:

Cellulose is a biomolecule and natural polymer which contain hundreds of carbon, hydrogen and oxygen atoms. It is the main substance of plant cell wall exist as a linear homopolysaccharide of glucose with β- 1,4 glycosidic linkage. Cellulose in the plants readily available in atmosphere as a significant plant biomass. A major obstacle for enzymatic hydrolysis is its crystalline and insoluble nature. Cellulose can be converted into glucose with the assistance of cellulolytic system. The bioconversion of cellulosic material mainly depends on the nature of cellulose source of cellulolytic enzyme, optimal condition for catalytic activity and production of enzymes. Endoglucanase is responsible for random cleavage of β- 1,4 glycosidic bonds along a cellulose chain. Exoglucanase is necessary for cleavage of non-reducing end of cellulose chain and splitting of the elementary fibrils from the crystalline cellulose. Agricultural land contained unwanted parts of crops and weeds which serves as a nutrient for cellulose degrading bacteria . The current study sought at the possible utilization of cellulose degrading bacteria from agricultural land for maximum cellulolytic potential at optimum conditions such as pH, temperature. Results showed that cellulose degradation (hydrolytic capacity) by isolate k04 was maximum ie. 7.1

KEYWORDS: *Cellulose, cellulolytic potential, endoglucanase, exoglucanase, cellulose degrading bacteria (K0).*

1. INTRODUCTION:

Cellulose is a biomolecule and natural polymer which contain hundreds of carbon, hydrogen and oxygen atoms Cellulose is a linear homopolysaccharide of 3000 or more repeating glucose residues with β- 1,4 glycosidic linkage. Cellulose is abundantly available in the environment in the form of plants as it is a major biomass of plants. It comprises 33 percent of all the vegetable biomass. Plants produce 4 X 10^9 tons of cellulose annually (6). Its crystalline nature and insoluble nature represents a big challenge for enzymatic hydrolysis. With the help of cellulolytic system cellulose can be converted to glucose. Different micro organism play an important role in conversion of lignocellulose waste into valuable products like biofuels produced by fermentation (7). Successful bioconversion of cellulosic material mainly depends on the nature of cellulose source of cellulolytic enzyme, optimal condition for catalytic activity and production of enzymes(8). Cellulase enzyme system comprises three classes of soluble extracellular enzymes ie β- 1,4 endoglucanase, β- 1,4 exoglucanase and β – glucosidase. Endoglucanase is responsible for random cleavage of β- 1,4 glycosidic bonds along a cellulose chain. Exoglucanase is necessary for cleavage of non-reducing end of cellulose chain and splitting of the elementary fibrils from the crystalline cellulose while β- 1,4glucosidase hydrolyses cellobiose and water soluble cellodextrin to glucose. (9,10). Farmland contained unwanted parts of crops and weeds which serves as a nutrient for cellulose degrading bacteria. The current study focused to examine the possible utilization of CDB from farmland for maximum cellulolytic potential at optimum conditions such as pH, temperature.

2. MATERIALS AND METHODS:

Sample collection: 1-gram soil sample was directly collected from agricultural land in Aurangabad region in sterilized screw cap tubes randomly. Sample was sieved and brought to laboratory for the isolation of cellulose degrading bacteria (K0). Isolation of cellulolytic bacteria: 1 gm of collected soil sample was mixed in 100 ml of sterile distil water. Serial dilutions up to 10^{-9} was prepared. A pour plate technique was used to isolate the cellulose degrading bacteria (CDB). 1 ml of diluted sample was mixed with cellulose agar media composed of KH_2PO_4-0.5 gm, $MgSO_4$-0.25 gm, cellulose-2.0 gm, gelatin-2.0 gm, agar- 15 gm and distil water- 1 L at pH 6.8 to 7.2 and 30 ^{0}C of temperature. After 48 hours of incubation selected colonies were streaked on Congo red agar media for the confirmation of cellulose degrading activity. Composition of Congo red agar is of KH_2PO_4-0.5 gm, $MgSO_4$-0.25 gm, cellulose-2.0 gm, gelatin-2.0 gm, agar- 15 gm, congo red -0.2 gm, distil water – 1L, pH- 6.8 to 7.2. Congo red used in the media act as an indicator for cellulose degradation as it provides rapid and sensitive test for cellulolytic bacteria. Colonies showing discoloration of congo red were taken as positive cellulose degrading bacteria (14). Hydrolysis capacity of positive isolates were determined by measuring diameter of clearing zone of colony (15).

Enzyme production: Positive isolates of cellulose degrading bacteria were cultured at 37 ^{0}C at 150 rpm in an enzyme production media composed of of KH2PO4-0.5 gm, MgSO4-0.25 gm, gelatin-2.0 gm, distil water- 1L and whatman filter paper No 1 (1 X 6 cm strip, 50 mg per 20 ml) at pH 6.8 to 7.2. After three days of incubation the broth

culture was centrifuged at 5000 rpm for 15 minutes and supernatant was collected and stored as a crude enzyme preparation.

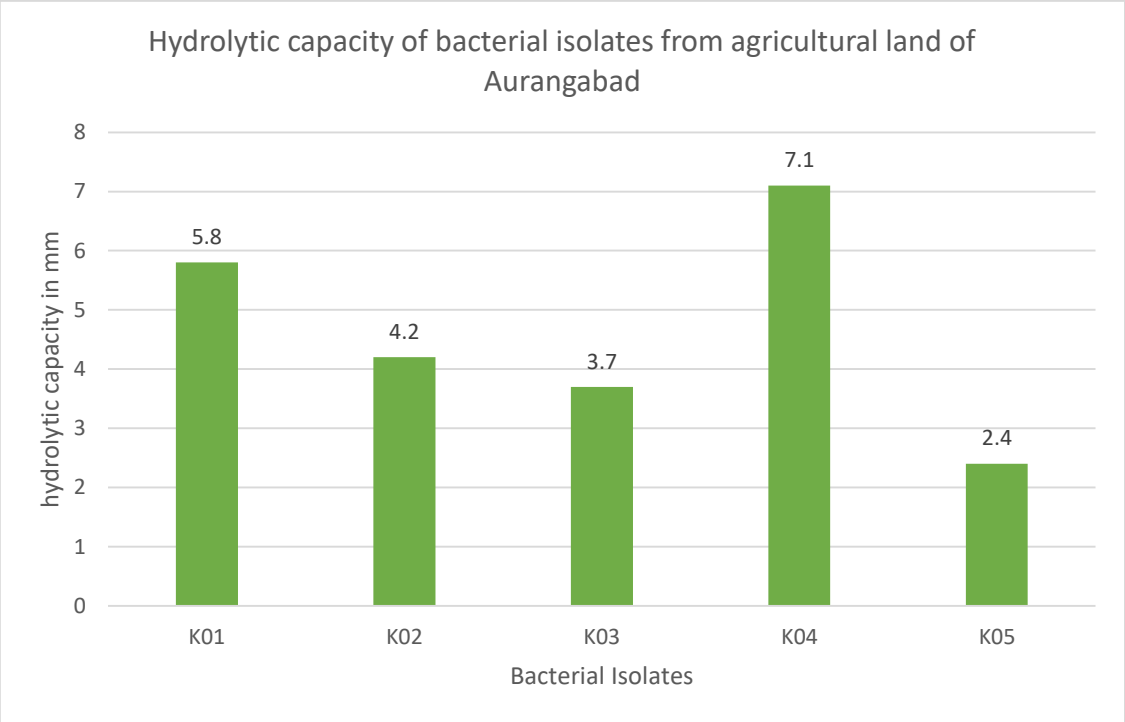
Enzyme assay: Cellulose activity was assayed by using 3,5- dinitrosalisic acid (DNS) reagent and released reducing sugar from filter paper was estimated. The cellulolytic activity was determined by incubating 0.5 ml of supernatant with 1.0 ml of 0.05 M sodium citrate buffer pH 4.8 containing whatman filter paper No 1 strip(1.0 X 6 cm ie 50 mg). After one hour incubation at 50^0C temperature the reaction was terminated by adding 3 ml of 3,5-dinitrosalisic acid (DNS) and 1 ml of reaction mixture. The amount of reducing sugar was estimated spectrophotometrically (16). One unit of enzymatic activity was defined as the amount of enzyme that releases 1µ mol reducing sugar per ml per minute.

3. RESULTS &DISCUSSIONS:

Isolation and screening of cellulose degrading bacteria: degradation of cellulosic material is a complex process and require participation of microbial cellulolytic enzymes. Habitats of the substrates are the best source for the isolation of cellulose degrading bacteria. Bacterial colonies cultured on cellulose agar media were selected to determine their cellulolytic potential on congo red agar media. Discoloration of colonies on media was observed in five colonies which are considered cellulose degrading bacteria and named, K0-1,K0-2, K0-3,K0-4,K0-5. Out of these five isolates K0-4 showed maximum hydrolysis capacity (HC) ie 7.1. The range of HC value is similar to range reported by Lu et al (18).

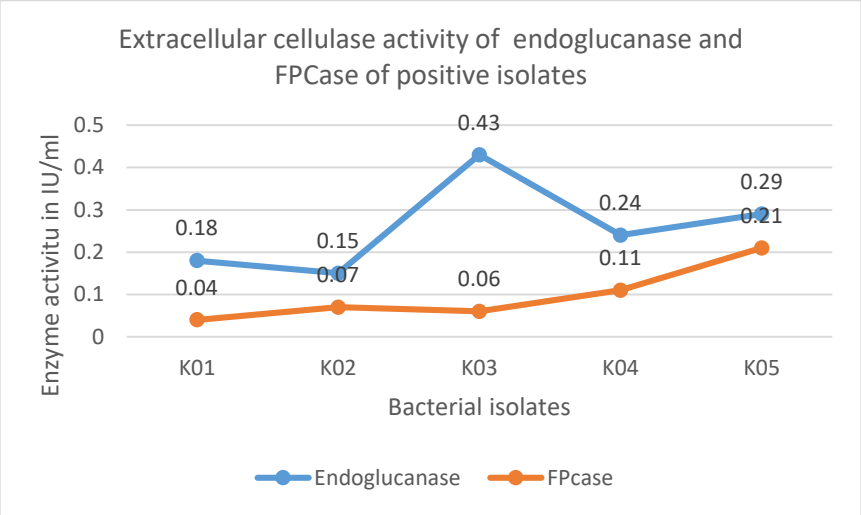
Table 1: Maximum clearing zone and Hydrolytic capacity (HC) of cellulose degrading bacteria (K0) on cellulose Congo red agar media.

Isolated Bacteria	Maximum clearing zone(mm)	HC value(Hydrolytic capacity)
K0 1	32	5.8
K0 2	28	4.2
K0 3	21	3.7
K0 4	37	7.1
K0 5	15	2.4



Graph 1: Maximum hydrolytic capacity in mm of isolated microorganisms on cellulose Congo red media

Cellulolytic potential: All the five isolates ie. K0-1, K0-2, K0-3, K0-4, K0-5 were selected for enzyme production and their respective cellulolytic activity was estimated.



Graph 2: Extracellular cellulase activity of endoglucanase and FPCase for positive isolates in three replicates.

The enzyme assay showed maximum cellulolytic activity for K03 with 0.43 IU/ml for endoglucanase and minimum for K02 with 0.15 IU/ml, similarly FPcase activity was observed maximum for K-05 with 0.21 IU/ml and minimum of 0.04 for K-01. The current study suggest that soil contain diverse type of microorganisms able to degrade cellulose by

Producing cellulose degrading enzyme.

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Physiochemical Analysis of Aqueous Extract of *Aegle marmelos* (Bael)

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***ABSTRACT**:*

In present study, an aqueous extract from Aegle marmelos (Bael), was determined the physiochemical study include macro, microelements, organic carbon, electrical conductivity and pH. Aegle marmelos (Bael) is used as a heart tonic. Aqueous extract has high pH therefore, it is helpful for the synthesis of base catalyzed chemical reactions and it act as Green catalyst. Aegle marmelos (Bael) is a source of Nitrogen, Potassium, Calcium, Zinc, Magnesium, Manganese, Iron and Phosphorus.

***KEYWORDS**: Aegle marmelos (Bael), Macro and Micro nutrients, pH, Electrical Conductivity.*

1. INTRODUCTION:

Aegle marmelos (L.) is a native plant of India. *Aegle marmelos* commonly known as "Bael" or wood apple or bilwa [1-3] (*Aegle marmelos* L.) is a dry-land plant belonging to the family *Rutaceae. A. marmelos* is burgeoning as a temple garden plant and its leaves are used to call for Lord Shiva. *A. marmelos* is a subtropical plant and develop to an altitude of 1,200 m altitude from sea level. It flourishes well in the dry forests mainly on hilly as well as plain areas. *A. marmelos* is a far apart; with a wide space distributed plant and found in India, Nepal, Vietnam, Laos, Cambodia, Sri Lanka, Myanmar, Ceylon, China, Pakistan, Bangladesh, Nepal, Sri Lanka, Java, Thailand, Indonesia, Malaysia, Tibet, Philippines and Fiji [4]. The bael is a blessed plant and it's all parts are very applicable, generally it is seen that if one part of any plant show any pharmacological effect then there is a major possibility that the other part give the same or related activity.

Fruit is beneficial in antidysentery, gastric troubles, digestive, antidiarrheal, constipation, laxative, tonic, stomachic, brain and heart tonic and additional importance such as antiviral activity while root bark shows action against intermittent fever and fish poison, gastric troubles, fever, heart disorders, palpitation, hypoglycemic, melancholia, anti-dog bite, antiamoebic, rheumatism [5] and stem bark are used as antipyretic and anti-inflammatory and anti-cancer activities. Abundant therapeutic activities of the plants bring about us to further develop a simple, rapid and precise chemo-profiling method for quality evaluation of different parts of *A. marmelos*.

In the present investigation physiochemical analysis [6-9] of aqueous extracts from *Aegle marmelos* or Bael. *It has medical importance value.*

Health benefits of Bael:

- Bael for Tuberculosis: In Ayurveda, it is used for the treatment of tuberculosis.
- Bael for Gynecological disorders: The regular consumption of Bael helps to prevent gynecological related issues.
- Bael for Urinary diseases: Use of bael leads you to overcome the problems of urinary diseases.
- Bael for Diabetes prevention: It has bitter pungent, full of antioxidants and helps to stimulate the pancreas to secrete insulin, which leads to lowering of blood sugar. The leaves can be utilized against diabetes.
- Bael for Digestive disorders: It supports intestinal biological formulations and protects the digestive system from ulceration, reduces the frequency of Irritable Bowel Syndrome (IBS), intestinal spasm thus beneficial in treating of diarrhea, dysentery, and other infections of Elementary canal.
- Bael for Fever prevention: The leaf juice with honey is helpful in prevention of fever.
- Bael for Epilepsy: Flowers are uses as epilepsy tonic.
- Bael Nutritional facts: It is rich in alkaloids, polysaccharides, antioxidants, beta carotene, vitamin C, Vitamin B, and many other bio-chemical substances. It also incorporates phosphorous, iron, protein, tannins, calcium, and fiber. The 100 gram of Bael include the following nutrients: Calorific value (136 Kcal), Moisture (60.5g), Protein (1.7g), Fat (0.3g), Minerals (1.8g), Fiber (2.8g), Thiamine (0.12mg), Niacin (1.2mg), Vitamin C (9 mg), Potassium (601mg) and Copper (0.22 mg), Carb (30.8mg), Calcium (80mg), Phosphorous (40mg), Iron (0.8mg), Beta carotene (53 UG).
- Bael for Piles treatment: The extract of unripe bael fruit is helpful in curing of piles and hemorrhoids.

- Bael fights ulcer: Due to its soothing effects on the digestive system, it leads to reduce the acidity level in the stomach thus useful in combating ulcers like gastric ulcers, gastro duodenal ulcers, etc.

Uses of Bael:

- Its juice is used to make drink and squashes, especially in summer season because of its sweet and pleasant nature.
- Bael tender leaves are used as salads.
- It is used to increase appetite.
- Its extract oil is used to cure respiratory problems.
- It is used in the preparation of candy, squash, toffee, pulp powder, and other eatable products.

Bael juice benefits:

- Bael juice is useful in curing of constipation because of its laxative properties.
- Bael juice gives great comfort in heartburn, acidity, hyperacidity and indigestion.
- If you are suffering from intestinal parasites, it is advisable to drink bael juice because of its antidote nature.
- Aegle marmelos juice is good for heart and brain. Bael juice mixed with Ghee is useful in prevention of heart disease. It is also used as a heart tonic.
- Chewing of raw leaves of Bel help to solve many gastric problems.
- Bael juice is rich in vitamin C, and good for scurvy treatment.

2. MATERIAL AND METHODS:

Collection of Plant materials:

Fresh dry fruit of Aegle marmelos or Bael from Shirala region of Maharashtra, then it dries completely up to two weeks, cut into small pieces, and grind to fine powder form. The powdered samples were hermetically sealed in clean covered bottles.

Chemicals: *All the chemicals were purchased from Merck, AR grade, and SD Fine.*

Instruments: *Conductivity Meter-Model EG-660, pH Meter Model EQ-610, Atomic Absorption Spectro-Photometer, Schimadzu Model–AAC-7000 and UV-Visible Spectrophotometer, Schimadzu,-Model UV-2700.*

Preparation of aqueous extractions: *Aqueous fruit extract of Aegle marmelos (Bael) prepared from the powdered sample of its and thermally treated by using muffle furnace at* 100^0C to obtain fine soft ash. The Ash was taken distilled water (50mL) in conical flask and carefully stirred for 1 hr. at room temperature. Then mixture was filtered through Whatman No.1 filter paper. Then filtrate was accumulated in fresh sterilized bottles for further use.

Experimental Photos:

3. RESULTS AND DISCUSSION:

The use of aqueous fruits extract of Bael for determined the physiochemical studies. Table 1 showed the pH of extract is 09.63 which is highly is basic nature (Table 1, entries 1).

Table 1: Physiochemical studies of aqueous fruit extract from *Aegle marmelos* (Bael).

Sr.No.	Parameter	Units	Value	Limit
1	pH	--	09.63	01-14
2	E.C.	Mhos/cm	1.02	01.02
3	Nitrogen (N)	%	1392	1320-1650
4	Phosphorous (P)	%	11-30	90
5	Potassium (K)	%	4753	2000-3000
6	Organic Carbon(C)	%	0.35	0.1-3.50
7	Calcium (Ca)	%	1.10	0.36-2.50
8	Magnesium(Mg)	%	0.10	0.26-1.20
9	Copper(Cu)	ppm	0.52	02-10
10	Iron(Fe)	ppm	0.99	01-03
11	Manganese (Mn)	ppm	1.00	01-05
12	Zinc(Zn)	ppm	20	10-30

Aqueous fruit extract has been significant role in Electrical Conductivity(Table 1, entries 2) and evaluation of macro as well as micro element such as Nitrogen (N), Phosphorus (P), Potassium(K), Organic Carbon, Calcium(Ca), Magnesium (Mg), Copper (Cu), Iron (Fe), Manganese (Mn), and Zinc (Zn). Overall, it observed that, in aqueous extract of aqueous fruits extract of Bael, *remarkable* source of Potassium(K) (Table 1, entries 5, Fig.1) and also more percentage of Nitrogen (N) (Table 1, entries 3, Fig.1).

The result showed that, incredible source of Potassium and Nitrogen and also showed good source of macro and micro elements in aqueous extracts (Table 1, Fig.1).

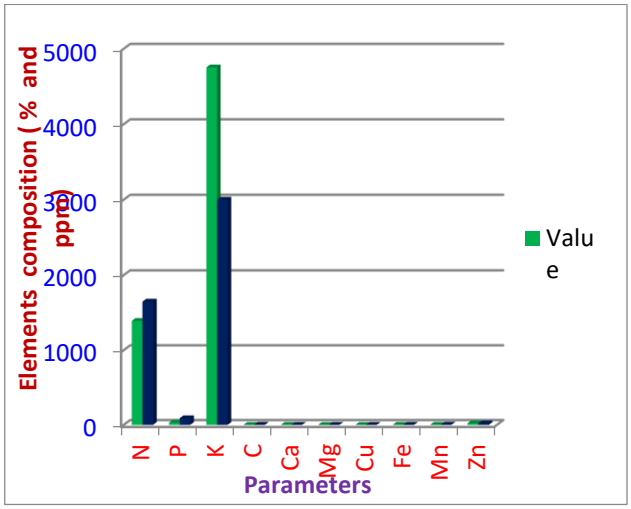

Figure 4 Physiochemical studies of aqueous fruit extract from *Aegle marmelos* (Bael).

4. CONCLUSION:

In Conclusion, We have investigated the rich source of Potassium, Nitrogen, and other parameters like pH, E.C. from aqueous fruit extract from *Aegle marmelos* (Bael). Aqueous fruit extract has high pH therefore, it is helpful for the synthesis of base catalyzed chemical reactions and it acts as Green catalyst.

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Spray Pyrolysis Deposition and Characterization Of Cobalt Ferrite Thin Film

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ABSTRACT:

The present investigation is related to the deposition of single phase nanocrystalline cobalt ferrite thin film on glass substrate using spray pyrolysis technique. The deposited film was annealed at 550^{o}C for 4 h and used for the further study. The film was characterized for their structural and magnetic properties by means of X-ray diffraction and Vibrating sample magnetometer technique at room temperature. The XRD analysis shows the presence of well oriented Bragg's peaks corresponding to cubic spinel structure. The particle size was estimated to be 18 nm. The hysteresis plots (M-H loop) shows ferrimagnetic behavior. Using M-H plot saturation magnetization (M_s), coercivity (H_c), remanence ratio (M_r/M_s) were obtained. The magnetic properties of cobalt ferrite shows better results compared to bulk ferrite. The magnetic parameters are in accordance with the other nano-size ferrites.

KEYWORDS*: Spray pyrolysis, Cobalt spinel ferrite thin film, Structural and magnetic properties.*

1. INTRODUCTION:

Spinel ferrites having the general formula MFe204 (M=divalent mental ion, Mn, Ni, Mg, Cu, Zn, Cd, etc.) are one of the most interesting class of magnetic material because of their many application like transformer cores, Antenna rod, Memory devices etc.[1] Apart from these application ferrites can also be used in gas and humidity sensors, magnetic drug delivery system etc due to their interesting electrical an magnetic properties. [2]. They pusses high electrical resistivity, low dielectric eddy current losses, high saturation magnetization, high permeability, high curie temperature compared to other magnetic materials they are chemical stable and can easily be produced in various forms .such as bulk nanocrystalline and thin film form. In recent year's spinel ferrite thin film have attracted much attention of researches for high density magnetic recording and magneto optical recording media, high frequency application [3]. Among the various spinel ferrite cobalt ferrite $CoFe_2O_4$ is well known for its good magnetic optical properties, excellent chemical stability. Spray pyrolysis technique offer an attractive route for better control of humginity, purity, morphology in the present work deposition of cobalt ferrite thin film by spray pyrolysis technique and its characterization by X-ray diffraction and pulse field hysteresis loop technique are presented.

2. EXPERIMENTAL TECHNIQUES:

Film Deposition

Cobalt ferrite ($CoFe_2O_4$) thin film was prepared by spray pyrolysis deposition (SPD) technique. Analytic reagent grade chemicals Co $(No_3)_2.6H_2O$ and Fe $(NO_3)_3.9H_2O$ were used as starting materials. The two metal nitrate solutions were dissolved separately in de-ionized water at the concentration of 0.1 M for both Co^{2+} and Fe^{3+} solution. Final solutions were prepared by mixing these two solutions in 1:2 volumetric proportions. Cobalt ferrite thin films were prepared by spraying the solution onto extremely cleaned glass substrate as it increases purity and homogeneity thin film.

3. RESULTS AND DISCUSSION:

Film formation

$CoFe_2O_4$thin film was deposited on glass substrate using spray pyrolysis deposition technique. The concentration ratio of Co^{2+} and Fe^{3+} ions was kept constant as 1:2 ratios. The ultrasonically clean glass substrate preheated was used for deposition the mixed solution of cobalt nitrate and iron nitrate was spared on glass substrate. By optimizing various parameters like pressure, distance, spray rate etc. The film was then annealed 550^{0}C. The reaction mechanism of ferrite thin film formation of $CoFe_2O_4$ is given below.

$$Co(No_3)_2 + 2Fe(No_3)_3 \xrightarrow{\Delta 823K} CoFe_2O_4 + 8No_2\uparrow + 2O_2\uparrow$$

Thickness Measurement

The property of thin film is strongly depending on thickens of the film due to surface phenomenon by optimizing the several parameters. Like nozzle diameter, pressure etc., the cobalt ferrite thin film with uniform thickness is produced. The film thickness was measured by thickness profiler and thickens of $CoFe_2O_4$ thin film was found to be 280 nm.

Structural Analysis

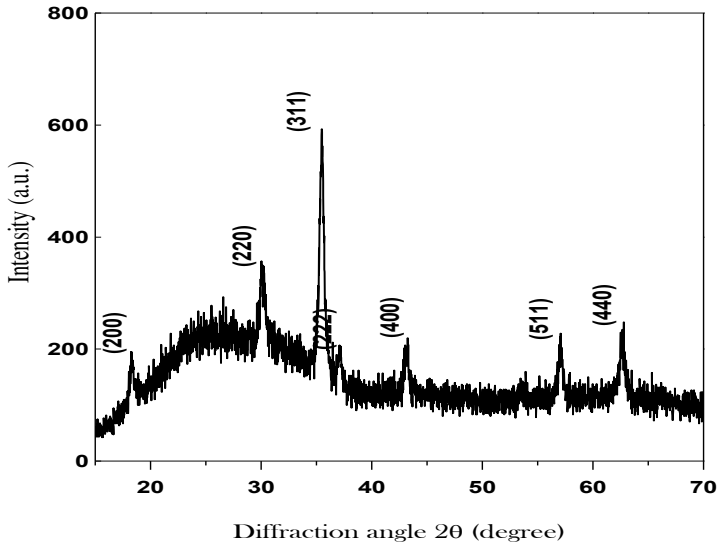

Fig.1.1: XRD diffraction pattern of cobalt ferrite thin film.

Cobalt ferrite thin film deposited on glass substrate was characterized by X- ray diffraction technique at room temperature using Cu-kα radiation. The XRD pattern was recorded in the 2θ range in the 20^0 to 70^0. **Fig. 1.1** represents the XRD pattern of $CoFe_2O_4$ ferrite thin film. The (200), (220), (311), (222) (400), (511) and (440) refection were observed in **Fig. 1.1**. This clearly gives the evidence of formation of single phase cubic spinel structure of cobalt ferrite. The intensity of the reflections observed in the XRD pattern reveled the existence of nano-sizegrains/fine grains. The crystallite size of film was intimated from the most intense peak (311) of the XRD pattern, by using the sherrer's formula [4].

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

Where, λ is wavelength of X- ray radiation,

β full width of diffraction line (311) at the half maximum intensity.

The crystallite size of the cobalt ferrite thin was found to be 18 nm. The several of structural parameter like lattice constant, X-ray density of the cobalt ferrite obtained from XRD data are given in the following **Table 1.1.**

Table-1.1 Structural and Magnetic Parameter

Sr.No.		1	2	3	4	5	6	7
Parameters	Structrural Parameters	Thickness (t)	Lattice constant (a)	Unit Cell Volume $(a)^3$	Crystallite size (D)	X-ray density (dx)	Bulk density (d_B)	Surface Roughness (Ra)
Observed Value		280nm	8.3738A	$587(A)^3$	18nm	5.3099 g/cm^3	5.2957 g/cm^3	6 nm

Magnetic Parameter	1	2	3	4
	Saturation magnetization (Ms)	Residual magnetization (Mr)	Coactivity (Hc)	Magneton number (n_B)
	25 emu/g	5 emu/g	180 Oe	1.1(μ_B)

Using XRD data lattice constant (a) and X-ray density (dx) was Calculated and are presented in **Table 1.1**.The Values of (a) and 'dx' are in reported range [5]. The surface roughness (Ra) of the film was calculated from AFM image and it is of the order of 6 nm.

The magnetic properties of the cobalt ferrite thin film were studied by vibrating sample magnetometer an applied magnetic field of 1Tesla at room temperature.

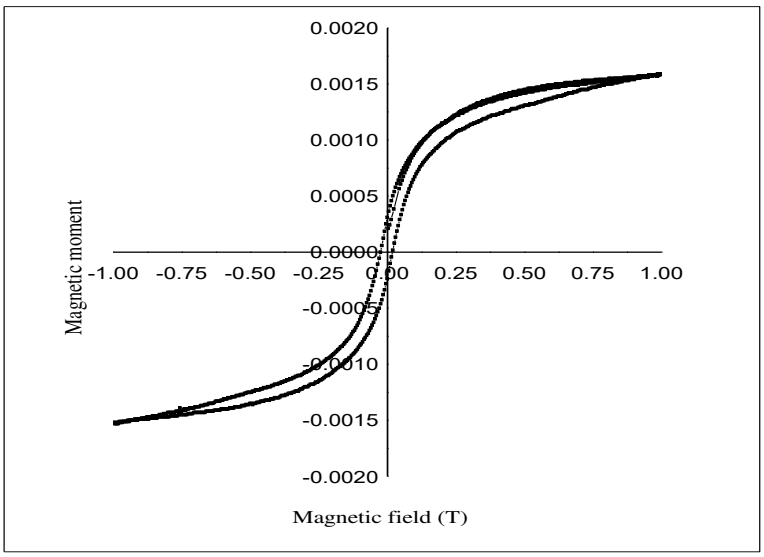

Fig.1.2: M-H Curve of cobalt ferrite thin film.

Fig. 1.2 shows the plot of magnetization (M) against applied field H. It is observed from that M-H curve of cobalt ferrite curve thin film saturate well at about 1 Tesla. Using hysteresis curve the saturation magnetization (Ms), residual magnetization (Mr) and coercivity (Hc) were obtained and their values are given in **Table 1.**

The value of Ms and Mr are quite low whereas corecivity is more indicating the nano crystalline nature of the cobalt ferrite thin film. However, in comparison with bulk magnetic data [6] these the present observations can be attributed to nano crystalline nature of the cobalt ferrite thin film.

4. CONCLUSIONS:

The deposition of cobalt ferrite thin film on to glass substrate was successfully achieved by spray pyrolysis techniques The nanocrystalline nature of the film was confirm from the crystallize size which is of the order of 18nm.The saturation magnetization Ms and remnant magnetization Mr are found to be low were as coactivity is sufficiently high.

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Study on Physico-chemical Water analysis from some selected Bore wells in Majalgaon city, Beed District. (MS)

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ABSTRACT:

Water is an important thing *for regulation and growth of all living organisms. Potable water is safe enough to be consumed by human, plants and animals. Water samples collected from* five *bore wells from Majalgaon city were subjected to physico-chemical and biological analysis. Physico-chemical analysis carried using titrimetric, spectro photometric method to evaluate the quality. The results showed that* $P^{H,}$ *temperature, turbidity, chloride, nitrate, and total hardness of all the bore well water samples were the permissible limits while magnesium and phosphate; samples gave values well above the permissible limits decided by WHO. Sample BW- 4 gave maximum of magnesium, sample BW-5 show highest values of phosphate. Also dissolved oxygen results showed higher values by sample BW- 3 .Generally results exhibited significant variation in the parameters studied on the samples. These samples could be attributed to the geographical positions and depth of the bore wells. Hence all these Bore well water samples are safe and suitable for domestic*, garden plantation *and drinking purpose.*

Keywords*: - Bore well, Physico-chemical analysis,* Majalgaon *city.*

1. INTRODUCTION: -

Water is the most important and abundance compounds of ecosystem. All living organisms on the earth need water for their survival and growth (Lamb1985). On earth planet have 70% of water and near about 80% of earth surface is covered by water out of which only small fraction is available for consumption. The rest of all water is closed water filled in sea and ocean ice slabs, glaciers. Ground water is defined as water that found underground in cracks and spaces in sand, soil and rocks. This source has two distinct functions, firstly it is a significant source of both urban and rural population's water supply and secondly it sustains many wetland ecosystems (Naiknaware 2018). The sources of ground water supply mostly depend upon the rainfall and resulting percolation of the water in the earth, another important factor is the type and quality of soil (Basavraja et al 2011).

But due to rising of human population, industrialization, uses of fertilizer in the agriculture and human domestic uses water is polluted. It is highly polluted with different contaminant. This contaminated polluted water absorbed in the earth surface. Therefore it is necessary that quality of drinking water should be checked at regular time interval, because due to use of contaminated drinking water should be suffer various diseases to human and animals (Adoni and Joshi 1987). Ground water is already used throughout wells and bore wells. Unfortunately underground water reservoirs are renewed only slowly by natural absorption. Ground water is available source of water supply, because it is unpolluted due to restricted movements of pollutant in soil profile (Kale N. N. 2007). However when water travels through the ground part of soil components dissolves in it, so it is usually hard, it may usually contain objectionable concentration of salt, such as metal iron, manganese, zinc etc. UNDP also reported that the water and sanitation crisis claims more lives through diseases than only war claims through guns (UNDP 2006). Near about 6 millions of people die each year from water sanitation and hygiene related causes. These all death occurs in developing world (WHO, 2008). Thus the quality as well as quantity of clean water supply is of vital signification for the welfare of mankind. Majalgaon city is lying to the Balaghat range of Beed district in Maharashtra state. It is less rain fall area, so location of Majalgaon is suitable for major source as bore water for drinking and domestic use purpose. Hence bore well water are major source of good water and have been increasingly commercialized for water required population of Majalgaon city.

The quality of this water not guaranteed and could cause health problem as a result of consumers drinking for such sources. This research investigated some physico-chemical and biological parameters of five bore well water constantly in uses by water vendors.

2. MATERIAL AND METHODS:-

Beed district is an administrative district in Maharashtra. It is situated in central place of Marathwada region out of eight districts in it. In this Beed district Majalgaon tehsil is most important for total economy of this district, so, more population run in Majalgaon city. These population need for regular living system needs water for human being and domestic animals.

For study water samples were collected from five bore well in Majalgaon city. These samples were collected using cleaned polyethylene bottles of one liter capacity for each labeled Tembhe Ganpati Bhat Galli BW-1, Bank Colony

BW-2, Ambedkar Chouk BW-3, Shivajinagar BW-4, Sanmitra Colony BW-5.This study samples were collected same time at evening 3:00 to 5:30 p.m.

These samples used for study of some physical parameters were analyzed on the bore well water samples at the site of collection. The temperature of each sample was measured and recorded using a calibrated thermometer in degree Celsius. The samples were then transferred to laboratory and they were kept in the refrigerator to preserve the quality of the sample prior to analysis. All the apparatus used for analysis were properly wash and rinsed and the reagents are all of analytical grade. Physico-chemical parameters determination by various standard method was used for P^H determination of the water samples, a digital P^H meter (Eligo Model) standardized with buffer solution of P^H 4 and P^H 7.2 was employed. The chemical parameters calcium, magnesium, alkalinity, Chloride and total hardness were determined by titrimetric method. Nitrates and phosphates were obtained using a double beam visible spectrophotometer (2203).All measurements were completed in triplicate and the mean values recorded in the table.

3. RESULTS AND DISCUSSION:-

The results of all physico-chemical and biological parameters obtained in five bore well samples are presented in the following table.

Physico-chemical and biological analysis of the Five Bore Well water samples in Majalgaon City.

Sr. No.	Parameters	BW-1	BW-2	BW-3	BW-4	BW-5
01	Temperature(°C)	28.6	29.5	30.4	29.7	30.2
02	P^H	8.4	7.8	8.2	7.1	7.6
03	Turbidity NTU	0.70	0.50	0.48	0.62	0.54
04	Chlorides ppm	69.3	69.2	84.9	115.2	81.4
05	Alkalinity ppm	120	102	112	92	125
06	Total hardness ppm	442	375	320	360	258
07	Calcium ppm	62	72	65	68	52
08	Magnesium ppm	52	82	77	42	62
09	Nitrates ppm	2.3	0.8	0.65	1.2	0.85
10	Phosphates ppm	1.6	2.1	2.8	0.8	2.9
11	Dissolved oxygen ppm	12.3	11.6	9.8	8.4	12.5
12	Biological oxygen demand	2.0	1.9	0.8	1.2	2.2
13	Chemical oxygen demand	5.6	7.6	8.2	4.4	6.8

The water samples temperature ranged between (28.6 to 30.4°C) with the bore well BW-3 having highest temperature and BW-1 have the lowest. Temperature values are known to depend on season and climate condition. The P^H values recorded in this work in between (7.1 to 8.4). The values observed within the permissible limits provided by WHO. The turbidity of bore well samples was found to be in the range of (0.40 to 0.80NTU). The values compared with the 5.0 NTU WHO permissible limits for potable water. Turbidity is due to the presence of colloidal particle from clay during rainfall, or from discharge of sewage and industrial waste.

The alkalinity is primarily due to carbonate, bicarbonate and hydroxide contents. Alkalinity, P^H and hardness affect the toxicity of many substances in the water sample BW-4(92ppm), showing minimum value of alkalinity and sample BW- 5 gives highest values (125ppm) of alkalinity.

The concentration of nitrate in water samples depends on the nitrification activity of microorganisms. The values of nitrates range (0.65 to 2.30). The values are well below 50 ppm(WHO) permissible limits of nitrate in the drinking water. High level of nitrate in drinking water is due to excessive use of agriculture fertilizers, domestic effluent, industrial sewage disposal (APHA 1989).

Water is contaminated with nitrate causing methemoglobinemia i.e. Blue baby syndrome in infant. Chloride values in the water samples ranges from (69.2 to 115.2 ppm). The concentration of chloride is lowest in sample BW-2 and highest in sample BW-4. The values were within the WHO (200ppm) limit for chloride. It may also get into surface water from several sources including rock, agricultural runoff waste water.

Total hardness of water samples were found to be in the range of (258 to 442 ppm). Bore well water sample BW- 1 showing highest hardness of water. Other water samples are in the normal range given by WHO./ Hardness value of ground water may be classified as soft >75ppm, Moderately soft>(75-150ppm),hard(150-300ppm), and very hard>300ppm. Total hardness less than 80 ppm may result in corrosive water, while hardness above 100ppm may result

in the need for more soap, during bathing and laundering form scum and curd causes yellowing of fabrics, excessive hardness may also lead to scale deposits in pipes, heaters and boilers.

The values of magnesium ranged between (44-80ppm) sample BW-4 showing lowest value but sample BW-2, showing highest value. Magnesium is a salt contribute to hardness and taste of water. Excessive magnesium may give water bitter taste, but it is not hazards to health.

The result of phosphate analysis in the samples ranged from (0.8-2.9ppm). All the bore well samples gave higher values than 0.5 ppm in the permissible limit. Phosphate stimulates the growth of plankton and aquatic plant. If excess of phosphate is enter in the water body stimulate growth of algae and aquatic plant that's choke up the water way and use up large amount of oxygen. This condition is known as eutrophication or over-fertilization of receiving waters.

Biological Oxygen Demand (BOD) is measure of organic material contamination in water specified by ppm. BOD is the amount of dissolve oxygen required for biochemical decomposition of organic compounds and oxidation of certain inorganic materials. High BOD decreases levels of dissolve oxygen. All water samples having BOD ranges within permissible limit. Chemical Oxygen Demands (COD) is another measure of organic material contamination in water specified ppm. COD is the amount of dissolve oxygen required to cause chemical oxidation of the organic material in water. Both BOD and COD are key indicators of the environment health of surface water supply. They are commonly used in waste water treatment but rarely in general water treatment by Mishra(1991).

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Tripropylammonium chlorochromates oxidation of p-nitrochalcone (pnc): kinetic and mechanistic study

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ABSTRACT:

The Kinetics of oxidation of P-nitrochalcone (PNC) by Tripropylammonium Chlorochromates [TriPACC] has been Studied Spectrophotometrically in presence of Sulphuric acid in aqueous acetic acid medium in the temperature range 295-320K.The reaction is first order with respect to both p-nitrochalcone (PNC) and TriPACC. There is no kinetic or spectral evidence for the formation of complex between TriPACC and p-nitrochalcone (PNC). The activation parameters for the slow step were computed and calculated. Effect of ionic strength and dielectric constant of medium has also been reported. A suitable mechanism has been proposed.

KEY WORDS: *P-nitrochalcone (PNC), Tripropylammonium Chlorochromates, Oxidation, Kinetics.*

1. INTRODUCTION:-

p-nitrochalcone (PNC) undergo a variety of chemical reactions and are found useful in the synthesis of variety of heterocyclic compounds. p-nitrochalcone (PNC) have been used as intermediate for the preparations of compounds having therapeutic value. Literature review reveals that p-nitrochalcone (PNC) derivatives exhibit diverse pharmacological activities such as potential cytotoxic agents, antimicrobial agents, antiviral, anti-inflammatory, anesthetics etc. Hence the study becomes important from the biological point of view.

An extensive literature survey reveals that the kinetics and mechanism of oxidation of chalcones have been carried out using various oxidants like trichloroisocyanuric acid (1), pyridinium chlorochromate (2), acid bromate (3), N-chloronicotinamide (4), hexacyanoferrate (III) (5), N-chlorosuccinimide (6), chloramine-T (7), morpholinium chlorochromate(8), peroxydisulphate(9) and periodate(10). The results of kinetics of oxidation of p-nitrochalcone (PNC) with TriPACC in aqueous acetic acid medium has been reported with a view to probe the mechanism of oxidation.

2. EXPERIMENTAL SECTION:-

All the chemicals and reagents were of analytical grade. All the solutions used in the study were prepared by using distilled acetic acid and doubly distilled water. Tripropylammonium Chlorochromates was prepared by the following method: chromium (VI) oxide (15.0g, o.150 mol) was dissolved in water in a polyethylene beaker and 40% hydrochloric acid (11.3 ml, 0.225 mol) was added with stirring at 0°C. To the resultant orange solution, tripropylammine (28.3 ml, 0.150 mol) was added drop wise with stirring to this solution over a period of 30 minutes and stirring was continued for 30 minutes at 0°C. The orange colored precipitate was filtered, washed with petroleum ether and dried in vacuum for 2 hours at room temperature [11]. Yield was 26 g (96%); MP was 144° C.

The Tripropylammonium Chlorochromates was stored in polyethylene bottle for long period of time. TriPACC was soluble in water, DMF, acetonitrile, acetone and DCM and was sparingly soluble in benzene, chloroform and hexane.

3. DETERMINATION OF STOICHIOMETRY AND PRODUCT ANALYSIS:-

The Stoichiometry of the reaction was determined by carrying out several sets of experiment with varying amount of (TriPACC) largely in excess over P-nitrochalcone (PNC) in 20% acetic acid by using 0.1N H_2SO_4. The remaining (TriPACC) was then analyzed Spectrophotometrically. The result indicated that 1 mole of alcohols react with 1 mole (TriPACC).

$$C_6H_5\text{-}CH{=}CH\text{-}COC_6H_5 + [C_3H_7]_3N^+H(CrO_3Cl) \xrightarrow{H^+} C_6H_5\text{-}COOH + C_6H_5\text{-}CH_2\text{-}CHO + [C_3H_7]_3NH(CrO_3H_2Cl)$$

The product analysis was carried out under kinetic conditions. In a typical experiment, P-nitrochalcone (PNC) (0.05 mol) and TriPACC (0.01) were made up to 50 ml in 20% acetic acid and kept in dark for about 24 hours to ensure the completion of the reaction. The solution was then treated with an excess (200 ml) of a saturated solution of 2, 4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept overnight in a refrigerator. The precipitated 2, 4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol and weighed again. The yield of DNP before and after recrystallization was 2.0 g (90%) and 1.7 g (75%) respectively. The DNP was found identical with the DNP of acetone by meting point. The products were also characterized by TLC, IR, and NMR spectra.

KINETIC MEASUREMENTS:-

The reactions were followed under pseudo-first-order conditions by keeping large excess (x 10 or greater) of the P-nitrochalcone (PNC) over TriPACC. The temperature was kept constant to +/- 0.1 K. The solvent was acetic acid. The reactions were followed by monitoring the decrease in the concentration of TriPACC spectrophotometrically at 350 nm for 80% completion of the reaction. The pseudo-first-order rate constants $K_{obs,}$ were evaluated from the linear (r=0.990-0.999) plots of log [TriPACC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within +/- 3%.

4. RESULT AND DISCUSSION:-

The results of oxidation of P-nitrochalcone (PNC) by TriPACC are represented as follows.

Effect of variation of concentration of P-nitrochalcone (PNC):-

The oxidation of P-nitrochalcone (PNC) with TriPACC in 20% of acetic acid in presence of sulphuric acid yields acetone. By keeping constant [TriPACC] and [H_2SO_4], the increase in [P-nitrochalcone (PNC)] increases the rate of reaction (Table-1). The plot of log of k_{obs} versus log [P-nitrochalcone (PNC)] for different initial concentration of P-nitrochalcone (PNC) is linear with unit slope demonstrate the first order dependence of rate on P-nitrochalcone (PNC) (Figure: 1)

Table 1: Effect of variation of [P-nitrochalcone (PNC)] on reaction rate

[TriPACC]= 0.001 M, [H_2SO_4] = 0.1 N, Temperature =303 k, AA = 20% (v/v)

(PNC)]	0.01M	0.02M	0.03M	0.04M	0.05M	0.06M	0.07M	0.08M
k x 10^3sec^{-1}	2.08	2.37	2.64	2.96	3.22	3.52	3.78	4.08

Effect of variation of concentration of TriPACC:-

At constant [P-nitrochalcone (PNC)] and [H_2SO_4], the increase in [TriPACC] increases the rate of reaction (Table-2). The plot of log k_{obs} verses log [TriPACC] for different initial concentration of TriPACC is linear with unit slope present the first-order dependence of rate on TriPACC.

Table 2: Effect of variation of [TriPACC] on reaction rate
[P-nitrochalcone (PNC)]= 0.01 M, [H_2SO_4] = 0.1 N, Temp =303 k, AA = 20% (v/v)

[T_{ri}PACC] Mole	0.001	0.0015	0.002	0.0025	0.003	0.0035	0.004	0.0045
k x 10^3sec^{-1}	2.08	2.36	2.58	2.87	3.08	3.31	3.55	3.79

Effect of variation of concentration of H^+:-

In order to study the effect the H^+ion concentration on the rate of oxidation reaction of P-nitrochalcone (PNC), the dependence of reaction rate has been investigated at different initial concentration of H_2SO_4. The rate of reaction increases with increase in [H_2SO_4] (Table-3). The plot of log K_{obs} verses log [H+]are also straight line with slope less than unity, Indicating a fractional order dependence on [H+].

Table 3: Effect of variation of [H_2SO_4] on reaction rate
[TriPACC]= 0.001 M, [(PNC)] = 0.01 M, Temp. =303 k, AA = 20% (v/v)

[H_2SO_4]	0.1M	0.2M	0.3M	0.4M	0.5M	0.6M	0.7M	0.8M
k x 10^3sec^{-1}	2.08	2.27	2.46	2.65	2.77	2.95	3.06	3.24

Effect of ionic strength:-

In the present investigation effect of salt on the rate of reaction is carried out. The salts selected are KCl, KBr, and KI. These will give effect of anion particularly halides on the rate of reaction. The divalent and trivalent cationic salt were also used such as $CaCl_2$, $Ca(NO_3)_2$, $Al(NO_{3)3}$ and K_2SO_4. The experiments were carried out under pseudo-first- order condition. These results were used to determine first order rate constant. The rate constants for the oxidation of P-nitrochalcone (PNC) in presence of different salt are shown in [Table 4]. From table it is clear that, the rate increases with increase in cationic charge and decreases with increase in anionic charge. In case of KCl the rate of reaction decreases with the addition of KCl, this is due to the formation of less reactive species [19] by interaction between Cl^- ion and protonated TriPACC.

Table 4: Effect of variation of [salts] on reaction rate

[TP]= 0.001 M, [(PNC)] = 0.01 M, [H_2SO_4] = 0.1 N, Temp. =303 k, AA = 20% (v/v)

Salts 0.1M	KCl	KBr	KI	$CaCl_2$	$Ca(NO_3)_3$	$Al(NO)_3$	K_2SO_4
k x 10^3sec^{-1}	2.07	2.38	2.39	2.48	2.76	2.98	2.34

Effect of solvent composition:-

At fixed [P-nitrochalcone (PNC)], [TriPACC] and [H^+], the rate of oxidation of P-nitrop-nitrochalcone (PNC) (PNC) with TriPACC increases with decrease in polarity of solvent (Table 5). This is due to polar character of transition state as compared to the reactant. The plot of log k_{obs} verses 1/D is linear with positive slope indicating ion- dipole type of reaction [20].

Table5: Effect of variation of Acetic Acid % on reaction rate

[TriPACC]= 0.001 M, [H_2SO_4] = 0.1 N, [P-nitrochalcone (PNC)] =0.01M, Temp=303 k

Acetic acid	10 %	20 %	30 %	40 %	50 %	60 %	70 %	80 %
k x 10^3sec^{-1}	1.95	2.08	2.25	2.37	2.49	2.57	2.73	2.86

Effect of temperature:-

The study of effect of temperature on rate of oxidation of P-nitrochalcone (PNC) by TriPACC has been subjected to different temperature range 293K to 313K by keeping the concentration of P-nitrochalcone (PNC) and reagent constant. Rate constants are given in [Table 6]. The plots of log of K_{obs} verses 1/T are linear (Figure: 2)

Table 6: Effect of variation of Temperatures on reaction rate

[TriPACC]= 0.001 M, [P-nitrochalcone (PNC)] = 0.01 M, [H_2SO_4] = 0.1 N, AA = 20% (v/v)

Temperatures (K)	293	298	303	308	313	318
k x 10^3sec^{-1}	1.28	1.79	2.08	2.46	2.89	3.18

Table 7: Activation Parameters

[TriPACC]= 0.001 M, [CH] = 0.01 M. [H_2SO_4] = 0.1 N, Temp. =303 k, AA = 20 % (v/v)

Activation parameters	**ΔE_a KJ mole^{-1}**	**$\Delta H^{\#}$KJmol^{-1}**	**$\Delta S^{\#}$JK^{-1}mole^{-1}**	**$\Delta G^{\#}$ KJ mole^{-1}**
	25.69	23.18	-222.06	88.83

Activation parameters are presented in [Table 7]. The negative values of entropy of activation reflect that the transition state is more rigid than initial state. The nearly constant ΔG value indicates that similar mechanism is operative for the oxidation of P-nitrochalcone (PNC).

These above observations suggest that the rate law can be written as shown

$$-\frac{d[T_{ri}PACC]}{dt} = k_3C_1$$

$$= \frac{k_3k_2[OxH^+][S]}{1+K_2[S]}$$

$$= \frac{k_3K_1K_2[Ox][H+][S]}{1+K_2[S]}$$

CONCLUSION:

The rate constants of the slow step involved in the mechanism were evaluated. Activation parameters were also computed. The negative value of $\Delta S^{\#}$ provides support to the formation of rigid transition state. The overall mechanism described here is consistent with product and kinetic studies.

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XRD and W-H analysis of sol-gel synthesized iron doped Zn-Cr oxide nanoparticles.

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ABSTRACT:

Zinc oxide nanoparticles have unique optical properties which have promising applications in luminescent devices. Pure and doped zinc oxides have several applications due to their unique structural and optical properties. Iron substituted Zn-Cr nano oxides were prepared by using the sol-gel auto-combustion method. X-ray diffraction patterns confirm the wurtzite crystal structure of the samples belonging to hexagonal crystal symmetry. Lattice constant 'a' varies from 3.2487Å to 3.2474Å and 'c' varies from 5.2043Å to 5.2029Å. Crystallite size was calculated by using well known Scherrer equation and W-H plots and it was observed within the nanometer range. The Williamson-Hall method was used to understand the changes observed in lattice strain. For $x \leq 0.02$, negative strain values are observed indicating the compressive type and for $x > 0.02$, positive strain values indicating the tensile type of strain.

KEY WORDS: *Zinc oxide, lattice constant, crystallite size, W-H analysis.*

1. INTRODUCTION:

Oxide semiconductors play an important role in the field of research because of their versatile applications in recent technology. These materials exhibit particle size dependent properties and therefore can be considered as the key materials in the technologically important components [1]. Recently, the demand of nano-sized semiconductors is increased because of their unique optical and electrical properties which are mostly useful in the fabrication of nano-sized multifunctional optoelectronic and electronic devices [2-5]. Among the metal oxides, zinc oxide has a commercial importance due to its major use in paints, rubber, catalyst, sensors, varistors as it exhibits semiconducting, piezoelectric and pyroelectric properties [6, 7]. Zinc oxide in nano-size has potential applications due to its altered properties than that of bulk size. Doping of various metal ions dramatically changes the structural, optical and electrical properties of zinc oxides [8-10].

In the recent past, several chemical methods have been employed to obtain the zinc oxide nanostructures by many researchers which includes chemical vapor deposition [11], thermal evaporation [12], hydrothermal [13], sol-gel auto ignition [14], electrochemical deposition [15], laser abolition [16], and sputter deposition [17]. In the present study we have adopted the sol-gel auto-ignition route in order to obtain the iron doped Zn-Cr oxide nanoparticles. The structural properties were studied by using X-ray diffraction method. Crystallite size and micro-strain observed in the samples were studied by using W-H analysis.

2. EXPERIMENTAL:

Nanoparticles of iron doped Zn-Cr oxide nanoparticles having general chemical formula $Fe_xZn_{0.95-x}Cr_{0.5}O$ (x = 0.0, 0.02, 0.04, 0.06, 0.08 and 1.0) were obtained by using sol-gel auto-ignition method. Analytical graded metal nitrates with high purity (Zinc nitrate, iron nitrate, and chromium nitrate) of the constituent elements were used as starting materials. All the starting materials were mixed with their weight proportion in sufficient amount of double distilled water. Citric acid was used as chelating agent and liquid ammonia was poured slowly in the solution to maintain the pH=7. Whole mixture was kept on hot plate and continuously stirrer at constant temperature of 90^0C. After couple of hours the solution becomes denser and the viscosity of the solution suddenly decreases and it converts into viscous sol. After few minutes the viscous sol converted into dried gel and burnt into ash by auto-ignition process. The burnt ash then sintered at 850^0C in order to obtain the final product in the form of fine particles at nano-scale level. The newly prepared samples were characterized by using X-ray diffraction technique. Room temperature XRD patterns of all the samples were collected in the 2θ range of 20^0 to 80^0 by using Cu-K radiations of wavelength 1.5405 Å.

3. RESULTS AND DISCUSSION:

Fig. 1 represents the X-ray diffractograms of $Fe_xZn_{0.95-x}Cr_{0.5}O$ nanoparticles. Diffraction peaks indexed for the planes (100), (002), (101), (102), (110), (103) (200), (112), (201), (004), and (202) are attributed to zinc oxide corresponds to the hexagonal (wurtzite) crystal structure of the samples. The secondary phase of Cr_2O_3 and Fe_2O_3 were also observed in the X-ray diffraction patterns of the samples. Broadening of the Bragg's lines clearly indicates the nanocrystalline nature of the samples. Lattice parameters 'a' and 'c' of all the samples were evaluated by using the following relation [18],

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (1)$$

When, h = 0 and k = 0 (i.e. for the planes (002) and (004)) then lattice parameter 'c' can be evaluated by using following relation,

$$c = ld \quad (2)$$

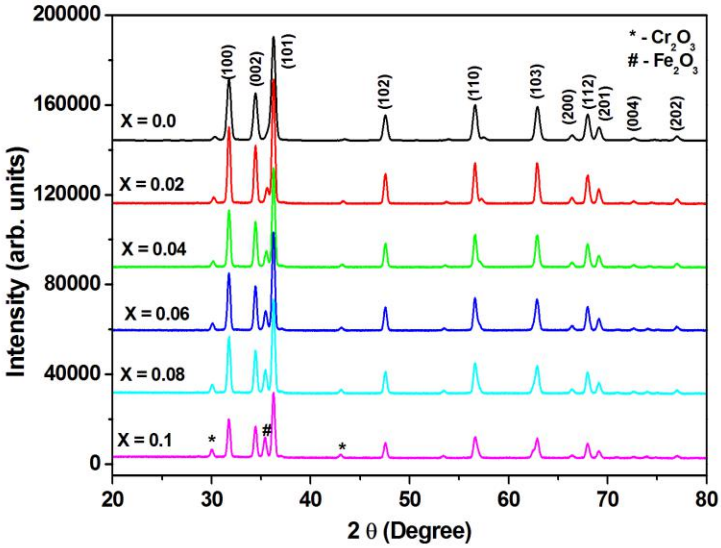

Fig. 1: X-ray diffraction patterns of $Fe_xZn_{0.95-x}Cr_{0.5}O$ nanoparticles

Calculated values of lattice parameters 'a' and 'c' for all the samples of the series $Fe_xZn_{0.95-x}Cr_{0.5}O$ are listed in Table 1. It can be seen that the lattice parameter 'a' decreases from 3.2487 Å to 3.2474 Å and 'c' decreases from 5.2043Å to 5.2029Å. The decrease in lattice parameter by the addition of Fe ions can be explained on the basis of difference in ionic radii. Here in the present series Fe ions having ionic radii 0.67Å replaces the Zn ions having relatively larger ionic radii 0.83Å [19]. The replacement of larger ions by smaller one reduces the size of unit cell and hence cell parameters decreases.

Table 1: Lattice constant (a), X-ray density (d_x), crystallite size (t) (XRD and W-H analysis), and micro-strain observed in $Fe_xZn_{0.95-x}Cr_{0.05}O$.

'x'	Lattice Parameter		'V'	'd_x'	't' (nm)		Strain
	'a' (Å)	'c' (Å)	$(Å)^3$	(gm/cc)	XRD	W-H analysis	
0.0	3.2487	5.2043	47.599	5.6352	17.565	17.81	-1.569×10^{-4}
0.02	3.2485	5.2041	47.590	5.6229	22.878	23.90	-3.848×10^{-6}
0.04	3.2482	5.2039	47.581	5.6106	23.014	25.45	2.089×10^{-4}
0.06	3.2479	5.2036	47.570	5.5985	23.204	26.92	3.133×10^{-4}
0.08	3.2476	5.2032	47.558	5.5866	23.277	27.90	5.150×10^{-4}
0.1	3.2474	5.2029	47.547	5.5745	23.443	28.85	5.950×10^{-4}

Unit cell volume of all the samples was estimated by using the relation $V = 0.866a^2c$ and the values are listed in Table 1. It can be observed that unit cell volume decreases with the substitution of Zn ions by Fe ions. This decrease in unit cell volume is attributed to the decrease in cell parameters. X-ray density was computed by using the relation discussed elsewhere [20] and it was obtained in the decreasing trend. The average crystallite size (t) was estimated by using the FWHM (β) values and Bragg's angles (θ_B) in well known Scherrer equation [20];

$$t = \frac{k\lambda}{\beta \cos\theta_B} \qquad (3)$$

where, λ is the wavelength of incident radiation (1.5405Å) and k is constant. Computed values of average crystalline size 't' varies from 17.565 nm to 23.443nm showing increasing trend with the addition of Fe ions in Zn-Cr oxides. The result indicates that the variation average crystallite size strongly depends on the Fe concentration. Increasing concentration of Fe ions promotes the crystallite growth. To confirm the nanocrystalline nature of the samples, Williamson-Hall method, which is another approach to estimate the average crystallite size was, employed [21]. This method gives the better information of crystallite size and contributions of micro-strains observed in the crystal lattice. By using the following W-H relation average crystallite size and micro-strain was obtained [22];

$$\beta \cos\theta = \left(\frac{K\lambda}{t_{W-H}} \right) + 4\varepsilon \sin\theta \qquad (4)$$

where, ε- is the micro-strain brought in the crystal lattice, λ-is the incident wavelength (1.5405Å) , K is the shape factor (K = 0.94 for the crystal having uniform size) and t_{W-H} is the average crystallite size obtained by the W-H analysis. W-H graphs plotted between $\beta \cos\theta$ and $4\varepsilon \sin\theta$ are shown in Fig. 2.

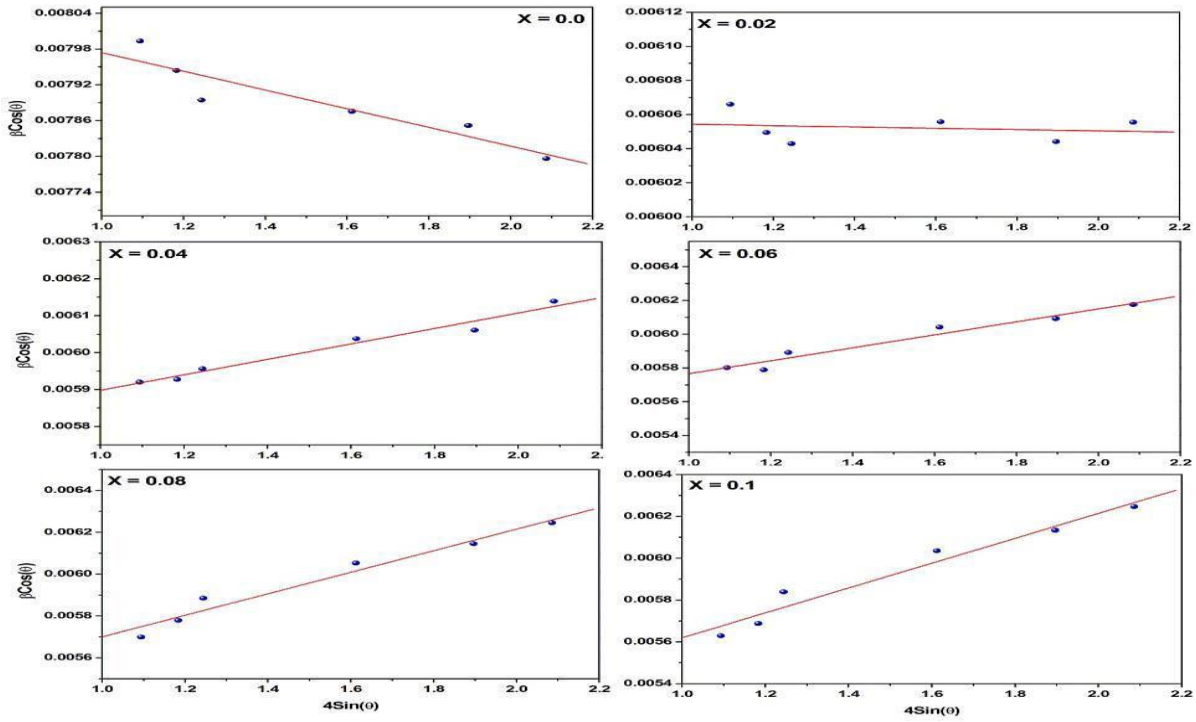

Fig. 2: W-H plots for the series $Fe_xZn_{0.95-x}Cr_{0.05}O$.

Average crystallite size from W-H plots was obtained from the Y-intercept and lattice strain was obtained from slope of the graph. The average crystallite size obtained from W-H plots increases from 17.81 nm to 28.85 nm which is in good agreement with the values obtained by using Scherrer equation. For the samples x ≤ 0.02, the lattice strain shows negative values indicating the compressive type of strain in the crystal lattice. As the concentration of Fe ion increases from x > 0.02, positive values of micro-strain are observed which indicates the tensile type of strain in the crystal lattice.

4. CONCLUSIONS:

Oxide nanoparticles of $Fe_xZn_{0.95-x}Cr_{0.5}O$ were successfully obtained by using sol-gel auto-ignition method. X-ray diffraction patterns confirm the hexagonal structure of the samples. Lattice parameter increases with the addition of Fe ions in Zn-Cr oxides which is related to the difference in ionic radii. Average crystallite size obtained from both Scherrer and W-H analysis is in nanometer range. For the samples x ≤ 0.02, compressive type strain is observed and for x > 0.02, tensile type strain is observed in the crystal lattice.

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Polyaniline composite, its Synthesis and suitable Dielectric Properties

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ABSTRACT:

Conducting polyaniline/Chromium oxide (PANI/Cr_2O_3) composites have been synthesized by in situ deposition technique by placing fine graded Cr_2O_3 in polymerization mixture of aniline. The PANI/Cr_2O_3 composites have been synthesized with various compositions viz., 05, 10, 15, 20 and 25 wt % of Cr_2O_3 in PANI. The ac conductivity was studied in the frequency range $10^2 – 10^6$ Hz. It is observed from the ac conductivity studies that the ac conductivity is found to be constant up to 10^5 Hz and there after it increases steeply which is a characteristic feature of disordered materials. The dielectric behavior was also investigated in the frequency range $10^2 – 10^6$ Hz. It is observed from the dielectric studies the value of dielectric constant increases up to 15 wt % and later it decreases. Similarly the imaginary dielectric constant increases up to 15 wt %, further it decreases rapidly up to 25 wt %. It is seen that the tan δ values increases up to 15 wt % and then decreases thereafter. At higher frequencies these composites exhibit almost zero dielectric loss the dimensions of Cr_2O_3 particles in the matrix have a greater influence on the conductivity values and the observed dielectric values.

KEYWORDS: *Conductivity, Polyaniline, Composites, Cr_2O_3, Dielectric Permittivity.*

1. INTRODUCTION:

Conducting polymers have made significant impact upon a number of different technologies since their introduction over twenty years ago. Applications range from optical and electrical devices (photovoltaic, transistors, batteries, etc) to antistatic packaging and various coating applications (membranes, shielding etc.) [1]. More recently, conductive polymers have been utilized as an effective medium for chemical sensing. A variety of conductive polymers have been evaluated using microelectronic devices, such as chemiresistors (interdigitated array transducers), quartz crystal microbalances (QCMs) and field-effect transistors (FETs). Examples of these studies include that of Kunugi et al. who utilized a specially modified QCM for making electrical and micro gravimetric measurements of the uptake of alcohols onto polypyrrole thin films [2], and of Josowicz and Janata who investigated the measurements of work function changes using a polypyrrole-coated FET for the detection of lower aliphatic alcohols [3]. Several companies, including Neotronics [4] and Aromas can [5], manufacture ‘electronic noses’ comprised of arrays of chemiresistor-based conductive polymer sensors.

The electrical transport in polymeric materials [6-7] has become an area of increasing interest in research because of the fact that these materials have great potential for solid state devices. Similarly, conducting polymer composites have attracted considerable interest in recent years because of their numerous applications in variety of electric and electronic devices. Conducting polymer composites with some suitable compositions of one or more insulating materials led to desirable properties [8]. These materials are especially important owing to their bridging role between the world of conducting polymers and that of nanoparticles. For application of conducting polymers, knowing how these conducting polymer composites will affect the behavior in an electric field in a long-standing problem and of great importance. The discovery of doping in conducting polymer has led to further dramatic increase in the conductivity of such conjugated polymers to values as high as 10^5 Scm^{-1}.

Among all conducting polymers, polyaniline (PANI) achieved widespread importance because of its unique conduction mechanism and environment stability. The survey of literature reveals that the detailed conductivity studies on PANI/Cr_2O_3 are scarce. In the present study, PANI and PANI/Cr_2O_3 composite (with varying weight percentage of chromium oxide in polyaniline) have been synthesized and studies have been made on the on AC conductivity as well as dielectric properties of PANI/Cr_2O_3 composites.

2. EXPERIMENTAL:

Aniline (AR grade) was purified by distillation before use and ammonium per sulphate [$(NH_4)_2S_2O_8$)], HCl were used as received. 0.1 mole aniline monomer is dissolved in 1 mole hydrochloric acid to form polyaniline. Fine graded pre-sintered chromium oxide (AR grade, SD-Fine Chem.) powder in the weight percentages (wt %) of 10, 20, 30, 40 and 50 is added to the polymerization mixture with vigorous stirring in order to keep the chromium oxide powder suspended in the solution. To this reaction mixture, [$(NH_4)_2S_2O_8$)] which is used as an oxidant is added slowly drop-wise with continuous vigorous stirring for the period of 4-6 hours at temperature 0-5^0 C. Polymerization of aniline takes

place over fine grade chromium oxide particles. The resulting precipitate is filtered under suction and washed with distilled water until the filtrate becomes colorless. Acetone is used to dissolve any unreacted aniline. After washing, the precipitate is dried under dynamic vacuum at 60-80^{0}C for 24 hrs to get resulting composites. In this way, five different polyaniline chromium oxide composites with different weight percentage of chromium oxide (10, 20, 30, 40 and 50) in polyaniline have been synthesized. All the composites are crushed into fine powder in an agate mortar in the presence of acetone medium. The composite powder so obtained is pressed to form pellets of 10mm diameter and thickness which varies from 2 to 2.75 mm. The electrical measurements on these samples were made using the silver paint as electrodes on both sides. AC conductivity measurements as well as dielectric property investigation were carried out at room temperature over frequency range 10^2-10^6 Hz using Hioki impedance analyzer 3532-50 (Japan). The characterization of polyaniline and its composites by spectroscopic methods is important, as it gives information not only about various molecular-levels interactions but also on the type of charge carriers.

3. RESULTS AND DISCUSSION:

Electrical measurements are known to be very sensitive for the study of electronic properties of materials. In amorphous systems, DC conductivity measurements are used to study the localization of electronic states, while AC conductivity measurements provide useful information concerning various relaxation phenomenons related to the electrical polarization process. In high frequency measurements, the characteristic hopping lengths and hopping rates of carriers between localized states can be determined. The low frequency data are however, more sensitive to slower relaxation process like the reorientation of dipoles, etc. In the latter case most relaxation process can be explained by the Debye theory of energy loss for dipole relaxations [9]. It is well known fact that frequency dependent complex conductivity in case of disordered materials such as polymers can arise from interfacial polarization at contacts, grain boundaries and other in homogeneities present in sample [10].

Figure 1 shows the variation of AC conductivity (σ_{ac}) as a function of frequency for PANI/Cr_2O_3 composites (different wt %). It is observed from figure 1. That in all the composites σ_{ac} remains constant up to 10^5 and thereafter increases steeply, which is characteristic feature of disordered materials. At higher frequencies, σ_{ac} increases because of contribution of polarons, which are moving along smaller and smaller distances in a polymer chain. Increase of σ_{ac} at higher frequencies is due to the charge motion in the amorphous region and this supports the presence of isolated polarons in this region [11].

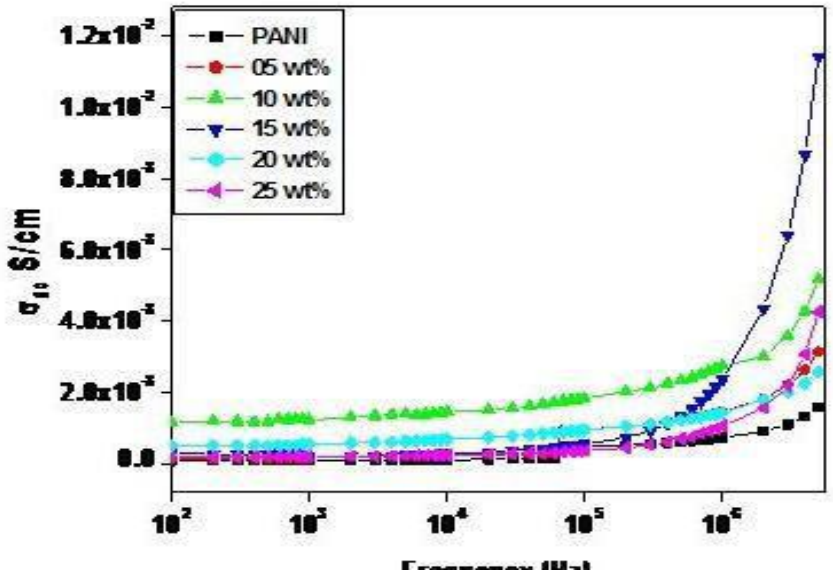

Figure 1: Variation of σ_{ac} as a function of frequency for Polyaniline – Cr_2O composites.

Figure 2 shows the variation of σ_{ac} as a function of wt % of Cr_2O_3 in polyaniline at two different frequencies and at room temperature. It is observed that in all the composites the conductivity increases up to 15 wt % of Cr_2O_3 in polyaniline and then decreases rapidly for 20 and 25 wt %. This may be due to the extended chain length of polyaniline which facilitate the hopping of charge carriers when the content of Cr_2O_3 is up to 15 wt %. Further decrease in conductivity for 20 and 25 wt % may be attributed due to the trapping of charge carrier hop [12].

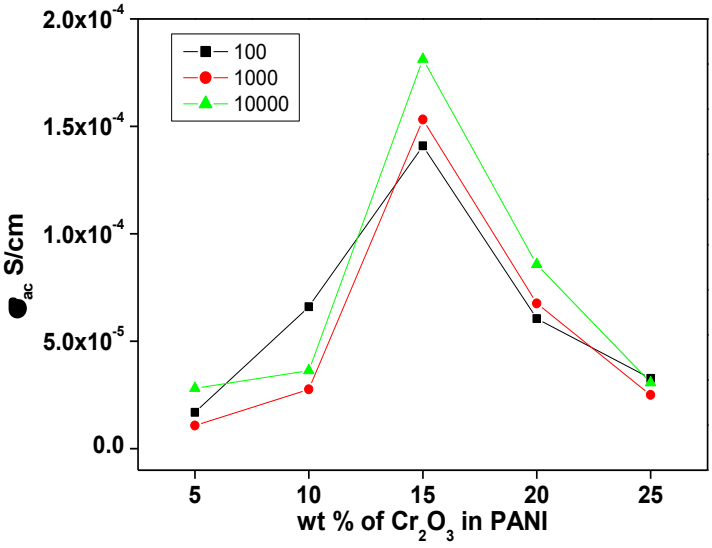

Figure 2: Variation of σ_{ac} as a function of wt % of Cr_2O_3 at different frequencies.

Dielectric materials – or, as they are also called, dielectrics – are such a media that has an ability to store, not conduct, electrical energy. A measure for this property is the permittivity or dielectric constant of the material. In fact, permittivity is only a higher-level invention to calculate approximately the electric response of matter. Matter – although electrically neutral – is composed of charged elements. The ideal dielectric does not allow the electrons to be carried around by the electric field. Instead, the force that an applied field exerts on charges displace these from their equilibrium positions, in which case there is a net displacement of positive charges in the direction of the electric field and electrons in the opposite direction. The separation of charges is equivalent to a dipole moment and the polarizability is a measure for the relation between dipole moment and electric field. Figure 3 represent the variation of dielectric constant (ε′) as a function of wt % of Cr_2O_3 at room temperature and at two different frequencies. It is observed that initially the values of dielectric constant increases up to 15 wt % and later it increases. ε′ exhibits high value at low frequency corresponding to bulk static dielectric constant ε_o and then decreases with increase in frequency, finally forming low value around 10^6 Hz, which may be attributed due to Debye-like relaxation mechanism [13 -14]. The variation of imaginary dielectric constant with wt % of Cr_2O_3 for PANI/Cr_2O_3 composites is shown in figure 4. It is clear from this figure that the imaginary dielectric constant deceases up to 10 wt %. Further it increases rapidly up to 15 wt % and decreases slowly up to 25 wt %. Imaginary dielectric constant ε″ is high at low frequency with changing concentration and this may be due to electric charges being displaced inside the polymer and / or their lower concentration [15-16]. Two possible causes may exist. The first one is increase in the counter anion size that led to an increasing interchain distance, which makes hopping between chains more difficult and hence resulting in reduction in conductivity. Another possible assumption depends on the changing concentration of Cr_2O_3. All these results go in accordance with the conductivity behavior. The observed change in conductivity is mainly responsible for the anomaly in the dielectric constant behavior of these composites.

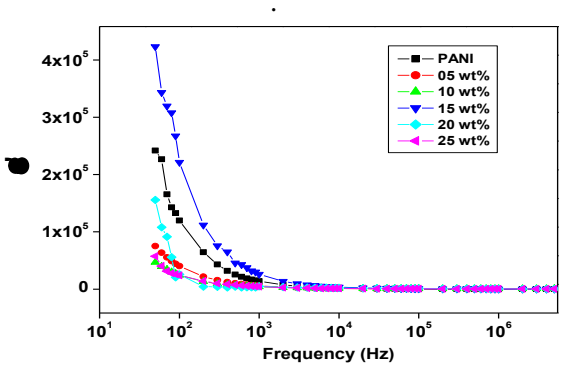

Figure 3: Variation of ε′ as a function of wt % of Cr_2O_3 at different frequencies.

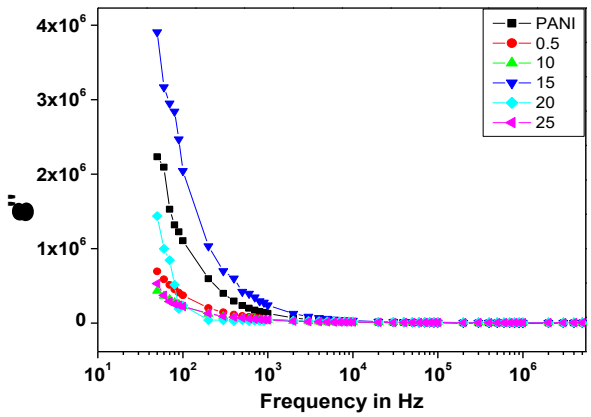

Figure 4: Variation of ε″ as a function of wt % of Cr_2O_3 at different frequencies.

Figure 5 shows the variation of tan δ as a function of wt % of Cr_2O_3 in polyaniline at room temperature and at two different frequencies. It is seen from the figure 5 that the tan δ values decreases up to 30 wt % and then increases thereafter. At higher frequencies these composites exhibit almost zero dielectric loss which suggests that these composites are lossless materials at frequencies beyond 1 MHz. The observed behavior is consistent with conductivity and dielectric constant results in these composites [17].

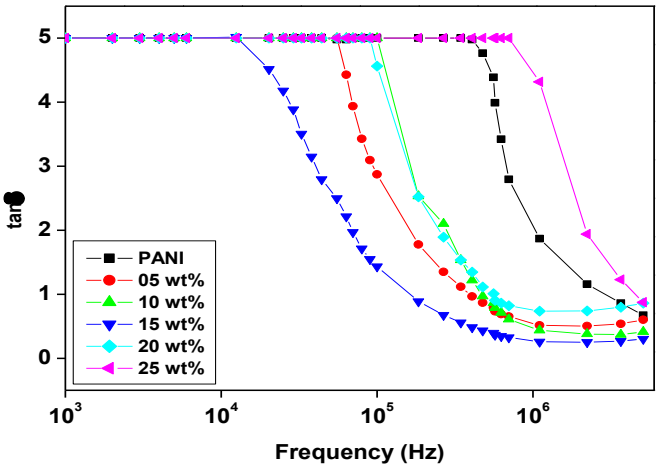

Figure 5: Variation of tan δ as a function of wt % of Cr_2O_3 at different frequencies

4. CONCLUSIONS:

Efforts have been made to synthesize polyaniline - Cr_2O_3 composites to tailor make their properties. The results of AC conductivity as well as dielectric property show a strong dependence on the wt % of Cr_2O_3 in polyaniline.

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Dielectric Properties of Lorazepam, Propanol Mixture Using Time Domain Reflectometry Technique

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ABSTRACT:

The dielectric relaxation study for Lorazepam and Propanol binary mixture has been carried out using the time domain reflectometry (T.D.R.) technique at temperature 283K, 288K, 293K and 298K and at different volume concentration, in the frequency range of 10MHz to 50 GHz. The dielectric parameters have been obtained from the complex permittivity spectra. The dielectric parameter shows change with temperature and concentration. The results obtained are used to interpret the nature and kind of solute-solvent interaction.

1. INTRODUCTION:

Lorazepam ($C_{15}H_{10}Cl_2N_2O_2$), is a medicine sold under the brand name. It is used to treat anxiety disorders, trouble sleeping. It is also used, along with other treatments, for acute coronary syndrome due to cocaine use. It is available as a generic medication [1]. Propanol (C_3H_8O) is a clear colorless liquid with a sharp musty odor like rubbing alcohol. Used in making pharmaceuticals, perfumes, lacquer formulations, dye solutions, antifreezes and other chemicals and products [2].

Above binary systems are studied for 06 different concentrations (0, 20, 40, 60, 80 and 100%) over the frequency range of 10 MHz to 50 GHz. Temperature dependent variations in dielectric parameters for four different temperatures (283, 288, 293 and 298K) are also reported for the systems. The dielectric constant and relaxation time have been determined. The static permittivity and relaxation time have been used to obtain the excess dielectric parameters, which give information related to molecular interaction. The obtained results are discussed on the basis of excess permittivity, excess inverse relaxation time.

2. EXPERIMENTAL:

The complex permittivity spectra are studied by using Time Domain Reflectometry. (T.D.R.). The Tektronix Digital Serial Analyzer sampling Oscilloscope (DSA8200) with 80E08 TDR Module has been used. Research work experimental part done at School of physics, Swami Ramanand Teerth Marathwada University. Nanded. Maharashtra. India. It generates a fast repetitive voltage pulse was fed through coaxial line system of impedance 50Ω. The time window used for the experiment is kept at 2 ns. The reflected pulse without sample and with sample are digitized in 2000 points and transferred to computer through USB device. TDR has up to 30GHz Bandwidth with 20ps reflected rise time and 18ps incident rise time. [3]

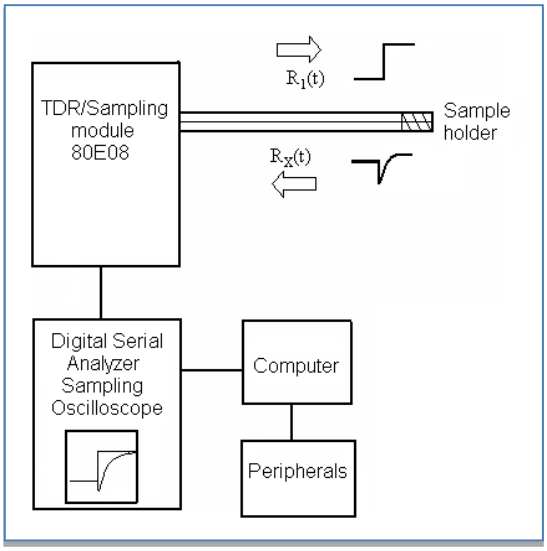

Fig.1 TDR Experimental block diagram

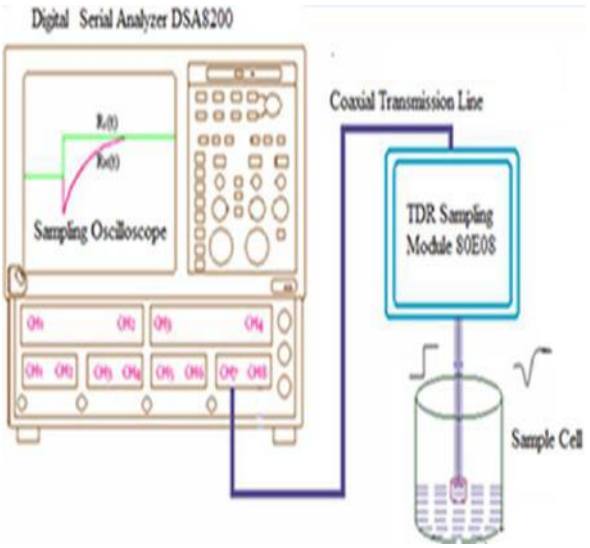

Fig.2 Experimental setup for TDR

Table 1. Physical constant of pure liquids

Sr. No.	Name of Compound	Molecular Formula	Permittivity Literature value (ε_s)	M.W. g/Mole	Density g/cm^3	Dipole Moment μ D	R. I.
1	Lorazepam	$C_{15}H_{10}Cl_2N_2O_2$	N.A.	321.2	1.52	N.A.	1.60
2	Propanol	C_3H_8O	20.1	60.09	0.803	1.68	1.3862

3. RESULT AND DISCUSSION:

Table: 2. Temperature dependent dielectric parameters for binary mixture of Lorazepam + Propanol.

Mole Fraction of Lorazepam	283K		288K		293K		298K	
	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)
0	316.00	315.9	316.00	315.9	316.00	304.2	263.00	263.4
0.0813	131.00	144.8	104.00	122.3	98.00	113.5	87.00	99.28
0.1910	99.40	143.1	93.50	113.1	75.50	106.2	66.00	98.34
0.3469	145.00	130.9	122.00	104.2	113.50	98.08	99.00	87.22
0.5862	143.00	99.41	113.00	91.54	106.00	75.49	98.00	66.38
1	81.80	81.78	61.50	61.66	57.00	57.13	47.00	47.27

Static Permittivity and Relaxation Time-

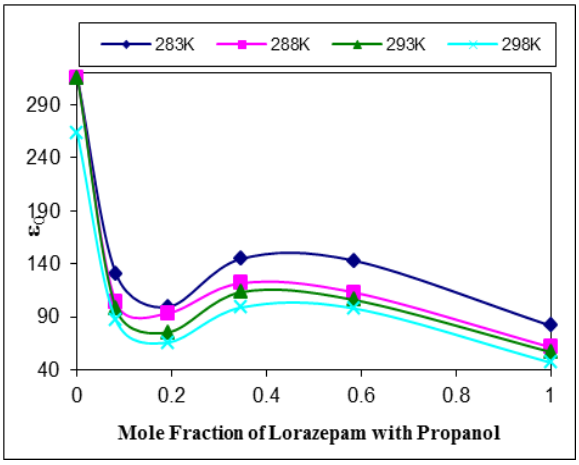

Fig. 3 Dielectric constant permittivity

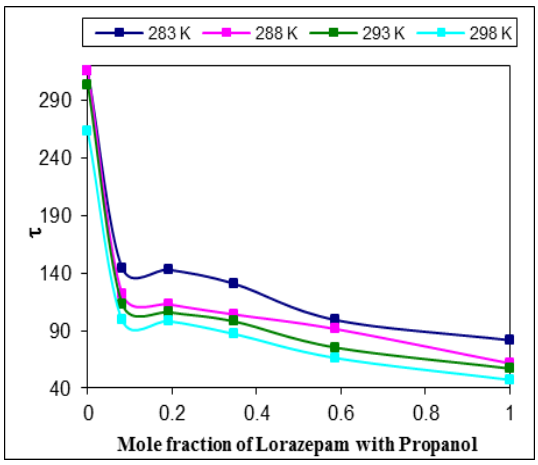

Fig. 4 Relaxation time

It can be seen that there is nonlinear relationship between the values of static dielectric constant (ε_s) and concentration of Lorazepam in the mixtures; it is decrease only at 40% mole fraction of Lorazepam. This suggests that there is weak intermolecular interaction between the molecules of mixture. And the relationship for the relaxation time (τ) is also nonlinear. The value of τ decreases with increase in mole fraction of Lorazepam. This suggests strong intermolecular interaction between Lorazepam and Propanol molecules [4]. The static permittivity and relaxation time decreases with increase in mole fraction of Lorazepam with Propanol indicate molecule rotate easily [5].

Excess Parameters-

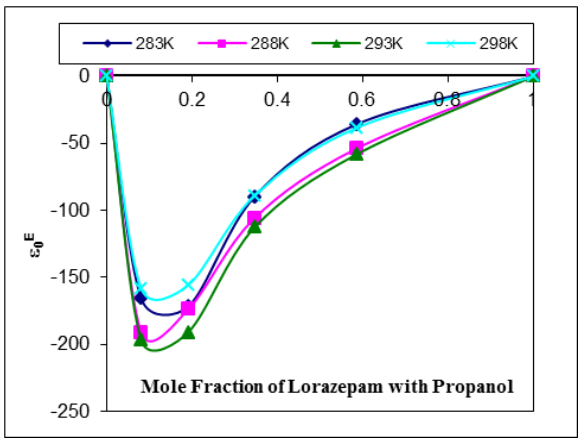

Fig. 5 excess permittivity

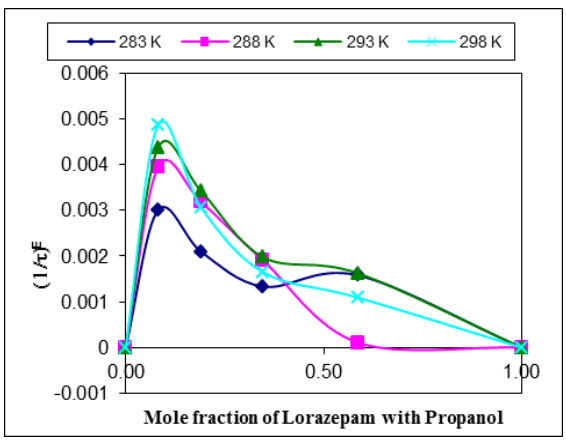

Fig. 6 excess relaxation time

From figure 3 it can be seen that $(\varepsilon_s)^E$is negative for all concentration of Lorazepam in the mixture for all temperature studied. This indicates that the molecules of mixture may form multimers structures in such a way that the effective dipoles get reduced [6-8]. This is due to the opposite alignment (antiparallel) of the dipoles in the mixture. For all the concentration the curves are more deviated at Propanol rich region. The behavior in $(1/\tau)^E$ is quite different as can be seen from figure 4. The values of $(1/\tau)^E$ are positive for all concentration of Lorazepam at all temperatures. This suggests that at for concentration of Lorazepam the molecular interaction produces a cooperative field and the effective dipoles have more freedom of rotation [9].

4. CONCLUSION:

It is concluded that, the value of static permittivity decreases at 20 & 40 % means weak interaction ant then comparative increase at 60 & 80 % means strong interaction takes place within this region. Relaxation time decreases continuously means molecule rotation becomes easier. Molecules of mixture may form multimers structures in such a way that the effective dipoles get reduced, molecular interaction produces a cooperative field and the effective dipoles have more freedom of rotation

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A Review on Synthetic Advances and Biological Aspects of Schiff Bases

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ABSTRACT:

Schiff bases are aldehyde - or ketone-like compounds in which the carbonyl group is replaced by an imine or azomethine functional group. They are widely used for industrial purposes and also exhibit a broad range of biological activities. This short review compiles examples of the most promising antimalarial, antibacterial, antifungal, and antiviral Schiff bases. An overview of synthetic methodologies used for the preparation of Schiff bases is also described.

KEY WORDS : *Schiff bases, thiazole, benzothiazole, anticancer , antifungal , antibacterial .*

1. INTRODUCTION:

Schiff bases are versatile ligands having imine or azomethine (–C=N–) functional group. They were first described by Hugo Schiff, German Chemist in 1864 and hence they are named so . Schiff bases are the backbone of large number of organic compounds and have enormous applications in many fields including analytical, biological, and inorganic chemistry . Schiff bases are well known for their wide range of applications and are useful intermediates in organic synthesis These compounds have intrinsic biological activities including anticancer [1-3],anti-inflammatory , antitubercular , antioxidant [4], antibacterial [5,6,] analgesic [7], antifungal and antifertility , herbicidal [8], anticonvulsant [9], anthelmintic and antiproliferative . Moreover, Schiff bases also exhibit fluorescence , photoluminescence , a potentiometric cation caring [10] and aggregation properties.

Schiff Compared to purely organic molecules, metal complexes have several advantages as a result of their varied reactivity pattern, structural diversity, and unique photo and electrochemical properties. To exploit these advantages, it is crucial to select good performing chelators with coordinating properties suitable for the proper stabilization of a given metal core . Inorganic compounds mainly transition metals have played an important role in the development of new metal based drugs .

The transition metal complexes with nitrogen, oxygen donor Schiff bases have elucidated importance among the researchers due to its varying applications in the field of bio Inorganic chemistry and biology. Some of the Schiff bases exhibit unusual configurations and structural labiality due to which they are sensitive to the molecular environment. Schiff base ligand may act as bidentate N,O-, tridentate N,O,O-, N,O,N-, N,O, S-, tetradentate N,N,O,O-, hexadentate N,N,O,O, S, S- donor ligand etc., which makes it suitable for complex formation. The ability of ligand to co-ordinate with transition metals leads to mononuclear or binuclear complexes or one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) metal-organic frame works. The complexes play an important role in the development of coordination chemistry related to enzymatic reactions, magnetism, catalysis and bioinorganic modelling studies.

The chemistry of the Schiff base ligands and their metal complexes evoke much current interest and encompasses a vast area of organometallic compounds and various aspects of bioinorganic chemistry.[11] Schiff bases are considered as privileged ligands because they are easily prepared by condensation of aldehydes or ketones with amines and are able to stabilize different metals in various oxidation states. The importance of Schiff base complexes for bioinorganic chemistry, biomedical applications, supramolecular chemistry, catalysis and material science, separation and encapsulation processes, and formation of compounds with unusual properties and structures has been well recognized and reviewed.[12]Large numbers of Schiff bases have shown to exhibit a wide range of biological activities, including antitumor[13] anti-bacterial, fungicidal and anticarcinogenic. properties. On the other hand, coordination compounds with heterocyclic Schiff base ligand has attracted much attention of the chemist in current years to find applications as potential drugs,[14,15] due to the presence of multifunctional groups [16,17].

In this review we present the general approaches along with greener methodologies to the synthesis of Schiff bases , we also highlight the most significant examples of compounds with most pharmacological activities to have been reported in literature, more emphasis has been given to thiazole and benzothiazole moieties.

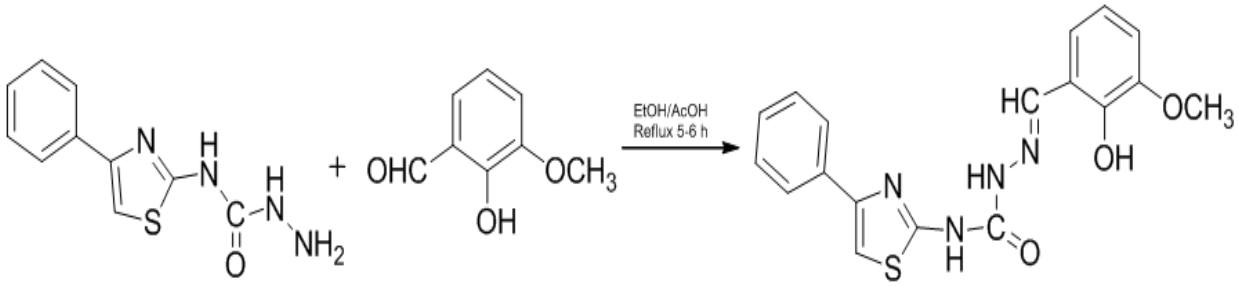
Synthetic development in thiazole moiety:

The excessive attention of synthesizing determined broad range of N and S chelating ligands as thiazole molecule have attracted significant interest. This is because thiazoles have a great pharmacological activity. Besides these atoms play an important role in the coordination of metals at the active sites of various metal biomolecules that have a therapeutic activity or serving as study models for metallo-enzymes [18-20] . Thiazoles are very important building

blocks in medicinal chemistry and can be found in numerous natural products (e.g. epothilone) and biologically important compounds including the anticancer drug dasatinib, antiviral clinical candidate TMC435350 and antidiabetic drug candidate MB06322 [21-23]. Recently, thiazoles found application in drug development for the treatment of allergies [24] , hypertension [25], inflammation [26], schizophrenia [27]bacterial[28] , HIV infections [29] , hypnotics, as fibrinogen receptor antagonist with antithrombotic activity and as new inhibitors of bacterial DNA gyrase B [30].

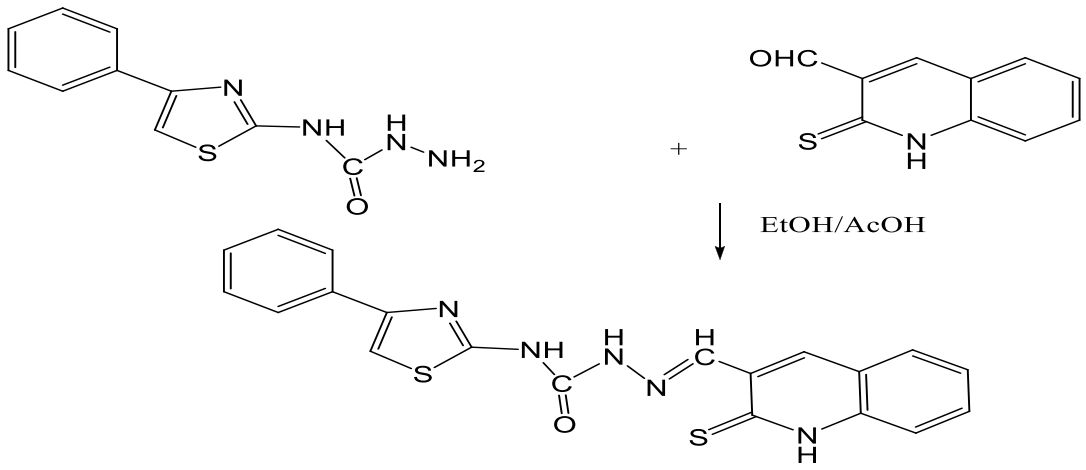
Many thaizole derivatives such as sulfathiazole, ritonvir, abafungi, blemycin and tiazofurin are well known as potent biologically active compounds.[13],[31].,Moreover, thiazoles are very important building blocks in medicinal chemistry and can be found in numerous natural products and biologically important compounds including anti-microbial, anti-inflammatory, anti-hypertensive, anti-HIV, anticancer and cytotoxic activity that can be well illustrated by the large number drugs in the market containing the moiety.[32,33] Thiazole ring also found applications in polymer, liquid crystals, photo-nucleases, fluorescent dyes, insecticides and antioxidants.[34,35] Their transition metal complexes have attracted a great deal of interest largely due to their ability to interact with DNA molecule.[36] These complexes that can bind or cleave DNA molecule at exact sites, plays an important role in genomic investigation and in photodynamic therapy against cancer.[37] It is well known that some coordination compounds can inhibit the growth of cancer cells by binding and damaging DNA.[38]

G. Y. Nagesh et.al[39] has been synthesized Schiff base complexes derived from thiazole and o- vanillin moieties , thermal behavior and biological evaluation of metal complexes were also investigated(Scheme 2. 1).



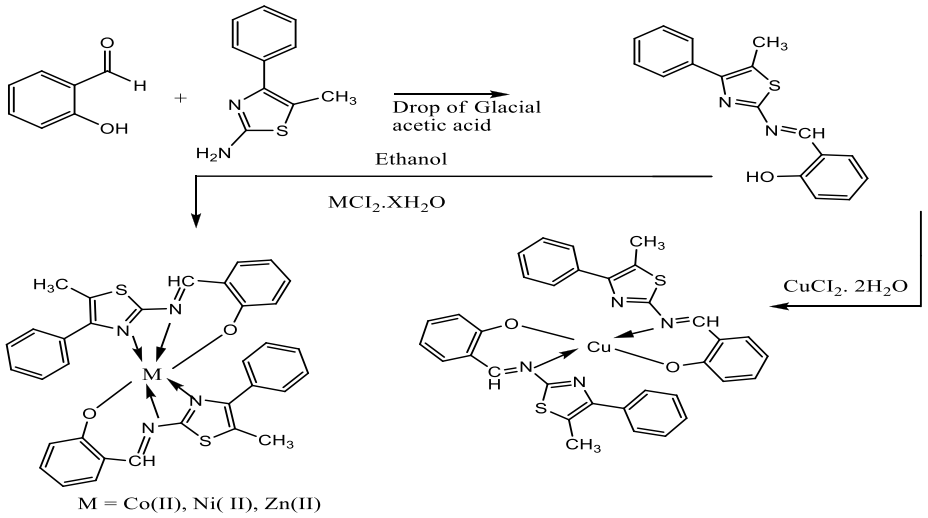
Scheme 2. 1:

M. Bennikallu Hire Mathada G. Y. Nagesh [40] have reported the synthesis of metal complexes of Schiff base Ligand Derived from Thiazole and Quinoline Moiety, these compounds were screened for antimicrobial, DNA Cleavage, and *In Vitro* Cytotoxic Studies (Scheme 2.2).



Scheme 2.2 :

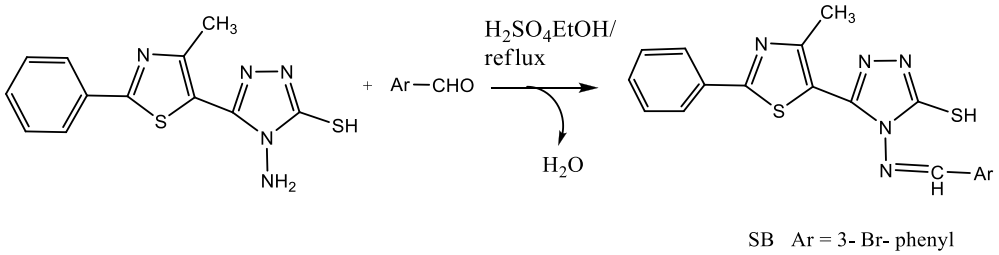
Metal complexes of Schiff bases derived from salicyaldehyde with 2-amino-4-phenyl-5-methyl thiazole was reported by Mokhles M. Abd-Elzaher et. al.[41] These authors have reported the anticancer activity against different human tumor cell lines: breast cancer MCF-7, liver cancer HepG2, lung carcinoma A549 and colorectal cancer HCT116 in comparison with the activity of doxorubicin for these complexes (Scheme 2. 3).



Scheme 2. 3 :

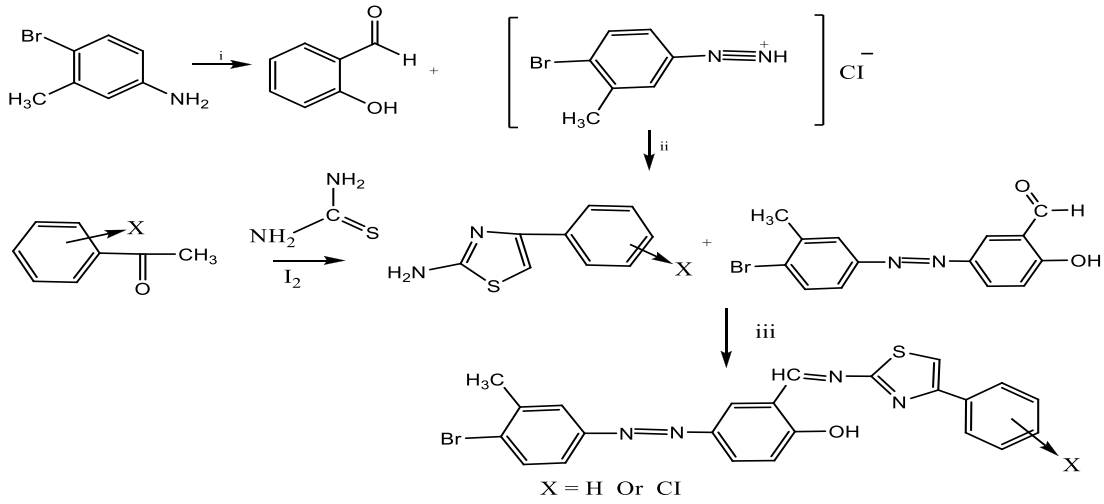
Synthesis of a novel Schiff base ligand 3-((4-phenylthiazol-2-ylimino) methyl)-2-hydroxybenzoic acid and its metal complexes, their characterization by different spectroscopic techniques and their antibacterial, antifungal, DNA cleavage and *in vitro* cytotoxicity property was reported by B. M. Kalshetty and coworkers [42].

Ejaz et. al.[43] described the synthesis of 2-aminothiazole-4-carboxylate Schiff bases and their antimicrobial evaluation against multidrug resistant strains and molecular docking .Ioana Baldea et. al.[44] have synthesized a novel thiazolyl Schiff base. The Schiff base also screened for antibacterial and antifungal effects and in vitro oxidative stress modulation on human endothelial cells (Scheme 2.4).



Scheme 2.4:

Biological investigation of novel metal complexes of 2-amino-4-substituted phenylthiazole Schiff bases have been reported by Jyotirmaya Sahoo, and Sudhir K. Paidesetty [45] (Scheme 2. 5).



Reaction condition : i) $NaNO_2$/HCI, 0-5 °c,diazodization; ii) 10% NaOH, Coupling reaction; iii Ethanol reflux, 2h,70°c

Scheme 2. 5 :

Benzothiazole Moiety

In recent years heterocyclic compounds analogues and derivatives have attracted wide attention due to their useful biological and pharmacological properties. Benzothiazole is among the usually occurring heterocyclic nuclei in many marine as well as natural plant products. Benzothiazole is a privileged bicyclic ring system with multiple applications. It is known to exhibit a wide range of biological properties including anticancer, antimicrobial, and antidiabetic, anticonvulsant, anti-inflammatory, antiviral, antitubercular activities.Alarge number of therapeutic agents are synthesized with the help of benzothiazole nucleus.During recent years there have been some interesting developments in the biological activities of benzothiazole derivatives. These compounds have special significance in the field ofmedicinal chemistry due to their remarkable pharmacological potentialities.

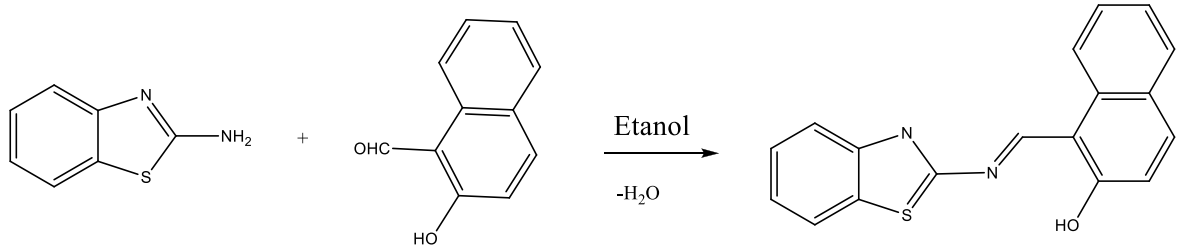
Being a heterocyclic compound, benzothiazole finds use in research as a starting material for the synthesis of larger, usually bioactive structures. Its aromaticitymakes it relatively stable; although, as a heterocycle, it has reactive sites, which allow for functionalization Scientific literature on different biological activities of benzothiazole Benzothiazole nucleus is found to possess a number of biological activities such as anticancer, antimicrobial, antidiabetic,anti-inflammatory, antiviral, antileishmanial, and antiviral Biological Aspects of Emerging Benzothiazoles Reviewd by Ruhi Ali and Nadeem Siddiqui [46].

Anticancer Activity. : Cancer is a serious worldwide health threat, killing almost seven million people a year, and poses great challenges to medical science. The global research efforts in this field are focused both on the development of new potent antineoplastic agents and on the discovery of novel biological targets. Novel benzothiazole-2-thiol derivatives were synthesized by Wang et al.[47], and their antiproliferative activities on HepG2 and MCF-7 cellswere investigated. Most compounds had inhibitory effects on cell growth, and some of them were more effective than cisplatin. Kumbhare et al. [48] synthesised benzothiazolylthiocarbamide using a catalytic amount of 4-dimethylaminopyridine (DMAP) followed by its chemoselective oxidativecyclization with 1,3-di-*n*-butylimidazolium tribromide[bbim][Br3] to afford the N-bis-benzothiazole derivatives. All the synthesized compounds were evaluated for cytotoxic activity against two human monocytic cell lines (U 937, THP-1) and a mouse melanoma cell line (B16-F10).

Antimicrobial Activity. The design of new compounds to deal with resistant bacteria and fungi has become one of the most important areas of antibacterial and antifungal research today since resistance of pathogenic bacteria and fungi toward available antimicrobial drugs is rapidly becoming a major problem worldwide. Thus the discovery of novel and potent antibacterial as well as antifungal agent is more demanding and challenging for chemists and pharmacists nowadays. Sahu et al. [49] have synthesized series of 4H-pyrimido[2,1-b][1,3]benzothiazole derivatives and evaluated their antibacterial activities against gram-positive and gram-negative bacteria, namely, *Staphylococcus aureus, Pseudomonas aeruginosa, Salmonella typhi, Escherichia coli, Bacillus cereus*, and *Providencia rettegeri*.

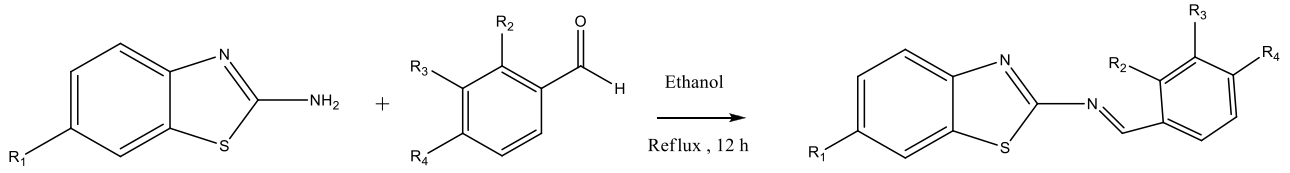
A new class of 4-arylhydrazono-1-benzothiazolyl-3- methylpyrazolin-5-ones and 4-arylazo-1-benzothiazolyl-3,5- dimethylpyrazoles were designed as pharmacophore hybrids between pyrazolinone/pyrazole and benzothiazole moiety by Amir et al. [50] and screened for antimicrobial activity.

Antidiabetic Activity : Diabetes mellitus is characterized by chronic hyperglycemia and belongs to a group of metabolic disorders with multiple etiologies. Recent estimates from the year 2000 indicate that there are 171 millionpeople in the world with diabetes, and this is projected to increase to 366 million by 2030. There is thus a growing need for effective therapies to achieve optimal glycemic control in the management of diabetes. N-(6-substituted- 1,3-benzothiazol-2-yl)benzenesulfonamide derivatives were synthesized and evaluated for their *in vivo* antidiabetic activity in a noninsulin-dependent diabetes mellitus rat model and also evaluated for 11-HSD1 and PTP-1B enzymes by Moreno-D´ıaz et al. [51]. A novel series of substituted (*E*)- 3-(Benzo[*d*]thiazol-2-ylamino)phenylprop-2-en-1-ones were synthesized and were evaluated for their antidiabetic activity by Patil et al. [52] The new ligand and their metal complxes has been synthesized from 2-aminobenzothiazole and 2- hydroxynaphthylaldehyde by condensation in ethanol by Sinan Saydam [53] (Scheme 3.1).



Scheme 3.1 :

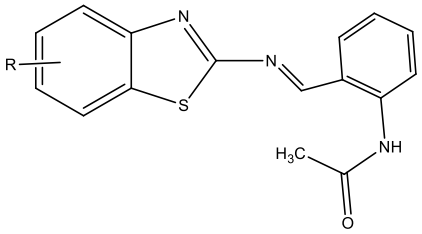
Kini S. G et. al.[54] studied synthesis and antimicrobial activity of Schiff bases derived from substituted 2- amino benzothiazole and substituted benzaldehyde (Scheme 3.2).



$R_1 = OCH_3$, OC_2H_5,CI
R_2 = F, CI
R_3 = OH, OCH_3, NO_2
R_4 = F, OCH_3, CH_3

Scheme 3.2:

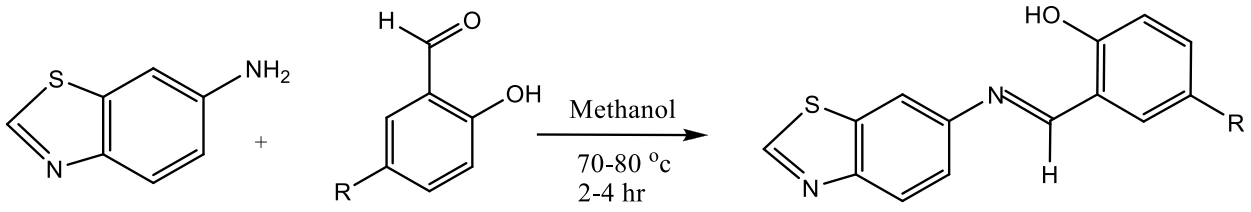
Zinc Complexes of Schiff Bases derived from reaction of 2-acetamidobenzaldehyde with substituted substituted 2-amino benzothiazole has been reported by Claudiu T. Supuran [55], these complexes were screened for antibacterial activity.



R = 4 -H ,4-CH_3 , 4-OCH_3 , 4-CI .6-NO_2 .6- SO_2CH_3

Fig 1

Binary complexes of Cu(II), Ni(II) and Co(II) were synthesized using two benzothiazole Schiff bases . DNA interactions and biocidal activity of metal complexes of benzothiazole Schiff bases have also been investigated by Shivaraj et.al [56] (Scheme 3.3).

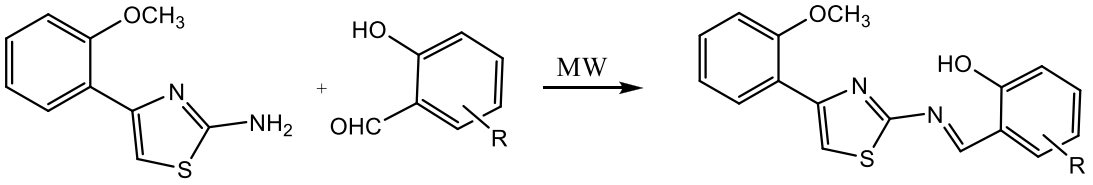


a) CI,
b) NO_2

Scheme 3.3:

Greener approach methodologies :

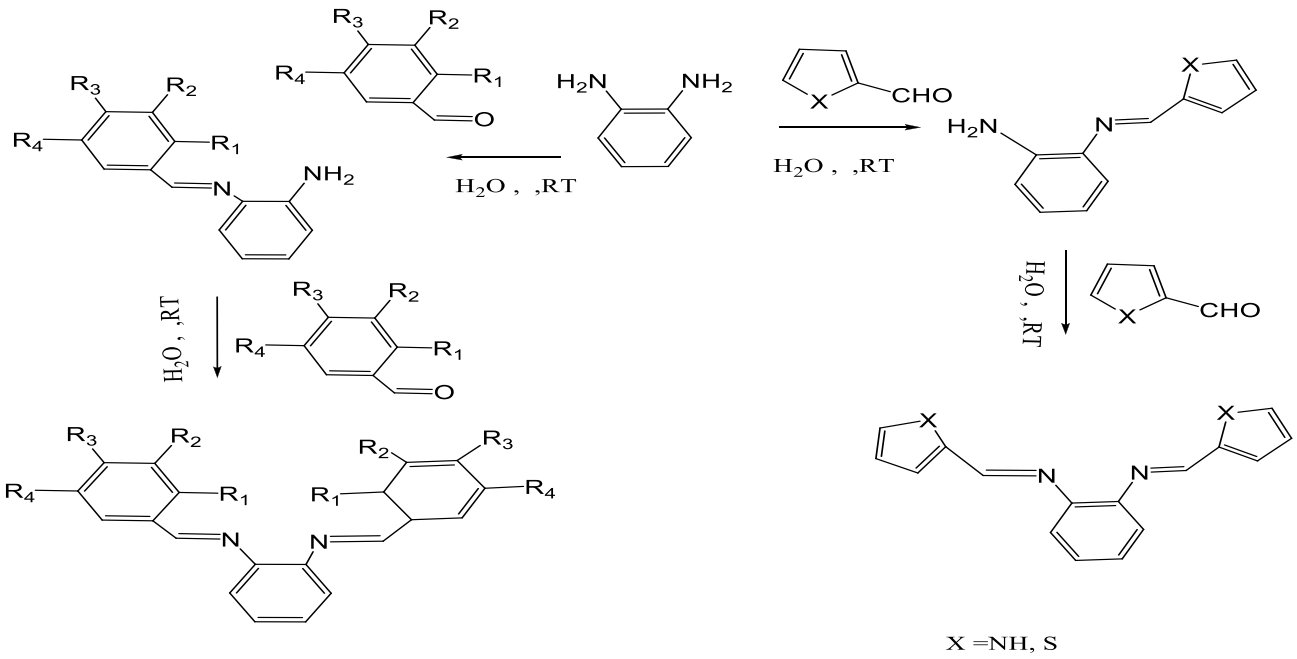
A simple and efficient one pot mechanochemical greener Route for the synthesis of salophen ligands and of the corresponding Zn, Ni, and Pd complexes have been reported by Johan Wouters and coworkers [57]. Prakash G. More et.al.[58] described the microwave irradiation synthesis and anti-biofilm activity of thiazole Schiff bases (Scheme 4.1).



R = H,3-CH_3,4 -CH_3, 5- CH_3 3-OCH_3 ,5-Br,

Scheme 4.1:

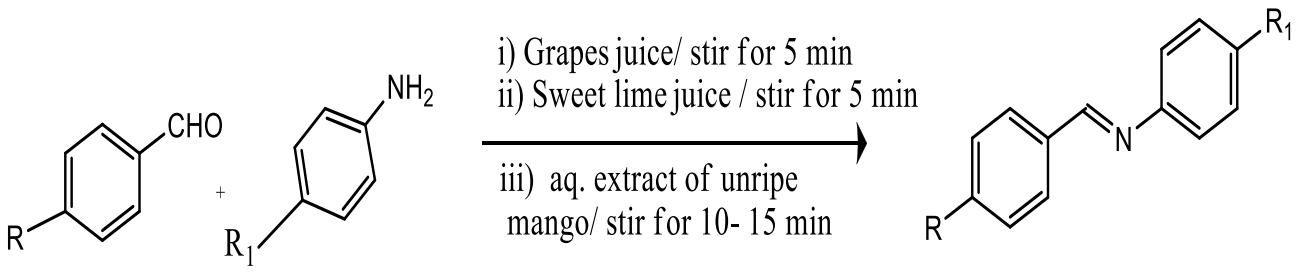
C. Naga Raju reported [59] Synthesis of Schiff's bases in aqueous medium green alternative approach with effective mass yield and high reaction rates.(Scheme 4.2)



Compound	R_1	R_2	R_3	R_4
1a/2a	OH	H	H	H
1b/2b	H	OH	H	H
1c/2c	H	H	OH	H
1d/2d	H	H	H	H
1e/2e	H	H	CI	H
1f/2f	OH	H	H	CI
1g/2g	OH	H	H	Br

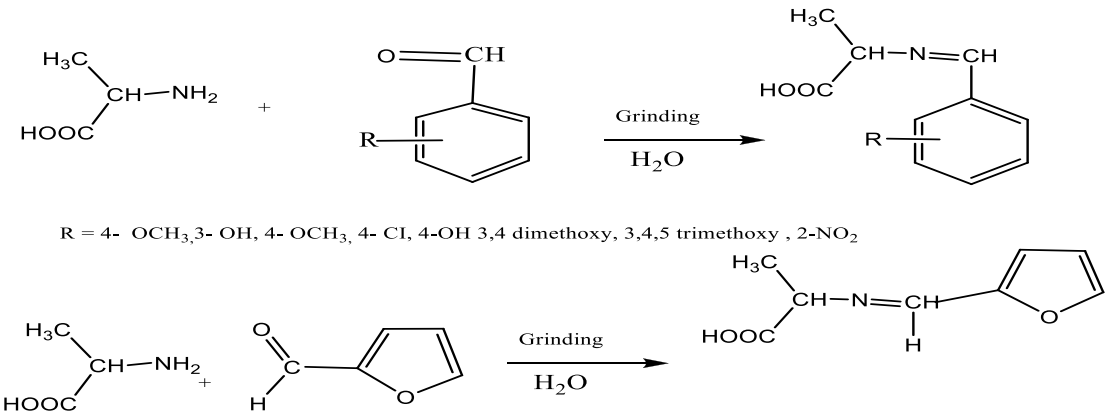
Scheme 4.2:

A series of salicylaldimine Schiff bases have been prepared from salicyladehyde and substituted aniline by microwave irradiation under solvent free condition in appropriate time by V.Nadaraj et. al.[60] .Garima Yadav and Jyoti V. Mani [61] have described the green synthesis of Schiff bases by using fruit juice as natural acid catalysts .(Scheme 4.3).



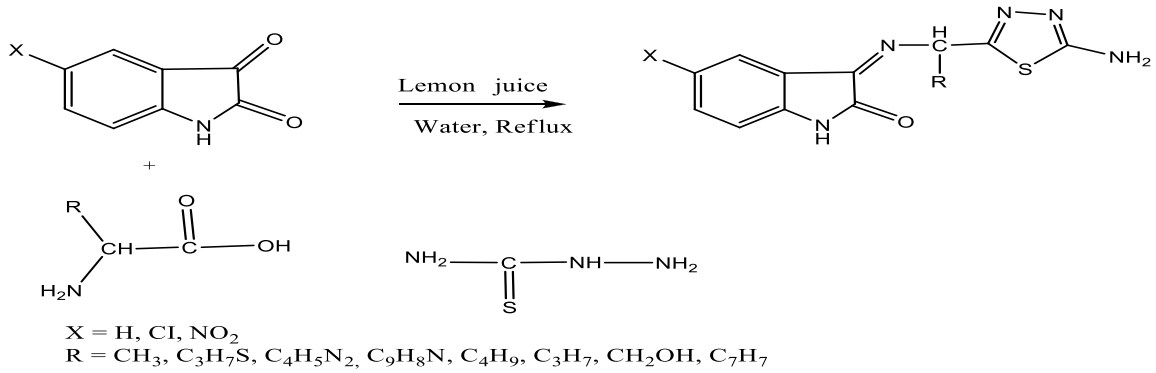
Scheme 4.3:

Harshita Sachdeva and coworkers reported [62] Operationally simple green synthesis of some Schiff bases using grinding chemistry technique and these compounds were screened for antimicrobial activities (Scheme 4.4).



Scheme 4.4:

Green chemical one-pot multicomponent condensation reaction of substituted 1*H*-indole-2,3-diones , various amino acids , and thiosemicarbazide is found to be catalyzed by lemon juice as natural acid using water as a green solvent to give the corresponding Schiff bases in good to excellent yields was described by Harshita Sachdeva and et. al. [63] these compoundes were screened for antibacterial and antifungal agent (Scheme 4.5).



Scheme 4.5:

Sunita Bhagat, and coworkers have reported [64] Synthesis of Some Salicylaldehyde-Based Schiff Bases in Aqueous Media . Synthesis of Thiazole Derivatives as Antimicrobial Agents by Green Chemistry Techniques such as microwave, ultrasound mediated technique has been reported by Serpil Demirci [65].

CONCLUSION :

The present review highlights the use of thiazole and benzothiazole moieties as template for development of newer therapeutic agents . Biological properties of the nucleus includes anticancer, antidiabetic ,antimicrobial, analgesic with proper designing and structure activity relationship of known thiazole and benzothiazole compounds , prospective compounds can be designed and synthesized for variety of biological activity.

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p-TSA catalyzed Multicomponent synthesis of 12-(substituted phenyl)-8*H*-benzo[5,6]chromeno[2,3-*d*]pyrimidine-9,11(10*H*,12*H*)-dione derivatives.

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ABSTRACT:

A simple procedure has been developed for the synthesis of 12-(substituted phenyl)-8H-benzo[5,6]chromeno[2,3-d]pyrimidine-9,11(10H,12H)-dione derivatives using β-Napthol, Barbituric acid and different substituted aromatic Aldehydes were refluxed in ethanol for certain time period using p-Toluenesulphonic acid (p-TSA) as phase transfer catalyst to form 12-(phenyl)-8H-benzo [5,6]chromeno[2,3-d]pyrimidine-9, 11(10H,12H)-dione derivatives.

KEYWORDS: *β-Napthol, Aromatic Aldehydes, Barbituric acid, p-TSA, MCRs.*

1. INTRODUCTION:

Multicomponent reactions (MCRs) have been useful for the synthesis of highly well-designed complex organic molecules and biologically active heterocyclic compounds from simple and willingly available preliminary materials.[1-3] These reactions have attracted extraordinary attention owing to their cleanness, good organization, selectivity, convergence, shorter reaction time, atom-economic unique -eness and environmentally benign.[4-5] As a commanding and widely employed synth- etic etiquette, MCRs provide a highly efficient platform for the rapid synthesis of various fused-ring products, in which the formation of two or more new rings is allowed.[6-9] Fused heterocyclic architectures are extensive in natural products and pharmaceutical molecules, informative their great capacity as a source of novel proficient compounds.[10-13] Multicomponent reactions (MCRs) play an important role in modern synthetic organic chemistry because they generally occur in a single pot and exhibit a high atom-economy and selectivity.

Multicomponent reaction reduces time and saves energy and raw material.[14] Over the past decade, various advanced sequential MCRs have been developed where 1,3-dicarbonyl derivatives are important synthetic intermediates due to its multiple functionalities that can be involved either as nucleophilic or electrophilic species in a large variety of synthetic transformation.[15] Their versatility and effectiveness as potential multicomponent substrates has been used in various MCRs such as Hantzsch 1,4-dihydropyridine synthesis,[16] Biginelli reaction[17] and Michael addition reaction.[18] Multicomponent reactions (MCRs) have emerged as an attractive and powerful strategy for organic synthesis compaired to multistep reactions because of the creation of numerous new bonds in a one-pot reaction, low number of reaction and purification steps, high atom economy, simple procedures, facile implementation and generally excellent yields of products.[19] Therefore, academic and industrial research groups have increasingly focused on the use of MCRs to synthesize a broad range of products [20-21] and development of MCRs can lead to new efficient synthetic methodologies to afford many small organic compounds in the field of modern organic, bioorganic, and medicinal chemistry.[22-24]

2. LITERATURE REVIEW:

Naphthopyrano pyrimidine and benzo chromeno pyrimidine dione and its derivatives have attracted attention because structural motifs of these compounds are very useful in medicinal and biological chemistry.[25]Also these compounds exhibit promising physiological,[26] hypolipidemic,[27] molluscicidal,[28] antifungal,[29] antitumor,[30] analgesic,[31] antibacterial[32] and anticonvulsant activities.[33]The synthesis of Naphtho- pyrano pyrimidines via earlier methods has been reported so far using formic acid,[34] indium(III) chloride,[35] iodine,[36] ZnO nanoparticles,[37] $H_4[SiW_{12}O_{40}]$,[38]L-proline,[39]poly(AMPS-coAA),[40]alum$KAl(SO_4)_2.12H_2O$,[41]$Al(H_2PO_4)_3$,[42] Fe_3O_4 @SiO_2,Fe_3O_4@MCM-4,[43] basic ionic liquid[44] and trichloroisocyanuric acid (TCCA).[45] Conversely, some of these methods often involve long reaction times, harsh reaction conditions and expensive catalysts. Thus, there is a need to develop a simple and cost-effective etiquette

for the synthesis of novel benzo chromeno pyrimidine dione derivatives and Naphthopyrano pyrimidines with biological importance

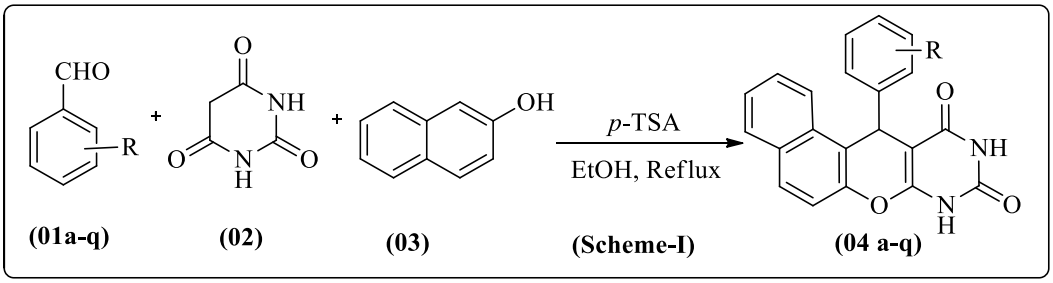
3. MATERIAL METHOD/ PRESENT WORK:

In present work, we have investigated the one pot three component synthesis of different substituted derivatives of 12-(phenyl)-8*H*-benzo[5,6]chromeno[2,3-*d*] pyrimidine-9,11(10*H*, 12*H*)-dione derivatives. The reaction followed by Knovengel condensation and then Michael addition reaction.

A mixture of *β*-Napthol (1mmol)(03), Barbituric acid (1mmol) (02) and different substituted aromatic Aldehyde(1mmol) (01a-q) was refluxed in ethanol for certain time period using *p*-Toluenesulphonic acid (*p*-TSA) (10 mol%) as a catalyst to form12-(phenyl)-8*H*-benzo[5,6]chromeno[2,3-*d*]pyrimidine-9, 11(10*H*,12*H*)-dione derivatives. Progress of the reaction was monitored by TLC. Solid formed was filtered, washed with water and recrystallized from ethanol to give (04 a-q). These obtained products (04 a-q) were completely characterized by IR, ^{1}H-NMR, Mass and ^{13}C-NMR spectroscopic technique and also elemental analysis.

4. RESULT AND DISCUSSION:

A mixture of *β*-Napthol (1mmole) (03), Barbituric acid (1 mmol) (02) and Aromatic aldehyde (1mmol) (04 a-q) was refluxed independently in ethanol using *p*-TSA as an efficient catalyst for certain period of time (Scheme-I).



It was considered as a model reaction (Scheme-I) for investigating the effectiveness of different solvent using catalytic amount of *p*-TSA (10mol %). Solvent optimization clearly noted that ethanol is the best solvent for the desired transformation due to fast reaction rate and high yield (Table-01). We have carried out the model reaction using different stoichiometric amount of catalyst. The catalyst screening result are summarized in (Table-02). It was observed that the excellent yield was achieved by using 10 mol% of *p*-TSA (Table-02).These synthesized products (VA-47a-q) were characterized from IR, ^{1}H-NMR, Mass and ^{13}C-NMR spectroscopic technique and also elemental analysis.

The *p*-TSA acting as phase transfer catalyst (PTC) that's why reaction mechanism was accelerated, *p*-Toluenesulphonic acid (PTSA) is commercially available and is a very cheap chemical, white solid, non-volatile that is soluble in water, alcohols, and other polar organic solvents. Most often, TsOH refers to the monohydrate, TsOH.H_2O. TsOH is a strong organic acid, about a million times stronger than benzoic acid. This catalyst can act as ecofriendly for a variety of organic transformations.

We propose tentative plausible mechanism for the formation of 12-(phenyl)-8*H*-benzo[5,6]chromeno[2,3-*d*]pyrimidine-9,11(10*H*,12*H*)-dione (04 a-q), in the presence of *p*-TSA. The overall, mechanism takes place according to Knoevenagel-Michael reaction (Scheme-I).The spectral and physical data of the compound is proved by agreement data.

Table.01. Optimization of the reaction conditions using different solvents.

Entry	Solvent	Reaction Time (h)	Yield (%)[b]
1	DMF	6.0	35
2	Ethylene glycol	5.5	50
3	THF	6.2	40
4	Acetonitrile	6.0	52
5	DCM	7.0	58
6	Ethanol	5.0	90
8	Water+Ethanol(1:1)	5.0	65

Reaction conditions: *β*-napthol **(1 mmol) (03)**, Barbituric acid **(1 mmol) (02)** and aromatic aldehyde **(1 mmol) (01)** was refluxed at 70 ^{0}C. [d] Isolated yields.

Table-02: Optimization Study for the amount of *p*-TSA.

Entry	Catalyst (mole %)	Temperature (^{0}C)	Reaction Time (h)	Yield %[b]
1	01	70	5.0	36
2	02	70	5.0	44
3	04	70	5.0	56
4	06	70	5.0	64
5	08	70	5.0	76
6	10	70	5.0	90
7	15	70	5.0	92

Reaction conditions: *β*-napthol **(1 mmol) (03)**, Barbituric acid **(1 mmol) (02)** and aromatic aldehyde **(1 mmol) (01)** was refluxed at 70 ^{0}C. [d] Isolated yields.

Probable Mechanism:

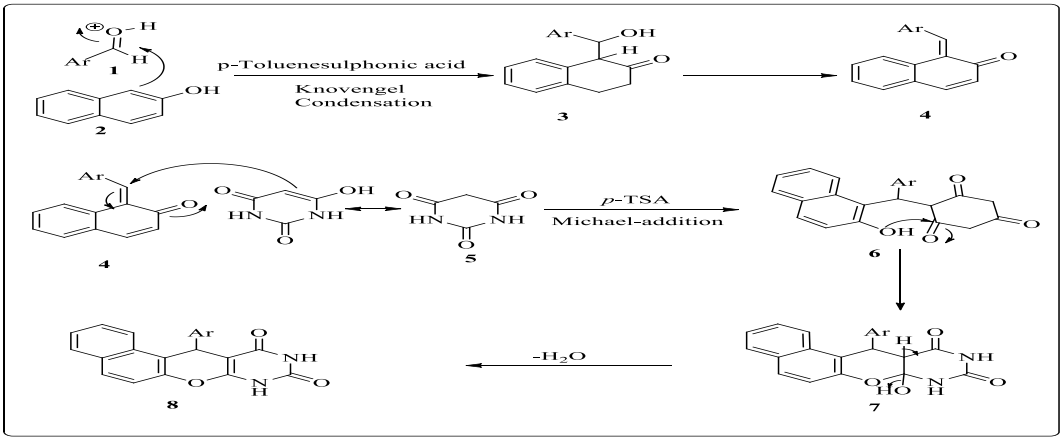
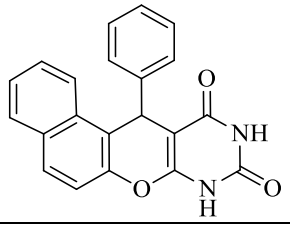
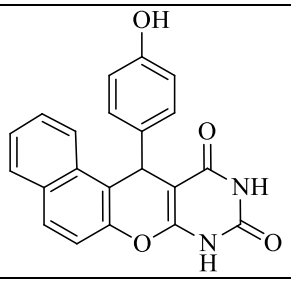
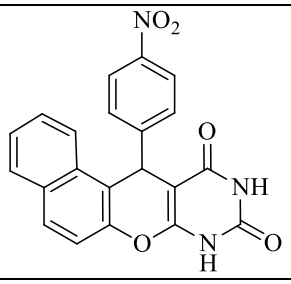
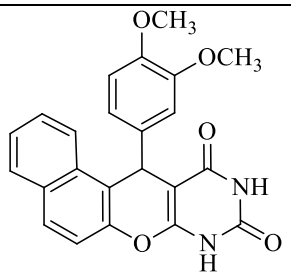
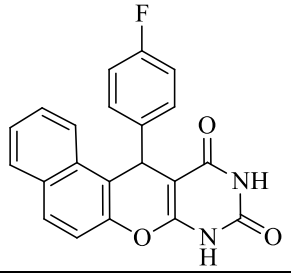
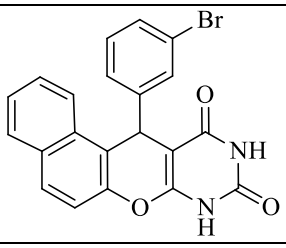
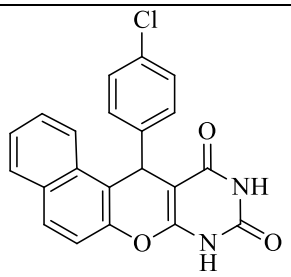
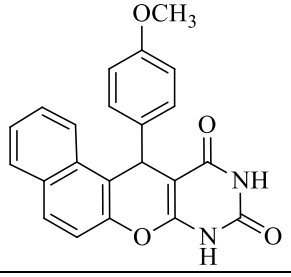
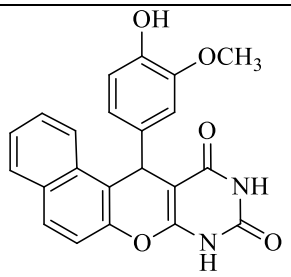
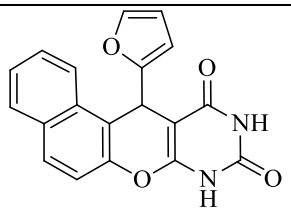
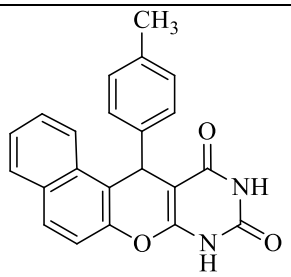
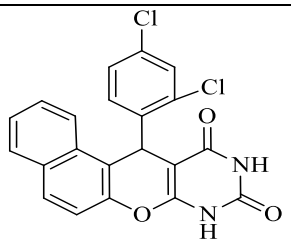
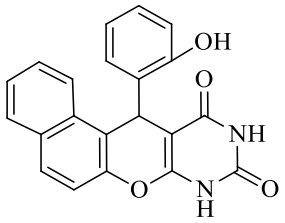
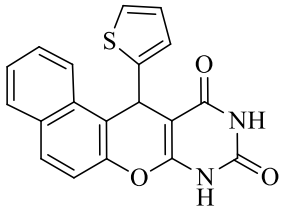
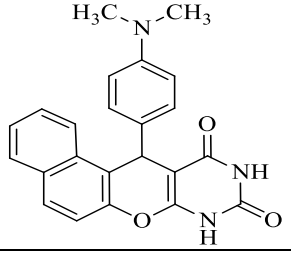
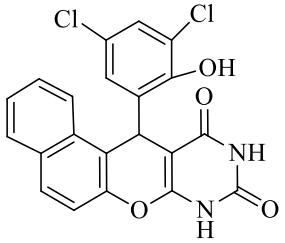
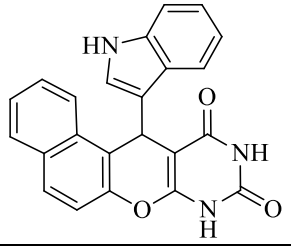


TABLE.03 Reaction Time, Yields and M.P.of 12-(phenyl)-8*H*-benzo[5,6]chromeno[2,3-*d*]pyrimidine-9,11(10*H*,12*H*)-dione derivatives.

Entry	Comp. code	Structure of compounds	Time (Hrs)	Yield (%)	M.P. (Obs. ^{0}C)	M.P. (Lit. ^{0}C)
1	04 a		5.2	80	275-277	276-278
2	04 b		5.0	90	248-250	250-252
3	04 c		5.5	78	304-306	305-307

4	04 d		5.0	90	288-289	288-290
5	04 e		5.2	82	278-279	280-282
6	04 f		5.5	77	262-264	265-266
7	04 g		5.2	82	298-300	301-302
8	04 h		5.0	86	257-259	258-260
9	04 i		5.0	84	284-286	286-288
10	04 j		6.5	72	272-274	274-276

11	04 k		5	86	279-280	280-281
12	04 l		5.5	74	290-291	291-292
13	04 m		5.5	80	250-252	252-254
14	04 n		6.5	70	266-268	268-270
15	04 o		5	87	274-276	276-278
16	04 p		5.0	80	305-306	306-308
17	04 q		6.0	70	277-278	278-279

4.1 EXPERIMENTAL:

Melting points of synthesized compounds were determined by open capillary tubes and uncorrected. Purity of all the products was routinely checked by thin layer chromatography (TLC) on pre-coated sheets of silica gel-C plates of 0.25 mm thickness using UV Chamber for detection. Perkin-Elmer FT-IR spectra were recorded in KBr pallets on infrared spectrophotometer. Bruckner advance spectrophotometer 300 or 400 MHz was used to record ^{1}H and ^{13}C-NMR spectra in DMSO-d_6 using TMS as internal standard. Mass spectra were recorded on FT-VC-7070 H Mass spectrometer using the EI technique at 70 eV.

5. SPECTRAL ANALYSIS: (FINDINGS)

1) **12-(4-nitrophenyl)-8*H*-benzo[5,6]chromeno[2,3-*d*]pyrimidine-9,11(10*H*,12*H*)dione.(04c)** (IR (KBr/cm^{-1}) 3234 (-NH), 3080 (Ar C-H), 1716 (-C=O), 1694 (Ar C=C), 1531 (-NO_2) cm^1; ^{1}HNMR (300MHz, DMSO d_6/ ppm); δ 4.75(1H,s,CH),7.32 (1H,d,Ar-H), 7.50 (2H,d,Ar-H), 7.60-7.72 (2H,t,Ar-H), 7.80 (H,d,Ar-H), 7.94 (1H,d,Ar-H), 8.15 (1H,d, Ar-H), 8.27 (1H,d,Ar-H) 11.30 (1H,s,NH), 11.86(1H,s,NH)EI-MS (m/z: RA %): 387 ($M^{+\cdot}$, 100%). ^{13}C NMR (300 MHz, DMSO–d_6/ppm) δ:37.1, 81.30, 118.91,122.12, 123.23, 123.24, 125.55, 125.55,128.56,128.86,133.57,145.48,151.29,151.81,154.12,157.93,164.10;Elemental analysis **:** Calculated data for $C_{21}H_{13}N_3O_5$; C, 65.12; H 3.38, N, 10.85. Found: C 65.06; H, 3.32; N, 10.20.
2) **12-(4-fluorophenyl)-8*H*-benzo[5,6]chromeno[2,3-*d*]pyrimidine-9,11(10*H*,12*H*) dione.(04e)** IR (KBr/cm^{-1}) 3262 (-NH), 3112 (Ar C-H), 1744 (-C=O),1354 (C-F) cm^{-1}; ^{1}HNMR(300MHz, DMSO d_6/ ppm); δ 4.75(1H,s,CH),6.90 (2H,d,Ar-H), 7.02 (2H,d,Ar-H), 7.25 (1H,d,Ar-H), 7.45 (2H,t,Ar-H), 7.65 (1H,d,Ar-H), 8.00 (1H,d,Ar-H), 8.20 (1H,d,Ar-H) 11.05 (1H,s,NH), 12.07(1H,s,NH). EI-MS (m/z: RA %): 360 ($M^{+\cdot}$, 100%); ^{13}CNMR (300MHz, DMSOd_6/ppm) δ: 37.10, 82.10, 116.56, 119.02, 122.10, 123.25, 126.34, 129.14, 130.02, 135.28, 142.37, 148.20, 150.70, 151.82, 156.13, 160 .40, 164.92.; Elemental analysis**:** Calculated data for $C_{21}H_{13}FN_2O_3$; C 70.00, H 3.64, N 7.77 Found: C 70.02, H 3.60, N 7.72)
3) **12-(4-chlorophenyl)-8*H*-benzo[5,6]chromeno[2,3-*d*]pyrimidine-9,11(10*H*,12*H*)-dione.(04.g)** IR (KBr/cm^{-1}) 3219 (-NH), 3091 (Ar C-H), 1755 (-C=O), 1288 (C-O-C), 792(C-Cl) cm^{-1}; ^{1}HNMR (300MHz, DMSO d_6/ ppm) δ: 4.85(1H,s,CH),7.12 (2H,d,Ar-H), 7.37-7.40 (2H,d,Ar-H), 7.52 (1H,d,Ar-H), 7.75 (2H,t,Ar-H), 7.85 (1H,d,Ar-H), 8.07 (1H,d, Ar-H), 8.20 (1H,d,Ar-H) 11.26 (1H,s,NH), 11.45 (1H,s,NH); EI-MS (m/z: RA %): 376 ($M^{+\cdot}$, 100%) ^{13}CNMR (300MHz, DMSOd_6/ppm) δ: 37.46, 81.30, 117.90, 119.03, 123.20, 125.70, 126.23, 128.82, 129.42, 131.80, 135.50, 146.70, 150.70, 151.90, 156.19, 163.00. Elemental analysis**:** Calculated data for $C_{21}H_{13}ClN_2O_3$; C 66.94, H 3.48, N 7.43 Found: C 66.90, H 3.39, N 7.3
4) **12-(4-methoxyphenyl)-8-*H*benzo[5,6]chromeno[2,3-*d*]pyrimidine-9,11(10*H*,12*H*)-dione.(04 h)** IR (KBr/cm^{-1}) 3211 (-NH), 3064(Ar C-H), 1732 (-C=O), 1269 (C-O-C) cm^{-1}; ^{1}HNMR (300MHz, DMSO d_6/ ppm) δ: 3.85 (3H,s,-OCH_3), 4.90 (1H,s,-CH), 7.05 (2H,d,Ar-H), 7.18 (2H,d,Ar-H), 7.35 (1H,d,Ar-H), 7.50 (1H,t,Ar-H), 7.60 (1H,t,Ar-H), 7.70 (1H,d,Ar-H), 8.05 (1H,d,Ar-H), 8.22 (1H,d,Ar-H) 11.16 (1H,s,NH), 11.29 (1H ,s,NH). ; EI-MS (m/z: RA %): 372 ($M^{+\cdot}$, 100%); ^{13}CNMR (300MHz, DMSOd_6/ppm) δ:38.12,82.00,115.20, 115.20,118.90,122.36,123.01,123.14,126.19,128.40,129.12,129.12,130.06,139.93,150.70,151.10,156.86,159.00,163.00 Elemental analysis**:** Calculated data for $C_{21}H_{13}N_3O_3$; C 70.96, H 4.33, N 7.52 Found: C 70.90, H 4.29, N 7.48)..

6. CONCLUSION:

We have proposed a novel efficient and eco-friendly synthesis of 12-(substituted phenyl)-8*H*-benzo[5,6]chromeno[2,3-*d*]pyrimidine-9,11(10*H*,12*H*)-dione derivatives by one-pot three component condensation reactions. The product can be easily isolated by simple work up technique, ecofriendly catalyst. Furthermore, the procedure offers a number of advantages including improved yields, simple experimental procedure, cleaner reactions and low cost which makes it a useful and attractive strategy with respect to economic and environmental advantages.

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Concentration Dependant Molecular Interaction of Substituted Ketimine Drugs in 75% Dichloromethane (DCM)-Water Mixture at 308 ± 1K.

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ABSTRACT:

In the present investigation, liquid properties such as density, relative viscosity, and specific viscosity of aromatic substituted ketimine drugs were measured under different concentration (0.01M, 0.008M, 0.006M, 0.004M & 0.002M) in 75% dichloromethane (DCM)-water mixture at 308 ± 1 K. The relation between viscosity (ηsp/√ C) and concentration of solution (√C) represented by plotting the graphs. These graphs prove the validity of Jones-Dole equation for both ligands by giving linear straight line. The intercept and slope of straight line gives value of A and B Coefficients. The large and small deviations in the values of 'A' give us an idea about the stronger and weaker solute-solvent interaction while the order or disorder introduced by solute in solvent is measured by the values of B coefficient. The experimental data were used to investigate the solute-solute and solute-solvent interaction of aromatic substituted ketimine drugs in 75% dichloromethane (DCM)-water mixture at 308 ± 1 K.

KEY WORDS: *Relative viscosity, specific viscosity, dichloromethane (DCM), etc.*

1. INTRODUCTION:

Viscosity is the physical property of liquids, which opposes the relative motion between two surfaces of liquids that are travelling at different velocities. In simple words viscosity describes a liquid internal resistance to flow and measure of its internal frictions. The measurement of viscosity of liquids has been widely used by chemists in order to know constitution of molecule, molecular weight of polymers, gradation of lubricants etc. Beside these viscosity measurements provides important information about solute-solute and solute-solvent interactions in aqueous and non-aqueous solutions. Many researchers have investigated solute-solute and solute-solvent interactions in aqueous and non-aqueous solutions. Jone-Dole [1] equation is applicable to investigate observed viscosity concentration dependence of dilute electrolyte solution. Moulik [2] and Einstein [3] have studied dependence of concentration of viscosity in concentrated electrolyte solution. D.V. Jahagirdar et al. [4] studied density, ultrasonic velocity and viscosity measurements of four pharmacologically significant drugs in methanol at 25°C. Thanuja et al. [5] Studied intermolecular interaction on binary mixtures of methyl orange–water system excess molar functions of ultrasonic parameters at different concentrations and at different temperatures. Biswajit Sinha et al. [6] investigated solute-solute and solute-solvent interactions of paracetamol in aqueous solution of β cyclodextrin at different temperature. Recently P. H. Parsania [7] studied molecular interactions in solutions of 1,1-bis(4-(2-oxopropoxy)phenyl)cyclohexane on ultrasonic velocity, density, and viscosimetric data. M. Tripathy et al. [8] investigated studies on the solute solvent interaction of nimesulide in aqueous solutions of hydrotropic agents at different temperatures and which shows that nimesulide in aqueous solutions of hydrotropic agents follows the order: sodium benzoate>nicotinamide>sodium salicylate>sodium bromide, which is the order of the basic nature of the aqueous solutions of these hydrotropic agents. These results suggest that at the lower hydrotropic concentration, weak ionic interaction and at higher hydrotropic concentration, the formation of molecular aggregates is the possible mechanisms of the hydrotropic solubilisation.

In the present work viscometric study of substituted ketimines drugs were carried out at different temperatures by preparing the solutions of different concentrations. The solutions of ligands were prepared in the 75% DCM-Water at different temperature (35°C, 37°C, 39°C, 41°C ±0.1^{0}C) and different concentration.

2. EXPERIMENTAL:

Material:

In the present research work solvent dichloromethane (DCM) of AR grade and freshly prepared doubly distilled water was used. The ligands used in the present investigation are

1. 5- Bromo-2-hydroxy-4-chloro (p-methyl phenyl) ketimine (L_A)
2. 5- Bromo-2-hydroxy-4-chloro (p-amino phenol) ketimine (L_B)

These ligands were synthesized by reported method [9].

Procedure:

The viscometric study of substituted ketimines were carried out by preparing the solutions of different concentrations such as, 0.01M, 0.008M, 0.006M, 0.004M & 0.002M in 75% dichloromethane (DCM)-water mixture at 308 ± 1 K. The densities of pure solvent and solutions of various concentrations were measured at different temperature using a specific gravity bottle. All the weighing were made on one pan digital balance (petit balance AD-50B) with an accuracy of ± 0.001 gm. Viscosities of the solutions were determined with the help of calibrated clean and dried Ostwald viscometer (± 0.11% $Kgm^{-1}s^{-1}$). The flow time of solutions were measured by using digital clock of Racer Company having error (±0.01Sec).

3. RESULT AND DISCUSSION:

To determine the relative and specific viscosity, the different concentration of the substituted α, β unsaturated ketimine solutions were prepared and there viscosities were measured with help of the following mathematical relation

$$(\eta_r) = (ds \times ts / dw \times tw) \times \eta_w \quad \text{.....(1)}$$

Where

η_r = Relative viscosity
η_w = Viscosity of water
ds = Density of solution
dw = Density of water
ts = Flow time for solution
tw = Flow time for water

The relative viscosities and density data of ligand solutions at different concentration are presented in table 1-2. The viscosity data have been analyzed by Jones–Dole equation.

$$(\eta_r - 1) / \sqrt{C} = \eta_{sp} / \sqrt{C} = A + B \sqrt{C} \quad \text{---------- (2)}$$

Where
A = Falkenhagen coefficient
B= Jones-Dole coefficient
C = Molar concentration of ligand solutions

The Falkenhagen coefficient (A) measures the solute-solute interaction, while Jones-Dole coefficient (B) measures the solute-solvent interaction. The graphs were plotted between $\eta_{sp}/\sqrt{C}$ against $\sqrt{C}$. the graphs for each system gives linear straight line showing validity of Jones–Dole equation. The slope of the straight line gives value of B-coefficient. The plot of $\eta_{sp}/\sqrt{C}$ against $\sqrt{C}$ shown in fig.1-2.

In the present investigation, the relative viscosity of solution of ligands A & B increases with increase in concentration of ligand solutions. The increase in viscosity with increase in concentration may be attributed to the increase in the interactions of solute-solvent. The relative viscosity of solutions increases with increase concentration which measures the in interaction of solute and solvent. The relation between viscosity ($\eta sp/\sqrt{C}$) and concentration of solution ($\sqrt{C}$) represented by plotting the graph (fig. 1-2). These graphs prove the validity of Jones-Dole equation for both ligands by giving linear straight line. The values of Jones-Dole coefficients especially B- coefficients are the slope of graph ($\eta sp/\sqrt{C}$) Vs ($\sqrt{C}$) while the values of Falkenhagen coefficient i.e. A-Coefficient are the intercept of graph of ($\eta sp/\sqrt{C}$) Vs ($\sqrt{C}$). The large and small deviations in the values of 'A' give us an idea about the stronger and weaker solute-solvent interaction respectively as shown in table 3. The order or disorder introduced by solute in solvent is measured by the values of B coefficient which shows either positive or negative values. In this work, the values of B-coefficients for both the ligands are negative it measures the effective thermodynamic volume of solute on accounts for solute-solvent interaction, it is known as a measure of disorder introduced by a solute into the solvent. Pandey et.al. [10] has shown that the solute with negative B-coefficient is characterized as 'surface breaker', signifying weak solute-solvent interactions for all systems. Therefore, the present work also supports this fact. Deosarkar et.al. [11] supported the fact that the viscosity increases with the concentration due to the presence of particles arises from the fact that, they lie across the fluid stream lines and are substituted to torsional force.

Conc(C) Mole/lit	**$\sqrt{C}$ $Mole^{-1/2}$ $lit^{-1/2}$**	**Density gm/cc**	**Time Flow (Sec)**	**Relative Viscosity $\eta_r = \eta/\eta 0$**	**Specific Viscosity $\eta_{sp} = \eta_r - 1$**	**$\eta_{sp}/\sqrt{C}$**
0.01	0.1	1.22419	64.5	1.605	0.604656	6.046562
0.008	0.0894	1.22329	63.0	1.566	0.566186	6.333181
0.006	0.0774	1.22238	62.6	1.555	0.555085	7.171636

0.004	0.0632	1.22148	60.5	1.502	0.501811	7.940043
0.002	0.0447	1.21604	55.3	1.367	0.366616	8.201697

Table 1: System-Ligand A (L_A)

Temp: (308 ±0.1) K Medium: 75% DCM-Water

Conc(C) Mole/lit	$\sqrt{C}$ $Mole^{-1/2}$ $lit^{-1/2}$	Density gm/cc	Time Flow (Sec)	Relative Viscosity $\eta_r = \eta/\eta_0$	Specific Viscosity $\eta_{sp} = \eta_r - 1$	$\eta_{sp}/\sqrt{C}$
0.01	0.1	1.22057	64.2	1.592	0.592470	5.924697
0.008	0.0894	1.21967	62.3	1.544	0.544201	6.087260
0.006	0.0774	1.21967	59.9	1.485	0.484713	6.262447
0.004	0.0632	1.21876	56.1	1.389	0.389487	6.162771
0.002	0.0447	1.21786	51.6	1.277	0.277087	6.198818

Table 2: System-Ligand B (L_B)

Temp: (308 ±0.1) K Medium: 75% DCM-Water

Table 3: A and B Coefficient values

Ligand + 75% DCM-Water	A	B (Lit/mol)
L_A	10.32	-42.464
L_B	6.43	-4.1696

Figure 1: Plot of $\sqrt{C}$ Vs. $\eta_{sp}/\sqrt{C}$

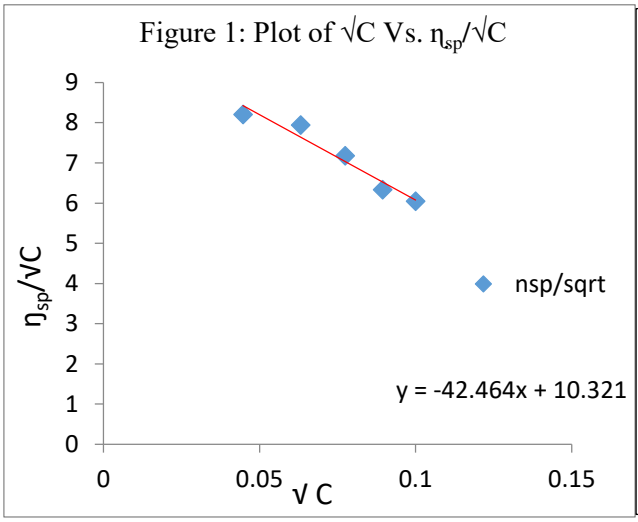
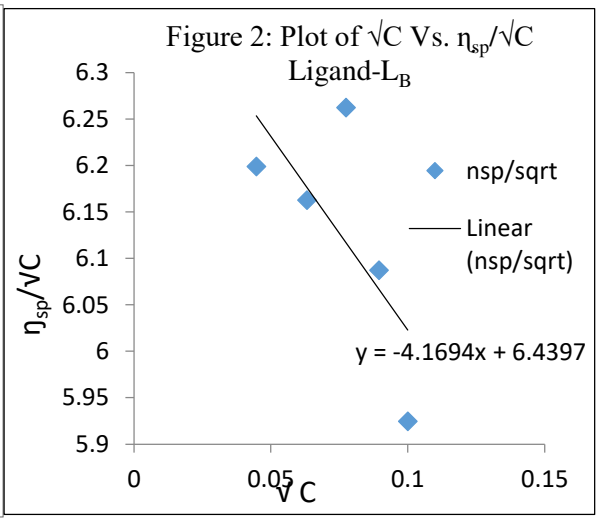


Figure 2: Plot of $\sqrt{C}$ Vs. $\eta_{sp}/\sqrt{C}$ Ligand-L_B



4. CONCLUSION:

In the present investigation, liquid properties such as density, relative viscosity, and specific viscosity of aromatic substituted ketimine drugs were measured under different concentration in 75% dichloromethane (DCM)-water mixture at 308 ± 1 K. From the experimental data it is concluded that both the ligands shows strong solute-solute and weak solute solvent interactions in aqueous solution.

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Multicomponent synthesis of hydrazino benzothiazole and its substituted derivatives

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ABSTRACT:

A Literature survey indicates that benzothiazole derivatives possess anti-inflammatory and anti-bacterial activity. 6-chloro-2-mercapto benzothiazole on reflux with different hydrazines in the presence of DMF and anhydrous K_2CO_3 gives 2-substituted hydrazino-6-chloro benzothiazole. The synthesized compounds were characterized by elemental analysis and spectral data.

KEY WORDS: *6-chloro-2-mercaptobenzothiazole, K_2CO_3, 2-substituted hydrazino-6-chloro benzothiazole*

1. INTRODUCTION:

Benzothiazole derivatives are an important class of heterocyclic compounds that exhibit a wide range of biological properties in medicinal and agricultural chemistry [1-5]. Further industrial applications as antioxidants [6,7], vulcanization accelerators [8,9], and a do pant in a light emitting organic electroluminescent devices [10] have also been reported. Many reports have appeared in the literature describing the formation of benzothiazoles via one of the two major routes. However, these methodologies suffer from one or more disadvantages, such as tedious workup, high temperature, prolonged reaction time, and toxic organic solvents such as DMF and DMSO.

Carrying out organic reactions in water has become highly desirable in recent years to meet environmental considerations. The use of water as a sole medium of organic reactions would greatly contribute to the development of environmentally friendly processes. It would be even more desirable to carry out catalytic organic reactions in water, which normally require delicate reaction conditions in order for the catalyst to be stable and yet reactive. In this context, in recent years much attention has been focused on Lewis acid-catalyzed organic reactions in water, and several reactions of this type have been already identified. Substituted benzothiazole is an important class of heterocyclic compounds that exhibits a wide range of biological properties such as inhibitors of stearoyl-coenzyme desaturase, antitumor, antimicrobial, LTD_4 receptor antagonist and the Gram-positive selective antibacterials [11-17].

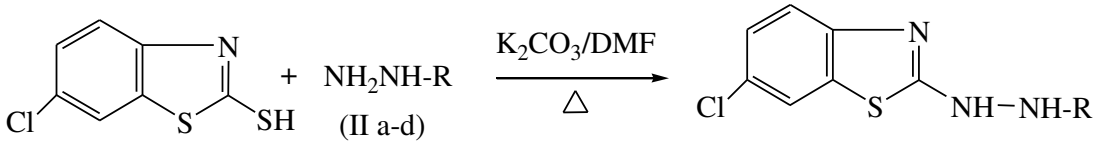
2. LITERATURE REVIEW:

Inspite of tremendous advance made in modern medicine, there are still a large number of aliments for which suitable drugs are yet to be found. Today, there is an need to develop safer drug for the treatment of pain. Hydrazino benzothiazole and isatin derivatives are an important class of organic heterocycles because of their potential activities are reported to be effective in CNS disorders such as convulsion [18] and depressions [19]. Indole and benzothiazoles its analogs constitute the active class of the compounds possessing wide spectrum of antimicrobial [20], anthelmintic [21], analgesic [22] , anti-inflammatory [23] and tuberculosis [24] activities. In view of our program to develop novel analgesic agents it was decided to synthesize substituted derivatives of hydrazino benzothiazole.

3. MATERIALS:

All melting points were determined in open capillary tube and were uncorrected. IR spectra were recorded with potassium bromide pellets technique, ^{1}H NMR spectra were recorded on AVANCE 300 MHz Spectrometer in DMSO using TMS as internal standard. Mass spectra were recorded on a FT VG-7070 H Mass Spectrometer using EI technique at 70 eV. All the reactions were monitored by Thin layer chromatography.

4. METHOD:



6-chloro-2-mercapto benzothiazole

(I)

2-substituted hydrazino-6-chloro benzothiazole

(III a-d)

5. DISCUSSION:

Preparation of 2-substituted hydrazino-6-chloro benzothiazole (III a.d):

6-chloro-2-mercapto benzothiazole on reflux independently with hydrazine hydrate, phenyl hydrazine/ 4-nitro phenyl hydrazine /2,4-dinitro phenyl hydrazine in the presence of DMF and anhydrous K_2CO_3 gives 2-substituted hydrazino-6-chloro benzothiazole. The synthesized compounds were characterized by elemental analysis and spectral data.

6. ANALYSIS:

The objectives of the present work are to synthesize certain hydrazino benzothiazole derivatives and study their antibacterial and anti-inflammatory activity in particular. Thus an attempt has been made in this direction. As expected substituted benzothiazoles exhibited antimicrobial activity some are equipotent to that of standard employed for comparison. Therefore a detailed study of toxicity is necessary. There is no such a thing as completely safe drug. Drugs are powerful tools which alter physiological processes for the better or for the worse.

7. FINDINGS: A novel compound synthesize to evaluate antibacterial and anti-inflammatory activity.

8. RESULT:

A society which wishes to benefit from them will not achieve all the benefits are for the biological testing do not always turn out as potential new drugs, but may be intended to serve as models for evaluation of hypothesis.

10. CONCLUSION:

In conclusion, a facile one pot synthesis has been developed for the title compounds using readily available starting materials. Thus, there is a network of reaction equilibria which all finally flow into an irreversible step yielding the product. 2-subtituted hydrazino-6-chloro benzothiazoles are responsible for antibacterial activity, but it is interesting to note that benzothiazole moieties when fused with other moieties showed a broad spectrum antibacterial activity. Hence in search of new generation of antibiotics it may be worthwhile to explore the possibility in this area by fusing different moieties and increase potency.

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Efficient synthesis and antibacterial screening of 2,6-diamino-6-phenyl pyrimidine-5-carbonitrile derivatives

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ABSTRACT:

One-pot three component synthesis of 2,6-diamino-6-phenyl pyrimidine-5-carbonitrile derivatives by the condensation of substituted Aromatic aldehydes, malononitrile and guanidine hydro-chloride in ethanol using iron acetylacetonate $Fe(acac)_3$ catalyst. The products have been assayed for their antimicrobial screening against Gram+ve and Gram-ve bacteria. Some of the products showed moderate activity when compared with known standard drug viz. penicillin at the same concentration 50µgm/ml. Spectroscopic tequeniques are very good tools for the identification of compounds. The structures have been confirmed by 1H NMR, ^{13}C-NMR, IR, and Mass spectral data.

KEYWORDS: *Aromatic aldehydes, Malononitrile, Guanidine Hydrochloride, Iron Acetylacetonate, Antimicrobial screening.*

1. INTRODUCTION:

Multicomponent reactions (MCRs), by virtue of their convergence, productivity, facile execution and generally high yields, have attracted much attention in the area of combinatorial chemistry [1–3]. Heterocycles are of significant biological and pharmaceutical importance and play vital roles in drug discovery process. Among these, the multicomponent synthesis of polyfunctionalized heterocyclic compounds has become more challenging in organic and medicinal chemistry [4–6]. Pyrimidines are one of the biologically substantial scaffolds due to their wide range of biological and pharmaceutical properties such as antihypertensive [7], antimicrobial [8, 9], antitumor [10], antimalarial [11], antioxidant [12] and protein kinase inhibitors [13]. Pyrimidines having amino group at positions 2 and 4 of the ring have been reported to exhibit application in Alzheimer's disease treatment [14]. Moreover, pyrimidine derivatives have played a significant role in agriculture as crop protection agents and in electro-optics as building blocks for calamitic liquid crystals [15]. Due to the valuable biological significance of pyrimidine compounds, the synthesis of pyrimidine derivatives has received considerable attention. Until today, a number of methods have been reported for the synthesis of pyrimidine rings by the use of 1,3-binucleophilic centers such as guanidine, amidines, urea, and thiourea [16–20] in the presence of different catalysts such as sodium acetate [21], Bi(NO3)3.5H2O [22], NaOH [23, 24], CuO microspheres [25], K_2CO_3 and tetra butyl ammonium bromide [26].

2. LITERATURE REVIEW:

Herein, with the aim to improve more efficient synthetic procedures, reduce the number of separate reaction steps, minimize by-products and in continuation of our efforts to the preparation of heterocyclic compounds [27-28], we sought to design, synthesize and evaluate antimicrobial activity of pyrimidine derivatives through MCRs. Herein, we report synthesis of 2,6-diamino-6-phenyl pyrimidine-5-carbonitrile derivatives by using commercially available aromatic aldehydes, malononitrile and guanidine hydrochloride in ethanol at 80^0C, as shown in Scheme 1.

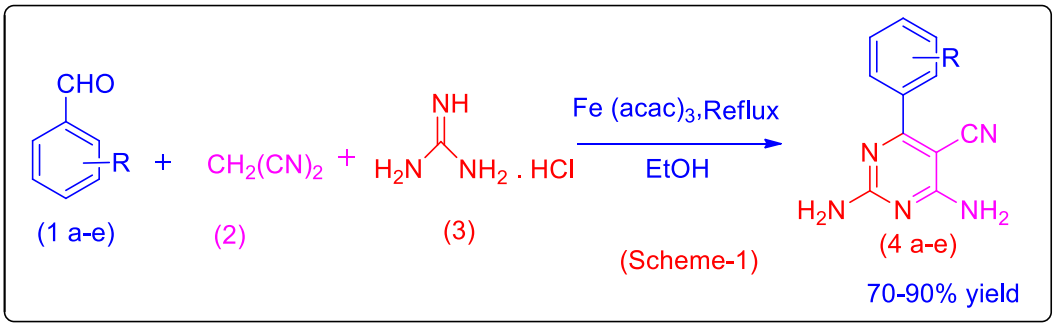
3. MATERIALS AND METHOD:

All the chemicals were obtained from Sigma Aldrich and Thomas Baker. These chemicals were applied without extra purification procedures. The reactions were carried out in dried glassware. The chemicals of analytical grade were procured from commercial sources and used as such without further purification. Open capillary tubes were used for melting points of isolated synthesized compounds and are uncorrected. Perkin-Elmer FTIR spectrophotometer was used for IR (KBr) spectra of compounds. Mass spectral data were recorded on liquid chromatography mass spectrometer (Shimadzu 2010Ev) using ESI probe. The ^{1}H and ^{13}C NMR spectra were recorded on spectrometer at 400MHz using TMS as an internal standard.

General procedure for the synthesis of 2,6-diamino-6-phenyl pyrimidine-5-carbonitrile derivatives (4a-e):

The equimolar mixture of aromatic aldehyde, (10 mmol), malononitrile (10 mmol) and $Fe(acac)_3$ (15 mole%) in 20 ml ethanol was stirred mechanically for at least 10 min, then guanidine hydrochloride (10 mmol) was added to the above reaction mixture and reaction mixture was refluxed till completion of reaction as monitored by TLC. After the completion of reaction, the reaction mixture was poured into ice-cooled water and neutralized by 1:1 HCl to get the desired product. The separated solid was filtered, washed with little distilled water to remove acid. Finally, the crude product was purified by recrystallisation from ethanol to get pure product in almost quantitative yield (Scheme 1).

4. RESULTS AND DISCUSSION:



We initially focused on optimization reaction condition. The reaction mixture of aromatic aldehyde, malononitrile and guanidine hydrochloride was refluxed independently in ethanol using $Fe(acac)_3$15 mole % as an efficient and novel catalyst, It was considered as a model reaction (**Scheme-1**) for investigating the effectiveness of different polar and non polar solvent using catalytic amount of $Fe(acac)_3$15 mmol %. Solvent optimization clearly noted that ethanol is the best solvent for the desired transformation due to fast reaction rate and high yield (Table1, entry 6). The other polar protic solvents gives moderate yield (Table1, entry 5), while other aprotic solvent like Acetonitrile, DMF, THF, DCM displayed slow reaction rates leading lower yield (Table-1, entry 1-4). We have carried out the model reaction using different stoichiometric amount of catalyst. The catalyst screening result are summarized in Table 2. It was observed that the excellent yield was achieved by using of Fe $(acac)_3$ 15 mole % (Table 2, entry 6).

Further investigating the influence of different parameters on the model reaction, we turned our attention towards the 2,6-diamino-6-phenyl pyrimidine-5-carbonitrile derivatives(**4 a-e**) using reaction of aromatic aldehyde **(1)**, malononitrile**(2),** and guanidine hydrochloride **(3),** was refluxed independently in ethanol using $Fe(acac)_3$15 mole % and the result are summarized in Table-3. With the both electron-poor and electron-rich benzaldhydes (Table-3, entries 1-5), the corresponding 2,6-diamino-6-phenyl pyrimidine-5-carbonitrile derivatives(**4a-e**) were obtained to excellent yields. These synthesized products **(4a-e)** were characterized from IR, ^{1}H-NMR, ^{13}C-NMR and Mass spectroscopic technique and elemental analysis.

TABLE-1: Optimization of the reaction conditions using different solvents[a]

Entry	Solvent	Reaction Time (h)	Yield (%)[b]
1	Acetonitrile	3.0	40
2	DCM	3.0	50
3	DMF	3.0	55
4	THF	3.0	62
5	Ethylene glycol	3.0	75
6	Ethanol-water	3.0	90

[a]***Reaction conditions:*** Aromatic aldehyde (10 mmol), Malononitrile (10 mmol) and guanidine hydrochloride (10 mmol) was refluxed.[b] Isolated yields.

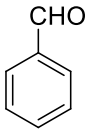
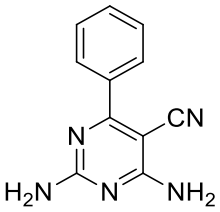
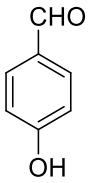
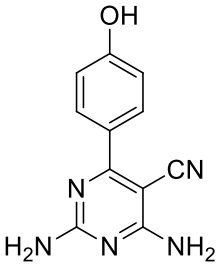
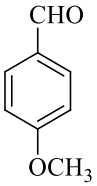
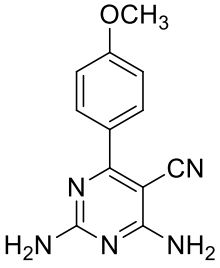
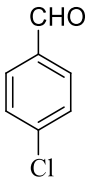
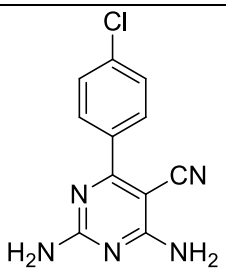
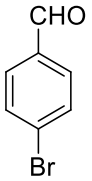
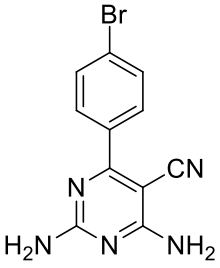
TABLE 2: Optimization Study for the amount Fe $(acac)_3$[a]

Entry	Catalyst (mole %)	Temperature (^{0}C)	Reaction Time (h)	Yield %[b]
1	01	80	3.0	45
2	02	80	3.0	50
3	05	80	3.0	55
4	08	80	3.0	60
5	10	80	3.0	70
6	15	80	3.0	90
7	20	80	3.0	92

[a]***Reaction conditions:*** Aromatic aldehyde (10 mmol), Malononitrile (10 mmol) and guanidine hydrochloride (10 mmol) was refluxed.

[b] Isolated yields.

Table 3: Aromatic aldehyde, Malononitrile and guanidine hydrochloride for the synthesis of **(4a-e)**[a]

Entry	Aldehyde (1a-e)	Products (4 a-e)	Time (h)	Yield (%)[b]	M.P. (^{0}C)
1		 **3a**	3.0	85	240-242
2		 **3b**	3.0	80	260-262
3		 **3c**	3.0	75	236-238
4		 **3d**	3.0	70	264-266
5		 **3e**	3.0	90	260-262

[a]***Reaction conditions:*** (1) (10 mmol), (2) (10 mmol), (3) (10 mmol) and ethanol in Fe $(acac)_3$ 15 mole % were refluxed.

[b] Isolated yield

Spectral Analysis:

2,4-diamino-6-phenyl pyrimidine-5-carbonitrile (4a):

M.P. 240-242^{0}C; Yield 85%; IR (KBr, *v*max, cm^{-1}), 3410, 3380, 3122, 2223; ^{1}H NMR (400MHz, DMSO-d_6, ppm) δ 7.04-7.38 (brs, 4H, 2NH$_2$), δ 7.40-7.80 (m, 5H, Ar-H); ^{13}C NMR (400 MHz, DMSO–d_6, ppm): *δ* 170.4, 168.6, 166.2, 135.6., 130.1, 129.4, 128.0, 116.4, 78.7; EI-MS (m/z: RA %): 211 (M$^{+\cdot}$, 100%). Elemental analysis Calculated data for $C_{11}H_9N_5$; C, 62.55; H, 4.29; N, 33.16; Found: C, 62.50; H, 4.36; N, 33.10.

2,4-diamino-6-(4-hydroxyphenyl)pyrimidine-5-carbonitrile (4b):

M.P. 260-262^{0}C; Yield 80%; IR (KBr, *v*max, cm^{-1}), 3395, 3374, 3256, 3022, 2230; ^{1}H NMR (400MHz, DMSO-d_6, ppm) δ 7.20-7.50 (brs, 4H, 2NH$_2$), δ 4.62 (s, 1H, OH), δ 7.14 (d, 2H, Ar-H), δ 7.68 (d, 2H, Ar-H); ^{13}C NMR (400 MHz, DMSO–d_6, ppm): *δ* 168.2, 167.4, 165.8, 155.6., 129.2, 118.0, 115.6, 78.9, 52.6; EI-MS (m/z: RA %): 227 (M$^{+\cdot}$, 100%). Elemental analysis Calculated data for $C_{11}H_9N_5O$; C, 58.14; H, 3.99; N, 30.82; Found: C, 58.10; H, 3.90; N, 30.88.

2,4-diamino-6-(4-methoxyphenyl)pyrimidine-5-carbonitrile (4c):

M.P. 236-238^{0}C; Yield 75%; IR (KBr, *v*max, cm^{-1}), 3436, 3390, 3110, 2910, 2218; ^{1}H NMR (400MHz, DMSO-d_6, ppm) δ 7.10-7.70 (brs, 4H, 2NH$_2$), δ 3.78 (s, 1H, CH$_3$), δ 6.90 (d, 2H, Ar-H), δ 7.40 (d, 2H, Ar-H); ^{13}C NMR (400 MHz, DMSO–d_6, ppm): *δ* 169.4, 167.6, 166.2, 160.3., 128.1, 120.0, 117.1, 79.2; EI-MS (m/z: RA %): 242 (M$^{+\cdot}$, 100%). Elemental analysis Calculated data for $C_{12}H_{11}N_5O$; C, 59.74; H, 4.60; N, 29.03; Found: C, 59.70; H, 4.60; N, 29.10.

2,4-diamino-6-(3-chlorophenyl)pyrimidine-5-carbonitrile (4d):

M.P. 264-266^{0}C; Yield 70%; IR (KBr, *v*max, cm^{-1}), 3466, 3374, 3145, 2215; ^{1}H NMR (400MHz, DMSO-d_6, ppm) δ 7.04-7.62 (brs, 4H, 2NH$_2$), δ 7.50 (d, 2H, Ar-H), δ 7.78 (d, 2H, Ar-H); ^{13}C NMR (400 MHz, DMSO–d_6, ppm): *δ* 170.2, 168.6, 167.5, 151.3., 130.1, 128.4, 119.2, 78.7; EI-MS (m/z: RA %): 245 (M$^{+\cdot}$, 100%). Elemental analysis Calculated data for $C_{11}H_8N_5Cl$; C, 53.78; H, 3.28; N, 28.51; Found: C, 53.80; H, 3.30; N, 28.20.

2,4-diamino-6-(4-bromophenyl)pyrimidine-5-carbonitrile (4e):

M.P. 260-262^{0}C; Yield 90%; IR (KBr, *v*max, cm^{-1}), 3472, 3360, 3130, 2290; ^{1}H NMR (400MHz, DMSO-d_6, ppm) δ 7.12-7.55 (brs, 4H, 2NH$_2$), δ 7.70 (d, 2H, Ar-H), δ 7.94 (d, 2H, Ar-H); ^{13}C NMR (400 MHz, DMSO–d_6, ppm): *δ* 168.4, 167.5, 166.2, 134.7., 132.8, 122.5, 115.4, 79.4; EI-MS (m/z: RA %): 289 (M$^{+\cdot}$, 100%). Elemental analysis Calculated data for $C_{11}H_8N_5Br$; C, 45.58; H, 2.84; N, 24.20; Found: C, 45.54; H, 2.78; N, 24.14.

Antimicrobial Activity:

We have used the *Agar* well diffusion method for assessment of the antimicrobial activity of newly synthesized compounds. On Muller-Hinton agar medium zone of inhibition were observed and zone diameter was recorded in mm against specific test microorganisms.

The synthesized compounds were accessed antimicrobial activity particularly antibacterial and antifungal. The antibacterial activity against Gram positive Staphylococcus aureus bacteria and Gram negative bacteria are Escherichia coli, Proteus vulgaris using standard drugs are Penicillin and Streptomycin. The antifungal activity screened against Aspergillus fumigatus, Aspergillus niger using Nystatin as standard drug.

The synthesized compounds **4b, 4c and 4e** showed good antibacterial activity against **Staphylococcus aureus** as compaired to standard drugs Penicillin and Streptomycin. The compounds **4a, 4b and 4e** showed good antibacterial activity against **Escherichia colias** compaired to standard drugs Penicillin and Streptomycin. The synthesized compounds **4b, 4d and 4e** showed good zone of inhibition against **Proteus vulgaris** as compaired to Penicillin and Streptomycin.

The synthesized compounds **4b, 4d and 4e** showed good zone of inhibition against **Aspergillus fumigatus** as compaired to Nystatin. The synthesized compounds **4c, 4d and 4e** shows good zone of inhibition against **Aspergillus niger** as compaired to Nystatin.

TABLE 4: Antimicrobial activity of tested compounds (4 a-e).

Sr. No.	Compounds	Zone of inhibition* (mm)				
		Bacterial Species			Fungal Species	
		Gram positive	Gram negative		*Aspergillusf umigatus*	*Aspergillus niger*
		Staphylococcus aureus	*Escherichia coli*	*Proteus vulgaris*		
01	**4a**	12	14	10	10	ND

02	**4b**	16	18	16	16	12
03	**4c**	18	12	10	10	20
03	**4d**	16	10	16	16	18
05	**4e**	20	18	14	18	14
Ref*	Penicillin	26 mm	40 mm	18 mm	-----	-----
	Streptomycin	40 mm	35 mm	34 mm	----	-----
	Nystatin (50 µgm/ml)	-----	-----	-----	40 mm	28 mm

ND= Not detected zone of inhibition under experimental condition.

5. CONCLUSION:

We have developed an operationally simple, eco-friendly, inexpensive and efficient, synthesis of tetramethyl-hexahydro-1*H*-xanthene-1,8(2*H*)-dione derivatives. The procedure offers several advantages including improved yields, cleaner reactions and low cost which makes it a useful and attractive strategy in view of economic and environmental advantages. Furthermore these compounds were evaluated for their antibacterial activity. Some of the compounds showed good activity against gram positive and gram negative bacterial strains.

ACKNOWLEDGMENTS:

Authors are grateful to Principal, Yeshwant Mahavidyalaya, Nanded for providing laboratory facilities, SRTMUN for sanctioning MRP (APDS/Uni.MRP/Sci.and technology-hem./2019-20/2819, UGC, New Delhi (File no.41-230/2012) (SR) Vishnu chemical Hyderabad, The Director, CSIR-IICT, Hyderabad for providing spectra.

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Solvent Free Efficient Approach for Synthesis of α-Hydroxy Phosphonates using an. K_2HPO_4/ Et_3N as a Catalyst

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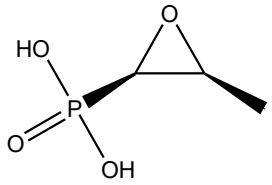
ABSTRACT:
A simple, efficient and neat method was established for one pot synthesis of α-hydroxy phosphonates from aromatic aldehyde and diethyl phosphite using an. K_2HPO_4/ Et_3N as a catalyst. Cheap and easily available catalyst, low toxicity, simple work-up procedure and solvent free reaction are gain point of these work.
KEY WORDS: *Cheap and easily available catalyst, Low toxicity, Simple work-up procedure, Solvent free.* Reaction.

1. INTRODUCTION:

Phosphonates are class of organic compounds containing R'-PO(OR)2 groups (where R, R' =alkyl, aryl); the structure of phosphonate compounds includes a tetra coordinate phosphorus atom in the +5 oxidation state that is connected to two alkoxy groups with P-O single bond and a formally double bonded oxygen (known as a phosphoryl group). The fourth group and the R of the two alkoxy groups can be a variety of species, so changes can be made chemically. Phosphonates are often used as the precursors to prepare the corresponding phosphonic acids. On the other hand, organophosphates (RO)3P(O) contain a phosphorus-oxygen bond in place of a phosphorus-carbon bond in organophosphonates. Phosphate is of key importance in cellular metabolism and is a important nutrient required for sustaining life. It is a main component for cellular structures, energy storage, and is involved in mediating cellular signalling pathways. For instance, phosphate is found in the backbone of DNA and RNA, high energy rich compounds (ATP, phosphoenolpyruvate) and is involved in enzyme catalysis. Within biological systems phosphorus is typically bound to four oxygen atoms in its fully oxidized state either as inorganic phosphate or as phosphate organic esters, amides and anhydrides.

2. LITERATURE REVIEW:

The α-hydroxy phosphonates are consequential class of organophosphorus compound which shows extensive applications in organic as well as in medicinal chemistry[1]. The synthesis of α-hydroxy phosphonates and their derivatives acquired much attention of organic chemists in recent years due to their important biological activities[2]. They exhibit broad range of biological activities like antibacterial[3], antiviral[4], anticancer[5], antioxidant[6], antifungal[7], insecticides[8], anti-HIV activities[9]. The α-hydroxy phosphonates and its derivatives have several utility in various areas covering biological and pharmaceutical industries due to physical and structural resemblance of phosphonic acid to biological active phosphate ester[10]. Phosphomycin (figure-1) is antibiotic drug which is analogue of phosphoenolpyruvate (PEP) clinically used for treatment of urinary tract and gastrointestinal infections.[11] In addition to this α-hydroxy phosphonates are also serve as a key precursor in the synthesis of other biologically active compounds such as α-amino[12], α-halo[13], α-keto[14] and α-acetoxy phosphonates[15].



Phosphomycin- an antibiotic drug
Figure-1

In Pudovik reaction, C-P bond is formed by synthesis of α-hydroxy phosphonates from aldehyde with dialkylphosphite under basic condition[16] while Abramov reaction is synthesis of α-hydroxy phosphonates from aldehyde and trialkylphosphite. Thus most important way for synthesis of α-hydroxy phosphonates involves reaction between aldehyde and di or trialkylphosphite in presence of basic catalyst such as ethyl magnesium bromide[17], LDA[18], KF on alumina[19], quinine[20], DBU[21], Magnesium oxide (MgO) [22] etc. while several acid catalyst such as HCl[23], oxalic acid[24], KH_2PO_4[25], camphor sulphonic acid[26] etc. have also been investigated for synthesis of α-hydroxy phosphonates and its derivatives. Although significant advances have been made in this route, but there is still some drawbacks such as harsh reaction condition, long reaction time, inadequate yield, use of toxic catalyst and environmental pollution caused by

utilization of organic solvents etc. Consequently, there is need for the further development to explored efficient and convenient method to synthesize such consequential scaffold.

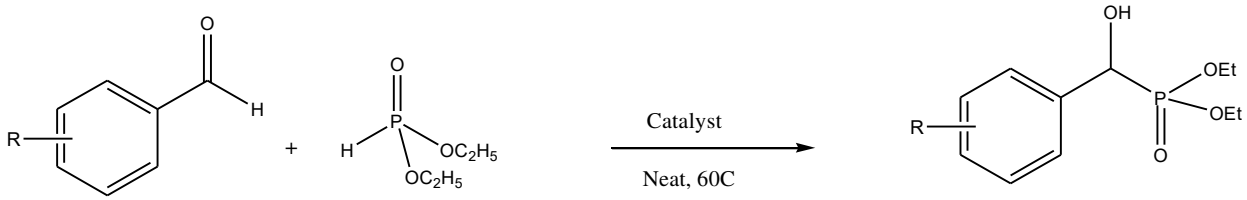
Now a days, solvent free reaction has offered more advantages than their homogenous counterparts due to increasing concern for the influence of organic solvents on the environment and also on human body[27]. So by considering all above fact, we herein report the investigation of an. K_2HPO_4/ Et_3N efficient, low cost and non-toxic catalyst for synthesis of α-hydroxy phosphonates by reaction of aldehyde and dialkylphosphite under solvent free condition. Compared with methods introduce above, our reaction shows advantages such as green route synthesis without using organic solvent, less reaction time, satisfactory yield, mild condition and easy work-up procedure.

3. MATERIALS AND METHODS:

All the reagents and chemicals were purchased from Sigma-Aldrich, Spectrochem and were used directly as received without further purification. The melting point were recorded on digital melting/boiling point apparatus of Labtronics make and found uncorrected. The progress of reaction was monitored by Thin layer chromatography was accomplished on precoated plates of TLC silica gel 60 F_{254}. 30% ethyl acetate in hexane solvent was used for TLC. Visualization was made with UV light (254 or 365nm).The ^{1}H NMR spectra were recorded on BRUKER- 400 MHz (Model: AV 400) spectrometer in $CDCl_3$ solvent using TMS as an internal standard and chemical shift is given as a delta.

Typical experiment procedure for synthesis of α-Hydroxy Phosphonates:

In a 50 ml round bottom flask, a mixture of aromatic aldehyde 1a (1mmol) and diethyl phosphite 2a (1 mmol) was stirred under solvent free condition at 60 ^{0}C in presence of an. K_2HPO_4:Et_3N (10:5 mol%) as a catalyst for 2 hours. The reaction was monitered by TLC and after the completion of reaction, the crushed ice was added to reaction mixture which results in formation of crude solid product, which was filtered through Buchner funnel and then washed with cold water. The crude product was recrystallized in ethanol solvent.



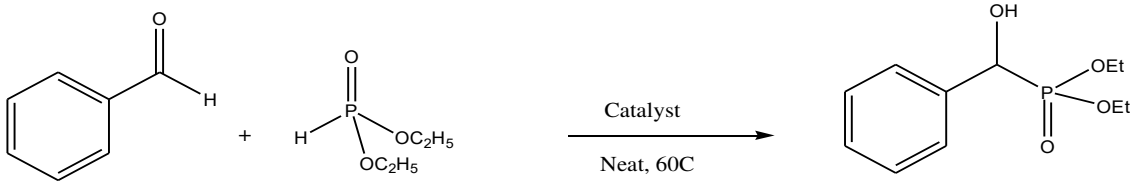
1a 2a 3a

figure-1

Scheme 1: Synthesis of α-Hydroxy Phosphonates

4. RESULT AND DISCUSSION:

At first endeavour, the reaction was carried out utilizing benzaldehyde (1 mmol) and diethyl phosphite (1 mmol) under solvent free condition at room temperature but progress of reaction was not visually examined on TLC even after stirring for longer time, (Table 1, Entry 1) then to the same reaction mixture, 10 mol % of K_2HPO_4 catalyst was integrated, then progress of reaction was visualized after stirring for 2 hours at 60^{0}C under solvent free condition (figure-2), but there is still demand of advancement in catalyst so we planned to utilize the strong organic basic catalyst with 10 mol % an. K_2HPO_4. As can visually perceived in Table-1, the desired product was obtained in moderate to good yield utilizing 1 mol % of different organic basic catalyst with 10 mol% an. K_2HPO_4. Utilizing pyridine, morpholine, pyrolidine and triethylamine as organic basic catalyst gives 3a in 50, 60, 65 and 75% yields respectively (Table 1, Entry 2-5).



1a 2a 3a

figure-2

Scheme 2: Synthesis of α-Hydroxy Phosphonates

Table-1: effect of various organic basic catalyst on synthesis of 3a

Entry	**Organic basic catalyst**	**Organic basic catalyst amount** (mol%)	**Time** (hrs)	**Yield** (%)
1	-	-	8	No reaction
2	Pyridine	1	4	50
3	Morpholine	1	3	60
4	Pyrolidine	1	4	65
5	Triethylamine	1	2	75
6	Triethylamine	2	2	85
7	Triethylamine	5	2	98

reaction condition: benzaldehyde (1 mmol.), diethyl phosphite (1 mmol), an.K_2HPO_4 (10 mol %), solvent free, temp. 60^0C

10 mol% an. K_2HPO_4/triethylamine catalyst produced greater yield of among all other catalyst, so we decided for optimization of triethylamine. The best result was obtained for 10:5 mol% of an. K_2HPO_4:Et_3N (table 1, entry 7). Therefore ideal reaction condition were established as: benzaldehyde (1 mmol), diethyl phosphite (1 mmol) and 10:5 mol% of an. K_2HPO_4:Et_3N at 60^0C temp. under solvent free condition.

The potency of the catalyst an. K_2HPO_4:Et_3N was compared with that of other catalyst reported earlier in synthesis of α-hydroxy phosphonates, 3a as a model product. from data summarized in table 2, entry 1-6, the superiority of an. K_2HPO_4:Et_3N catalyst over other mention catalyst with respect to yield, cost, easy work-up and product isolation (table 2, entry 7). The influence of solvent such as ethanol, toluene, dichloromethane and dioxane was investigated, and it was observed that excellent yield of the product was obtained when the reaction was carried out under solvent-free conditions. (table 2, entry 7-11) It may be due to under solvent-free conditions, the concentration of catalyst leads to higher reaction rates than the same reaction in the presence of solvent.

Table-2: Comparison of catalyst and influence of solvent.

Entry	**Catalyst (conc.)**	**Solvent**	**Time (hrs)**	**Temp. (°C)**	**Yield (%)[ref]**
Comparison of Catalyst					
1	HCl (100 g/mol%)	Diethyl ether	24	0	74[23]
2	K_2HPO_4[a] (5g/mol%)	Neat	5[c]	rt))	86[25]
3	MgO (0.2g)	Neat	2	rt	90[22]
4	Camphor Sulphonic Acid[a] (10 g/mol%)	Neat	0.5	rt	91[26]
5	KF-alumina (0.6g)	Neat	2	rt	96[19]
6	Oxalic acid[b] (10g/mol%)	Neat	1.5	80	98[24]
7	an. K_2HPO_4:Et_3N (10:5 mol%)	Neat	2	60	98This work
Influence of solvent					
7	an. K_2HPO_4:Et_3N (10:5 mol%)	Ethanol	3	60	60
8	an. K_2HPO_4:Et_3N (10:5 mol%)	Toluene	4	60	40
9	an. K_2HPO_4:Et_3N (10:5 mol%)	Dichloromethane	2	60	65
10	an. K_2HPO_4:Et_3N (10:5 mol%)	Dioxane	4	60	50
11	an. K_2HPO_4:Et_3N (10:5 mol%)	Neat	2	60	98

reaction condition: benzaldehyde (1 mmol), diethyl phosphite (1 mmol), catalyst
[a]Using triethyl phosphite ,[b]Using trimethyl phosphite,[c]time in min.

Next, we utilized the optimal conditions to elongate the substrate scope by using a series of alternative phosphonates. As summarized in Table 3, the standard reaction conditions were found to be compatible with a wide range of phosphonates. These results showed that *α*-hydroxylation was realized in good yields irrespective of the nature and the position of the aryl substituents of the dimethyl benzylphosphonate.

Entry	**Comp.**	**Aldehyde**	**Time (hrs)**	**M.P.°C found**	**M.P. °C reported[ref]**	**Yield (%)**
1	3a	Benzaldehyde	2	74-75	75-76	98
2	3b	4-Methyl benzaldehyde	1.5	95-96	94-95	96
3	3c	4-Methoxy benzaldehyde	1.5	120-122	120-121	94
4	3d	3-Nitro benzaldehyde	1.5	80-82	81-82	98

5	3e	2-Fluro benzaldehyde	2	88-89	-	92
6	3f	4- Fluro benzaldehyde	2	78-79	-	90
7	3g	4-Chloro benzaldehyde	1.5	68-70	67-68	92
8	3h	2-Chloro benzaldehyde	1.5	75-77	74-75	93
9	3i	4- Nitro benzaldehyde	1.5	88-90	87-88	95
10	3j	Thiophene 2-aldehyde	2	67-68	-	84
11	3k	Salicyldehyde	2	70-73	-	88
12	3l	Cyclohexanone	5	No Reaction		
13	3m	Propenone	5	No Reaction		
14	3n	Acetophenone	5	No Reaction		

Spectral data:

Compound 3a

^{1}HNMR: ($CDCl_3$) δ(ppm): 7.26-7.49 (m, 5H, Ar-H), 5.03 (d,1H, CH), 3.94-4.10 (q, 4H, OCH_2), 1.19-1.28 (t, 6H, CH_3).

5. CONCLUSION:

In summery we have developed novel route for synthesis of α-hydroxyphosphonatesand its derivatives using an. K_2HPO_4:Et_3N with excellent yield using non-toxic, eco-friendly catalyst. The present method has advantage of mild reaction condition, easy work-up, short reaction time and excellent yield are advantages of this work without use of expensive and hazardous solvent.

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Solar Cell - A smiconductor having future in near future

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ABSTRACT:

A solar cell is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect, which is physical and chemical phenomenon.[1] Assemblies of solar cells are used to make solar modules that generate electrical power from sunlight, as distinguished from a "solar thermal module" or "solar hot water panel". A solar array generates solar power using solar energy. Solar cells are a form of photoelectric cell. Individual solar cells are combined to form modules known as solar panels.A solar cell is basically a p-n junction diode, although its construction it is little bit different from conventional p-n junction diodes. A very thin layer of p-type semiconductor is grown on a relatively thicker n-type semiconductor. We then apply a few finer electrodes on the top of the p-type semiconductor layer. Just below the p-type layer there is a p-n junction. We also provide a current collecting electrode at the bottom of the n-type layer. We encapsulate the entire assembly by thin glass to protect the ***solar cell*** *from any mechanical shock.*

KEYWORDS: *p-n junction diode.*

1. INTRODUCTION:

Solar energy is radiant light and heat from the Sun that is harnessed using a range of ever-evolving technologies such as solar heating, photovoltaics, solar thermal energy, solar architecture, molten salt power plants and artificial photosynthesis.[1][2]. It is an essential source of renewable energy, technologies are broadly characterized into passive solar or active solar depending on how they capture and distribute solar energy or convert it into solar power. Active solar techniques- photovoltaic systems, concentrated solar power, and solar water heating to harness the energy. Passive solar techniques - orienting a building to the Sun, selecting materials with favorable thermal mass or light-dispersing properties, and designing spaces that naturally circulate air. The large magnitude of solar energy available makes it a highly appealing source of electricity. The United Nations Development Programme in its 2000 World Energy Assessment found that the annual potential of solar energy was 1,575–49,837 exajoules (EJ). This is several times larger than the total world energy consumption, which was 559.8 EJ in 2012.[3][4].

In 2011, the International Energy Agency said that "the development of affordable, inexhaustible and clean solar energy technologies will have huge longer-term benefits. It will increase countries' energy security through reliance on an indigenous, inexhaustible, and mostly import-independent resource, enhance sustainability, reduce pollution, lower the costs of mitigating global warming, and keep fossil fuel prices lower than otherwise. These advantages are global. Hence the additional costs of the incentives for early deployment should be considered learning investments; they must be wisely spent and need to be widely shared".[1]

1.1 Working of solar cell :

Fig. 1 SOLAR PLATES

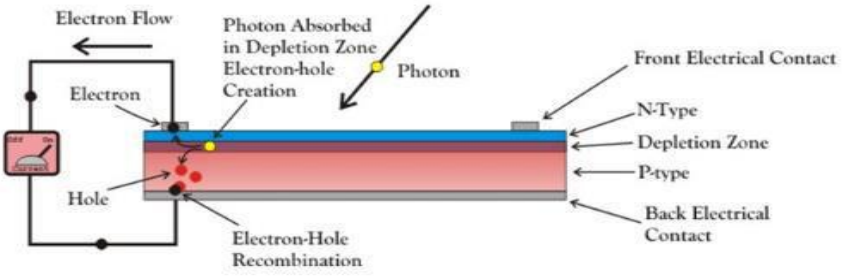

Fig. 1.1 structure of splar plate

When light reaches the p-n junction, the light photons can easily enter in the junction, through very thin p-type layer. The light energy, in the form of photons, supplies sufficient energy to the junction to create a number of electron-hole pairs. The incident light breaks the thermal equilibrium condition of the junction. The free electrons in the depletion region can quickly come to the n-type side of the junction. Similarly, the holes in the depletion can quickly come to the p-type side of the junction. Once, the newly created free electrons come to the n-type side, cannot further cross the junction because of barrier potential of the junction. Similarly, the newly created holes once come to the p-type side cannot further cross the junction became of same barrier potential of the junction. As the concentration of electrons

becomes higher in one side, i.e. n-type side of the junction and concentration of holes becomes more in another side, i.e. the p-type side of the junction, the p-n junction will behave like a small battery cell. A voltage is set up which is known as photo voltage. If we connect a small load across the junction, there will be a tiny current flowing through it.

Thin-film photovoltaic cells can use less than 1% of the expensive raw material (silicon or other light absorbers) compared to wafer-based solar cells, leading to a significant price drop per Watt peak capacity. There are many research groups around the world actively researching different thin-film approaches and/or materials.[5]

One particularly promising technology is crystalline silicon thin films on glass substrates. This technology combines the advantages of crystalline silicon as a solar cell material (abundance, non-toxicity, high efficiency, long-term stability) with the cost savings of using a thin-film approach.[6][7]

2. NEED OF THE STUDY:

There are currently many research groups active in universities and research institutions around the world.
This research can be categorized into three areas:

- Making current technology solar cells cheaper and/or more efficient to effectively compete with other energy sources;
- Developing new technologies based on new solar cell architectural designs;
- Developing new materials to serve as more efficient energy converters from light energy into electric current or light absorbers and charge carriers.

3. LIMITATION OF THE STUDY :

High cost of installation , Low efficiency , During cloudy environment, rainy season, at night solar energy will not be avialable to us.

4. CONCLUSION:

As technology will advance and emerge with new and more cost effective devices, the solar cell/ plates will be avialable at affordable prices to each one of us.

These days the aim of government is also focusing on use of solar energy/ renewable energy sources to fullfill the requirements of energy at many levels.

The encouragement will lead to research of many small effective devies working on solar energy that will help to reach energy demands at daily individual level to industrial levels.

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New Agricultural Innovation Systems and Small Holder Participation in Modern Farm in Village, Mandur

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ABSTRACT:

In this paper, different samples of soil from Shirala Tahasil were collected and the various physicochemical parameters such as pH, electrical conductivity, organic carbon, phosphorous, nitrogen, potassium, sodium and calcium carbonate and micronutrient were tested. Many soils along the Wasatch front content naturally higher N, P, and K. With the regular use of fertilizer it is observed that basic fertility level is low and after conditioning the soil with treatment of spent wash the result showed that fertility level has increased. But, it is not recommended to have an over fertilizer dose to establish a basic fertility level. A soil test is the best method to indicate whether N, P, K fertilizer is needed or not. It is recommended that home gardeners have their soil to be tested. It is concluded that level of N, P, K contents was increased after giving spent wash treatment.

KEY WORDS: *Soil, fertility, micronutrients*

1. INTRODUCTION:

Shirala is a small town located in western Maharashtra, India's most prosperous state. During the Rashtrakuta period the region was ruled by Shilaharas. (From 765 to 1020) The major source of income for people in this Shirala Tahasil is from agriculture. Recently, a dozen of small-scale agro-industries have been set in Maharashtra Industrial Development Corporation (MIDC) area near Shirala. With special economic concessions offered due to remoteness of the area, the MIDC has attracted number of investors in relatively short time. The desirable properties of soil quality should include adequate amount of micronutrient and other nutrient at all time, a relatively high organic content, pH value near neutrality, moderate temperature. The factor of good quality of soil is required for development of the rural areas and developing nations [5-7] to reduce environmental problem. Industries also think about this problem. Different industries create a variety of waste water pollutants; which are difficult and costly to treat. The use of industrial waste as soil improvement has generated curiosity in recent time. The wastewater produced continuously could furnish the needs of irrigated crops The ever-increasing amount of distillery spent wash and its disposal has stimulated the need for developing new technologies to process this effluent efficiently and economically including growth and yield of different crops in agriculture [8-11.] If this spent wash will use in soil to improve soil quality then it will helpful to Industry, Farmers and automatically to the nation.

2. MATERIALS AND METHOD:

For understanding the influence of pH, Conductivity (E.C.), Nitrogen, Phosphorous, Potassium, Calcium & organic carbon as well as microelements are Copper, Iron, Manganese and Zinc on growth of crop and for improvement different sources of fertilizers are available. But in absence of fertilizer to improve soil content Nitrogen, Phosphorous, Potassium, Calcium & organic carbon as well as microelements are Copper, Iron, Manganese and Zinc by using spent wash. Collection of the Sample as per the recommended procedure.[1-2] When general fertility is to be found out, number of samples to be collected varies according to size of plot. However, 50-100 samples per hectare are required for such experiment purpose. For determination of pH take 20 gm oven dried soil sample in 100 ml distilled water. Stirr for about an hour at regular intervals. Allow to settle the solids. Determine the pH of supernatant using pH meter. Take 20 gm of oven dried soil sample in 100 ml distilled water and keep on shaker for one hour. Filter or pour off supernatant and measure the conductivity of liquid with conductivity meter. Determination of Nitrogen is carried out by using Kjeldahl distillation assembly. Calculation, Available Nitrogen % = B.R. * N of H_2SO_4 * 0.0141 * 100 / wt of sample (gm)

Phosphorous is extracted from the soil with sodium Bi-carbonate extract at pH 8.5 and it determined by using Spectrophotometer. Calculation **-** From the graph reading calculate % of P in soil sample by back calculation.

P kg/ha = % P * 20000

P % as P_2O_5 = % P * 2.29

P % as PO_4 = % P * 3.06

Take 10 ml Potassium Solution of stock solution and dilute to 100ml, Weigh 2 gm of oven dried soil sample. Add 100 ml neutral ammonium acetate extraction. Shake for half an hour intermittently and filter the content. Use the clear filtrate for determination of K. Calculation,

K% = Value from graph (mg/l) * total volume prepared / 10000 * wt of sample (gm)

Take 2 gm dried soil, add 100 ml ammonium acetate extract. Keep it for hour with intermittent mixing. Decant and filter the suspension through filter paper. Determination of Calcium should be carried out and calculated by,

Calcium % = A * 400.8 * V / v * 10000 * S A= Volume of EDTA required in ml.

V= Total volume of extract prepared in ml.

v= Volume of extract taken for titration in ml.

S= Weight of soil.

Take 20 ml filtrate add 100 mg Murexide indicator, and 5 ml 1.0 N NaOH. Titrate with 0.01 M EDTA till the purple colour appears. For determination of Magnesium 2 ml ammonia buffer and 100 mg eriochrome black T indicator and 0.01 M EDTA solution is used.

Calculation, Mg% = (B-A) * 400.8 * V / v *10000 * 1.645 * S

A= volume of EDTA required for Ca determination B= volume of EDTA requirement for titration in ml

V= Total volume of soil extract prepared in ml. v = volume of extract taken for titration in ml

S= weight of soil sample (gm)

The organic matter present in the soil is digested with excess of potassium dichromate and sulphuric acid and residual and residual unutilized dichromate is the titrated with ferrous sulphate. After determination of organic carbon the organic matter in the soil can be calculated as,

% organic matter = % organic carbon * 1.724

The factor 1.724 is based on the assumption that carbon is only 58% of the organic matter.

3. RESULTS AND DISCUSSION:

The samples are collected as per the recommended procedure from Mandur village before using spent wash (original sample) are analyzed and the results are summarized as follow.

Table 3.1 Results of the Pretreatment analysis of the soil

Sr. No.	Parameter	Unit	Limit	Analysis of Soil before spent wash.
1	pH	-	6.5-8.5	8.00
2	E-Conductivity	mhos/cm	<4.0	0.11
3	Nitrogen	Kg/ha	100-200	134.00
4	Phosphorous	Kg/ha	30-40	24.53
5	Potassium	Kg/h	110-280	226.00
6	Organic Carbon	%	>0.50	0.61
7	Calcium	%	0.1-3.2	0.50
8	Copper (Cu)	ppm	0.3-0.5	1.18
9	Iron (Fe)	ppm	2.5-4.5	2.92
10	Manganese (Mn)	ppm	1.0-2.0	2.72
11	Zinc (Zn)	ppm	0.5-1.2	0.84

As we perform experiments to analyze, soil samples collected from Mandur Shirala Tahasil before using spent wash. All result was collect in (table 3.1) , pH was observed in the range 8.0 , Conductivity (E.C.) was observed in the range 0.11 Nitrogen was observed in the range 134.00 kg/ha Phosphorous was observed in the range 24.53 kg/ha. Potassium was observed in the range 226.00kg/ha Calcium was observed in the range 0.50 % and organic carbon was

observed in the range 0.61 % as well as microelements are Copper are found in the range 1.18 ppm. Iron was found in the range 2.92 ppm. Manganese are found 2.72 ppm in between them. Zinc was found to be it the range 0 .84 ppm. [11-19] The samples are collected from the same plot as per the recommended procedure from Mandur village after using spent wash analyzed the results are summarized as follows -

Table 3.1.2 Results of the after treatment analysis of the soil

Sr. No.	Parameter	Unit	Limit	Analysis of Soil after spent wash.
1	pH	-	6.5-8.5	7.00
2	E-Conductivity	mhos/cm	<4.0	0.90
3	Nitrogen	Kg/ha	100-200	234.00
4	Phosphorous	Kg/ha	30-40	224.00
5	Potassium	Kg/ha	110-280	3080.00
6	Organic Carbon	%	>0.50	1.85
7	Calcium	%	0.1-3.2	1.20
8	Copper (Cu)	ppm	0.3-0.5	1.95
9	Iron (Fe)	ppm	2.5-4.5	3.10
10	Manganese (Mn)	ppm	1.0-2.0	2.90
11	Zinc (Zn)	ppm	0.5-1.2	1.84

Similarly, soil samples collected from same regions of Shirala Tahasil after using spent wash in same plot. All results are collected in(Table 3.1.2). Conclusions made from above results are given. pH was observed in the range 7.0, Conductivity (E.C.) was observed in the range 0.90. Nitrogen was observed in the range 234.0 kg/ha. Phosphorous was observed in the range 224.00 Kg/ha. Potassium was observed in the range 3080.0 kg/ha .Calcium was observed in the range 1.20 % & organic carbon was observed in the range 1.85 % as well as microelements are Copper are found in the range 1.95 ppm. Iron was found in the range 3.10 ppm, Manganese are found 2.90 ppm. Zinc was found to be it the range 1.84 ppm. The (Table 3.1.3) shows comparative analysis of the soil treatment results.

Table 3.1.3 Comparative analysis of the soil

Sr. No.	Parameter	Sample (II-I)
1	pH	-1
2	E-Conductivity	0.79
3	Nitrogen	100
4	Phosphorous	199.47
5	Potassium	2854
6	Organic Carbon	1.24
7	Calcium	0.7
8	Copper (Cu)	0.77
9	Iron (Fe)	0.18
10	Manganese (Mn)	0.18
11	Zinc (Zn)	1

4. CONCLUSION:

In this paper, soil conditioning treatment by using spent wash is presented. After using spent wash, actual improvement was observed in the range (Table 3.1.2) Conductivity (E.C.) 0.79 Nitrogen 100 kg/ha Phosphorous 199.47 kg/ha. Potassium 2854 kg/ha Calcium 0.7 % & organic carbon 1.24% as well as microelements are Copper are found in the range 0.77 ppm. Iron 0.18 ppm. Manganese are found 0.18 ppm, Zinc 1 ppm. Only pH value decreased remaining all value was increased. This indicates that instead of fertilizers farmers can use spent wash and save the money. This will be beneficial to farmers as comparative to fertilizers.

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Substituted pyrazole chalcones: a physicochemical study

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ABSTRACT:
A series of some new pyrazole based chalcones were prepared by the conventional Claisen-Schmidt condensation method under mild reaction condition. All the synthesized products were characterized by the spectroscopic and analytical measurements. Furthermore, all the synthesized compounds were study for physicochemical study

KEY WORDS: *Pyrazole-chalcones, Conductivity, Density, pH meter.*

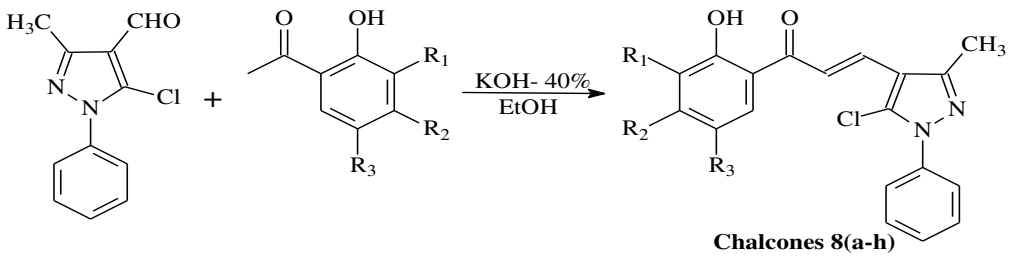
1. INTRODUCTION:

Chalcones are also called as α, β-unsaturated ketones. They are precursors of flavonid biosynthesis. They can be obtained from natural sources or by synthesis. The presence of (functional group) chalcones confers biological properties, i.e. bacteriostatic/ bactericidal activity [1-8]. Chalcones are of a high interest due to their use as starting materials in the synthesis of a series of various heterocyclic compounds and especially chalcones bearing oxygenated function on the aromatic rings are the precursors of all flavonoids. Thus the synthesis of chalcones has generated vast interest to organic as well as for medicinal chemist. This class exhibits a broad spectrum of biological properties including antinociceptive, anti-inflammatory, antitumor, antibacterial, antifungal and antileischmanial. On other side Pyrazole ring has wide applications in medicinal chemistry. It is also reported that, pyrazole derivatives are gained synthetic interest in recent years due to their broad spectrum of biological properties like anti-inflammatory, analgesic, antibacterial, and antifungal activities due to this we decided to study on physicochemical aspect of pyrazole based chalcones.[9-16] These compounds have applications in various other fields also [17, 18]. However,literature survey reveals that very less work has been done to study the physicochemical properties such as density, solubility, conductance, dissociation constant etc of chalcones.

These physical properties such as density, molecular mass and specific volume is very useful in the evaluation of various thermodynamics properties of chemical materials. Conductometry method is useful to various biological processes [19-20]. Further, solution crystallization is a key step for industrial purification process, which control product quality such as purity, yield, and crystal size distribution [21-22]. Another physical parameter such as dissociation constant plays an important role in various analytical processes and is used to determine stereo- chemical and conformational structures, directions of nucleophilic and electrophilic attack, stability of intermediates etc. [23, 24] The knowledge of dissociation constant is important to understand transport behavior, solubility, binding to receptors, lipophilicity and mechanism of action of certain pharmaceutical samples [24]. Therefore in the present study some physicochemical properties such as density, dissociation constant and conductance of some newly synthesized chalcones in solutions of different solvents are considered for study.

2. MATERIALS AND METHOD:

A mixture of substituted acetophenone (1 mmol), substituted aldehyde (1 mmol) and KOH (2. mmol, with a minimum of H_2O) were taken in ethanol and stirred at 50-60^0 C temperature for one hour. The reaction went to completion within determined by TLC. The products were isolated by acidification of the cool diluted acid solution and obtained solid product was filtered and washed with 2x5 mL water and recrystallized by aqueous acetic acid to give pure product



Chalcones 8(a-h)

Entry	Product	Mol. Formula	Yield %	M.P. (°C)	R_1	R_2	R_3
1	3A	$C_{19}H_{14}O_2N_2Cl_2$	86	168	H	H	Cl

2	3B	$C_{19}H_{13}O_2N_2Cl_2I$	88	174	I	H	Cl
3	3C	$C_{19}H_{13}O_2N_2Cl_2Br$	89	152	Br	H	Cl
4	3D	$C_{19}H_{13}O_2N_2Cl_3$	91	141	Cl	H	Cl
5	3E	$C_{20}H_{16}O_2N_2Cl_2$	86	128	H	CH_3	Cl
6	3F	$C_{20}H_{15}O_2N_2Cl_2I$	88	156	I	CH_3	Cl
7	3G	$C_{20}H_{15}O_2N_2Cl_2Br$	90	185	Br	CH_3	Cl
8	3H	$C_{20}H_{17}O_2N_2Cl$	85	132	H	H	CH_3

Table -1-: Physico-chemical data synthesized chalcone derivatives 3(a-h)

Table 1 shows physical constants such as molecular formula, molecular weight, melting point, % yield, etc. of all the synthesized compounds.

Experimental: eight different chalcones have been synthesized and their general structure is given in Figure 1. The structures of all the synthesized compounds were confirmed by IR, 1H NMR and mass spectral data.

Physicochemical studies: All the synthesized chalcones were recrystallized from. Solvents such as chloroform and alcohol were used for the physicochemical studies. All these solvents were purified by standard methods. It was found to be 99.99%. For the determination of dissociation constant, $CHCl_3$ water binary mixture was used. The selection of solvents in different physicochemical study is due to solubility and other practical problems.

Conductance: Solutions of different concentrations were made in alcohol and CHCl3 of all of the synthesized compounds. The conductance of pure solvents and of solutions was measured using Equip-tronics conductivity meter (Model No. 664) at 298 K. The cell constant was 0.1 cm^{-1} at 298 K.

PH metric Studies For all the synthesized compounds, following two sets of mixtures were prepared.(1) 2 ml HNO_3 (0.01 M) + 4 ml $NaNO_3$ (0.01 M) + 19 ml alcohol (2) 2 ml HNO_3 (0.01 M) + 4 ml $NaNO_3$ (0.01 M) + 2 ml ligand solution (15 ppm) + 17 ml alcohol Thus, total volume of each set of solution was 25 ml and ethyl alcohol: water ratio was 90:10(v/v).

For each set of solution, pH was measured after each addition of 0.5 ml NaOH till there was no change in absorbance. A Equiptronic pH meter (Model No. EQ 664) was used for the pH determination. pH meter was calibrated by known buffer solutions. The glass electrode and a saturated calomel electrode were used as indicator and reference electrodes respectively.

Density: for measuring density of different chalcones solutions of different concentration were prepared in different solvents such as ethyl alcohol and chloroform density of each solution and pure solvents were measured at 298 K

3. RESULTS AND DISCUSSION :

Density: The density of each compound was evaluated using the following relation:

$1/\rho12 = g1/\rho1 + g2/\rho2$ where ρ1, ρ2 and ρ12 are the density of pure solvent, pure solute

(i.e., synthesize compound and solution respectively. g1 and g2 are the weight fractions of solvent and solute respectively. The slope of plot of $1/g1\rho12$ versus g1/g2 gives $1/\rho2$.

Density of compounds can be evaluated theoretically by using the equation:

$$\rho = KM/NA\sum\Delta Vi$$

Table 2 shows variation of conductance with concentration of both the solvents.

Compound Code	Experimental density,g/.cm3		Theoretical density,g/cm3
	C2H5OH	CHCl3	
3A	1.1248	1.3215	1.1702
3B	1.141	1.3662	1.1621
3C	1.1506	1.3821	1.1811
3D	1.1732	1.4131	1.2230
3E	1.1621	1.4021	1.1932
3F	1.1524	1.3224	1.1822
3G	1.1432	1.3112	1.1662
3H.	1.1612	1.3215	1.1745

Where ρ the density of the compound, K is packing fraction (0.599), M is the molecular weight of the compound, NA is the Avogadro's number and ΔVi is the volume increment of the atoms and atomic groups present in the compound. Table 2 shows the experimental and theoretical values of density.

It is observed that there is deviation between experimental and theoretical density values. Further, for the same compound, density in the two solvents is different. The values are much higher in chloroform than in ethyl alcohol. The different values in different solvents suggest that interactions play an important role. In solutions, molecular interactions exist which differ in different solvents. Further, these interactions differ due to different substitutions in compounds. Due to these interactions, there may be some changes in volume, which affects density. Thus, different density values in different solvents and deviation between experimental and theoretical density values suggest the presence of intermolecular interactions between solute and solvent molecules.

Conductance: The measured conductance of all the compounds in studied solvents was corrected by subtracting the conductance of pure solvent. Using corrected conductance (k), specific conductance (κ) and equivalent conductance (λc) were evaluated. The equations used for calculating specific conductance (κ) and equivalent conductance (λc) $\Lambda c = 1000.k / C$

C is the concentration (g. equi./lit) of solution. K is specific conductance and Λc is equivalent conductance.

Figure -1

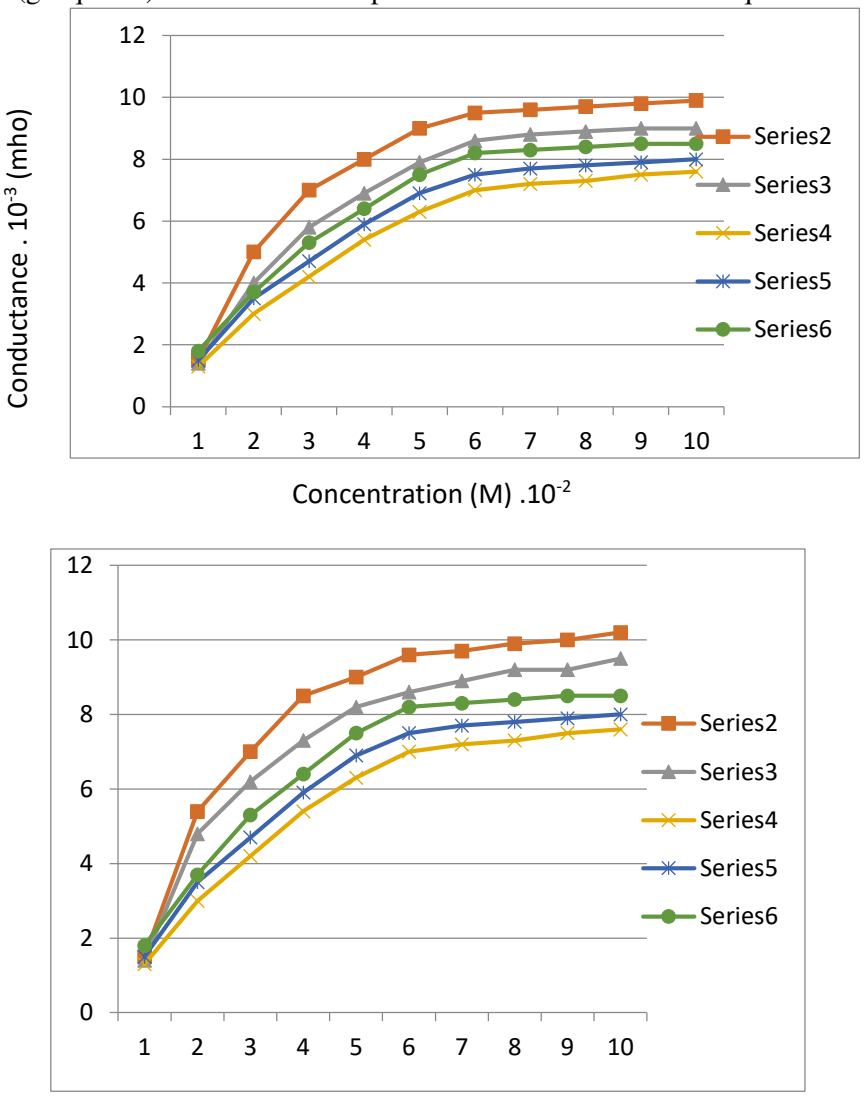


Figure -1 shows variation of conductance with concentration for both the solvents.

It is clear from the figure that there is increase in conductance of the solution with concentration and values are slightly less in ethyl alcohol then in chloroform and also at lower concentration there is slight increase in conductance and as concentration is higher slow increase in conductance is observed.

Figure-2

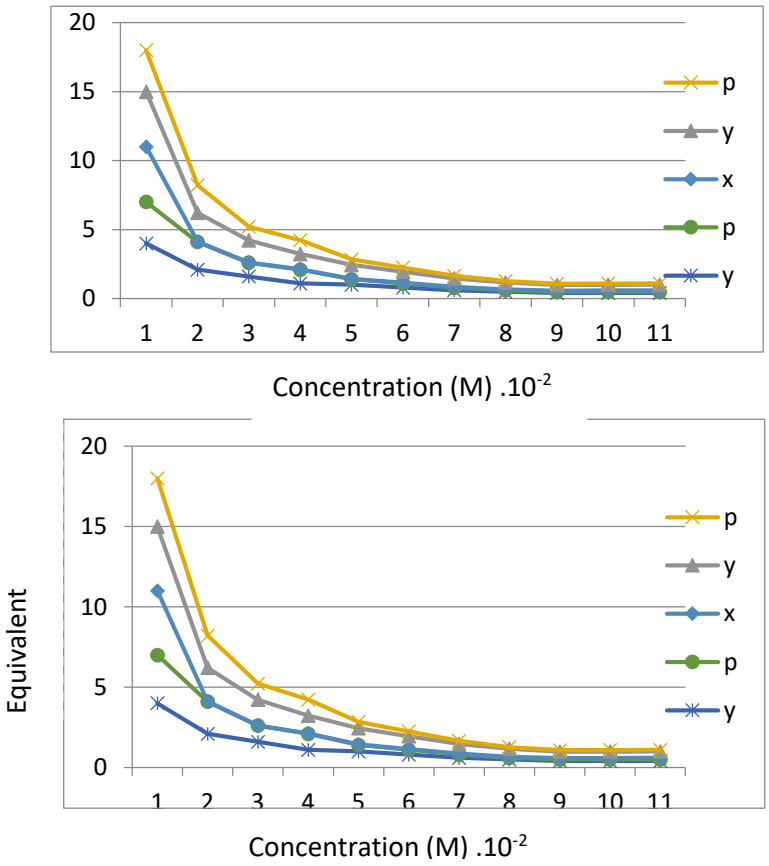


Figure-2 shows variation of equivalent conductance with squre root of concentration for ethyl alcohol and chloroform

It is clear that the compounds show a variation in behavior with change in concentration of solvents It is observed that for all electrolytic in nature in alcohol. However, in CHCl3 strong electrolytic behavior is observed. Different thermodynamic parameters were determined for these synthesized chalcones solutions Such as ΔH_S is the heat of solution and The change in Gibb's free energy during solubility process can be calculated by intercept of the plot of

lnx versus 1/T by following equation: $\Delta G = -RT^*$ intercept

$\Delta S = (\Delta H - \Delta G) / T$

All the thermodynamic parameters are given in Table 3.

Table - 3

Compound Code	C_2H_5OH			$CHCl_3$		
	ΔH (cal/.mol)	ΔG (kcal/mol)	ΔS (cal/mol)	ΔH (cal/mol)	ΔG (kcal/mol)	ΔS (Cal/mol)
3A	250.93	3.7552	-10.243	240.83	2.3453	-9.5781
3B	271.44	4.5403	-12.654	251.48	3.4173	-10.4751
3C	238.43	4.1292	-10.387	258.73	3.1763	-9.1932
3D	310.54	3.8537	-10.474	338.45	4.3214	-10.824
3E	355.76	3.6583	-8.876	374.93	4.1734	-9.1028
3F	240.22	3.0172	-10.998	248.13	4.1657	-9.1065
3G	368.11	3.6144	-12.098	363.71	5.1434	-10.2298
3H	412.67	3.1353	-13.434	451.23	4.8265	-10.2341

It has been observed from the table that for all the compounds which are synthesized ΔH_S and ΔG values is positive whereas ΔS values are negative. It is because stronger bonds are broken and weaker bonds are formed, energy is consumed and so, ΔH_S become positive this indicates endothermic dissolution of compounds where the enthalpy term contributes to an unfavorable positive value of ΔG. Therefore positive values of ΔG indicate that the dissolution process is not spontaneous and also negative value of entropy which is measure of randomness indicates less randomness in solutions

Dissociation Constant: By measuring pH values the dissociation constant can be determined by equation

$$pKa = pH + \log [BH+]/[B]$$

Rearrangement of above equation gives

$\text{Log}[BH+]/[B] = pH - pka$ A plot of left hand side versus pH will yield a straight line and $pH = pK_a$ when ratio of

$\log [BH^+]/[B] = 0$. [44].

The concentrations of BH^+ and B can be determined

Compound code	3A	3B	3C	3D	3E	3F	3G	3H
Average Pka Values	10.23	10.45	10.34	10.76	9.43	9.56	8.77	10.87

Spectrophotometrically by measuring the absorbance at particular wavelength.

Table 4 shows the Pka values for the studied compounds. It is observed that substitution group affects the dissociation constant as expected.

CONCLUSIONS:

In this paper, we studied physicochemical parameter of different synthesized chalcones such as density, conductivity, Pka values that provides useful information about the reactivity of chalcones such as variation in experimental and theoretical value of density. Conductance measurement is also a easy way to know about the reactivity of chalcones along with these different thermo dynamical parameters were determined.

ACKNOWLEDGEMENT

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Aliquat 336 catalysed Knoevenagel condensation at room temperature

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ABSTRACT:

Knoevenagel condensation of aromatic aldehydes with active methylene compounds malononitrile, proceeds smoothly in the presence of Aliquat 336 as catalyst at room temperature without solvent, to produce products of good purity and in high yields. The reactions occur at room temperature giving excellent yields of the products. All the reactions were performed under mild reaction conditions, shorter reaction time and in high yields. All the synthesized compounds were characterized by IR, ^{1}HNMR, Mass.

KEYWORDS: *Knoevenagel condensation, active methylene compounds, Aliquat 336.*

1. INTRODUCTION:

The Knoevenagel condensation of aldehydes with active methylene compounds is an important and widely employed method for carbon–carbon bond formation in organic synthesis(1) There have been several modifications of the reaction such as the Doebner modification, Hantzsch pyridine synthesis, the Feist–Benary furan synthesis and the Gewald reaction, all contain a step of Knoevenagel reaction with numerous applications in the synthesis of fine chemicals,(2) hetero Diels–Alder reactions(3) and in synthesis of carbocyclic as well as hetero- cyclic(4) compounds of biological significance. The reactions are usually catalysed by bases(5) such as amines, ammonia or sodium ethoxide in organic solvents. Lewis acids,(6) surfactants,(7) zeolites(8) and heterogeneous catalysts(9) have also been employed to catalyse the reactions. Similarly, the use of ionic liquids(10) pave a new path for such organic synthesis. The use of environmentally benign solvents like water(11) and solvent-free reactions represent very powerful green chemical technology procedures from both the economical and synthetic point of view. They not only reduce the burden of organic solvent disposal, but also enhance the rate of many organic reactions. Therefore, efforts have been made to perform the Knoevenagel condensation in aqueous medium as well as in the absence of solvents(12) which are usually catalysed by Lewis acids,(12a) or base(12e,f)and require drastic conditions.(12b–d) Some of these reactions are performed on solid supports, promoted by infrared,(13a) ultrasound or microwave(13b,c) heating.

Aliquat 336 is a water insoluble quaternary ammonium salt made by the methylation of tri octyl / decyl amine, which is capable of forming oil soluble salts of anionic species at neutral or slightly alkaline pH. Aliquat 336 is a versatile and affordable cation source for an entirely new family of hydrophobic ionic liquids.(14) It can form salts with anions over a wider pH range than primary, secondary or tertiary amines. For this reason Aliquat 336 finds application in environments from acid to slightly alkaline pH. It is used as a phase transfer catalyst(15)

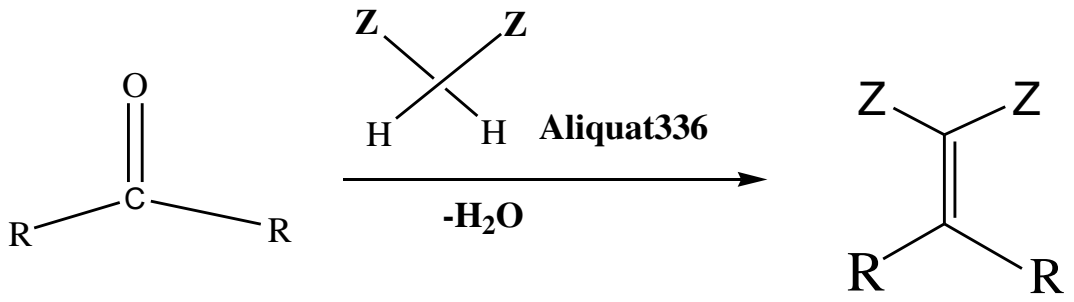
Here in the present work we have attempted to discover the role of Aliquat336 as a catalyst in Knoevenagel reaction .We are successful in a one pot protocol for the synthesis of 3,4 dimethoxybenzyllidene malanonitrile by just stirring the equimolar mixture of malanonitrile, 3,4-dimethoxybenzaldehyde, in presence of catalytic amount of Aliquat336 .The structure of the derivative was confirmed based on the spectral data .

2. MATERIALS & METHOD:

Aldehydes , malononitrile & Aliquat336 were procured from Sd-fine chem. All melting points were determined in open capillaries on Kumar's melting point apparatus. 1H NMR spectra were recorded on Mercury Plus Varian in $CDCl_3$ at 400 MHz using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer FTIR using KBr discs. Mass spectra were recorded on Micromass Quatrro II using electrospray Ionization technique, showing (m+1) peak as a base peak. The test for the purity of products and the progress of the reactions were accomplished by TLC on Merck silica gel plates. General procedure : Synthesis of 3,4-Dimethoxy-benzylidene malononitrile. In a 100 ml round bottom flask 1 mmole of malanonitrile (0.066gm) is warmed 5 min on magnetic stirrerand mixed with 1 mmole of benzaldehyde 0.166gm alongwith catalytic amount of Aliquat336 and warmed on mechanical stirrer for 3 minutes and then5 ml water is added to get yellow solid .The completion of reaction checked by T.L.C. The reaction mixture was poured on ice contained a beaker to obtain the product .The solidified substance was filtered and recrystallized from ethanol.

3. RESULT & DISCUSSION:

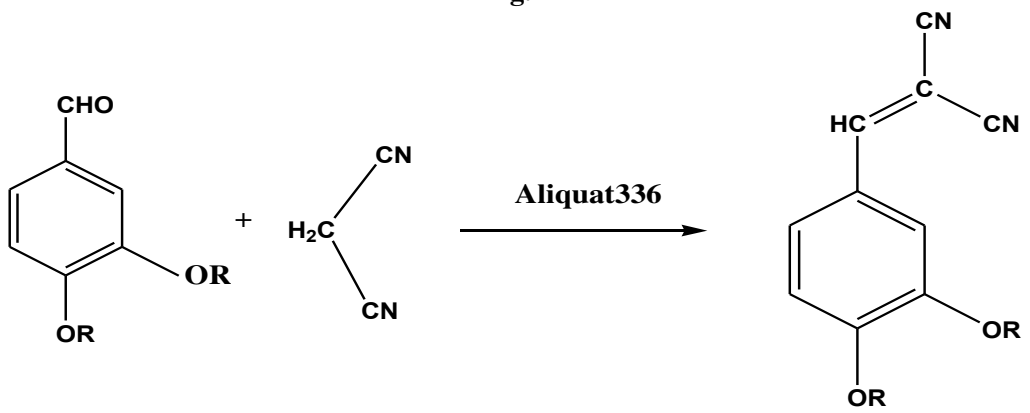
Here in the present work we have attempted to discover the role of Aliquat336 as a catalyst in Knoevenagel reaction .We are successful in a one pot protocol for the synthesis of 3,4 dimethoxybenzyllidene malanonitrile by just stirring the equimolar mixture of malanonitrile, 3,4-dimethoxybenzaldehyde, in presence of catalytic amount of Aliquat336 .The structure of the derivative was confirmed based on the spectral data .



In this reaction the carbonyl compound is an aldehyde or a ketone .The catalyst is usually a weakly basic amine .The active hydrogen component has the following for_Z–CH2-Z or Z–CHR–Z such as diethyl malonate, Meldrum's acid, ethyl acetoacetate or malonic acid, or cyanoacetic acid. Z–CHR1R2 such as nitromethane.
where Z is an electron withdrawing functional group .Z must be powerful enough to facilitate deprotonation to the enolate ion even with a mild base .Using a strong base in this reaction would induce self-condensation of the aldehyde or ketone.

4. ANALYSIS:
Molecular Formula =C12H10N2O2
Molecular Weight 214.23=Exact Mass 214= Molecular Composition Calculated found
C 67.3)67.28%0 (%H (4.75%)4.71%N)13.0813.05(%
H NMR: d ppm 7.14-7.87)m,3H,Ar (3.85)S,3H,OMe (3.86)S,3H,OMe (6.88)S,1H,CH(
IR)KBr:(cm-1) 3080-3030= (C-H ;)3050.83 (Ar .C-H;)2235-2215 (CN;)1604±3(C=C;)1160.03(O-CH3

Fig.1



5. CONCLUSION:
Thus, we have successfully synthesized 3,4 dimethoxy benzylidine malononitrile by using Aliquat 336 Knoevanagel condensation reaction .A highly efficient and simple method has been described for the catalysed synthesis of this compound, The present condensation completes with the principle of green chemistry.

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Synthesis and antibacterial screening of series of α-aminophosphonates derivatives of 2-chloro quinolines 3-carbaldehyde and aminophenol

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ABSTRACT:

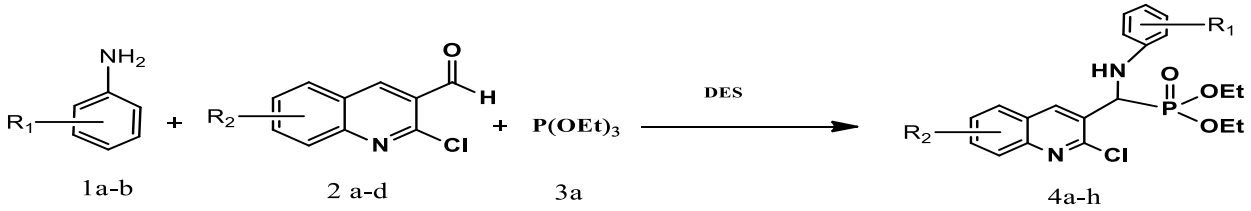
A new Schiff base, bioactive 2-chloro quinolines 3-carbaldehyde novel quinolines-containing α-aminophosphonates, A series of a-aminophosphonate derivatives containing aminophenol moiety have been synthesized by using eco-friendly catalyst (ChCl / $ZnCl_2$) and evaluated for their antibacterial activities against two clinical strains Gram-positive and Gram negative applying Agar disc diffusion method, Minimal Inhibition Concentration (MIC) and Minimal Bactericidal Concentration (MBC) methods. The compounds have been characterized by elemental analysis, TLC, IR and NMR spectra. The aminophosphonates and their synthetic precursors have significant bactericide activity with totalities of bacterial strains used.

KEYWORDS: *quinolines 3-carbaldehyde, aminophenol, Deep Eutectic solvent.*

1. INTRODUCTION:

Aminophosphonate derivatives, structural referents of the corresponding α-amino acids, constitute significant class of organophosphorus compounds on credit of their handy biological activity [(1)]. In general, low mammalian toxicity of these compounds ready them for use in agriculture and medicine [(2)]. α-aminophosphonates have fascinated interest since they are studied as structural analogues of α-amino acids and they act as conceivable antibiotic [(3)], antimicrobial [(4)], antitumor [(5)] and antioxidants agents [(6)]. They also have numerous applications in the agricultural industry [(7)]. It has the same effective against parasites such as Toxoplasma and Cryptosporidium that cause opportunistic infections in AIDS patients α -aminophosphonates were observed to be efficient in constraining growth of plasmodium falciparum causes malaria [(8)]. α-aminophosphonates have been found to act as inhibitors of specific enzymes as HIV protease, suppress the growth of various tumours and viruses [(9)]. For that motive, the synthesis of α -aminophosphonates enjoys substantial attention and significant progress has been made to develop more efficient methods for the synthesis of these compounds [(10)]. The 'one-pot' three component reaction Kabachnik-Fields reaction is the most suitable methods for the synthesis of α-aminophosphonates because of its usefulness and high yields.

Quinolines [(11)] are an important class of heterocyclic compounds and have been curtained for biological activities such as bactericidal, [(12)] antitumor, [(13)] anti-inflammatory, [(14)] antimalarial [(15)] activities. Quinolines such as 2-chloroquinoline-3-carbaldehyde occupy a prominent position as they are key intermediates for further annellation and for various functional group interconversions.[(16)] It is also reported that organophosphates are potent pesticides, which have wide variety of application.[(17)]Recently, some new vinyl phosphates have been reported as potent inhibitors of phosphatase[(18)] and phosphodiesterase.[(19)]In recent work we have expanded the synthesis of series of α-aminophosphonates initiating from aminophenol as primary amine. The present research work is designed at comparing the antibacterial activity with the molecules to understand the activity.



R_2=6,7,8- CH_3,OCH_3,H R_1= p-OH, o-OH 0r p -NO_2

Scheme1-one pot synthesis of α-aminophosphonates with aminophenol using DES

2. MATERIALS:

2-Chloroquinoline-3-carbaldehydes were prepared in the laboratory by the reported procedure and were purified by column chromatography over silica gel (60–120 mesh, ortho/para-aminophenol, triethylphosphite, were precured from sigma Aldrich. Acetonitrile, N, N-Dimethylformamide (DMF), absolute ethanol, choline chloride, methanol and hexane were procured from S.D. Fine-chem. All melting points were determined in open capillaries on Kumar's melting point apparatus. 1H NMR spectra were recorded on Mercury Plus Varian in$CDCl_3$at 400 MHz using TMS as an internal

standard. IR spectra were recorded on a Perkin-Elmer FTIR using KBr discs. Mass spectra were recorded on Micromass Quatrro II using electrospray Ionization technique, showing (m+1) peak as a base peak. The test for the purity of products and the progress of the reactions were accomplished by TLC on Merck silica gel plates. Catalyst preparation: In this study, the ionic liquids used were synthesized according to the procedure reported in the literature.[20]

3. METHOD:

Procedure for synthesis 4a) ***diethyl ((2-chloroquinolin-3-yl) ((4-hydroxyphenyl) amino) methyl) phosphonate*** **-** A mixture of para-aminophenol (0.01 mol) and 2-Chloroquinoline-3-carbaldehydes (0.01 mol) was stirred at room temperature for 1 h then triethylphosphite (0.01 mol) was added dropwise. Stirring was continued at room temperature for another 30 min, after which the mixture was added to the stirring solution of Choline chloride in $ZnCl_2$ as catalyst (10mol%) and heated under reflux in an oil bath at 80^0C for an appropriate time. Water (20 mL) was added to the cooled reaction mixture and extracted with DCM (2× 20 mL). The combined organic extract was washed with water (2 × 10 mL), separated, dried over K_2SO4 and filtered. Product was isolated by preparative plate chromatography eluted with n-hexane: EtOAc (1:1). It is important to note that the catalysts were recycled by simple extraction of the product from the reaction mixture. The other compounds 4b to 4f were prepared employing a procedure similar to that described for compound.IR (KBr):3580 cm^{-1} (b) -OH), 3311 cm−1 (-NH) ; 1234 cm−1 (P-O); 1032 cm−1(P-O-C) 1H NMR ($CDCl_3$, δ ppm): 1.05 (t, 3H, O CH_2-CH_3, J = 8 Hz); 1.35 (t, 3H, O CH_2-CH_3,J = 8 Hz); 3.7 (m, 1H, O CH_2-CH_3); 3.9 (m, 1H, O CH_2-CH_3); 4.2 (m, 2H, O CH_2-CH_3); 5.4 (d, 1H, NH CH P O, J = 24 Hz); 6.3–6.5 (m, 3H, Ph-H, C_2,C_4,C_6); 7.0 (dd, 1H, Ph H, C_5,J = 8 Hz); 7.5 (t, 1H, Quinolin-H, C_5,J = 8 Hz); 7.69 (t, 1H, Quinolin-H, C_6,J = 8 Hz); 7.75 (d,1H, Quinolin-H, C_7,J = 8 Hz); 7.99 (d, 1H, Quinolin-H, C_8,J = 8 Hz); 8.34 (d, 1H, Quinolin H, C_4,J = 8 Hz). ES-MS: m/z 420.1(m+1) and 422.2 (m+3). Elemental analysis: $C_{20}H_{22}ClN_2O_4P$ Calcd.: C: 57.08%, H: 5.27%, N: 6.66 %; Found: C: 56.72%, H: 5.95%, N: 6.61%.

4b) ***Diethyl ((2-chloro-6-methylquinolin-3-yl) ((4-hydroxyphenyl) amino) methyl) phosphonate:***

IR (KBr):3585 cm^{-1} (b) -OH) 3300 cm−1 (NH) ; 1230 cm−1 (P-O) ; 1023 cm−1(P-O-C) ^{1}H NMR ($CDCl_3$, δ ppm): 1.05 (t, 3H, O CH_2-CH_3,J = 8 Hz); 1.38 (t, 3H, O CH_2-CH_3,J = 8 Hz); 2.48 (s, 3H, Quinolin-CH_3); 3.68 (m, 1H, O CH_2-CH_3); 3.88 (m, 1H, O CH_2-CH_3); 4.22 (m, 2H, O CH_2-CH_3); 5.16 (s, 1H, CH-NH Ph); 5.33 (d, 1H, NH CH P-O, J = 24 Hz); 6.28–6.42 (m, 3H, Ph H, C_2,C_4,C_6); 7.02 (dd, 1H, Ph H, C_5,J = 8 Hz); 7.5 (d, 1H, Quinolin-H, C_7,J = 8 Hz); 7.6 (s, 1H, Quinolin-H, C_5); 7.9 (d,1H, Quinolin-H, C_8,J = 8 Hz); 8.3 (d, 1H, Quinolin-H, C_4,J = 8 Hz). ES-MS: m/z 434.1 (m+1) and 436.2 (m+3). Elemental analysis: $C_{21}H_{24}ClN_2O_4P$ Calcd.: C: 58.14%, H: 5.56%, N: 6.44%; Found: C: 57.65%, H: 5.31%, N: 6.24%.

4c) ***Diethyl ((2-chloro-7-methylquinolin-3-yl) ((4-hydroxyphenyl) amino) methyl) phosphonate:***

IR (KBr): 3580 cm^{-1} (b) -OH) 3315 cm^{-1} (NH) ; 1235cm−1 (P-O) ; 1021 cm−1(P-O-C) ^{1}H NMR ($CDCl_3$, δ ppm): 1.07 (t, 3H, O CH_2-CH_3,J = 8 Hz); 1.38 (t, 3H, O CH_2-CH_3,J = 8 Hz); 2.49 (s, 3H, Quinolin-CH_3); 3.68 (m, 1H, O CH_2-CH_3); 3.88 (m, 1H, O CH_2-CH_3); 4.22 (m, 2H, O CH2-CH3); 5.14 (s, 1H, CH-NH Ph); 5.3 (d, 1H, NH CH P-O, J = 24 Hz); 6.29–6.45 (m, 3H, Ph H, C_2,C_4,C_6); 7.05 (dd, 1H, Ph H, C5,J = 8 Hz); 7.5 (d, 1H, Quinolin-H, C7,J = 8 Hz); 7.6 (s, 1H, Quinolin-H, C5); 7.9 (d,1H, Quinolin-H, C_8,J = 8 Hz); 8.2 (d, 1H, Quinolin-H, C_4,J = 8 Hz). ES-MS: m/z 434.1 (m+1) and 436.2 (m+3). Elemental analysis: $C_{21}H_{24}ClN_2O_4P$ Calcd.: C: 58.14%, H: 5.56%, N: 6.44%; Found: C: 57.64%, H: 5.29 %, N: 6.21%.

4d) ***Diethyl ((2-chloro-6-methylquinolin-3-yl) ((2-hydroxyphenyl) amino) methyl) phosphonate***

IR (KBr): 3554 cm^{-1} (b) -OH) 3333 cm^{-1} (NH) ; 1254cm−1 (P-O) ; 1060 cm^{-1}(P-O-C) ^{1}H NMR ($CDCl_3$, δ ppm): 1.08 (t, 3H, O CH_2-CH_3, J = 8 Hz); 1.34 (t, 3H, O-CH_2-CH_3,J = 8 Hz); 2.45 (s, 3H, Quinolin-CH_3); 3.62 (m, 1H, O CH_2-CH_3); 3.82 (m, 1H, O CH_2-CH_3); 4.24 (m, 2H, O CH2-CH3); 5.12 (s, 1H, CH-NH Ph); 5.34 (d, 1H, NH CH P-O, J = 24 Hz); 6.20–6.45 (m, 3H, Ph H, C_2,C_4,C_6); 7.06 (dd, 1H, Ph H, C_5,J = 8 Hz); 7.5 (d, 1H, Quinolin-H, C_7,J = 8 Hz); 7.6 (s, 1H, Quinolin-H, C_5); 7.9 (d,1H, Quinolin-H, C_8,J = 8 Hz); 8.2 (d, 1H, Quinolin-H, C_4,J = 8 Hz). ES-MS: m/z 434.1 (m+1) and 436.2 (m+3). Elemental analysis: $C_{21}H_{24}ClN_2O_4P$ Calcd.: C: 58.00%, H: 5.56%, N: 6.44%; Found: C: 57.34%, H: 5.31%, N: 6.35%.

4e) ***Diethyl ((2-chloro-7-methylquinolin-3-yl) ((2-hydroxyphenyl) amino) methyl) phosphonate:***

IR (KBr): 3550 cm^{-1} (b) -OH) 3305 cm^{-1} (NH) ; 1245cm−1 (P-O) ; 1025 cm−1(P-O-C) ^{1}H NMR ($CDCl_3$, δ ppm): 1.07 (t, 3H, O CH_2-CH_3, J = 8 Hz); 1.38 (t, 3H, O CH_2-CH_3,J = 8 Hz); 2.49 (s, 3H, Quinolin-CH_3); 3.68 (m, 1H, O CH_2-CH_3); 3.88 (m, 1H, O CH_2-CH_3); 4.22 (m, 2H, O CH2-CH3); 5.14 (s, 1H, CH-NH Ph); 5.3 (d, 1H, NH CH P-O, J = 24 Hz); 6.29–6.45 (m, 3H, Ph H, C_2,C_4,C_6); 7.05 (dd, 1H, Ph H, C5,J = 8 Hz); 7.5 (d, 1H, Quinolin-H, C7,J = 8 Hz); 7.6 (s, 1H, Quinolin-H, C5); 7.9 (d,1H, Quinolin-H, C_8,J = 8 Hz); 8.2 (d, 1H, Quinolin-H, C_4,J = 8 Hz). ES-MS: m/z 434.1

(m+1) and 436.2 (m+3). Elemental analysis: $C_{21}H_{24}ClN_2O_4P$ Calcd.: C: 58.00%, H: 5.56%, N: 6.44%; Found: C: 57.34%, H: 5.31%, N: 6.35%.

4f) ***diethyl ((2-chloro-6-methoxyquinolin-3-yl) ((4-nitrophenyl) amino) methyl) phosphonate***

IR (KBr): 3535 cm^{-1} (b) -OH) 3343 cm^{-1} (NH); 1227 cm^{-1} (P O); 1035 cm^{-1}(P- O- C) ^{1}H NMR ($CDCl_3$, δ ppm): 1.07 (t, 3H, O CH_2-CH_3,J = 8 Hz); 1.36(t, 3H, O-CH_2-CH_3,J = 8 Hz); 3.69 (m, 1H, O-CH_2-CH_3); 3.87 (s, 3H, Quinolin OCH_3); 3.9 (m, 1H, O CH_2CH_3); 4.22 (m, 2H, O CH_2 CH_3); 5.16 (s, 1H, CH NH Ph); 5.36 (d, 1H, NH CH P O, J = 24 Hz); 6.28–6.5 (m, 3H, Ph-H, C_2,C_4,C_6);; 6.9 (s, 1H, Quinolin-H, C5); 7.0 (dd, 1H, Ph-H, C5,J = 8 Hz); 7.33 (d, 1H, Quinolin-H, C7,J = 8 Hz); 7.88 (d, 1H, Quinolin-H, C_8,J = 8 Hz); 8.22 (d, 1H, Quinolin-H, C_4,J = 8 Hz).ES-MS: m/z 470.1 (m+1) and 472.11 (m+3).Elemental analysis: $C_{21}H_{23}ClN_3O_6P$ Calcd.: C: 52.56%, H:4.83%, N: 8.76%; Found: C: 52.62%, H: 4.90%, N: 8.15%.

4g) ***Diethyl ((2-chloro-8-methoxyquinolin-3-yl) ((4-hydroxyphenyl) amino) methyl) phosphonate****:*

IR (KBr): 3600 cm^{-1} (b) -OH) 3342 cm^{-1} (NH); 1231cm^{-1} (P O); 1035 cm^{-1}(P- O- C) ^{1}H NMR ($CDCl_3$, δ ppm): 1.07 (t, 3H, O CH_2-CH_3,J = 8 Hz); 1.36(t, 3H, O-CH_2-CH_3,J = 8 Hz); 3.69 (m, 1H, O-CH_2-CH_3); 3.87 (s, 3H, Quinolin OCH_3); 3.9 (m, 1H, O CH_2CH_3); 4.22 (m, 2H, O CH_2 CH_3); 5.16 (s, 1H, CH NH Ph); 5.36 (d, 1H, NH CH P O, J = 24 Hz); 6.28–6.5 (m, 3H, Ph-H, C_2,C_4,C_6);; 6.9 (s, 1H, Quinolin-H, C5); 7.0 (dd, 1H, Ph-H, C5,J = 8 Hz); 7.33 (d, 1H, Quinolin-H, C7,J = 8 Hz); 7.88 (d, 1H, Quinolin-H, C_8,J = 8 Hz); 8.22 (d, 1H, Quinolin-H, C_4,J = 8 Hz).ES-MS: m/z 450.1 (m+1) and 452.11 (m+3).Elemental analysis: $C_{21}H_{24}ClN_2O_5P$ Calcd.: C: 55.94%, H: 5.37%, N: 6.21%; Found: C: 55.62%, H: 5.90%, N: 6.15%.

Evaluation of antimicrobial activity

Antimicrobial screening

The antibacterial activities of the diethyl α-aminophosphonates were screened for their antimicrobial activity against two gram-negative and two gram-positive bacterial strains using disc diffusion method [(21)]. Briefly, two calculated amounts of the compounds were dissolved in DMSO in three different vials for getting solutions having concentrations of 50 mg/ml and 100 mg/ ml respectively. They were then applied on filter paper disc. Standard chloramphenicol (100 mg/ml) was used as positive control and DMSO as negative control. Both experimental and control discs were placed in petri dishes seeded with organism in nutrient agar medium. The petri dishes were kept in a refrigerator at 4 C for 24 h to ensure diffusion of the test materials. Finally, they were incubated at 37 ± 1 C for 24 h and all experiments were done as triplicates. The antibacterial activity was determined by measuring the diameter of zone of inhibition in mm. determination of MIC and MBC Each bacterium has a level of antibiotic which will inhibit growth but not kill the organisms. This is called the minimum inhibitory concentration.

Table 1 Minimum inhibitory concentration MIC and MBC of 4a, 4b, 4c, 4d, 4e,4f and 4g.

	B. subtilis			*S.aureus*			*E. coli*			*P. aeruginosa*		
	MIC	MBC	MBC/MIC (effect)	MIC	MBC	MBC/MIC (effect)	MIC	MBC	MBC/MIC (effect)	MIC	MBC	MBC/MIC (effect)
4a	32	128	4(+)	16	128	8(+)	8	64	8(-)	64	256	4(+)
4b	16	64	4(+)	32	64	2(-)	16	126	8(+)	32	128	4(-)
4c	32	128	4(-)	16	64	4(+)	32	128	4(+)	128	256	2(+)
4d	64	256	4(+)	8	16	2(+)	16	32	2(+)	32	128	4(+)
4e	8	64	8(-)	64	256	4(+)	128	256	2(-)	64	256	4(-)
4f	32	256	8(+)	32	128	4(-)	32	128	4(+)	8	64	8(+)
4g	64	256	4(+)	64	128	2(-)	64	256	4(+)	16	126	8(-)

(+) bactericidal effect, (-) bacteriostatic effect.

Related to this, a higher antibiotic concentration will kill the organisms. This is called the minimum bactericidal concentration. By understanding the concepts in determining antibiotic concentrations compared to the MIC and MBC, we can make rational decisions in determining how successful antibiotic treatment is likely to be[22]. The Minimum Inhibitory Concentration (MIC) and Minimum Bactericidal Concentration (MBC) of 4a-4g were determined by serial dilution technique against the above-mentioned pathogenic bacteria [23]. 4a-4g were used from a concentration of 0.25 mg/ml to 256 mg/ml. A control test-tube containing only medium (nutrient broth medium) was used to confirm the sterility of the medium. Bacterial suspension (10 ml) containing 102 cells/ml was inoculated into all tubes. All of the test tubes were incubated at 37 ± 1 C and observed for bacterial growth for 24 h for MIC and 95 h (4 days) for MBC determinations after inoculation for 24 h, the test tube with no visible growth of the microorganism was taken to represent the MIC value of the sample in mg/ml. MBC, in which no viable organism occurred was determined by keeping the test tubes which was used for MIC determination for four days. After four days, bacterial growth was observed and MBC was determined at lowest concentrations where no bacterial growth was observed. The action of an antibacterial on the bacterial strains can be characterized with two parameters such as Minimum inhibitory concentration (MIC) and Minimum bactericidal concentration (MBC). According to the ratio MBC/MIC, we appreciated antibacterial activity. If the ratio MBC/MIC4, the effect was considered as bactericidal but if the ratio MBC/MIC>4, the effect was defined as bacteriostatic [24].

4. CONCLUSION:

In the present study, the synthesis of series of aminophosphonates from Ortho and Para aminophenol via Kabachnik-Fields reaction. In vitro antimicrobial screening of the synthesized of a-aminophosphonates showed good antibacterial activity against some pathogenic Gram-positive and Gram-negative bacteria. The results also indicate that the difference in the chemical structure of the aminophosphonates affects the microbiological activity. The good activity of synthesized compounds 4c and 4f is probably attributed to the presence of pharmacologically active nitro groups attached to phenyl group of aromatic aldehydes. When the substitution of these groups is replaced by hydrogen or methoxy groups, a sharp decrease in activity against most of strains was observed. Compounds 4b and 4e exhibited better activity compared to that of standard Chloramphenicol against all the bacterial strain. Further the result showed that Gram-positive exhibited better activity than Gram-negative organism. The theoretical calculations carried out for the studied molecules 4a-4f, are also conducted for analysis of electrostatic characteristics of compounds.

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Trichloroacetic acid catalyzed synthesis of 1-(benzothiazolylamino) methyl-2-naphthol under solvent free condition

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ABSTRACT:

The present protocol has been synthesized 1-(benzothiazolylamino)methyl-2-naphthol derivatives by condensation reaction of 2-naphthol, aldehydes, and 2-aminobenzothiazole catalyzed by trichloroacetic acid under solvent free reaction conditions. The note worthy advantages of this protocol is inexpensive reagent, high yield, short reaction time and simple procedure.

1. INTRODUCTION :

One-pot multi-component reactions have attracted a considerable attention in organic synthesis as they can produce the target products in a single operation without isolating the intermediates and thus reducing the reaction time and energy [1, 2]. Multi-component contribute to the requirements of an environment friendly process by reducing multistep synthesis, energy consumption, less amount of solvents or no solvents and waste material production. 2-AminoBenzothiazoles as inimitable frames are presented a broad spectrum of pharmacological and biological properties [3]. Simplicity in electron transfer in the firefly luciferine cycle is reason of their different acts,[4] through antitumor,[5] and antidiabetic activity[6] to Alzheimer disease tracer,[7] and anticancer agent in pharmaceutical chemistry[8]. Also, benzothiazoles are commercially momentous as reactive dyes,[9] hair dyes, agrochemical fungicides, acaricides, herbicides, insecticides, plant desiccants, and defolicants [10-11].

2. LITERATURE REVIEW:

Synthesis of amidoalkyl naphthols can be carried out by the multi-component condensation of aldehydes, 2-naphthols and amide/urea in the presence of Lewis or Bronsted acid catalysts such as citric acid [12] chlorosulphonic acid [13], *p*-toluene sulphonic acid [14], $NaHSO_4.H_2O$ [15], $Fe(HSO_4)_3$ [16], has been used to carry out the synthesis.

However some of the above reported methods suffer from disadvantages such as long reaction times, the use of expensive reagents, low yields of products, high catalyst loading, corrosive reagents, strongly acidic conditions and the use of an additional microwave oven, or ultrasonic irradiation.

3. MATERIALS AND METHOD:

All chemicals, reagents and solvents were purchased from S. D. Fine, Spectrochem, Alfa aesar, and Loba chemical companies and used further without purification. We have taken melting points by an open capillary tube method and are uncorrected. Progress of the reaction was tested by using alumina TLC plates (Merck 60 F_{250}). ^1H & ^{13}C NMR spectra of synthesized heterocyclic compounds were tested by 400 & 100 MHz Bruker Avance spectrometer respectively in DMSO solvents and using tetramethylsilane (TMS) as an internal standard and the value of chemical shift is in the δ scale and *J* value is in hertz (Hz).

General procedure for the synthesis of 1-(benzothiazolylamino)methyl-2-naphthol

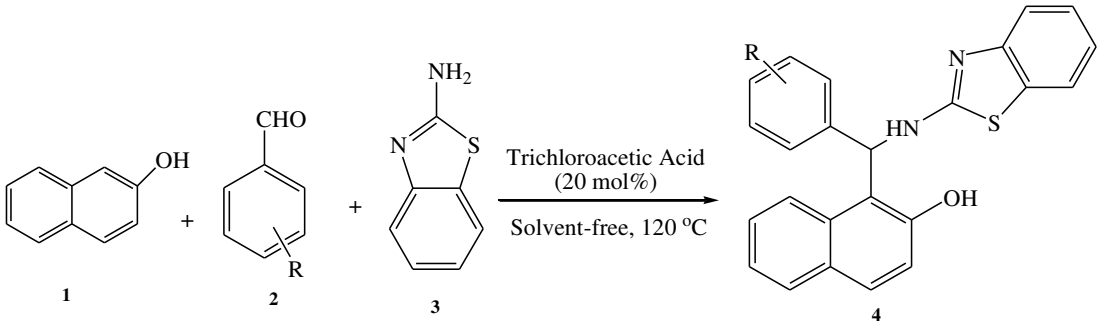
In round bottom flask the mixture of 2-naphthol (1 mmol), aromatic aldehyde (1 mmol) and 2-aminobenzothiazoles (1.2 mmol), Trichloroacetic acid (20 mol %) was added. The mixture was stirred at 120 ^0C for an appropriate time period. After completion of reaction (TLC check), the crude product was cooled to room temperature and washed with ice-cold water and separated by filtration. The pure product was obtained by recrystallization using ethyl alcohol.

Spectral Analysis:

1-((benzo[d]thiazol-2-ylamino)(2-hydroxy-3-methoxyphenyl)methyl)naphthalen-2-ol

Yield: (97 %); m.p. 201-204 °C ; IR (KBr, cm^{-1}): 3366 (N-H), 3141 (O-H), 1632 (C=N); ^1H NMR (400 MHz, DMSO-d6): δ = 3.74 (S, 3H, OCH_3), 6.67 (t, 1H, J=7.6 Hz, HAr), 6.82 (d, 1H, J=7.6 Hz, HAr), 6.96 (t, 1H, J=7.6 Hz, HAr), 7.01 (d, 1H, J=7.2 Hz, HAr), 7.14-7.40 (m, 6H, HAr,1Hbenzylic), 7.61 (d, 1H, J=7.2 Hz, HAr), 7.71 (d, 1H, J=8 Hz, HAr), 7.76 (d, 1H, J=8 Hz, HAr), 8.18 (d, 1H, J=8.4 Hz, HAr), 8.64 and 8.79 (brs, 2H, NH and OH), 9.95 (brs, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d6): δ = 50.90, 56.12, 56.27, 110.81, 118.29, 118.53, 118.86, 119.16, 121.13, 121.24,

122.66, 123.43, 125.81, 126.42, 128.82, 129.30, 130.96, 132.17, 133.22, 144.29, 147.79, 151.68, 152.69, 153.66, 166.27.

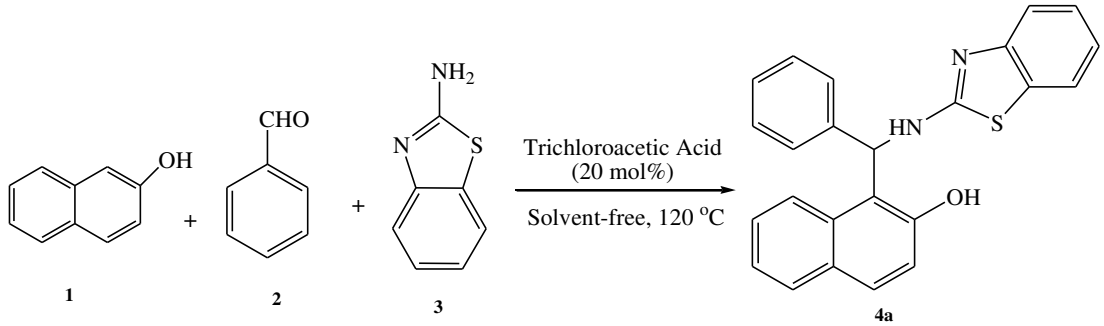


Scheme 1. Synthesis of 1-(benzothiazolylamino)methyl-2-naphthol

4. RESULTS AND DISCUSSION:

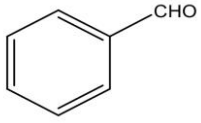
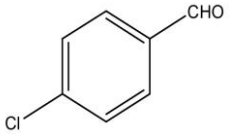
For our initial study, reaction of benzaldehyde, 2-naphthol, 2-aminobenzothiazoles and trichloroacetic acid as catalyst was considered as a standard model reaction (Scheme 2). Model reaction in the absence of catalyst did not lead to product formation. It means intervention of catalyst was must for initiation of the reaction. So, the catalytic activity of trichloroacetic acid as an organopromoter was investigated on the model reaction under solvent-free condition. To study, the temperature effect on reaction rate, the model reaction was performed at different temperature 90, 100, 120 and 125°C temperature. Temperature of 120 °C found to carry out the reaction efficiently in 78 % yield.

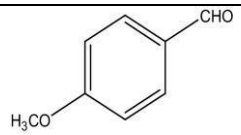
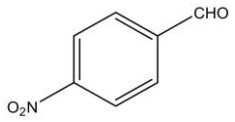
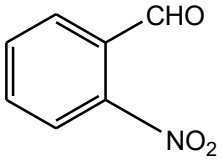
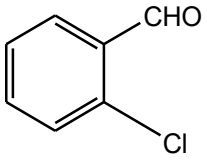
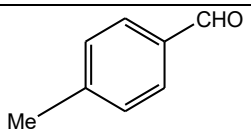
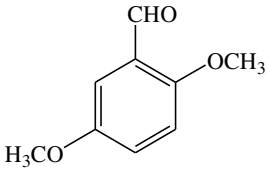
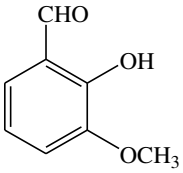
Any further increase in temperature failed to enhance the reaction rate substantially, while lowering the temperature below 120 °C, slow down the reaction rate (Table 2). To know the exact requirement of catalyst for the transformation, we investigated the model reaction using different concentrations of trichloroacetic acid such as 5, 10, 15, 20 and 25 mol%. 20 mol % catalysts were found to be optimum (Table 2). Further, increasing amount of catalyst concentration but did not improve the yield of the product. All result summarized in Table 1.



Scheme 2. 1-((benzo[d]thiazol-2-ylamino)(phenyl)methyl)naphthalen-2-ol

Table 1 Synthesis of 1-(benzothiazolylamino)methyl-2-naphthol catalyzed by Trichloroacetic acid[a]

Entry	Aldehydes	Products	Time (h)	Yield, (%)[a]	M.P. °C
1		**4a**	1.5	78	241-243
2		**4b**	1	86	234-237

3		**4c**	1	84	183-185
4		**4d**	1	85	248-250
5		**4e**	1.5	74	183-185
6		**4f**	1.5	76	212-214
7		**4g**	1.5	80	115-118
8		**4h**	1.5	76	208-210
9		**4i**	1.5	78	201-204

Reaction Condition: 2-naphthol (1 mmol), aromatic aldehyde (1 mmol) and 2-aminobenzothiazoles (1.2 mmol), Trichloroacetic acid (10 mol %) at 120 °C, [b]Isolated Yield.

Table 2. Optimization of catalyst concentration at different temperatures.

Entry	Amount of Catalyst (mol %)	Time (h)	Temperature °C	Yield[a] (%)
1	--	3	120	Trace
2	5	2.5	120	45
4	10	2	120	55
5	15	1.5	120	65
6	**20**	**1.5**	**120**	**78**
7	25	1.5	120	78
8	20	1.5	90	71

9	20	1.5	100	74
10	20	1.5	125	78

[a] Isolated yield.

5. CONCLUSION:

In the present method has developed an efficient and mild protocol for the synthesis of 1-(benzothiazolylamino)methyl-2-naphthol from the condensation reaction of 2-naphthol, aromatic aldehyde and 2-aminobenzothiazole using trichloroacetic acid under solvent free reaction conditions. The key advantages of this method have the inexpensive catalyst, shorter reaction time, solvent-free condition, easy work up and excellent yields.

ACKNOWLEDGMENTS:

Authors are thankful to Principal, Late K.G. Kataria College, Daund-413 801[M.S.]-India, Maharashtra (India) for providing necessary laboratory facilities to carry out this work.

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Facile and efficient synthesis of 1-(benzothiazolylamino) methyl-2-naphthol catalyzed by succinic acid

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ABSTRACT:
The present protocol has been synthesized 1-(benzothiazolylamino)methyl-2-naphthol derivatives by condensation reaction of 2-naphthol, aldehydes, and 2-aminobenzothiazole catalyzed by succinic acid under solvent free reaction conditions. The noteworthy advantages of this protocol is inexpensive reagent, eco-friendly, high yield, short reaction time and easy handling and simple procedure.

KEY WORDS: *Succinic acid, Solvent free, aromatic aldehydes, 2-aminobenzothiazole, β-Naphthol.*

1. INTRODUCTION :

One-pot multi-component reactions have attracted a considerable attention in organic synthesis as they can produce the target products in a single operation without isolating the intermediates and thus reducing the reaction time and energy [1, 2]. Multi-component contribute to the requirements of an environment friendly process by reducing multistep synthesis, energy consumption, less amount of solvents or no solvents and waste material production. One such example is the synthesis of amidoalkyl naphthols. Compounds bearing 1, 3-amino oxygenated functional groups are ubiquitous to a variety of biologically important natural products and potent drugs including a number of nucleoside antibiotics and HIV protease inhibitors, such as ritonavir and lipinavir. [3] Amidoalkyl naphthols have attracted strong interest to their useful biological and pharmacological properties such as adrenoceptor blocking, antihypertensive, and Ca^{2+} channel blocking activities [4-8]. Amidoalkyl naphthols are also important synthetic building blocks and are used as precursors for the synthesis of 1-aminomethyl-2-naphthol derivatives, which exhibit important cardiovascular activity [9]. The hypotensive and bradycardiac affects of these compounds have been evaluated [10].

Synthesis of amidoalkyl naphthols can be carried out by the multi-component condensation of aldehydes, 2-naphthols and amide/urea in the presence of Lewis or Bronsted acid catalysts such as chlorosulphonic acid [11], p-toluene sulphonic acid [12], $NaHSO_4.H_2O$ [13], $Fe(HSO_4)_3$ [14], $Sr(OTf)_2$ [15], Iodine [16], hetropoly acid $K_5CoW_{12}O_{40}.3H_2O$ [17], and hetropoly acid catalysts like cation-exchange resins [18] and silica supported perchloric acid [19,20] has been used to carry out the synthesis.

However some of the above reported methods suffer from disadvantages such as long reaction times, the use of expensive reagents, low yields of products, high catalyst loading, corrosive reagents, strongly acidic conditions and the use of an additional microwave oven, or ultrasonic irradiation.

2. EXPERIMENTAL:

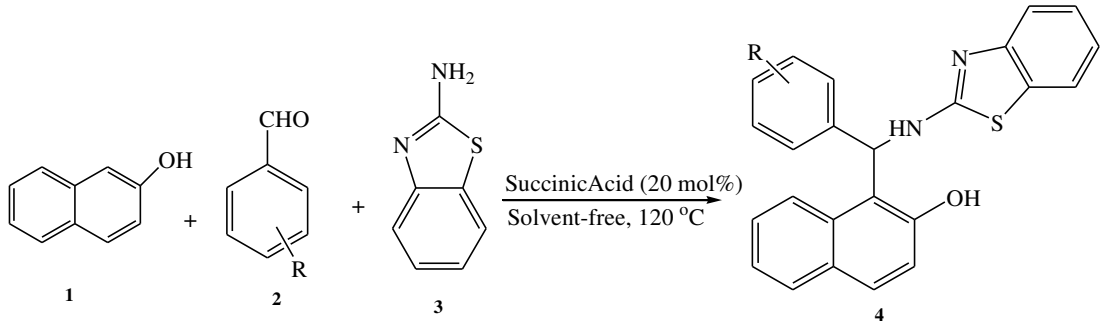
All chemicals, reagents and solvents were purchased from S. D. Fine, Spectrochem, Alfa aesar, and Loba chemical companies and used further without purification. We have taken melting points by an open capillary tube method and are uncorrected. Progress of the reaction was tested by using alumina TLC plates (Merck 60 F_{250}). ^{1}HNMR spectra of synthesized heterocyclic compounds were tested by 400 MHz Bruker Avance spectrometer respectively in DMSO solvents and using tetramethylsilane (TMS) as an internal standard and the value of chemical shift is in the δ scale and *J* value is in hertz (Hz).

General procedure for the synthesis of 1-(benzothiazolylamino)methyl-2-naphthol

In round bottom flask the mixture of 2-naphthol (1 mmol), aromatic aldehyde (1 mmol) and 2-aminobenzothiazoles (1.2 mmol), Succinic acid (20 mol %) was added. The mixture was stirred at 120 ^{0}C for an appropriate time period. After completion of reaction (TLC check), the crude product was cooled to room temperature and washed with ice-cold water and separated by filtration. The pure product was obtained by recrystallization using ethyl alcohol.

1-((benzo[d]thiazol-2-ylamino)(2,5-dimethoxyphenyl)methyl)naphthalen-2-ol

Yield: 94 %; m.p. 208-210 °C ; IR (KBr, cm^{-1}): 3368 (N-H), 3060 (O-H), 1628 (C=N); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.50 and 3.64 (2s, 6H, $2OCH_3$), 6.76 (d, 1H, *J*=8.4 Hz, HAr), 6.84 (d, 1H, *J*=8.8 Hz, HAr), 6.98 (d, 1H, *J*=7.2 Hz, HAr), 7.15-7.45 (m, 7H, HAr,1Hbenzylic), 7.63 (d, 1H, *J*=7.6 Hz, HAr), 7.71 (d, 1H, *J*=8.8 Hz, HAr), 7.77 (d, 1H, *J*=8Hz, HAr), 8.26 (d, 1H, *J*=8.4 Hz, HAr), 8.61 (brs, 1H, NH), 9.92 (S, 1H, OH);

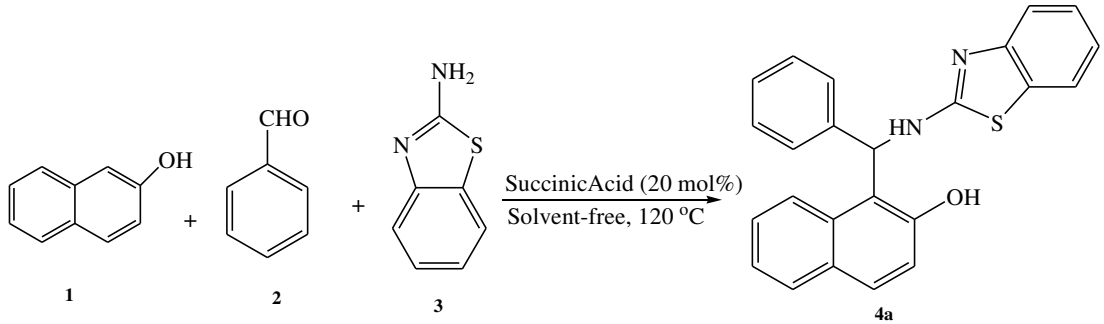


Scheme-1 Synthesis of 1-(benzothiazolylamino)methyl-2-naphthol

3. RESULTS AND DISCUSSION:

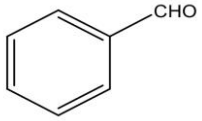
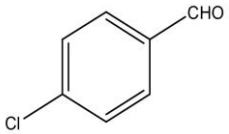
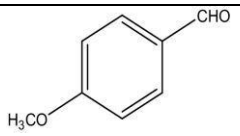
For our initial study, reaction of benzaldehyde, 2-naphthol, 2-aminobenzothiazoles and succinic acid as catalyst was considered as a standard model reaction (Scheme 2). Model reaction in the absence of catalyst did not lead to product formation. It means intervention of catalyst was must for initiation of the reaction. So, the catalytic activity of succinic acid as an organopromoter was investigated on the model reaction under solvent-free condition. To study, the temperature effect on reaction rate, the model reaction was performed at different temperature 90, 100, 120 and 125°C temperature. Temperature of 120 °C found to carry out the reaction efficiently in 87 % yield.

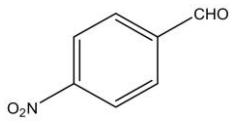
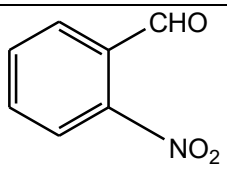
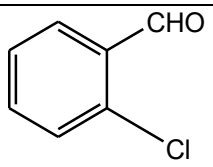
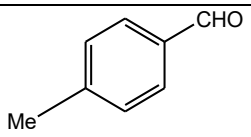
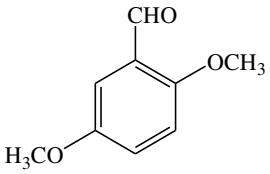
Any further increase in temperature failed to enhance the reaction rate substantially, while lowering the temperature below 120 °C, slow down the reaction rate (Table 2). To know the exact requirement of catalyst for the transformation, we investigated the model reaction using different concentrations of succinic acid such as 5, 7, 10, 15, 20 and 25 mol%. 20 mol % catalysts were found to be optimum (Table 2). Further, increasing amount of catalyst concentration but did not improve the yield of the product. All result summarized in Table 1.



Scheme 2 1-((benzo[d]thiazol-2-ylamino)(phenyl)methyl)naphthalen-2-ol

Table 1 Synthesis of 1-(benzothiazolylamino)methyl-2-naphthol catalyzed by succinic acid[a]

Entry	Aldehydes	Products	Time (Min.)	Yield, (%)[a]	M.P. °C
1		**4a**	20	87	241-243
2		**4b**	18	90	234-237
3		**4c**	20	86	183-185

4		**4d**	18	90	248-250
5		**4e**	30	85	183-185
6		**4f**	25	88	212-214
7		**4g**	20	87	115-118
8		**4h**	25	85	208-210

Reaction Condition: 2-naphthol (1 mmol), aromatic aldehyde (1 mmol) and 2-aminobenzothiazoles (1.2 mmol), Succinic acid (10 mol %) at 120 °C, [b]Isolated Yield.

Table 2. Optimization of catalyst concentration at different temperatures.

Entry	Amount of Catalyst (mol %)	Time (min.)	Temperature °C	Yield[a] (%)
1	--	120	120	Trace
2	5	90	120	55
3	7	60	120	65
4	10	45	120	70
5	15	30	120	75
6	**20**	**20**	**120**	**87**
7	25	20	120	88
8	20	30	90	80

9	20	25	100	82
10	20	20	125	86

[a] Isolated yield.

4. CONCLUSION:

In summary, present protocol developed an efficient, mild and cleans for the synthesis of 1-(benzothiazolylamino)methyl-2-naphthol from the condensation reaction of 2-naphthol, aromatic aldehyde and 2-aminobenzothiazole using succinic acid under solvent free reaction conditions. Moreover this method has the advantages of shorter reaction time, solvent-free condition, easy work up and excellent yields.

ACKNOWLEDGMENTS:

Authors are thankful to Principal, Kalikadevi (ACS) College, Shirur (Kasar) District- Beed, Maharashtra (India) for providing necessary laboratory facilities to carry out this work.

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Synthesis and characterization of imidazole containing pyrazole

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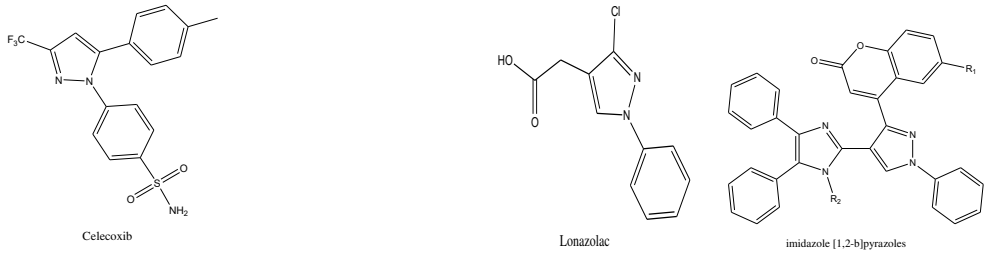
ABSTRACT:

Multicomponent reactions (MCRs) and one-pot process include synthesis of Pyrazole derivatives containing Imidazole from benzile, substituted 1H pyrazole 4-carbaldehydes and ammonium acetate using UHP. Imidazole and its derivatives are potential bioactive agents due to their wide spectrum of pharmacological activities like antibacterial, fungicidal[1] , sympathomimetic activity[2] , anti-retrovirus activity and pharmaceutical compositions

Key Words: *Multicomponent reactions, one pot process, benzyl, benzoin, UHP, Pyrazole derivatives.*

1. INTRODUCTION:

Pyrazole is a heterocyclic compound characterized by a 5-membered ring of three carbon atoms and two adjacent nitrogen atoms. Pyrazole is a weak base, with pK_b 11.5 (pK_a of the conjugated acid 2.49 at 25 °C). The pyrazole ring is found within a varietyof pesticides as fungicides, insecticides and herbicides, including fenpyro ximate, fipronil, tebufenpyrad and tolfenpyrad.[15]. Pyrazole moieties are listed among the highly used ring systems for small molecule drugs by the US FDA [16] Many natural products, especially alkaloids, contain the imidazole ring. These imidazoles share the 1,3-C_3N_2 ring but feature varied substituents. This ring system is present in important biological building blocks, such as histidine and the related hormone histamine. Many drugs contain an imidazole ring, such as certain antifungal drugs, the nitroimidazole series of antibiotics, and the sedative midazolam. Multicomponent reactions (MCRs) allow the capitulator of complex molecules in a one-pot process and show an accessible enforcement, high atom-economy and high selectivity. MCRs usually afford good-to-high yields, deserve simple work-up procedure and are fundamentally different and more efficient than classic two-component and stepwise reactions[1]. Imidazole are aromatic heterocyclic compound. It is five member ring contain three carbon and two Nitrogen. It is present in one and three position. One position nitrogen is pyrrole type nitrogen and three position nitrogen is pyridine type nitrogen. It also known as the 1,3 diazole[9]. Imidazole is amphoteric in nature. That is can function as both an acid and as a base. The acid the Pka of imidazole is 14.5 making it less acidic than carboxylic acid, phenols but slightly more acidic than alcohol. The acidic proton is the one bond to nitrogen and basic site of another nitrogen with the lone pair[10]. Imidazole is highly polar compound as the evidence by calculate dipole moment is 3.67D. it is highly soluble in polar solvent such as water(polarity of water is 9.0)[13]. The imidazole ring structure is often found in different biological system. Like vitamin-B12 ,Histamine and Biotin have imidazole nucleus in there core structure. It is also include in many synthetic drugs molecules such as Cimetidine, Azomycin and Metronidazole. Drugs containing the imidazole structure have a broad scope in clinical medicine[14]. Imidazole containing molecules found in more versatile biological activity. It is exhibit in Antibacterial[8,9,10,13] Anticancer[4,9,10,13] Anti-tubercular[9,13] Anti-fungal[8,9,13] Anti-analgesic[9,13] Antimicrobial[3,7,8,] Antihelmintic agent[3] Antidepressant[5,9] Antibacterial[7,9] Antiviral[9] Anti-HIV[13] activity. Pyrazole is also important heterocyclic compound and its derivatives have found different in Agriculture and Medicine. It is shows Anti-tuberculater[16], Antimicrobial Activity[16], anti-fungal[16] activity.



Some Reported important commercial drugs

2. LITERATURE REVIEW:

Imidazole and its derivatives are potential bioactive agents due to their wide spectrum of pharmacological activities like antibacterial, fungicidal[1] , sympathomimetic activity[2] , anti-retrovirus activity and pharmaceutical compositions effective for the treatment of retrovirus infection such as human immunodeficiency syndromes[3] . Encouraged by diverse biological activities and in continuation of the research work on bioactive heterocycles. It was intended to design and synthesized some new imidazole and its derivatives

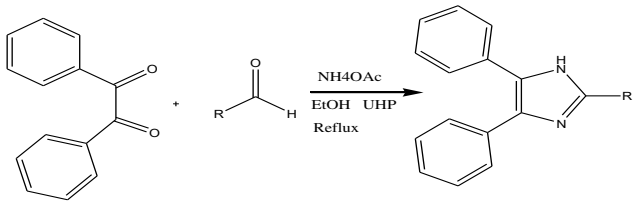
3. EXPERIMENTAL:

Materials and Apparatus

The chemicals and solvents were purchased from commercial suppliers (Merck, S.D. fine and Spectrochem) and they were used without purification prior to use. Melting points were recorded by open tube capillary method and are uncorrected. The progress of the reaction and the purity of the compounds were monitored by thin-layer chromatography (TLC), using analytical silica gel plates (Merck 60 F250). 1H NMR and 13C NMR spectra were recorded on 400 and 100 MHz, respectively. NMR spectra were obtained in CDCl3 solutions and are reported as parts per million (ppm) downfield from tetramethylsilane (TMS).

General Procedure for the Synthesis

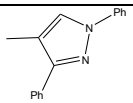
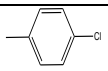
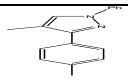
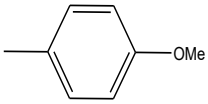
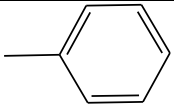
A mixture of benzil or benzoin (1.0 mmol), an aldehyde (1.0 mmol), NH4OAc (4.0 mmol) and UHP (10 mol %) was taken in round bottom flask fitted with the condenser. The mixture in RB is refluxed with EtOH as a solvent. After refluxing the progress of the reaction was monitored by taking TLC after a specific time interval. After observing disappearance of reactant spots it was concluded reaction is over. After completion of the reaction, refluxing was stopped and the crude product was isolated by filtration of the reaction mixture and washing of the precipitate with H2O for removal of impurities. Pure products were obtained via agitating and re-crystallization by EtOH.



Scheme 1. Synthesis of 2,4,5-trisubstituted imidazoles catalyzed by UHP

RESULT:

The following various Pyrazole derivatives containing Imidazole were synthesized from benzile, substituted 1H pyrazole 4-carbaldehydes and ammonium acetate

Sr. No	R group	Yield in %	M.P. in ^{0}C	Time in hrs
1.		84	216	3.0
2.		85	264	2.0
3.		78	252	3.0
4.		77	235	3.0
5.		86	226	2.5
6.		82	213	2.5

5. DISCUSSION:

To explore the use of UHP as a catalyst, a reaction of Benzile with different aldehydes was conducted as a standard model reaction for the preparation of imidazole (Scheme 1). The reaction in the absence of catalyst did not give any desired product. To determine the exact amount of the catalyst, we investigated the model reaction using different concentrations of aldehydes. During this study, we observed that if we take aldehyde containing pyrazole then different derivatives containing pyrazole as well as imidazole an be prepared which is having widw range of applications. UHP was proved to be an efficient catalyst to conduct the reaction smoothly. Ethanol was found to be superior solvents in terms of both yield and reaction time for this transformation.

SPECTRAL ANALYSIS:

1,3-diphenyl-1H-pyrazole derivative 13C NMR (100 MHz, CDCl3) δ ppm: δ 129.3, 135.8, 133.1, 127.5, 129.3, 128.8, 129.3, 123.1, 115.2, 150.0, 15.2, 139.7, 120.2, 129.4, 126.3, 129.4, 120.2, 133.1, 127.5, 129.3, 128.8, 129.3, 127.5; 1H NMR (400 MHz, CDCl3) δ ppm: δ 7.65 (1H, s, Ar-H), 2.05 (3H, s, $-CH_3$), 7.03 (5H, m, Ar-H), 7.48 (2H, d, J = 8.1 Hz, Ar-H), 7.32 (2H, d, J = 8.1 Hz, Ar-H) , 7.22 (1H, t, Ar-H), 13.4(1H, s, NH), 7.48(4H, d, Ar-H), 7.32(4H, t, Ar-H), 7.22(2H, t,Ar-H)

1-chloro-benzene derivative ^{13}C NMR (100 MHz, CDCl3) δ ppm: δ 129.3, 135.8, 133.1, 127.5, 129.3, 128.8, 129.3,136.5, 130.5, 128.8, 131.3, 128.8, 130.5, 24.3; ^{1}H NMR (400 MHz, CDCl3) δ ppm: δ 7.00 (2H, m, Ar-H), 7.15 (2H, t, Ar-H), 2.35 (3H, m, $-CH_3$) 7.32 (2H, d, J = 8.1 Hz, Ar-H) , 7.22 (1H, t, Ar-H), 13.4(1H, s, NH), 7.48(4H, d, Ar-H), 7.32(4H, t, Ar-H), 7.22(2H, t,Ar-H).

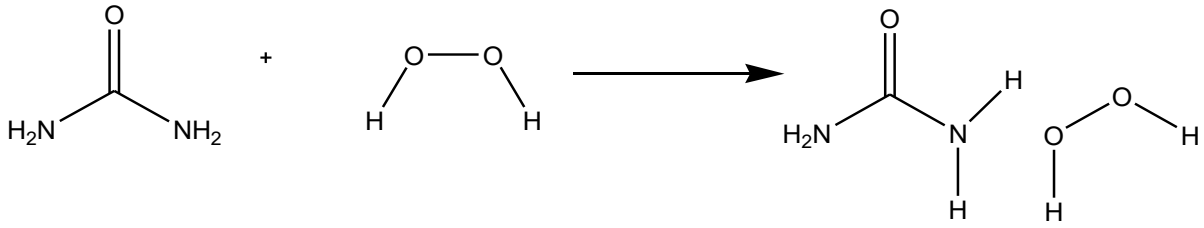
3-(4-fluorophenyl)-1-phenyl-1H-pyrzole derivative; 13C NMR (100 MHz, CDCl3) δ ppm: δ 129.3, 135.8, 133.1, 127.5, 129.3, 128.8, 129.3,129.1, 116.0, 162.9, 116.0, 129.1, 128.7, 150.0, 123.1, 115.2, 9.2, 139.7, 120.2, 129.4, 126.3, 129.4, 120.2; 1H NMR (400 MHz, CDCl3) δ ppm: δ 7.46 (2H, q, Ar-H), 7.03 (2H, t, Ar-H), 7.65 (1H, s, Ar-H), 2.05 (3H, s, $-CH_3$), 7.3 (5H, m, Ar-H) 7.32 (2H, d, J = 8.1 Hz, Ar-H) , 7.22 (1H, t, Ar-H), 13.4(1H, s, NH), 7.48(4H, d, Ar-H), 7.32(4H, t, Ar-H), 7.22(2H, t,Ar-H).

1-phenyl-3-p-tolyl-1H-pyrazole derivative; ^{13}C NMR (100 MHz, CDCl3) δ ppm: δ 129.3, 135.8, 133.1, 127.5, 129.3, 128.8, 129.3, 127.4, 129.6, 138.4, 129.6, 127.4, 130.1, 24.3, 150.0, 123.1, 115.2, 9.2, 139.7, 120.2, 129.4, 126.3, 129.4, 120.2; 1H NMR (400 MHz, CDCl3) δ ppm: δ 7.46 (2H, q, Ar-H), 7.03 (2H, t, Ar-H), 7.65 (1H, s, Ar-H), 2.05 (3H, s, $-CH_3$), 7.3 (5H, m, Ar-H).

Methoxy benzene derivative; ^{13}C NMR (100 MHz, CDCl3) δ ppm: δ 130.7, 130.1, 114.2, 157.7, 114.2, 130.2, 55.9, 129.3, 135.8, 133.1, 127.5, 129.3, 128.8, 129.3, 127.4, 129.6, 138.4, 129.6, 127.4, 130.1, 24.3; 1H NMR (400 MHz, CDCl3) δ ppm: δ 7.22 (1H, t, Ar-H), 13.4(1H, s, NH), 7.48(4H, d, Ar-H), 7.32(4H, t, Ar-H), 7.22(2H, t,Ar-H), 6.95(2H, q, Ar-H) 6.65 (2H, q, Ar-H), 3.37 (3H, s, $-CH_3$)

PREPARATION OF UHP:

For the preparation of the compound, urea (which is stable to oxidizing agents such as hydrogen peroxide) is dissolved in 30% hydrogen peroxide (molar ratio 2:3) at temperatures below 60 °C. On cooling, hydrogen peroxide - urea precipitates in the form of small platelets. Dry and use the UHP in synthesis of imidazole



6. CONCLUSION:

It is possible to synthesis pyrazole by using benzyl, aldehyde, NH_4OAc and UHP it is also possible to synthesis pyrazole derivative of imidazole. If imidazole containing aldehyde is used in this reaction then there is formation of pyrazole derivative of imidazole which may show biological activity this can be a important biological building blocks, such as histidine and the related hormone histamine. The advantage of the reaction is this is one pot synthesis with just condensation of benzyl and aldehyde and the catalyst used is UHP.

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Synthesis and Characterization of Some New Aryl Substituted Cinnamoyl-2-Pyrazoline Derivatives

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ABSTRACT:

Synthesis and characterization of some new biologically active 3, 5-diaryl-1-cinnamyol-2-pyrazolines is reported. A new class of of 1-cinnamoyl-2-pyrazoline derivatives were synthesized by the treatment of appropriate chalcones with cinnamoyl hydrazide using acetic acid in polyethylene glycol-400 as reaction solvent under mild reaction condition. Structures of the newly synthesized compounds were confirmed by the spectral analysis. The advantage of this method is simple, easy work up, shorter reaction time and without use of catalyst is reported.

KEYWORDS: *PEG-400, Substituted chalcones, Cinnamoyl-2-Pyrazolines;*

1. INTRODUCTION:

Nitrogen containing pyrazolines are heterocyclic compounds of five membered unsaturated ring structure having three carbon atoms and two nitrogen atoms in adjacent positions. Several pyrazoline derivatives possess important pharmacological activities and therefore they are useful materials in drug research. 2-Pyrazolines are biologically active scaffolds with a variety of biological activities like antimicrobial [1], antitubercular [2], anti-inflammatory [3], anticancer [4], antitumor [5], anticonvulsant [6], and anti-HIV [7]. Some of the pyrazoline derivatives are also reported to possess anti-inflammatory [8], antidiabetic [9] and antidepressant properties [10]. Cinnamic acid derivatives, especially those combining the cinnamoyl moiety with hydroxyl groups, present strong free radical scavenging properties [11]. Acids, esters, amides, hydrazides and related derivatives of cinnamic acid with such activities are reported in the literature for their health benefits [12-13].

Literature survey revealed that, as far as the different pyrazolines are concerned, 2-pyrazoline derivatives became the most frequently studied pyrazolines, various methods are used for the preparations of 2-pyrazolines. The treatment of chalcones with hydrazines seems to be the most popular for this purpose. Keeping these biological observations of pyrazolines in mind along with social responsibilities and in continuation of our work on the synthesis of biologically active heterocyclic compounds [14-16], it was planned to synthesize some new series of 2-pyrazoline derivatives containing cinnamoyl moiety under mild condition.

2. EXPERIMENTAL METHODS:

Melting points were determined by in an open capillary method and are uncorrected. The chemicals and solvents used for laboratory grade and were purified. IR spectra were recorded (in KBr pallets) on Shimadzu spectrophotometer. ^{1}H NMR spectra were recorded (in DMSO-d_6) on Avance-300 MHz spectrometer using TMS as an internal standard. The mass were recorded on EI-Shimadzu-GC-MS spectrometer.

General experimental procedure for the synthesis of chalcones (1a-h)

Equimolar mixture of substituted acetophenone (1 mmol), and aromatic aldehyde (1 mmol) was mixed in 15 mL polyethylene glycol-400 (PEG-400) taken in 100 mL conical flask. Then 2-3 mL of saturated solution of KOH (aprox 40%) was added into the flask. The solution becomes reddish brown color. The reaction mixture was kept for overnight at room temperature. On the next day morning, the completion of the reaction was monitored by TLC. After completion of the reaction, then the contents of the flask were poured into 50 mL ice cold water. The corresponding solid was separated then filtered. The crude product was recrystallized from suitable solvent. The yield and M.P. of the product was noted.

Similarly, all the compounds were synthesized by the same procedure. The physical and analytical data of the compounds were mentioned in Table-1.

General procedure for the synthesis of 1-Cinnamoyl-2-pyrazoline 3(a-h)

An equimolar mixture of chalcone (**1a)** (1 mmol) and cinamoyl hydrazide **2** (1 mmol) was mixed in 20 mL poly ethylene glycol-400 (PEG-400) taken in 50 mL round bottom flask. The catalytic amount of glacial acetic acid (1-2 ml) was added into the flask. The reaction mixture was stirred on magnetic stirrer at 50 °C for 1 hr. The completion of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature and poured into cold water. The solid was separated then filtered. The crude product **(3a)** was recrystallized from ethanol solvent. The yield and M.P. of the product was determined.

Similarly, all the compounds were synthesized by the same procedure. The physical and analytical data of the compounds was mentioned in Table-2.

1-Cinnamoyl-3-(2-hydroxy-5-chlorophenyl)-5-(4- chlorophenyl)-2-pyrazoline (3a)
IR (KBr, cm^{-1}): 1615, 1645, 3232; ^1H NMR (DMSO-d_6, δ ppm): 3.11 (dd, 1H, H_A), 3.72 (dd, 1H, H_B), 5.31 (dd, 1H, H_X), 6.11 (s, 1H, -OH); 6.71-7.95 (m, 14H, Ar-H+CH=CH), 11.52 (s, 1H, -OH); EIMS (*m/z*): 418 (M^+), 420 (M+2); Anal. Calcd. For $C_{24}H_{19}N_2O_3Cl$: C, 68.82; H, 4.57; N, 6.69%. Found: C, 68.69; H, 4.42; N, 6.52%

1-Cinnamoyl-3-(4-chlorophenyl)-5-(4-hydroxyphenyl)-2-pyrazoline (3b)
IR (KBr, cm^{-1}): 1610, 1648, 3256; ^1H NMR (DMSO-d_6, δ ppm): 3.21 (dd, 1H, H_A), 3.84 (dd, 1H, H_B), 5.26 (dd, 1H, H_X), 6.19 (s, 1H, -OH); 6.78-8.15 (m, 15H, Ar-H+CH=CH); EIMS (*m/z*): 402 (M^+), 404 (M+2); Anal. Calcd. For $C_{24}H_{19}N_2O_2Cl$: C, 71.55; H, 4.75; N, 6.95%. Found: C, 71.42; H, 4.86; N, 6.88%

1-Cinnamoyl-3-(4-chlorophenyl)-5-(4-chlorophenyl)-2-pyrazoline (3c)
IR (KBr, cm^{-1}): 1618, 1646, 3056; ^1H NMR (DMSO-d_6, δ ppm): 3.16 (dd, 1H, H_A), 3.81 (dd, 1H, H_B), 5.34 (dd, 1H, H_X), 6.85-8.35 (m, 16H, Ar-H+CH=CH); EIMS (*m/z*): 420 (M^+); Anal. Calcd. For $C_{24}H_{18}N_2OCl_2$: C, 68.42; H, 4.31; N, 6.65%. Found: C, 68.36; H, 4.46; N, 6.78%

1-Cinnamoyl-3-(4-chlorophenyl)-5-(4-bromophenyl)-2-pyrazoline (3d)
IR (KBr, cm^{-1}): 1610, 1642, 3025; ^1H NMR (DMSO-d_6, δ ppm): 3.08 (dd, 1H, H_A), 3.62 (dd, 1H, H_B), 5.12 (dd, 1H, H_X), 6.81-8.21 (m, 16H, Ar-H+CH=CH); EIMS (*m/z*): 464 (M^+); Anal. Calcd. For $C_{24}H_{18}N_2OClBr$: C, 61.89; H, 3.91; N, 6.01%. Found: C, 61.76; H, 3.98; N, 5.91%

1-Cinnamoyl-3-(2-hydroxy-5-chlorophenyl)-5-(4- bromophenyl)-2-pyrazoline (3e)
IR (KBr, cm^{-1}): 1616, 1645, 3245; ^1H NMR (DMSO-d_6, δ ppm): 3.22 (dd, 1H, H_A), 3.65 (dd, 1H, H_B), 5.28 (dd, 1H, H_X), 6.86-8.28 (m, 14H, Ar-H+CH=CH), 11.28 (s, 1H, -OH); EIMS (*m/z*): 480 (M^+); Anal. Calcd. For $C_{24}H_{18}N_2O_2ClBr$: C, 59.83; H, 3.77; N, 5.81%. Found: C, 59.92; H, 3.86; N, 5.68%

1-Cinnamoyl-3-(2-hydroxy-5-fluorophenyl)-5-(4- methoxyphenyl)-2-pyrazoline (3f)
IR (KBr, cm^{-1}): 1612, 1640, 3256; ^1H NMR (DMSO-d_6, δ ppm): 3.26 (dd, 1H, H_A), 3.38 (s, 3H, $-OCH_3$), 3.72 (dd, 1H, H_B), 5.21 (dd, 1H, H_X), 6.82-8.41 (m, 14H, Ar-H+CH=CH), 11.62 (s, 1H, -OH); EIMS (*m/z*): 416 (M^+); Anal. Calcd. For $C_{25}H_{21}N_2O_2F$: C, 72.11; H, 5.08; N, 6.73%. Found: C, 72.24; H, 5.19; N, 6.61%

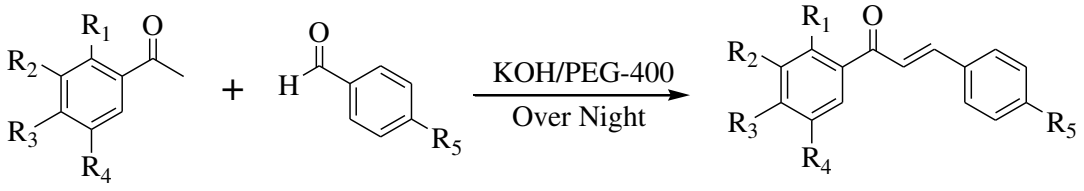
1-Cinnamoyl-3-(4-methylphenyl)-5-(4- methoxyphenyl)-2-pyrazoline (3g)
IR (KBr, cm^{-1}): 1618, 1648, 3072; ^1H NMR (DMSO-d_6, δ ppm): 2.32 (s, 3H, $-CH_3$), 3.26 (dd, 1H, H_A), 3.41 (s, 3H, $-OCH_3$), 3.61 (dd, 1H, H_B), 5.28 (dd, 1H, H_X), 6.91-8.52 (m, 15H, Ar-H+CH=CH); EIMS (*m/z*): 396 (M^+); Anal. Calcd. For $C_{26}H_{24}N_2O_2$: C, 78.76; H, 6.11; N, 7.07%. Found: C, 78.64; H, 6.19; N, 7.18%

1-Cinnamoyl-3-(2-hydroxy-5-chlorophenyl)-5-(4- chlorophenyl)-2-pyrazoline (3h)
IR (KBr, cm^{-1}): 1615, 1648, 3281; ^1H NMR (DMSO-d_6, δ ppm): 3.21 (dd, 1H, H_A), 3.71 (dd, 1H, H_B), 5.31 (dd, 1H, H_X), 6.88-8.56 (m, 14H, Ar-H+CH=CH), 11.52 (s, 1H, -OH); EIMS (*m/z*): 436 (M^+); Anal. Calcd. For $C_{24}H_{18}N_2O_2Cl_2$: C, 65.91; H, 4.15; N, 6.41%. Found: C, 65.82; H, 4.26; N, 6.54%

3. RESULTS AND DISCUSSION:

Recently, polyethylene glycol-400 prompted reactions [17-20] have attracted the attention of organic chemists due to their solvating ability and aptitude to act as a phase transfer catalyst, negligible vapor pressure, easy recyclability, ease of work-up, eco-friendly nature and economical cost. With our recent success on the development of new selective environmentally friendly methodologies using polyethylene glycol (PEG-400) [21-23] as a solvent for the preparation of biologically active compounds, herein we report the synthesis of some new cinnamoyl 2-pyrazolines derivatives by the cyclization reaction of chalcones with cinnamoyl hydrazide using catalytic amount of acetic acid in PEG-400 as an efficient reaction solvent.

The starting chalcones **1(a-h)** were prepared by the Claisen-Schmidt condensation method. The aromatic acetophenones and aldehydes were mixed in PEG-400 taken in a conical flask. The aqueous KOH solution was added to it and kept for overnight. On the next day morning, the progress of the reaction was monitored by the TLC and worked up with water to yielded corresponding chalcones **1(a-h)** (Scheme-1, Table-1). The synthesis of 1-cinnamoyl-2-pyrazoline derivatives **3(a-h)** were prepared by the condensation of chalcones with cinnamoyl hydrazide **(2)** using catalytic amount of AcOH in PEG-400 as an efficient reaction solvent system.



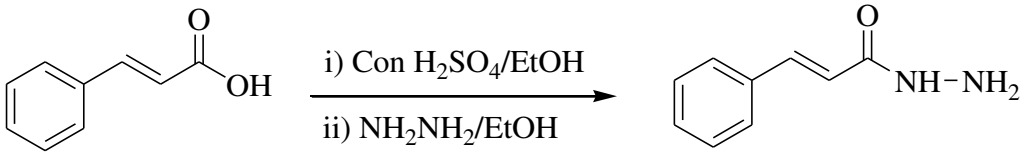
Acetophenones Aldehydes Chalcones **1(a-h)**

Scheme-1: Synthesis of chalcones using KOH in PEG-400 **1(a-h)**

Table-1: The physical and analytical data of synthesized chalcone derivatives

Entry (1a-h)	Substitution					Mol. Formula	Yield (%)	M.P (°C)
	R_1	R_2	R_3	R_4	R_5			
a	OH	H	H	Cl	OH	$C_{15}H_{11}O_3Cl$	90	130-132
b	H	H	Cl	H	OH	$C_{15}H_{11}O_2Cl$	85	127-129
c	H	H	Cl	H	Cl	$C_{15}H_{10}OCl_2$	95	134-136
d	H	H	Cl	H	Br	$C_{15}H_{10}OBrCl$	92	116-118
e	OH	H	H	Cl	Br	$C_{15}H_{10}O_2BrCl$	86	96-98
f	OH	H	H	F	OMe	$C_{16}H_{13}O_3F$	85	138-140
g	H	H	CH_3	H	OMe	$C_{17}H_{16}O_2$	86	106-108
h	OH	H	H	Cl	Cl	$C_{15}H_{10}O_2Cl_2$	90	126-128

The cinnamoyl hydrazide was prepared by the classical esterification method. The synthesis of cinnamoyl hydrazide was carried out from the esterification of cinnamic acid with ethanol in conc.H_2SO_4 followed by the treatment with hydrazine hydrate under reflux condition to yielded corresponding cinnamoyl hydrazide (Scheme-2). This formed cinnamoyl hydrazide was used as intermediate for the synthesis of cinnamoyl 2-pyrazolines.

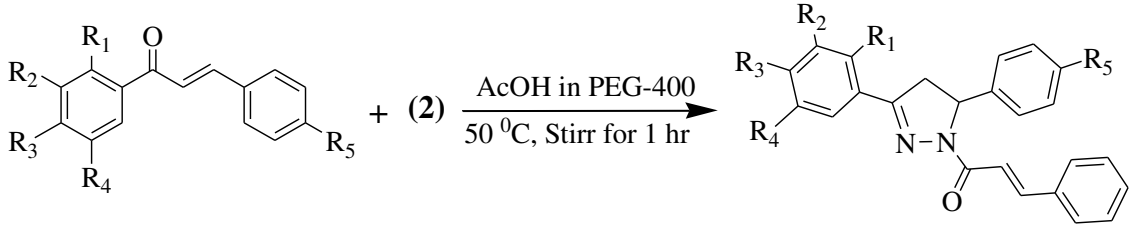


Cinnamic acid

Cinnamoyl hydrazide **(2)**

Scheme-2: Synthesis of Cinnamoyl hydrazide

Now, the cinnamoyl hydrazide **(2)** intermediate was treated with different chalcone derivatives **1(a-h)** for the period of one hour using catalytic amount of acetic acid in polyethylene glycol-400 as reaction solvent to formed corresponding 1-cinnamoyl 2-pyrazolines (Scheme-3, Table-2). The catalytic amount of acetic acid was used in combination with PEG-400; the reaction was completed very smoothly in high yield. Encouraged by the results, we focused our attention to variety of substituted chalcones. In all cases, the reaction proceeded efficiently in high yields under mild reaction temparature using catalytic amount of acetic acid in PEG-400 as an alternative reaction solvent.



Chalcones **1(a-h)**

Cinnamoyl 2-pyrazolines **3(a-h)**

Scheme-3: Synthesis of 1-cinnamyol 2-pyrazolines **3(a-h)**

All the structures of all newly synthesized compounds were characterized by the spectroscopic methods. The IR spectra of the products showed a characteristic band between 1600-1620 cm^{-1} referring to C=N double band between the N-2 and C-3 atoms. The IR spectrum of the products were also showed 1640-1660 cm^{-1}revealed to C=O of cinnamoyl group. In the ^1H NMR spectra of 2-pyrazolines, the three hydrogen atoms attached to the C-4 and C-5 carbon atoms of the heterocyclic ring gave an ABX spin system proved the 2-pyrazoline structure. Phenolic proton appeared as a singlet near δ 11.0-13.0 due to the hydrogen bonding, while other aromatic and aliphatic protons were observed at excepted regions. The mass spectra of the 1-cinnamyol 2-pyrazolines derivatives were showed molecular ion peak corresponding to their molecular formula.

Table-2: The physical and analytical data of synthesized 1-cinnamoyl 2-pyrazolines

Product	Substitution					Mol. Formula	Yield (%)	M.P. (°C)
	R_1	R_2	R_3	R_4	R_5			
3a	OH	H	H	Cl	OH	$C_{24}H_{19}N_2O_3Cl$	90	218-220
3b	H	H	Cl	H	OH	$C_{24}H_{19}N_2O_2Cl$	85	182-184

3c	H	H	Cl	H	Cl	$C_{24}H_{18}N_2OCl_2$	92	192-194
3d	H	H	Cl	H	Br	$C_{24}H_{18}N_2OClBr$	80	212-214
3e	OH	H	H	Cl	Br	$C_{24}H_{18}N_2O_2BrCl$	85	208-210
3f	OH	H	H	F	OMe	$C_{25}H_{21}N_2O_3F$	90	174-176
3g	H	H	CH_3	H	OMe	$C_{26}H_{24}N_2O_2$	82	232-234
3h	OH	H	H	Cl	Cl	$C_{24}H_{18}N_2O_2Cl_2$	86	164-166

4. CONCLUSION:

In summary, we synthesized some new aryl substituted cinnamoyl 2-pyrazolines developed with simple and efficient system. The reaction of substituted chalcones with cinnamoyl hydrazide using catalytic amount of glacial acetic acid in polyethylene glycol (PEG-400) as an efficient reaction solvent at mild reaction condition is described. The advantages of the present protocol are the simple and easy work up procedure, high yields of products and shorter reaction time is reported. The without use of catalyst is feature of this methodology.

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Study of the ground states of SiC molecule.

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ABSTRACT:
The diatomic SiC molecule is spectroscopically studied by many workers. The accurate ground state constants of these molecules derived from latest Fourier Trnsform spectroscopic analysis are used to construct the RKRV curve. The Hulbert-Hirschfelder, extended Rydberg and Zavitsas potential functions are used and are compared with RKRV curve. The error curve is also studied.
KEYWORDS*: Hulbert-Hirschfelder, extended Rydberg and Zavitsas potential functions*

1. INTRODUCTION:

The knowledge of potential energy curves is of prime importance in the study of diatomic molecular spectra [1]. In the calculations of F.C. factors, dissociation energies and thermodynamic quantities etc, the studies of potential energy curves are necessary. The empirical potential energy functions like Hulbert-Hirschfelder [2,3], extended Rydberg [4,5] and Zavitsas function [6,7] are usually applied and the potential energy curves are drawn. For all these calculations the Rydberg Klien Rees- Vanderslice RKRV [8-11] curves are essential. Naturally to compute the turning points of various vibrational levels the accurate spectroscopic constants are required. The empirical potential functions also require these molecular constants. In the present study the potential energy curves for the ground electronic states are constructed for the diatomic molecule viz SiC.

2. CHOICE OF MOLECULES AND EXPERIMENTAL DETAILS:

The diatomic silicon carbide (SiC) is known to be an important constituent of the interstellar dust grains. The infrared vibrational spectra of SiC (solid phase) has been observed in 10 micrometer region of an electromagnetic spectrum [12]. The first near IR spectrum of SiC was reported by Peter Bernath et. al. [13]. They observed the spectrum around 6103 cm^{-1}, wherein the use of a Hollow Cathode lamp was made as an excitation source. The band at 6103 cm^{-1} was assigned as a (0,0) band of the $d^1\Sigma$-$b^1\Pi$ electronic transition. Later using same source a band at 4578 cm^{-1} was also observed by Brazier et al [14] and they assigned it as a (0,0) band of $A^3\Sigma$-$X^3\Pi$ system. Cerenicharo et. al. [15] reported a laboratory study of the pure rotational spectrum of SiC in the $X^3\Pi$ state and also detected this molecule in the circumsteller envelope of the late type of star IRC + 10216.

The laser induced fluorescence (LIF) spectrum of $C^3\Pi$-$X^3\Pi$ band system was studied for the first time by Ebben et. al. [16,17]. They produced SiC by using pulsed laser vaporization of silicon in combination with a supersonic expansion, where the carbon was thought to be present in an impurity form in a silicon sample. Butenhoff and Rohlfing [18] observed the $C^3\Pi$-$X^3\Pi$ band of SiC during a search for the SiC_2 spectrum, utilizing jet cooled laser vaporization and analyzed many vibrational bands including v=0 to 5 of the X state. Wienkoop et.al [19] applied Faraday Laser Magnetic Resonance (LMR) to the study of the (1,0) band in the ground state $X^3\Pi$, $\Omega = 2$ & measured three rotational transitions.

Although Brazier et. al [14] assigned 4578 cm^{-1} band to (0,0) of the $A^3\Sigma$-$X^3\Pi$ electronic transition, the theoretical study [20,21] and matrix isolation study [22] indicated that, this band should have been assigned as (1,0).

The FT studies [23] of an infrared emission study of a positive column of the discharge tube ment for this purpose of excitation has shown three bands in the 4578, 3723 and 2770 cm^{-1} regions which were assigned the (1,0), (0,0) and (0,1) bands respectively of $A^3\Sigma$-$X^3\Pi$ electronic transition. The FT spectrum was recorded on a Bruker IFS 120 HR in the region 1800-8000 cm^{-1} with an apodized resolution of 0.037 cm^{-1}. The CaF_2 beam splitter and a liquid nitrogen cooled InSb detector were used. Total 268 scans gave a better Signal to Noice ratio and the spectrum was calibrated with $^{12}C^{16}O$ lines near 2150 cm^{-1}. The molecular constants derived from the analysis are presented in Table 1.

3. THE POTENTIAL ENERGY FUNCTIONS:

The Hulbert-Hirschfelder potential function*:*

This function [2,3] is an extension of a Morse function and is defined as follows.

$$U_{H\text{-}H}(r) = D_e \{ [1- \exp(-x)]^2 + cx^3 (1 + bx) e^{-2x} \} \quad \text{..... (1)}$$

Where $x = x_1(r - r_e)$; $x_1 = (\omega_e x_e / B_e)^{1/2} / r_e$

$c = 1 + a_1(D_e/ ao)^2$; $b = 2 - \{[(7/12) - (D_e - (a_2 / a_o))] /c \}$ $a_o = \omega_e^2 / 4 B_e$; $a_1 = - 1 - \{\omega_e x_e / (6B_e)^2 \}$ and

$a_2 = (5/4)\, a_1 - (2/3)\, (\omega_e x_e / B_e)$

This function employees the spectroscopic constants like ω_e, $\omega_e x_e$, B_e and D_e etc. The potential energies $U_{H\text{-}H}$ could be calculated by substituting the values of the constants and r values obtained from the RKRV data and the relevant parameters.

The extended Rydberg Potential function

Murrell and Sorbie [4] and Huxley and Murrell [5] have suggested a potential function, which is based on the force field parameters and is similar to Rydberg potential function. It has the form

$$U_{exR} = D_e - D_e \{ 1 + a_1\rho + a_2\rho^2 + a_3\rho^3]e^{-a/\rho} \quad \text{…….. (2)}$$

Where $\rho = r - r_e$; a_1, a_2 and a_3 are the constants defined through following discussions. These constants should not be confused with the constants appearing in H-H function. The constant a_1 is determined from the solution of the following quartic equation :

$$D_e a_1^4 - 6 f_2 a_1^2 - 4 f_3 a_1 - f_4 = 0 \quad \text{…….. (3)}$$

The parameters f_2 , f_3 , f_4 are called force field parameters and are defined as :

$$f_2 = 4 \pi^2 \mu \omega_e^2 c^2$$

$$f_3 = - (3 f_2 / r_e) [1 + (\alpha_e \omega_e / 6 B_e)^2]$$

$$f_4 = (f_3 / r_e)^2 \{15[1 + (\alpha_e \omega_e / 6B_e^2)] - (8\omega_e x_e / B_e)\}$$

Usually the largest positive root of equation (3) is selected as a_1. The other parameters a_2, a_3 and a_4 appearing in equation (2) could be calculated from following equations:

$$a_2 = (1/2) [a_1^2 - (f_2 / D_e)]$$

$$a_3 = (a_1 a_2 - (a_1^3/3) - (f_3/6D_e)]$$

This potential function was studied further and was compared with Dimitreva– Zenevich [24] potential function by Bhartiya and Behere[25]. This potential was applied by Birajdar [26] to a large number of molecules and found to give satisfactory results.

The Zavitsas potential energy function.

This recently suggested potential function by Zavitsas [6,7] is based on electronegativities of the constituent atoms forming a diatomic molecule. This function is also a modification of Morse function but the constant β appearing in Morse function is no more a constant in this function. The function is

$$U_z (r) = D_e [\exp (-2 \beta_\pm x) - 2 \exp (\beta_\pm x)]$$

…….. (4)

$$\beta_M = 8.486 (k_N)^{1/2} \quad ; \quad x = r - r_e \quad , \quad \text{Where } k_N = k_e / D_e .$$

The variables $\beta_\pm$ are calculated separately for $r < r_e$ and $r > r_e$.

For $r < r_e$ $\quad \beta_- = \beta_M \{ 1 + m\, u^{1/2} \}$

For $r > r_e$ $\quad \beta_+ = \beta_M \{ 1 + a_1 u^{1/2} + a_2 u^n + a_3 u^{3n} + a_4 u^{5n} \}$

Where, $\quad u = \exp (-2 \beta_M x) - 2 \exp (-\beta_M x) + 1$

For all species $a_1 = -0.32m$; $a_2 = 0.15$; $a_3 = 0.2 - 0.6m$ and $a_4 = (0.21\text{-}3m)\, (\Delta \chi)^{2.}$

m and n are calculated as follows **:**

$$m = - 0.025 r_e + [0.70 \exp (- 7.41 \times 10^3 k_N r_N) / z_1 z_2] + 0.042 \; | \Delta \chi |$$

And

$$n = 0.70 - 0.03r_e + 0.096 / (10^3 \times k_N r_N - 0.3) + [0.55 (\Delta \chi)^2 / r_e^{1/2}]$$

Where $r_N = r_e / D_e$

Zavitsas has taken D_e in kcal /mol , bond length in A^o and ω_e in cm^{-1} , μ is in amu the electronegativity difference $|\Delta \chi|$ is from Pauling scale[27]. We also retained same units but finally converted the energies in cm^{-1} which otherwise come in kilocalories .

4. COMPUTATIONAL PROCEDURE:

The data of turning points i.e. r_{min} and r_{max} values obtained from RKRV curves of SiC molecule is substituted in equations 1, 2 and 4 respectively for H-H, extended Rydberg and Zavitsas potential functions along with the corresponding parameters shown in Table 2. The potential energies obtained plotted against r values yield a potential energy curve for that potential for that particular molecule. For comparison purposes all the potential energy curves of each molecule are drawn on same scale along with their respective RKRV curve. These curves are shown in Fig 1 to 4 along with their error curves i.e. the % deviation from RKRV energies.

5. RESULTS AND DISCUSSION:

The PE curves are drawn which shows PE's around 60% of the D_e. Specifically SiC(61%) The Zavitsas Potential energy curve distinctly deviate from RKR. As per discussion with Zavitsas, the potential is mainly suitable for covalent molecules rather than ionic molecules. Moreover the electro negativity values of the atoms forming a diatomic molecule also can cause deviations. The H-H and Extended Rydberg potential functions almost overlap on each other and fall in between the Zavitsas and RKR curves. The error comparison shows that nearly 3 to 4% deviations occur in the potential energies from RKR values.

Table 1: Spectroscopic constants of the ground states of SiC molecule

Molecule/Constants	M	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	D_e	r_e	References
SiC	8.39792238	965.16	5.910	--	0.67976	0.00538	37582.2645	1.7182	28,29,30,31

Note: All constants are in cm^{-1} except r_e, which is in Å and μ, is in amu

Table.2: Parameters of H-H, extended Rydberg and RPC potentials for the ground state of SiC molecule

H-H Parameters	a_0	a_1	a_2	c	b	x_1
	342596.6	-2.87292	4.52092	4.847131	0.196881	1.757227

Extended Rydberg Parameters	a_1	a_2	a_3
	1.785623	-1.46661	0.601271

Zavitsas Parameters	Bm	κ_ε	κ_v	r_n	Z_1	Z_2	e_1	e_2	M	N	a_1	a_2	a_3	a_4
	1.758	4.61	0.043	0.016	3.8	2.9	1.9	2.55	-0.02	1.074	0.005	0.15	0.209	0.108

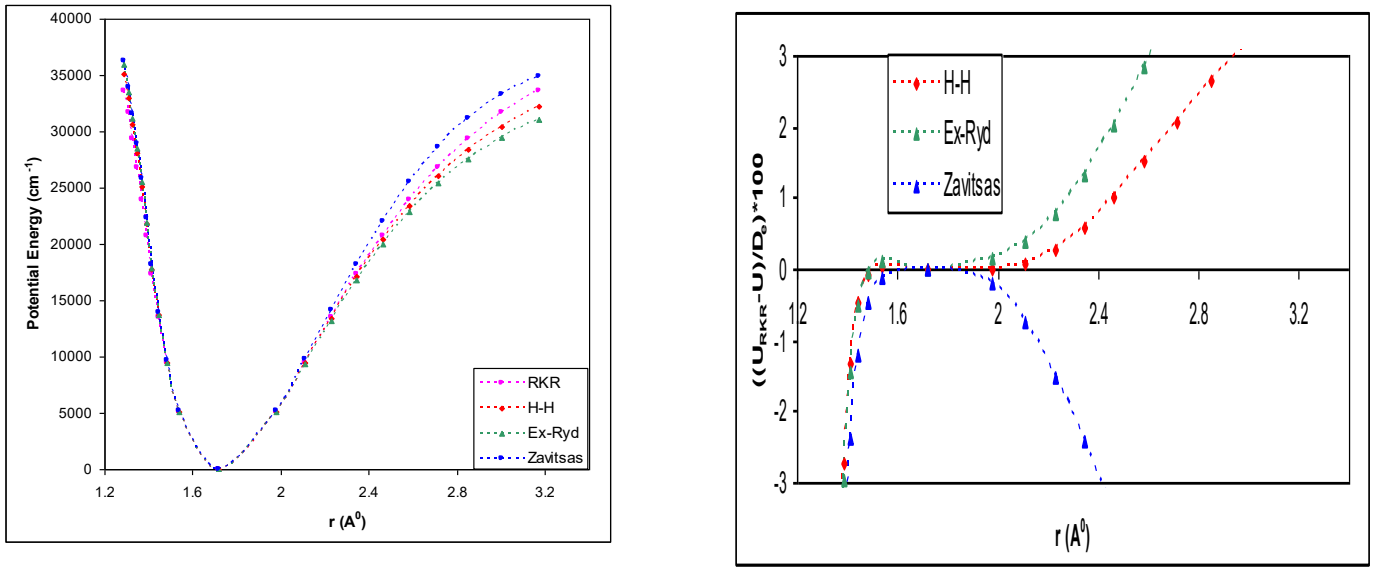

Figure 1 (a): RKR, H-H, Extended- Rydberg & Zavitsas Potential energy curves for the ground state of SiC molecule

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Ionic Liquid Assisted Green Synthesis of 2-Phenylimidizo [4,5-f][1,10]-Phenanathroline

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ABSTRACT:
A range of 2-phenylimidazo [4,5-f] [1,10]-phenanthroline have been synthesized in very good yield under solvent-free conditions by grinding 1,10,phenanthroline-5dione,aromatic aldehydes and ammonium acetate in the presence of [HBim]BF_4 as catalyst. The short reaction time, clean reaction, and easy workup make this protocol practically economical attractive and efficient.

KEYWORD:*2-phenylimidazo [4,5-f] [1,10]- phenanthroline, aldehydes, 1,10, phenanthroline-5-dione , ammonium acetate.*

1. INTRODUCTION:

The Ru(II) metal complexes of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline has been attracted considerable attention of chemist for many years[1],because their utilities in DNA structure prob[2-3]. The heterocyclic compounds with fused imidazopyridine ring system represent an important class of ligand not only for their theoretical interest but also from a pharmacological point of view. These heterocyclic structures forms the skeleton of natural alkaloids[4] which act as neuromuscular blocking agent[5], reversible inhibitors of the H^+, K^+, ATPase enzyme[6] with a potent anti-secretory activity[7] and sedative hypnotics of the nervous system[8]. The imidazole-[1,5-a]pyridine is a basic structure of synthetic drugs such as Pirmogrel, with human clinical application as effective platelets aggregation and thromboxane synthase inhibitors[9] moreover, N, N-Bidentate ligands with mixed five and six membered heterocycles are a desirable class of compounds in pursuit of structural diversity to enhance the physical and chemical properties in particular, 1-pyridylimidazo-[1,5-a]-pyridines possessing a bidentate structural feature with a pyridyl nucleus adjacent to a fused imidazole have emerged as a new class of ligand which is a potential positive inotropic agents[10,11].

Literature survey shows that synthesis of 2-phenylimidazo [4,5-*f*] [1,10]- phenanthroline has various routs like from 1,10,phenanthroline--5.6-dione with aldehyde in the presence of ammonium acetate in acetic acid[12] and anhydrous $ZnCl_2$ mediated the formation of 2-4,5-diphenyl-2-pyridin-2-yl-1H-imidazol-1-yl in methanol[13] and molecular iodine[14].

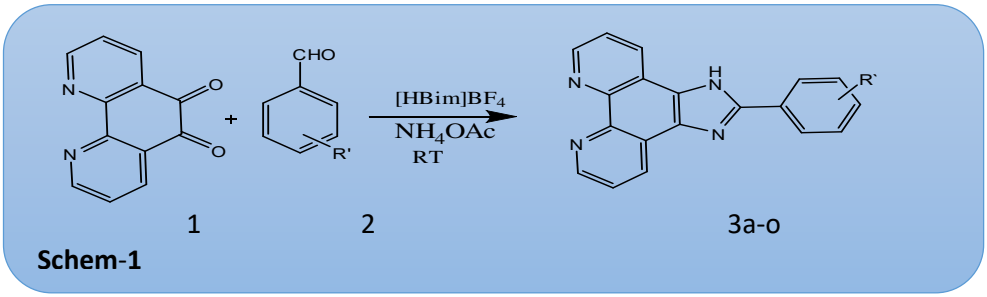
Most routes involve reaction of a 2-amino methyl pyridine with acylation followed by cyclization with phosphorus oxy chloride or polyphosphoric acid[15] or thiocyclation followed by ring closure using DCC or mercuric salts[16] Imidazo-[1,5-a]-pyridines were also obtained from 2-cynopyridine by the Vilsmeir reaction[17] or by reaction with Schiff bases in the presence of three steps from the dipyridyl ketone.[18-22] . In 1882, Radziszewski report the first time synthesis of 2,4,5-triphenyl imidazoles[23-24] and using nitriles and esters[25] also reported by using potassium ferrocynide[26].Siddiqui et al[27-28] report the green synthesis of 1-pyridyl imidazo[1,5-a]pyridines at room temperature in the presence of ionic liquid.

However these methods require prolong and exotic reaction condition. Thus the development of a new method for the synthesis of imidazoles derivatives would be highly desirable. Here we report an easy procedure for synthesizing of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline in the presence [HBim]BF_4 and ammonium acetate under solvent free condition with excellent yield and easy work up.

2. MATERIAL AND METHODS:

Synthesis of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline :

Mixture of benzaldehyde(1mmol)1,10-phenanthroline-5,6-dione,(1mmol),NH_4OAC(2.5mmol) and [HBim]BF_4 (10mmol) were ground together in a mortar with a pestle at room temperature for appropriate time as shown in table-1 .Completion of reaction is confirmed by TLC the mixture was further purified by column chromatography by using methanol : benzene and recrystallised from methanol.



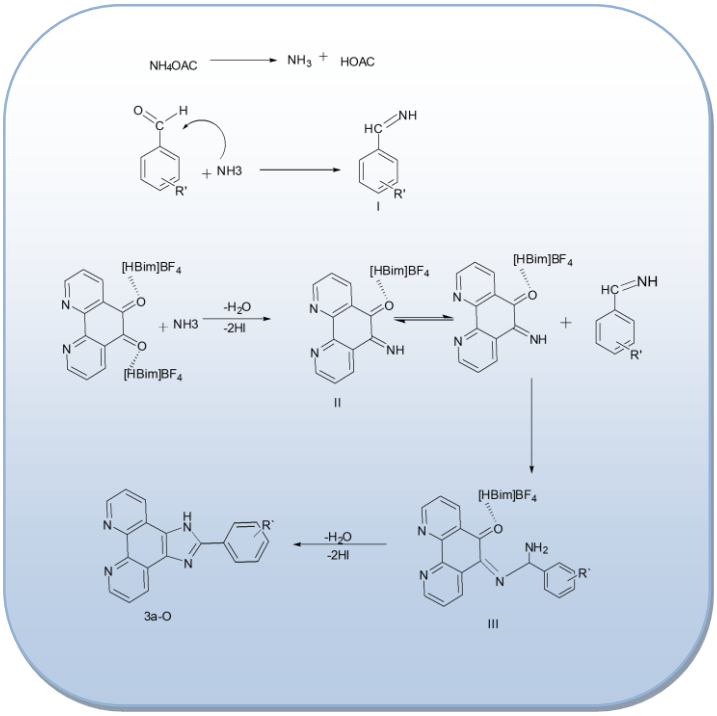
Schem-1

Many of the synthetic protocols for imidazole derivatives reported so far suffer from one or more disadvantages such as harsh reaction condition, poor yield, prolong reaction times, or use of hazardous and often expensive catalysts.

Recently ionic liquid has received considerable attention as an inexpensive, nontoxic, readily available catalyst for various organic transformation[29]offering the corresponding products in excellent yield with high selectivity. The mild Lewis acidity associated with ionic liquid enhanced its usage in organic synthesis to realize several organic transformation using stioichiometric levels to catalytic amount. Owing to numerous advantages associated with this eco-friendly element, ionic liquid has been explored as a powerful catalyst for various organic transformations. During the course of our studies towards the development of new routes to the synthesis of biologically active heterocycles.

Schem-2 Possible mechanism of the synthesis of 3a-o

The ammonium acetate is acting as a nitrogen source for the formation of imines I. Due to the high selectivity



the [HBim]BF4 ionic liquid attached to the both carbonyl group of 1,10-phenanthroline give an intermediate II which cyclized to form product via intermediate III as mention in scheme-2.

By getting this result, we have extended this protocol to a variety of aldehydes and summarized in Table 1. This protocol is rapid and efficient for the preparation of several2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline from both electrons efficient as well as electron deficient aromatic aldehydes. Electron-withdrawing groups enhance the rate of the reaction as compare to the electron-donating group. Aliphatic aldehyde were also used as starting carbonyl compounds for the same reaction. The *ortho* and *para* substituents activate the aromatic ring of aldehydes and increase the rate of the reaction. While *meta* substitution requires somewhat greater time as compared to the *o/p* substituents. A nearly stiochiometric amount of ammonium acetate was used in the course of the reaction, whereas previously a many-fold excess of ammonium acetate was required. This is an additional advantage of the novel methodology.Here we report an easy procedure for synthesizing of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline catalyzed by inexpensive, easily available and nontoxic [HBim]BF_4 in the presence of ammonium acetate under solvent free condition with excellent yield and easy work up.

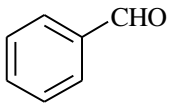
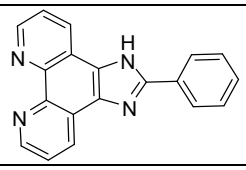
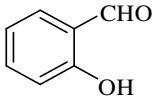
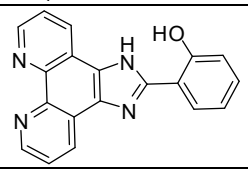
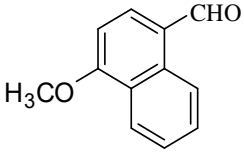
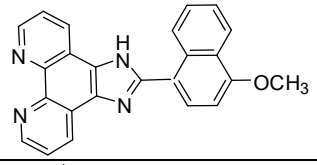
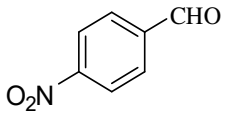
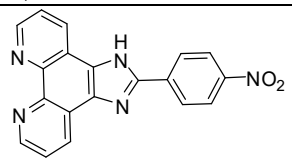
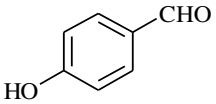
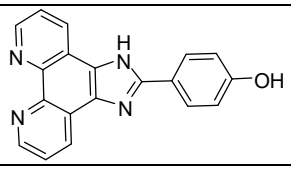
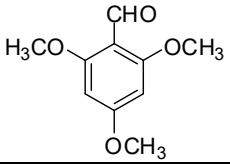
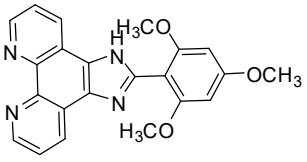
3. RESULTS AND DISCUSSION:

In conclusion, molecular iodine was found to be a mild and effective catalyst for the formation of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline in excellent yields. The uses of this inexpensive
and easily available catalyst under solvent-free conditions make this protocol practical and economically attractive. The simple work-up procedure, mild reaction conditions, selectivity, and
very good yields make our methodology a valid contribution to the existing processes in the field
of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline derivatives synthesis.

The formation of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline are confirmed by spectral analysis. The IR spectra of 4-N,N-dimethyl-2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline shows absorption at 1687,2257 and 3355cm-

[1] corresponding to the C=N, NH and tertiary amino group respectively. The [1]HNMR spectra shows 1H(s) δ=2.0,for NH gr, 6H(s) δ=3.00 for methyl group,4H(d) δ=6.65-7.30for aromatic benzene, 4H(d) δ=8.00-8.81,2(H) δ=7.26 mass 207(M^+),185,165,127. these result shows the confirmation of the formation 4-N,N-dimethyl-2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline(3i).

Table-1: Synthesis of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline :

Entry	Aldehyde	Product	Time(sec).	Yield (%)
3a			18	80
3b			20	90
3c			16	89
3d			10	80
3e			14	88
3f			15	90

[a]Products were characterized by [1]H NMR, [13]C NMR, Mass, elemental analysis and comparison with authentic sample, [b]Isolated yield after column chromatography.

4. EXPERIMANTAL:

General procedure for the synthesis of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline(3a-f):

A mixture of benzaldehyde(1mmol), 1,10-phenanthroline 5,6-dione(1mmol), ammonium acetate (20mmol) and [HBim]BF_4 (10mmol) were grind together in a mortar with pestle at room temperature for appropriate time **Table-1** after completion of reaction confirmed by TLC . The crude was further purified by column chromatography by using petroleum ether: ethyl acetate (9:1) eluent and get the corresponding 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline **.** The products **3(a-f)** were confirmed by comparison with authentic sample, [1]H NMR, [13]C NMR, mass, elemental analysis and melting points.

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Oxidation of m-chlorochalcone (MCC) by Tripropylammonium Chlorochromates: Kinetic and Mechanistic Study

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ABSTRACT:
The Kinetics of oxidation of m-chalorochalcones by Tripropylammonium Chlorochromates [TriPACC] has been Studied Spectrophotometrically in aqueous acetic acid medium in the temperature range 292-318K.The reaction is first order with respect to both m-chlorochalcone (MCC) and TriPACC. There is no kinetic or spectral evidence for the formation of complex between TriPACC and m-chlorochalcone (MCC). The activation parameters for the slow step were computed and calculated. Effect of ionic strength and dielectric constant of medium has been reported. A suitable mechanism has been proposed.
Key words: *m-chlorochalcone (MCC), Tripropylammonium Chlorochromates, Oxidation, Kinetics.*

1. INTRODUCTION:-

An extensive literature survey reveals that the kinetics and mechanism of oxidation of m-chlorochalcone (MCC) have been carried out using various oxidants like trichloroisocyanuric acid (1), pyridinium chlorochromate (2), acid bromate (3), N-chloronicotinamide (4), hexacyanoferrate (III) (5), N-chlorosuccinimide (6), chloramine-T (7), morpholinium chlorochromate(8), peroxydisulphate(9) and periodate(10). m-chlorochalcone (MCC) undergo a variety of chemical reactions and are found useful in the synthesis of variety of heterocyclic compounds. m-chlorochalcone (MCC) have been used as intermediate for the preparations of compounds having therapeutic value. Literature review reveals that m-chlorochalcone (MCC) derivatives exhibit diverse pharmacological activities such as potential cytotoxic agents, antimicrobial agents, antiviral, anti-inflammatory, anesthetics etc. Hence the study becomes important from the biological point of view. The results of kinetics of oxidation of m-chlorochalcone (MCC) with TriPACC in aqueous acetic acid medium has taken for study.

2. EXPERIMENTAL SECTION:-

All the chemicals and reagents were of analytical grade. All the solutions used in the study were prepared by using distilled acetic acid and doubly distilled water. Tripropylammonium Chlorochromates was prepared by the following method: chromium (VI) oxide (15.0g, o.150 mol) was dissolved in water in a polyethylene beaker and 40% hydrochloric acid (11.3 ml, 0.225 mol) was added with stirring at 0°C. To the resultant orange solution, tripropylammine (28.3 ml, 0.150 mol) was added drop wise with stirring to this solution over a period of 30 minutes and stirring was continued for 30 minutes at 0°C. The orange colored precipitate was filtered, washed with petroleum ether and dried in vacuum for 2 hours at room temperature [11]. Yield was 26 g (96%); MP was 144° C.
The Tripropylammonium Chlorochromates was stored in polyethylene bottle for long period of time. TriPACC was soluble in water, DMF, acetonitrile, acetone and DCM and was sparingly soluble in benzene, chloroform and hexane.

DETERMINATION OF STOICHIOMETRY AND PRODUCT ANALYSIS:-

The Stoichiometry of the reaction was determined by carrying out several sets of experiment with varying amount of (TriPACC) largely in excess over m-chlorochalcone (MCC) in 20% acetic acid by using 0.1N H_2SO_4. The remaining (TriPACC) was then analyzed Spectrophotometrically. The result indicated that 1 mole of alcohols react with 1 mole (TriPACC).

$$C_6H_5\text{-}CH{=}CH\text{-}COC_6H_5 + [C_3H_7]_3N^+H(CrO_3Cl) \xrightarrow{H^+} C_6H_5\text{-}COOH + C_6H_5\text{-}CH_2\text{-}CHO + [C_3H_7]_3NH(CrO_3H_2Cl)$$

The product analysis was carried out under kinetic conditions. In a typical experiment, m-chlorochalcone (MCC) (0.05 mol) and TriPACC (0.01) were made up to 50 ml in 20% acetic acid and kept in dark for about 24 hours to ensure the completion of the reaction. The solution was then treated with an excess (200 ml) of a saturated solution of 2, 4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept overnight in a refrigerator. The precipitated 2, 4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol and weighed again. The yield of DNP before and after recrystallization was 2.0 g (90%) and 1.7 g (75%) respectively. The DNP was found identical with the DNP of acetone by meting point. The products were also characterized by TLC, IR, and NMR spectra.

KINETIC MEASUREMENTS:-

The reactions were followed under pseudo-first-order conditions by keeping large excess (x 10 or greater) of the m-chlorochalcone (MCC) over TriPACC. The temperature was kept constant to +/- 0.1 K. The solvent was acetic

acid. The reactions were followed by monitoring the decrease in the concentration of TriPACC spectrophotometrically at 350 nm for 80% completion of the reaction. The pseudo-first-order rate constants $K_{obs,}$ were evaluated from the linear (r=0.990-0.999) plots of log [TriPACC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within +/- 3%.

3. RESULT AND DISCUSSION:-

The results of oxidation of Chalcone by TriPACC are represented as follows.

Effect of variation of concentration of Chalcone:-

The oxidation of m-chlorochalcone (MCC) with TriPACC in 20% of acetic acid in presence of sulphuric acid yields acetone. By keeping constant [TriPACC] and [H_2SO_4], the increase in (MCC) increases the rate of reaction (Table-1). The plot of log of k_{obs} versus log (MCC) for different initial concentration of m-chlorochalcone (MCC) is linear with unit slope demonstrate the first order dependence of rate on m-chlorochalcone (MCC)

Table 1: Effect of variation of m-chlorochalcone (MCC) on reaction rate

[TriPACC]= 0.001 M, [H_2SO_4] = 0.1 N, Temperature =303 k, AA = 20% (v/v)

(MCC)	0.01M	0.02M	0.03M	0.04M	0.05M	0.06M	0.07M	0.08M
k x 10^3sec^{-1}	2.06	2.35	2.64	2.94	3.22	3.50	3.78	4.08

Effect of variation of concentration of TriPACC:-

At constant m-chlorochalcone (MCC) and [H_2SO_4], the increase in [TriPACC] increases the rate of reaction (Table-2). The plot of log k_{obs} verses log [TriPACC] for different initial concentration of TriPACC is linear with unit slope present the first-order dependence of rate on TriPACC.

Table 2: Effect of variation of [TriPACC] on reaction rate

[MCC]= 0.01 M, [H_2SO_4] = 0.1 N, Temp =303 k, AA = 20% (v/v)

[T_{ri}PACC] Mole	0.001	0.0015	0.002	0.0025	0.003	0.0035	0.004	0.0045
k x 10^3sec^{-1}	2.06	2.33	2.58	2.84	3.08	3.31	3.55	3.79

Effect of variation of concentration of H^+:-

In order to study the effect the H^+ion concentration on the rate of oxidation reaction of m-chlorochalcone (MCC), the dependence of reaction rate has been investigated at different initial concentration of H_2SO_4. The rate of reaction increases with increase in [H_2SO_4] (Table-3). The plot of log K_{obs} verses log [H+]are also straight line with slope less than unity, Indicating a fractional order dependence on [H+].

Table 3: Effect of variation of [H_2SO_4] on reaction rate

[TriPACC]= 0.001 M, (MCC) = 0.01 M, Temp. =303 k, AA = 20% (v/v)

[H_2SO_4]	0.1M	0.2M	0.3M	0.4M	0.5M	0.6M	0.7M	0.8M
k x 10^3sec^{-1}	2.06	2.26	2.43	2.60	2.75	2.91	3.06	3.24

Effect of ionic strength:-

In the present investigation effect of salt on the rate of reaction is carried out. The salts selected are KCl, KBr, and KI. These will give effect of anion particularly halides on the rate of reaction. The divalent and trivalent cationic salt were also used such as $CaCl_2$, $Ca(NO_3)_2$, $Al(NO_{3)3}$ and K_2SO_4. The experiments were carried out under pseudo- first-order condition. These results were used to determine first order rate constant. The rate constants for the oxidation of Chalcone in presence of different salt are shown in [Table 4]. From table it is clear that, the rate increases with increase in cationic charge and decreases with increase in anionic charge. In case of KCl the rate of reaction decreases with the addition of KCl, this is due to the formation of less reactive species [19] by interaction between Cl^- ion and protonated TriPACC.

Table 4: Effect of variation of [salts] on reaction rate

[TP]= 0.001 M, (MCC) = 0.01 M, [H_2SO_4] = 0.1 N, Temp. =303 k, AA = 20% (v/v)

Salts 0.1M	KCl	KBr	KI	$CaCl_2$	$Ca(NO_3)_3$	$Al(NO)_3$	K_2SO_4
k x 10^3sec^{-1}	2.07	2.38	2.38	2.47	2.76	2.98	2.34

Effect of solvent composition:-

At fixed [MCC], [TriPACC] and [H^+], the rate of oxidation of m-chlorochalcone (MCC) with TriPACC increases with decrease in polarity of solvent (Table 5). This is due to polar character of transition state as compared to the reactant. The plot of log k_{obs} verses 1/D is linear with positive slope indicating ion- dipole type of reaction [20].

Table5: Effect of variation of Acetic Acid % on reaction rate
[TriPACC]= 0.001 M, $[H_2SO_4]$ = 0.1 N, [MCC] =0.01M, Temp=303 k

Acetic acid	10 %	20 %	30 %	40 %	50 %	60 %	70 %	80 %
k x 10^3sec^{-1}	1.95	2.06	2.21	2.34	2.46	2.58	2.72	2.86

Effect of temperature:-

The study of effect of temperature on rate of oxidation of m-chlorochalcones by TriPACC has been subjected to different temperature range 293K to 313K by keeping the concentration of m-chlorochalcone (MCC) and reagent constant. Rate constants are given in [Table 6]. The plots of log of K_{obs} verses 1/T are linear.

Table 6: Effect of variation of Temperatures on reaction rate
[TriPACC]= 0.001 M, [MCC] = 0.01 M, $[H_2SO_4]$ = 0.1 N, AA = 20% (v/v)

Temperatures (K)	293	298	303	308	313	318
k x 10^3sec^{-1}	1.27	1.69	2.06	2.44	2.88	3.28

Table 7: Activation Parameters
[TriPACC]= 0.001 M, [MCC] = 0.01 M. $[H_2SO_4]$ = 0.1 N, Temp. =303 k, AA = 20 % (v/v)

Activation parameters	**ΔE_a KJ mole^{-1}**	**$\Delta H^{\#}$KJmol^{-1}**	**$\Delta S^{\#}$JK^{-1}mole^{-1}**	**$\Delta G^{\#}$ KJ mole^{-1}**
	25.67	23.15	-220.06	89.83

Activation parameters are presented in [Table 7]. The negative values of entropy of activation reflect that the transition state is more rigid than initial state. The nearly constant ΔG value indicates that similar mechanism is operative for the oxidation of m-Chlorochalcone.

These above observations suggest that the rate law can be written as shown

$$-\frac{d[T_{ri}PACC]}{dt} = k_3C_1$$

$$= \frac{k_3k_2[OxH^+][S]}{1+K_2[S]}$$

$$= \frac{k_3K_1K_2[Ox][H+][S]}{1+K_2[S]}$$

4. CONCLUSION:

The rate constants of the slow step involved in the mechanism were evaluated. Activation parameters were also computed. The negative value of $\Delta S^{\#}$ provides support to the formation of rigid transition state. The overall mechanism described here is consistent with product and kinetic studies.

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Dimethylaminopyridine catalyzed one pot synthesis of α-aminophosphonates from 2-chloroquinoline-3-carbaldehydes

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ABSTRACT:
A simple one pot and high yielding method was developed for the synthesis of α-aminophosphonates from 2-chloroquinoline-3-carbaldehyde, aniline and triethylphosphite in the presence of Dimethylaminopyridine (DMAP) as catalyst. All the synthesized compounds were characterized by IR, ^{1}HNMR and Mass spectroscopy.
KEY WORDS: *2-chloroquinoline-3-carbaldehyde, aniline, triethylphosphite and DMAP.*

1. INTRODUCTION:

Quinoline ring systems represent a major class of heterocyclic compounds in which benzene ring is fused with pyridine heterocyclic ring system. Quinolines are known also as benzo[*b*]pyridine and 1-azanaphthalene with one nitrogen atom in one benzene ring and none in the other ring or at the ring junction. Heterocycles containing a nitrogen atom possess high and interesting medicinal and pharmaceutical properties.(1–4) Montelukast is a drug used as an antiasthma agent.(5) In addition, quinolines are the main core of many types of natural products,(6,7) drugs,(8–10) and were found in many synthetic heterocyclic compounds in order to enhance the biological and medicinal properties. Compounds incorporating quinoline ring system exhibited various biological,(11,12) and pharmaceutical activities *e.g.* anti-tuberculosis,(13) antiplasmodial,(14) antibacterial,(15,16) antihistamine,(17) antifungal,(18) antimalarial,(19,20) anti-HIV,(21) anticancer,(22) anti-infammatory,(23,24) anti-hypertensive,(25) and antioxidant activities.(26) In addition, the use of quinolines as tyro kinase PDGF-RTK inhibitor,(27) inositol 5^0-phosphatase (SH_2),(28) DNA gyrase B inhibitors as *Mycobacterium tuberculosis*,(29) and DNA topoisomerase inhibitors,(30) were reported.

Generally, *α*-aminophosphonates are prepared in the presence of Lewis acids or bases by the addition of phosphorous nucleophiles to the imines. Lewis acids such as $SnCl_4$, $SnCl_2$, $ZrCl_4$, $ZnCl_2$ and $MgBr_2$ have been used as catalysts for such reactions.(31-33) Recently, Lewis and Bronsted acids such as $LiClO_4$,(34) $InCl_3$,(35) lanthanide triflates,(36) $TaCl_5$-SiO_2,(37) montmorillonite clay-MW,(38) Al_2O_3- MW,(39) CF_3COOH(40) were found to be effective in the preparation of *α*-aminophosphonates. However, many of these procedures require expensive reagents, long reaction times and suffer from poor yields. These reactions cannot be carried out in one-step by the reaction between a carbonyl compounds, amine and dialkylphosphite.(41) 4-(Dimethylamino)pyridine (DMAP) is a catalyst of outstanding utility in a variety of group-transfer reactions, such as the acylation of alcohols and amines.(42-46) Despite the frequent use of DMAP itself and the recent development of chiral DMAP derivatives for applications in stereoselective catalysis,(47-54) the mechanisms of even the most simple DMAP-catalyzed reactions, such as the acetylation of alcohols with acetic anhydride, have not yet been studied in detail. A recent review of the mechanistic characteristics of this reaction highlighted the importance of the deprotonation step as well as the influence of the auxiliary base on the catalytic activity of DMAP.(44) Hence we were interested in the synthesis of α-aminophosphonates using DMAP as versatile catalyst, In the Search of better reaction condition for the synthesis of α-aminophosphonates using 2-chloroquinoline-3-carbaldehyde, we have developed a solvent-free reaction condition with excellent yield using DMAP catalyst at room temperature.

2. MATERIALS & METHOD:

2-Chloroquinoline-3-carbaldehydes were prepared in the laboratory by the reported procedure and were purified by column chromatography over silica gel (60–120 mesh). 3-fluoroaniline, 2-methylaniline, triethylphosphite, DMAP were procured from Lancaster. All melting points were determined in open capillaries on Kumar's melting point apparatus. 1H NMR spectra were recorded on Mercury Plus Varian in $CDCl_3$ at 400 MHz using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer FTIR using KBr discs. Mass spectra were recorded on Micromass Quatrro II using electrospray Ionization technique, showing (m+1) peak as a base peak. The test for the purity of products and the progress of the reactions were accomplished by TLC on Merck silica gel plates.

EXPERIMENTAL PROCEDURE:

2a) Diethyl (3-fluorophenylamino)(2-chloroquinolin-3-yl)methylphosphonate:

To a mixture of 2-Chloroquinoline-3-carbaldehyde (0.95 g, 5 mmol), 3-fluoroaniline (0.65 g, 6 mmol) and triethylphosphite (1.66 g, 10 mmol) was added DMAP in catalytic amount. The progress of the reaction was monitored on TLC using Hexane: Ethyl acetate (8:2) as the solvent system. After the completion of the reaction, poured ice cold water in the reaction mass to get the solid product. Filtered the solid and washed with water and dried in oven at 50 ^{0}C for 8.0 h (dry wt. 1.90 g, yield 91%).

3. RESULTS & DISCUSSION:

In continuation of our work related to phosphorus chemistry,(55-60) we were earlier synthesized α-aminophosphonates using quinoline moiety in two steps. In the first step, imines of 2-chloroquinoline-3-carbaldehyde were synthesized from 2-chloroquinoline-3-carbaldehyde and aniline then converted to α-aminophosphonates using TMSCl and triethylphosphite in the next step. Now we were synthesized α-aminophosphonates from 2-chloroquinoline-3-carbaldehyde and aniline using triethylphosphite in the presence of DMAP as catalyst (Scheme -1, Table-1). All the compounds were synthesized using this methodology in excellent yields. All the compounds synthesized were unequivocally characterized based on analytical data.

4. ANALYSIS:

2a) Diethyl (3-fluorophenylamino)(2-chloroquinolin-3- yl)methylphosphonate:

IR (KBr): 3311 cm^{-1} (-NH); 1234 cm^{-1} (P = O); 1032 cm^{-1}(P- O - C)

1H NMR (CDCl3, δ ppm): 1.05 (t, 3H, O-CH_2-CH_3) ;1.35 (t, 3H, O-CH_2-CH_3); 3.7 (m, 1H, O-CH_2-CH_3); 3.9 (m, 1H, O-CH_2-CH_3); 4.2 (m, 2H, O-CH_2-CH_3); 5.4 (d, 1H, -NH-CH-P= O); 6.3–6.5 (m, 3H, Ph-H,C_2,C_4,C_6); 7.0 (dd, 1H, Ph-H,C_5); 7.5 (t, 1H, Quinolin-H,C_5); 7.69 (t, 1H, Quinolin-H,C_6); 7.75 (d,1H, Quinolin-H,C_7); 7.99 (d, 1H, Quinolin-H,C_8); 8.34 (d, 1H, Quinolin-H,C_4).

ES-MS: m/z 423.1 (m+1) and 425.1 (m+3).

2b) Diethyl (3-fluorophenylamino)(2-chloro6-methylquinolin-3-yl)methylphosphonate:

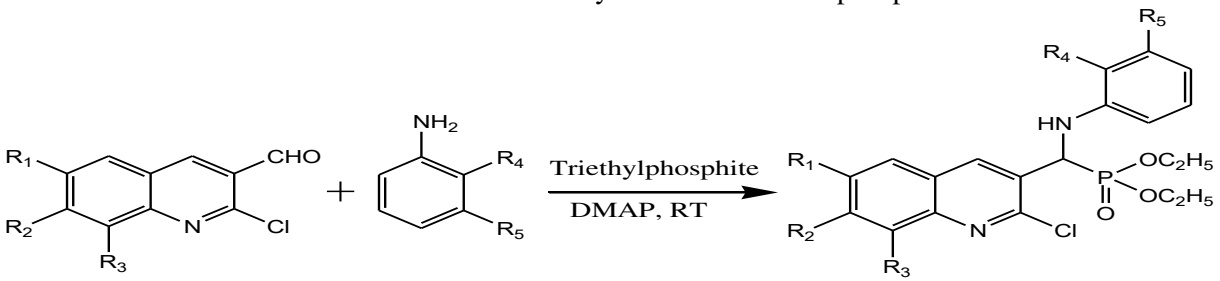
IR (KBr): 3305 cm^{-1} (-NH); 1230 cm^{-1} (P = O); 1022 cm^{-1}(P-O-C)

1H NMR (CDCl3, δ ppm): 1.05 (t, 3H, O-CH_2-CH_3); 1.38 (t, 3H, O-CH_2-CH_3); 2.48 (s, 3H, Quinolin-CH_3); 3.68 (m, 1H, O-CH_2-CH_3); 3.88 (m, 1H, O-CH_2-CH_3); 4.22 (m, 2H, O-CH_2-CH_3); 5.16 (s, 1H, -CH-NH-Ph); 5.35(d, 1H, -NH-CH-P=O); 6.28–6.42 (m, 3H, Ph-H,C_2,C_4,C_6); 7.02 (dd, 1H, Ph-H,C_5); 7.5 (d, 1H, Quinolin-H, C_7);7.6 (s, 1H, Quinolin-H,C_5); 7.9 (d,1H, Quinolin-H,C_8); 8.3 (d, 1H,Quinolin-H,C_4).

ES-MS: m/z 437.1 (m+1) and 439.2 (m+3).

Figures/ Tables.

Scheme-1: DMAP Facilitated Synthesis of α-Aminophosphonates



1a-p **2a-p**

Table-1: DMAP Facilitated Synthesis of α-Aminophosphonates

Entry	R_1	R_2	R_3	R_4	R_5	Reaction Time min	Yield %	M.P. ℃
2a	H	H	H	H	F	40	91	146–148
2b	CH_3	H	H	H	F	45	92	136–138
2c	H	CH_3	H	H	F	40	94	163–165
2d	H	H	CH_3	H	F	40	92	113–115
2e	OCH_3	H	H	H	F	45	91	153–155
2f	H	OCH_3	H	H	F	45	94	155–157
2g	OC_2H_5	H	H	H	F	40	92	160–162
2h	H	H	C_2H_5	H	F	40	90	159–161
2i	H	H	H	CH_3	H	45	91	139–141
2j	CH3	H	H	CH_3	H	40	92	104–106
2k	H	CH3	H	CH_3	H	45	90	143–145
2l	H	H	CH3	CH_3	H	40	92	160–162
2m	OCH3	H	H	CH_3	H	40	91	98–100
2n	H	OCH3	H	CH_3	H	45	92	126–128
2o	OC_2H_5	H	H	CH_3	H	40	91	146–148
2p	H	H	C_2H_5	CH_3	H	40	90	133–135

5. CONCLUSION:

In conclusion, a new methodology was developed for the synthesis of new α-aminophosphonate derivatives from 2-chloroquinoline-3-carbaldehydes and aniline using triethylphosphite and DMAP as catalyst. All the reactions were performed under mild reaction conditions, shorter reaction time and in quantitative yields (Table-I). The methodology developed will be of much use to combinatorial chemist.

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Stability constant of binary and ternary complexes of some medicinal ligand with metal ion in aqua-organic media

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ABSTRACT:
pH-metric studies were used for the simultaneous equilibrium of Nickel (II) and Copper (II) with Ranitidine as medicinal ligand and Glycine amino acid. In present study Glycine is used as primary ligand and Ranitidine as secondary ligand. Stability constant of these complexes were measured at 25 ± 0.5^0C *in aqua-organic media. Result of stability constant of complexes were calculated by using SCOGS software program.*
Key Words: *pH-metric studies, Medicinal ligand, aqua-organic media.*

1. INTRODUCTION:

pH-metric studies have been used from decades for the determination of stability constant. pH-meter is a very simple set-up of the instrument, so it is very frequently used technique. The present study deals with the stability constant of Ranitidine and Glycine with metal ion in aqua-organic media. Metal ions play very important role in the formation of stable complexes and also of interest to the analytical chemists and bio-inorganic researchers.

J. Bjerrum and Ido Leden's work enlightened the interest in the investigation of equilibrium of metal-chelates. Schwarzenback and Ackermann[1] found that the stability of chelates decreases with increase of the size of ring. In similar way the stability of complexes increases with basicity of the substituted ligands due to steric effect [2-4].

2. LITERATURE SURVEY:

Solvent mixtures are important reactions media. The solvent can effect on the chemical reactions in a pure solvent as well as the binary mixture is entirely different. Therefore, we decided to study the effect of the solvent on the stability of the metal-ligand complexes [5], using different acids with Cu (II) as metal ion.

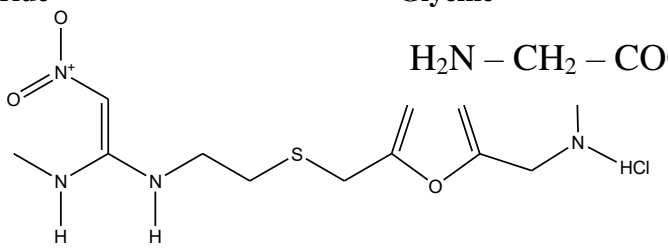
The metal ions Mn, Fe and Ni with amino acids Histidine, Glutamic acid, proline and L-aspartic acid using aqua-organic solvents [6].

For the present study, an attempt has been made for the determination of the stability constant of binary and ternary complexes of Ni (II) and Cu (II) with Ranitidine and Glycine.

3. MATERIAL AND METHOD:

All the chemicals used were of Sd-fine chemical ltd. The metal nitrates as well as Glycine and Ranitidine from Pharmaceuticals. The solution prepared for pH-metric titrations in glass distilled water and standardized. The titration was carried out at constant temperature, similarly the glasswares used are calibrated by standard method described in Vogel [7].

Ranitidine Hydrochloride **Glycine**



$H_2N - CH_2 - COOH$

Glycine was first amino acid isolated from a protein. It is important in the biosynthesis of amino acid serine, the co-enzyme glutathione, purines and heme a vital part of hemoglobin.

The ranitidine is in a class of medications called H_2 blockers. It decreases the amount of acid in stomach.

All the pH-metric titrations were carried out by LI – 612 ELICO INDIA. pH-meter (accuracy 0.01 unit), in an inert atmosphere, which was obtained by bubbling oxygen free nitrogen gas.

4. ANALYSIS, DISCUSSION:

The present study has great importance in biological processes [8]. As amino acid glycine is organic compound in which – NH_2 and – COOH group are present. Ranitidine has NO_2, – NH group, which play key role in stability of complexes.

The results of Protonation constants of ligand are given in table 1.

Table 1: Protonation constants of ligand

Ligand	Aqueous		50% ethanol	
	Log K_1^H	Log K_2^H	Log K_1^H	Log K_2^H
Glycine	5.31	7.26	4.69	3.66
Ranitidine	9.96	4.97	8.112	3.436

Table 2: Metal ligand stability constants

Metal ion	Aqueous ligands		50% ethanol	
	Glycine	Ranitidine	Glycine	Ranitidine
Ni (II)	4.32	5.030	7.281	4.718
Cu (II)	3.46	6.58	3.234	2.50

The metal-ligand stability constants of ligands with metal ions were obtained at 1:5:5 ratio at (25 ± 0.5^{0}c) and ionic strength maintained at 1.0 M $NaClO_4$ in aqua-organic media.

The stability constant of mixed ligand complexes of Ni(II) and Cu(II) with glycine as primary ligand and Ranitidine as secondary ligand was given in table no. 3.

The Δ log k values observed are positive, which give them extra stability.

Table 3: Stability constant of Mixed-ligand complexes

Metal ion	Mixed ligand system	log KMXY		Δ log k	
		Aqueous	50%	Aqueous	50%
Ni (II)	Glycine + Ranitidine	5.30	2.61	5.69	0.92
Cu (II)	Glycine + Ranitidine	6.00	0.56	7.13	2.32

The present work shows the stability constant for mixed-ligand complexes is positive range, and confirmed the complexation between the metal and ligand.

Zine [9] reported that ternary complexes of amino acids show positive log K values. Medicinal drug is a system of scientific knowledge and having many applications for improving human health treatment and prevention of diseases [10].

5. RECOMMENDATIONS:

The work is original and has not been submitted to any other journal at same time for publication.

6. CONCLUSION:

The stability constant of Glycine and Ranitidine shows positive logk value, that confirms the complexation between metal and ligand.

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Green Chemistry and Sustainable Development

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ABSTRACT:

The chemical industry plays a fundamental role in sustaining the world economy and underpinning future technologies and scientific advances in new materials, less toxic products, renewable energy sources, environmental protection, industrial processes with energy efficiency and renewable raw materials. Green Chemistry or Sustainable Chemistry aims, under greater societal expectations, for a sustainable global future of the planet Earth, for the design of chemical products that eliminate the use of hazardous substances for man and the environment. In this respect Green Chemistry fields initiated in the 1990s are rapidly developing technological innovations providing the most environmentally suitable solutions for a sustainable development of future science and technology. Green Chemistry offers enhanced chemical process economics, concomitant with a reduced environmental burden. Green Chemistry can be applied to design environmentally benign synthetic protocols, to produce life-saving medicines, environmentally friendly agrochemicals, new enzymes for biocatalytic chemical processes, innovative renewable energy sources, energy efficiency in chemical reactions, and innovative materials while minimizing environmental impact.

KEY WORDS: *Green chemistry, Benign Chemistry, Environment, Sustainable development.*

1. INTRODUCTION:

Green Chemistry is defined as invention, design, development and application of chemical products and processes to reduce or to eliminate the use and generation of substances hazardous to human health and environment [1]. The green chemistry revolution is providing an enormous number of challenges to those who practice chemistry in industry, education and research. With these challenges however, there are an equal number of opportunities to discover and apply new chemistry, to improve the economics of chemical manufacturing and to enhance the much-tarnished image of chemistry. Green chemistry is a philosophy and study of the design of products or substance.es that will not involve materials harmful to the environment. The ideal scenario is to virtually stop pollution before it can even begin through the use of non-pollutants. Green chemistry is a relatively new area of chemistry that emerged by the need to reduce the hazardous effect of chemicals and to reduce the amount of environmental pollution that chemicals have. All these will be discussed in this article.

The Green Chemistry revolution provides an enormous number of opportunity to discover and apply new synthetic approaches using alternative feedstock; Eco friendly reaction conditions, energy minimization and the design of less toxic and inherently safer chemicals. The origin and basis of Green Chemistry for achieving environmental and economic prosperity is inherent in a sustainable world. One important element of sustainable chemistry is commonly defined as the chemical research aiming at the optimization of chemical processes and products with respect to energy and material consumption, inherent safety, toxicity, environmental degradability, and so on [2].

While considering progress has been made in environmental chemistry, Green Chemistry, and the environmental assessment of chemical products, however, the societal aspect of sustainable chemistry remains to be fully recognized in all branches of chemical research. One prerequisite for this is the inclusion of sustainable chemistry into chemical education from the very beginning. Green Chemistry is the utilization of set of principles that reduces or eliminates the use or generation of hazardous substances in design, manufacture and application of chemical products. In practice, Green Chemistry is taken to cover a much broader range of issues than the definition covers [3].

As well as using and producing better chemicals with less waste, Green Chemistry also involves reducing other associated environmental impacts [3]., including reduction in the amount of energy used in chemical processes. Consequently, there have been efforts to achieve environmentally benign synthesis and various acts have been passed to control and treat pollution, in an endeavor to encourage industries and academics to devise novel technologies, processes and educational materials, discouraging the formation or use of hazardous substances. Green Chemistry is not different from traditional chemistry in as much as it embraces the same creativity and innovation than has always been central to classical chemistry. However, there lies a difference in that historically synthetic chemists have not been seen to rank the environment very high in their priorities. But with the increase in environmental consciousness throughout the world, there is a challenge for chemists to develop new products, processes and services that achieve necessary social, economic and environmental objectives [4].

Since the types of chemicals and the types of transformations are much varied, so are the Green Chemistry solutions that have been proposed. Developed 'The twelve Principles of Green Chemistry' that serve as guidelines for practicing chemists in developing and assessing how green a synthesis, compound, process or technology is [5].

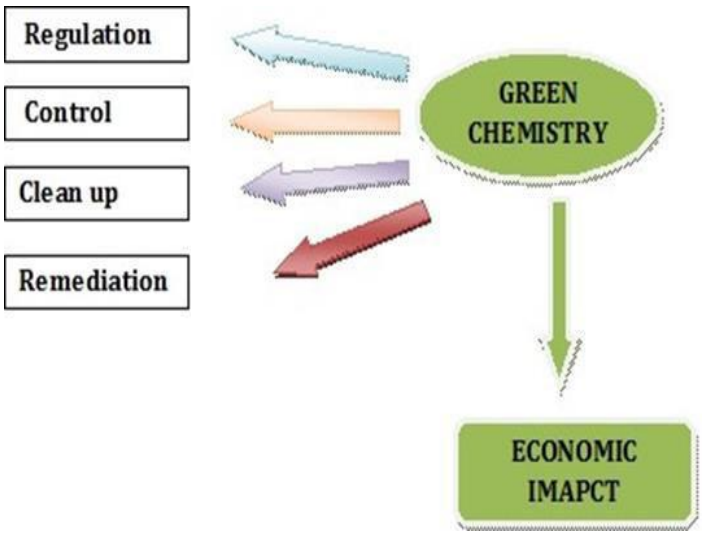

Fig. 1 Green chemistry scenario

2. HISTORY OF GREEN CHEMISTRY:

The term green chemistry was first used in 1991 by P.T. Anastas in a special program launched by the US Environmental Protection Agency (EPA) to implement sustainable development in chemistry and chemical technology by industry, academia and government. In 1995 the annual US Presidential Green Chemistry Challenge was announced. Similar awards were soon established in European countries. In 1996 the Working Party on Green Chemistry was created, acting within the framework of International Union of Applied and Pure Chemistry. One year later, the Green Chemistry Institute (GCI) was formed with chapters in 20 countries to facilitate contact between governmental agencies and industrial corporations with universities and research institutes to design and implement new technologies. The first conference highlighting green chemistry was held in Washington in 1997. Since that time other similar scientific conferences have soon held on a regular basis. The first books and journals on the subject of green chemistry were introduced in the 1990s, including the Journal of Clean Processes and Products (Springer-Verlag) and Green Chemistry, sponsored by the Royal Society of Chemistry. Other journals, such as Environmental Science and Technology and the Journal of Chemical Education, have devoted sections to green chemistry.

3. UNDERSTAND THE ORIGINS OF GREEN CHEMISTRY:

It is a modern science of chemistry that deals with the application of environmentally friendly chemical compounds in the various areas of our life such as industrial uses and many others. This area of chemistry had been developed by the need to avoid chemical hazards that organic and inorganic compounds had on the body of humans and animals. Most chemical compounds whether they are naturally made or are synthesized in the laboratory have negative effects on the human body although they are beneficial on a commercial basis. Especially notable are organic compounds which can easily penetrate the hydrophobic skin layer and enter the body. There it can exert an effect by binding to macromolecules in the body and alter their structure or interfere with their normal metabolism [6].

4. CONCEPTS OF GREEN CHEMISTRY:

The concept of green chemistry incorporates a new approach to the synthesis, processing and application of chemical substances in such manner as to reduce threats to health and environment. This new approach is also known as:

- Environmentally benign chemistry
- Clean chemistry
- Atom economy
- Benign-by-design chemistry

Green Chemistry or environmentally benign chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Green chemistry was developed by virtue of the need to overcome this hazardous effect that toxic compounds exert on the body. This relatively new area of chemistry uses water as the medium of chemical reactions that are done in the laboratory. Chemical reactions are usually done in a medium that is called solvent. An exception is reactions that take place in the gas phase where there is no need for medium there. Sometimes chemical reactions are done in a neat fashion. Namely, the reacting compounds are mixed and reacted together with the need for a solvent. This is one of the methods that are used in green chemistry to avoid pollution and the hazardous effect of the volatile solvent. As a chemical philosophy, green chemistry applies to organic chemistry, inorganic chemistry, biochemistry, analytical chemistry and physical chemistry to minimize west, utilize renewable resources. [6-11].

5. GLOBAL RECOGNITION OF GREEN CHEMISTRY:

AUSTRALIA: The Royal Australian Chemical Institute (RACI) presents Australia's Green Chemistry Challenge Awards;
CANADA: The Canadian Green Chemistry Medal is an annual award given to any individual or group for promotion and development of green chemistry;
ITALY: Green Chemistry activities in Italy Centre on interuniversity consortium known as INCA. In 1999, INCA has given three awards annually to industry for applications of green chemistry;
JAPAN: In Japan, The Green & Sustainable Chemistry Network (GSCN), formed in 1999, is an organization consisting of representatives from chemical manufacturers and researcher;
UK: In the United Kingdom, the Crystal Faraday Partnership, a non-profit group founded in 2001, awards businesses annually for incorporation of green chemistry;
USA: United States Environmental Protection Agency (EPA);
NOBEL PRIZE: The Nobel Prize Committee recognized the importance of green chemistry in 2005 by awarding Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock the Nobel Prize for Chemistry for "the development of the metathesis method in organic synthesis."

6. THE BASIC PRINCIPLES OF GREEN CHEMISTRY:

Green Chemistry is commonly presented as a set of twelve principles proposed by Anastas and Warner 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 has been created.
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 methods 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 effect their desired function while minimizing toxicity.
Safer Solvents and Auxiliaries
The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
Design for Energy Efficiency
Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
Use of Renewable Feedstocks
A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
Reduce Derivatives
Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
Catalysis
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
Design for Degradation
Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
Real-time analysis for Pollution Prevention
Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
Inherently Safer Chemistry for Accident Prevention
Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

7. INDUSTRIAL INTEREST IN GREEN CHEMISTRY:

Many forward-looking companies are embracing Green Chemistry, not only to protect the environment and to create good public relations, but also because it is often beneficial to the bottom line it is also estimated to cost US industries between $ 100 and $ 150 billion per year to comply with environmental regulations. In addition, cleaning up hazardous waste sites will cost hundreds of billions of dollars. In many companies, the cost of dealing with environmental regulations often exceeds their expenditure for research. Larger companies budget close to $ 1 billion per year for environmental compliance. If a company can significantly reduce this expenditure, then these funds can be spent in more productive areas and result in an improved bottom line. Thus, Green Chemistry (pollution prevention) is not only good for the environment but also for industry [12].

8. GREEN CHEMISTRY IN EDUCATION:

Convincing chemists to think in an environmentally friendly manner begins with education. The idea of including Green Chemistry in chemistry education was first put forward in 1994. Few Green chemistry textbooks have also been published [13]. Graduates, post graduates teachers and researchers will find these books of immense use. Both Environmental Protection Agency (EPA) and American Chemical Agency (ACS) have recognized the importance of bringing Green Chemistry to the class room and the laboratory. Together they have launched a significant campaign to develop Green Chemistry educational materials and to encourage the 'greening' of the chemistry curriculum[1]. Student involvement in Green Chemistry principles and practices is essential to the integration the environmentally benign technologies in academia and industry. ACS Student Affiliate Chapters may be recognized as "green" chapters by engaging in at least three Green Chemistry activities during the academic year. Suggestions for these activities include: Hosting a Green Chemistry speaker

- Organizing an interdisciplinary Green Chemistry workshop on campus.
- Working with a local company on a Green Chemistry project.
- Developing a Green Chemistry activity with a local school.
- Converting a current laboratory experiment into a greener one.
- Organizing a Green Chemistry poster sessions on campus.
- Distributing a Green Chemistry Newsletter to the local community.
- Designing a green Chemistry web page.

9. PROGRESS IN GREEN CHEMISTRY:

Over the past decade, green chemistry has convincingly demonstrated how fundamental scientific methodologies can be devised and applied to protect human health and the environment 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, biosorption, 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 dimethylcarbonate (DMC) production DMC is a versatile and environmentally innocuous material for the chemical industry. 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:

$COCl_2 + 2CH_3OH \rightarrow CH_3OCOOCH_3$ (DMC) + 2HCl

Alternative route for the production of DMC:

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

$2CuCl + 2CH_3OH + 1/2O_2 \rightarrow 2Cu(OCH_3)Cl + H_2O$

$2Cu(OCH_3)Cl + CO \rightarrow 2CuCl + CH_3OCOOCH_3$

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.

Extraction of gold:

This can involve numerous ferrous and sulphur oxidizing bacteria, such as Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans (also referred to as Thiobacillus). For example, bacteria catalyse the breakdown of the mineral arsenopyrite (FeAsS) by oxidising the sulphur and metal (in this case arsenic ions) to higher oxidation states whilst reducing dioxygen by H_2 and Fe3+. This allows the soluble products to dissolve.

$FeAsS(s) \rightarrow Fe^{2+}(aq) + As^{3+}(aq) + S^{6+}(aq)$

This process occurs at the cell membrane of the bacteria. The electrons pass into the cells and are used in biochemical processes to produce energy for the bacteria to reduce oxygen molecules to water. In stage 2, bacteria oxidise Fe^{2+} to Fe^{3+} (whilst reducing O_2).

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

They then oxidise the metal to a higher positive oxidation state. With the electrons gained, they reduce Fe^{3+} to Fe^{2+} to continue the cycle. The gold is now separated from the ore and in solution.

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°C, 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.[14].

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 waste water.

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. [15]. 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 tbutyl ether (MTBE) to the petrol pool. MTBE has high octane and by use of electric vehicles powered by fuel cells.

10. GREEN CHEMISTRY IN DAY-TO-DAY LIFE:

Biodegradable Plastics:

Non-biodegradable plastics are making a giant heap of waste material on earth. Minnesota makes food containers from polylactic acid called as ingeo. Scientist at nature works converted corn starch into a resin that is just as strong as the rigid petroleum based plastic and is currently used for making containers such as water bottles, yogurt pots etc. BASF developed a compostable polyester film called Eco flux they are using for making fully biodegradable bags made from this film with cassava starch and calcium carbonate. Theses bags completely decompose into water, CO2 and biomass in industrial composting systems. Use of these bags in place of conventional plastics bags , the kitchen and yard waste will quickly vitiate in municipal corporation system[16].

Ecofriendly Paint:

Oil based 'alkyd 'paints give off large amount of volatile organic compounds (VOCs) as it dries and cures. These VOC's have many environmental effects. Procter & Gamble and Cork composites & polymers established a mixture of soya oil and sugar to be used in place of petroleum petrochemicals derived paints resins and solvents which reduced the hazardous volatiles by 50%. Chermpol MPS, paint formulation use these bio based sepose oils to replace petroleum based solvents and create paint which is safer to use. Sherwin William established water based acrylic alkyd paints from recycled soda bottle plastic (PET), acrylics and soya bean oil. These paints give performance benefits of alkyds and low VOC content of acrylics. In alone 2010 enough quantity of these paints were manufactured to eliminate 362,874Kg of VOC's [17-18].

Green Bleaching agents:

Conventionally during manufacturing of good quality white paper, lignin from wood used for it, is removed by placing small pieces of wood into a bath of sodium hydroxide and sodium sulphide followed by its reaction with chlorine. Chlorine during the process also reacts with aromatic rings of the lignin to form chlorinated dioxins and chlorinated furans. These compounds being carcinogens, cause health problems. Terrence Collins of cambegie mellon university developed a green bleaching agent which involves use of H_2O_2 as a bleaching agent in the presence of some activators such as TAML[19] which catalysis the fast conversion of H_2O_2 into hydroxyl radicals that cause bleaching. This bleaching agent breaks down lignin in a shorter time and at much lower temperature .It can be used in laundry and results in lesser use of water [20].

Putting out fires the green way:

The conventionally used chemical firefighting foams used worldwide discharge toxic substances into environment contaminating water and deleting ozone layer. A new Foam called pyro cool has now been invented to put out fires effectively without producing toxic substances as in other firefighting materials [21].

Green dry cleaning of clothes:

Percholoroethylene (perc) is the solvent most commonly used in dry cleaning clothes. Perc ($Cl_2C = CCl_2$) is suspected to be carcinogenic and it contaminates ground water on its disposal. A new technology known as micell technology is developed by Joseph De Simons [22], Timothy Remark and James Mc clain in which liquid carbon dioxide can be used as a safer solvent along with a surfactant to dry clean clothes. This method is now being used commercially by some dry cleaners. Dry cleaning machines have been modified for using this technology so carcinogen PERC is replaced by green solvent [15].

Turning turbid water clear in green way:

Conventionally, municipality and industrial waste water is made clear by the use of Alum. Alum is found to increase toxic ions in treated water which causes Alzheimer's disease. The tamarind seed kernel powder has been found as effective and economic agent to make waste water clear as alum.

Biofuels:

It can be obtained from biomass which may be obtained from sugar cane, corn, rapeseed, straw, wood, animal and agriculture residues. For example: Bio-diesel which is produced from oil or fat by a process called '' trans esterification'' when burnt in diesel engine with hydrocarbons is found to reduce the petroleum fuel consumption as well as the generation of toxic gaseous substances[23].

Lighter vehicles preparation, reduced costs and carbon dioxide emission:

The modern synthetic polyesters has been found to reduce the quantity of foam used in the seats of the car, decreasing its weight sufficiently which decreases the fuel consumption and carbon dioxide emission into atmosphere.

New Lighting technologies:

Organic light emitting diodes (OLEDS) an example of new lighting technologies produce more light with lower energy consumption.

Use of Unleaded petrol:

The higher the octane number better is the quality of petrol. Octane number of petrol these days is increased without addition of lead components such as tetra ethyl lead (TEL) .Unleaded petrol is obtained by adding methyl tertiary butyl ether (MTBE) which supplies oxygen of petrol and hence reducing the formation of per-oxy compounds [24].

Use of Nonpetroleum fuels

Power Alcohol:

When ethyl alcohol is used in an internal combustion engines, it is called '' power alcohol ''. It is mixed with Gasoline in the ratio of 4:1 in order to increase its octane number. As in India ethyl alcohol is prepared from molasses, a dark brown mother liquor residue left after the crystallization of sugar thus an enormous amount of residue is consumed and hence reduces the pollution [25].

Benzol:

It is obtained as side product during coal carbonization. It is also obtained from the fractional distillation of light oil. It is a mixture of benzene (70%), Toluene (18%) and Xylenes (6%) with some other hydrocarbons. It can be used as a component of motor fuels due to its high anti knocking value and hence it reduces the fuels consumption as well as generation of toxic pollutants.

11. CONCLUSION:

The expansion of Green Chemistry over the course of the past decade needs to increase at an accelerated pace if molecular science is to meet challenges of sustainability. It has been said that the revolution of one day becomes the new orthodoxy of the next Green Chemistry is applied and must involve the successful implementation of more environmentally friendly chemical processes and product design. Most importantly we need the relevant scientific, engineering, educational and other communities to work together for sustainable future through Green Chemistry.

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Role of dopant L-Methionine concentration in modifying optical properties of parent Zinc Thiourea Sulphate Nonlinear crystal

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ABSTRACT:

The recent investigation was aimed to explore the influence of varying concentration of amino acid L-methionine on decisive optical properties of zinc thiourea sulphate (ZTS) crystal. The traditional slow solvent evaporation technique has been adapted to grow L-methionine zinc thiourea sulphate (LM-ZTS) crystal at room temperature. The influence of 0.2 M% &0.3M % L- Methionine on optical transparency and optical constants of ZTS crystal in range of 200-900 nm has been ascertained by means of UV visible spectral analysis, to discuss the technological impetus of mixed crystal for optical devices. The optical study revealed that 0.2 M % LM-ZTS crystal has higher transmission with lower cut off wave length. The extinction coefficient, refractive index, reflectance and polarizability of 0.2 M % LM-ZTS found to belower than 0.3 M % LM-ZTS crystal. Also the direct band gap determined by the Tauck's plot method of 0.2 M % LM-ZTS is wider than 0.3 M % LM-ZTS. All these parameters show the usability of LM- ZTS crystal for various opto-electronic device applications.

KEYWORD: *Crystal growth, Excitation coefficient, Optical constant.*

1. INTRODUCTION:

In past decade many research groups have done extensive research on semi organic thiourea metal complexes. Among thiourea metal complex pure and doped zinc thiourea sulphate outstands as a potential candidate that seeks huge demand in technologies like high power lasers, opto-electronics, frequency conversion, high speed information processing [1-3]. Amino acid play a vital role in the field of NLO crystal as they exhibit natural chiral properties and crystallize in the non-Centro symmetric space group, which are an essential criteria for nonlinearoptical device applications. The enhancement in different characteristics properties of ZTS crystals has been evident from literature due to addition of L-cysteine, L-serine, Nd^{3+}, urea [4-7]. Thus in order to imitate foresaid desirable properties amino acid L-methionine is doped in different concentration in ZTS crystal by employing UV visible spectral analysis and its detail optical parameters to confirm its superiority for various opto-electronics applications.

2. EXPERIMENTAL PROCEDURE:

Zinc thiourea sulphate (ZTS) salt was synthesized by gradually dissolving merck made analytical reagent (AR) grade zinc sulphate and thiourea in double distilled water in the molar ratio of 1:3. The recrystallization of technique has been used to enhance the purity of ZTS salt. Amino acid L- methionine with 0.2 mole% and 0.3mole% was added into the super saturated solution of ZTS with constant stirring for 4 hours. The 0.2 mole% and 0.3mole% LM-ZTS solution was filtered using whatmans filter paper in a beaker and kept for slow evaporation at ambient temperature. The grown crystalsof 0.2 mole% and 0.3mole% LM-ZTS were obtained within a period of 20 days as shown in Fig.1.

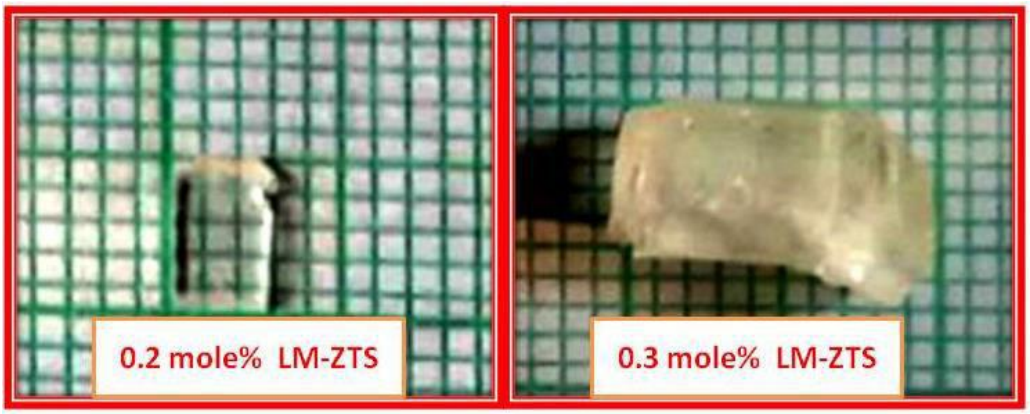


Fig.1. Photograph of 0.2 mole% and 0.3mole% LM-ZTS Crystals.

3. RESULT AND DISCUSSION:

UV-visible study

Shimadzu make UV-2450 spectro-photometer was used in the range of 200-900 nanometers to study the optical transparency and optical parameters of both 0.2mole% & 0.3mole%LM-ZTS crystal of thickness 2mm. The recorded transmittance spectra are shown in Fig.2 (a). In entire visible region of wavelength, 0.2mole% LM-ZTS exhibits higher transmittance and lower cut off wavelength as compared to 0.3mole% LM-ZTS crystal. Higher optical transmittance with lower cut off of 0.2mole% LM-ZTS wavelength is more suitable for NLO and UV-tunable laser device applications [8].

Band gap: The optical band gap of 0.2M% and 0.3M% has been evaluated from Tauc's plot using relation $(\alpha h\nu)^2=A(h\nu-E_g)$, where A is a constant, α is linear absorption coefficient, hν is incident photon energy and E_g is optical band gap. The optical band gap of 0.2M% & 0.3M% LM- ZTS crystal is found to be 3.73 eV&3.5 eV as shown in Fig 2(b). The lower absorption and wide optical band gap makes 0.2M% LM-ZTScrystal a potential candidate for electro optic applications [9].

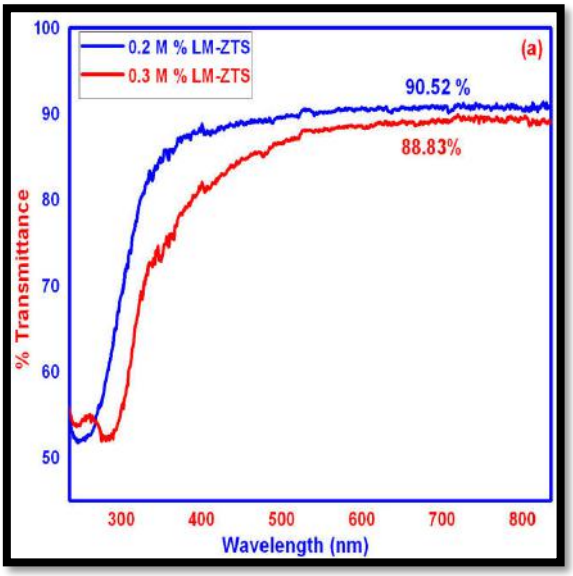


Fig.2(a) Transmittance spectra.

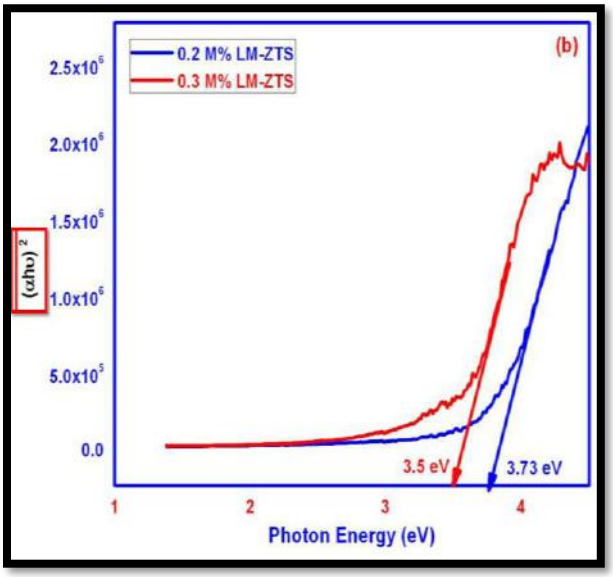


Fig.2(b) Band Gap by Tauck's plot.

Linear optical constants

The detailed study of optical constants helps to identify the most suitable crystal for opto-electronic device applications [10].The extinction coefficient of LM-ZTS crystals was observed to be decreasing with wavelength Fig 2(c) which confirms semi conducting nature of material.

The plot of polarizability vs wavelength is depicted in Fig 2(d).The low polarizability in entire UV region, 200-900 nm decreases the dielectric nature of material. The lower dielectric indicates better conversion efficiency. [11]. The extinction coefficient and polarizability of .2M% LM-ZTS crystal is lower than 0.3 M% LM-ZTS crystal, which confirms its superior conductivity than 0.3 M% LM-ZTS crystal.Lower refractive index and reflectance of 0.2M% LM-ZTS crystal than 0.3 M% LM-ZTS crystal as shown in Fig 2(e) and Fig 2(f), make it suitable for anti-reflection coating in solar thermal devices and optical device fabrications [12-13].

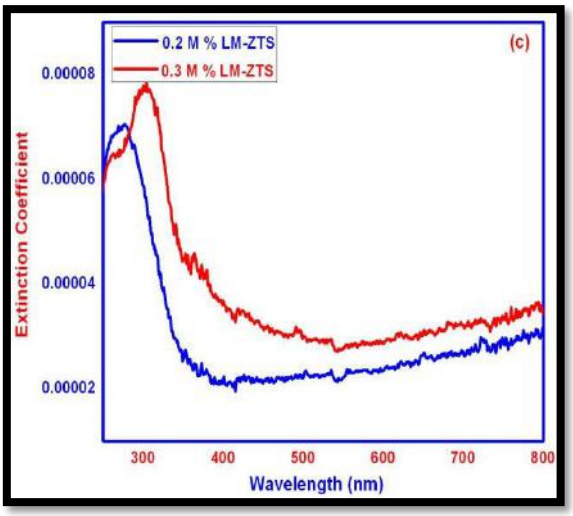


Fig.2. (c) Extinction Coefficient

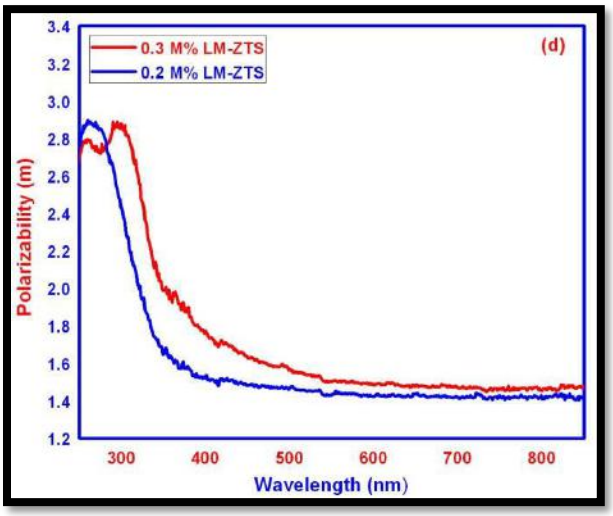
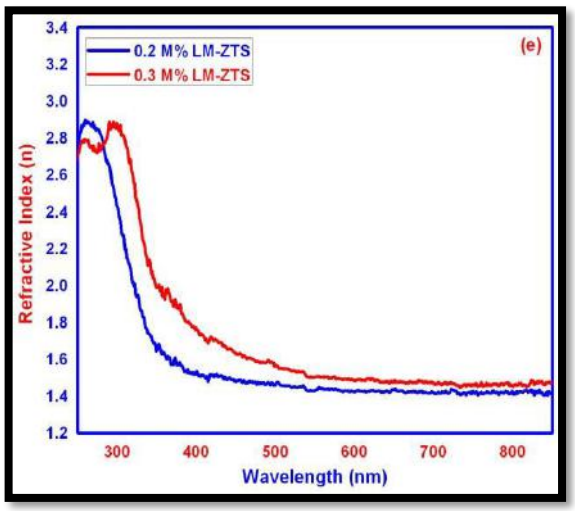


Fig.2. (d) Polarizability



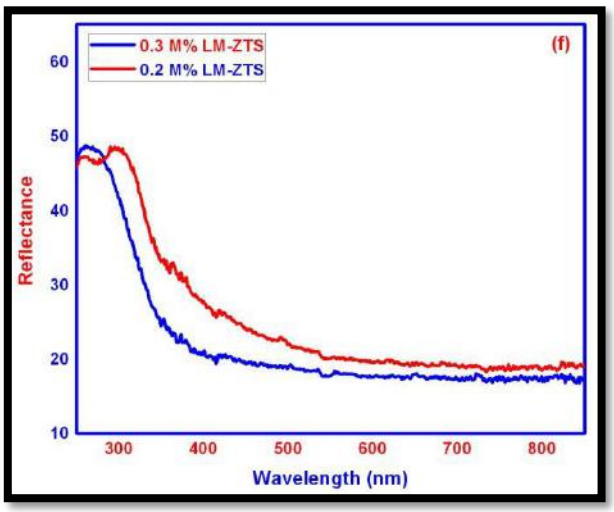


Fig.2 (e) Refractive Index vs. Wavelength **Fig.2. (f) Reflectance vs. Wavelength**

4. CONCLUSION:

In present investigation 0.2M% LM-ZTS and 0.3 M% LM-ZTS single crystalswere successfully grown by traditional slow solvent evaporation technique in order to explore the effect of concentration of amino acid L-methionine on optical properties of parent ZTS crystal. The UV-visible study shows that the presence of L-methionine enhanced the optical-transparency of ZTS crystal. In particular the 0.2M% concentration ofL-methionine has enhanced the optical transmittance of parent ZTS crystal than 0.3M% L-methionine.The optical band gap is found to be 3.73 eV for 0.2M%LM-ZTS &3.5 eV for 0.3 M%LM-ZTS crystal. The linear optical constants such as extinction coefficient, polarizability, refractive index, and reflectance confirmed the lower values for 0.2M%LM-ZTS than 0.3 M%LM-ZTS. Hence from the present investigation, it is thus confirmed that 0.2M% ZTS crystal has superior optical properties than0.3 M% LM-ZTS.

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Removal of Methyl Orange and Methyl red onto Activated Charcoal prepared from Used Black Tea

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ABSTRACT:

An adsorbent was prepared from used black tea (UBT) leave for adsorption of methyl orange (MO) and methyl red (MR) from aqueous solution. The tea leaves were used as precursors for the preparation of Activated charcoal (AC) in the present study. The prepared charcoal was activated by using H_2SO_4 activation method is self-generated atmosphere using an oven (temperature at 600^oC). The characteristic of AC was determined by Fourier transform infrared spectroscopy, (FTIR) and observed by Scanning electron microscopy (SEM). SEM indicated that the surface of AC became clean and the porous structure after activation. The adsorption equilibrium and kinetics of Methyl orange and Methyl red on activated charcoal were examined at 300K. The removal efficiency was tested with respect to adsorbent dose, P^H, time, concentration of adsorbent etc. Further experimental data was analyzed to study the Langmuir, Freundlich and Temkin adsorption isotherm. The kinetics of sorption was well correlated using the pseudo-first order rate equation and the value of correlation coefficient R^2 shows that activated carbon was found to be good adsorbent.

KEY WORDS: *Adsorption, Activated charcoal, Isotherm,Kinetic, Used black tea, Methyl orange, Methyl red.*

1. INTRODUCTION:

Dyes are widely used by textile industries to color their products. One of the major problems concerning textile waste waters is coloured effluent. This wastewater contains a variety of organic compounds and toxic substances, which are harmful to fish and other aquatic organism[1].

Wastewaters commonly contain moderate concentrations (10-200 mg L^{-1}) of dyestuffs, contributing significantly to the pollution of aquatic ecosystems. The reactive dyes, which represent the largest class of dyes used in textile processing industries, are almost azo compounds, *i.e*., molecules with one or several azo (N=N) bridges linking substituted aromatic structures. These dyes are designed to be chemically and photolytically stable. They exhibit a high resistance to microbial degradation and are highly persistent in natural environment. The release of these compounds into the environment is undesirable, not only for aesthetic reasons, but also because many azo dyes and their breakdown products are toxic and/or mutagenic for life [2,3.]

Conventionally, chemical coagulation/flocculation, ozonation, adsorption, oxidation, electrochemical treatment, filtration and floatation *etc*., are all means used for the removal of dyestuffs. Although they can remove dyes partially, their initial investment and operational costs are so high that they can be widely used in dyeing and finishing industries, especially in developing countries[4-6]. Among these processes, adsorption has been found to be superior to other techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitivity of toxic substances. Adsorption is the process by which solid adsorbent can attract a component in water to its surface and form an attachment via.a physical or chemical bond, thus removing the component from fluid phase (Demirbas et al.,2008). Activated carbon known for its unique properties including porous structure, high specific surface area and large sorption capacities (Dural et.al.2011). It is also an excellent adsorbent and can be widely used for variety of purposes such as purification and separation, in the abatement of hazardous contaminants, in municipal and industrial wastewater treatment, as a catalyst support in medicine, and in the recovery of valuable metals, etc. The most widely used adsorbent with great success because of its high adsorption capacity, but its use is limited due to its high cost, has led to a search for cheaper substitutes. Natural materials that are available in large quantities may have potential as inexpensive sorbents. Due to their low-cost, after these materials have been expended, they can be discarded without expensive regeneration. The abundance and availability of agricultural byproducts make them good sources of raw materials for activated carbons. Material such as rice bran, sugarcane bagasse pith, bagasse fly ash, pomogranate peel, coconutshell, *Ulva lactuca*and *Sargassum*, *Azadirachtaindica*leaf, hazelnut shell, Coirpith, orange peel, walnut shells, *etc*., as adsorbents for the removal of dyes from wastewaters[1,5-17].

In the present study activated carbon was prepared from low-cost adsorbent (used black tea leaves) as an adsorbent for the removal of methyl orange dye and methyl red from aqueous solution. The effect of different parameters such as P^H, contact time, adsorbent dose and initial dye concentration were investigated. The kinetic data and equilibrium data on batch adsorption studies were carried out to understand the adsorption process.

2. MATERIALS:

Methyl orange (MO) is a kind of the p-amino azobenzene(p-AAB) and Methyl red (2-(N, N-dimethyl-4-aminophenyl) azobenzene carboxylic acid), also called C.I Acid Red 2, an indicator dyes were used as adsorbate. However, the aqueous solution of MO is poisonous and irritating. All chemical used in the present research work were of analytical grade and purchased from Sigma Aldrich.

The stock solution of 1000ppm of MO and MR was prepared and subsequently their solution of desired concentration was prepared. Thus, removal of MO from aqueous solution is of great significance chemicals as used as model to study the adsorption capacity of bio sorbent. The structural formulas of the dyes are presented in the figure 1 and 2.

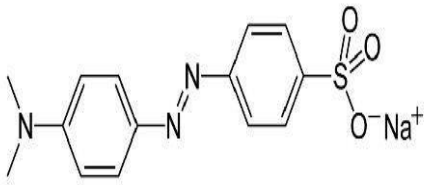

Fig1: Structure of Methyl Orange (MO)

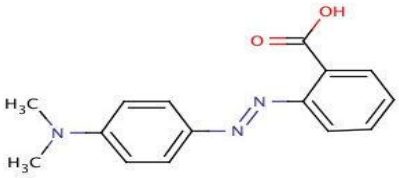

Fig. 2: Structure of Methyl red (MR)

Table 1: Some characteristic of the azo dyes Methyl orange and Methyl Red

Dye	Methyl orange	Methyl red
Chemical class	Anionic dye	Anionic dye
CAS number	547-58-0	493-52-7
Color Index number	13025	10303
Molecular formula	$C_{14}H_{14}N_3NaO_3S$	$C_{15}H_{15}N_3O_2$
Molecular weight	327.33g/mol	269.3g/mol

3. METHOD:

Preparation of activated charcoal. The raw material used was used black tea (UBT). UBT was washed with distilled water and dried. The dried tea leaves were soak with H_2SO_4 solution for two days. Then it was filtered till P^H was neutral then the residue dried. The dried mixture was kept into a furnace and heated to 600°C for 2 hours. After cooling the UBT was taken out and was used for further analysis.

3.2 Characterization of Activated charcoal: Infra-red spectroscopy provides qualitative information of characteristic functional groups on the surface of activated charcoal. The FTIR spectrum of activated charcoal prepared from UBT taken by "**FTIR – 4100 JASCO MODEL**" is shown in figure.

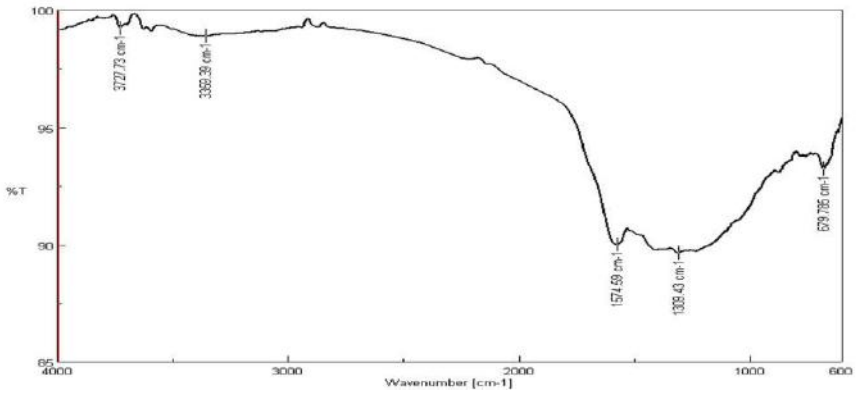

Fig: 3 FTIR of Activated Charcoal prepared from used UBT:

IR Frequency (cm^{-1})	Bond	Functional group
3727.73	O-H stretching vibrations	Alcohol, phenol
3359.39	N-H stretching vibrations	Amine
1574.59	N-O stretching	Nitro group
1309.43	C-H bending	Alkanes
679.785	Double bond C-H bending	Aromatic or Alkene

Table No. 2 Interpretation of spectra for activated charcoal prepared from UBT

SEM Observations:

The morphology of activated charcoal before and after activation is shown in the figure 4 and 5. The surface of the activated charcoal was rough, as shown in micrographs at low magnification. Under magnification, a porous structure was seen, which was beneficial for adsorption of dye. After activation, the porous structure was maintained, thus indicating that the initial structure of charcoal was not damaged in the activation process. The spherical pores with average size of nearly about 0.35µm.

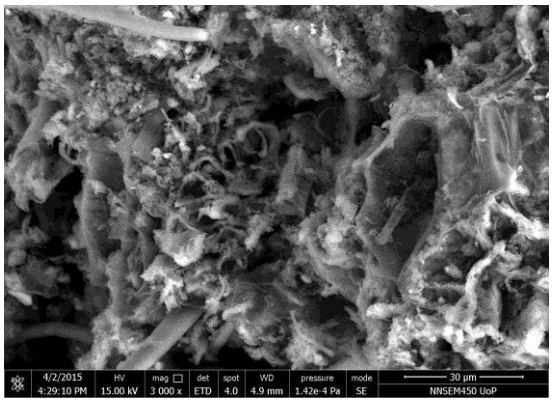

Fig.4 SEM image for activated charcoal

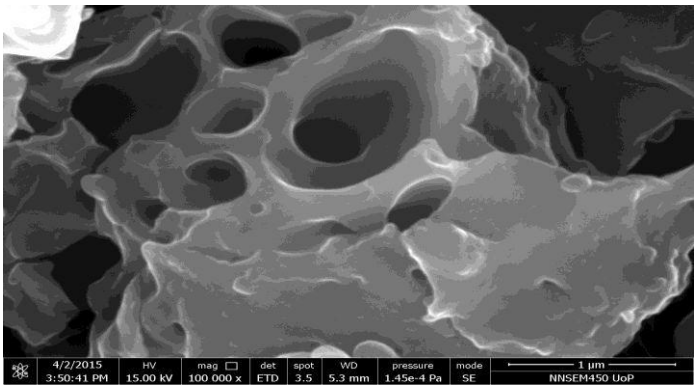

Fig.5 SEM image for Activated charcoal

Adsorbate Materials:

The stock solution of 1000ppm of MO and MR was prepared and subsequently their solutions of desired concentration were prepared. The maximum wavelength of dilute methyl red and methyl orange solutions were found using colorimetric (Equiptronicmodel EQ650A colorimeter).

Adsorption Equilibrium:

Adsorption equilibrium test were conducted for removal of methyl red and methyl orange in aqueous solution. Very dilute solutions of dyes were first used to prepare a standard calibration of dye samples. The effects of contact time, pH of aqueous dye solution, concentrations of methyl orange were studied. For each test, a known mass of activated charcoal was weighed into a 250ml Erlenmeyer flask and a predetermined volume of methyl red or methyl orange and solution of known concentration was added. The flask with its content, was then shaken at 120 rpm and dye sample withdrawn at regular time interval or after equilibrium as appropriate. The withdrawn sample was centrifuged at 500rpm for 5minute and residual dye in supernatant was determine by measuring its absorbance at maximum wavelength using colorimeter (Equiptronic model EQ650A colorimeter).

$$q_e = \frac{(C_0 - C_e)\,V}{W} \qquad (1)$$

$$\%R = \frac{(C_o - C_e)}{C_o}\,X\,100 \qquad (2)$$

Where Co and Ce (mg/l) are the initial and equilibrium concentration of methyl red or methyl orange respectively, V (L) is the volume of the dye, W(g) mass of activated charcoal used.

4. RESULTS AND DSCUSSION:

Effect of contact time of Methyl red and methyl orange dye on AC adsorption:

The effect of contact time of methyl red and methyl orange on activated charcoal adsorption capacity significantly increased from 20 to 120 minutes adsorption equilibrium was reached. The initial high adsorption rate may have been due to high driving force accelerating molecules to the surface of activating charcoal and interacting with numerous active sites. The decrease in the adsorption may be attributed to decreased number of active adsorption site and long-range diffusion effect of molecules. The equilibrium adsorption capacity was reached up to 2 hours.

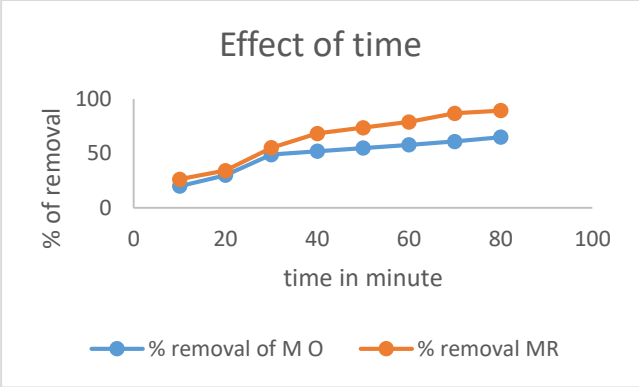

Fig 6 Effect of time on Methyl orange and Methyl red removal efficiency using UBT as an adsorbent

Effect of Initial P^H of Methyl red and methyl orange dye on AC adsorption:

The effect of P^H values on the adsorption capacity of methyl red (MR) and methyl orange (MO) on activated charcoal was shown in fig.7.when the P^H value of Methyl red and methyl orange solution increased from 2 to 10, At P^H =4 the adsorption capacity of Methyl red onto activated charcoal and the removal rate is 66.0%.and for methyl orange is at P^H = 9, % removal of methyl orange is 60%.

The effect of P^H values on the adsorption capacity of MR and MO on activated charcoal were shown in fig. 7.

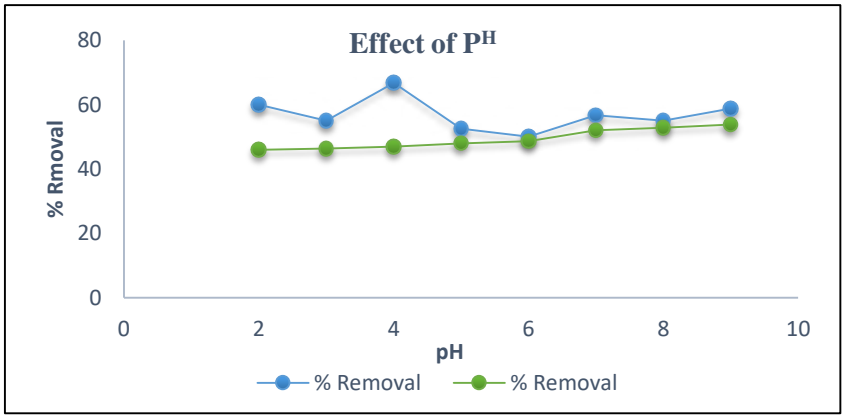

Fig 7: Effect of P^H for MO (orange line) and MR (Blue line) dye removal efficiency using UBT as an adsorbent

Effect of adsorbent dose for methyl red and methyl orange dye adsorption:

To optimize the adsorbent dose for methyl red and methyl orange adsorption from the aqueous solution. Adsorption was carried out with different sorbent dosages. The dose of adsorbent was varied from 0.1 to 1.5g per 100ml dye solution at concentration 100mg/l. The amount of methyl red and methyl orange dye adsorbed by different masses of adsorbent is presented in the fig.8. The percentage removal of MO (orange line) and MR (Blue) increased with increase in dose of adsorbent. This may be due the increase in availability of surface-active sites resulting from the increased dose and conglomeration of adsorbent.

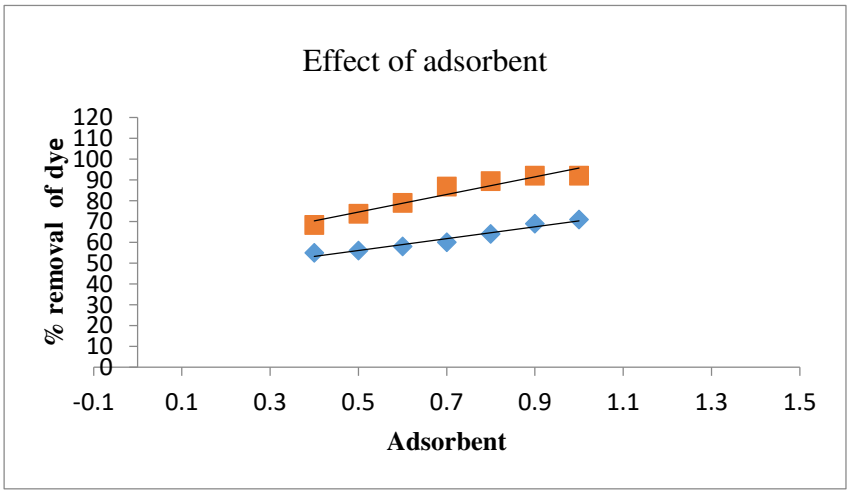

Fig.8: Effect of adsorbent for MO (orange) and MR (Blue) dye removal efficiency Using on prepared activated charcoal of UBT as an adsorbent

Adsorption equilibrium study:

Equilibrium data, commonly known as adsorption isotherms, are basic requirement for the design of adsorption systems. To discover the adsorption capacity of activated carbon prepared from tea leaves, the experimental data points were fitted to Langmuir and Freundlich isotherm equation 5and 6and the constant parameter of these equations were calculated (Fig 9 and 10.).

Langmuir isotherm

The Langmuir equation relates to the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature. This model assumes **monolayer** adsorption, where adsorption can occur at definite sites. The Langmuir equation can be written in the following form (Zhang et.al.2009; Chiou and Li2002; Langmuir1918):

$$q_e = \frac{q_m K_L C_e}{\frac{1}{KL} + C_e} \qquad (3)$$

The equation is often written as

$$\frac{c_e}{q_e} = \frac{1}{q_m} K_L + \frac{C_e}{q_m} \qquad (4)$$

Where, Ce (mg L^{-1}) is the equilibrium concentrations of methyl orange and methyl red (mg/L), q_e, the amount of adsorbate per unit mass of adsorbent (mg g^{-1}), $K_L$is the Langmuir constant (Lmg^{-1}) and q_m is the amount of adsorption corresponding to maximum adsorption capacity (mg g^{-1}). The value of q_m is recognized as the adsorption capacity, which is commonly a measure of adsorption ability of an adsorbent. When Ce/q_e was plotted against Ce straight line with slope $1/q_m$ was obtained (Fig.9 and Fig 10) indicating that adsorption of methyl orange and methyl red on activated carbon produced from used tea leaves follow the Langmuir isotherm. The values of q_m and K_L are given in the table 4.

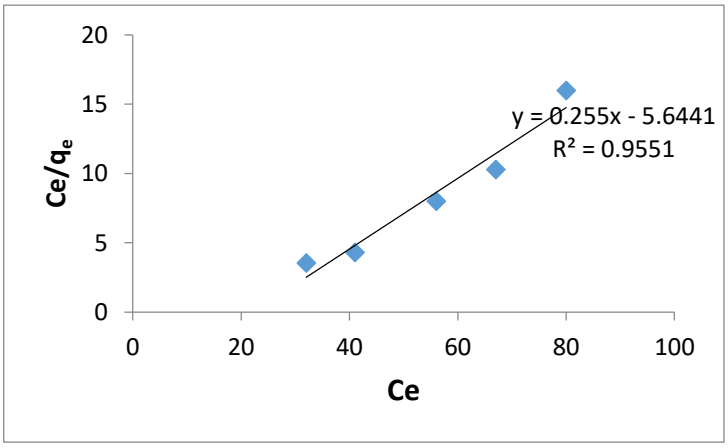

Fig 9: Langmuir isotherm plot for Methyl red dye adsorption on prepared activated charcoal of UBT

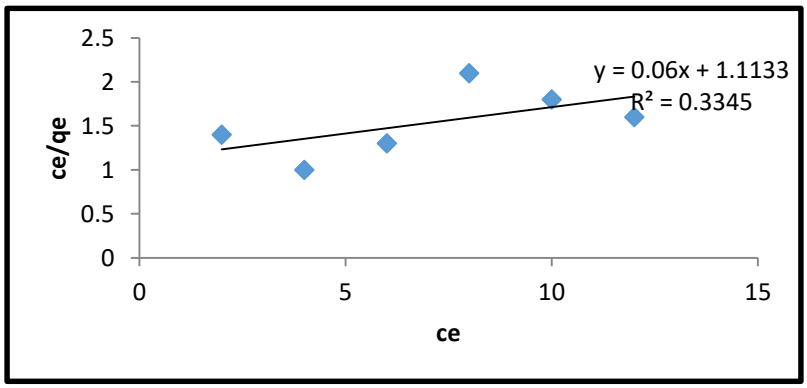

Fig.10. Langmuir isotherm plot for Methyl orange dye adsorption on prepared activated charcoal of UBT

Freundlich Adsorption Isotherm:

The Freundlich equation was developed mainly to allow for an empirical account of the variation in adsorption heat with concentration of an adsorbate (vapor or solute) on an energetically heterogeneous surface.

$$log q_e = log K_f + {}^{1}/_{n} log C_e \qquad (5)$$

Here q_e is the mass of adsorbate adsorbed per unit mass of adsorbent (mg g $^{-1}$), C_e is the equilibrium concentration of adsorbate (mg L $^{-1}$) for methyl red and methyl orange . K_f indicates adsorption capacity and n an intensity factor of the adsorption process, which varies with the heterogeneity of the adsorbent. The adsorption is more favourable when 1/n is greater. The fractional values of 1/n ranged between 0 and 1.

The value of 1/n and the constants K_f were calculated from the intercept and slope of the plot of logq_e vs.logC_e. Figure 12 shows the linear plot of Freundlich isotherm for adsorption lies between 0 and 1 is a degree of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero.

The calculated parameters are shown in Table 3.

The experimental data were used for Langmuir model, Freundlich model and Temkin model corresponding to monolayer coverage of the binding sites availed in the adsorbent[2].

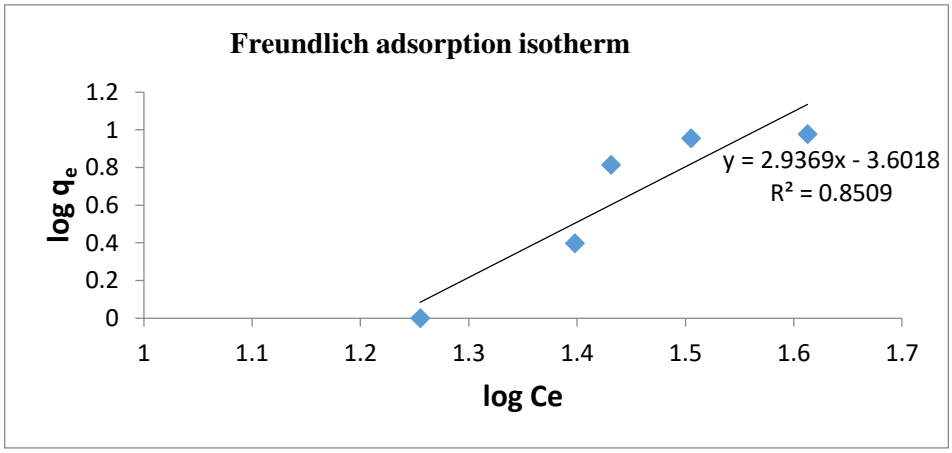

Fig. 11 Freundlich isotherm for Methyl red dye adsorption on prepared activated charcoal of UBT

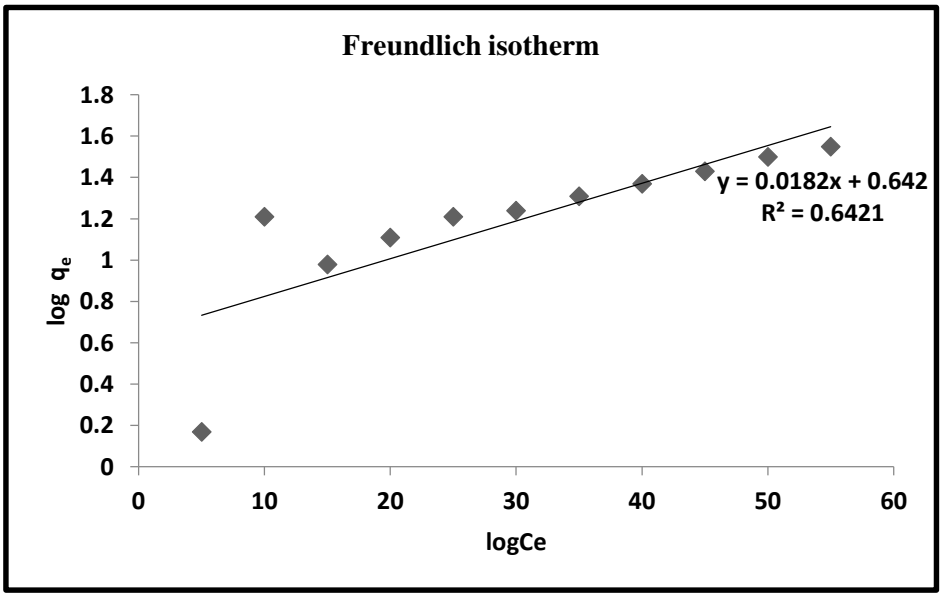

Fig .12 Freundlich isotherm for Methyl orange dye adsorption On prepared activated charcoal of UBT

Temkin isotherm:

$$q_e = B \log K_t + B \log C_e \qquad (6)$$

Where B =RT/b represent the heat of adsorption,T is the absolute temperature (K), R is the universal gas constant (J K^{-1} mol^{-1}), 1/b indicates the adsorption potential of the adsorbent and k_t (L mg^{-1}) is the equilibrium binding constant corresponding to the maximum binding energy. The plot of q_e vs log C_e allows the determination of isotherm constants B (J mol^{-1}) and K_t (L mg^{-1}). (table.3).

The calculated value of heat of adsorption from the slope illustrated in Table 3, indicates that the adsorption of methyl red and methyl orange. On prepared activated carbon from used black tea leaves follows mechanism of chemisorption.

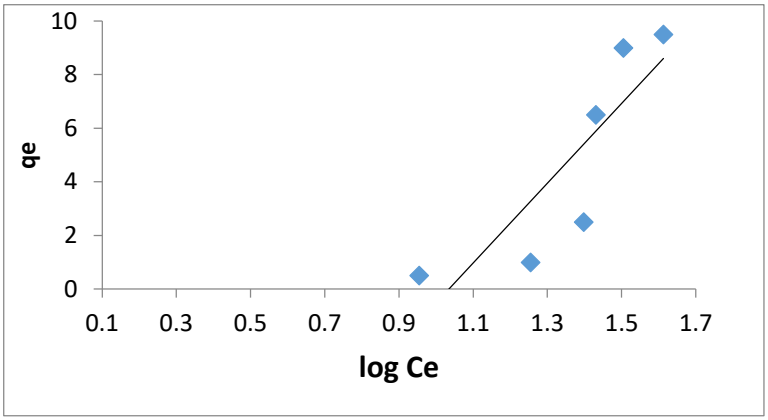

Fig.13 Temkin isotherm for methyl red dye adsorption on prepared activated charcoal of UBT

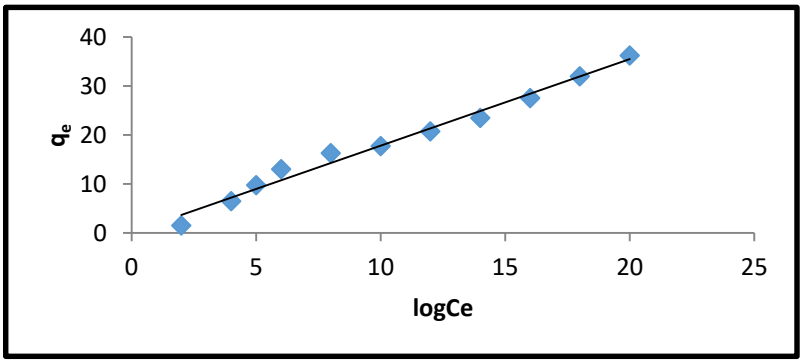

Fig.14 Temkin isotherm for methyl orange dye adsorption on prepared activated of UBT

Dye	Langmuir K_L	q_{max}	R^2	Freundlich K_F	N	R^2	Temkin B	K_t	R^2
Methyl orange	1.17	16.66	0.334	5.56	3.15	0.642	10.16	5.78	0.984
Methyl red	23.03	17.76	0.995	0.2157	1.17	0.850	6.68	0.4153	0.731

Table 3 Adsorption isotherm constant for Methyl red and ethyl orange at 300 K

Adsorption kinetics:

In the adsorption process,the behaviour was determined by the spread of the adsorbate to the adsorbent and by the adsorption rate of the adsorbate on the surface of the adsorbent . Two kinetics model are commonly used to describe the adsorption behaviour of dye molecules from aqueous solution on to the adsorbent: pseudo first order and pseudo second order kinetic models.

The pseudo first order kinetics model can be expressed as follows:

$$\ln(q_e - q_t) = lnq_e - K_1 t \qquad (7)$$

Where q_e is methyl orange or methyl red amount of adsorbed onto the unit weight of adsorbent at equilibrium (mgg^{-1}),

q_t is methyl orange or methyl red amount of adsorbed onto the unit weight of adsorbent at t time t (mg/g), and k_1 is the rate constant ($Lmin^{-1}$) of the pseudo first order kinetics model.

The correlation coefficients (R^2) of the pseudo first order model were more uniform and higher than those of the pseudo second order kinetic equation is

$$t/q_t = 1/K_2 q_e^2 + 1/q_e\ t \qquad (8)$$

Where K_2 (g/mg) is the rate constant of adsorption. By plotting a curve of t/q_e against t and k_2 can be determined. The correlation coefficient values at 100mg/lit concentration are lower than 0.90.

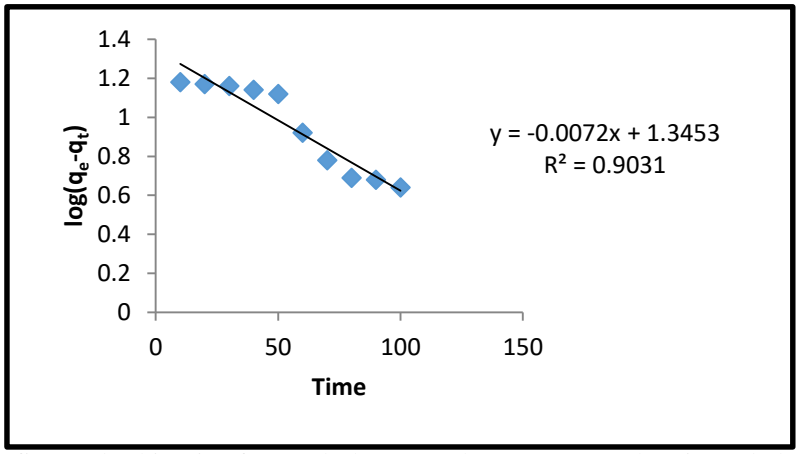

Fig15.Pseudo-first order kinetics for methyl orange dye on prepared activated charcoal of UBT

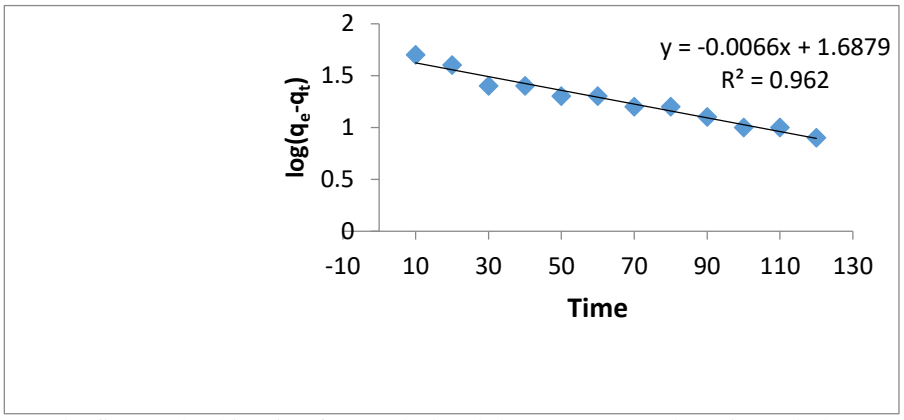

Fig16. Pseudo-first order kinetics for methyl red dye on prepared Activated charcoal of UBT

Table 4: Pseudo-first order kinetics for Methyl red and methyl orange at 300 K

Pseudo first order kinetics			
Dye	K_1	q_e	R^2
Methyl orange	0.0165816	22.15	0.9031.
Methyl red	0.0151998	48.74	0.962

Intraparticle diffusion:

The mechanism of sorption is either film diffusion controlled, or particle diffusion controlled.

$$q_t = k_{id}\ t^{1/2} + C \qquad (9)$$

Where k_{id} (mg/g) and C (mg/g) are the intra particle diffusion rate constant and intercept respectively, reflecting the significance of boundary layer or mass transfer effect.

The plot of q_t Vs $t^{1/2}$ is plotted and k_{id} was determined. The intraparticle diffusion was not only rate controlling step but also significant in the sorption process, especially at the initial reaction period (Hameed et.al.2009). If the diffusion mechanism was controlled by intraparticle diffusion, then the intercept C should cross the origin.

As per Weber-Morris model intercepts for MO and MR are nonzero i.e., not crossing the origin; thus, it showed that intraparticle diffusion was not rate limiting.

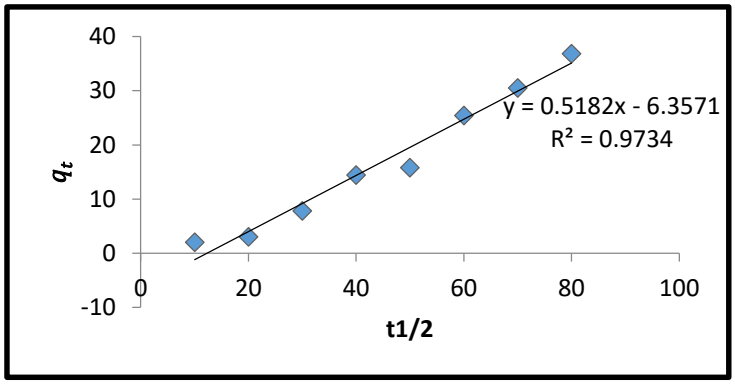

Fig.17 Intra particle diffusion for methyl orange dye on prepared activated charcoal of UBT

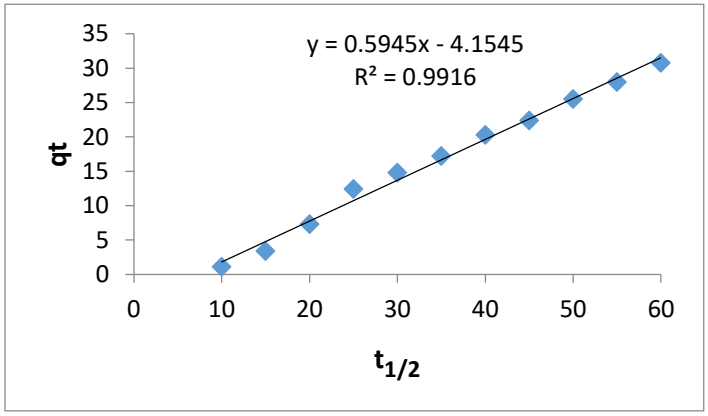

Fig.18 Intra particle diffusion for methyl red dye on prepared Activated charcoal of UBT

5. CONCLUSION:

In this work, the activated charcoal prepared from Used black tea had been used as an adsorbent for the removal reactive methyl red and methyl orange dye from aqueous solution. Adsorption behavior was describe as monolayer Langmuir type isotherm. The Langmuir isotherm for methyl red better fit (R^2=0.995) than for Methyl orange. While Temkin isotherm for methyl orange better fit (R^2=0.984) than methyl red (R^2=0.731) confirms chemisorption. Kinetic studies showed that adsorption of methyl red and methyl orange dyes on prepared activated charcoal follows pseudo-first order kinetic model. Intraparticle diffusion for methyl red and methyl orange dyes on prepared activated charcoal were studied.

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The Effect of Seed Size and Depth of Planting on Banana Plants Production

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ABSTRACT:

Investigating the performance of banana plant under planting holes dimensions could provide sustainable way of improving growth rate and high crop yield in agriculture. Bananas are cultivated specifically for both local consumption and commercially sold to the market. To achieve high yield of production some parameters have to be set correctly, these parameters are hole depth, spacing and seedling size. Small scale farmers in Murang'a County in Kenya are mostly involved in the production of banana as a staple food and thereafter sell the surplus in the local markets. One of the main problem being experienced by these farmers is that they lack information regarding these parameters which as result poor production due to their poor planting methods. Moreover, weak banana plant fails to itself properly due to heavy weight when it starts bearing fruits. A deep hole helps to reduce formation of high erosion activities which may stop banana plants toppling (falling) in the advent of wind. A field experiment was carried out to study the effect of depth and spacing on growth and yield of banana under general conditions. These experiments were conducted in a block of fields designed to have six treatments comprising of six different seedlings of different sizes. Three holes dug having length, depth and spacing (2mx3m, 1.8mx3.6m and 1.8mx1.8m) and then were replicated twice. Seedlings parameters like height were (273.27cm) and diameter of a stem (13.60) ware recorded the highest in S_1 (with spacing 50cm×50cm). This study determine the effect of hole dimensions and seedling size before planting. Growth rate, the number of fruits per plant is also recorded. Seedling sizes didn't show much significant in growth rate at early stages but planting pit dimensions showed significant differences on development of fruits. Holes dimensions influenced fruits length, weight and number of fruits per plant. Fruit weight and length increased with increased planting depth. Results obtained in this study show that seedling size does not show much effect on yields during planting at proper length and depth.

KEY WORDS: *Banana, small scale farmers, seedling, planting depth, fruit size and weight.*

1. INTRODUCTION:

Banana (*Musa paradisiaca* spp.) is the most commonly grown crop by small scale farmers in Muranga County in Kenya as one of the staple food for most communities around Mt Kenya. These farmers generally experience many problems concerning the production of banana fruits. One of the main problems is a weak stem that fail to hold the plant upright. Lack of knowledge in farmers especially those who prefer not to plant new seedlings every season may face weak stem banana plants. This results on weak and unhealthy plants that lead to low productions of banana fruits yields. In practical, one should dig deep and wide holes as possible. Planting holes should be at least 2 m deep by 2.5 m length. The deep hole helps to increase formation of high mat that reduce the risks for plants toppling (falling) in the advent of wind. Banana suckers should be placed and buried in a depth of about 10 cm. More loose soil is then added so that the sucker has about 15 cm above the junction of the pseudostem and a bit has the "eye" buried to a similar depth. Since most farmers have small pieces of land, a lot of care should be taken to achieve production of high yield. In most areas, one acre of banana should have about 850 – 1100 plants and the average production varies from 50 thousand fruit units for plantain and 80 thousand fruit units for banana per acre. Temperature and moisture affect seedling growth rate and production yield of banana. This happens when the seedlings are planted deeply in the soil. The appropriate planting depth varies due to many parameters like type of soil hardness. A deeper hole gives a moderate and an average temperature in the soil which is closely approximates normal air temperature. Use of proper holes dimensions during planting offers numerous benefits to the agricultural developments. Investigating the performance of banana plant under holes dimensions could provide sustainable way of improving growth rate and high crop yield in agriculture. Problems of poor planting techniques are difficult to avoid under low fertile soil conditions. Few studies have been conducted to investigate the weekly performances of banana plant in different conditions in Kenya. This is important because of the high population increase, which demand high crop yield for better sustainable livelihood, particularly among the rural people. Our objective was to investigate the performance of bananas plants from planting time, growth period to maturity period and yield performance. Different planting conditions managed in the same climate and same parameters are investigated on weekly basis.

Fig: 1. Banana plantation in kaharati maragua muranga county.

2. MATERIALS AND METHODS:

Site description

The experiment was conducted in one of the farm in Ann Ngugi's land, 5 km away from the town city of Maragua, Murang'a county Kenya; located within latitude 0.8551° S and longitude 37.1634° E. The topography of the site is semi hilly belonging to red soil.

Fig; 2. Banana spacing in maragua muranga

Experimental field management exercise

A field-crop experiment was designed to test the plant growth rate and yield performance of local banana seedlings under different planting parameters. Six holes which have been sustainably managed with same materials and environmental conditions. In the process of these seedlings management exercise, all holes were treated equally with same organic fertilizers. Six Soil holes of different dimensions were dug, two S1 (15 cm length x 20 cm depth), two S2 (40 cm length x 50 cm depth) and two S3 (50 cm length x 50 cm depth). Organic samples were supplied to these holes and about 1000 ml of water was poured for planting seedlings. Six seedlings of different sizes i.e. two small seedlingsT1 (15 cm), two medium size T2 (25 cm) and larger seedlings T3 (60 cm). 10,000 ml of water were poured twice every day (morning and evening) for two weeks. This is to enhance seedlings roots to establish as well decomposition of organic materials that added in the hole. This test lasted for a period of one year. The nine resultant samples were evaluated using the same red soil. Observations on banana plant parameters like plant height (cm), pseudostem girth (cm) and leaves size and length were recorded in each replication of all treatments.

Fig; 3. Mrs Ann Ngugi showing how a weak banana stems is supported.

Table 1: The summary of hole and seedlings physical parameters properties

Hole measurement dimensions parameters (cm)	seedlings measurement (cm)
S1 (15 cm length x 20 cm depth)	**T1** (15 cm height)
S2 (40 cm length x 50 cm depth)	**T2** (25 cm height)
S3 (60 cm length x 50 cm depth)	**T3** (60 cm height)
S4 (15 cm length x 20 cm depth)	**T4** (60 cm height)
S5 (40 cm length x 50 cm depth)	**T5** (60 cm height)
S6 (60 cm length x 50 cm depth)	**T6** (15 cm height)
S7 (15 cm length x 20 cm depth)	**T1** (25 cm height)
S8 (40 cm length x 50 cm depth)	**T2** (15 cm height)
S9 (60 cm length x 50 cm depth)	**T3** (25 cm height)

Field plants direct observation test

This involves regular visiting to the field and observes any changes to every seedling plants. The control soil unit was taken separately. However, a sample representative of each banana seedlings was measured on weekly basis. The parameters used in this measurement exercise are: stem height, stem diameter size, leaf width size, and leaf length for plant growth performances (Figure 1). While the number of fruits per plant, number of lines per bunch, and shapes of fruit in each plant were used for yield performances' assessment as designed (Figure 3). Besides, the measurements of plant parameters were made by means of tape measure, and data were verified consequently. Initially the intervals for all the measurements were taken after 1 week later changed to 5 weeks and 5 weeks.
(15/12/2019–05/01/2020), after 3 weeks (5/01/2020–26/01/2020), after 5 weeks (19/07/2020–24/08/2020) etc. The first Banana yield was finally harvested on 30 October, 2020 after 340-420 days (58 weeks). The banana bunch harvested was used to determine the number of lines per bunch as well as the number of fruits on each plant.

Fig: pit dimension

3. DISCUSSION:

The results of this finding have further confirm the better performance of plant growth and yield productivity under a maximum pit dimensions. Throughout the period of banana plant growth (over 400 days), the entire banana plants seem to have grown-up perfectly with few physical deformity. The performances of plant growth in term of stem height and leaf length show a remarkable attraction for using plant and animal organic materials under poor soil conditions. There was rapid improvement in term of stem height, stem diameter size, leaf length, leaf size and number of fruits per plant.

Future Perspective

In today's scenario it is almost impossible to avoid soil changes because of where you come from due to soil structures and compositions. Banana growing usage in our day-to-day life cannot be avoided. However, now it has been felt across the world that along with beneficial perspective they may also have benefits to human health endpoints. Therefore, it is required to overcome all the limitations of previous studies and to follow-up suitable standardised methodologies

4. CONCLUSION:

In conclusion, the present study confirms the assumption that banana plant is very likely to perform better under deep pit soil condition if all management requirements are provided in the right time. Banana Plants growth rate were reported positively well in first few months after planting. Performances in yield in all samples were equally confirmed positively. We conclude that well-spaced deep hole managed with organic materials provides a good performance atmosphere for banana plants growth in crop production. Likewise, the results suggested that banana grown under a hole (60 cm length x 50 cm depth) perform better in term of plant growth and yield production. This proved to be the best dimension for getting maximum yield.

ACKNOWLEDGEMENT

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Ammine Gas Monitoring: polypyrrole –nickel chloride doped films Sensor

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ABSTRACT:

In present study we have developed Polypyrrole –Nickel chloride doped thin films polymeric compositesl. These films were synthesized by chemical oxidative polymerization in aqueous acidic medium. This polymeric composites were characterized by U.V.-visible, FTIR spectroscopy, surface morphology by Scanning electron microscope (SEM).Their electrical conductivity was measured by four probe techniques. The linear Ohmic behaviour observed by I-V characteristics. Gas monitoring properties of the sensor was checked against hazardous gases like Trimethyl amine (TMA) and Ammonia .The sensor shows almost stable and repeatable response up to 10-800ppm.. The increase in sensitivity is discussed in terms of increased in resistivity, due to surface modification of dopant to improved electrical and environmental stability of sensor.

KEYWORDS*: polymer, polypyrrole, Nickel Chloride, Conducting polymer, Ammine gas and Gas sensor.*

1. INTRODUCTION:

The polymeric composites are arising as one of the most important materials in the 20th century, the utilization of polymers moves from primarily passive materials, for holding the dynamic materials with valuable electronic, optical, energy stockpiling, and mechanical properties. Inspite the fact that directing polymers are known as new materials in working of their properties, the main work portraying the blend of a directing polymer was distributed in the nineteenth century. In 1862, Henry Lethe by arranged polyaniline by anodic oxidation of aniline, which was conductive, and appeared electrochromic conduct. For over thirty years, formed natural polymers were known as the best applicants due to their one of kind electrical vehicle properties too as their possible utility in the arising innovation (1). Electrically conducting polymers are synthesized either by reduction or by oxydations réactions, which is called doping process, giving materials with electrical conductivities up to 105 S/cm.

Among the leading polymers, polypyrrole has attracted significant consideration because of its high conductivity, simple preparation, stability, and good mechanical and electrochemical properties. It shows a wide scope of surface conductivities ($10{-}3$ Scm$-1 < \sigma <$ 100Scm-1) contingent upon the usefulness and replacement example of the monomer and the nature of the counter ion or dopant. There are other potential application of polypyrrole, for example, chip-in-chip connector, microwave protecting, and erosion assurance (2). Aside from these, polypyrrole is widely utilized in sensor applications since they give steady and permeable network to the gas part and likewise encourages the e-move measure (3). Additionally, polypyrrole offers another class of materials in organic and biomedical applications including biosensors (4).

The present investigation deals with a study of the influence of nickel chloride dopant on synthesis of Polypyrrole doped thin films. These synthesized films were characterized by U.V.-visible, Fourier transform Infrared spectroscopy (FTIR), surface morphology by Scanning Electron Microscopy (SEM), electrical conductivity and I-V characteristics. The gas sensing behavior for monitoring of TMA and ammonia gas vapors at room temperature from 10-800ppm concentration.

2. METHOD AND MATERIALS:

Analytical-reagent-grade Pyrrole, nickel choride and anhydrous iron (III) chloride (AR-grade) were obtained and used in the present study. Pyrrole monomer was purified by distillation under reduced pressure and stored in dark at 10^{o}C. Each process was done with double distilled conductivity water. (qualigen fine–chem. India) were used.

Synthesis of Polypyrrole and Polypyrrole-Ni Composites-.

For chemical polymerisation of pyrrole, FeCl3 was used as an oxidant 1.5 mL of pyrrole having 1N solution was dissolved in 10 mL of Aqueous ferric chloride solution with doped with 5 ml of nickel chloride in ethanol and stirred for 10min was added drop wise to the solution of pyrrole. Nickel chloride was varied in, 0.5N,1N,1.5N and 2N, added to the polypyrrole solution. This reaction mixture was stirred for 3 hr with magnetic stirrer in order to disperse NiCl2 in the polymer solution and inserted glass plate to obtained coated uniform thin films. The obtained product was filtered and washed thoroughly with distilled water in order to remove the unreacted pyrrole and excess ferric chloride. The samples were vacuum-dried for 1 hr at 60–70Oc.

3. RESULTS& DISCUSSION:

UV-Visible spectra -UV-visible spectroscopy is a very sensitive tool for the study of Polypyrrole doped thin films protonation and more precisely for the elucidations of the dopant Nickel chloride into the thin films. UV-visible study selected those films, which have uniform, and good sensor response time. These sample films were dissolved in (DMSO) solvent, and then the UV-visible spectra recorded in the range 200-700 nm. The sample yields sharp peaks within 360-380nm and a broad band at 480-570nm wavelength ranges. In DMSO the sample, however exhibits broad peak around 610 nm indicating formation of emerladine base. Fig-1.

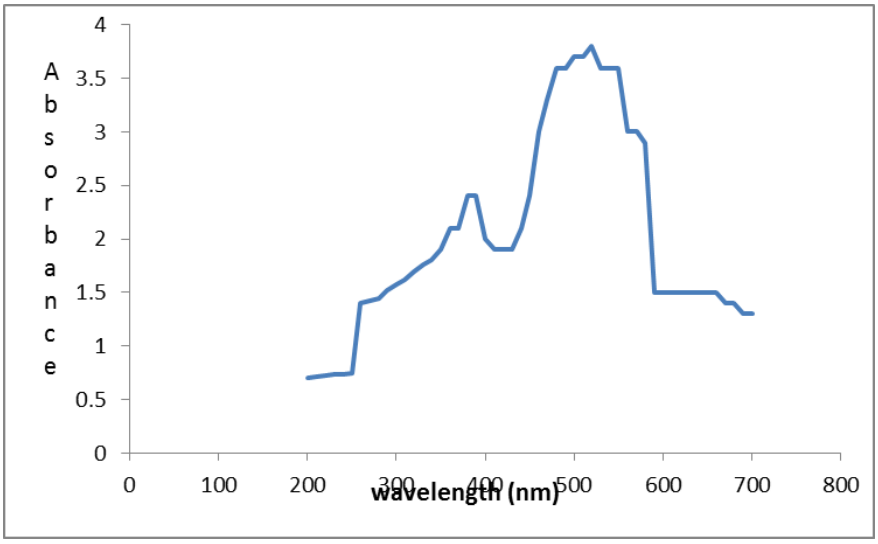

Fig-1.1UV-Visible spectra of Py-Ni doped films –

FTIR-spectra

The FTIR- spectra of doped Nickel Chloride in polypyrrole composites thin films were recorded in the range of 4000-400 cm-1 using DMSO as solvent The principal characteristics band occurrence indicates the type of functional group present in the polymer. The medium strong band observed at 3400 cm-1 suggests the presence of N-H stretch. The spectra shows the peak at 1660 cm-1, which is due the presence of C=C group of aromatic benzonids ring. The observed medium intensity band in the region 1410-1433 cm-1 suggests the presence of C-N stretch). Nickel Chloride in Pyrrole material (doublet) splits into triplets and shifts towards lower frequency at 1313 cm-1. leading to exposure of the hidden C-N+ group as (NH, +NH2, +NH=, C=N+) in Nickel Chloride in Pyrrole depends on the nature and percentage of doping which may effect the population of charge defect center (polaron and bipolaron) and ultimately the electrical conductivity. The C-O stretching vibrations in plane and out of plane, the bending vibration were observed at 1085cm-1 and 702 cm-1.

The entire characteristics of band confirm the presence of doped conducting Nickel Chloride in Pyrrole thin films in Fig-2.1

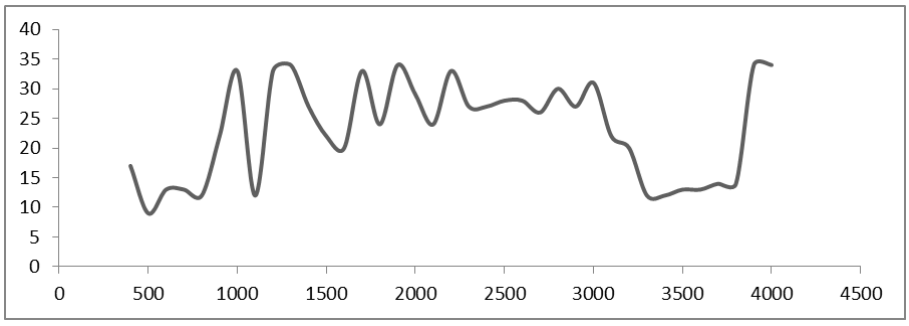

Fig 2.1 The FTIR spectra of 1) Py-Ni doped

SEM study

A typical SEM image of 0.5M nickel chloride doped polypyrrole films having uniform and good stability. This film is shown in fig-3. Therefore SEM images give first hand information about a molecular level combination of the components and possibility for application as gas sensors. This thin films surface morphology study indicates that the films have porous surface and uniform in nature, which is one of the essential conditions for gas sensors.

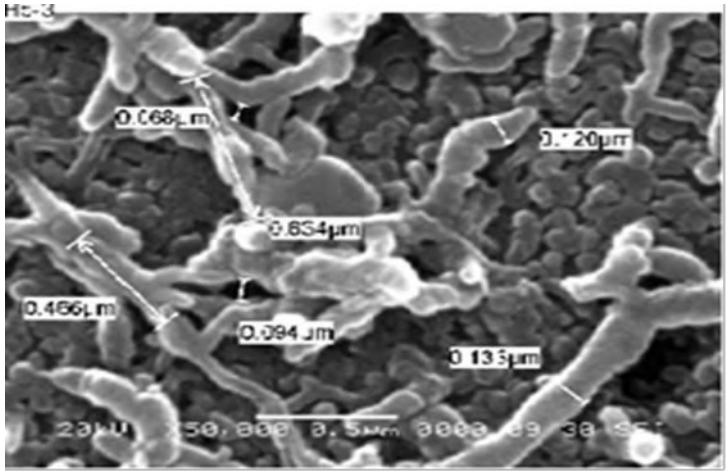

Fig.3.1 SEM of Py-Ni doped

I-V characteristics-

The electrical conductivity of the synthesized Nickel Chloride in polypyrrole films studied at room temperature by four probe indigenous developed computer controlled (I-V) system. It is observed that, with the increasing concentration level, the electrical conductivity of thin films gradually increases.

The current-voltage (I-V) characteristics of synthesized films were studied to ensure an Ohmic behavior of all thin films samples. A linear relationship of I-V curve is shown in fig-4.

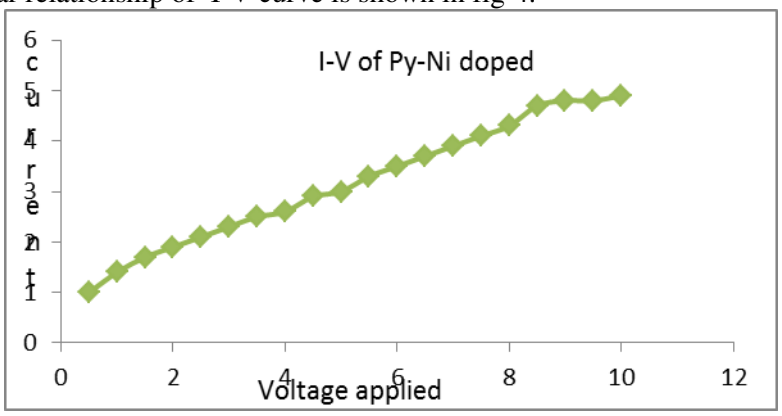

Fig-.4.1:I-V curve of Py-Ni doped

Magnetization- The magnetization (M) versus the applied magnetic field (H) for polypyrrole doped Nickel chloride nanoparticles. The value of saturation magnetization (Ms), remnant magnetization (M) and coercivity (Ho) for polypyrrole doped Nickel chloride were 6.43emu/g, 1.22emu/g.

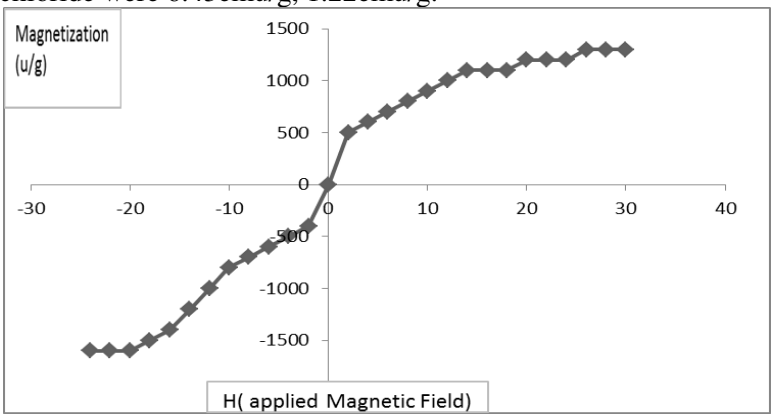

Fig-5.1: Magnetic hysteresis loops of polypyrrole doped Nickel chloride

TMA and ammonia Gas sensing behaviors-

The synthesized polypyrrole doped Nickel chloride thin films were studied for ammonia and TMA gas at room temperature (303k) by using indigenous developed computer controlled gas sensing system. Initially the films

were allowed to saturate for half an hour before exposing to ammonia & TMA gas. The film was first exposed for five minutes to predefined concentration of ammonia &TMA gas, and then it was exposed to air to recover initial resistance for five to seven minutes .The same process repeated for 10-800 ppm concentration for both gases. The change in resistance of the gas exposed and its recovery were measured. The barrier height increases when absorption of TMA and ammonia gas concentration in ppm increases. This change in resistance is found to be linearly increasing for this thin film.

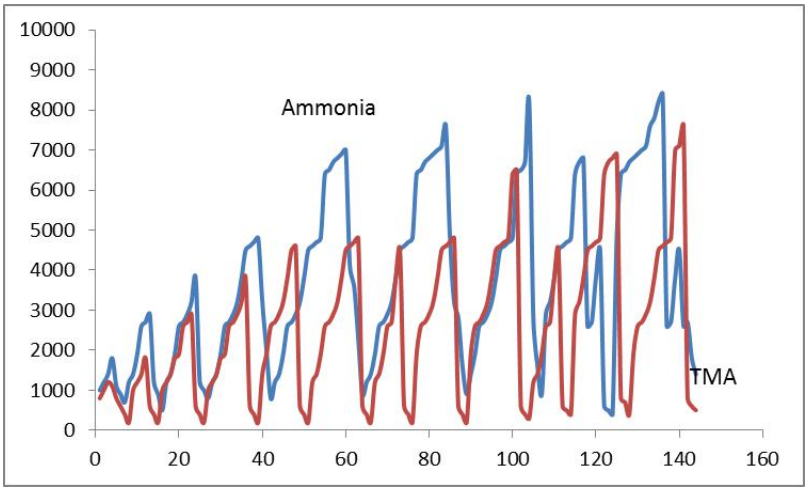

Fig-6.1: TMA and ammonia Gas Monitoring 10-800ppm

4. CONCLUSION:

This study describes the synthesis of Ppy-nickel chloride doped composite films using chemical bath deposition method and successful fabrication of chemiresistive ammine sensors based on Ppy-Ni composite films for ammine leakage detection at room temperature. Several characterization techniques such as FTIR and SEM analysis confirmed that Nickel were successfully incorporated into the on Ppy-Ni matrix. Effect of different concentration of nickel chloride on structural, electrical and gas sensing properties Ppy-Ni composite films The synthesis composite films with nickel chloride 3 doping showed highest conductivity with a value of 28.24 × 10-4 Scm−1 among all the other Ppy-Ni composites. The results obtained in the present study for 0.5N nickel chloride in Ppy-Ni composite films based for ammine as well as TMA gas sensors. This synthesis films were response at lower 10ppm level to higher 800 ppm concentration of ammine gases.

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LASER TRANSMITTER POWERED BY ARDUINO WITH DIFFERENT SENSORS USED FOR OPTICAL MEASUREMENT

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ABSTRACT:

This paper demonstrates the characteristics of laser transmitter powered by Arduino. The laser transmitter is used to transmit light beam on the object. The laser light ray is much focused and almost having no divergence over small distances. The Arduino powered Lasers KY-008 module can be used as emitting laser source for measurement in digital holography and many other optical applications. The design is novel, affordable and has good beam quality. Use any Ardunio with 5 Volts, can emit visible light, usually emit at a focused red dot having a 650nm beam. Do not generate enough heat to require special cooling devices. Because of these many advantages over other types of lasers, Lasers KY-008 module can be used for many applications in research like measurement in digital holography. This paper proposes the use of Arduino powered Lasers KY-008 module together with light detectors in optical measurement.

KEYWORDS: *Arduino Lasers KY-008 module, light sensor, light detector and optical applications.*

1. INTRODUCTION:

The single most expensive component required in the holography recording is the laser. Diode lasers are inexpensivewhen buying and easy to power. Physics labs in many colleges and high schools usually use Helium-neon lasersthat emit around 1mW output beam. These lasers are very expensive for any ordinary labs. They are expensive to purchase.A newGreen He-Ne Lasers - 543 nmgoes for about $1,800 to $2,950 compared with Lasers KY-008 module, which cost around $25.A Helium-neon Laser Power Supply for 1.5mW - 2.0mW AC cost around $350.00 while Lasers KY-008 module is a 5volts powered by Arduino. However, due to a low cost, many colleges and high school would go for Lasers KY-008 module in their labs. KY-008 which emit 650nm wavelength, 5V,it also emit 100mW,finally it emits a small intense focused beam of visible red light. The module can be used with an Arduino,Light Dependent Resistor and photo resistor module to perform basic remote signaling.Holography is a technique that creates and then records the light patterns that results from interference between two light beams, reference and object beams. Reference beam is propagated directly on the recording material while the object beam must first interact with the object material by either getting transmitted through or either gets reflected by the object material in the system. The light source for this technique is a laser beam which must have some characteristics like coherence length, good power stability, wavelength range.

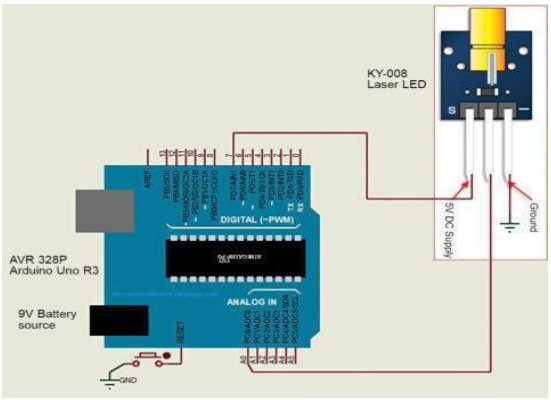

Fig:1. Lasers KY-008 module connected to Arduino

2. LITERATURE REVIEW:

Arun Anand [5], The Baroda university of engineering and Technology has successfully conducted several laser experiments in digital holography and digital tomography and many optical measurement using lasers. To date other organizations have also conducted many laser communication demonstrations worldwide and the time has come when Lasers KY-008 module should be integrated in the experiments systems. Karatina University has recently carried out the first experiment successful in optical measuring via Lasers KY-008 module. This paper presents recent activities on Lasers KY-008 module experiments in the colleges and high school labs for future generation.

2.1 Need of study

The project basically to encourage colleges and high schools to use Lasers KY-008 module for many optical experiments that require laser beam. It works on the principle of interference and distance measuring. If by any means the LASER light is interrupted the distance will be measured the object is more transmit more energy. The laser is a concentrated light source that puts out a straight beam of light of a single color.The LDR is sensitive to light and puts out a voltage when the laser light hits it. When the laser beam is interrupted and can't reach LDR, its voltage output changes, and eventually annealed using Arduino.

3. METHOLOGY:

KY-008 Laser Transmitter module

Two main uses for KY-008 laser module involve 'tripwire' detecting and using it as a pointer. Lasers are a great way to draw distances and limits as they shoot straight often at very long distances. Coupled with a photo resistor or specialized laser detecting module can be used to detect a breach in the path of the laser. The KY-008 Transmitter module emits a small dot-shaped, red laser beam which is almost collimating beam. The module is powered from microcontroller Arduino output pin which draws approximately 30mA to 40mA. Below figure shows KY-008 Laser transmitter module. It emits a beam consists of a 650nm red laser diode head and a resistor. The Operating voltage KY-008 Transmitter module is 5V and Output Power is 5mW. Working temperature is ranging from 10°C ~ 40°C [14°F to 104°F]. Dimensions are about 18.5mm x 15mm [0.728in x 0.591in]. It has three pins i.e. From left to right pin 1 is signal output, pin number 2 is +5 volts (DC), and pin 3 is GND. Theoretically it measures up to 1000 cm.

Fig:2. Lasers KY-008 module

Test code for KY-008 Laser transmitter module
Testing the Code for the Arduino KY-008 Laser Transmitter module

```
int blinkTimer = 500;
int pinNo = 10;
void setup ()
{
pinMode (pinNo, OUTPUT);
}
void loop ()
{
digitalWrite (pinNo, HIGH);
delay (blinkTimer);
digitalWrite (pinNo, LOW);
delay (blinkTimer);
}
//middle pin is +, right pin is -, and left pin is data

void setup ()
{
pinMode (13, OUTPUT); // define the digital output interface 13 feet
}
void loop () {
digitalWrite (13, HIGH); // open the laser head
delay (1000); // delay one second
digitalWrite (13, LOW); // turn off the laser head
delay (1000); // delay one second
```

Arduino Uno Board

Hardware

Arduino Uno microcontroller is based on the ATmega328, 32 KB flash memory. It is designed as a variety of microprocessors and controllers. It consists of 14 digital input/output pins, 6 analog inputs, a 16 MHz quartz crystal oscillators, a USB connection, a power jack as well as reset button. The Arduino Uno can control on an external supply from 6 to 20 volts but the recommended range is 7 to 12 volts because voltage regulator may overheat thus damaging Arduino Uno. The board can be programmed with Arduino Software (IDE).Some boards look a bit different from the one below, but most Arduinos have the majority of these components in common:

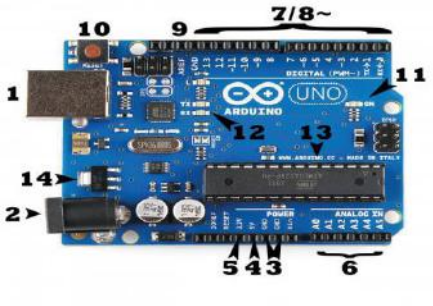

Fig:3. Arduino Board

SOFTWARE

Arduino IDE is open source software that is mainly used for writing and compiling the code into the Arduino Module. IDE stands for Integrated Development Environment, introduced by Arduino.cc. In this software code can be written in either C or java script. A program is written on the IDE Arduino is called a sketch. The main code, also known as a sketch, created on the IDE platform will ultimately generate a Hex File which is then transferred and uploaded in the controller on the board. The IDE environment mainly contains two basic parts: Editor and Compiler where former is used for writing the required code and later is used for compiling and uploading the code into the given Arduino Module. Arduino programs are divided into 3 parts.

Structure, Values and Functions

The Light Dependent Resistor

Light Dependent Resistor (LDR) is made from a piece of exposed semiconductor material such as Cadmium Sulphide. An LDR is a component that has a (variable) resistance that changes with the light intensity that falls upon it. This change its electrical resistance from several thousand Ohms in the dark to only a few hundred Ohms when light falls upon it by creating hole-electron pairs in the material. This allows it to be used in light sensing circuits. The net effect is an improvement in its conductivity with a decrease in resistance for an increase in illumination. Variation in resistance with changing light intensity.

Fig:4. Typical LDR

Typical LDR (Light Dependent Resistor) resistance vs light intensity graph

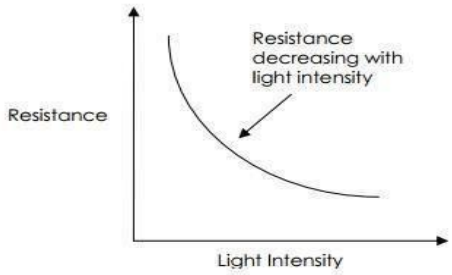

Fig:5. Typical LDR resistance vs light intensity graph

The most common type of LDR has a resistance that falls with an increase in the light intensity falling upon the device (as shown in the image above). The resistance of an LDR may typically have the following resistances:

Daylight = 5000Ω

Dark = 20000000Ω

Testing the Code for the Arduino LDR Sensor

```
int LDR sensorPin = A0; // select the input pin for LDR
int LDR sensorValue = 0; // variable to store the value coming from the sensor
void setup() {
Serial.begin(9600); //sets serial port for communication
}
void loop() {
LDR sensorValue = analogRead(LDR sensorPin); // read the value from the sensor
```

```
Serial.println(LDR sensorValue); //prints the values coming from the sensor on the screen

delay(100);

}
```

CODE:

```
int ldr = A0, button = 2, relay = 3, threshold = 512;
void setup()
{
  pinMode (ldr,INPUT);
  pinMode(button,INPUT_PULLUP);
  pinMode(relay,OUTPUT);
}
void loop()
 {
  int val = analogRead(ldr);
   while(val < threshold)
{
    bool k = digitalRead(button);
    if(k != 0)
{
      digitalWrite(relay, HIGH);
    }
    else {
      break;
    }
   }
  digitalWrite(relay, LOW);
  delay(1);
```

CONCLUSIONS

In this manuscript we have examined the feasibility of using KY-008 Laser Transmitter module for optical measuring techniques. We have investigated some fundamental difficulties associated with some universities and high school optics labs and suggested several practical and theoretical solutions to overcome them. We have demonstrated the effectiveness of our solutions with experimental results. The principle of KY-008 Laser Transmitter module on optical measurement by using Arduino is analyzed. However, KY-008 Laser Transmitter module for measurement method has the larger advantage than using He-Nelaser with lowcost, less power supply and fast processing characteristics. Future research direction is to solve the measurement optical difficulties in the lab which already exist. The main point of this work is to examine the feasibility of low-cost optical measurement.

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DIELECTRIC CONSTANT STUDY OF POLYANILINE – ZINC FERRITE (PANI - ZnFe2O4) COMPOSITES

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ABSTRACT:

Chemical route for the synthesis of polymer composites with oxide materials enhances the composite technology. Polyaniline (PANI) and Polyaniline-Zinc Ferrite (PANI - $ZnFe_2O_4$) composite material was prepared by insitu polymerization of aniline with Zinc Ferrite (PANI - $ZnFe_2O_4$) as composite material. Variation in the oxide composition with polymer matrix is maintained to know its detailed changes. The dielectric behavior is also investigated in the frequency range 10^2–10^7 Hz at room temperature. The dimensions of Zinc Ferrite ($ZnFe_2O_4$) particles in the matrix have a greater influence on the observed dielectric values.

KEYWORDS: *Synthesis, Composites, Dielectric Constant, Polyaniline, Zinc Ferrite ($ZnFe_2O_4$).*

1. INTRODUCTION:

The technological importance of basic research and its development on conducting polymer has been carried for new properties and applications [1]. Zinc Ferrite ($ZnFe_2O_4$) is a materials shows good electrical and optical properties [2-3]. Various techniques have been used for the preparation of Magnesium stanate materials [4-6]. More recently, there has been considerable attention on the synthesis of $ZnFe_2O_4$ with additional properties for potential applications [7-8] However, new approach on conducting polymer composite materials integrates the technology of conducting polymeric materials. Metal oxide inserted Polymers constitute polymer composites, which are well studied for its properties [9-11]. Conducting polymers have a variety of applications in various fields, such as in Industry, Scientific and in medical (ISM) fields. Applications like anticorrosion, static coating electromagnetic shielding etc., comes under first generation. Second Generation of electric polymers have applications such as transistors, LEDs, solar cells, batteries etc.Controlled conductivity, high temperature resistance, low cost and ease of bulk preparation make these materials attractive in the engineering and scientific world. Among conducting polymers, polyaniline is the most extensively studied polymer obtained by simple chemical or electrochemical route. Polymeric materials have become an area of increasing interest in research because of the fact that these materials have great potential for solid state devices [12-13]. This polyaniline has received much attention because of its high electrical conductivity and ease of preparation at low cost. The demand of high quality materials for electromagnetic compatibility is alarmingly increasing [14]. Metal oxides dispersed polymer composites have attracted a great deal of interest from researchers, because they frequently exhibit unexpected hybrid properties synergistically derived from both components. Zinc Ferrite ($ZnFe_2O_4$)is one of the examples of oxide material, which is known for progressive properties and applications [15]. Composite of Zinc Ferrite ($ZnFe_2O_4$) dispersed PANI with variable compositions my lead to desirable properties and new applications. These materials are especially important owing to their bridging role between the worlds of conducting polymers [16-18]. In this paper, we describe the synthesis of PANI and Zinc Ferrite ($ZnFe_2O_4$) dispersed PANI composite materials through insitu polymerization method. Dielectric study of the as prepared PANI composite material is also well studied for its dielectricbehavior.

2. EXPERIMENTAL:

Materials andMethods

Ammonium persulphate $(NH4)_2S_2O_8$, Hydrochloric acid (HCl) and Zinc Ferrite ($ZnFe_2O_4$) used were of AR grade. Doubly distilled water and aniline is used as a solvent and a monomer. Polyaniline is prepared by oxidative method and Polyaniline composites were prepared by insitu polymerization method with dispersion of Zinc Ferrite in polyaniline.

Synthesis of Polyaniline/ Zinc Ferrite ($ZnFe_2O_4$) Composites

Aniline was dissolved in 1m HCl to form polyaniline (PANI). Zinc Ferrite ($ZnFe_2O_4$) was added to PANI solution with vigorous stirring to keep the Zinc Ferrite ($ZnFe_2O_4$) suspended in the solution. To this reaction mixture, 0.1M of ammonium persulphate [$(NH_4)_2S_2O_8$], which acts as an oxidant, was added slowly with continuous stirring for 4-6 hours at 0-5^{O}C. The precipitated powder recover was vacuum-filtered and washed with deionizer water. Finally, the resultant precipitate was dried in an oven for 24 hours to achieve a constant weight. In the similar manner pure PANI is prepared without adding Zinc Ferrite

PANI/ Zinc Ferrite ($ZnFe_2O_4$) composites were prepared in weight percent ratio in which the concentration of Zinc Ferrite (10, 30, and 50wt %) was varied. The test samples to be used were prepared in pellet form of diameter

10mm and thickness 3mm by applying pressure of 7t using Pye-Unicam dye. The contacts for these composites were made using silver paste as electrodes on both sides.

AC conductivity measurements were carried out at room temperature over the frequency range 10^2-10^7Hz using the Hiokie LCR Q meter.

3. RESULTS & DISCUSSION:

Polyaniline – Zinc Ferrite ($ZnFe_2O_4$)composites

Figure 1 shows the variation of ε' as a function of frequency for polyaniline – Zinc Ferrite ($ZnFe_2O_4$) composites (different wt %). it is observed that, the dielectric constant is quite high at low frequency and decreases with increase in applied frequency but 30wt% of composite shows maximum value. The observed behavior may be due to Debye like relaxation mechanism taking place in all these materials.

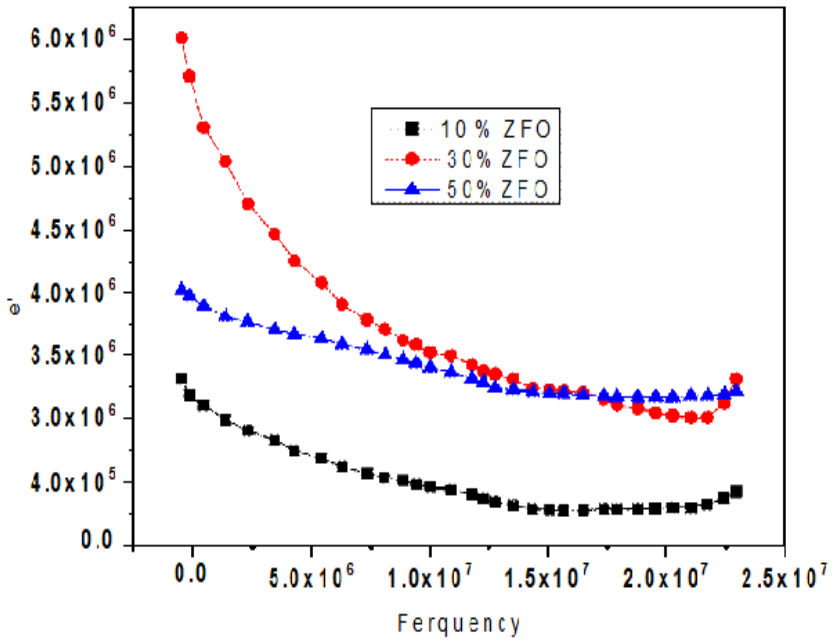

Figure 1: Variation of Dielectric constant as a function of frequency for Polyaniline – Zinc Ferrite ($ZnFe_2O_4$) composites

4. CONCLUSION:

Polyaniline composites with different weight percentages of Zinc Ferrite ($ZnFe_2O_4$) in PANI were synthesized by chemical oxidative polymerization of monomer aniline. The results of Dielectric constant show a strong dependence on the weight percent of Zinc Ferrite ($ZnFe_2O_4$) in polyaniline.

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BIODIVERSITY STUDIES ON ORDER OF AGARICALESFROM AURANGABAD DISTRICT OF MAHARASHTRA, INDIA

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ABSTRACT:

Studies on biodiversity of order Agaricalesspecies are need to protecting more importance becouse many macrofungi are heading for extinct or facing the threat of extinction. Macrofungal speciesare important for functioning and stabilityof ecosystem as well as known for high nutritional value and medicinal properties. Extremely inattentive has been given to conservation of macrofungal biodiversity as compare to other flora and fauna even they are main constituent of the ecosystem.Present study deals with the biodiversity of Agaricales species were recorded from six places of Aurangabad, Maharashtra state. In this research surveya total of 40 macrofungal species and 22 genera of 13 families were collected. Most diversity and highest species comes under the family Agariaceae rather than other families. Termitomyces, Agaricus andVolvariellais most dominant genus recorded in study area.

KEYWORDS: *Macrofungi, Agaricales, biodiversity, Aurangabad.*

1. INTRODUCTION:

The order Agaricales in the class Agaricomycetes is the largest and most multifariousness order of the phylum basidiomycota that include of species which havingfleshy and gills bearing sporocarp as a distinctive character. But nowadays, members of Agaricales are classified based on molecular phylogenetic and thus they may or may not have gills as well as typical mushroom shaped fruiting bodies.(Hawksworth, 2001, Kark, 2007). The order has 33 extant families, 413 genera, and more than 13,000 described species (Kirk *et al.* 2008).Most of Agaricales species popped out during rainy season and survive in different niches in the different terrestrial ecosystems of the all the continents ranging from arctic to tropics but they are found more in tropical areas rather in temperate areas.Agaricales can survivein all different terrestrial ecosystems whereas some species show preference for a certain type of natural habitat with a particular substrate. Based on the substrate preferences, they have commonly been referred to as bryophilous, coprophilous, fungicolous, lignicolous, humicolous, parasitic and saprotrophs. Numerous species of Agaricales also include termitesymbionts (Termitophilic) or even nematode predators or may form mutualistic ectomycorrhizal association with roots of vascular plants. Which are key functional constituent of a forest ecosystem allow plants towards better nutrient uptake, crucial under unfavorable edaphic conditions (Brown *et al*., 2006, Hawksworth, 1991).

An estimated 8000 plants and 7000 to 10000 fungal species occupied in ectomycorrhizal fungi symbiosis (Taylor and Alexander 2005). An Ectomycorrhiza (ECM) fungus helps to break down the complex minerals and organic substances in the soil and transfer nutrients to the tree. ECM fungi are the common and dominant mycorrhizal type of boreal and temperate forests, about 95% of roots of trees colonized by ectomycorrhizal symbiosis. Many mushrooms species have been used in folk medicine for thousands of years as a natural food having potential value in increase immune system and maintaining health of the human body. Mushrooms have been used as medicine since the Neolithic and Paleolithic eras (Samorini, 2001).

Agaricales have been known to humans since many years and used as food and medicine purpose. More than 100 medicinal mushrooms have been identified with their bioactive metabolites, such as phenolic compounds, polypeptides, triterpenes and steroids have been successfully used for the treatment of cancer, cardiovascular diseases, diabetes mellitus and neurodegenerative diseases etc. (Barros *et al*. 2007, Benjarong *et al.* 2015, Lin *et al.* (2013) Villares *et al*. 2012).

2. MATERIALS AND METHODS:

All the Specimens were collected during first flush of morning (June 2016-October 2017) in subsequent field trips from different areas of Aurangabad city, Maharashtra state (GPS Coordinates is N 19° 53' 47" - E 75° 23' 54"). The morphological and ecological characteristics were noted as well as color photographs were taken in the field on current time. Macrofungal specimens were collected with the help of mushroom hunting tools were used for collection of samples. The macrofungal samples were wrapped in aluminum foil paper and kept separately in a basket, polythene bags and containers in order to keep away from contamination. As soon as possible after returning from the field immediately applied biochemical test on fresh samples of different species and genera for identification purpose. Studied the detail microscopic characteristics of species was observed under the light microscope in addition to micro photographed by Digi Eye camerafixed to OLYMPUS CX 21 bright field light microscope.

Table No. 1:Occurrence of macrofungi in different locations of Aurangabad

Sr. No.	Name of the Macrofungal Taxa	Site I	Site II	Site III	Site IV	Site V	Site VI
1)	*Agaricus arvensis* Schaeff.	+	-	-	-	-	-
2)	*Agaricus grandiomyces* Zhou & Zhao	+	-	-	-	-	-
3)	*Agaricus martinicensis* Pegler	-	+	-	-	+	-
4)	*Agaricus placomyces* Peck.	+	-	-	-	-	+
5)	*Amanita cokeri* (E.-J.Gilbert & Kuhner)	-	-	+	+	+	-
6)	*Bovista sp.*	-	-	+	+	-	+
7)	*Chlorophyllum molybdites* (G. Mey.)	+	+	-	+	-	-
8)	*Conocybe apala* (Fr.: Fr.) Arnolds	-	-	+	-	-	-
9)	*Conocybe tenera* (Schaeff: Fries) Fayod.	-	-	+	-	-	-
10)	*Coprinellus domesticus* (Bolton) Vilgalys, Hopple & Johnson	-	-	-	-	+	-
11)	*Coprinellus flocculosus* (DC)Vilgalys, Hopple & Johnson	-	-	-	-	+	-
12)	*Coprinellus micaceus* (Bull.) Vilgalys, Hopple & Johnson	-	-	+	-	+	+
13)	*Coprinopsis cinera* (Bull.Fr.) Redhead, Vilgalys and Moncalvo	-	-	+	-	-	+
14)	*Coprinopsis picacea* (Bull.Fr.) Redhead, Vilgalys &Moncalvo	-	-	+	-	-	-
15)	*Coprinus comatus* (O.F. Mull.) Pers.	+	+	-	-	-	-
16)	*Gymnopus confuens* (Pers.)	+	-	+	-	-	+
17)	*Inocybe alba*	+	-	+	-	+	-
18)	*Inocybe purpureoflavida* Vrinda & Pradeep	-	-	+	-	-	-
19)	*Leucoagaricus leucothites* (Vittad.) Wasser	-	-	+	+	+	-
20)	*Leuagaricus sp.*	+	-	-	+	+	-
21)	*Leucocoprinus brebissionii* (Godey) Locq.	+	-	-	-	-	-
22)	*Leucocoprinus cretaceous* (Bull.) Locq.	+	-	+	-	-	-
23)	*Leucocoprinus fragilissimus* (Berk. &Curtis)Pat.	+	+	+	-	-	-
24)	*Macrolepiota procera* (Scop.Fr.) Singer	+	-	+	-	-	-
25)	*Neonothopanus hygrophanus* (Mont.) De Kesel & Degreef	-	+	-	-	+	-
26)	*Panaeolus papilioneus*	-	+	-	+	-	-
27)	*Parasola plicatilis* (Curtis) Fr. Redhead, Vilgalys & Hopple	+	+	+	-	-	-
28)	*Pleurotus ostreatus* (Jacq.) P. Kumm.	+	-	+	-	-	-
29)	*Psilocybe cubensis* (Earle)Singer.	+	-	-	-	-	-
30)	*Schizophyllum commune* Fr.	-	+	+	-	-	+
31)	*Termitomyces clypeatus* Heim.	+	-	-	-	+	-
32)	*Termitomyces globules* R. Heim & Gooss.-Font.	+	-	+	-	-	-
33)	*Termitomyces heimii* Natarajan	+	-	+	-	-	-
34)	*Termitomyces reticulatus* Van der Westh. & Eicker	+	-	+	-	-	-
35)	*Termitomyces umkowaan* (Cooke & Massee) D.A. Reid	+	-	+	-	-	-
36)	*Volvariella bombycina* (Schaeff. Fr.) Singer	-	+	+	-	-	-
37)	*Volvariella bombycina* var. *flaviceps* (Murrill) Shaffer.	+	+	+	-	-	+
38)	*Volvariella taylorii* (B. & Br.) Singer.	+	-	+	-	-	-
39)	*Volvariella volvaceae* (Bull.) Singer.	-	+	+	-	-	+
40)	*Xanthagaricus sp.*	-	+	+	-	+	+

Site I- Dr. B. A. M. U. Campus, Site II- Goga baba hills, Site III- Himayatbagh,
Site IV-Kanchanwadi, Site V- Mukundwadi, Site VI- Waluj, ("+" Present "-" Absent)

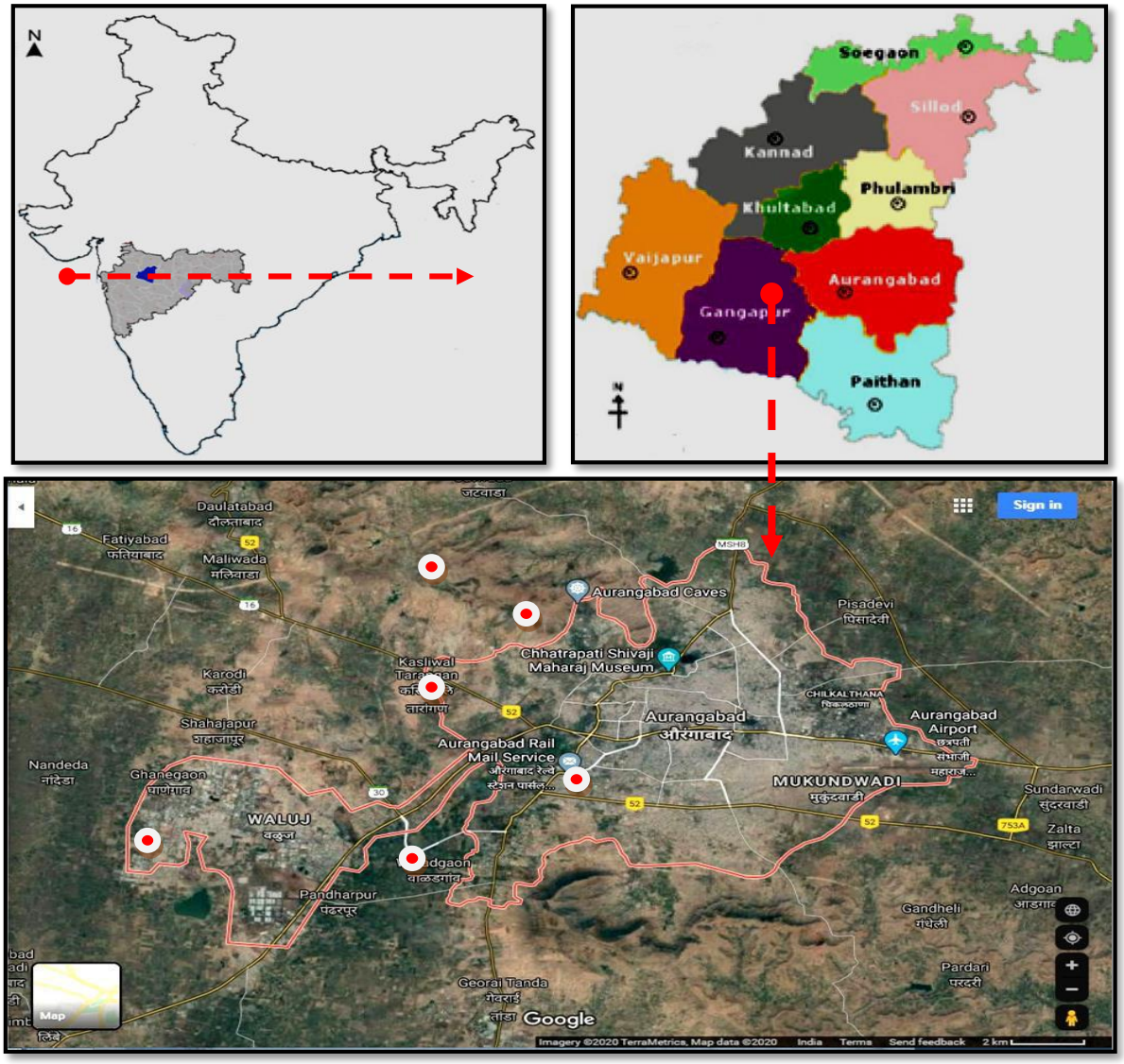

Figure no. 1: Arial view of the location of selected sampling sites.

3. RESULTS AND DESCUUSION:

The diversity and distribution of Agaricales have been done first time in the selected location of Maharashtra State. The locations of research area (Figure No. 1) seem to make available a wide range of habitats for the growth of Agaricales belonging 13 families which having 22 genera with 40 species (Table No. 1). A total of 13 families such as Agariaceae, Amanitaceae, Bolbitiaceae, Coprinaceae, Inocybaceae, Lepiotaceae, Lyophyllaceae, Marasmiaceae, Pleurotaceae, Pluteaacae, Psathyrellaceae, Schizophyllaceae, Strophariaceae were recorded in which 6 genera and 12 species comes under the Agariaceae which is highest as compare to other families. Highest number of 5 species comes under the *Termitomyces* genera followed by *Agaricus* and *Volvariella* (4), *Leucocoprinus* and *Coprinellus* (3),*Leucoagaricus*, *Conocybe*, *Inocybe* and *Coprinopsis* (2), remaining *Amanita, Bovista*, *Chlorophyllum*, *Coprinus, Gymnopus, Macrolepiota, Neonothopanus,Panaeolus*, *Parasola, Psilocyb, Schizophyllum, Xanthagaricus* each genera having single species.Based on the substrate preferenceshighest 16soil and humus loving mushrooms(Humicolous) recorded followed by 12 wood inhabiting mushrooms(Lignicolous), 5 grown on termites mound (Termitophilic), 3dung inhabiting mushroom (Coprophilous) and 4 associated with plants and grasses (Mycorrhizal) (Table No. 1.1 and Figure No. 1.2). On the basis of collections 22 species recorded from Dr. Babasaheb Ambedkar Marathwada University Campus, 12 species from Gogababa Hills,06 species from Kanchanwadi, 11 species from Mukundwadi, 09 species from Waluj area and 26 species fromHimayatbagh which are most dominant and having diversity area in Aurangabad (M.S.). *Termitomyces, Agaricus* and*Volvariella*are most dominant genus as well as Agariaceae family having maximum genera were collected in study area.

Table No. 1.1:Diversity of mushrooms in different habitat

Sr. No.	Habitat	No. of Species	Percentage
1)	Lignicolous	12	30%

2)	Humicolous	16	40%
3)	Termitophilous	5	13%
4)	Coprophilous	3	8%
5)	Mycorrhizal	4	10%

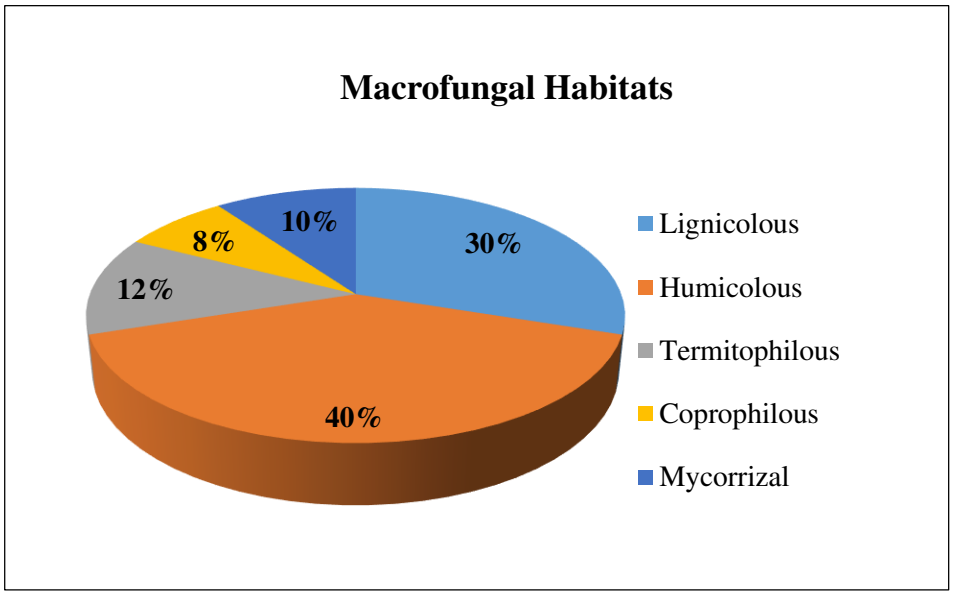

Fig. No. 2 :Substrate specificity of the macrofungi grown in the sampling station.

4. CONCLUSION:

The present investigation deals with the biodiversity as well as distributional study of macrofungal flora from Aurangabad district (M.S.). In thisinvestigation total 40 species were recorded which belongs from family Agariaceae (12 species), Amanitaceae (1 species), Bolbitiaceae (3 species), Coprinaceae (2 species), Inocybaceae (2 species), Lepiotaceae (1 species), Lyophyllaceae(5 species), Marasmiaceae (2 species), Pleurotaceae (1 species), Pluteaacae(04 species), Psathyrellaceae (5 species), Schizophyllaceae (1 species)and Strophariaceae(1 species). In thisresearch study fungal species of Agariaceae family were mostdominant as compare to other. Outof six selected sites there was rich fungal basidiomata recordedfromHimayatbagh area.On the basis of our research found that selected locations are treasure house for growth of macrofungal sporocarps and having great scope for to exploration of diversity of macrofungal flora to new researcher and mushroom hunters.

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TIME EVOLUTION OF LEAD FROM LEAD ACETATE IN ELECTRODEPOSITION

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ABSTRACT:

Electro deposition is well studied and systematically explored area. The Electro deposition, viscous fingering, dendritic crystal growth, and DLA (Diffusion Limited Aggregation) have received the major attention. We studied electrodeposition in circular cell geometry with a view to explore the growth rate of different portions of the dendritic patterns.Such dendritic patterns show interesting characteristics and in most of the cases are fractals obeying scale invariance over a wide range of length of scale. It is interesting to note that the dendrites with a few branches when observedshow microstructures that are of interest from the point of material science and newer materials with non-conventional characteristics. In this paper study of growth of dendritic patterns in electro deposition using circular cell geometry and the development of different branches is observed and rate of growth analyzed. We also studied the time course of evolution of the fractal patterns grown by electro deposition using Lead Acetate solution. The rate of growth is studied from the point of linear growth, detailed findings are presented.

KEYWORDS: *Electrodeposition, dendritic patterns, electrolysis, faraday's laws.*

1. INTRODUCTION:

The growth of dendritic crystals has paying attention of scientific interest for nearly half a century because the resulting symmetrical but complex forms are not well understood. The Electro deposition, viscous fingering, dendritic crystal growth, and DLA (Diffusion Limited Aggregation) [1, 2, 3] have received the major attention. The concept of fractal and non-fractal aggregation is applicable in physics especially in turbulence [4,5], polymerization,[6,7]. Flocculation, coagulation, dendritic growth, crystallization. Gelation process also exhibit self-similarity and fractal character in many cases. The practical importance and fundamental principle of Diffusion limited growth processes has motivated extensive studies in the past years. Electro-deposition processes [8, 9] are well suited for experimental studies of growth of fractals and dendritic patterns. For the purpose of forecasting the trends of the random events like prices of shares in the share market, the concept of Fractal model is being effectively used [10, 11].

We studied growth of dendritic patterns in electrodeposition using circular cell geometry the development of different branches is monitored and rate of growth analysed. It was found that the concentration of the solution strongly influences the structure and textures of electro deposition . Few dendritic patterns obtained under different cell operating conditions and their characterization is presented. We also studied the time course of evolution [12] of the fractal patterns grown by electro deposition using Lead Acetate solution.

2. BASICS OF ELECTRODEPOSITION:

Electro deposition is the process of coating a thin layer of one metal on top of a different metal to modify its surface properties. Done to achieve the desired electrical and corrosion resistance, reduce wear & friction, improve heat tolerance and for decoration. [13,14]

Growth of dendritic patterns using circular cell geometry is basically electrolysis that is governed by Faradays laws of electrolysis. The electro deposition under study is governed by Faradays laws of electrolysis, however, there are two competing processes i.e. the ionic motion due to applied electric field and the random motion of the molecules at room temperature that tend to make it DLA like situ situation. Faraday's first law of electrolysis states that the mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred at that electrode.[15] Quantity of electricity refers to electrical charge, typically measured in coulomb. The second law states that for a given quantity of electricity (electric charge), the mass of an elemental material altered at an electrode is directly proportional to the element's equivalent weight. The equivalent weight of a substance is its molar mass divided by an integer that depends on the reaction undergone by the material.

Faraday's laws can be summarized by $m = \left(\frac{Q}{F}\right) \cdot \left(\frac{M}{z}\right)$ .....(1)

Where ,m be the mass of the substance altered at an electrode

Q be the total electric charge passed through the substance
F = 96,485 C mol-1 is the Faraday constant
M be the molar mass of the substance
z be the valency number of ions of the substance (electrons transferred per ion)
andM / z is the same as the equivalent weight of the substance deposited.

For Faraday's first law, M, F, and z are constants, so that the larger the value of Q the larger m will be. For Faraday's second law, Q, F, and z are constants, so that the larger the value of M / z (equivalent weight) the larger m will be. In the simple case of constant-current electrolysis, Q = It leading to $m = \left(\frac{It}{F}\right) \cdot \left(\frac{M}{z}\right)$

and then to $n = \left(\frac{It}{F}\right) \cdot \left(\frac{1}{z}\right)$ .....(2)

where , n be the amount of substance ("number of moles") transformed: n = m / M
t be the total time for which the constant current applied.

3. EXPERIMENTAL SETUP:

The electro deposition cell was mounted providing leveling arrangement with suitable arrangement for illumination from both the sides. Three milky lamps were used on back side and one on the top side of the electro deposition cell. A video camera was mounted right at the top of the cell for video recording of the growth of the electro deposition. A still camera was also kept ready for photographing the growth at suitable stages for high resolution images for further processing. The power supply used was a regulated power supply with a adjustable range from 0 – 30 V DC. The power-supply was capable of delivering a maximum current of 2 A Dc. During most of the experiment we used constant voltage conditions for electro deposition. To study time course of evolution of the dendritic patterns, real time videos were recorded during the electrodeposition process and selected frames at definite time interval were extracted for analysis.

The time course of evolution of the dendritic patterns presented here is for growth at a cell operating voltage of 12V DC and molarity of Lead Acetate solution was 0.5. The movie was recorded for 140 sec.. The video file was then processed and frames were separated at intervals of 20 sec. Figure 1 below shows these frames indicating different stage of growth of the electro deposition. The first frame at t = 0 is not included.

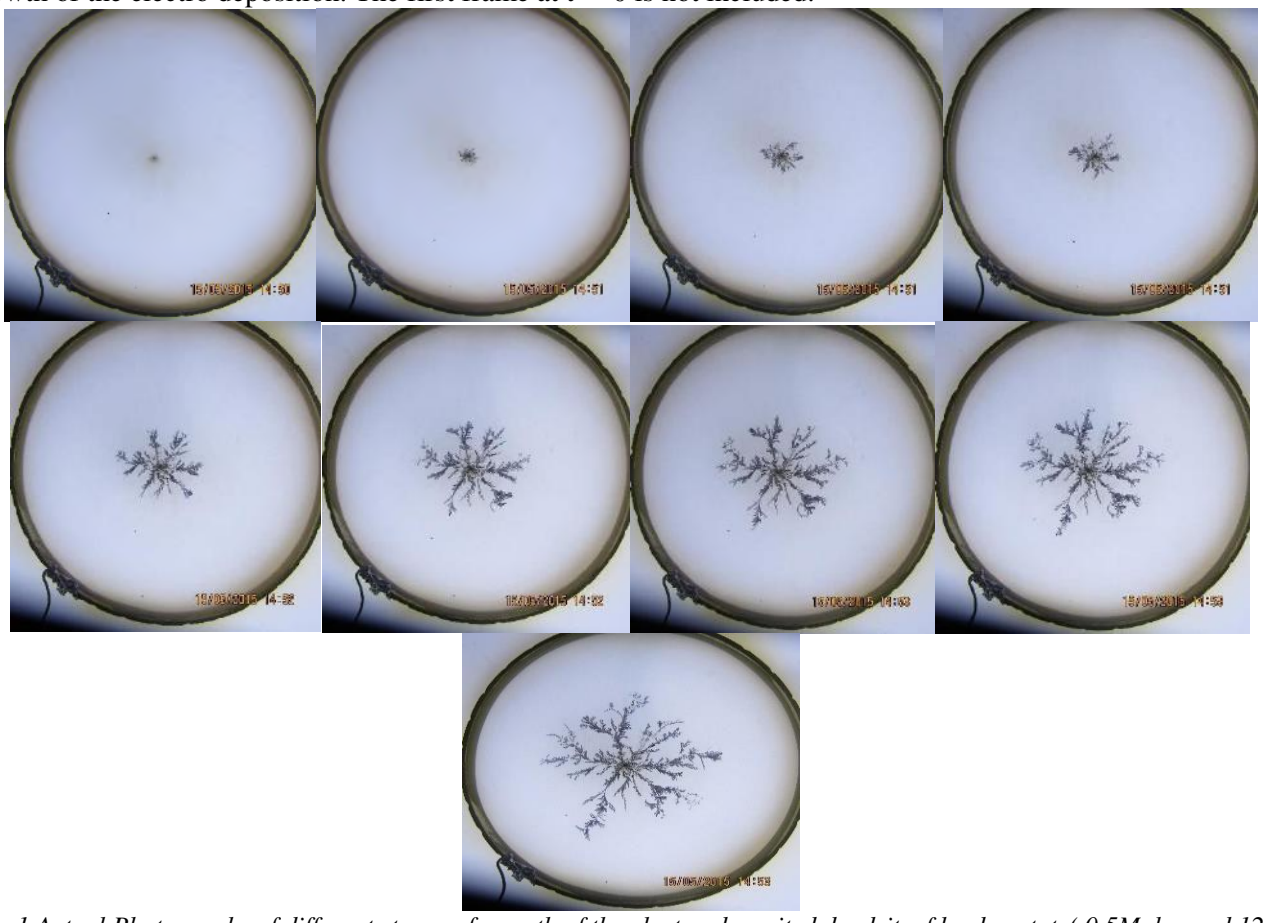

Fig.1 Actual Photographs of different stages of growth of the electro-deposited dendriteof lead acetate(0.5Molar and 12V)

After separating the frames, the images were converted to 2 bit black and white images, selecting suitable threshold. After converting the images to 1 bit images, the images were independently edited to remove the image of outer anode for further analysis of the images.

As can be seen from the fully grown pattern at t = 140 sec., there are primary and secondary branches are seen, however six prominent main primary branches could be identified. In fact these branches appear to be smooth and linearly growing branches however a closer examination under higher resolution reveals the branching is almost continuous at different length scale. Primary branches have secondary and tertiary branches that in turn possess lot of complex and intricate branching pattern that makes the deposit more or less porous with low bulk density.

We measured the length of all the six main branches in each of the 6 frames selected. The method used was to find the x and y coordinates of the tip of the selected branch and knowing the coordinates of the center, the length was calculated using the distance formula:

$$d = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2} \quad \ldots\ldots \quad (3)$$

From the coordinates of the tip of branch and centre of deposit, the length of the six different branches were calculated at the interval of 20 sec. using the distance formula shown in equation 3. From the length of the branches so calculated in pixels, the lengths were converted in to mm using the resolution of the picture which was 180 pixels per inch. Using the information of the length of each branch at different stages of growth (at an interval of 20 sec) the growth velocity was estimated in mm / sec. Table1 shows the length of different branches in pixels and Table 2 shows the distance in mm for all the six branches at different stages of progress of the growth of the dendritic pattern. Table 3 shows the growth velocity (in mm/sec) at different stages of growth. Table below gives the length of the six branches (in pixels) at interval of 20sec.

Table –1 showing the growth of various branches in Pixels

Time(sec)		0	20	40	60	80	100	120	140
Branch Length for Branch (pixel)	1	0	76.7	210	262	314	380	422	554
	2	0	101	245	290	360	409	438	504
	3	0	134	305	401	469	565	612	696
	4	0	85.9	225	285	315	342	400	481
	5	0	58	185	252	296	378	490	616
	6	0	103	84	300	353	407	416	529

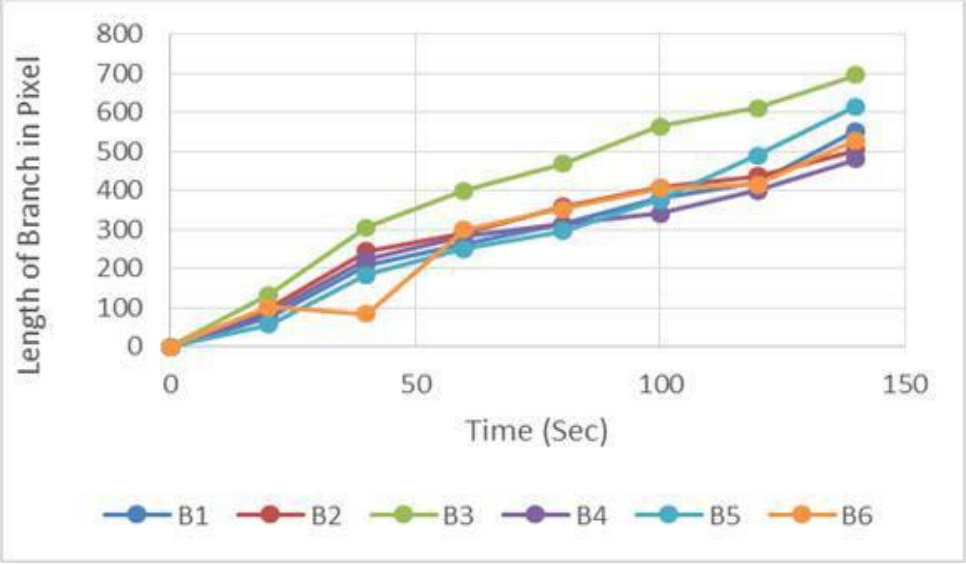

Fig. 2 Showing the progress of length (in pixel) of various branches with time in sec.
Table below gives the length of the six branches (in mm) at interval of 20 Sec.

Table – 2 showing the growth of various branches in mm.

Time (Sec)	Branch length in mm					
	1	2	3	4	5	6
0	0	0	0	0	0	0
20	1.08	1.42	1.89	1.21	0.82	1.45
40	2.97	3.46	4.31	3.17	2.61	1.19
60	3.7	4.1	5.66	4.02	3.56	4.23
80	4.43	5.08	6.62	4.45	4.17	4.98
100	5.36	5.77	7.98	4.82	5.33	5.74
120	5.96	6.19	8.64	5.65	6.92	5.86
140	7.81	7.11	9.82	6.79	8.69	7.46

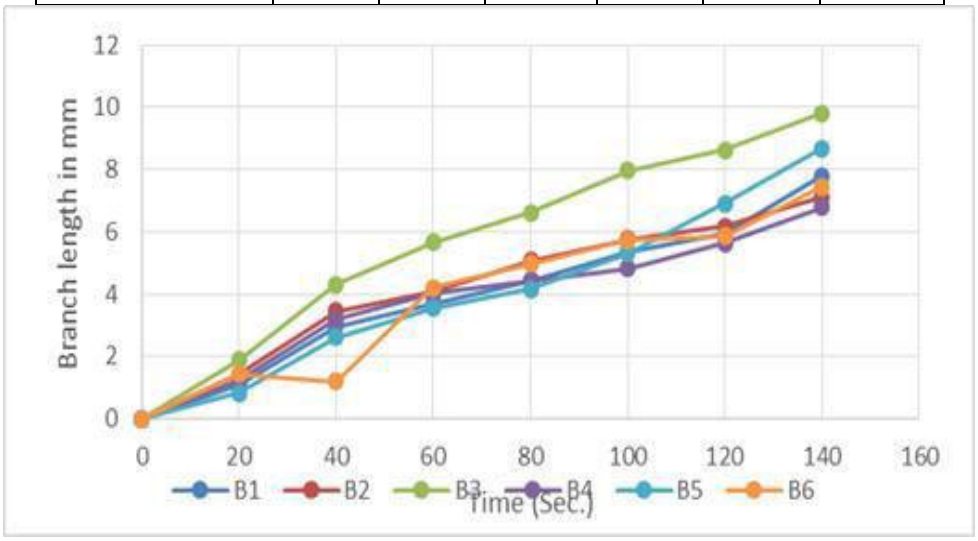

Fig. 3 Showing the progress of the length of the six branches (in mm) at interval of 20 Sec.

Table below gives the growth velocity of the six branches (in mm/sec) at interval of 20Sec.

Table – 3 showing the growth velocity of various branches in mm/sec.

Time Step		0	20	40	60	80	100	120	140
Velocity of the brance in mm/s	1	0	0.054084	0.148491	0.185006	0.221616	0.268111	0.297955	0.390576
	2	0	0.071	0.173	0.205	0.254	0.289	0.309	0.355
	3	0	0.09	0.22	0.28	0.33	0.4	0.43	0.49
	4	0	0.06	0.16	0.2	0.22	0.24	0.28	0.34
	5	0	0.04	0.13	0.18	0.21	0.27	0.35	0.43
	6	0	0.07	0.06	0.21	0.25	0.29	0.29	0.37

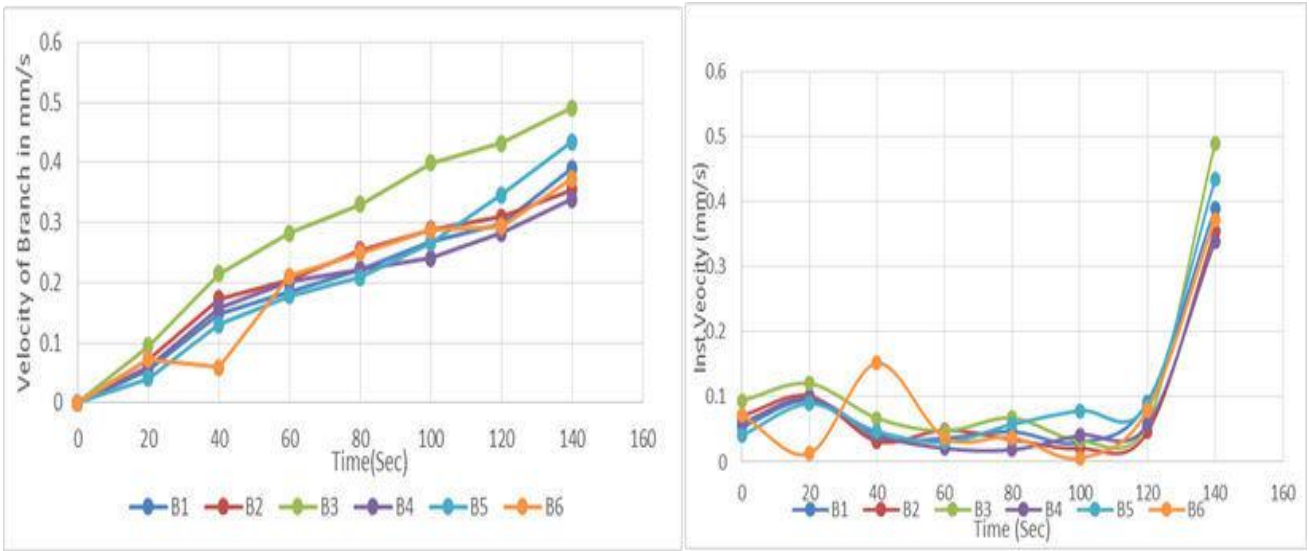

Fig. 4 Showing the growth velocity of various branches in mm/sec. with time.

The time course of evolution of the different branches could be more clearly presented in the form of a plot of the size of individual branches as a function of time. Fig.4 shows the size (in mm) of different branches of the electro deposited dendritic pattern of Fig 1 at different stages of growth. The time step in this plot is 20 sec and the 6th time step corresponds to a time of 140sec of growth. It is seen from Fig 4 that the growth during the initial stages is slower for branches 1,2,3 and 5 till about 3 minutes and thereafter the rate of growth picks up for these branches.

Thereafter up to about 140 sec the growth is similar for almost all the six branches. It is the characteristic of DLA like processes that the well-developed branches tend to grow faster than those that remain under developed. This is also known as masking effect. As a consequence of this few branches are found to grow faster than the others. As is seen that Fig 4, after a time of 40 sec (step 2), branch No 6, that was slower has now become fastest growing branch. Branches 3, 5 and 6 are among faster growing branches and Branches 1 ,2 and 4 are among the slower growing branches.

The growth velocity of different branches of electrodeposited pattern shown in Fig 1. is shown in figure 5. The growth velocity is calculated as cumulative growth divided by the time taken, this is the average growth velocity of the respective branch It is seen from the figure that growth velocity is increasing with time. The growth velocity discussed above is the average growth velocity of individual branches calculated on the basis of the total length of the branch at a certain stage and the time corresponding to that stage. However it was found of interest to study the instantaneous velocity as a function of time.

4. CONCLUSION:

Time course of evolution of the dendritic patterns in electrodeposition revealed that during the initial phase of growth, up to a time of 40 sec, the growth is fast and later on gradually increases the growth rate . This is due to the fact that as growth proceeds the distance between cathode and anode shortens and at a fixed cell operating voltage the electric field becomes stronger, at the same time with the increase in the size of the growth the net area exposed increases much faster contributing the a faster decrease in current density.

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Determination of Lead in *Cassia Siemea* leaf spectrophotometrically

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ABSTRACT:

A spectrophotometric method for the determination of trace amounts of Pb(II) in aqueous samples of Cassia Siemea leaf is reported. The leaves of the plants were studied for lead concentration simultaneously in 2019 and 2020 . the plants that were selected were one from isolated place and one from road side site in the central part of Aurangabad city. It was found that the road side plants showed high content of lead on leaves as compared to that of isolated place.

KEYWORDS: *Lead, Cassia Siemea leaf, spectrophotometrically.*

1. INTRODUCTION:

Lead compounds used as anti-knocking agents in automobile fuels cause air pollution. In paces with heavy vehicular traffic the lead content may be as high as 5-10 µg/m^3. Studies have shown that about 60 % of the lead in the environment comes from lead alkyls used for boosting octane number of gasoline. Presence of even amount of Pb (II) in environmental samples causes environmental pollution and many fatal diseases including dysfunction of renal blood system and neurological systems. Pb (II) easily deposits in kidney, blood, nervous system, reproductive system, brain and cellular process. Acute lead poisoning can result in colic shock, severe anemia and irreversible brain damage [1-2]. The determination of trace amounts of lead (Pb) is very important for the purpose of environmental screening. In this context a large number of spectrometric methods are reported for determination of lead [3-6]. The present study was planned to determine the prevalence of lead in Cassia Siemea leaf samples collected from Aurangabad district.

2. EXPERIMENTAL PROCEDURE:

Leave samples were collected from Central Aurangabad from an isolated place and road side place for the analysis of lead spectroscopically.

Principle: Lead on the surfaces is dissolved by shaking the nitric acid solution. /the lead is extracted as the dithizone complex in to methylene chloride at pH above 9. The intensity of the complex is measured spectrophotometrically and compared to a calibration curve prepared similarly from lead standards to calculate the amount of lead.

3. PROCEDURE:

Preparation of calibration curve:

This should be done at the time the samples are to be analyzed. The chelate formation and solvent extraction are to be performed in vials. To each of six labeled vials added ammonia cynide sulfite solution in different quantities and shake for about one minute. By using one of the standard the absorbance from 400-600nm is measure to determine wavelength of maximum absorption. Plot absorbance against microgram of lead used for preparation of calibration curve.

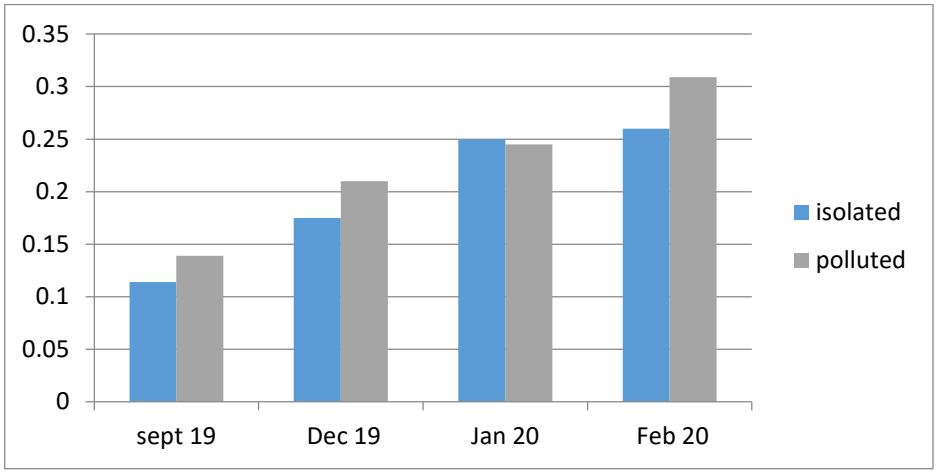
Determination of lead leaves:

For each flask containing leaf sample 0.1 M HNO_3 is added and heated to 70 ^oC. Add to this thymol blue indicator and added drop wise 2M NH_3 until blue color appears. Add some more drops so that the solution smell of ammonia. To this solution 60mL of ammonia-cynide-sulfite solution and 25 ml of dithizone solution is added and proceed with the extraction measurement as with the standard.

4. RESULTS AND DISCUSSION:

Experiment carried out for *Cassia Siemea* leaf for the determination of lead concentration.

Sr. No	Month	O.D		Conc. µg/lit	
		Isolated	Polluted	Isolated	Polluted
1	September 2019	0.125	0.145	0.114	0.139
2	December 2019	0.195	0.265	0.175	0.210
3	January 2020	0.260	0.273	0.250	0.245
4	February 2020	0.290	0.340	0.260	0.309



Graph showing the variation of concentration of lead at isolated place and polluted place

In the present study it can be revealed from the graph that as time period increases there is increase in the concentration of lead from 2019 to 2020. It is also investigated that the concentration of lead is more at polluted place as compared to isolated place.

Kanda Artwell[7] et al studied concentrations of different metals Cr, Cu, Fe, Mn, and Pb in leaves, leaf brew and infusion extracts of the tea alternate, *L. javanica* collected from seven sites, were determined and they found that the dietary contribution of Cu, Cr, Fe, and Mn from the consumption of tea beverage was higher in the leaf infusion than the brew of *L. javanic*.

Farouk S Nas[8] et al studied The effect of lead on plants in terms of growing and biochemical parameters and concluded that lead is non essential element for plant but, it accumulates in different parts of plant and negatively affects various physiological processes such as photosynthesis, respiration, mineral nutrition, membrane structure and properties and gene expression.

Mansoure Hatamian[9] studied the Interaction of lead and cadmium on growth and leaf morphophysiological characteristics of European hackberry (*Celtis australis*) seedlings and found high amounts of Pb and Cd were applied to plants along with high soil available Pb and Cd during 6 months via irrigation water. The results showed that application of Cd and Pb significantly reduced hackberry growth characteristics; however, the plant growth reduction was minor under relatively high amounts of applied heavy metals compared to many other studies.

Adnan M. Massadeh[10] et al studied Distribution of Heavy Metals in Some Tree Leaves along the Main Road in an Agricultural Area selecting four plants and found that The tree leaf samples, washed and unwashed, were analyzed for lead (Pb), cadmium (Cd), copper (Cu), and zinc (Zn) by atomic absorption spectrophotometry. All heavy-metals were present in concentrations of the samples were significantly higher than their counterparts of the control, indicating heavy-metal pollution was taking place.

5. CONCLUSION:

It is found that the concentration of lead in polluted leaf is more than isolated leaf. Hence different steps must be taken by the government and industries to control the lead pollution.

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Dielectric Relaxation and Thermodynamic Parameters of Iso-Amyl Alcohol, Ethylenediamine and their Binary Mixtures in 1,4 - Dioxan

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ABSTRACT: *The values of dielectric constant ($\in'$) and loss factor ($\in''$) have been experimentally determined for Iso-amyl alcohol, ethylenediamine and their binary mixture in 1-4, dioxan at different temperatures 9.85 GHz microwave frequency. The values of $\in'$ and $\in''$ have been used to evaluate the relaxation time (τ) and dipole moment (μ) by employing Gopala Krishna's method. Thermodynamic parameters also have been calculated for dielectric relaxation as well as for viscous flow process. The nonlinear behavior of relaxation time with mole fraction reveals presence of solute-solute molecular association in the mixture.*

KEYWORDS*: Relaxation time, Dipole moment, Dielectric relaxation, Thermodynamic parameters.*

1. INTRODUCTION:

Dielectric relaxation in the mixture of polar liquids in non-polar solvent has evoked considerable interest. Since in these systems apart from self-association, there is possibility of hetro-association. The dielectric relaxation depends upon the molecular size, shape, intra and intermolecular interaction. Therefore, study of dielectric relaxation can be used for knowledge of internal rotation, complex formation, solute-solute and solute-solvent molecular association in the mixture. Several workers [1-6] have done extensive work on dielectric behaviour of polar liquids and their binary mixtures in non-polar solvent. In the present chapter the dielectric relaxation study of Iso-amyl alcohol (*IAA),* ethylenediamine (*EDA*) and their binary mixtures in 1,4-dioxan is carried out for different mole fraction of *EDA* at different temperature. The study is expected to provide better understanding of the nature of molecular association in the mixture.

2. LITERATURE REVIEW:

Dielectric relaxation studies of polar molecules in non-polar solvent from microwave absorption have been frequently attempted by a number of research workers [1-6]. Rajesh Kumar [1] et al., have calculated the relaxation time (τ), dipole moment (μ) and energy parameters of binary mixtures of N-methyl formamide (*NMF*) and dimethylsuphoxide (*DMSO*) in benzene and predicted solute-solute type of molecular association in the mixture. Rana and Vyas [2] have evaluated relaxation time (τ) and distributed parameters for 3-bromo aniline and its mixtures with 1-propanol in dilute solution of benzene. They found more than one relaxation processes in the system and interaction between constituent molecules In the present chapter the dielectric relaxation study of Iso-amyl alcohol (*IAA),* ethylenediamine (*EDA*) and their binary mixtures in 1,4-dioxan is carried out for different mole fraction of *EDA* at different temperature. The study is expected to provide better understanding of the nature of molecular association in the mixture.

3. MATERIAL AND METHOD:

Iso-amyl alcohol (*IAA*) and ethylenediamine (*EDA*) A.R. Grade supplied by M/s S.D. Fine Chemicals were used without further purification. 1,4-dioxane AR grade supplied by M/s E-Merk India Ltd., also used without further purification. The liquids were mixed according to their proportions by volume and kept for six hours to ensure good thermal equilibrium.The X-band microwave bench was used to measure wavelength in dielectric (λ_d) and voltage standing wave ratio (*VSWR*) using short circuit plunger. To hold the liquid sample in the cell, a thin mica window whose *VSWR* and attenuation were neglected, is introduced between the cell and rest of microwave bench. is switched on.

The dielectric constant ($\in'$) and dielectric loss ($\in''$) of *nPA, EDA* and their binary mixtures at different temperature were calculated by using following equations [12]

$$\in' = \left(\frac{\lambda_o}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \qquad [1]$$

$$\in'' = \left(\frac{2}{\pi}\right)\left(\frac{\lambda_o}{\lambda_d}\right)^2\left(\frac{\lambda_g}{\lambda_d}\right)\left(d\rho/dn\right) \qquad [2]$$

where λ_o, λ_c, λ_g and λ_d are the free space wavelength, the cutoff wavelength, guide wavelength and wavelength in dielectric respectively. ρ is the inverse voltage standing wave ratio (*VSWR*) and $d\rho/dn$ is the slope of ρ versus *n* where *n* = 1,2,3------ such that $n\frac{\lambda_d}{2}$ represents the length of dielectric filled in wave guide. The values of λ_d, $d\rho/dn$ for different weight fraction of solute in 1,4-dioxan. The calculated values of ($\in'$) and ($\in''$) for different concentration and at different temperatures have been utilized in evaluating the relaxation time (τ) and dipole moment (μ) following Gopal Krishna's [7] method.

$$x = \frac{\in'^2 + \in' + \in''^2 - 2}{(\in'+2)^2 + \in''^2} \qquad [3]$$

$$y = \frac{3\in'}{(\in'+2)^2 + \in''^2} \qquad [4]$$

$$\tau = \frac{\lambda_o}{2\pi c} \times \frac{dy}{dx} \qquad [5]$$

$$\mu = \left[\frac{9KTM}{4\pi Nd} \times \left\{1 + \left(\frac{dy}{dx}\right)^2 \frac{dx}{dw}\right\}\right]^{1/2} \qquad [6]$$

where *c* is the velocity of electromagnetic waves, *k* is the Boltzman's constant, *N* is Avogadro's number, *M* is molecular weight of solute, *d* is the density of the solvent, *T* is absolute temperature, and *w* is the weight fraction of solute. The slope of the line drawn between *x* and *y* used for determining the value of relaxation time (τ) and the slope of line *x* and *w* used for calculating the dipole moment (μ).

The energy parameters, free energy (ΔF_τ), enthalpy (ΔH_τ) and the entropy of activation (ΔS_τ) for the dielectric relaxation process and the corresponding parameters for the viscous flow (ΔF_η), (ΔH_η) and (ΔS_η) have been calculated using the Eyrings equations [13].

$$\tau = \left(\frac{h}{KT}\right) \times \exp\left(\frac{\Delta F_t}{RT}\right) \qquad [7]$$

$$\Delta F_\tau = \Delta H_\tau - T\Delta S_\tau \qquad [8]$$

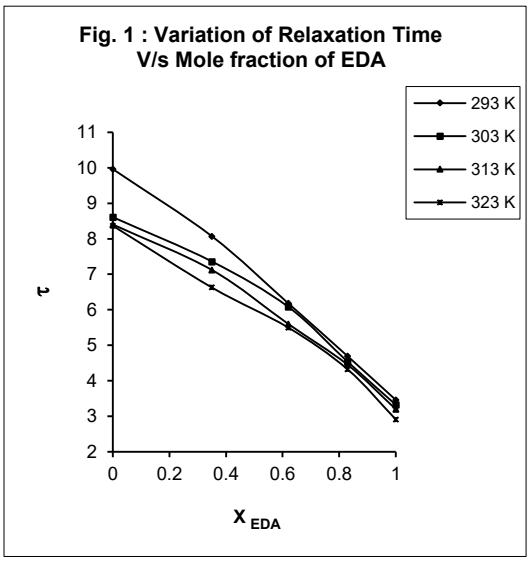
$$\eta = \left(\frac{hN}{V}\right).\ \exp\left(\frac{\Delta F_\eta}{RT}\right) \qquad [9]$$

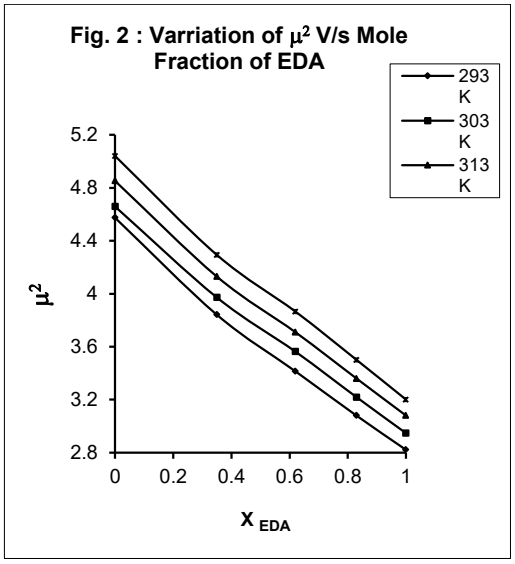
and $$\Delta F_\eta = \Delta H_\eta - T\,\Delta S_\eta \qquad [10]$$

where *V* is molar volume, η is the viscosity of the pure solvent and *K* is Boltzmann's constant other symbols have their usual meaning.

4. RESULT AND DISCUSSION:

The values of dielectric constant ($\in'$), dielectric loss($\in''$) and relaxation time (τ) for different weight fraction of solute of Iso-Amyl alcohol, ethylenediamine and their binary mixtures in 1,4-dioxan at different temperatures are shown in table 1





The values of relaxation time are observed to decrease systematically with increase in temperature from 20°C to 50°C for pure components as well as for binary mixtures. This may be due to increase in molar volume of the solute also due to the increase in the size of dipole with increase in temperature. Similar result has been predicted by Rajesh et al.[1] Fig. 1 shows variation of relaxation time (τ) with increase in the mole fraction of EDA. The relaxation time varies non-linearly with increase in mole fraction of EDA at all temperature. The non-linear variation of relaxation time shows the presence of solute – solute molecular association in the mixture. [8-9]

Fig. 2 shows non-linear variation of μ^2 with mole fraction of *EDA*. The deviation from linearity of μ^2 may be attributed to the presence of solute-solute molecular association through hydrogen bonding. [14,15]

The energy parameters ($\Delta F_\tau, \Delta H_\tau$ and ΔS_τ) for dielectric relaxation process and the energy parameters ($\Delta F_\eta, \Delta H_\eta$ and ΔS_n) for viscous flow process have been compared as shown in table 2. From table it is found free energy of activation increases with increase in temperature. With increase in temperature, the thermal agitation increases and dipole requires more energy to be an active. It is also found that free energy of activation (ΔF_τ) for dielectric relaxation process is less than the free energy of activation (ΔF_η) for the viscous flow process. This may be explained on the basis that dielectric relaxation process involves the rotation of the molecules whereas in the viscous flow process, the rotation as well as the translation motion of the molecules is involved. Similar kind of results have been shown by several research workers. [1, 11] The enthalpy of activation (ΔH_η) for viscous flow process is greater than the enthalpy of activation (ΔH_τ) for dielectric relaxation process The entropy of activation (ΔS_τ) for dielectric relaxation process is found to be negative, indicating cooperative environment of the system. [14,23] Again negative entropy of activation suggest activated state is more ordered than normal state of system. [24]

Table – 1 The values of dielectric constant ($\in'$), dielectric loss($\in''$) and relaxation time (τ) for different weight fraction of solute of Iso-Amyl alcohol, ethylenediamine and their binary mixtures in 1,4-dioxan at different temperatures.

Temperature →		293°K			303°K			313°K			323°K		
Solute %	Wt. Fraction	$\in'$	$\in''$	τ ps	$\in'$	$\in''$	τ ps	$\in'$	$\in''$	τ ps	$\in'$	$\in''$	τ ps
IAA 100%	0.0373	2.862	0.253	9.96	2.738	0.217	8.61	2.655	0.175	8.40	2.602	0.147	8.37
	0.0727	2.919	0.329		2.887	0.285		2.767	0.234		2.710	0.208	
	0.1050	3.018	0.405		2.856	0.338		2.826	0.302		2.796	0.269	
	0.1356	3.087	0.479		3.052	0.442		3.018	0.392		2.887	0.332	
IAA (65%) + *EDA* (35%)	0.0388	2.826	0.264	8.07	2.767	0.232	7.36	2.738	0.199	7.12	2.655	0.179	6.63
	0.0748	2.950	0.374		2.887	0.332		2.856	0.294		2.796	0.257	
	0.1082	3.087	0.470		3.066	0.429		3.018	0.388		2.950	0.343	
	0.1392	3.233	0.556		3.196	0.509		3.160	0.469		3.087	0.421	
IAA (38%) + *EDA* (62%)	0.0378	2.950	0.325	6.18	2.826	0.278	6.08	2.796	0.241	5.60	2.767	0.209	5.50
	0.0765	3.018	0.374		2.919	0.317		2.887	0.282		2.858	0.253	
	0.1105	3.393	0.604		3.311	0.534		3.196	0.458		3.160	0.415	
	0.1421	3.478	0.647		3.435	0.602		3.393	0.548		3.311	0.489	

IAA (17%) + *EDA* (83%)	0.0406 0.0780 0.1126 0.1447	2.856 3.087 3.160 3.478	0.273 0.368 0.437 0.554	4.69	2.862 3.018 3.123 3.393	0.238 0.328 0.394 0.486	4.53	2.796 2.919 3.087 3.311	0.205 0.284 0.352 0.433	4.45	2.767 2.887 3.052 3.233	0.182 0.253 0.323 0.385	4.32
EDA (100%)	0.0417 0.0801 0.1154 0.1482	2.767 3.087 3.338 3.537	0.271 0.335 0.384 0.438	3.46	2.738 3.065 3.312 3.478	0.192 0.304 0.363 0.386	3.32	2.710 3.018 3.286 3.393	0.170 0.273 0.334 0.340	3.20	2.682 2.975 3.258 3.367	0.178 0.223 0.286 0.319	2.91

Table –2. The values of free energy of activation (ΔF_τ , ΔF_η), enthalpy of activation (ΔH_τ , ΔH_η) and entropy of activation (ΔS_τ , ΔS_n) for IAA, EDA and their binary mixtures in 1,4-diaxon at different temperatures.

Solute %	Temp. °K	ΔF_τ K cal/mole	ΔH_τ K cal/mole	ΔS_τ cal/mole	ΔF_η K cal/mole	ΔH_η K cal/mole	ΔS_n cal/mole
IAA (100%)	293 303 313 323	2.39 2.41 2.49 2.59	0.637	-5.98 -5.85 -5.92 -6.02	3.231 3.232 3.225 3.167	4.033	2.738 2.644 2.581 2.680
IAA (65%) + *EDA* (35%)	293 303 313 323	2.27 2.31 2.38 2.44	0.233	-6.95 -6.85 -6.86 -6.83	3.231 3.232 3.225 3.167	4.033	2.738 2.644 2.581 2.680
IAA (38%) + *EDA* (62%)	293 303 313 323	2.11 2.20 2.24 2.32	0.252	-6.34 -6.43 -6.35 -6.40	3.231 3.232 3.225 3.167	4.033	2.738 2.644 2.581 2.680
IAA (17%) + *EDA* (83%)	293 303 313 323	1.95 2.02 2.09 2.16	0.307	-5.60 -5.65 -5.69 -5.74	3.231 3.232 3.225 3.167	4.033	2.738 2.644 2.581 2.680
EDA (100%)	293 303 313 323	1.78 1.83 1.89 1.91	0.429	-4.597 -4.630 -4.667 -4.585	3.231 3.232 3.225 3.167	4.033	2.738 2.644 2.581 2.680

5. CONCLUSION:

- The non-linear variation of relaxation time suggests the solute-solute molecular association in the mixture.
- Solute-solvent interaction has been concluded from temperature dependent of dipole moment values in pure *IAA, EDA* and their binary mixtures.
- Studies of thermodynamic parameters suggest that, the dielectric process involves rotation of molecules where as viscous flow process involves rotational as well as translational motion of molecules.
- Negative values of entropy of activation for dielectric relaxation process indicates that, the activated state is more ordered than normal state of molecules.

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