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( 7th January, 2021 )

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7th January, 2021

Seminar Proceedings Issue – 21

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Dr. Chirag M. Patel
(Research Culture Society & Publication)

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

And

Research Culture Society
International Conference  
on  
Advances in Material Science and Nano-Technology  

07th January 2021  

Seminar Proceedings Issue – 21

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President’s Message

“Imagination is more important than knowledge. For knowledge is limited, whereas imagination embraces the entire world, stimulating progress, giving birth to evolution.”  Albert Einstein

The vital force of education aims at utilization of life forces through the aesthetic activity and this could be achieved through audio visual methods improved methods of learning and dynamic participation of students, teachers and society in the process of advancement. The Founder of Sir Sayyed College always guided us to be with the technology. It gives me immense pleasure to know that Physics & Chemistry Departments of our Sir Sayyed College are going to organize One day International e-Seminar on Advances in Material Science and Nano-Technology. The theme of the Seminar is challenging to the academic institutions and the research scholars. I send my warm greetings and hope that participants, researchers and scientists will discuss the innovations in Advances in Material Science and Nano-Technology.

I congratulate and wish that the seminar will be a grand success.

Dr. Shamama Parveen
President, RECWS
Principal’s Message

“One machine can do the work of fifty ordinary men. No machine can do the work of one extraordinary man.”  

Albert Hubbard

We feel proud to host this One day International e-seminar on “Advances in Material Science and Nano-Technology. The devoted and committed teacher, Prof. Mohd Tilawat Ali established this college that could meet the demands of changing times. Prof. Mohd Tilawat Ali named this college after legendary SIR SAYYED AHMED KHAN, an optimistic social reformer and visionary. The college is busy in imparting quality education to the mass. This international seminar provides an ideal academic platform for the researchers and the scientists to present their latest research findings.

I congratulate Computer and the physics Departments and send warm greetings for the success of the seminar.

Dr. Shaikh Kabeer Ahmed
Principal
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.
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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
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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.

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 radiolabeled 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 constrains1-3.

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 drugs4. Simple and precise HPTLC methods were developed for the simultaneous estimation of two anti-inflammatory drugs (curcumin and galangin). The method was tailored to analyze both drugs in their commercial dosage form (capsules) with no interference fromingREDIENTS. 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 mobilephase. Detection and quantification was achieved at 404 nm through spectrodensitometricanalysis5.

The selection of mobile phase is based on adsorbent material used as stationary phase and physical and chemical properties of the 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 by ion 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 pentanesulphonate (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/v/v)6.

RESULT AND DISCUSSION-
Emtricitabine is 4-amino-5-fluoro-1-[(2R,5S)-2-(hydroxymethyl)-1,3-oxathiolan-5-yl]-2-(1H)-pyrimidin-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 9-[(1R)-2-(6-amino-9H-purin-9-yl)-1-methylethoxy]methyl phosphonic acid (Figure II). Tenofovir belongs to a class of antiretroviral drugs known as nucleotide analogue reverse transcriptase inhibitors (nRTIs), which block reverse transcriptase, an enzyme crucial to viral production in HIV-infected people. Literature review revealed that UV10-14, HPLC15-23 and HPTLC19-22 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 Guidelines23.

EXPERIMENTAL SECTION-

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).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Emtricitabine</th>
<th>Tenofovir</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linearity range</td>
<td>320-1120 ng/spot</td>
<td>480-1680 ng/spot</td>
</tr>
<tr>
<td>correlation coefficient (r²)</td>
<td>0.998</td>
<td>0.999</td>
</tr>
<tr>
<td>Slope</td>
<td>8.02</td>
<td>2.52</td>
</tr>
<tr>
<td>Intercept</td>
<td>178.8</td>
<td>50.14</td>
</tr>
</tbody>
</table>

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).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Emtricitabine</th>
<th>Tenofovir</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOD</td>
<td>30.24</td>
<td>51.90</td>
</tr>
<tr>
<td>LOQ</td>
<td>91.64</td>
<td>157.29</td>
</tr>
</tbody>
</table>

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.(ngiband) Intra day Inter day

<table>
<thead>
<tr>
<th>Drug</th>
<th>Concentration (ng band)</th>
<th>%mean</th>
<th>SD</th>
<th>%RSD</th>
<th>%mean</th>
<th>SD</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emtricitabine</td>
<td>800</td>
<td>99.90</td>
<td>0.73</td>
<td>0.73</td>
<td>99.96</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>Tenofurir</td>
<td>1200</td>
<td>99.98</td>
<td>0.72</td>
<td>0.72</td>
<td>99.73</td>
<td>0.82</td>
<td>0.82</td>
</tr>
</tbody>
</table>

*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 Tenofurir 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 Tenofurir respectively.

<table>
<thead>
<tr>
<th>Drug</th>
<th>Level of % recovery</th>
<th>% mean</th>
<th>SD</th>
<th>% R.S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emtricitabine</td>
<td>80%</td>
<td>99.59</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>100%</td>
<td>99.23</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>120%</td>
<td>98.68</td>
<td>0.65</td>
<td>0.65</td>
</tr>
<tr>
<td>Tenofurir</td>
<td>80%</td>
<td>98.59</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>100%</td>
<td>99.93</td>
<td>0.24</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>120%</td>
<td>100.63</td>
<td>1.64</td>
<td>1.64</td>
</tr>
</tbody>
</table>

*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).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>% RSD for Emtricitabine*</th>
<th>% RSD for Tenofurir*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobile phase composition (± 0.1 ml)</td>
<td>99.05</td>
<td>98.95</td>
</tr>
<tr>
<td>Amount of mobile phase (± 1.0 %)</td>
<td>99.08</td>
<td>98.55</td>
</tr>
<tr>
<td>Time from spotting to chromatography (5 min)</td>
<td>98.86</td>
<td>99.14</td>
</tr>
<tr>
<td>Time from chromatography to scanning (10 min)</td>
<td>98.94</td>
<td>98.90</td>
</tr>
</tbody>
</table>

*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 Tenofurir 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 Tenofurir 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 Tenofurir 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.

<table>
<thead>
<tr>
<th>Stress condition</th>
<th>Drug</th>
<th>Mass balance</th>
<th>Rf values of degradation Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid hydrolysis (0.1N HCl)</td>
<td>Emtricitabine</td>
<td>99.99</td>
<td>0.15, 0.24</td>
</tr>
<tr>
<td></td>
<td>Tenofovir</td>
<td>99.12</td>
<td>0.14, 0.29, 0.79</td>
</tr>
<tr>
<td>Alkali hydrolysis (0.1N NaOH)</td>
<td>Emtricitabine</td>
<td>100.10</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>Tenofovir</td>
<td>98.96</td>
<td>0.02</td>
</tr>
<tr>
<td>Oxidation (3%H₂O₂)</td>
<td>Emtricitabine</td>
<td>99.96</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>Tenofovir</td>
<td>100.02</td>
<td>0.37, 0.58</td>
</tr>
</tbody>
</table>

Table VI: Results of Forced Degradation studies

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.

REFERENCES:

7. www.drugbank.ca/drugs/DB08864
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 of β-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.

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. 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 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. It has been employed numerous times successfully as a key step in natural product synthesis as well as in medicinal chemistry. 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. 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 as well. Most Mannich reactions are catalyzed by Lewis acid or Brønsted acid. In recent years, the researchers continued to study new synthetic methods and new catalysts including TMG32, Sm(OTf)3, Fe(HSO4)3/SiO2, triphenylphosphine, nano-Mn(HSO4)2, Zeolite were reported. Variety of asymmetric versions of Mannich reaction have been reported.

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, anti-HIV, anti-cancer, anti-fungal, anti-malarial 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 diastereoselectivity, non-reusable solvents, poor yields etc. Encouraged by the all this researched literature along with pyridinium supported ionic liquid reagents and catalysts 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.

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>
<thead>
<tr>
<th>Entry</th>
<th>Temperature °C</th>
<th>Time (h)</th>
<th>Yielda (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>1.5</td>
<td>65</td>
</tr>
<tr>
<td>3</td>
<td>70</td>
<td>1</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>1</td>
<td>65</td>
</tr>
</tbody>
</table>

aData all the products were purified using column chromatography and confirmed with melting point m.p. 118–120° C

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactant 1</th>
<th>Reactant 2</th>
<th>Product</th>
<th>Yielda (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>2a</td>
<td>4a</td>
<td>92%</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>2b</td>
<td>4b</td>
<td>96%</td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>2c</td>
<td>4c</td>
<td>78%</td>
</tr>
<tr>
<td>4</td>
<td><img src="image1.png" alt="Structure 1a" /></td>
<td><img src="image2.png" alt="Structure 2d" /></td>
<td><img src="image3.png" alt="Structure 4d" /></td>
<td>83%</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td><img src="image1.png" alt="Structure 1a" /></td>
<td><img src="image2.png" alt="Structure 2e" /></td>
<td><img src="image3.png" alt="Structure 4e" /></td>
<td>77%</td>
</tr>
<tr>
<td>6</td>
<td><img src="image1.png" alt="Structure 1b" /></td>
<td><img src="image2.png" alt="Structure 2b" /></td>
<td><img src="image3.png" alt="Structure 4f" /></td>
<td>86%</td>
</tr>
<tr>
<td>7</td>
<td><img src="image1.png" alt="Structure 1b" /></td>
<td><img src="image2.png" alt="Structure 2e" /></td>
<td><img src="image3.png" alt="Structure 4g" /></td>
<td>79%</td>
</tr>
<tr>
<td>8</td>
<td><img src="image1.png" alt="Structure 1b" /></td>
<td><img src="image2.png" alt="Structure 2f" /></td>
<td><img src="image3.png" alt="Structure 4h" /></td>
<td>88%</td>
</tr>
<tr>
<td>9</td>
<td><img src="image1.png" alt="Structure 1b" /></td>
<td><img src="image2.png" alt="Structure 2b" /></td>
<td><img src="image3.png" alt="Structure 4i" /></td>
<td>82%</td>
</tr>
<tr>
<td>10</td>
<td><img src="image1.png" alt="Structure 1b" /></td>
<td><img src="image2.png" alt="Structure 2a" /></td>
<td><img src="image3.png" alt="Structure 4j" /></td>
<td>85%</td>
</tr>
<tr>
<td>11</td>
<td><img src="image1.png" alt="Structure 1b" /></td>
<td><img src="image2.png" alt="Structure 2g" /></td>
<td><img src="image3.png" alt="Structure 4k" /></td>
<td>79%</td>
</tr>
<tr>
<td>12</td>
<td><img src="image1.png" alt="Structure 1c" /></td>
<td><img src="image2.png" alt="Structure 2d" /></td>
<td><img src="image3.png" alt="Structure 4l" /></td>
<td>80%</td>
</tr>
<tr>
<td>13</td>
<td><img src="image1.png" alt="Structure 1c" /></td>
<td><img src="image2.png" alt="Structure 2h" /></td>
<td><img src="image3.png" alt="Structure 4m" /></td>
<td>85%</td>
</tr>
</tbody>
</table>
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%.

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.

Conclusion:

A microwave assisted simple and efficient synthetic method has been testified for a variety of \( \beta \)-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 \( \beta \)-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): \( \delta \) (ppm) = 1.60-1.89 (m, 8H), 2.32-2.41(q, 1H, \( j = 20\)Hz), 3.76(s, 3H), 4.57-4.60(d, 1H, \( j = 12\)Hz), 6.50-7.30 (m, 9H).

\(^1\)H NMR of (2-((phenylamino)(P-Tolyl)methyl)cyclohexanone) (4d):-
\(^{1}\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta\) (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, \(j = 8\)Hz), 4.47-4.59(d, 1H, \(j = 8\)Hz), 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): \(\delta\) (ppm) = 1.28-1.84 (m, 8H), 2.35-2.84 (m, 3H), 3.76(s, 3H), 4.41-4.45(d, 1H, \(j = 16\)Hz), 4.87(s, 1H), 6.50-7.26(m, 9H)

\(^{13}\)C-NMR (CDCl\(_3\), 100 MHz): \(\delta\) (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): \(\delta\) (ppm) = 1.26-2.47(m, 10H), 2.93-2.98(t, \(j = 8\)Hz), 4.55-4.58(d, \(j = 12\)Hz), 4.69(s, 1H), 6.47-7.57(m, 9H)

\(^{13}\)C-NMR (CDCl\(_3\), 100 MHz): \(\delta\) (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-((2-chlorophenyl) (Phenylamino)methyl)cycloheptanone (4m):

\(^{1}\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta\) (ppm) = 1.59-2.42 (m,10H), 3.25-3.32(t, \(j = 8\)Hz), 5.86-5.91(d, \(j = 20\)Hz), 6.47-6.56 (m, 2H), 7.03-7.50 (m, 7H).

\(^{13}\)C-NMR (CDCl\(_3\),100 MHz): \(\delta\) (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): \(\delta\) (ppm) = 1.26-1.89 (m, 10H), 2.36-2.93 (q, \(j = 20.4\) Hz), 4.45-4.49(d, \(j = 16\)Hz), 4.80 (s, 1H), 6.53-7.30 (m, 14H)

\(^{13}\)C-NMR (CDCl\(_3\),100 MHz): \(\delta\) (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

References:

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

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].

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/cm³.

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.

Theory:-

The specific acoustic impedance[11] is given by ,

$$Z = \frac{U}{\rho}$$

Where ‘$U$’ is the ultrasonic velocity (of the mixture) and ‘$\rho$’ is the density of the mixture.

The adiabatic compressibility[11] is given by,

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

Where, ‘$U$’ and ‘$\rho$’ are the velocity and density of liquid mixture.

The general formula for calculating the excess parameters [1-3] is given below

$$A^E = A_m - (x_1 M_1 + (1 - x_1)M_2)$$
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

$$A^E = x_1x_2 \sum_{i=0}^{n} A_i (1 - 2x_2)^i$$

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

**Result and Discussion:**

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

<table>
<thead>
<tr>
<th>Volume fraction of acrylonitrile</th>
<th>Density (g/cm$^3$)</th>
<th>Viscosity (cP)</th>
<th>Velocity (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.023</td>
<td>0.440</td>
<td>1286</td>
</tr>
<tr>
<td>0.1</td>
<td>1.003</td>
<td>0.434</td>
<td>1298</td>
</tr>
<tr>
<td>0.2</td>
<td>0.983</td>
<td>0.418</td>
<td>1312</td>
</tr>
<tr>
<td>0.3</td>
<td>0.939</td>
<td>0.405</td>
<td>1327</td>
</tr>
<tr>
<td>0.4</td>
<td>0.917</td>
<td>0.397</td>
<td>1342</td>
</tr>
<tr>
<td>0.5</td>
<td>0.890</td>
<td>0.389</td>
<td>1359</td>
</tr>
<tr>
<td>0.6</td>
<td>0.870</td>
<td>0.383</td>
<td>1374</td>
</tr>
<tr>
<td>0.7</td>
<td>0.846</td>
<td>0.375</td>
<td>1391</td>
</tr>
<tr>
<td>0.8</td>
<td>0.828</td>
<td>0.369</td>
<td>1409</td>
</tr>
<tr>
<td>0.9</td>
<td>0.805</td>
<td>0.368</td>
<td>1427</td>
</tr>
<tr>
<td>1</td>
<td>0.796</td>
<td>0.360</td>
<td>1454</td>
</tr>
</tbody>
</table>

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.
Negative values of acoustic impedance 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

Negative 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.

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 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.

Acknowledgment: All Authors are thankful to Prof. A. G. Murugkar, department of Physics, Dr. Babasaheb Ambedkar Marathwada University Aurangabad for kind support, guidance provided.
References:

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

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 serious global threat to the surrounding environment affecting all living creatures. 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. 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.

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.

Numerous traditional methods like precipitation, ultra-filtration, electrode-deposition, reverse osmosis, electrochemical treatments, membrane filtration, evaporation, flotation, oxidation–reduction, and biosorption for elimination of heavy metal from aqueous solution. 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 secondary pollutants. Adsorption is most commonly method used for heavy metals removal from water.

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. Recently, the innovative development of nanoscience and nanotechnology has shown significant potential for the remediation of environmental concerns. 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.

The nano-sized metal oxides like titanium oxides, ferric oxides, aluminium oxides, magnesium oxides, zinc oxide, and copper oxides 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.

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.
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 the separation and decantation of adsorbate was done and the 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.

RESULT AND DISCUSSION:

Effect of pH:

The adsorption of Cd onto CON suggests the electrostatic attraction particularly at a relatively low pH. As the pH value increases from 3 to 11 decrease 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.

![Figure (1): Effect of pH](image1)

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.

![Figure (2): Effect of concentration of metal ion](image2)
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 remains unsaturated which decreases unit adsorption during the adsorption process.\textsuperscript{15}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{effect_of_amount_adsorbed.png}
\caption{Effect of amount of adsorbent}
\end{figure}

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.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{effect_of_time.png}
\caption{Effect of time}
\end{figure}

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.\textsuperscript{16}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{effect_of_temperature.png}
\caption{Effect of temperature}
\end{figure}
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\(^\text{17}\) 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\(^\text{22}\) as in figure (6).

The Langmuir isotherm is stated in terms of important characteristic dimensionless constant separation factor or equilibrium factor \(R_L\) as suggested by the nature of the isotherm is below:

<table>
<thead>
<tr>
<th>(R_L) Value</th>
<th>Types of Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_L &gt; 1)</td>
<td>Unfavorable</td>
</tr>
<tr>
<td>(R_L = 1)</td>
<td>Linear</td>
</tr>
<tr>
<td>(0 &lt; R_L &lt; 1)</td>
<td>Favorable</td>
</tr>
<tr>
<td>(R_L = 0)</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

For non-ideal adsorption, the Freundlich isotherm may be used involving heterogeneous sorption\(^\text{18}\). 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 in figure (7).

**CONCLUSION:**
Investigational results shows that the use of copper oxide 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 have 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. Copper oxide 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 $\rho$ due to the impact of gamma radiation on the Co-Zn ferrite system

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ABSTRACT:
Resistance of the Co,Zn,Fe$_{204}$ samples is measured after irradiation with Co$^{60}$ $\gamma$-radiation and compared with that prior to irradiation. The aim of the present work is to shed light on the effect of $\gamma$ -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.

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 synthesise 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 are known to be sensitive to chemical composition, microstructure, type and amount of doping. [5,6,7] etc

EXPERIMENTAL:

Sample preparation
Samples of the system Co$_{1-x}$Zn$_x$Fe$_{204}$ ($x = 0.0,0.2$) were prepared by using the usual ceramic technique (Josulu and Sobhanadri, 1980)[8]. The ferrites were prepared by the conventional double-stage sintering process. The very pure COO, ZnO, Fe$_2$O$_3$(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$^{60}$ $\gamma$ –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.

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 ($\log \rho$) 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

$$\rho = \rho_0 \exp \left[ -\frac{E_g}{kT} \right]$$

where,

- $E_g$ is activation energy in eV,
- $\rho_0$ is temperature dependent factor,
- $k$ is Boltzmann constant
- $T$ is absolute temperature.

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].

\[ \text{Fig. 1(a) and (b): Variation of } \log \rho \text{ with } 1000/T \text{ of } \text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4 \text{ for } x = 0.0 \text{ and } x = 0.2 \]

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,

\[
\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+} + e^- 
\]

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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11. Shaikh A.K (2009), *Effect of gamma radiation on some physical properties of ferrite,* DrBAMU, Aurangabad
Structural and Electrical Properties of Ti$^{4+}$ Substituted Ni-ferrite Synthesized by Solid State Reaction Method

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#corresponding author: cmkale1973@gmail.com

ABSTRACT:
Tetravalent Ti-doped Ni-ferrite with generic formula Ni$_{1+x}$Ti$_x$Fe$_{2-2x}$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$_x$Fe$_{2-2x}$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. The XRD data was used to determine lattice constant ‘a’ of the system with an accuracy ± 0.002 A.U. The lattice constant of ferrite system Ni$_{1+x}$Ti$_x$Fe$_{2-2x}$O$_4$ decreases with Ti$^{4+}$ substitution. 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 indicating semiconducting nature of the samples. The observed decreasing nature of d. c. electrical resistivity may be attributed to decrease in the electron hopping 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, activation energy.

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 losses 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$_x$Fe$_{2-2x}$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$_2$O$_3$) 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°C 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°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° to 80°. 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\(_x\)Fe\(_{2-2x}\)O\(_4\) system

X-ray powder diffraction (XRD) patterns of Ni\(_{1+x}\)Ti\(_x\)Fe\(_{2-2x}\)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\(_x\)Fe\(_{2-2x}\)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\(_x\)Fe\(_{2-2x}\)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 1

<table>
<thead>
<tr>
<th>Ti content x</th>
<th>Lattice constant ‘a’ (Å)</th>
<th>Particle Size (Å)</th>
<th>X-Ray density (gm/cm(^3))</th>
<th>Bulk density (gm/cm(^3))</th>
<th>Porosity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.332</td>
<td>453.9</td>
<td>4.041</td>
<td>3.729</td>
<td>7.72</td>
</tr>
</tbody>
</table>
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,

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

where, $\Delta E$ 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 plots of Ti content x (=0.1 and 0.2) of Ni$_{1+x}$Ti$_x$Fe$_{2-2x}$O$_4$ system](image-url)
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

<table>
<thead>
<tr>
<th>Ti content $x$</th>
<th>Activation energy (eV)</th>
<th>$\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_F$</td>
<td>$E_P$</td>
</tr>
<tr>
<td>0.0</td>
<td>0.305</td>
<td>0.699</td>
</tr>
<tr>
<td>0.1</td>
<td>0.203</td>
<td>0.385</td>
</tr>
<tr>
<td>0.2</td>
<td>0.259</td>
<td>0.325</td>
</tr>
<tr>
<td>0.3</td>
<td>0.296</td>
<td>0.359</td>
</tr>
<tr>
<td>0.4</td>
<td>0.283</td>
<td>0.709</td>
</tr>
<tr>
<td>0.5</td>
<td>0.234</td>
<td>0.411</td>
</tr>
<tr>
<td>0.6</td>
<td>0.151</td>
<td>0.340</td>
</tr>
<tr>
<td>0.7</td>
<td>0.188</td>
<td>0.581</td>
</tr>
</tbody>
</table>

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 ($Fe^{3+} \leftrightarrow Fe^{2+}$, $Ni^{2+} \leftrightarrow Fe^{3+}$, $Fe^{2+}$, $Ni^{3+}$) [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 great er than that in ferrimagnetic region.

5. ACKNOWLEDGMENT

One of the authors (CMK) is thankful to Prof. K. M. Jadhav, (Dr. B. A. M. U. Aurangabad) for their consistant help and cooperation while fruitful discussion.

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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-substituted 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 tumorigenicity, 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 druglikeness 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 drug1. The molecular properties involved molecular weight, hydrophobicity, electronic distribution, hydrogen bond acceptors and donors, solubility, and other concerned properties2.

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 druglike properties may help to achieve decent pharmacodynamics 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 drugs3.

Now generally the Lipinski’s rule of Five (RO5) is used to determine the drug likeness of the evaluated drug molecules4. 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 druglikeness of a molecule is important for the screening the drug like molecules.

Methods for druglikeness 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 druglikeness 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 organism5. There is no consideration for pharmacodynamics 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. Druglikeness was a broad term used to define absorption, distribution metabolism, excretion and toxic (ADMET) properties of a drug molecule6-11.

Heterocyclic compounds it may be natural or synthetic have been immensely explored for their prifound applicability in the field of industrial, agricultural and medicinal chemistry. Cinnamamide containing heterocyclic moiety with a various of biological properties2, like central nervous system depressant, anticonvulsant, muscle relaxant, anti-allergic, antineoplastic, antitumor, anesthetic, analgesic and anti-infective activities and anti-infective activities12-15, etc. In agrochemical field, insecticidal, their avian repellent, herbicidal activities, and several excellent cinnamamide
are fungicides. Inspire of wide range of their applications and very less attention is paid towards the synthesis of cinnamamides 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 physico-chemical properties like clogP, 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 tumorogenic, mutagenic, irritation, and reproduction effectivity and various physico-chemical properties like clogP, solubility, drug-likeness and drug score were calculated by the methodology developed by Data warrior software of Osiris property explorer.

The (E)-3-Substituted phenyl- 1-piperidino-2-propen-1-one Cinnamamides and (2E)-1-(piperazine-1-yl)-3-substituted 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](image1)

![Fig.2- Structure of (E)-3-phenyl-1-Piperidino-2-Propen-1-one Cinnamamide.](image2)

2.1 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:

\[
ds = \prod \left( \frac{1}{2} + \frac{1}{2} s_i \right) \cdot \prod f_i
\]

\[
s = \frac{1}{1 + e^{ap+q}}
\]
Where, $ds$ is the drug score, $si$ are the contributions calculated directly from $c\text{LogP}$, $\log S$, molecular weight and drug-likeness. Parameters $a$ and $b$ are $(1, -5)$, $(0.012, -6)$ and $(1, 0)$ for $c\text{LogP}$, molecular weight and drug-likeness, 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.

Piperidine heterocyclic compounds (D1 to D4)

- A1 to A4 Benzaldehyde with all substitution as follows-

\[
\text{Ph}_3\text{P}=\text{C}=\text{N} \quad \text{NH}
\]

(B) Ph$_3$P=CO

Reflux
Dry Benzene

Piperazine heterocyclic compounds (E1 to E4)

\[
\text{Ph}_3\text{P}=\text{C}=\text{N} \quad \text{NH}
\]

(C) Ph$_3$P=CO

Reflux
Dry Benzene

\[
\text{Reflux} \quad \text{Dry Benzene}
\]

Available online on – WWW.IJIRMF.COM
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-prop-1-one Cinnamamides and (2E)-1-(piperazine-1-yl)-3-substituted 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, ¹H NMR, 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>
<thead>
<tr>
<th>Sr. No.</th>
<th>Entries</th>
<th>Mol. Formula</th>
<th>Mol. Weight</th>
<th>Yield in %</th>
<th>M.P. in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>D1</td>
<td>C₁₄H₁₇ON</td>
<td>215</td>
<td>62</td>
<td>162</td>
</tr>
<tr>
<td>2</td>
<td>D2</td>
<td>C₁₅H₁₉O₂N</td>
<td>245</td>
<td>64</td>
<td>174</td>
</tr>
<tr>
<td>3</td>
<td>D3</td>
<td>C₁₆H₁₇O₂N</td>
<td>275</td>
<td>70</td>
<td>186</td>
</tr>
<tr>
<td>4</td>
<td>D4</td>
<td>C₁₇H₁₉O₂N</td>
<td>305</td>
<td>64</td>
<td>202</td>
</tr>
<tr>
<td>5</td>
<td>E1</td>
<td>C₁₃H₁₆N₂O</td>
<td>216</td>
<td>72</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>E2</td>
<td>C₁₄H₁₈N₂O₂</td>
<td>246</td>
<td>84</td>
<td>136</td>
</tr>
<tr>
<td>7</td>
<td>E3</td>
<td>C₁₅H₂₀N₂O₃</td>
<td>276</td>
<td>82</td>
<td>181</td>
</tr>
<tr>
<td>8</td>
<td>E4</td>
<td>C₁₆H₂₂N₂O₄</td>
<td>306</td>
<td>74</td>
<td>229</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Entries</th>
<th>Molecular Formula</th>
<th>Mol. Wt.</th>
<th>% C (calculated)</th>
<th>% H (calculated)</th>
<th>% O (calculated)</th>
<th>% N (calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>D1</td>
<td>C₁₄H₁₇ON</td>
<td>215</td>
<td>78.10 (78.14)</td>
<td>7.96 (7.91)</td>
<td>7.43 (7.44)</td>
<td>6.51 (6.51)</td>
</tr>
<tr>
<td>2</td>
<td>D2</td>
<td>C₁₅H₁₉O₂N</td>
<td>245</td>
<td>73.44 (73.47)</td>
<td>7.81 (7.76)</td>
<td>13.04 (13.06)</td>
<td>5.71 (5.71)</td>
</tr>
<tr>
<td>3</td>
<td>D3</td>
<td>C₁₆H₂₁O₂N</td>
<td>275</td>
<td>69.79 (69.82)</td>
<td>7.69 (7.64)</td>
<td>17.43 (17.45)</td>
<td>5.09 (5.09)</td>
</tr>
<tr>
<td>4</td>
<td>D4</td>
<td>C₁₇H₂₃O₂N</td>
<td>305</td>
<td>66.86 (66.89)</td>
<td>7.59 (7.54)</td>
<td>20.96 (20.98)</td>
<td>4.59 (4.59)</td>
</tr>
<tr>
<td>5</td>
<td>E1</td>
<td>C₁₃H₁₆N₂O</td>
<td>216</td>
<td>72.19 (72.22)</td>
<td>7.46 (7.40)</td>
<td>7.40 (7.40)</td>
<td>12.95 (12.96)</td>
</tr>
<tr>
<td>6</td>
<td>E2</td>
<td>C₁₄H₁₈N₂O₂</td>
<td>246</td>
<td>68.27 (68.29)</td>
<td>7.37 (7.32)</td>
<td>12.99 (13.00)</td>
<td>11.37 (11.38)</td>
</tr>
<tr>
<td>7</td>
<td>E3</td>
<td>C₁₅H₂₀N₂O₃</td>
<td>276</td>
<td>65.27 (65.22)</td>
<td>7.30 (7.25)</td>
<td>17.37 (17.39)</td>
<td>10.14 (10.14)</td>
</tr>
<tr>
<td>8</td>
<td>E4</td>
<td>C₁₆H₂₂N₂O₄</td>
<td>306</td>
<td>62.73 (62.75)</td>
<td>7.24 (7.19)</td>
<td>20.89 (20.92)</td>
<td>9.14 (9.15)</td>
</tr>
</tbody>
</table>
Table-3:- Drug likeness properties of piperidino/ piperazine cinnamamides:

<table>
<thead>
<tr>
<th>Entry</th>
<th>Molecular Formula</th>
<th>Mol. Wt.</th>
<th>cLogP</th>
<th>Solubility</th>
<th>TPSA</th>
<th>Drug-likeliness Value</th>
<th>Drug Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>C13H17ON</td>
<td>215</td>
<td>2.83</td>
<td>-2.58</td>
<td>20.31</td>
<td>-0.93</td>
<td>0.57</td>
</tr>
<tr>
<td>D2</td>
<td>C13H19O2N</td>
<td>245</td>
<td>2.48</td>
<td>-2.29</td>
<td>40.54</td>
<td>0.57</td>
<td>0.75</td>
</tr>
<tr>
<td>D3</td>
<td>C13H18O2N</td>
<td>275</td>
<td>2.69</td>
<td>-2.62</td>
<td>38.77</td>
<td>2.26</td>
<td>0.84</td>
</tr>
<tr>
<td>D4</td>
<td>C13H12O2N</td>
<td>305</td>
<td>2.62</td>
<td>-2.64</td>
<td>48.00</td>
<td>3.43</td>
<td>0.86</td>
</tr>
<tr>
<td>E1</td>
<td>C13H16N2O</td>
<td>216</td>
<td>1.52</td>
<td>-1.56</td>
<td>32.34</td>
<td>-0.93</td>
<td>0.57</td>
</tr>
<tr>
<td>E2</td>
<td>C13H14N2O2</td>
<td>246</td>
<td>1.54</td>
<td>-1.58</td>
<td>41.57</td>
<td>0.53</td>
<td>0.35</td>
</tr>
<tr>
<td>E3</td>
<td>C13H20N2O3</td>
<td>276</td>
<td>1.38</td>
<td>-1.60</td>
<td>50.8</td>
<td>2.26</td>
<td>0.85</td>
</tr>
<tr>
<td>E4</td>
<td>C16H22N2O4</td>
<td>306</td>
<td>1.31</td>
<td>-161</td>
<td>60.03</td>
<td>3.43</td>
<td>0.86</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Entry</th>
<th>Mutagenic</th>
<th>Tumorogenic</th>
<th>Irritation</th>
<th>Reproduction effect</th>
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<tr>
<td>1</td>
<td>D1</td>
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<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>2</td>
<td>D2</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>3</td>
<td>D3</td>
<td>None</td>
<td>None</td>
<td>High</td>
<td>None</td>
</tr>
<tr>
<td>4</td>
<td>D4</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>5</td>
<td>E1</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>6</td>
<td>E2</td>
<td>None</td>
<td>None</td>
<td>High</td>
<td>None</td>
</tr>
<tr>
<td>7</td>
<td>E3</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>8</td>
<td>E4</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
</tbody>
</table>

3.1 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-

  1HNMR-(400 MHz, CDCl3, δ ppm)- 1.2(m), (2H), CH2; 1.4(m), (4H) CH2; 3.4(t), (4H), 2CH2-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) 1685, 1600; Mass: m/z (%): 215.13 (100) (M)+, 216.0 (15.50).

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

  1HNMR-(400 MHz, CDCl3, δ ppm)- 1.2(m),(2H), CH2; 1.4(m), (4H) CH2; 3.4(t), (4H), 2CH2-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-CH3).

  **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

  1HNMR (400 MHz, CDCl3) 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

  1HNMR(400 MHz, CDCl3): 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=CHC6H5) 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 piperazidine 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.

REFERENCES:

Dielectric Estimation of Loss Factor and Field Strength Using TDR

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cShivaji Arts, Commerce and science college Kannad…431103(MS)

4Corresponding author: shaikhyh@gmail.com

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:

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

2.2 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 \( \varepsilon^*(\omega) \) 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 \( \varepsilon' \) and \( \varepsilon'' \) 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:

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

(1)

Where, \( \varepsilon_0 \) is static permittivity, \( \varepsilon_\infty \) is permittivity at high frequency, \( \tau \) is relaxation time, \( \alpha \) and \( \beta \) are the empirical parameters for the distribution of relaxation time between 0 and 1. The Havriliak-Negami function includes the Cole-Cole [12] (\( \beta=1 \)), Cole-Davidson [13] (\( \alpha=0 \)) and Debye [14] (\( \alpha=0, \beta=1 \)) 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 \( \tan\delta \) has been calculated by making use of [15]

\[
\tan\delta = \frac{\varepsilon''}{\varepsilon'}
\]  

(2)

\[
\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty
\]  

(3)

3. Results and discussion:-

![Figure 1](image)

The cole-cole plot (\( \varepsilon' \) vs \( \varepsilon'' \) plot) for ETOH-1-PENT binary mixture at 25 °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 \( \tan\delta \) according to varying concentrations of 1-pentanol in ethanol. Several workers have reported [17] that \( \tan\delta \) is the angle between polarization and the field which in turn yields the loss factor. At concentration 0.5 of 1-pentanol \( \tan\delta \) is highest this manifest angle between the polarization and the field is greater at concentration 0.5 which 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 \( \tan\delta \) 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](image2.png)

**Figure 2**

Variations of $\tan \delta$ with volume fraction of 1-pentanol

![Figure 3](image3.png)

**Figure 3**

Variations of $\Delta \varepsilon$ with volume fraction of 1-pentanol

4. Conclusions:-

The cole-cole plot for ethanol-1-pentanol binary mixture exhibits Debye behavior. The study of $\tan \delta$ 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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References:

Why simulate?

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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:
2.1 Types of Analysis:

2.1.1 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.

2.1.2 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.

2.1.3 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.

2.1.4 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.

2.1.5 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.

2.1.6 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.

2.1.7 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.

REFERENCES:

Synthesis, In Vitro Antimicrobial Activities Evaluation of Some Novel 3-Hydroxy-4H-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 % H2O2 using methanol as solvent in the presence of 20 % NaOH in ice cold condition (0-5 °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, 1H 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 moniliforme and Aspergillus flavus, using Penicilin 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.

INTRODUCTION:
Flavonoids are well known group of naturally occurring aromatic oxygen containing heterocyclic compounds. They broadly distributed in different plants kingdom and are found in many fruits, vegetables, tea and in red wines. They constitute most of yellow, red 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 antidepressant15 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-4H-chromen-4-one (4a–j) having substituted halogens, dimethylamo and methyl groups with an aim to find new most active in vitro antibacterial and antifungal agents.

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 1H-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-4H-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-4H-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 °C, then added 30% H2O2 (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-4H-chromen-4-one derivatives.
ANTIMICROBIAL ACTIVITY:

In vitro antibacterial activity:

The synthesized substituted 3-hydroxy-4H-chromen-4-one compounds were screened for their antibacterial activity by using agar cup method 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 37°C for 24 hrs. The penicillin is the standard drug used for antibacterial comparison purpose. The corresponding pure substituted 3-hydroxy-4H-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 37°C for 24 hrs, and then the zones of inhibition were recorded.

In vitro antifungal activity:

The antifungal activity of substituted 3-hydroxy-4H-chromen-4-one compounds (4a-j) were screened against four plant pathogenic and mold fungi, such as *Aspergillus niger*, *penicillium chrysogenum*, *Fusarium monelliforme* and *Aspergillus flavus*. The antifungal activities of the synthesized 3-hydroxy-4H-chromen-4-one compounds were assessed by poisoned plate method. 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°C of the rate 100 mg/mL PDA. The medium was poured in sterilized petri-plates and allowed to solidify. The medium was poured in sterilized petri-plates 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 37°C for 24 hrs, and then the zones of inhibition were recorded.

RESULTS AND DISCUSSION:

In this research work we have synthesized the novel substituted 3-hydroxy-4H-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-4H-chromen-4-one derivatives didn’t give violet coloration with FeCl₃ solution and pink coloration with concentrated H₂SO₄. The structures of newly synthesized compounds have been confirmed by spectral data. The IR spectra of substituted 3-hydroxy-4H-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 ¹H 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

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

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Entry</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>Molecular Formula</th>
<th>Molecular weight</th>
<th>Yield in (%)</th>
<th>Melting point ⁰C</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>4a</td>
<td>I</td>
<td>H</td>
<td>I</td>
<td>C₁₁H₁₃O₃I₂N</td>
<td>533</td>
<td>78</td>
<td>221</td>
</tr>
<tr>
<td>2</td>
<td>4b</td>
<td>I</td>
<td>H</td>
<td>CH₃</td>
<td>C₁₈H₁₉O₃I₂N</td>
<td>421</td>
<td>80</td>
<td>230</td>
</tr>
<tr>
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<td>Cl</td>
<td>H</td>
<td>Cl</td>
<td>C₁₇H₁₅O₂Cl₂N</td>
<td>349</td>
<td>75</td>
<td>225</td>
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<tr>
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<td>I</td>
<td>H</td>
<td>Cl</td>
<td>C₁₇H₁₇O₂ICl₂N</td>
<td>441</td>
<td>80</td>
<td>227</td>
</tr>
<tr>
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<td>H</td>
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<td>C₁₈H₁₉O₂Br₂N</td>
<td>374</td>
<td>75</td>
<td>220</td>
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<tr>
<td>6</td>
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<td>198</td>
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<td>76</td>
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<td>8</td>
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<tr>
<td>10</td>
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</table>
proton of ortho-hydroxyl group in the phenyl ring of chalcone which clearly indicates the formation of substituted 3-hydroxy-4H-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-4H-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’-dimethylamino-phenyl)-3-hydroxy-4H-chromene-4-one (4e) and 8-bromo-6-chloro-2-(4’-dimethylamino-phenyl)-3-hydroxy-4H-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’-dimethylamino-phenyl)-3-hydroxy-4H-chromene-4-one (4b), 8-iodo-6-bromo-2-(4’-dimethylamino-phenyl)-3-hydroxy-4H-chromene-4-one (4h) and compounds 8-bromo-2-(4’-dimethylamino-phenyl)-3-hydroxy-4H-chromene-4-one (4j) does not showed activity against E. coli while compounds 8-iodo-6-chloro-2-(4’-dimethylamino-phenyl)-3-hydroxy-4H-chromene-4-one (4d), 8-iodo-6-bromo-2-(4’-dimethylammino-phenyl)-3-hydroxy-4H-chromene-4-one (4h) and compound 8-bromo-2-(4’-dimethylamino-phenyl)-3-hydroxy-4H-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-4H-chromene-4-one (4e), 8-bromo-6-methyl-2-(4’-dimethylamino-phenyl)-3-hydroxy-4H-chromene-4-one (4e), 8-bromo-6-chloro-2-(4’-dimethylamino-phenyl)-3-hydroxy-4H-chromene-4-one (4f) and 8-iodo-6-bromo-2-(4’-dimethylamino-phenyl)-3-hydroxy-4H-chromene-4-one (4h) showed maximum antibacterial activity against Bacillus subtilis as compared with standard drug with zone of inhibition 17mm, 18mm, 22mm 17mm and 18mm respectively as compare to zone of inhibition 22mm. The compounds 6, 8-dichloro-2-(4’-dimethylamino-phenyl)-3-hydroxy-4H-chromene-4-one (4e), 8-bromo-6-chloro-2-(4’-dimethylamino-phenyl)-3-hydroxy-4H-chromene-4-one (4f), 6, 8-dichloro-2-(4’-dimethylamino-phenyl)-3-hydroxy-4H-chromene-4-one (4g) and 8-iodo-6-bromo-2-(4’-dimethylamino-phenyl)-3-hydroxy-4H-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-4H-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-4H-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 chrysogenum, Fusarium monelliforme and Aspergillus flavus. The antifungal activity data showed in Table No. 3. The study revealed that the newly synthesized 3-hydroxy-4H-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-4H-chromene-4-one (4c), 8-Iodo-6-choro-2-(4’-dimethylamino-phenyl)-3-hydroxy-4H-chromene-4-one(4d) and 8-bromo-2-(4’-dimethylamino-phenyl)-3-hydroxy-4H-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-4H-chromene-4-one compounds.

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

Yield 80%, melting point 230°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), δ 3.0 - 3.1 ppm (s, 6H, N-(CH₃)), 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-4H-chromene-4-one (4c):

Yield 75%, Melting Point: 225°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), δ 3.0 - 3.2 ppm (s, 6H, N-(CH₃)), 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-4H-chromene-4-one (4e):

Yield 75%, Melting Point: 220°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), δ 2.1 - 2.3 (s, 3H, CH₃), δ 2.9 - 3.2 (s, 6H, N-(CH₃)), 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

Available online on – WWW.IJIRMF.COM
8-Bromo-6-Chloro-2-(4'-dimethylamino-phenyl)-3-hydroxy-4H-chromen-4-one (4f):–
Yield 82%, Melting Point: 98°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), ¹H NMR (DMSO): δ 2.0 - 2.3 (s, 3H, CH₃), δ 2.8 - 3.2 (s, 6H, N-(CH₃)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-4H-chromen-4-one (4i):–
Yield 82%, Melting point: 195°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), ¹H NMR (DMSO): δ 2.2 - 2.4 ppm (s, 3H, CH₃), δ 3.0 - 3.2 ppm (s, 6H, N-(CH₃)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-4H-chromen-4-one (4j):–
Yield 82%, Melting point: 98°C, IR (KBr): 1587 cm⁻¹ (>C=C< str), 1290 cm⁻¹ (>C-O str), 1614 cm⁻¹ (>C=O pyrone ring), ¹H NMR (DMSO): δ 3.0-3.2 ppm (s, 6H, N-(CH₃)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-4H-chromen-4-one derivatives (4a-j)

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Entry</th>
<th>molecular formula</th>
<th>Antibacterial activity (Zone of Inhibition in mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Escherichia coli</td>
</tr>
<tr>
<td>1</td>
<td>4a</td>
<td>C₁₀H₁₈O₃I₂N</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>4b</td>
<td>C₁₀H₁₈O₂I₂N</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>4c</td>
<td>C₁₀H₁₈O₂Cl₂N</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>4d</td>
<td>C₁₀H₁₈O₂I₂Cl₂N</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>4e</td>
<td>C₁₀H₁₈O₂Br₂N</td>
<td>17</td>
</tr>
<tr>
<td>6</td>
<td>4f</td>
<td>C₁₀H₁₈O₂Br₂Cl₂N</td>
<td>13</td>
</tr>
<tr>
<td>7</td>
<td>4g</td>
<td>C₁₀H₁₈O₂Br₂Cl₂N</td>
<td>16</td>
</tr>
<tr>
<td>8</td>
<td>4h</td>
<td>C₁₀H₁₈O₂Br₂N</td>
<td>--</td>
</tr>
<tr>
<td>9</td>
<td>4i</td>
<td>C₁₀H₁₈O₂Br₂Cl₂N</td>
<td>15</td>
</tr>
<tr>
<td>10</td>
<td>4j</td>
<td>C₁₀H₁₈O₂Br₂Cl₂N</td>
<td>--</td>
</tr>
<tr>
<td>+ve Control DMSO</td>
<td></td>
<td></td>
<td>-ve</td>
</tr>
<tr>
<td>Penicilline</td>
<td></td>
<td></td>
<td>12</td>
</tr>
</tbody>
</table>

(– = No Antibacterial activity)

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

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Entry</th>
<th>molecular formula</th>
<th>Antifungal activity (Zone of Inhibition in mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aspergillus niger</td>
</tr>
<tr>
<td>1</td>
<td>4a</td>
<td>C₁₀H₁₈O₃I₂N</td>
<td>-ve</td>
</tr>
<tr>
<td>2</td>
<td>4b</td>
<td>C₁₀H₁₈O₃I₂N</td>
<td>-ve</td>
</tr>
<tr>
<td>3</td>
<td>4c</td>
<td>C₁₀H₁₈O₂Cl₂N</td>
<td>-ve</td>
</tr>
<tr>
<td>4</td>
<td>4d</td>
<td>C₁₀H₁₈O₂I₂Cl₂N</td>
<td>-ve</td>
</tr>
<tr>
<td>5</td>
<td>4e</td>
<td>C₁₀H₁₈O₂Br₂N</td>
<td>RG</td>
</tr>
<tr>
<td>6</td>
<td>4f</td>
<td>C₁₀H₁₈O₂Br₂Cl₂N</td>
<td>RG</td>
</tr>
<tr>
<td>7</td>
<td>4g</td>
<td>C₁₀H₁₈O₂Br₂N</td>
<td>RG</td>
</tr>
<tr>
<td>8</td>
<td>4h</td>
<td>C₁₀H₁₈O₂Br₂Cl₂N</td>
<td>-ve</td>
</tr>
<tr>
<td>9</td>
<td>4i</td>
<td>C₁₀H₁₈O₂Br₂Cl₂N</td>
<td>-ve</td>
</tr>
<tr>
<td>10</td>
<td>4j</td>
<td>C₁₀H₁₈O₂Br₂Cl₂N</td>
<td>-ve</td>
</tr>
<tr>
<td>+ve Control DMSO</td>
<td></td>
<td></td>
<td>+ve</td>
</tr>
<tr>
<td>-ve Control (Griseofulvin)</td>
<td></td>
<td></td>
<td>-ve</td>
</tr>
</tbody>
</table>

([+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 %)]

**CONCLUSION:**

In this work, we have demonstrated the synthesis of 3-hydroxy-4H-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-4H-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.

REFERENCES:


Removal of Indigo dye from wastewater using novel reactive absorptive material

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³Department of Agronomy and Plant Breeding, Karaj Branch, Islamic Azad University, College of, Karaj branch, Islamic Azad University, Alborz, Iran

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-TiO₂ 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.

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-TiO₂ 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.

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 TiO₂, 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].

**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>
<thead>
<tr>
<th>Bentonite(gr)</th>
<th>(gr) Final Product</th>
<th>%Removal COD (100ppm Indigo dye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.094</td>
<td>34.17</td>
</tr>
<tr>
<td>0.05</td>
<td>0.134</td>
<td>41.72</td>
</tr>
<tr>
<td>0.07</td>
<td>0.178</td>
<td>47.34</td>
</tr>
<tr>
<td>0.10</td>
<td>0.199</td>
<td>64.36</td>
</tr>
<tr>
<td>0.12</td>
<td>0.201</td>
<td>62.68</td>
</tr>
<tr>
<td>0.15</td>
<td>0.202</td>
<td>61.25</td>
</tr>
<tr>
<td>0.17</td>
<td>0.202</td>
<td>58.83</td>
</tr>
<tr>
<td>0.20</td>
<td>0.205</td>
<td>54.15</td>
</tr>
</tbody>
</table>

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>
<thead>
<tr>
<th>ACV(gr)</th>
<th>(gr) Final Product</th>
<th>%Removal COD (200ppm Indigo dye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.187</td>
<td>52.43</td>
</tr>
<tr>
<td>0.02</td>
<td>0.199</td>
<td>64.36</td>
</tr>
<tr>
<td>0.03</td>
<td>0.207</td>
<td>73.21</td>
</tr>
<tr>
<td>0.04</td>
<td>0.209</td>
<td>58.87</td>
</tr>
<tr>
<td>0.05</td>
<td>0.210</td>
<td>44.64</td>
</tr>
</tbody>
</table>

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>
<thead>
<tr>
<th>EGDMA(gr)</th>
<th>(gr) Final Product</th>
<th>%Removal COD (200ppm Indigo dye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.171</td>
<td>65.76</td>
</tr>
<tr>
<td>0.50</td>
<td>0.207</td>
<td>73.21</td>
</tr>
<tr>
<td>0.75</td>
<td>0.261</td>
<td>82.30</td>
</tr>
<tr>
<td>1.00</td>
<td>0.224</td>
<td>66.19</td>
</tr>
<tr>
<td>1.25</td>
<td>0.189</td>
<td>61.97</td>
</tr>
</tbody>
</table>

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.

![Figure 1: Picture of TEM electronic microscope and XRD diffraction pattern from sample of TiO$_2$](image)

**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.

![Figure 2: SEM images of Chitosan-Bentonite-TiO$_2$ with different resolution](image)

**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 CH bond, in 1856.16 cm$^{-1}$ with a CO bond.
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.

![Fig. 3 FTIR diagram of Chitosan (a) [9] and Chitosan-Bentonite-TiO\(_2\) (b)](image)

**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 °C with an associated large exotherm and again at around 330 °C. The lower thermal stability is expected due to newly formed bonds. However for the purpose of water decontamination, stability upto 220 °C is quite sufficient.

![Fig. 4 Thermogravimetric analysis diagram of Chitosan-Bentonite-TiO\(_2\)](image)

**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 $2\theta = 10^\circ$ and $20^\circ$ disappeared, and a very weak and broad peak appeared at $2\theta = 20^\circ$. 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 $2\theta = 25$-$38$-$48$-$55$-$63$-$75$-$82$ which conform to the Anatase phase JCPDS standard.

![Fig. 5 X Ray Diffraction pattern](image)

### 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 considerably 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](image)

### 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](image)
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](image)

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 2θ = 10° and 20° disappears, and a very weak and broad peak appears at 2θ = 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.

References:

5. V. K. Gupta, J. Environmental management 90., 8, 2313 (2009)
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.

Key words : Adulterant, appearance, profit, FSSAI and safe food.

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

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


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

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

Source: Spink et al. (2011)

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 in Vanaspati ghee. Artificial colours and dyes are used in the sweets to improve appearance and aroma.

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 powder 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 being 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.

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

<table>
<thead>
<tr>
<th>Items</th>
<th>Adulterants</th>
<th>Interface</th>
<th>Reason for Adulteration</th>
<th>Health effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chilli powder</td>
<td>Brick Powder</td>
<td>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.</td>
<td>To increase the quantity</td>
<td>Stomach disorder</td>
</tr>
<tr>
<td>Colour impurity</td>
<td>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.</td>
<td>To improve the texture and feel of spices</td>
<td>Can cause cancer</td>
<td></td>
</tr>
<tr>
<td>Starch</td>
<td>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.</td>
<td>To improve the bulk</td>
<td>Stomach disorder</td>
<td></td>
</tr>
<tr>
<td>Turmeric powder</td>
<td>Any powder (Starch, wheat)</td>
<td>Add few drops of toilet cleaner to the sample. Instant pink / violet</td>
<td>To increase the quantity and</td>
<td>Stomach Disorder, Neurotoxic,</td>
</tr>
<tr>
<td>Material (e.g., flour, etc.)</td>
<td>Description</td>
<td>Test Method</td>
<td>Result</td>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-------------</td>
<td>-------------</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td>Metanil yellow</td>
<td>Colour which disappears on dissolution with water, indicates pure turmeric. If colour persists hence metanil yellow is present.</td>
<td>Texture of powder.</td>
<td>(Nagraja and Desiraja, 1993), hepatotoxic (Saxena and Sharma, 2015)</td>
<td></td>
</tr>
<tr>
<td>Chalk powder</td>
<td>Also, if the mixture releases small bubbles, it indicates the presence of chalk powder.</td>
<td>Not very toxic but may causes stomach disorder, kidney stone.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead chromate</td>
<td>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 teaspoon with 5 ml of water and add a few drops of toilet cleaner. Pink colour indicates the presence of lead chromate.</td>
<td>Can damage all of the body system, including the heart, intestines, bones, kidneys, teeth, reproductive organs and the nervous and immune systems (Newman, 2018)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Asafoetida (hing)</td>
<td>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.</td>
<td>To increase the quantity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soapstone, other earthy matter</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black pepper</td>
<td>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.</td>
<td>To increase the quantity and making more profit.</td>
<td>Dhanya et al., 2009</td>
<td></td>
</tr>
<tr>
<td>Papaya seeds, light berries, etc.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cumin seeds (Jeera)</td>
<td>Grass seeds coloured with charcoal dust</td>
<td>Rub cumin seeds on palm turns black</td>
<td>To increase the bulk</td>
<td></td>
</tr>
<tr>
<td>Dhaniya powder</td>
<td>Horse dung</td>
<td>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.</td>
<td>To increase the quantity</td>
<td></td>
</tr>
<tr>
<td>Grass seeds</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saffron</td>
<td>Coloured dried tendrils of maize cob</td>
<td>Genuine Saffron will not break easily but artificial saffron breaks. Artificial saffron lose colour before lasting whereas real saffron continues to give colour till end</td>
<td>To increase the quantity</td>
<td></td>
</tr>
<tr>
<td>Coloured dried tendrils of maize cob</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clove</td>
<td>Magnesium, salt, sand, earth</td>
<td>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.</td>
<td>To increase profit</td>
<td>Philip et al., 2001</td>
</tr>
</tbody>
</table>
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. Cassia 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

<table>
<thead>
<tr>
<th>Items</th>
<th>Adulterants</th>
<th>Interface</th>
<th>Reason for Adulteration</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arhar</td>
<td>Kesari dal</td>
<td>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.</td>
<td>To increase quantity</td>
<td></td>
</tr>
<tr>
<td>Metanil yellow</td>
<td></td>
<td>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.</td>
<td>To enhance texture of yellow dal</td>
<td>Stomach Disorder Neurotoric⁷, hepatotoxic⁸</td>
</tr>
<tr>
<td>All yellow pulses (Chana, Arhar, Dhuli, Moong, etc.)</td>
<td>Lead Chromate</td>
<td>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</td>
<td></td>
<td>Can damage all of the body systems, including heart, intestines, bones, teeth, kidneys and reproductive organs, nervous and immune system (Newman, 2018)</td>
</tr>
</tbody>
</table>

### Table 5. Tests for milk and milk products

<table>
<thead>
<tr>
<th>Items</th>
<th>Adulterants</th>
<th>Interface</th>
<th>Reason for Adulteration</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milk</td>
<td>Water</td>
<td>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 leaving a white trail behind it whereas the drop of milk adulterated with water will flow immediately without leaving any mark.</td>
<td>To increase the quantity of milk</td>
<td></td>
</tr>
<tr>
<td>Synthetic milk (mixture of water, area, soap, or detergent, stabilizer, sodium hydroxide, vegetable oil and salt)</td>
<td>Urea / detergent or soap / sodium hydroxide</td>
<td>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.</td>
<td>To make profit / money.</td>
<td></td>
</tr>
</tbody>
</table>
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>
<thead>
<tr>
<th>Food Items</th>
<th>Adulterants</th>
<th>Interface</th>
<th>Reason for Adulteration</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mustard oil and Coconut oil</td>
<td>Argemone oil</td>
<td>Heat the mixture of oil with little amount of toilet cleaner for 2-3 min. Red colour appears</td>
<td>To increase the quantity and consistency</td>
<td>Epidemic dropsy, Carcinogenic (Babu et al., 2007)</td>
</tr>
<tr>
<td>Coconut oil</td>
<td>Cheap oils</td>
<td>Freeze the oil in refrigerator for 1-2 hr, some oil remains in liquid form</td>
<td>To increase the quantity</td>
<td></td>
</tr>
<tr>
<td>Honey</td>
<td>Sugar syrup, Glucose solution or starch</td>
<td>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.</td>
<td>To increase the quantity</td>
<td>Harmful for diabetic patients</td>
</tr>
<tr>
<td>Bura Sugar</td>
<td>Washing, Chalk Powder</td>
<td>1. Effervescence with toilet cleaner. 2. To the solution of bura powder in water add 1/4 tea spoon of haldi, will turn red.</td>
<td>To increase quantity and its consistency</td>
<td>May cause kidney stone</td>
</tr>
<tr>
<td>Jaggery</td>
<td>Metanil yellow</td>
<td>Dissolve jaggery in water then add toilet cleaner to it, colour changes to Magenta</td>
<td>To enhance the texture</td>
<td>Stomach disorder, Neurotoxic, hepatotoxic</td>
</tr>
<tr>
<td>Tea and Coffee</td>
<td>Iron Filling</td>
<td>Move a magnet over tea or coffee, iron filling will click to it.</td>
<td>To increase quantity and weight</td>
<td></td>
</tr>
<tr>
<td>Tea coloured leaves</td>
<td>Rub leaves on white paper, artificial colour comes out on paper</td>
<td>To increase quantity and profit</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Used tea</td>
<td>Tea leaves sprinkled on wet fitter paper. Pink or red spots on paper show colour</td>
<td>To earn more profit</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coffee</td>
<td>Chicory, Tamarind seeds powder and date seed powder</td>
<td>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</td>
<td>To earn more profit</td>
<td>Patrizia et al., 2010 Downey et al., 1997</td>
</tr>
</tbody>
</table>
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.

Table 7. Tests for vegetables and fruits

<table>
<thead>
<tr>
<th>Food Items</th>
<th>Adulterants</th>
<th>Interface</th>
<th>Reason for Adulteration</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green vegetables (Beans, Spinach, Parmal, Capsicum, Lady finger, Tori, Frozen matar, Bitter guard Kakora etc.)</td>
<td>Sprinkled or dipped in solution of malachite</td>
<td>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.</td>
<td>To give attractive and fresh look</td>
<td>Cause carcinogenesis, mutagenesis, chromosomal fractures, teratogenicity and respiratory toxicity (Mani and Bharagava, 2016)</td>
</tr>
<tr>
<td>Apple</td>
<td>Coated with wax</td>
<td>Scratch the surface of apple with the help of knife, if some semisolid mass comes out, it is coated with wax</td>
<td>To prevent weight loss</td>
<td></td>
</tr>
<tr>
<td>Black berries (Jamun)</td>
<td>Dipped in solution of crystal violet</td>
<td>Dip Jamuns in lukewarm water for 5 min. purple colour appears in water</td>
<td>Improve the brightness</td>
<td>Cause mitotic poison, potent careinogen and clastogene promoting tumor growth (Mani and Bharagava, 2016)</td>
</tr>
</tbody>
</table>

List of chemicals used (Available at home)

i. Toilet cleaner : Dil/con. HCl (Hydrochloric acid)
ii. Nail paint remover : Acetone
iii. Washing Soda : Sodium carbonate (Na₂CO₃)
iv. Edible Soda : Sodium bicarbonate (NaHCO₃)
v. Vinegar : 5% acetic and (CH₃COOH)
vii. Lemon juice : Citric acid
vii. Turmeric powder : Indicator
viii. Tincture Iodine : Iodine (I₂)
ix. Wax

1. 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.

2. 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.

3. 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).

4. Vegetables and fruits

A systemic fungicide (benomyl) in applied to vegetables to inhibit the growth of microorganisms and to avoid spoilage (Gahukar, 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.

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.

References:


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 range 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→ 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 → M2+2e, while the cathode has reduction: 2H+2e→ 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-d₆); δ: 1.54 (t, 3H for CH₃), 3.01 (m, 2H for CH₂), 5.83 (s, 1H for OH), 6.87–7.17 (m, 4H, Aromatic).

3. Electrochemical measurements

Al 5025 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-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol](image-url)
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 potentio-dynamic 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.

4. 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$_{3}$O$_{5}$S) 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:
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.

<table>
<thead>
<tr>
<th>Concentration (mM)</th>
<th>R_s (ohm cm$^2$)</th>
<th>R_ct (ohm cm$^2$)</th>
<th>CPE$_{dl}$</th>
<th>C$_{dl}$ (mFcm$^{-2}$)</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.4512</td>
<td>0.0778</td>
<td>924.6</td>
<td>0.914</td>
<td>338.7</td>
</tr>
<tr>
<td>0.05</td>
<td>0.4251</td>
<td>0.7607</td>
<td>5050</td>
<td>0.706</td>
<td>375.1</td>
</tr>
<tr>
<td>0.10</td>
<td>0.3251</td>
<td>0.7694</td>
<td>3812</td>
<td>0.728</td>
<td>820.9</td>
</tr>
<tr>
<td>0.20</td>
<td>0.3672</td>
<td>0.7808</td>
<td>2065</td>
<td>0.773</td>
<td>954.7</td>
</tr>
<tr>
<td>0.40</td>
<td>0.3935</td>
<td>0.7796</td>
<td>1690</td>
<td>0.806</td>
<td>365.9</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5417</td>
<td>0.8509</td>
<td>435.4</td>
<td>0.854</td>
<td>266.2</td>
</tr>
</tbody>
</table>

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

Table 2
CPE 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.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Concentration (mM)</th>
<th>R_s (ohm cm$^2$)</th>
<th>R_ct (ohm cm$^2$)</th>
<th>CPE$_{dl}$</th>
<th>C$_{dl}$ (mFcm$^{-2}$)</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>Blank</td>
<td>0.2540</td>
<td>0.0779</td>
<td>924.6</td>
<td>0.914</td>
<td>338.7</td>
</tr>
<tr>
<td>30</td>
<td>0.5</td>
<td>0.5509</td>
<td>0.8480</td>
<td>435.4</td>
<td>0.854</td>
<td>266.2</td>
</tr>
<tr>
<td>40</td>
<td>Blank</td>
<td>0.2481</td>
<td>0.2205</td>
<td>4526</td>
<td>0.928</td>
<td>502.0</td>
</tr>
<tr>
<td>40</td>
<td>0.5</td>
<td>0.2299</td>
<td>0.3519</td>
<td>500.2</td>
<td>0.831</td>
<td>398.5</td>
</tr>
<tr>
<td>50</td>
<td>Blank</td>
<td>0.2315</td>
<td>0.1511</td>
<td>1634.01</td>
<td>0.731</td>
<td>835.9</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
<td>0.2127</td>
<td>0.3380</td>
<td>507.5</td>
<td>0.832</td>
<td>266.1</td>
</tr>
<tr>
<td>60</td>
<td>Blank</td>
<td>0.1840</td>
<td>0.1103</td>
<td>2172.87</td>
<td>0.840</td>
<td>920.8</td>
</tr>
<tr>
<td>60</td>
<td>0.5</td>
<td>0.1699</td>
<td>0.2501</td>
<td>451.4</td>
<td>0.869</td>
<td>554.5</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Concentration (mM)</th>
<th>b_a (V dec^{-1})</th>
<th>b_c (V dec^{-1})</th>
<th>I_{corr} (mA cm^{-2})</th>
<th>--E_{corr} (mV vs SCE)</th>
<th>Corrosion rate (mpy)</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.1360</td>
<td>0.1298</td>
<td>659.00</td>
<td>489.00</td>
<td>7.6010</td>
<td>0.00</td>
</tr>
<tr>
<td>0.05</td>
<td>0.1291</td>
<td>0.1286</td>
<td>601.00</td>
<td>478.00</td>
<td>7.0040</td>
<td>10.53</td>
</tr>
<tr>
<td>0.10</td>
<td>0.1139</td>
<td>0.1209</td>
<td>408.00</td>
<td>468.00</td>
<td>4.8360</td>
<td>40.01</td>
</tr>
<tr>
<td>0.20</td>
<td>0.1021</td>
<td>0.1179</td>
<td>339.00</td>
<td>456.00</td>
<td>4.0150</td>
<td>48.60</td>
</tr>
<tr>
<td>0.40</td>
<td>0.0887</td>
<td>0.1140</td>
<td>180.00</td>
<td>449.00</td>
<td>2.0380</td>
<td>74.39</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6012</td>
<td>0.4029</td>
<td>44.590</td>
<td>390.00</td>
<td>0.0529</td>
<td>93.21</td>
</tr>
</tbody>
</table>

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 anodical (b_a) and cathodic tafels (b_c) 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>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Concentration (mM)</th>
<th>Potential Dynamic Parameter (PD)</th>
<th>Corrosion rate (mpy)</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>Blank</td>
<td>$b_a$ (Vdec$^{-1}$) $b_c$ (Vdec$^{-1}$) $i_{corr}$ (mAcm$^{-2}$) $E_{corr}$ (mV vsSCE)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.1360 0.1298</td>
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<td></td>
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</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.0711 0.1063</td>
<td>134.00 540.00 13.7200 76.05</td>
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<td></td>
</tr>
<tr>
<td>50</td>
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<td>0.9692 0.7201 819.00 669.00 114.7980 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>Blank</td>
<td>4.0200 2.0296 1559.00 680.00 630.4000 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.1389 0.1430</td>
<td>0998.00 464.00 1015.9000 35.93</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 6. The potenio-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 Morphology**

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.
5. 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.

References:


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.

Key words: Aryl hydrazine: phenyl hydrazine: carbonyl compound, aromatic carbonyl compound, Grinding, room temperature, hydrazones etc

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, antimarial, 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, antimarial, 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].

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.

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.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Hydrazone 3</th>
<th>R</th>
<th>R1</th>
<th>R2</th>
<th>Time(min)</th>
<th>Yielda (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3a</td>
<td>H</td>
<td>H</td>
<td>n-C5H11</td>
<td>3</td>
<td>90</td>
</tr>
</tbody>
</table>

Scheme-2 Possible mechanism of (3) hydrazone

Table 1:- Synthesis of Arylhydrazone(3)
<table>
<thead>
<tr>
<th>No.</th>
<th>Formula</th>
<th>Melting Points</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td><img src="image1" alt="Compound 2" /></td>
<td>3b H H</td>
<td>5 92</td>
</tr>
<tr>
<td>3</td>
<td><img src="image2" alt="Compound 3" /></td>
<td>3c H CH3</td>
<td>5 91</td>
</tr>
<tr>
<td>4</td>
<td><img src="image3" alt="Compound 4" /></td>
<td>3d H CH3</td>
<td>4 94</td>
</tr>
<tr>
<td>5</td>
<td><img src="image4" alt="Compound 5" /></td>
<td>3e H H</td>
<td>3 95</td>
</tr>
<tr>
<td>6</td>
<td><img src="image5" alt="Compound 6" /></td>
<td>3f NO2 H</td>
<td>5 91</td>
</tr>
<tr>
<td>7</td>
<td><img src="image6" alt="Compound 7" /></td>
<td>3g NO2 H</td>
<td>5 93</td>
</tr>
<tr>
<td>8</td>
<td><img src="image7" alt="Compound 8" /></td>
<td>3h NO2 CH3</td>
<td>6 94</td>
</tr>
<tr>
<td>9</td>
<td><img src="image8" alt="Compound 9" /></td>
<td>3i NO2 CH3</td>
<td>4 91</td>
</tr>
<tr>
<td>10</td>
<td><img src="image9" alt="Compound 10" /></td>
<td>3j Cl H</td>
<td>3 92</td>
</tr>
<tr>
<td>11</td>
<td><img src="image10" alt="Compound 11" /></td>
<td>3k Cl H</td>
<td>5 91</td>
</tr>
<tr>
<td>12</td>
<td><img src="image11" alt="Compound 12" /></td>
<td>3l Cl CH3</td>
<td>3 93</td>
</tr>
<tr>
<td>13</td>
<td><img src="image12" alt="Compound 13" /></td>
<td>3m Cl CH3</td>
<td>5 92</td>
</tr>
</tbody>
</table>

**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.
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.

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).

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.

Antimycobacterial Activity:-
Antimycobacterial drugs are used in the treatment of diseases caused by members of the Mycobacterium genus, 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]nicotinic acid aryldene-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.

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

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). 1H NMR spectra were recorded on a Bruker AC-200 (MHz) spectrometer in CDCl3/ 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):
\[ \text{IR (cm}^{-1}\text{)} 3418,70,3329,95,2859,1680,90,1599,86,1352,1121,24,667,68 \]
\[ \text{HNMR(CDCl}_3\text{), } \delta 6.81(1H, d), 7.20 (1H, d), 7.35(1H, d), 11.12(1H, s), 7.50(1H, t), 1.31 (2H, six), 1.31 (2H, six), 0.90 (3H, t) \]
\[ \text{Mass } 199(M^+) 182,173,157,143,130,115,103,89,77, C_{13}H_{25}N_2 \text{ Anal.Calcd C 76.10,H 10.40,N 13.70 Found C 76.05,H 10.31,N 13.64} \]

3-Methyl-1-phenyl-1H-pyrazol-5-(4H)-1-ethylidene-2-phenylhydrazine (3b):
\[ \text{IR (cm}^{-1}\text{)} 3223,23,1665,99,1498,96,1215,74, 669,02 \]
\[ \text{HNMR(CDCl}_3\text{), } \delta 6.81(1H,d), 7.20 (1H, d), 7.35(1H, d), 11.12(1H, s), 7.50(1H, t), 2.3 (1H,d), 1.94 (1H,d),7.94(2H,d), 7.34 (2H,d) 7.19(1H,d) Mass 292(M^+), 275,201,185,171,155,133,118,105,93,77,65, C_{17}H_{18}N_4O \text{ Anal.Calcd C 69.70,H 7.20,N 18.10,O 5.20 Found C 69.65,H 7.14,N 18.05 ,O 5.15} \]
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
$^1$HNMR(CDC$_3$), $\delta$ 6.81 (1H,d), 7.70 ( 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., 188,181,165,152,126,120,115,105,98,93,87,77,63 C$_{14}$H$_{14}$N$_2$ Anal.Calcld C 79.99,H 6.80,N 13.40
Found C 79.79,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, 1.81(1H,m), 0.86 (1H,q)
Mass 176(M$^+$),167,144,119,105,91,77. C$_{14}$H$_{14}$N$_2$ Anal.Calcld C 74.99,H 19.20,N 15.15
Found C 74.96,H 9.15,N 15.09

1-benzylidene-2-phenyl hydrazine (3e):
IR (cm$^{-1}$) 1731(M$^+$), 1631,141,116,102,87,74. C$_{14}$H$_{14}$N$_2$ Anal.Calcld C 74.99,H 9.15,N 15.09

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Molecular interaction of acetonitrile - 1, 2 Dichloroethane mixtures at 15°C 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°C 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.

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=\(\equiv\)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°C 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 - 0.7857 gm cm\(^{-3}\); mol. wt. - 41.05
1, 2 Dichloroethane -density: 1.256 gm cm\(^{-3}\); mol.wt.-98.96

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 \(R_1(t)\) 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.

DATA ANALYSIS
The time dependent data were processed to obtain complex reflection coefficient spectra from 10 MHz to 20 GHz using Fourier transformation [5, 6] as

\[
\left(\frac{R_1(t)-R_x(t))}{[R_1(t)+R_x]}\right) e_{o} - e_{\infty} \left(1 + j\omega \tau\right)^{-1}
\]

is angular frequency, d is the effective pin length and \(j=\sqrt{-1}\).

bilinear calibration method [3].
-squares fit method \(^8\) was used to determine the values of dielectric parameters. In Eq.(2), \(\varepsilon_0\) is the static dielectric constant, \(\varepsilon_\infty\) is the limiting high-frequency dielectric constant and \(\tau\) is the relaxation time

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

\[
\frac{4\pi N \mu^2 \rho}{9kT} g_f = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0 (\varepsilon_\infty + 2)^2}
\]

where \(\mu\) is dipole moment in gas phase, \(\rho\) is density at temperature \(T\), \(M\) is molecular weight, \(k\) is Boltzmann constant, \(N\) 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

\[
\frac{4\pi N \mu^2 \rho}{9kT} g_{eff} = \frac{(\varepsilon_{0m} - \varepsilon_{xm})(2\varepsilon_{0m} + \varepsilon_{xm})}{\varepsilon_{0m} (\varepsilon_{xm} + 2)^2}
\]

where \(\phi_1\) and \(\phi_2\) 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

\[
\frac{4\pi N \left( \frac{\mu_1^2 \rho_1}{M_1} \phi_1 + \frac{\mu_2^2 \rho_2}{M_2} \phi_2 \right) g_{eff} = \frac{(\varepsilon_{0m} - \varepsilon_{xm})(2\varepsilon_{0m} + \varepsilon_{xm})}{\varepsilon_{0m} (\varepsilon_{xm} + 2)^2}}{9kT}
\]

where \(g_{eff}\) is the effective Kirkwood correlation factor for a binary mixture, with \(\phi_1\) and \(\phi_2\) 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.](image-url)
According to equation (6), a linear relationship is expected which will give a straight line when plotted $f_B$ against $\phi_2$. 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 $\phi_2$ of ACN at 15°C is given in Figure 2.

To fit the experimental data, Eq.(6) has been modified \[f_B = 1 - \left[a - (a-1)\phi_2\right]\phi_2\] (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.

**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 cellulotic 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. Exogluanase 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

Key Words: Cellulose, cellulolytic potential, endoglucanase, exoglucanase, cellulose degrading bacteria (K0).

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 109 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 cellulotic 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 celledextrin 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.

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 KH2PO4-0.5 gm, MgSO4-0.25 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 °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 KH2PO4-0.5 gm, MgSO4-0.25 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 °C at 150 rpm in an enzyme production media composed 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°C 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.

RESULTS and DISCUSSIONS:

Isolation and screening of cellulose degrading bacteria: degradation of cellullosic 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.

<table>
<thead>
<tr>
<th>Isolated Bacteria</th>
<th>Maximum clearing zone(mm)</th>
<th>HC value (Hydrolytic capacity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K0 1</td>
<td>32</td>
<td>5.8</td>
</tr>
<tr>
<td>K0 2</td>
<td>28</td>
<td>4.2</td>
</tr>
<tr>
<td>K0 3</td>
<td>21</td>
<td>3.7</td>
</tr>
<tr>
<td>K0 4</td>
<td>37</td>
<td>7.1</td>
</tr>
<tr>
<td>K0 5</td>
<td>15</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Graph 1: Maximum hydrolytic capacity in mm of isolated micro organisms 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.
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.

ACKNOWLEDGE

Author is very much thankful to Dr. Shaikh Kabeer Ahmed, principal, Sir Sayyed College, Aurangabad for providing all the necessary facilities for this work.

REFERENCES:


Physiochemical Analysis of Aqueous Extract of Aegle marmelos (Bael)

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Email: gopinathskhansole@gmail.com

Abstract: In present study, an aqueous extract from Aegle marmelos (Bael), was determined the physiochemical study include macro, micro elements, 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 its 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 antisyentery, 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:

2.1 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.

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


2.4 Preparation of aqueous extractions: Aqueous fruit extract of Aegle marmelos (Bael) prepared from the powdered sample of it’s and thermally treated by using muffle furnace at 100°C 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.

2.5 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>
<thead>
<tr>
<th>Sr.No.</th>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>--</td>
<td>09.63</td>
<td>01-14</td>
</tr>
<tr>
<td>2</td>
<td>E.C.</td>
<td>Mhos/cm</td>
<td>1.02</td>
<td>01.02</td>
</tr>
<tr>
<td>3</td>
<td>Nitrogen (N)</td>
<td>%</td>
<td>1392</td>
<td>1320-1650</td>
</tr>
<tr>
<td>4</td>
<td>Phosphorus (P)</td>
<td>%</td>
<td>11-30</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>Potassium (K)</td>
<td>%</td>
<td>4753</td>
<td>2000-3000</td>
</tr>
<tr>
<td>6</td>
<td>Organic Carbon(C)</td>
<td>%</td>
<td>0.35</td>
<td>0.1-3.50</td>
</tr>
<tr>
<td>7</td>
<td>Calcium (Ca)</td>
<td>%</td>
<td>1.10</td>
<td>0.36-2.50</td>
</tr>
<tr>
<td>8</td>
<td>Magnesium(Mg)</td>
<td>%</td>
<td>0.10</td>
<td>0.26-1.20</td>
</tr>
<tr>
<td>9</td>
<td>Copper(Cu)</td>
<td>ppm</td>
<td>0.52</td>
<td>02-10</td>
</tr>
<tr>
<td>10</td>
<td>Iron(Fe)</td>
<td>ppm</td>
<td>0.99</td>
<td>01-03</td>
</tr>
<tr>
<td>11</td>
<td>Manganese (Mn)</td>
<td>ppm</td>
<td>1.00</td>
<td>01-05</td>
</tr>
<tr>
<td>12</td>
<td>Zinc(Zn)</td>
<td>ppm</td>
<td>20</td>
<td>10-30</td>
</tr>
</tbody>
</table>

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).
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.

5. ACKNOWLEDGMENTS:
Authors are grateful to Principal, D. A. B. N. College, Chikhali for providing elemental analysis and laboratory facilities.

REFERENCES:
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°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:

Spinell 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 passes 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$_2$O$_4$ 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:

2.1. Film Deposition

Cobalt ferrite (CoFe$_2$O$_4$) thin film was prepared by spray pyrolysis deposition (SPD) technique. Analytic reagent grade chemicals Co (NO$_3$)$_2$.6H$_2$O and Fe (NO$_3$)$_3$.9H$_2$O 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:

3.1. Film formation

CoFe$_2$O$_4$ 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°C. The reaction mechanism of ferrite thin film formation of CoFe$_2$O$_4$ is given below.

$$\text{Co(NO}_3\text{)}_2 + 2\text{Fe(NO}_3\text{)}_3 \xrightarrow{\Delta 523\text{K}} \text{CoFe}_2\text{O}_4 + 8\text{NO}_2 \uparrow + 2\text{O}_2 \uparrow$$

3.2. 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$_2$O$_4$ thin film was found to be 280 nm.

3.3. Structural Analysis

![Fig.1.1: XRD diffraction pattern of cobalt ferrite thin film.](image)

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 20 range in the 20$^0$ to 70$^0$. Fig. 1.1 represents the XRD pattern of CoFe$_2$O$_4$ ferrite thin film. The (200), (220), (311), (222) (400), (511) and (440) reflection 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-size grains/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, $\lambda$ is wavelength of X-ray radiation,

$\beta$ 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>
<thead>
<tr>
<th>Sr.No.</th>
<th>Parameters</th>
<th>Observed Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Thickness (t)</td>
<td>280nm</td>
</tr>
<tr>
<td>2</td>
<td>Lattice constant (a)</td>
<td>8.3738A</td>
</tr>
</tbody>
</table>
Using XRD data lattice constant (a) and X-ray density (dx) was calculated and are presented in Table 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 1Tesa at room temperature.

![M-H Curve of cobalt ferrite thin film.](image)

**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 coercivity 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.

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

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vnaiiknaware77@gmail.com

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, spectrophotometric method to evaluate the quality. The results showed that 

Introduction:
Water is the most important and abundance compounds of ecosystem. All living organisms on the earth need water for their survival and growth (Lamb 1985). 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 unpoluted 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 isGroup is of vital signification for the welfare of mankind. Majalgaon city is lying to the Bagalhat 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.

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 washed and rinsed and the reagents are all of analytical grade. Physico-chemical parameters determination by various standard method was used for pH determination of the water samples, a digital pH meter (Eligo Model) standardized with buffer solution of pH 4 and pH 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.

**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.**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Parameters</th>
<th>BW-1</th>
<th>BW-2</th>
<th>BW-3</th>
<th>BW-4</th>
<th>BW-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>Temperature(°C)</td>
<td>28.6</td>
<td>29.6</td>
<td>30.4</td>
<td>29.7</td>
<td>30.2</td>
</tr>
<tr>
<td>02</td>
<td>pH</td>
<td>8.4</td>
<td>7.8</td>
<td>8.2</td>
<td>7.1</td>
<td>7.6</td>
</tr>
<tr>
<td>03</td>
<td>Turbidity NTU</td>
<td>0.70</td>
<td>0.50</td>
<td>0.48</td>
<td>0.62</td>
<td>0.54</td>
</tr>
<tr>
<td>04</td>
<td>Chlorides ppm</td>
<td>69.3</td>
<td>69.2</td>
<td>84.9</td>
<td>115.2</td>
<td>81.4</td>
</tr>
<tr>
<td>05</td>
<td>Alkalinity ppm</td>
<td>120</td>
<td>102</td>
<td>112</td>
<td>92</td>
<td>125</td>
</tr>
<tr>
<td>06</td>
<td>Total hardness ppm</td>
<td>442</td>
<td>375</td>
<td>320</td>
<td>360</td>
<td>258</td>
</tr>
<tr>
<td>07</td>
<td>Calcium ppm</td>
<td>62</td>
<td>72</td>
<td>65</td>
<td>68</td>
<td>52</td>
</tr>
<tr>
<td>08</td>
<td>Magnesium ppm</td>
<td>52</td>
<td>82</td>
<td>77</td>
<td>42</td>
<td>62</td>
</tr>
<tr>
<td>09</td>
<td>Nitrates ppm</td>
<td>2.3</td>
<td>0.8</td>
<td>0.65</td>
<td>1.2</td>
<td>0.85</td>
</tr>
<tr>
<td>10</td>
<td>Phosphates ppm</td>
<td>1.6</td>
<td>2.1</td>
<td>2.8</td>
<td>0.8</td>
<td>2.9</td>
</tr>
<tr>
<td>11</td>
<td>Dissolved oxygen ppm</td>
<td>12.3</td>
<td>11.6</td>
<td>9.8</td>
<td>8.4</td>
<td>12.5</td>
</tr>
<tr>
<td>12</td>
<td>Biological oxygen demand</td>
<td>2.0</td>
<td>1.9</td>
<td>0.8</td>
<td>1.2</td>
<td>2.2</td>
</tr>
<tr>
<td>13</td>
<td>Chemical oxygen demand</td>
<td>5.6</td>
<td>7.6</td>
<td>8.2</td>
<td>4.4</td>
<td>6.8</td>
</tr>
</tbody>
</table>

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 pH 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, pH 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.

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.

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, 0.150 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, tripropylamine (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 P-nitrochalcone (PNC) in 20% acetic acid by using 0.1N H2SO4. The remaining (TriPACC) was then analyzed Spectrophotometrically. The result indicated that 1 mole of alcohols react with 1 mole (TriPACC).

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

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 Kobs 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%.

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 [H2SO4], the increase in [P-nitrochalcone (PNC)] increases the rate of reaction (Table-1). The plot of log of kobs 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>
<thead>
<tr>
<th>[PNC]</th>
<th>0.01M</th>
<th>0.02M</th>
<th>0.03M</th>
<th>0.04M</th>
<th>0.05M</th>
<th>0.06M</th>
<th>0.07M</th>
<th>0.08M</th>
</tr>
</thead>
<tbody>
<tr>
<td>k x 10^3 sec^-1</td>
<td>2.08</td>
<td>2.37</td>
<td>2.64</td>
<td>2.96</td>
<td>3.22</td>
<td>3.52</td>
<td>3.78</td>
<td>4.08</td>
</tr>
</tbody>
</table>

Effect of variation of concentration of TriPACC:-

At constant [P-nitrochalcone (PNC)] and [H2SO4], the increase in [TriPACC] increases the rate of reaction (Table-2). The plot of log kobs versus log [TriPACC] for different initial concentration of TriPACC is linear with unit slope present the first-order dependence of rate on TriPACC.

<table>
<thead>
<tr>
<th>[TriPACC] Mole</th>
<th>0.001</th>
<th>0.0015</th>
<th>0.002</th>
<th>0.0025</th>
<th>0.003</th>
<th>0.0035</th>
<th>0.004</th>
<th>0.0045</th>
</tr>
</thead>
<tbody>
<tr>
<td>k x 10^3 sec^-1</td>
<td>2.08</td>
<td>2.36</td>
<td>2.58</td>
<td>2.87</td>
<td>3.08</td>
<td>3.31</td>
<td>3.55</td>
<td>3.79</td>
</tr>
</tbody>
</table>

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 H2SO4. The rate of reaction increases with increase in [H2SO4] (Table-3). The plot of log kobs versus log [H+]are also straight line with slope less than unity, Indicating a fractional order dependence on [H+].

<table>
<thead>
<tr>
<th>[H2SO4]</th>
<th>0.1M</th>
<th>0.2M</th>
<th>0.3M</th>
<th>0.4M</th>
<th>0.5M</th>
<th>0.6M</th>
<th>0.7M</th>
<th>0.8M</th>
</tr>
</thead>
<tbody>
<tr>
<td>k x 10^3 sec^-1</td>
<td>2.08</td>
<td>2.27</td>
<td>2.46</td>
<td>2.65</td>
<td>2.77</td>
<td>2.95</td>
<td>3.06</td>
<td>3.24</td>
</tr>
</tbody>
</table>

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 CaCl2, Ca(NO3)2, Al(NO3)3 and K2SO4. 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.

| [TP] | 0.001 M, [PNC] = 0.01 M, [H2SO4] = 0.1 N, Temp. =303 k, AA = 20% (v/v) |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| k x 10^3 sec^-1 | 2.08 | 2.27 | 2.46 | 2.65 | 2.77 | 2.95 | 3.06 | 3.24 |
Salts 0.1M  |  KCl | KBr | KI | CaCl₂ | Ca(NO₃)₂ | Al(NO₃)₃ | K₂SO₄  
--- | --- | --- | --- | --- | --- | --- | ---  
k x 10³ sec⁻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-nitro-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 kₜₐₐₜ verses 1/D is linear with positive slope indicating ion- dipole type of reaction [20].

Table 5: Effect of variation of Acetic Acid % on reaction rate
[TriPACC]= 0.001 M, [H₂SO₄] = 0.1 N, [P-nitrochalcone (PNC)] =0.01M, Temp=303 k

<table>
<thead>
<tr>
<th>Acetic acid</th>
<th>10 %</th>
<th>20 %</th>
<th>30 %</th>
<th>40 %</th>
<th>50 %</th>
<th>60 %</th>
<th>70 %</th>
<th>80 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>k x 10³ sec⁻¹</td>
<td>1.95</td>
<td>2.08</td>
<td>2.25</td>
<td>2.37</td>
<td>2.49</td>
<td>2.57</td>
<td>2.73</td>
<td>2.86</td>
</tr>
</tbody>
</table>

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 Kₜₐₐₜ 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, [H₂SO₄] = 0.1 N, AA = 20% (v/v)

<table>
<thead>
<tr>
<th>Temperatures (K)</th>
<th>293</th>
<th>298</th>
<th>303</th>
<th>308</th>
<th>313</th>
<th>318</th>
</tr>
</thead>
<tbody>
<tr>
<td>k x 10³ sec⁻¹</td>
<td>1.28</td>
<td>1.79</td>
<td>2.08</td>
<td>2.46</td>
<td>2.89</td>
<td>3.18</td>
</tr>
</tbody>
</table>

Table 7: Activation Parameters
[TriPACC]= 0.001 M, [CH] = 0.01 M, [H₂SO₄] = 0.1 N, Temp. =303 k, AA = 20 % (v/v)

<table>
<thead>
<tr>
<th>Activation parameters</th>
<th>∆Eₐ KJ mole⁻¹</th>
<th>∆H# KJmol⁻¹</th>
<th>∆S# JK⁻¹mole⁻¹</th>
<th>∆G# KJ mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25.69</td>
<td>23.18</td>
<td>-222.06</td>
<td>88.83</td>
</tr>
</tbody>
</table>

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 ∆G 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
\[
\frac{d[\text{TriPACC}]}{dt} = k_3 C_1 \\
= k_3 k_2 [OxH⁺][S] \\
= \frac{k_3 k_2 [OxH⁺][S]}{1 + K_2 [S]} \\
= \frac{k_3 k_1 K_2 [Ox][H⁺][S]}{1 + K_2 [S]} \\
\]

CONCLUSION:–
The rate constants of the slow step involved in the mechanism were evaluated. Activation parameters were also computed. The negative value of ∆S# provides support to the formation of rigid transition state. The overall mechanism described here is consistent with product and kinetic studies.

Acknowledgement:–
The author is very much thankful to Dr. Shamama Parveen, President, RECWS, Aurangabad and Dr. Shaikh Kabeer Ahmed, Principal, Sir Sayyed College, Aurangabad, for providing laboratory facilities.
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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 ≤ 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.

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, varistor 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.

EXPERIMENTAL:
Nanoparticles of iron doped Zn-Cr oxide nanoparticles having general chemical formula Fe xZn 0.95–xC r x 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°C. 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°C 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 20 range of 20° to 80° by using Cu-Kα radiations of wavelength 1.5405Å.
RESULTS AND DISCUSSION:

Fig. 1 represents the X-ray diffractograms of Fe\textsubscript{x}Zn\textsubscript{0.95-x}Cr\textsubscript{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\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{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],

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

(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,

\[ c = ld \]  

(2)

Calculated values of lattice parameters ‘a’ and ‘c’ for all the samples of the series Fe\textsubscript{x}Zn\textsubscript{0.95-x}Cr\textsubscript{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\textsubscript{x}), crystallite size (t) (XRD and W-H analysis), and micro-strain observed in Fe\textsubscript{x}Zn\textsubscript{0.95-x}Cr\textsubscript{0.5}O.

<table>
<thead>
<tr>
<th>‘x’</th>
<th>Lattice Parameter</th>
<th>‘Y’ (Å\textsuperscript{3})</th>
<th>‘d\textsubscript{x}’ (gm/cc)</th>
<th>‘t’ (nm)</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>3.2487 5.2043</td>
<td>47.599</td>
<td>5.6352</td>
<td>17.565</td>
<td>17.81</td>
</tr>
<tr>
<td>0.02</td>
<td>3.2485 5.2041</td>
<td>47.590</td>
<td>5.6229</td>
<td>22.878</td>
<td>23.90</td>
</tr>
<tr>
<td>0.04</td>
<td>3.2482 5.2039</td>
<td>47.581</td>
<td>5.6106</td>
<td>23.014</td>
<td>25.45</td>
</tr>
<tr>
<td>0.06</td>
<td>3.2479 5.2036</td>
<td>47.570</td>
<td>5.5985</td>
<td>23.204</td>
<td>26.92</td>
</tr>
<tr>
<td>0.08</td>
<td>3.2476 5.2032</td>
<td>47.558</td>
<td>5.5866</td>
<td>23.277</td>
<td>27.90</td>
</tr>
<tr>
<td>0.1</td>
<td>3.2474 5.2029</td>
<td>47.547</td>
<td>5.5745</td>
<td>23.443</td>
<td>28.85</td>
</tr>
</tbody>
</table>
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 (\( \beta \)) values and Bragg’s angles (\( \theta_B \)) in well known Scherrer equation [20];

\[
t = \frac{k\lambda}{\beta \cos \theta_B}
\]

where, \( \lambda \) 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 23.443 nm 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];

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

where, \( \varepsilon \) is the micro-strain brought in the crystal lattice, \( \lambda \) is the incident wavelength (1.5405 Å), 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.

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 \( x \leq 0.02 \), 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.
CONCLUSIONS:

Oxide nanoparticles of Fe$_x$Zn$_{0.95-x}$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 $x \leq 0.02$, 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$_2$O$_3$) composites have been synthesized by in situ deposition technique by placing fine graded Cr$_2$O$_3$ in polymerization mixture of aniline. The PANI/Cr$_2$O$_3$ composites have been synthesized with various compositions viz., 05, 10, 15, 20 and 25 wt % of Cr$_2$O$_3$ 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$^3$ 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$_2$O$_3$ particles in the matrix have a greater influence on the conductivity values and the observed dielectric values.

Keywords: Conductivity, Polyaniline, Composites, Cr$_2$O$_3$, 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$^4$ 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$_2$O$_3$ are scarce. In the present study, PANI and PANI/Cr$_2$O$_3$ 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$_2$O$_3$ composites.

2. Experimental:
Aniline (AR grade) was purified by distillation before use and ammonium per sulphate [(NH$_4$)$_2$S$_2$O$_8$], 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, [(NH₄)₂S₂O₈] which is used as an oxidant is added slowly dropwise with continuous vigorous stirring for the period of 4-6 hours at temperature 0-5°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°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 10²-10⁶ 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 phenomena 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 inhomogeneities present in sample [10].

Figure 1 shows the variation of AC conductivity ($\sigma_{ac}$) as a function of frequency for PANI/Cr₂O₃ composites (different wt %). It is observed from figure 1. That in all the composites $\sigma_{ac}$ remains constant up to $10^5$ and thereafter increases steeply, which is characteristic feature of disordered materials. At higher frequencies, $\sigma_{ac}$ increases because of contribution of polaron, which are moving along smaller and smaller distances in a polymer chain. Increase of $\sigma_{ac}$ 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 2 shows the variation of $\sigma_{ac}$ as a function of wt % of Cr₂O₃ 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 Cr₂O₃ 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 Cr₂O₃ 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 1: Variation of $\sigma_{ac}$ as a function of frequency for Polyaniline – Cr₂O₃ composites.

Figure 2: Variation of $\sigma_{ac}$ as a function of wt % of Cr₂O₃ 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. 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. 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: Variation of $\varepsilon'$ as a function of wt % of Cr$_2$O$_3$ at different frequencies.

Figure 4: Variation of $\varepsilon''$ as a function of wt % of Cr$_2$O$_3$ at different frequencies.
Figure 5 shows the variation of tan δ as a function of wt % of Cr₂O₃ 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 Cr₂O₃ at different frequencies](image)

4. Conclusions:

Efforts have been made to synthesize polyaniline - Cr₂O₃ composites to tailor make their properties. The results of AC conductivity as well as dielectric property show a strong dependence on the wt % of Cr₂O₃ in polyaniline.

References:

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.

Introduction- Lorazepam (C15H10Cl2N2O2), 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 (C3H8O) 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.

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]
Table 1. Physical constant of pure liquids

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of Compound</th>
<th>Molecular Formula</th>
<th>Permittivity Literature value (ε_s)</th>
<th>M.W. g/Mole</th>
<th>Density g/cm^3</th>
<th>Dipole Moment µ D</th>
<th>R. I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lorazepam</td>
<td>C15H10Cl2N2O2</td>
<td>N.A.</td>
<td>321.2</td>
<td>1.52</td>
<td>N.A.</td>
<td>1.60</td>
</tr>
<tr>
<td>2</td>
<td>Propanol</td>
<td>C3H8O</td>
<td>20.1</td>
<td>60.09</td>
<td>0.803</td>
<td>1.68</td>
<td>1.3862</td>
</tr>
</tbody>
</table>

Result and Discussion

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

<table>
<thead>
<tr>
<th>Mole Fraction of Lorazepam</th>
<th>283K</th>
<th>288K</th>
<th>293K</th>
<th>298K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ε_s</td>
<td>τ (ps)</td>
<td>ε_s</td>
<td>τ (ps)</td>
</tr>
<tr>
<td>0</td>
<td>316.00</td>
<td>315.9</td>
<td>316.00</td>
<td>315.9</td>
</tr>
<tr>
<td>0.0813</td>
<td>131.00</td>
<td>144.8</td>
<td>104.00</td>
<td>122.3</td>
</tr>
<tr>
<td>0.1910</td>
<td>99.40</td>
<td>143.1</td>
<td>93.50</td>
<td>113.1</td>
</tr>
<tr>
<td>0.3469</td>
<td>145.00</td>
<td>130.9</td>
<td>122.00</td>
<td>104.2</td>
</tr>
<tr>
<td>0.5862</td>
<td>143.00</td>
<td>99.41</td>
<td>113.00</td>
<td>91.54</td>
</tr>
<tr>
<td>1</td>
<td>81.80</td>
<td>81.78</td>
<td>61.50</td>
<td>61.66</td>
</tr>
</tbody>
</table>

Static Permittivity and 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

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].

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 [9].

Acknowledgement- The authors wish to acknowledge the Department of Physics Dr. Babasaheb Ambedkar Marathwada University Aurangabad, Department of Physics Swami Ramanand Teerth Marathwada University Nanded, Department of Physics Milliya Arts, Science and Management Science College Beed.

References:

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 antimarial, 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, antitumor, antimicrobial, 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, anti-inflammatory, antioxidant, antibacterial, analgesic, antifungal and antifertility, herbicidal, anticonvulsant, anthelmintic and antiproliferative. Moreover, Schiff bases also exhibit fluorescence, photoluminescence, a potentiometric cation caring 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 frameworks. 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. 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. Large numbers of Schiff bases have shown to exhibit a wide range of biological activities, including antitumor, 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, due to the presence of multifunctional groups.

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.

2. 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. Thiazoles are very important building blocks in the preparation of metal complexes.
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 anti-diabetic drug candidate MB06322\textsuperscript{21-23}. Recently, thiazoles found application in drug development for the treatment of allergies\textsuperscript{24}, hypertension\textsuperscript{25}, inflammation\textsuperscript{26}, schizophrenia\textsuperscript{27}, bacterial\textsuperscript{28}, HIV infections\textsuperscript{29}, hypnotics, as fibrinogen receptor antagonist with antithrombotic activity and as new inhibitors of bacterial DNA gyrase B\textsuperscript{30}.

Many thiazole derivatives such as sulfathiazole, ritonvir, abafungi, blemycin and tiazofurin are well known as potent biologically active compounds\textsuperscript{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 of drugs in the market containing the moiety\textsuperscript{32,33}. Thiazole ring also found applications in polymer, liquid crystals, photo-nuclease, fluorescent dyes, insecticides and antioxidants\textsuperscript{34,35}. Their transition metal complexes have attracted a great deal of interest largely due to their ability to interact with DNA molecule\textsuperscript{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\textsuperscript{37}. It is well known that some coordination compounds can inhibit the growth of cancer cells by binding and damaging DNA\textsuperscript{38}.

G. Y. Nagesh et al\textsuperscript{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](image1)

M. Bennikallu Hire Mathada G. Y. Nagesh\textsuperscript{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 \textit{In Vitro} Cytotoxic Studies (Scheme 2.2).

![Scheme 2.2](image2)

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\textsuperscript{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).
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. Ejaz et. al. 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. 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.

Biological investigation of novel metal complexes of 2-amino-4-substituted phenylthiazole Schiff bases have been reported by Jyotirmaya Sahoo, and Sudhir K. Paisesetty (Scheme 2.5).
3. Benzothiazole Moiety

In recent years heterocyclic 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. A large 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 of medicinal 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 aromaticity makes 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, anti-inflammatory, antiviral, antileishmanial, and antiviral.

Benzothiazole has special significance in the field of medicinal chemistry due to their remarkable pharmacological potentialities. Developing new potent antineoplastic agents and on the discovery of novel biological targets. Novel benzothiazole-2-thiol derivatives were synthesized by Wang et al.\textsuperscript{47}, and their antiproliferative activities on HepG2 and MCF-7 cells were investigated. Most compounds had inhibitory effects on cell growth, and some of them were more effective than cisplatin. Kumbhare et al.\textsuperscript{48} synthesised benzothiazolylthiocarbamide using a catalytic amount of 4-dimethylaminopyridine (DMAP) followed by its chemoselective oxidative cyclization 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).

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.\textsuperscript{47}, and their antiproliferative activities on HepG2 and MCF-7 cells were investigated. Most compounds had inhibitory effects on cell growth, and some of them were more effective than cisplatin. Kumbhare et al.\textsuperscript{48} synthesised benzothiazolylthiocarbamide using a catalytic amount of 4-dimethylaminopyridine (DMAP) followed by its chemoselective oxidative cyclization 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.\textsuperscript{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 rettgeri.

A new class of 4-arylhydrazono-1-benzothiazol-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.\textsuperscript{50} and screened for antimicrobial activity.

Antidiabetic Activity: Diabetes mellitus is characterized by chronic hyperglycemia and belongs to a group of metabolic disorders with different etiologies. Recent estimates from the year 2000 indicate that there are 171 million people 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’iaz et al.\textsuperscript{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.\textsuperscript{52}. The new ligand and their metal complexes has been synthesized from 2-aminobenzothiazole and 2-hydroxynaphthaldehyde by condensation in ethanol by Sinan Saydam\textsuperscript{53} (Scheme 3.1).

![Scheme 3.1](image-url)

**Scheme 3.1:**
Kini S. G et. al.\textsuperscript{54} studied synthesis and antimicrobial activity of Schiff bases derived from substituted 2- amino benzothiazole and substituted benzaldehyde (Scheme 3.2).
Scheme 3.2:

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

\[
\begin{align*}
R_1 &= OCH_3, OC_2H_5, CI \\
R_2 &= F, CI \\
R_3 &= OH, OCH_3, NO_2 \\
R_4 &= F, OCH_3, CH_3
\end{align*}
\]

\[R = 4-H, 4-CH_3, 4-OCH_3, 4-Cl, 6-NO_2, 6-SO_2CH_3\]

Fig 1

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

Scheme 3.3:

4. 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)
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. \(^6\). Garima Yadav and Jyoti V. Mani \(^6\) 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 \(^6\) operationally simple green synthesis of some Schiff bases using grinding chemistry technique and these compounds were screened for antimicrobial activities (Scheme 4.4).

<table>
<thead>
<tr>
<th>Compound</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>R₄</th>
</tr>
</thead>
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<td>OH</td>
<td>H</td>
<td>H</td>
<td>H</td>
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<td>1b/2b</td>
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<td>1d/2d</td>
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<td>H</td>
<td>H</td>
<td>H</td>
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<td>1e/2e</td>
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<td>H</td>
<td>CI</td>
<td>H</td>
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<tr>
<td>1f/2f</td>
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<td>H</td>
<td>H</td>
<td>CI</td>
</tr>
<tr>
<td>1g/2g</td>
<td>OH</td>
<td>H</td>
<td>H</td>
<td>Br</td>
</tr>
</tbody>
</table>
Green chemical one-pot multicomponent condensation reaction of substituted 1H-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. these compounds were screened for antibacterial and antifungal agent (Scheme 4.5).

![Image of Scheme 4.5](image_url)

**Scheme 4.5:**
Sunita Bhagat, and coworkers have reported 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 Serpel Demirci.

**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, antiadhesive, 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.

**References:**


Ashok R.Karad¹, Anilkumar G.Jadhav¹, Navanand B. Wadwale², Gopinath S. Khansole³, Sunil S. Choudhare⁴, Sachin S.Tiwade⁵, Swapnil V.Nawhate⁶and Vijay N. Bhosale⁶⁶

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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.

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 cleaness, 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-dicarboxyl 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 reaction¹⁷ and Michael addition reaction.¹⁸ Multicomponent reactions (MCRs) have emerged as an attractive and powerful strategy for organic synthesis compared 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

LITERATURE REVIEW:
Naphthopyranopyrimidine 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 antibacterial³² and anticonvulsant activities.³³ The synthesis of Naphtho- pyranopyrimidines via earlier methods has been reported so far using formic acid,³⁴ indium(III) chloride,³⁵ iodine,³⁶ ZnO nanoparticles,³⁷ H₃[SiW₁₂O₄₀],³⁸ L-proline,³⁹ poly(AMPs-co-MAA),⁴₀ aluminKAl(SO₄)₂·12H₂O,⁴¹ Al(H₂PO₄)₃,⁴² Fe₃O₄, @SiO₂-Fe₂O₃@MCM-4,⁴³ basic ionic liquid⁴⁴ 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

**MATERIAL METHOD/ PRESENT WORK:**

In present work, we have investigated the one pot three component synthesis of different substituted derivatives of 12-(phenyl)-8H-benzo[5,6]chromeno[2,3-d] pyrimidine-9,11(10H, 12H)-dione derivatives. The reaction followed by Knoevenagel 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 form 12-(phenyl)-8H-benzo[5,6]chromeno[2,3-d]pyrimidine-9, 11(10H,12H)-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, 1H-NMR, Mass and 13C-NMR spectroscopic technique and also elemental analysis.

**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 effectivene ss 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, 1H-NMR, Mass and 13C-NMR spectroscopic technique and also elemental analysis.

The p-TSA acting as phase transfer catalyst (PTC) that’s why reaction mechanism was accelerated, p-Toluene sulfonic 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.H2O. 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)-8H-benzo[5,6]chromeno[2,3-d]pyrimidine-9,11(10H,12H)-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.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Reaction Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMF</td>
<td>6.0</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>Ethylene glycol</td>
<td>5.5</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>THF</td>
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<td>40</td>
</tr>
<tr>
<td>4</td>
<td>Acetonitrile</td>
<td>6.0</td>
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<tr>
<td>5</td>
<td>DCM</td>
<td>7.0</td>
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<tr>
<td>6</td>
<td>Ethanol</td>
<td>5.0</td>
<td>90</td>
</tr>
<tr>
<td>8</td>
<td>Water+Ethanol(1:1)</td>
<td>5.0</td>
<td>65</td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mole %)</th>
<th>Temperature (°C)</th>
<th>Reaction Time (h)</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
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<td>2</td>
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<td>8</td>
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</tr>
</tbody>
</table>
Reaction conditions: \(\beta\)-naphthol (1 mmol) (03), Barbituric acid (1 mmol) (02) and aromatic aldehyde (1 mmol) (01) was refluxed at 70 °C. \([d]\) Isolated yields.

Probable Mechanism:

![Probable Mechanism Diagram]

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.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Comp. code</th>
<th>Structure of compounds</th>
<th>Time (Hrs)</th>
<th>Yield (%)</th>
<th>M.P. (Obs. °C)</th>
<th>M.P. (Lit. °C)</th>
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<tr>
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<td>![Structure 1]</td>
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<td>275-277</td>
<td>276-278</td>
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<tr>
<td>2</td>
<td>04 b</td>
<td>![Structure 2]</td>
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<td>248-250</td>
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<tr>
<td>3</td>
<td>04 c</td>
<td>NO$_2$</td>
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<tr>
<td>5</td>
<td>04 e</td>
<td>F</td>
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<tr>
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<tr>
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<td>11</td>
<td>04 k</td>
<td><img src="image2" alt="Chemical Structure" /></td>
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<td>12</td>
<td>04 l</td>
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<td>70</td>
<td>277-278</td>
<td>278-279</td>
</tr>
</tbody>
</table>
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. Bruker advance spectrophotometer 300 or 400 MHz was used to record 1H and 13C-NMR spectra in DMSO-d6 using TMS as internal standard. Mass spectra were recorded on FT-VC-7070 H Mass spectrometer using EI technique at 70 eV.

SPECTRAL ANALYSIS:(FINDINGS)

1) 12-(4-nitrophenyl)-8H-benzo[5,6]chromeno[2,3-d]pyrimidine-9,11(10H,12H)dione.(04c) (IR (KBr/cm⁻¹) 3234 (-NH), 3080 (Ar-C-H), 1716 (-C=O), 1694 (Ar C=C), 1531 (-NO₂) cm⁻¹; 1HNMR (300MHz, DMSO d6/ 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⁺, 100% ). 13C NMR (300 MHz, DMSO-d6/ppm) δ:37.1, 81.30, 118.91,122.12, 123.23, 123.24, 125.55, 125.55, 125.56,128.86,133.57,145.48,151.29,151.81,154.12,157.93,164.10; Elemental analysis : Calculated data for C21H13N2O5; C, 65.12; H 3.38, N, 10.85. Found: C 65.06; H, 3.32; N, 10.20.

2) 12-(4-fluorophenyl)-8H-benzo[5,6]chromeno[2,3-d]pyrimidine-9,11(10H,12H) dione.(04e) IR (KBr/cm⁻¹) 3262 (-NH), 3112 (Ar-C-H), 1744 (-C=O),1354 (C-F) cm⁻¹; 1HNMR (300MHz, DMSO d6/ 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⁺, 100% ); 13CNMR (300MHz, DMSOds/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 C22H11F3N2O3; C 70.00, H 3.64, N 7.77 Found: C 70.02, H 3.60, N 7.72)

3) 12-(4-chlorophenyl)-8H-benzo[5,6]chromeno[2,3-d]pyrimidine-9,11(10H,12H)-dione.(04g) IR (KBr/cm⁻¹) 3219 (-NH), 3091 (Ar-C-H), 1755 (-C=O), 1288 (C-O-C), 792(C-Cl) cm⁻¹; 1HNMR (300MHz, DMSO d6/ 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⁺, 100% ); 13CNMR (300MHz, DMSOds/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 C22H11Cl2N2O3; C 66.94, H 3.48, N 7.43 Found: C 66.90, H 3.39, N 7.3

4) 12-(4-methoxyphenyl)-8H-benzo[5,6]chromeno[2,3-d]pyrimidine-9,11(10H,12H)-dione.(04 h) IR (KBr/cm⁻¹) 3211 (-NH), 3064(Ar-C-H), 1732 (-C=O), 1269 (C-O-C) cm⁻¹; 1HNMR (300MHz, DMSO d6/ ppm) δ: 3.85 (3H,s,-OCH3), 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,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⁺, 100% ); 13CNMR (300MHz, DMSOds/ppm) δ:38.12,82.00,115.20, 115.20,118.90,122.36,123.01,123.14,126.19,128.40,129.12,129.12,130.06,139.93,150.70,151.10,156.86,159.00,1 63.00 Elemental analysis: Calculated data for C23H13N2O5; C 70.96, H 4.33, N 7.52 Found: C 70.90, H 4.29, N 7.48).

CONCLUSION:

We have proposed a novel efficient and eco-friendly synthesis of 12-(substituted phenyl)-8H-benzo[5,6]chromeno[2,3-d]pyrimidine-9,11(10H,12H)-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.

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.

REFERENCES:

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 (νsp/√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°C) and different concentration.

2. EXPERIMENTAL:

2.1 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].

2.2 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⁻¹s⁻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

\[ \eta_r = \frac{\eta}{\eta_0} \]

\[ \eta_d = \frac{\eta_d}{\eta_0} \]

Where

\[ \eta_r \] = Relative viscosity
\[ \eta_w \] = Viscosity of water
\[ \eta_d \] = Density of solution
\[ \eta_s \] = Density of solution
\[ \eta_f \] = Flow time for solution
\[ \eta_t \] = 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.

\[ \left( \frac{\eta_r - 1}{\sqrt{C}} \right) = \eta_{sp}/\sqrt{C} = A + B \sqrt{C} \]  

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 (\( \eta_{sp}/\sqrt{C} \)) 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.

<table>
<thead>
<tr>
<th>Table 1: System-Ligand A (L_A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp: (308 ±0.1) K</td>
</tr>
<tr>
<td>Conc(C) Mole/lit</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
</tbody>
</table>
Table 2: System-Ligand B ($L_B$)

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

Table 3: A and B Coefficient values

<table>
<thead>
<tr>
<th>Ligand + 75% DCM-Water</th>
<th>A</th>
<th>B (Lit/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_A$</td>
<td>10.32</td>
<td>-42.464</td>
</tr>
<tr>
<td>$L_B$</td>
<td>6.43</td>
<td>-4.1696</td>
</tr>
</tbody>
</table>

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.

REFERENCES:

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$_2$CO$_3$ 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$_2$CO$_3$, 2-substituted hydrazino-6-chloro benzothiazole

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 dopant 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].

LITERATURE REVIEW:

Inspite of tremendous advance made in modern medicine, there are still a large number of ailments 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.

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.

METHOD:

\[
\text{Cl} \quad \text{S} \quad \text{SH} \quad + \quad \text{NH}_2\text{NH-R} \quad (\text{II a-d}) \quad \xrightarrow{\text{K}_2\text{CO}_3/\text{DMF}} \quad \triangle \quad \text{Cl} \quad \text{N} \quad \text{S} \quad \text{NH} \quad \text{NH-R} \quad (\text{III a-d})
\]

6-chloro-2-mercapto benzothiazole  
2-substituted hydrazino-6-chloro benzothiazole
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 K2CO3 gives 2-substituted hydrazino-6-chloro benzothiazole. The synthesized compounds were characterized by elemental analysis and spectral data.

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.

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

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.

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-substituted 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.

REFERENCES:
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 techniques are very good tools for the identification of compounds. The structures have been confirmed by 1H NMR, 13C NMR, IR, and Mass spectral data.

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

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 and tetra butyl ammonium bromide [26].

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°C, as shown in Scheme 1.

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 ¹H and ¹³C 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).

RESULT 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 benzaldehydes (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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Reaction Time (h)</th>
<th>Yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetonitrile</td>
<td>3.0</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>DCM</td>
<td>3.0</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>DMF</td>
<td>3.0</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>3.0</td>
<td>62</td>
</tr>
<tr>
<td>5</td>
<td>Ethylene glycol</td>
<td>3.0</td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td>Ethanol-water</td>
<td>3.0</td>
<td>90</td>
</tr>
</tbody>
</table>

$^a$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)$_3$ 

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mole %)</th>
<th>Temperature ($^\circ$C)</th>
<th>Reaction Time (h)</th>
<th>Yield %$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>01</td>
<td>80</td>
<td>3.0</td>
<td>45</td>
</tr>
<tr>
<td>2</td>
<td>02</td>
<td>80</td>
<td>3.0</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>05</td>
<td>80</td>
<td>3.0</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>08</td>
<td>80</td>
<td>3.0</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>80</td>
<td>3.0</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>80</td>
<td>3.0</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>80</td>
<td>3.0</td>
<td>92</td>
</tr>
</tbody>
</table>
**Reaction conditions:** Aromatic aldehyde (10 mmol), Malononitrile (10 mmol) and guanidine hydrochloride (10 mmol) was refluxed.

**Isolated yields.**

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde (1a-e)</th>
<th>Products (4 a-e)</th>
<th>Time (h)</th>
<th>Yield (%)**</th>
<th>M.P. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CHO</td>
<td><img src="image" alt="Product 3a" /></td>
<td>3.0</td>
<td>85</td>
<td>240-242</td>
</tr>
<tr>
<td>2</td>
<td>OH CHO</td>
<td><img src="image" alt="Product 3b" /></td>
<td>3.0</td>
<td>80</td>
<td>260-262</td>
</tr>
<tr>
<td>3</td>
<td>CHO OCH₃</td>
<td><img src="image" alt="Product 3c" /></td>
<td>3.0</td>
<td>75</td>
<td>236-238</td>
</tr>
<tr>
<td>4</td>
<td>Cl CHO</td>
<td><img src="image" alt="Product 3d" /></td>
<td>3.0</td>
<td>70</td>
<td>264-266</td>
</tr>
<tr>
<td>5</td>
<td>Br CHO</td>
<td><img src="image" alt="Product 3e" /></td>
<td>3.0</td>
<td>90</td>
<td>260-262</td>
</tr>
</tbody>
</table>

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

**Isolated yield**

**Spectral Analysis:**

2,4-diamino-6-phenyl pyrimidine-5-carbonitrile (4a):
M.P. 260-262°C; Yield 80%; IR (KBr, νmax, cm⁻¹), 3466, 3374, 3145, 2215; ¹H NMR (400 MHz, DMSO-d₆, ppm) δ 7.04-7.62 (s, 8H, 2NH₂), 6.90 (d, 2H, Ar-H), 5.74 (s, 1H, OH), 4.62 (s, 1H, OH), 3.78 (s, 2H, CH₂), δ 6.90 (d, 2H, Ar-H), 6.74 (d, 2H, Ar-H); ¹³C NMR (400 MHz, DMSO-d₆, ppm): δ 168.4, 167.5, 166.2, 134.7, 132.8, 122.5, 117.1, 79.2; EI-MS (m/z: RA %): 289 (M⁺, 100%). Elemental analysis Calculated data for C₁₉H₁₁N₃O; C, 59.70; H, 3.60; N, 29.10. Found: C, 59.80; H, 3.50; N, 29.10.

2.4-diamino-6-(4-hydroxyphenyl)pyrimidine-5-carbonitrile (4b):
M.P. 260-262°C; Yield 80%; IR (KBr, νmax, cm⁻¹), 3395, 3374, 3256, 3022, 2230; ¹H NMR (400 MHz, DMSO-d₆, ppm) δ 7.04-7.38 (brs, 4H, 2NH), δ 7.40 (d, 2H, Ar-H), δ 7.10 (d, 2H, Ar-H); ¹³C NMR (400 MHz, DMSO-d₆, 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⁺, 100%). Elemental analysis Calculated data for C₁₀H₇N₅C; C, 62.55; H, 4.29; N, 33.16. Found: C, 62.50; H, 4.36; N, 33.10.

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

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

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Compounds</th>
<th>Zone of inhibition (mm)</th>
<th>Bacterial Species</th>
<th>Fungal Species</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Staphylococcus aureus</td>
<td>Escherichia coli</td>
</tr>
<tr>
<td>01</td>
<td>4a</td>
<td>12</td>
<td>14</td>
<td>10</td>
</tr>
<tr>
<td>02</td>
<td>4b</td>
<td>16</td>
<td>18</td>
<td>16</td>
</tr>
<tr>
<td>03</td>
<td>4c</td>
<td>18</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>03</td>
<td>4d</td>
<td>16</td>
<td>10</td>
<td>16</td>
</tr>
<tr>
<td>05</td>
<td>4e</td>
<td>20</td>
<td>18</td>
<td>14</td>
</tr>
<tr>
<td>Ref²</td>
<td>Penicillin</td>
<td>26 mm</td>
<td>40 mm</td>
<td>18 mm</td>
</tr>
<tr>
<td></td>
<td>Streptomycin</td>
<td>40 mm</td>
<td>35 mm</td>
<td>34 mm</td>
</tr>
<tr>
<td></td>
<td>Nystatin (50 μg/ml)</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
</tbody>
</table>

ND = Not detected zone of inhibition under experimental condition.
CONCLUSION:
We have developed an operationally simple, eco-friendly, inexpensive and efficient, synthesis of tetramethyl-hexahydro-1H-xanthen-1,8(2H)-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.

REFERENCES:


Solvent Free Efficient Approach for Synthesis of α-Hydroxy Phosphonates using an. K$_2$HPO$_4$/Et$_3$N as a Catalyst

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Abstract: An simple, efficient and neat method was established for one pot synthesis of α-hydroxy phosphonates from aromatic aldehyde and diethyl phosphite using an. K$_2$HPO$_4$/Et$_3$N 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

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.

LITERATURE REVIEW:
The α-hydroxy phosphonates are consequential class of organophosphorus compound which shows extensive applications in organic as well as in medicinal chemistry1. The synthesis of α-hydroxy phosphonates and their derivatives acquired much attention of organic chemists in recent years due to their important biological activities2. They exhibit broad range of biological activities like antibacterial3, antiviral4, anticancer5, antioxidant6, antifungal7, insecticides8, anti-HIV activities9. 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 ester10. 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-amino12, α-halo13, α-keto14 and α-acetoxy phosphonates15.

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 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 dialkylphosphite in presence of basic catalyst such as ethyl magnesium bromide, LDA, KF on alumina, quinine, DBU, Magnesium oxide (MgO) etc. while several acid catalyst such as HCl, oxalic acid, KH₂PO₄, camphor sulphonic acid 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. So by considering all above fact, we herein report the investigation of an. K₂HPO₄/Et₃N 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.

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 F254, 30% ethyl acetate in hexane solvent was used for TLC. Visualization was made with UV light (254 or 365nm). The ¹H NMR spectra were recorded on BRUKER- 400 MHz (Model: AV 400) spectrometer in CDCl₃ 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°C in presence of an. K₂HPO₄/Et₃N (10:5 mol%) as a catalyst for 2 hours. The reaction was monitored 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.

![Scheme 1: Synthesis of α-Hydroxy Phosphonates](image)

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 K₂HPO₄ catalyst was integrated, then progress of reaction was visualized after stirring for 2 hours at 60°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. K₂HPO₄. 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. K₂HPO₄. 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).
Scheme 2: Synthesis of α-Hydroxy Phosphonates

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Organic basic catalyst</th>
<th>Organic basic catalyst amount (mol%)</th>
<th>Time (hrs)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>8</td>
<td>No reaction</td>
</tr>
<tr>
<td>2</td>
<td>Pyridine</td>
<td>1</td>
<td>4</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>Morpholine</td>
<td>1</td>
<td>3</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>Pyrolidine</td>
<td>1</td>
<td>4</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>Triethylamine</td>
<td>1</td>
<td>2</td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td>Triethylamine</td>
<td>2</td>
<td>2</td>
<td>85</td>
</tr>
<tr>
<td>7</td>
<td>Triethylamine</td>
<td>5</td>
<td>2</td>
<td>98</td>
</tr>
</tbody>
</table>

Reaction condition: benzaldehyde (1 mmol.), diethyl phosphite (1 mmol), an. K₂HPO₄ (10 mol%), solvent free, temp. 60°C.

10 mol% an. K₂HPO₄/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. K₂HPO₄:Et₃N (table 1, entry 7). Therefore ideal reaction condition were established as: benzaldehyde (1 mmol), diethyl phosphite (1 mmol) and 10:5 mol% of an. K₂HPO₄:Et₃N at 60°C temp. under solvent free condition.

The potency of the catalyst an. K₂HPO₄:Et₃N 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. K₂HPO₄:Et₃N 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.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (conc.)</th>
<th>Solvent</th>
<th>Time (hrs)</th>
<th>Temp. (℃)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Comparison of Catalyst</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>HCl (100 g/mol%)</td>
<td>Diethyl ether</td>
<td>24</td>
<td>0</td>
<td>74[23]</td>
</tr>
<tr>
<td>2</td>
<td>K₂HPO₄a (5g/mol%)</td>
<td>Neat</td>
<td>5c</td>
<td>rt</td>
<td>86[25]</td>
</tr>
<tr>
<td>3</td>
<td>MgO (0.2g)</td>
<td>Neat</td>
<td>2</td>
<td>rt</td>
<td>90[22]</td>
</tr>
<tr>
<td>4</td>
<td>Camphor Sulphonic Acida (10 g/mol%)</td>
<td>Neat</td>
<td>0.5</td>
<td>rt</td>
<td>91[26]</td>
</tr>
<tr>
<td>5</td>
<td>KF-alumina (0.6g)</td>
<td>Neat</td>
<td>2</td>
<td>rt</td>
<td>96[19]</td>
</tr>
<tr>
<td>6</td>
<td>Oxalic acidb (10g/mol%)</td>
<td>Neat</td>
<td>1.5</td>
<td>80</td>
<td>98[24]</td>
</tr>
</tbody>
</table>
Influence of solvent

<table>
<thead>
<tr>
<th>Entry</th>
<th>Comp.</th>
<th>Aldehyde</th>
<th>Time (hrs)</th>
<th>M.P. °C found</th>
<th>M.P. °C reported</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>an. K$_2$HPO$_4$:Et$_3$N (10:5 mol%)</td>
<td>Neat</td>
<td>2</td>
<td>60</td>
<td>98</td>
<td>This work</td>
</tr>
<tr>
<td>8</td>
<td>an. K$_2$HPO$_4$:Et$_3$N (10:5 mol%)</td>
<td>Ethanol</td>
<td>3</td>
<td>60</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>9</td>
<td>an. K$_2$HPO$_4$:Et$_3$N (10:5 mol%)</td>
<td>Toluene</td>
<td>4</td>
<td>60</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>an. K$_2$HPO$_4$:Et$_3$N (10:5 mol%)</td>
<td>Dichloromethane</td>
<td>2</td>
<td>60</td>
<td>-</td>
<td>65</td>
</tr>
<tr>
<td>11</td>
<td>an. K$_2$HPO$_4$:Et$_3$N (10:5 mol%)</td>
<td>Dioxane</td>
<td>4</td>
<td>60</td>
<td>-</td>
<td>50</td>
</tr>
</tbody>
</table>

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.

**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$_3$).

**CONCLUSION:**

In summery we have developed novel route for synthesis of α-hydroxyphosphonates and its derivatives using an. K$_2$HPO$_4$:Et$_3$N 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.
REFERENCES:

Solar Cell - A semiconductor 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 photovoltaic 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 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.

Working of solar cell:
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]

Fig. 1

Fig. 1.1
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]

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:
1. Making current technology solar cells cheaper and/or more efficient to effectively compete with other energy sources;
2. Developing new technologies based on new solar cell architectural designs;
3. Developing new materials to serve as more efficient energy converters from light energy into electric current or light absorbers and charge carriers.

LIMITATION OF THE STUDY:

High cost of installation, Low efficiency, During cloudy environment, rainy season, at night solar energy will not be available to us.

CONCLUSION:

As technology will advance and emerge with new and more cost effective devices, the solar cell/plates will be available 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 fulfill the requirements of energy at many levels. The encouragement will lead to research of many small effective devices working on solar energy that will help to reach energy demands at daily individual level to industrial levels.

REFERENCES:
New Agricultural Innovation Systems and Small Holder Participation in Modern Farm in Village, Mandur

A. B. Patil, S. M. Patil, M. G. Chikalkar

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 H2SO4 * 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 P2O5 = % P * 2.29
P % as PO4 = % 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, 
\[ K\% = \frac{\text{Value from graph (mg/l) } \times \text{total volume prepared}}{10000 \times \text{wt of sample (gm)}} \]
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, 
\[ \text{Calcium }\% = \frac{A \times 400.8 \times V}{v \times 10000 \times S} \]
where 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 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, 
\[ \text{Calcium }\% = \frac{A \times 400.8 \times V}{v \times 10000 \times S} \]
where 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 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, 
\[ \% \text{ organic matter} = \frac{\% \text{ organic carbon} \times 1.724}{1.724} \]
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

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Parameter</th>
<th>Unit</th>
<th>Limit</th>
<th>Analysis of Soil before spent wash.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>-</td>
<td>6.5-8.5</td>
<td>8.00</td>
</tr>
<tr>
<td>2</td>
<td>E-Conductivity</td>
<td>mhos/cm</td>
<td>&lt;4.0</td>
<td>0.11</td>
</tr>
<tr>
<td>3</td>
<td>Nitrogen</td>
<td>Kg/ha</td>
<td>100-200</td>
<td>134.00</td>
</tr>
<tr>
<td>4</td>
<td>Phosphorous</td>
<td>Kg/ha</td>
<td>30-40</td>
<td>24.53</td>
</tr>
<tr>
<td>5</td>
<td>Potassium</td>
<td>Kg/h</td>
<td>110-280</td>
<td>226.00</td>
</tr>
<tr>
<td>6</td>
<td>Organic Carbon</td>
<td>%</td>
<td>&gt;0.50</td>
<td>0.61</td>
</tr>
<tr>
<td>7</td>
<td>Calcium</td>
<td>%</td>
<td>0.1-3.2</td>
<td>0.50</td>
</tr>
<tr>
<td>8</td>
<td>Copper (Cu)</td>
<td>ppm</td>
<td>0.3-0.5</td>
<td>1.18</td>
</tr>
<tr>
<td>9</td>
<td>Iron (Fe)</td>
<td>ppm</td>
<td>2.5-4.5</td>
<td>2.92</td>
</tr>
<tr>
<td>10</td>
<td>Manganese (Mn)</td>
<td>ppm</td>
<td>1.0-2.0</td>
<td>2.72</td>
</tr>
<tr>
<td>11</td>
<td>Zinc (Zn)</td>
<td>ppm</td>
<td>0.5-1.2</td>
<td>0.84</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Parameter</th>
<th>Unit</th>
<th>Limit</th>
<th>Analysis of Soil after spent wash.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>-</td>
<td>6.5-8.5</td>
<td>7.00</td>
</tr>
<tr>
<td>2</td>
<td>E-Conductivity</td>
<td>mhos/cm</td>
<td>&lt;4.0</td>
<td>0.90</td>
</tr>
<tr>
<td>3</td>
<td>Nitrogen</td>
<td>Kg/ha</td>
<td>100-200</td>
<td>234.00</td>
</tr>
</tbody>
</table>
Similarly, soil samples collected from same regions of Shirala Tahasal 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 224.0 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 in the range 1.84 ppm. The Table 3.1.3 shows comparative analysis of the soil treatment results.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Parameter</th>
<th>Sample (II-I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Phosphorous</td>
<td>Kg/ha 30-40</td>
</tr>
<tr>
<td>5</td>
<td>Potassium</td>
<td>Kg/ha 110-280</td>
</tr>
<tr>
<td>6</td>
<td>Organic Carbon</td>
<td>% &gt;0.50</td>
</tr>
<tr>
<td>7</td>
<td>Calcium</td>
<td>% 0.1-3.2</td>
</tr>
<tr>
<td>8</td>
<td>Copper (Cu)</td>
<td>ppm 0.3-0.5</td>
</tr>
<tr>
<td>9</td>
<td>Iron (Fe)</td>
<td>ppm 2.5-4.5</td>
</tr>
<tr>
<td>10</td>
<td>Manganese (Mn)</td>
<td>ppm 1.0-2.0</td>
</tr>
<tr>
<td>11</td>
<td>Zinc (Zn)</td>
<td>ppm 0.5-1.2</td>
</tr>
</tbody>
</table>

Similarly, soil samples collected from same regions of Shirala Tahasal 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 224.0 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 in 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

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Parameter</th>
<th>Sample (II-I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>E-Conductivity</td>
<td>0.79</td>
</tr>
<tr>
<td>3</td>
<td>Nitrogen</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>Phosphorous</td>
<td>199.47</td>
</tr>
<tr>
<td>5</td>
<td>Potassium</td>
<td>2854</td>
</tr>
<tr>
<td>6</td>
<td>Organic Carbon</td>
<td>1.24</td>
</tr>
<tr>
<td>7</td>
<td>Calcium</td>
<td>0.7</td>
</tr>
<tr>
<td>8</td>
<td>Copper (Cu)</td>
<td>0.77</td>
</tr>
<tr>
<td>9</td>
<td>Iron (Fe)</td>
<td>0.18</td>
</tr>
<tr>
<td>10</td>
<td>Manganese (Mn)</td>
<td>0.18</td>
</tr>
<tr>
<td>11</td>
<td>Zinc (Zn)</td>
<td>1</td>
</tr>
</tbody>
</table>

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.

REFERENCES:

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Substituted pyrazole chalcones: a physicochemical study

Shaikh Abdul Baseer, Momin Nishat Parveen

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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, PHmeter

INTRODUCTION:
Chalcones are also called as α, β-unsaturated ketones. They are precursors of flavonoid 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 antileishmanial. 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.

MATERIALS and METHOD:
A mixture of substituted acetophenone (1 mmol), substituted aldehyde (1 mmol) and KOH (2. mmol, with a minimum of H2O) were taken in ethanol and stirred at 50-60°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.
Table -1-: Physico-chemical data synthesized chalcone derivatives 3(a-h)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Mol. Formula</th>
<th>Yield %</th>
<th>M.P. (°C)</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3A</td>
<td>C_{10}H_{14}O_{2}N_{2}Cl_{2}</td>
<td>86</td>
<td>168</td>
<td>H</td>
<td>H</td>
<td>Cl</td>
</tr>
<tr>
<td>2</td>
<td>3B</td>
<td>C_{10}H_{13}O_{2}N_{2}Cl_{2}I</td>
<td>88</td>
<td>174</td>
<td>I</td>
<td>H</td>
<td>Cl</td>
</tr>
<tr>
<td>3</td>
<td>3C</td>
<td>C_{10}H_{13}O_{2}N_{2}Cl_{2}Br</td>
<td>89</td>
<td>152</td>
<td>Br</td>
<td>H</td>
<td>Cl</td>
</tr>
<tr>
<td>4</td>
<td>3D</td>
<td>C_{10}H_{13}O_{2}N_{2}Cl_{3}</td>
<td>91</td>
<td>141</td>
<td>Cl</td>
<td>H</td>
<td>Cl</td>
</tr>
<tr>
<td>5</td>
<td>3E</td>
<td>C_{20}H_{16}O_{2}N_{2}Cl_{2}</td>
<td>86</td>
<td>128</td>
<td>H</td>
<td>CH_{3}</td>
<td>Cl</td>
</tr>
<tr>
<td>6</td>
<td>3F</td>
<td>C_{20}H_{15}O_{2}N_{2}Cl_{2}I</td>
<td>88</td>
<td>156</td>
<td>I</td>
<td>CH_{3}</td>
<td>Cl</td>
</tr>
<tr>
<td>7</td>
<td>3G</td>
<td>C_{20}H_{15}O_{2}N_{2}Cl_{2}Br</td>
<td>90</td>
<td>185</td>
<td>Br</td>
<td>CH_{3}</td>
<td>Cl</td>
</tr>
<tr>
<td>8</td>
<td>3H</td>
<td>C_{20}H_{17}O_{2}N_{2}Cl</td>
<td>85</td>
<td>132</td>
<td>H</td>
<td>H</td>
<td>CH_{3}</td>
</tr>
</tbody>
</table>

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 CHCl_{3} of all 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

**RESULT AND DISCUSSION**

Density: The density of each compound was evaluated using the following relation:

\[ \frac{1}{\rho_{12}} = g_1/\rho_1 + g_2/\rho_2 \]

where \( \rho_1, \rho_2 \) and \( \rho_{12} \) are the density of pure solvent, pure solute and synthesized compound and solution respectively. \( g_1 \) and \( g_2 \) are the weight fractions of solvent and solute respectively. The slope of plot of \( 1/g_1\rho_{12} \) versus \( g_1/g_2 \) gives \( 1/\rho_2 \).
Density of compounds can be evaluated theoretically by using the equation:

\[ \rho = \frac{K M}{N_A \sum \Delta V_i} \]

Where \( \rho \) is the density of the compound, \( K \) is packing fraction (0.599), \( M \) is the molecular weight of the compound, \( N_A \) is the Avogadro’s number and \( \Delta V_i \) is the volume increment of the atoms and atomic groups present in the compound. Table 2 shows the experimental and theoretical values of density.

<table>
<thead>
<tr>
<th>Compound Code</th>
<th>Experimental density, g/cm³</th>
<th>Theoretical density, g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2H5OH</td>
<td>1.1248</td>
<td>1.3215</td>
</tr>
<tr>
<td>CHCl3</td>
<td>1.3215</td>
<td>1.1702</td>
</tr>
<tr>
<td>3A</td>
<td>1.41</td>
<td>1.3662</td>
</tr>
<tr>
<td>3B</td>
<td>1.141</td>
<td>1.1621</td>
</tr>
<tr>
<td>3C</td>
<td>1.1506</td>
<td>1.3821</td>
</tr>
<tr>
<td>3D</td>
<td>1.1732</td>
<td>1.4131</td>
</tr>
<tr>
<td>3E</td>
<td>1.1621</td>
<td>1.4021</td>
</tr>
<tr>
<td>3F</td>
<td>1.1524</td>
<td>1.3224</td>
</tr>
<tr>
<td>3G</td>
<td>1.1432</td>
<td>1.3112</td>
</tr>
<tr>
<td>3H</td>
<td>1.1612</td>
<td>1.3215</td>
</tr>
</tbody>
</table>

Table 2 shows variation of conductance with concentration of both the solvents. 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 (\( \kappa \)) and equivalent conductance (\( \lambda_c \)) were evaluated. The equations used for calculating specific conductance (\( \kappa \)) and equivalent conductance (\( \lambda_c \)) are:

\[ \lambda_c = 1000 \cdot \frac{k}{C} \]

\( C \) is the concentration (g, equi./lit) of solution. \( k \) is specific conductance and \( \lambda_c \) is equivalent conductance.
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 than 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 shows variation of equivalent conductance with square 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 ΔHₛ 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:  
\[ ΔG = -RT \times \text{intercept} \]
\[ ΔS = (ΔH - ΔG) / T \]

It has been observed from the table that for all the compounds which are synthesized ΔHₛ and ΔG values are positive whereas ΔS values are negative. It is because stronger bonds are broken and weaker bonds are formed, energy is consumed and so, ΔHₛ 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

\[ pK_a = pH + \log [BH^+] / [B] \]

Rearrangement of above equation gives

\[ \log [BH^+] / [B] = pH - pK_a \]

A plot of left hand side versus pH will yield a straight line and pH=pKₐ when ratio of \[ \log [BH^+] / [B] =0. \] [44].

The concentrations of BH⁺ and B can be determined spectrophotometrically by measuring the absorbance at particular wavelength.

<table>
<thead>
<tr>
<th>Compound code</th>
<th>Average Pka Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>3A</td>
<td>10.23</td>
</tr>
<tr>
<td>3B</td>
<td>10.45</td>
</tr>
<tr>
<td>3C</td>
<td>10.34</td>
</tr>
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<td>3D</td>
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</tr>
<tr>
<td>3H</td>
<td>10.87</td>
</tr>
</tbody>
</table>

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 which 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 The Authors would like to thank Principal Dr. Shaikh Kabeer Ahmed, Sir Sayyed College for providing necessary instrumentation facility.

REFERENCES:
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, 1H NMR, Mass.

Key words: Knoevenagel condensation, active methylene compounds, Aliquat 336.

INTRODUCTION & LITERATURE REVIEW:

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, Hannsche 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 base1(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-dimethoxybenzylidene malononitrile by just stirring the equimolar mixture of malononitrile, 3,4-dimethoxybenzaldehyde, in presence of catalytic amount of Aliquat336 .The structure of the derivative was confirmed based on the spectral data.

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 CDCl3 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 Quattro 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 malononitrile (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.

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 dimethoxybenzylidene malononitrile by just stirring the equimolar mixture of malononitrile, 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 \( Z-\text{CH}_2-Z \) or \( Z-\text{CHR} \) such as diethyl malonate, Meldrum's acid, ethyl acetoacetate or malonic acid, cyanoacetic acid, \( Z-\text{CHR} \text{R}_2 \) 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.

**ANALYSIS:**

Molecular Formula =C12H10N2O2

Molecular Weight 214.23=Exact Mass 214= Molecular Composition Calculated found

\[ \text{C} 67.3\%67.280 \text{ (\%H \ (\%4.75)\%4.71N \ )13.0813.05(\%} \]

H NMR: 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)

**CONCLUSION/SUMMARY:**

Thus, we have successfully synthesized 3,4 dimethoxy benzylidene 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.

**REFERENCES:**


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 α-aminophosphonate derivatives containing aminophenol moiety have been synthesized by using eco-friendly catalyst (ChCl / ZnCl₂) 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.

Key Words: quinolines 3-carbaldehyde, aminophenol, Deep Eutectic solvent.

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.

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 Quattro 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.

**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°C 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$_2$SO$_4$ 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): 3358 cm$^{-1}$ (b) -OH; 3311 cm$^{-1}$ (NH); 1234 cm$^{-1}$ (PO); 1032 cm$^{-1}$ (PO-C) 1H NMR (CDCl$_3$, δ ppm): 1.05 (t, 3H, O CH$_2$-CH$_3$); 3.13 (t, 3H, O CH$_2$-CH$_3$); 4.23 (m, 2H, O CH$_2$-CH$_3$); 5.13 (s, 1H, CH-NH Ph); 5.35 (d, 1H, NH CH P-O, J = 24 Hz); 6.71–6.5 (m, 3H, Ph-H, C$_6$H$_5$); 7.51 (d, 1H, Quinolin-H, C$_6$J = 8 Hz). 7.75 (d, 1H, Quinolin-H, C$_6$J = 8 Hz). 8.49 (s, 1H, Quinolin-H, C$_6$J = 8 Hz). ES-MS: m/z 420.1 (m+1) and 442.2 (m+3). Elemental analysis: C$_{20}$H$_{21}$Cl$_2$N$_2$O$_2$P Calcd.: C: 57.08%, H: 5.27%, N: 6.66 %; Found: C: 57.65%, H: 5.59%, 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$^{-1}$ (PO); 1023 cm$^{-1}$ (PO-C) 1H NMR (CDCl$_3$, δ ppm): 1.05 (t, 3H, O CH$_2$-CH$_3$); 3.13 (t, 3H, O CH$_2$-CH$_3$); 4.23 (m, 2H, O CH$_2$-CH$_3$); 5.13 (s, 1H, CH-NH Ph); 5.35 (d, 1H, NH CH P-O, J = 24 Hz); 6.71–6.5 (m, 3H, Ph-H, C$_6$H$_5$); 7.51 (d, 1H, Quinolin-H, C$_6$J = 8 Hz). 7.75 (d, 1H, Quinolin-H, C$_6$J = 8 Hz). 8.49 (s, 1H, Quinolin-H, C$_6$J = 8 Hz). ES-MS: m/z 420.1 (m+1) and 442.2 (m+3). Elemental analysis: C$_{20}$H$_{21}$Cl$_2$N$_2$O$_2$P Calcd.: C: 57.08%, H: 5.27%, N: 6.66 %; Found: C: 57.65%, H: 5.59%, N: 6.61%

4c **Diethyl (2-chloro-7-methylquinolin-3-yl) ((4-hydroxyphenyl) amino) methyl) phosphonate**:
IR (KBr): 3580 cm$^{-1}$ (b) -OH; 3311 cm$^{-1}$ (NH); 1234 cm$^{-1}$ (PO); 1032 cm$^{-1}$ (PO-C) 1H NMR (CDCl$_3$, δ ppm): 1.05 (t, 3H, O CH$_2$-CH$_3$); 3.13 (t, 3H, O CH$_2$-CH$_3$); 4.23 (m, 2H, O CH$_2$-CH$_3$); 5.13 (s, 1H, CH-NH Ph); 5.35 (d, 1H, NH CH P-O, J = 24 Hz); 6.71–6.5 (m, 3H, Ph-H, C$_6$H$_5$); 7.51 (d, 1H, Quinolin-H, C$_6$J = 8 Hz). 7.75 (d, 1H, Quinolin-H, C$_6$J = 8 Hz). 8.49 (s, 1H, Quinolin-H, C$_6$J = 8 Hz). ES-MS: m/z 420.1 (m+1) and 442.2 (m+3). Elemental analysis: C$_{20}$H$_{21}$Cl$_2$N$_2$O$_2$P Calcd.: C: 57.08%, H: 5.27%, N: 6.66 %; Found: C: 57.65%, H: 5.59%, N: 6.61%

4d **Diethyl (2-chloro-6-methylquinolin-3-yl) ((4-hydroxyphenyl) amino) methyl) phosphonate**:
IR (KBr): 3580 cm$^{-1}$ (b) -OH; 3311 cm$^{-1}$ (NH); 1234 cm$^{-1}$ (PO); 1032 cm$^{-1}$ (PO-C) 1H NMR (CDCl$_3$, δ ppm): 1.05 (t, 3H, O CH$_2$-CH$_3$); 3.13 (t, 3H, O CH$_2$-CH$_3$); 4.23 (m, 2H, O CH$_2$-CH$_3$); 5.13 (s, 1H, CH-NH Ph); 5.35 (d, 1H, NH CH P-O, J = 24 Hz); 6.71–6.5 (m, 3H, Ph-H, C$_6$H$_5$); 7.51 (d, 1H, Quinolin-H, C$_6$J = 8 Hz). 7.75 (d, 1H, Quinolin-H, C$_6$J = 8 Hz). 8.49 (s, 1H, Quinolin-H, C$_6$J = 8 Hz). ES-MS: m/z 420.1 (m+1) and 442.2 (m+3). Elemental analysis: C$_{20}$H$_{21}$Cl$_2$N$_2$O$_2$P Calcd.: C: 57.08%, H: 5.27%, N: 6.66 %; Found: C: 57.65%, H: 5.59%, N: 6.61%

4e **Diethyl (2-chloro-7-methylquinolin-3-yl) ((4-hydroxyphenyl) amino) methyl) phosphonate**:
IR (KBr): 3580 cm$^{-1}$ (b) -OH; 3311 cm$^{-1}$ (NH); 1234 cm$^{-1}$ (PO); 1032 cm$^{-1}$ (PO-C) 1H NMR (CDCl$_3$, δ ppm): 1.05 (t, 3H, O CH$_2$-CH$_3$); 3.13 (t, 3H, O CH$_2$-CH$_3$); 4.23 (m, 2H, O CH$_2$-CH$_3$); 5.13 (s, 1H, CH-NH Ph); 5.35 (d, 1H, NH CH P-O, J = 24 Hz); 6.71–6.5 (m, 3H, Ph-H, C$_6$H$_5$); 7.51 (d, 1H, Quinolin-H, C$_6$J = 8 Hz). 7.75 (d, 1H, Quinolin-H, C$_6$J = 8 Hz). 8.49 (s, 1H, Quinolin-H, C$_6$J = 8 Hz). ES-MS: m/z 420.1 (m+1) and 442.2 (m+3). Elemental analysis: C$_{20}$H$_{21}$Cl$_2$N$_2$O$_2$P Calcd.: C: 57.08%, H: 5.27%, N: 6.66 %; Found: C: 57.65%, H: 5.59%, N: 6.61%
(m+1) and 436.2 (m+3). Elemental analysis: C_{21}H_{23}Cl_{2}N_{5}O_{4}P 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); 1231cm⁻¹ (P O); 1035 cm⁻¹ (P - O - C) H NMR (CDCl₃, δ ppm): 1.07 (t, 3H, O CH₂-CH₃, J = 8 Hz); 1.36(t, 3H, O CH₂-CH₃, J = 8 Hz); 3.69 (m, 1H, O CH₂-CH₃); 3.87 (s, 3H, Quinolin OCH₃); 3.9 (m, 1H, O CH₂CH₃); 4.22 (m, 2H, O CH₂CH₃); 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, C₅,C₆,C₀); 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, C₅,J = 8 Hz); 8.22 (d, 1H, Quinolin-H, C₆,J = 8 Hz); ES-MS: m/z 470.1 (m+1) and 472.11 (m+3).Elemental analysis: C_{21}H_{23}Cl_{2}N_{5}O_{4}P 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) H NMR (CDCl₃, δ ppm): 1.07 (t, 3H, O CH₂-CH₃, J = 8 Hz); 1.36(t, 3H, O CH₂-CH₃, J = 8 Hz); 3.69 (m, 1H, O CH₂-CH₃); 3.87 (s, 3H, Quinolin OCH₃); 3.9 (m, 1H, O CH₂CH₃); 4.22 (m, 2H, O CH₂CH₃); 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, C₅,C₆,C₀); 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, C₅,J = 8 Hz); 8.22 (d, 1H, Quinolin-H, C₆,J = 8 Hz); ES-MS: m/z 450.1 (m+1) and 452.11 (m+3).Elemental analysis: C_{21}H_{23}Cl_{2}N_{5}O_{4}P 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.

<table>
<thead>
<tr>
<th></th>
<th>B. subtilis</th>
<th>S.aureus</th>
<th>E. coli</th>
<th>P. aeruginosa</th>
</tr>
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<tr>
<td></td>
<td>MIC (mg/ml)</td>
<td>MIC (mg/ml)</td>
<td>MIC (mg/ml)</td>
<td>MIC (mg/ml)</td>
</tr>
<tr>
<td>4a</td>
<td>32</td>
<td>128</td>
<td>8(+</td>
<td>64</td>
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<tr>
<td>4b</td>
<td>16</td>
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<tr>
<td>4g</td>
<td>64</td>
<td>256</td>
<td>4(+)</td>
<td>64</td>
</tr>
</tbody>
</table>

(+): 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/MIC>4, the effect was considered as bactericidal but if the ratio MBC/MIC<4, the effect was defined as bacteriostatic (24).

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.

REFERENCES:

(17) Engel R., (1992), Phosphorus Containing Insecticides, Handbook of Organophosphorus Chemistry (Marcel Dekker: New York, Ch. 16.
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 noteworthy advantages of this protocol is inexpensive reagent, high yield, short reaction time and simple procedure.

Key Words: Trichloroacetic 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. 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 defoliants [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], NaHSO₄.H₂O [15], Fe(HSO₄)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 F₂₅₄). ¹H & ¹³C 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).

3.1 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 °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.

3.2 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, OCH₃), 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,1Hbenzyllic), 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); ¹³C 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. RESULT 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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehydes</th>
<th>Products</th>
<th>Time (h)</th>
<th>Yield, (%)</th>
<th>M.P. °C</th>
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<td>241-243</td>
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</table>
Reaction Condition: 2-naphthol (1 mmol), aromatic aldehyde (1 mmol) and 2-aminobenzothiazoles (1.2 mmol), Trichloroacetic acid (10 mol %) at 120 °C, bIsolated Yield.

Table 2. Optimization of catalyst concentration at different temperatures.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amount of Catalyst (mol %)</th>
<th>Time (h)</th>
<th>Temperature °C</th>
<th>Yield* (%)</th>
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<td>10</td>
<td>20</td>
<td>1.5</td>
<td>125</td>
<td>78</td>
</tr>
</tbody>
</table>

*aIsolated 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.

REFERENCES:
Facile and efficient synthesis of 1-(benzothiazolylamino) methyl-2-naphthol catalyzed by succinic acid

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2Department of Chemistry, Kalikadevi Art’s, Commerce & Science College, Shirur (Ka.) Dist. Beed-413 249 [M.S.-] India.

Email: uddhav21@gmail.com

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 note worthy 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.

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 pharmaceutical properties such as adrenoceptor blocking, antihypertensive, and Ca2+ 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], NaHSO4.H2O [13], Fe(HSO4)3 [14], Sr(OTf)2 [15], Iodine [16], metopoly acid K2CoW12O40.3H2O [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.

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 molting points by an open capillary tube method and are uncorrected. Progress of the reaction was tested by using alumina TLC plates (Merck 60 F254). 1H NMR 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 °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-(benzothiazol-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); 1H NMR (400 MHz, DMSO-d6): δ = 3.50 and 3.64 (2s, 6H, 2OCH3), 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);
Result 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.

**Table 1 Synthesis of 1-(benzothiazolylamino)methyl-2-naphthol catalyzed by succinic acid**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehydes</th>
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<th>Time (Min.)</th>
<th>Yield, (%)</th>
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Reaction Condition: 2-naphthol (1 mmol), aromatic aldehyde (1 mmol) and 2-aminobenzothiazoles (1.2 mmol), Succinic acid (10 mol %) at 120 °C, *Isolated Yield.

Table 2. Optimization of catalyst concentration at different temperatures.

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<th>Entry</th>
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</tbody>
</table>

*Isolated yield.

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.
References:

Synthesis and characterization of imidazole containing pyrazole

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\textsuperscript{2}P. G. Department of Chemistry, Sir Sayyed College of Art’s, Commerce & Science, Aurangabad- 431 001 [M.S.]- India

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Abstract: Multicomponent reactions (MCRs) and one-pot process include synthesis of Pyrazole derivatives containing Imidazole from benzile, substituted \textit{IH} 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\textsuperscript{1}, sympathomimetic activity\textsuperscript{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 \( \text{pK}_b \) 11.5 (\( \text{pK}_a \) of the conjugated acid 2.49 at 25 °C). The pyrazole ring is found within a variety of pesticides as fungicides, insecticides and herbicides, including fenpyroximate, fipronil, tebufenpyrad and tolfenpyrad\textsuperscript{[15]}. Pyrazole moiety is listed among the highly used ring systems for small molecule drugs by the US FDA \textsuperscript{[16]} Many natural products, especially alkaloids, contain the imidazole ring. These imidazoles share the 1,3-C\textsubscript{2}N\textsubscript{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 capillitator 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\textsuperscript{[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\textsuperscript{[9]}. Imidazole is amphoteric in nature. That is can function as both an acid and as a base. The acid the \( \text{pK}_a \) 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\textsuperscript{[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)\textsuperscript{[13]}. The imidazole ring structure is often found in different biological system. Like vitamin-B12 , Histamine and Biotin have imidazole nucleus in there 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\textsuperscript{[14]}. Imidazole containing molecules found in more versatile biological activity. It is exhibit in Antibacterial\textsuperscript{[8,9,10,13]} Anticancer\textsuperscript{[4,9,10,13]} Anti-tubercular\textsuperscript{[9,13]} Anti-fungal\textsuperscript{[8,9,13]} Anti-analgesic\textsuperscript{[9,13]} Antimicrobial\textsuperscript{[3,7,8,]} Antihelmintic agent\textsuperscript{[3]} Antidepressant\textsuperscript{[5,9]} Antibacterial\textsuperscript{[7,9]} Antiviral\textsuperscript{[9]} Anti-HIV\textsuperscript{[13]} activity. Pyrazole is also important heterocyclic compound and its derivatives have found different in Agriculture and Medicine. It is shows Anti-tuberculosis\textsuperscript{[16]}, Antimicrobial Activity\textsuperscript{[16]}, anti-fungal\textsuperscript{[16]} activity.

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**

3.1 **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 CDCl\(_3\) 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), NH\(_4\)OAc (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 H\(_2\)O for removal of impurities. Pure products were obtained via agitating and re-crystallization by EtOH.

![Diagram of synthesis](image)

**Scheme 1.** Synthesis of 2,4,5-trisubstituted imidazoles catalyzed by UHP

4. **Result**

The following various Pyrazole derivatives containing Imidazole were synthesized from benzil, substituted 1H pyrazole 4-carbaldehydes and ammonium acetate

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<th>Sr. No</th>
<th>R group</th>
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</table>
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 can be prepared which is having wide 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.

5. 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, -CH3), 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  13C 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; 1H NMR (400 MHz, CDCl3) δ ppm: δ 7.00 (2H, m, Ar-H),
7.15 (2H, t, Ar-H), 2.35 (3H, m, -CH₃) 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-pyrazole derivative; 13C NMR (100 MHz, CDCl₃) δ ppm: δ 129.3, 135.8, 133.1, 127.5, 129.3, 128.9, 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, -CH₃), 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; 13C 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, 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, -CH₃), 7.3 (5H, m, Ar-H).

Methoxy benzene derivative; 13C 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, 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, -CH₃), 7.3 (5H, m, Ar-H).

6. 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

\[
\begin{align*}
\text{H}_2\text{N} & \quad + \quad \text{O} - \text{O} - \text{O} \\
\text{O} & \quad \text{H} & \quad \text{O} & \quad \text{H} \\
\text{H}_2\text{N} & \quad \text{N} & \quad \text{H} & \quad \text{O} & \quad \text{H}
\end{align*}
\]

7. Conclusion
It is possible to synthesis pyrazole by using benzyl, aldehyde, NH₄OAc 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-cinnamoyl-2-pyrazolines is reported. A new class 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. 1H NMR spectra were recorded (in DMSO-d6) 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 overnight at room temperature. On the next day morning, the completion of the reaction was monitored by TLC. After completion of the reaction, the then 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 (3a-h)

An equimolar mixture of chalcone (1a) (1 mmol) and cinamoyl hydrazide (1 mmol) was mixed in 20 mL polyethylene 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-d₆, δ ppm): 3.11 (dd, 1H, Hα), 3.72 (dd, 1H, Hβ), 5.31 (dd, 1H, Hγ), 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 C₂₅H₁₈N₂O₂Cl: 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-d₆, δ ppm): 3.21 (dd, 1H, Hα), 3.84 (dd, 1H, Hβ), 5.26 (dd, 1H, Hγ), 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 C₂₅H₁₈N₂O₂Cl: 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-bromophenyl)-2-pyrazoline (3c)

IR (KBr, cm⁻¹): 1618, 1664, 3056; ¹H NMR (DMSO-d₆, δ ppm): 3.16 (dd, 1H, Hα), 3.81 (dd, 1H, Hβ), 5.34 (dd, 1H, Hγ), 6.85-8.35 (m, 16H, Ar-H+CH=CH); EIMS (m/z): 420 (M⁺); Anal. Calcd. For C₂₅H₁₈N₂O₂Br: 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-d₆, δ ppm): 3.08 (dd, 1H, Hα), 3.62 (dd, 1H, Hβ), 5.12 (dd, 1H, Hγ), 6.81-8.21 (m, 16H, Ar-H+CH=CH); EIMS (m/z): 464 (M⁺); Anal. Calcd. For C₂₅H₁₈N₂O₂ClBr: 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-d₆, δ ppm): 3.22 (dd, 1H, Hα), 3.65 (dd, 1H, Hβ), 5.28 (dd, 1H, Hγ), 6.86-8.28 (m, 14H, Ar-H+CH=CH); 11.28 (s, 1H, -OH); EIMS (m/z): 480 (M⁺); Anal. Calcd. For C₂₅H₁₈N₂O₂ClBr: 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): 1620, 1640, 3256; ¹H NMR (DMSO-d₆, δ ppm): 3.26 (dd, 1H, Hα), 3.38 (s, 3H, -OCH₃), 3.72 (dd, 1H, Hβ), 5.21 (dd, 1H, Hγ), 6.82-8.41 (m, 14H, Ar-H+CH=CH); 11.62 (s, 1H, -OH); EIMS (m/z): 416 (M⁺); Anal. Calcd. For C₂₅H₁₈N₂O₂F: 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-d₆, δ ppm): 2.32 (s, 3H, -CH₃), 3.26 (dd, 1H, Hα), 3.41 (s, 3H, -OCH₃), 3.61 (dd, 1H, Hβ), 5.28 (dd, 1H, Hγ), 6.91-8.52 (m, 15H, Ar-H+CH=CH); EIMS (m/z): 396 (M⁺); Anal. Calcd. For C₂₅H₂₀N₂O₂: 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-d₆, δ ppm): 3.21 (dd, 1H, Hα), 3.71 (dd, 1H, Hβ), 5.31 (dd, 1H, Hγ), 6.88-8.56 (m, 14H, Ar-H+CH=CH); 11.52 (s, 1H, -OH); EIMS (m/z): 436 (M⁺); Anal. Calcd. For C₂₅H₁₈N₂O₂Cl: 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

Scheme-1: Synthesis of chalcones using KOH in PEG-400 (1a-h)

Table-1: The physical and analytical data of synthesized chalcone derivatives

<table>
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<tr>
<th>Entry</th>
<th>Substitution</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
<th>R5</th>
<th>Mol. Formula</th>
<th>Yield (%)</th>
<th>M.P (°C)</th>
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<td>a</td>
<td>OH H H Cl OH</td>
<td>C15H15O2Cl</td>
<td>90</td>
<td>130-132</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>b</td>
<td>H H H OH Cl</td>
<td>C15H15O2Cl</td>
<td>85</td>
<td>127-129</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>H H Cl H Cl</td>
<td>C15H15OCl2</td>
<td>95</td>
<td>134-136</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>H H Cl H Br</td>
<td>C15H16OBrCl</td>
<td>92</td>
<td>116-118</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>OH H H Cl Br</td>
<td>C15H16OBrCl</td>
<td>86</td>
<td>96-98</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>OH H H F OMe</td>
<td>C15H15O3F</td>
<td>85</td>
<td>138-140</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>g</td>
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<td>C15H15O2</td>
<td>86</td>
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<td>C15H15O2Cl2</td>
<td>90</td>
<td>126-128</td>
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<td></td>
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</table>

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. H2SO4 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 + H2SO4/EtOH + NH2NH2/EtOH → Cinnamoyl hydrazide (2)

Scheme-2: Synthesis of Cinnamoyl hydrazide

Now, the cinnamoyl hydrazide (2) intermediate was treated with different chalcone derivatives (1a-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 temperature using catalytic amount of acetic acid in PEG-400 as an alternative reaction solvent.

Chalcones (1a-h) + AcOH in PEG-400 (50 °C, Stirr for 1 hr) → Cinnamoyl 2-pyrazolines (3a-h)

Scheme-3: Synthesis of 1-cinnamoyl 2-pyrazolines (3a-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=O double bond 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-cinnamoyl 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

<table>
<thead>
<tr>
<th>Product</th>
<th>Substitution</th>
<th>Mol. Formula</th>
<th>Yield (%)</th>
<th>M.P. (°C)</th>
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<tbody>
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<td>3a</td>
<td>OH H H Cl OH</td>
<td>C_{20}H_{19}N_{2}O_{2}Cl</td>
<td>80</td>
<td>218-220</td>
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<td>3b</td>
<td>H H Cl H OH</td>
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<td>85</td>
<td>182-184</td>
</tr>
<tr>
<td>3c</td>
<td>H H Cl H Cl</td>
<td>C_{20}H_{18}N_{2}O_{2}Cl</td>
<td>92</td>
<td>192-194</td>
</tr>
<tr>
<td>3d</td>
<td>H H Cl H Br</td>
<td>C_{20}H_{18}N_{2}O_{3}Cl</td>
<td>80</td>
<td>212-214</td>
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<tr>
<td>3e</td>
<td>OH H H Cl Br</td>
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<td>85</td>
<td>208-210</td>
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<tr>
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<td>C_{20}H_{21}N_{2}O_{2}F</td>
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<td>174-176</td>
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<td>232-234</td>
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<td>C_{20}H_{18}N_{2}O_{2}Cl</td>
<td>86</td>
<td>164-166</td>
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</table>

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.

5. Acknowledgements:

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References:


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 Transform 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 \(d^2\Sigma^+_b \rightarrow \Pi\) 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\(^3\)\(\Sigma^+_g \rightarrow \Pi\) system. Cerenicharo et. al. [15] reported a laboratory study of the pure rotational spectrum of SiC in the X\(^2\)\(\Pi\) state and also detected this molecule in the circumstellar envelope of the late type of star IRC +10216.

The laser induced fluorescence (LIF) spectrum of C\(^2\)\(\Pi\)-X\(^2\)\(\Pi\) 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\(^2\)\(\Pi\)-X\(^2\)\(\Pi\) 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\(^2\)\(\Pi\), \(\Omega = 2\) & measured three rotational transitions.

Although Brazier et. al [14] assigned 4578 cm\(^{-1}\) band to (0,0) of the A\(^3\)\(\Sigma^+_g \rightarrow \Pi\) 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\(^3\)\(\Sigma^+_g \rightarrow \Pi\) 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 CaF2 beam splitter and a liquid nitrogen cooled InSb detector were used. Total 268 scans gave a better Signal to Noise 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.

\[
U_{HH}(r) = D_e \left(1 - \exp(-x)\right)^2 + c x^3 (1 + b x) e^{-2x}
\]

Where \(x = x(r - r_e)\); \(x_1 = (\omega_e x_e / B_e)^{1/2} / r_e\); \(c = 1 + a_1(D_e / a_0)^2\); \(b = 2 - \{(7/12) - (D_e - (a_2 / a_0)) / c\}\) \(a_0 = \omega_e^2 / 4 B_e\); \(a_1 = -1 - (\omega_e x_e / (6B_e)^2)\) and \(a_2 = (5/4) a_1 - (2/3) (\omega_e x_e / B_e)\)

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This function employees the spectroscopic constants like \(\omega_e\), \(\omega_e x_e\), \(B_e\) and \(D_e\) etc. The potential energies \(U_{H-H}\) could be calculated by substituting the values of the constants and \(r\) values obtained from the RKR curve 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

\[
U_{\text{exR}} = D_e - D_e \{1 + a_1 \rho + a_2 \rho^2 + a_3 \rho^3\} e^{-\beta \rho} \quad \text{............. (2)}
\]

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 \(a_4\) is determined from the solution of the following quartic equation:

\[
D_e a_1^2 - 6 f_2 a_1^2 - 4 f_3 a_1 - f_4 = 0 \quad \text{............. (3)}
\]

The parameters \(f_2\), \(f_3\), \(f_4\) are called force field parameters and are defined as:

\[
f_2 = 4 \pi^2 \mu \omega_e^2 c^2
\]

\[
f_3 = -3z(3f/\rho) [1 + (\omega_e x_e / 6 B_e)^2]
\]

\[
f_4 = (f/\rho)^2 (15 [1 + (\omega_e x_e / 6 B_e)^2]) \left(\frac{8 \omega_e x_e}{B_e}\right)
\]

Usually the largest positive root of equation (3) is selected as \(a_4\). The other parameters \(a_2, a_3\) and \(a_4\) appearing in equation (2) could be calculated from following equations:

\[
a_2 = \left(\frac{1}{\sqrt{2}}\right) [a_1^2 - (f_e / D_e)]
\]

\[
a_3 = (a_2 - a_1^2 - 3/3) - (f_e / 6D_e)
\]

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 \(\beta\) appearing in Morse function is no more a constant in this function. The function is

\[
U_e (r) = D_e \left[\exp\left(-2 \beta_e x\right) - 2 \exp\left(\beta_e x\right)\right] \quad \text{............. (4)}
\]

\[
\beta_e = 8.486 \left(\frac{k_e}{m}\right)^{1/2} : x = r - r_e \quad \text{Where} \quad k_e = k_e / D_e.
\]

The variables \(\beta_e\) are calculated separately for \(r < r_e\) and \(r > r_e\).

For \(r < r_e\) \(\beta_e = \beta_e \{1 + \mu u^{1/2}\}\)

For \(r > r_e\) \(\beta_e = \beta_e \{1 + a_1 u^{1/2} + a_2 u^n + a_3 u^{3n} + a_4 u^{5n}\}\)

Where \(u = \exp(-2 \beta_e x) - 2 \exp(-\beta_e x) + 1\)

For all species \(a_1 = 0.32m; a_2 = 0.15; a_3 = 0.2 - 0.6m\) and \(a_4 = (0.21-3m) (\Delta \chi) 2\)

\(m\) and \(n\) are calculated as follows:

\[
m = 0.025r_e + [0.70 \exp(-7.41 \times 10^3 k_e (\Delta \chi) / z_1 z_2 + 0.042] (\Delta \chi) 1
\]

And

\[
n = 0.70 - 0.03r_e + 0.096 / (10^3 \times k_e \times r_e - 0.3) + [0.35 (\Delta \chi)^2 / r_e^{1/2}]
\]

Where \(r_e = r_e / D_e\)

Zavitsas has taken \(D_e\) in kcal/mol, bond length in \(A^0\) and \(\omega_e\) in cm\(^{-1}\), \(\mu\) 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.

### 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.

### 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

<table>
<thead>
<tr>
<th>Molecule/Constants</th>
<th>M</th>
<th>c_e</th>
<th>c_xe</th>
<th>c_ye</th>
<th>B_e</th>
<th>a_e</th>
<th>D_e</th>
<th>r_e</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>8.39792238</td>
<td>965.16</td>
<td>5.910</td>
<td>--</td>
<td>0.67976</td>
<td>0.00538</td>
<td>37582.2645</td>
<td>1.7182</td>
<td>28,29,30,31</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>H-H Parameters</th>
<th>a₀</th>
<th>a₁</th>
<th>a₂</th>
<th>c</th>
<th>b</th>
<th>x₁</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>342596.59</td>
<td>-2.8729195</td>
<td>4.5209202</td>
<td>4.8471305</td>
<td>0.1968806</td>
<td>1.7572269</td>
</tr>
<tr>
<td>Extended Rydberg Parameters</td>
<td>a₁</td>
<td>a₂</td>
<td>a₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.785623</td>
<td>-1.466607</td>
<td>0.601271</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zavitsas Parameters</td>
<td>B_m</td>
<td>κ_e</td>
<td>κ_n</td>
<td>r_n</td>
<td>Z₁</td>
<td>Z₂</td>
</tr>
<tr>
<td></td>
<td>1.757554</td>
<td>4.609516</td>
<td>0.042908</td>
<td>0.015994</td>
<td>3.8</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Figure 1 (a): RKR, H-H, Extended- Rydberg & Zavitsas Potential energy curves for the ground state of SiC molecule
REFERENCES:


Ionic Liquid Assisted Green Synthesis of 2-Phenylimidazo [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-5-dione, 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 and efficient.

KEYWORD: 2-phenylimidazo [4,5-f][1,10]-phenanthroline, aldehydes, 1,10-phenanthroline-5-dione, ammonium acetate.

INTRODUCTION:-

The Ru(II) metal complexes of 2-phenylimidazo [4,5-f][1,10]-phenanthroline have been attracted considerable attention of chemists for many years\(^1\), because their utilities in DNA structure prob\(^2\). 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 form the skeleton of natural alkaloids\(^3\) which act as neuromuscular blocking agent\(^3\), 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-alpyridine 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 agent\(^10\). 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 dipropyld ketone. In 1882, Radziszewski report the first time synthesis of 2,4,5-triphenyl imidazoles\(^23\), and using nitriles and esters\(^25\) also reported by using potassium ferrocynide\(^26\). Siddiqui et al\(^27\) 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 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.

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\(_4\)OAc(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.
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 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 transformations using stochiometric 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.

\[
\begin{align*}
\text{NH}_4\text{OAC} & \quad \rightarrow \quad \text{NH}_3 + \text{HOAC} \\
\end{align*}
\]

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 2-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 stochiometric 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]BF4 in the presence of ammonium acetate under solvent free condition with excellent yield and easy work up.

Result 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 ¹H NMR spectra shows 1H(s) δ=2.0, for NH group, 6H(s) δ=3.00 for methyl group, 4H(d) δ=6.65-7.30 for 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 :**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde</th>
<th>Product</th>
<th>Time(sec.)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>CHO</td>
<td><img src="image1.png" alt="Image" /></td>
<td>18</td>
<td>80</td>
</tr>
<tr>
<td>3b</td>
<td>CHO</td>
<td><img src="image2.png" alt="Image" /></td>
<td>20</td>
<td>90</td>
</tr>
<tr>
<td>3c</td>
<td>CHO</td>
<td><img src="image3.png" alt="Image" /></td>
<td>16</td>
<td>89</td>
</tr>
<tr>
<td>3d</td>
<td>CHO</td>
<td><img src="image4.png" alt="Image" /></td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>3e</td>
<td>CHO</td>
<td><img src="image5.png" alt="Image" /></td>
<td>14</td>
<td>88</td>
</tr>
<tr>
<td>3f</td>
<td>CHO</td>
<td><img src="image6.png" alt="Image" /></td>
<td>15</td>
<td>90</td>
</tr>
</tbody>
</table>

*aProducts were characterized by ¹H NMR, ¹³C NMR, Mass, elemental analysis and comparison with authentic sample, bIsolated yield after column chromatography.*

**EXPERIMENTAL:**

**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]BF₄ (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, ¹H NMR, ¹³C NMR, mass, elemental analysis and melting points.

**Acknowledgment:** Author thankful to Department of Chemistry, B. Raghunath College, Parbhani.

**References:**

Oxidation of m-chlorochalcone (MCC) by Tripropylammonium Chlorochromates: Kinetic and Mechanistic Study

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Abstract: The Kinetics of oxidation of m-chlorochalcones 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.

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.

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, 0.150 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, tripropylamine (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$_2$SO$_4$. The remaining (TriPACC) was then analyzed Spectrophotometrically. The result indicated that 1 mole of alcohols react with 1 mole (TriPACC).

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

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 \( k_{\text{obs}} \) 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%.

### 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\(_2\)SO\(_4\)], the increase in (MCC) increases the rate of reaction (Table-1). The plot of log of \( k_{\text{obs}} \) 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>
<thead>
<tr>
<th>( \text{[MCC]} )</th>
<th>0.01M</th>
<th>0.02M</th>
<th>0.03M</th>
<th>0.04M</th>
<th>0.05M</th>
<th>0.06M</th>
<th>0.07M</th>
<th>0.08M</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k \times 10^3 \text{sec}^{-1} )</td>
<td>2.06</td>
<td>2.35</td>
<td>2.64</td>
<td>2.94</td>
<td>3.22</td>
<td>3.50</td>
<td>3.78</td>
<td>4.08</td>
</tr>
</tbody>
</table>

#### Table 1: Effect of variation of m-chlorochalcone (MCC) on reaction rate

[\([\text{TriPACC]} = 0.001 \text{ M}, [\text{H}_2\text{SO}_4] = 0.1 \text{ N}, \text{Temperature} = 303 \text{ k}, \text{AA} = 20\% (v/v)\) ]

At constant m-chlorochalcone (MCC) and [H\(_2\)SO\(_4\)], the increase in [TriPACC] increases the rate of reaction (Table-2). The plot of log \( k_{\text{obs}} \) verses log [TriPACC] for different initial concentration of TriPACC is linear with unit slope present the first-order dependence of rate on TriPACC.

<table>
<thead>
<tr>
<th>([\text{TriPACC}]) Mole</th>
<th>0.001</th>
<th>0.0015</th>
<th>0.002</th>
<th>0.0025</th>
<th>0.003</th>
<th>0.0035</th>
<th>0.004</th>
<th>0.0045</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k \times 10^3 \text{sec}^{-1} )</td>
<td>2.06</td>
<td>2.33</td>
<td>2.58</td>
<td>2.84</td>
<td>3.08</td>
<td>3.31</td>
<td>3.55</td>
<td>3.79</td>
</tr>
</tbody>
</table>

#### Table 2: Effect of variation of [TriPACC] on reaction rate

[\([\text{MCC]} = 0.01 \text{ M}, [\text{H}_2\text{SO}_4] = 0.1 \text{ N}, \text{Temp.} = 303 \text{ k}, \text{AA} = 20\% (v/v)\) ]

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\(_2\)SO\(_4\). The rate of reaction increases with increase in [H\(_2\)SO\(_4\)] (Table-3). The plot of log \( K_{\text{obs}} \) versus log [H+]are also straight line with slope less than unity, Indicating a fractional order dependence on [H\(^+\)].

<table>
<thead>
<tr>
<th>([\text{H}_2\text{SO}_4])</th>
<th>0.1M</th>
<th>0.2M</th>
<th>0.3M</th>
<th>0.4M</th>
<th>0.5M</th>
<th>0.6M</th>
<th>0.7M</th>
<th>0.8M</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k \times 10^3 \text{sec}^{-1} )</td>
<td>2.06</td>
<td>2.26</td>
<td>2.43</td>
<td>2.60</td>
<td>2.75</td>
<td>2.91</td>
<td>3.06</td>
<td>3.24</td>
</tr>
</tbody>
</table>

#### Table 3: Effect of variation of [H\(_2\)SO\(_4\)] on reaction rate

[\([\text{TriPACC]} = 0.001 \text{ M}, (\text{MCC}) = 0.01 \text{ M}, \text{Temp.} = 303 \text{ k}, \text{AA} = 20\% (v/v)\) ]

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\(_2\)SO\(_4\). 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>
<thead>
<tr>
<th>([\text{TP}] = 0.001 \text{ M}, (\text{MCC}) = 0.01 \text{ M}, [\text{H}_2\text{SO}_4] = 0.1 \text{ N}, \text{Temp.} = 303 \text{ k}, \text{AA} = 20% (v/v))</th>
<th>([\text{Salts} 0.1\text{M}])</th>
<th>KCl</th>
<th>KBr</th>
<th>KI</th>
<th>CaCl(_2)</th>
<th>Ca(NO(_3))(_2)</th>
<th>Al(NO(_3))(_3)</th>
<th>K(_2)SO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k \times 10^3 \text{sec}^{-1} )</td>
<td>2.07</td>
<td>2.38</td>
<td>2.38</td>
<td>2.47</td>
<td>2.76</td>
<td>2.98</td>
<td>2.34</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Acetic acid</th>
<th>10 %</th>
<th>20 %</th>
<th>30 %</th>
<th>40 %</th>
<th>50 %</th>
<th>60 %</th>
<th>70 %</th>
<th>80 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k \times 10^3) (\text{sec}^{-1})</td>
<td>1.95</td>
<td>2.06</td>
<td>2.21</td>
<td>2.34</td>
<td>2.46</td>
<td>2.58</td>
<td>2.72</td>
<td>2.86</td>
</tr>
</tbody>
</table>

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>
<thead>
<tr>
<th>Temperatures (K)</th>
<th>293</th>
<th>298</th>
<th>303</th>
<th>308</th>
<th>313</th>
<th>318</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k \times 10^3) (\text{sec}^{-1})</td>
<td>1.27</td>
<td>1.69</td>
<td>2.06</td>
<td>2.44</td>
<td>2.88</td>
<td>3.28</td>
</tr>
</tbody>
</table>

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 \(\Delta G\) 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

\[
-\frac{d[T_{\alpha}\text{PACC}]}{dt} = k_3C_1
\]

\[
= k_3k_2[OxH^+][S] \frac{1}{1 + K_2[S]} = k_3K_1K_2[Ox][H^+][S] \frac{1}{1 + K_2[S]}
\]

CONCLUSION:-
The rate constants of the slow step involved in the mechanism were evaluated. Activation parameters were also computed. The negative value of \(\Delta S^0\) provides support to the formation of rigid transition state. The overall mechanism described here is consistent with product and kinetic studies.

Acknowledgement:-
The author is very much thankful to the Dr. Shamama Parveen, President, RECWS and Dr. Shaikh Kabeer Ahmed, Principal, Sir Sayyed College, Aurangabad, for providing laboratory facilities.

REFERENCES:-


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, 1HNMR and Mass spectroscopy.

Key Words: 2-chloroquinoline-3-carbaldehyde, aniline, triethylphosphite and DMAP.

INTRODUCTION & LITERATURE REVIEW:

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-inflammatory,(23,24) anti-hypertensive,(25) and antioxidant activities.(26) In addition, the use of quinolines as tyrosine kinase PDGF-R TK inhibitor,(27) inositol 5'-phosphatase (SH2),(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 phosphorus nucleophiles to the imines. Lewis acids such as SnCl₄, SnCl₂, ZrCl₄, ZnCl₂ and MgBr₂ have been used as catalysts for such reactions.(31-33) Recently, Lewis and Bronsted acids such as LiClO₄,(34) InCl₃,(35) lanthanide triflates,(36) TaCl₅-SiO₂,(37) montmorillonite clay-MW,(38) Al₂O₃-MW,(39) CF₃COOH(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.

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 CDCl₃ 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 Quattro 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 °C for 8.0 h (dry wt. 1.90 g, yield 91%).

RESULT & 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 triethylphosphate 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.

ANALYSIS:

2a) Diethyl (3-fluorophenylamino)(2-chloroquinolin-3-yl)methylphosphonate:
IR (KBr): 3311 cm⁻¹ (-NH); 1230 cm⁻¹ (P=O); 1234 cm⁻¹ (P - O - C)
1H NMR (CDC13, δ ppm): 1.05 (t, 3H, O-CH₂); 2.48 (s, 3H, Quinolin-CH₃); 3.68 (m, 1H, O-CH₂); 4.22 (m, 2H, O-CH₂); 5.4 (d, 1H, -NH-CH-P=O); 6.3 (m, 1H, -NH-CH-P=O); 7.0 (dd, 1H, Ph-H,C); 7.6 (s, 1H, Quinolin-H,C); 7.69 (t, 1H, Quinolin-H,C); 7.75 (d,1H, Quinolin-H,C); 7.99 (d, 1H, Quinolin-H,C); 8.34 (d, 1H, Quinolin-H,C).
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); 1232 cm⁻¹ (P = O); 1032 cm⁻¹ (P-O-C)
1H NMR (CDC13, δ ppm): 1.05 (t, 3H, O-CH₂); 2.48 (s, 3H, Quinolin-CH₃); 3.88 (m, 1H, O-CH₂); 4.22 (m, 2H, O-CH₂); 5.16 (s, 1H, -CH-NH-Ph); 5.35(d, 1H, -NH-CH-P=O); 6.28–6.42 (m, 3H, Ph-H,C, C=O); 7.02 (dd, 1H, Ph-H,C); 7.5 (d, 1H, Ph-H,C); 7.69 (t, 1H, Quinolin-H,C); 7.75 (d,1H, Quinolin-H,C); 7.99 (d, 1H, Quinolin-H,C); 8.3 (d, 1H, Quinolin-H,C).
ES-MS: m/z 437.1 (m+1) and 439.2 (m+3).

Scheme-1: DMAP Facilitated Synthesis of α-Aminophosphonates

Table-1: DMAP Facilitated Synthesis of α-Aminophosphonates

<table>
<thead>
<tr>
<th>Entry</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>R₄</th>
<th>R₅</th>
<th>Reaction Time min</th>
<th>Yield %</th>
<th>M.P. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>F</td>
<td>40</td>
<td>91</td>
<td>146–148</td>
</tr>
<tr>
<td>2b</td>
<td>CH₅</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>F</td>
<td>45</td>
<td>92</td>
<td>136–138</td>
</tr>
<tr>
<td>2c</td>
<td>H</td>
<td>CH₃</td>
<td>H</td>
<td>H</td>
<td>F</td>
<td>40</td>
<td>94</td>
<td>163–165</td>
</tr>
<tr>
<td>2d</td>
<td>H</td>
<td>H</td>
<td>CH₃</td>
<td>H</td>
<td>F</td>
<td>40</td>
<td>92</td>
<td>113–115</td>
</tr>
<tr>
<td>2e</td>
<td>OCH₃</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>F</td>
<td>45</td>
<td>91</td>
<td>153–155</td>
</tr>
</tbody>
</table>
CONCLUSION:

In conclusion, a new methodology was developed for the synthesis of new α-aminophosphonate derivatives from 2-chloroquinoline-3-carbaldehyde 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.

Acknowledgement:
The authors are thankful to the IICT Hyderabad for providing laboratorial facilities.

REFERENCES:

Stability constant of binary and ternary complexes of some medicinal ligand with metal ion in aqua-organic media

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Email: drayeshanuzhat101@gmail.com
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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°C 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.

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].

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.

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

H2N – CH2 – 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 H2 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.
Analysis, Discussion:

The present study has great importance in biological processes [8]. As amino acid glycine is organic compound in which – NH₂ and – COOH group are present. Ranitidine has NO₂, – NH group, which play key role in stability of complexes.

The results of Protonation constants of ligand are given in table 1.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Aqueous</th>
<th>50% ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Log K₁H</td>
<td>Log K₂H</td>
</tr>
<tr>
<td>Glycine</td>
<td>5.31</td>
<td>7.26</td>
</tr>
<tr>
<td>Ranitidine</td>
<td>9.96</td>
<td>4.97</td>
</tr>
</tbody>
</table>

Table 2: Metal ligand stability constants

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Aqueous ligands</th>
<th>50% ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Glycine</td>
<td>Ranitidine</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>4.32</td>
<td>5.030</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>3.46</td>
<td>6.58</td>
</tr>
</tbody>
</table>

The metal-ligand stability constants of ligands with metal ions were obtained at 1:5:5 ratio at (25 ± 0.5°C) and ionic strength maintained at 1.0 M NaClO₄ 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>
<thead>
<tr>
<th>Metal ion</th>
<th>Mixed ligand system</th>
<th>log K₉Xₐ</th>
<th>Δ log k</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Aqueous</td>
<td>50%</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>Glycine + Ranitidine</td>
<td>5.30</td>
<td>2.61</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>Glycine + Ranitidine</td>
<td>6.00</td>
<td>0.56</td>
</tr>
</tbody>
</table>

The present work shows the stability constant for mixed-ligand complexes is positive range, and confirmed the complexion 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].

Recommendations: The work is original and has not been submitted to any other journal at same time for publication.

Conclusion: The stability constant of Glycine and Ranitidine shows positive log k value, that confirms the complexion between metal and ligand.

References:
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 substances 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].
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 waste, utilize renewable resources. [6-11].

5. GLOBAL RECOGNITION OF GREEN CHEMISTRY:

5.1 AUSTRALIA: The Royal Australian Chemical Institute (RACI) presents Australia’s Green Chemistry Challenge Awards;

5.2 CANADA: The Canadian Green Chemistry Medal is an annual award given to any individual or group for promotion and development of green chemistry;

5.3 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;

5.4 JAPAN: In Japan, The Green & Sustainable Chemistry Network (GSCN), formed in 1999, is an organization consisting of representatives from chemical manufacturers and researcher;

5.5 UK: In the United Kingdom, the Crystal Faraday Partnership, a non-profit group founded in 2001, awards businesses annually for incorporation of green chemistry;

5.6 USA: United States Environmental Protection Agency (EPA);

5.7 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 [5]. The principles comprise instructions for professional chemists to implement new chemical compound, and new synthesis and technological processes.

6.1. Prevention
It is better to prevent waste than to treat or clean up waste after it has been created.

6.2. Atom Economy
Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

6.3. 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.

6.4. Designing Safer Chemicals
Chemical products should be designed to effect their desired function while minimizing toxicity.

6.5. 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.

6.6. 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.

6.7. Use of Renewable Feedstocks
A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

6.8. 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.

6.9. Catalysis
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

6.10. 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.

6.11. 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.
6.12. 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. 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 feedstocks and starting materials, bio-catalysis, green solvent, biosorption, designing safer chemicals, energy and waste management.

9.1 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.

\[
\% \text{ Atom economy} = 100 \times \left(\frac{\text{FW of product}}{\text{FW of reactants}}\right)
\]

9.2 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:

\[
\text{COCl₂} + 2\text{CH₃OH} \rightarrow \text{CH₃OCOOCH₃ (DMC)} + 2\text{HCl}
\]

Alternative route for the production of DMC:

This involves the use of copper chloride (CuCl₂), methanol (CH₃OH), oxygen (O₂) and carbon monoxide.

\[
2\text{CuCl₂} + 2\text{CH₃OH} + 1/2\text{O₂} \rightarrow 2\text{Cu(OC₃H₃)Cl} + \text{H₂O}
\]

\[
2\text{Cu(OC₃H₃)Cl} + \text{CO} \rightarrow 2\text{CuCl} + \text{CH₃OCOOCH₃}
\]

9.4 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.

9.5 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 dioxide by H₂ and Fe³+. This allows the soluble products to dissolve.

\[
\text{FeAsS(s)} \rightarrow \text{Fe}^{2+}(aq) + \text{As}^{3+} (aq) + 5\text{e}^- \text{(aq)}
\]

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 Fe²⁺ to Fe³⁺ (whilst reducing O₂).

\[
\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-
\]

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

9.6 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 (T_c = 31.3°C, P_c = 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].

9.7 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.

9.8 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:

10.1. 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].

10.2. 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’s [17-18].

10.3. 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 H₂O₂ as a bleaching agent in the presence of some activators such as TAML[19] which catalysis the fast conversion of H₂O₂ 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].
10.4. Putting out fires the green way:
The conventionally used chemical firefighting foams used worldwide discharge toxic substances into the 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].

10.5. Green dry cleaning of clothes:
Perchloroethylene (perc) is the solvent most commonly used in dry cleaning clothes. Perc (Cl₂C = CCl₂) 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 McClain 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].

10.6. 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.

10.7. 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].

10.8. 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.

10.9. New Lighting technologies:
Organic light emitting diodes (OLEDs) an example of new lighting technologies produce more light with lower energy consumption.

10.10. 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].

10.11. Use of Nonpetroleum fuels
10.11.1 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].

10.11.2 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.

REFERENCES:
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\% & 0.3 M\% 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 be lower 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.

Keywords: crystal growth, extinction 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 \cite{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\textsuperscript{3+}, urea \cite{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 0.3 mole\% was added into the super saturated solution of ZTS with constant stirring for 4 hours. The 0.2 mole\% and 0.3 mole\% LM-ZTS solution was filtered using whatmans filter paper in a beaker and kept for slow evaporation at ambient temperature. The grown crystal of 0.2 mole\% and 0.3 mole\% LM-ZTS were obtained within a period of 20 days as shown in Fig.1.

Fig.1. Photograph of 0.2 mole\% and 0.3 mole\% LM-ZTS Crystals.
3. RESULT AND DISCUSSION:

3.1 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].

3.2 Band gap:
The optical band gap of 0.2M% and 0.3M% has been evaluated from Tauc’s plot using relation (αhv)²=A(h-ν-Eg), 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].

3.3 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(e) 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].
4. CONCLUSION:

In present investigation 0.2M% LM-ZTS and 0.3 M% LM-ZTS single crystals were 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 of L-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 than 0.3 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 H₂SO₄ activation method is self-generated atmosphere using an oven (temperature at 600°C). 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, P¹, 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 R² shows that activated carbon was found to be good adsorbent.

Key Words: Adsorption, Activated charcoal, Isotherm, Kinetic, Used black tea, Methyl orange, Methyl red

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 organism¹.

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 countries⁴-⁶. 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 lactucaand Sargassum, Azadirachta indica leaf, hazelnut shell, Coirpith, orange peel, walnut shells, etc., as adsorbents for the removal of dyes from wastewaters 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 pH, 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.

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)](structure_methyl_orange.png)  ![Fig. 2: Structure of Methyl red (MR)](structure_methyl_red.png)

### Table 1: Some characteristic of the azo dyes Methyl orange and Methyl Red

<table>
<thead>
<tr>
<th>Dye</th>
<th>Methyl orange</th>
<th>Methyl red</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical class</td>
<td>Anionic dye</td>
<td>Anionic dye</td>
</tr>
<tr>
<td>CAS number</td>
<td>547-58-0</td>
<td>493-52-7</td>
</tr>
<tr>
<td>Color Index number</td>
<td>13025</td>
<td>10303</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C_{14}H_{14}N_{3}NaO_{3}S</td>
<td>C_{15}H_{16}N_{3}O_{2}</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>327.33g/mol</td>
<td>269.3g/mol</td>
</tr>
</tbody>
</table>

METHOD:

3.1 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_{2}SO_{4} solution for two days. Then it was filtered till pH 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](ftir.png)
3.3 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.

3.4 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 (Equiptronic model EQ650A colorimeter).

3.5 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).

\[
q_e = \frac{(C_o - C_e) V}{W} \tag{1}
\]

\[
\%R = \frac{(C_o - C_e)}{C_o} \times 100 \tag{2}
\]

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.

<table>
<thead>
<tr>
<th>IR Frequency (cm⁻¹)</th>
<th>Bond</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3727.73</td>
<td>O-H stretching vibrations</td>
<td>Alcohol, phenol</td>
</tr>
<tr>
<td>3359.39</td>
<td>N-H stretching vibrations</td>
<td>Amine</td>
</tr>
<tr>
<td>1574.59</td>
<td>N-O stretching</td>
<td>Nitro group</td>
</tr>
<tr>
<td>1309.43</td>
<td>C-H bending</td>
<td>Alkanes</td>
</tr>
<tr>
<td>679.785</td>
<td>Double bond C-H bending</td>
<td>Aromatic or Alkene</td>
</tr>
</tbody>
</table>

Table No. 2 Interpretation of spectra for activated charcoal prepared from UBT

Fig.4 SEM image for activated charcoal

Fig.5 SEM image for Activated charcoal
4 RESULTS AND DISCUSSION:

4.1 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.

![Effect of time on Methyl orange ssand Methyl red removal efficiency using UBT as an adsorbent](image)

Fig 6: Effect of time on Methyl orange and Methyl red removal efficiency using UBT as an adsorbent.

4.2 Effect of Initial pH of Methyl red and methyl orange dye on AC adsorption:

The effect of pH values on the adsorption capacity of methyl red (MR) and methyl orange (MO) on activated charcoal was shown in fig. 7. When the pH value of Methyl red and methyl orange solution increased from 2 to 10, the adsorption capacity of Methyl red onto activated charcoal and the removal rate is 66.0%. and for methyl orange is at pH = 9, % removal of methyl orange is 60%.

The effect of pH values on the adsorption capacity of MR and MO on activated charcoal were shown in fig. 7.

![Effect of pH for MO (orange line) and MR (Blue line) dye removal efficiency using UBT as an adsorbent](image)

Fig 7: Effect of pH for MO (orange line) and MR (Blue line) dye removal efficiency using UBT as an adsorbent.

4.3 Effect of adsorbent dose for methyl red and methyl orange dye adsorption:

To optimise 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.
4.4 Adsorption equilibrium study:
Equilibrium data, commonly known as adsorption isotherms, are basic requirements 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 equations and 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 Li 2002; Langmuir 1918):

\[ q_e = \frac{q_m K_L C_e}{K_L + C_e} \]  

The equation is often written as

\[ \frac{c_e}{q_e} = \frac{1}{q_m} K_L + \frac{c_e}{q_m} \]  

Where, \( C_e \) (mg L\(^{-1}\)) is the equilibrium concentration 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
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.

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]  

(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 \(\log q_e\) vs. \(\log C_e\). 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\(^2\).
Temkin isotherm:

\[ q_e = B \log K_t + B \log C_e \] 

(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.12 Freundlich isotherm for Methyl orange dye adsorption
On prepared activated charcoal of UBT

Fig.13 Temkin isotherm for methyl red dye adsorption
on prepared activated charcoal of UBT
4.5 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:

\[
\ln(q_e - q_t) = ln q_e - K_1 t
\]

(7)

Where \(q_e\) is methyl orange or methyl red amount of adsorbed onto the unit weight of adsorbent at equilibrium (mg/g), \(q_t\) is methyl orange or methyl red amount of adsorbed onto the unit weight of adsorbent at time \(t\) (mg/g), and \(K_1\) is the rate constant (L/min) 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

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t
\]

(8)

Where \(K_2\) (g/mg) is the rate constant of adsorption. By plotting a curve of \(t/q_t\) against \(t\) and \(K_2\) can be determined. The correlation coefficient values at 100mg/lit concentration are lower than 0.90.
**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

<table>
<thead>
<tr>
<th>Dye</th>
<th>K&lt;sub&gt;1&lt;/sub&gt;</th>
<th>q&lt;sub&gt;e&lt;/sub&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl orange</td>
<td>0.0165816</td>
<td>22.15</td>
<td>0.9031</td>
</tr>
<tr>
<td>Methyl red</td>
<td>0.0151998</td>
<td>48.74</td>
<td>0.962</td>
</tr>
</tbody>
</table>

**Intraparticle diffusion:**

The mechanism of sorption is either film diffusion controlled, or particle diffusion controlled.

\[ q_t = k_{id} t^{1/2} + C \]  \hspace{1cm} (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 \( \log(q_e - q_t) \) 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** Intraparticle diffusion for methyl orange 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 described as monolayer Langmuir-type isotherm. The Langmuir isotherm for methyl red better fits (R²=0.995) than for methyl orange. While Temkin isotherm for methyl orange better fits (R²=0.984) than methyl red (R²=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.

REFERENCES:


The Effect of Seed Size and Depth of Planting on Banana Plants Production

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2University of Nairobi, Kenya
1Sir Sayyed College, Aurangabad, India(M.S.)
E-mail: jack_kihiko@yahoo.com.

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 S1 (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.
2.0 MATERIALS AND METHODS

2.1 Site description
The experiment was conducted in one of the farms 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.

2.2 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 seedlings T1 (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.
### Table 1: The summary of hole and seedlings physical parameters properties

<table>
<thead>
<tr>
<th>Hole measurement dimensions parameters (cm)</th>
<th>seedlings measurement (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 (15 cm length x 20 cm depth)</td>
<td>T1 (15 cm height)</td>
</tr>
<tr>
<td>S2 (40 cm length x 50 cm depth)</td>
<td>T2 (25 cm height)</td>
</tr>
<tr>
<td>S3 (60 cm length x 50 cm depth)</td>
<td>T3 (60 cm height)</td>
</tr>
<tr>
<td>S4 (15 cm length x 20 cm depth)</td>
<td>T4 (60 cm height)</td>
</tr>
<tr>
<td>S5 (40 cm length x 50 cm depth)</td>
<td>T5 (60 cm height)</td>
</tr>
<tr>
<td>S6 (60 cm length x 50 cm depth)</td>
<td>T6 (15 cm height)</td>
</tr>
<tr>
<td>S7 (15 cm length x 20 cm depth)</td>
<td>T1 (25 cm height)</td>
</tr>
<tr>
<td>S8 (40 cm length x 50 cm depth)</td>
<td>T2 (15 cm height)</td>
</tr>
<tr>
<td>S9 (60 cm length x 50 cm depth)</td>
<td>T3 (25 cm height)</td>
</tr>
</tbody>
</table>

#### 2.3 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.

#### 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.

#### 4. 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.
5. 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:

The authors acknowledge Miss Ruth Gathoni kinyua from Farming systems Kenya for helping us with vital information regarding this research work. The original results of this paper was collected by Ann Ngugi as part of her PhD research activities, therefore, we show our gratitude to her and wish her a superior success in finishing her program at University of Nairobi, UON.

References:

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 composites. 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.

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 < σ < 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.

MATERIALS:
Analytical-reagent-grade Pyrrole, nickel chloride 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°C. Each process was done with double distilled conductivity water. (qualigen fine–chem. India) were used.

METHOD:
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.
DISCUSSION & RESULT:

1) 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 emeraldine base. Fig-1.

2) 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 benzonoids 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.

3) 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.
4) 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.

5) 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.
6) 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.

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 S cm⁻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.

REFERENCES:

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.

Key Words: permittivity, excess permittivity, relaxation time, excess inverse relaxation time, time domain reflectometry

INTRODUCTION:

Lorazepam (C15H10Cl2N2O2), 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 [•]. Propanol (C3H8O) is a clear colourless liquid with a sharp musty odor like rubbing alcohol. Used in making pharmaceuticals, perfumes, lacquer formulations, dye solutions, antifreezes and other chemicals and products [•]. 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.

EXPERIMENTAL: The complex permittivity spectra are studied by using Time Domain Reflectometry. (T.D.R.). The Tekronix 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. [1]

Table 1. Physical constant of pure liquids

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of Compound</th>
<th>Molecular Formula</th>
<th>Permittivity Literature value (ε_r)</th>
<th>M.W. g/Mole</th>
<th>Density g/cm³</th>
<th>Dipole Moment µ D</th>
<th>R. I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lorazepam</td>
<td>C15H10Cl2N2O2</td>
<td>N.A.</td>
<td>321.2</td>
<td>1.52</td>
<td>N.A.</td>
<td>1.60</td>
</tr>
<tr>
<td>2</td>
<td>Propanol</td>
<td>C3H8O</td>
<td>20.1</td>
<td>60.09</td>
<td>0.803</td>
<td>1.68</td>
<td>1.3862</td>
</tr>
</tbody>
</table>
RESULT AND DISCUSSION:

<table>
<thead>
<tr>
<th>Mole Fraction of Lorazepam</th>
<th>283K</th>
<th>288K</th>
<th>293K</th>
<th>298K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon_s$</td>
<td>$\tau$ (ps)</td>
<td>$\varepsilon_s$</td>
<td>$\tau$ (ps)</td>
</tr>
<tr>
<td>0</td>
<td>316.00</td>
<td>315.90</td>
<td>316.00</td>
<td>315.90</td>
</tr>
<tr>
<td>0.0813</td>
<td>131.00</td>
<td>144.80</td>
<td>104.00</td>
<td>122.30</td>
</tr>
<tr>
<td>0.1910</td>
<td>99.40</td>
<td>143.10</td>
<td>93.50</td>
<td>113.10</td>
</tr>
<tr>
<td>0.3469</td>
<td>145.00</td>
<td>130.90</td>
<td>122.00</td>
<td>104.20</td>
</tr>
<tr>
<td>0.5862</td>
<td>143.00</td>
<td>99.41</td>
<td>113.00</td>
<td>91.54</td>
</tr>
<tr>
<td>1</td>
<td>81.80</td>
<td>81.78</td>
<td>61.50</td>
<td>61.66</td>
</tr>
</tbody>
</table>

It can be seen that there is nonlinear relationship between the values of static dielectric constant ($\varepsilon_s$) 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 [2]. The static permittivity and relaxation time decreases with increase in mole fraction of Lorazepam with Propanol indicate molecule rotate easily [3].

EXCESS PARAMETERS:

From figure 5 it can be seen that (ε) 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 [4-6]. 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/τ) is quite different as can be seen from figure 6. The values of (1/τ) 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 [7].

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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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 Arduino 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 inexpensive when buying and easy to power. Physics labs in many colleges and high schools usually use Helium-neon lasers that emit around 1mW output beam. These lasers are very expensive for any ordinary labs. They are expensive to purchase. A new Green He-Ne Lasers - 543 nm goes 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.

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.

3. 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.

4. METHODOLOGY

4.1 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.

4.2 Test code for KY-008 Laser transmitter module
Testing the Code for the Arduino KY-008 Laser Transmitter module

```c
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

```c
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
}
```

Fig:2. Lasers KY-008 module
4.3 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:

![Arduino Board](Fig:3. Arduino Board)

4.4 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

4.5 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

![Typical LDR](Fig:4. Typical LDR)

Typical LDR (Light Dependent Resistor) resistance vs light intensity graph

![Typical LDR 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

```c
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-Ne laser with low cost, 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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ABSTRACT:

Chemical route for the synthesis of polymer composites with oxide materials enhances the composite technology. Polyaniline (PANI) and Polyaniline-Zinc Ferrite (PANI - ZnFe\(_2\)O\(_4\)) composite material was prepared by in situ polymerization of aniline with Zinc Ferrite (PANI - ZnFe\(_2\)O\(_4\)) 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\(^8\) Hz at room temperature. The dimensions of Zinc Ferrite (ZnFe\(_2\)O\(_4\)) particles in the matrix have a greater influence on the observed dielectric values.

Keywords: Synthesis, Composites, Dielectric Constant, Polyaniline, Zinc Ferrite (ZnFe\(_2\)O\(_4\)).

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\(_2\)O\(_4\)) is a material 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\(_2\)O\(_4\) 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\(_2\)O\(_4\)) is one of the examples of oxide material, which is known for progressive properties and applications [15]. Composite of Zinc Ferrite (ZnFe\(_2\)O\(_4\)) 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\(_2\)O\(_4\)) dispersed PANI composite materials through in situ polymerization method. Dielectric study of the as prepared PANI composite material is also well studied for its dielectric behavior.

2. EXPERIMENTAL:

Materials and Methods

Ammonium persulphate (NH\(_4\))\(_2\)S\(_2\)O\(_8\), Hydrochloric acid (HCl) and Zinc Ferrite (ZnFe\(_2\)O\(_4\)) 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 in situ polymerization method with dispersion of Zinc Ferrite in polyaniline.

Synthesis of Polyaniline / Zinc Ferrite (ZnFe\(_2\)O\(_4\)) Composites

Aniline was dissolved in 1m HCl to form polyaniline (PANI). Zinc Ferrite (ZnFe\(_2\)O\(_4\)) was added to PANI solution with vigorous stirring to keep the Zinc Ferrite (ZnFe\(_2\)O\(_4\)) suspended in the solution. To this reaction mixture, 0.1M of ammonium persulphate [(NH\(_4\))\(_2\)S\(_2\)O\(_7\)], which acts as an oxidant, was added slowly with continuous stirring for 4-6 hours at 0-5\(^\circ\)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$_2$O$_4$) 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 $10^2$-$10^7$Hz using the Hioki LCR Q meter.

3. RESULTS AND DISCUSSION:

**Polyaniline – Zinc Ferrite (ZnFe$_2$O$_4$) composites**

Figure 1 shows the variation of $\varepsilon'$ as a function of frequency for polyaniline – Zinc Ferrite (ZnFe$_2$O$_4$) 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$_2$O$_4$) composites](image)

4. CONCLUSION:

Polyaniline composites with different weight percentages of Zinc Ferrite (ZnFe$_2$O$_4$) 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$_2$O$_4$) in polyaniline.

REFERENCES:

BIODIVERSITY STUDIES ON ORDER OF AGARICALES FROM AURANGABAD DISTRICT OF MAHARASHTRA, INDIA

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ABSTRACT: Studies on biodiversity of order Agaricales species are need to protecting more importance because many macrofungi are heading for extinct or facing the threat of extinction. Macrofungal species are important for functioning and stability of 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 survey a total of 40 macrofungal species and 22 genera of 13 families were collected. Most diversity and highest species comes under the family Agaricaeae rather than other families. Termitomyces, Agaricus and Volvariella is 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 having fleshy 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 survive in 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, fungicocolous, lignicolous, humicolous, parasitic and saprotrophs. Numerous species of Agaricales also include termite symbionts (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 camera fixed to OLYMPUS CX 21 bright field light microscope.
Table No. 1: Occurrence of macrofungi in different locations of Aurangabad

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of the Macrofungal Taxa</th>
<th>Site I</th>
<th>Site II</th>
<th>Site III</th>
<th>Site IV</th>
<th>Site V</th>
<th>Site VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Agaricus arvensis Schaeff.</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Agaricus grandiomyces Zhou &amp; Zhao</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Agaricus martiniicensis Pegler</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Agaricus placomyces Peck.</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>5</td>
<td>Amanita cokeri (E.-J.Gilbert &amp; Kuhner)</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Bovista sp.</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>Chlorophyllum molybdites (G. Mey.)</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Conocybe apala (Fr.: Fr.) Arnold</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Conocybe tenera (Schaeff: Fries) Fayod.</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>Coprinellus domesticus (Bolton) Vilgalys, Hopple &amp; Johnson</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>11</td>
<td>Coprinellus flocculosus (DC) Vilgalys, Hopple &amp; Johnson</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>Coprinellus micaceus (Bull.) Vilgalys, Hopple &amp; Johnson</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>Coprinopsis cinera (Bull.Fr.) Redhead, Vilgalys and Moncalvo</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>14</td>
<td>Coprinopsis picacea (Bull.Fr.) Redhead, Vilgalys &amp; Moncalvo</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>Coprinus comatus (O.F. Mull.) Pers.</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>Gymnopus confuens (Pers.)</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>17</td>
<td>Inocybe alba</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>18</td>
<td>Inocybe purpureoflavida Vrinda &amp; Pradeep</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>19</td>
<td>Leucoagaricus leucothites (Vittad.) Wasser</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>Leuagaricus sp.</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>21</td>
<td>Leucocoprinus brebissinii (Godey) Locq.</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>22</td>
<td>Leucocoprinus cretaceous (Bull.) Locq.</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>23</td>
<td>Leucocoprinus fragilissimus (Berk. &amp; Curtis) Pat.</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>Macrolepiota prosera (Scop.Fr.) Singer</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>Neonothopanus hygrophanus (Mont.) De Kesel &amp; Degreef</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>26</td>
<td>Panaeolus papilloneus</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>27</td>
<td>Parasola plicatilis (Curtis) Fr. Redhead, Vilgalys &amp; Hopple</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>28</td>
<td>Pleurotus ostreatus (Jacq.) P. Kumm.</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>29</td>
<td>Psilocybe cubensis (Earle) Singer.</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>Schizophyllum commune Fr.</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>31</td>
<td>Termitomyces clypeatus Heim.</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>32</td>
<td>Termitomyces globules R. Heim &amp; Gooss.-Font.</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>33</td>
<td>Termitomyces heimii Natarajan</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>34</td>
<td>Termitomyces reticulatus Van der Westh. &amp; Eicker</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>35</td>
<td>Termitomyces umkowaan (Cooke &amp; Masssee) D.A. Reid</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>36</td>
<td>Volvariella bombycina (Schaeff. Fr.) Singer</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>37</td>
<td>Volvariella bombycina var. flaviceps (Murrill) Shaffer.</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>38</td>
<td>Volvariella taylorii (B. &amp; Br.) Singer.</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>39</td>
<td>Volvariella volvaceae (Bull.) Singer.</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>40</td>
<td>Xanthagaricus sp.</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>
3. RESULT AND DISCUSSION:

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, Pluteaceae, 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), Leucocarpinus and Coprinellus (3), Leucoagaricus, Conocybe, Inocybe and Coprinopsis (2), remaining Amanita, Bovista, Chlorophyllum, Coprinus, Gymnopus, Macrolepiota, Neonothopanus, Panaeolus, Parasola, Psilocybe, Schizophyllum, Xanthagaricus each genera having single species. Based on the substrate preferences highest 16 soil and humus loving mushrooms (Humicolous) recorded followed by 12 wood inhabiting mushrooms (Lignicolous), 5 grown on termites mound (Termitophilic), 3 dung 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 from Himayatbagh 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

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Habitat</th>
<th>No. of Species</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>Lignicolous</td>
<td>12</td>
<td>30%</td>
</tr>
<tr>
<td>2)</td>
<td>Humicolous</td>
<td>16</td>
<td>40%</td>
</tr>
<tr>
<td>3)</td>
<td>Termitophilous</td>
<td>5</td>
<td>13%</td>
</tr>
<tr>
<td>4)</td>
<td>Coprophilous</td>
<td>3</td>
<td>8%</td>
</tr>
<tr>
<td>5)</td>
<td>Mycorrizal</td>
<td>4</td>
<td>10%</td>
</tr>
</tbody>
</table>

4. CONCLUSION:

The present investigation deals with the biodiversity as well as distributional study of macrofungal flora from Aurangabad district (M.S.). In this investigation total 40 species were recorded which belongs from family Agaricaceae (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), Pluteacae (04 species), Psathyrellaceae (5 species), Schizophyllaceae (1 species) and Strophariaceae (1 species). In this research study fungal species of Agaricaceae family were most dominant as compare to other. Out of six selected sites there was rich fungal basidiomata recorded from Himayatbagh 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.

5. REFERENCES

Time Evolution of Lead from Lead Acetate in electrodeposition

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\textsuperscript{2}PES College of Engineering, Aurangabad – 431001
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\textsuperscript{2}\textsuperscript{**}Shivaji College Kannad, Dist.: Aurangabad India-431103

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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 observed show 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 electrolysis 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) \textsuperscript{[1, 2, 3]} have received the major attention. The concept of fractal and non-fractal aggregation is applicable in physics especially in turbulence \textsuperscript{[4,5]}, polymerization,\textsuperscript{[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 \textsuperscript{[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 \textsuperscript{[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 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. \textsuperscript{[13,14]}

Growth of dendritic patterns using circular cell geometry is basically electrolysis that is governed by Faraday’s laws of electrolysis. The electro deposition under study is governed by Faraday’s 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.\textsuperscript{[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

\[
m = \left(\frac{Q}{F}\right) \cdot \left(\frac{M}{z}\right) \quad \text{(1)}
\]

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)

and \(\frac{M}{z}\) 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 \(\frac{M}{z}\) (equivalent weight) the larger \(m\) will be. In the simple case of constant-current electrolysis, \(Q = It\) leading to

\[
\begin{align*}
  m &= \left(\frac{It}{F}\right) \left(\frac{M}{z}\right) \\
  n &= \left(\frac{It}{F}\right) \left(\frac{1}{z}\right)
\end{align*}
\]

\[
\text{..........(2)}
\]

where \(n\) be the amount of substance (“number of moles”) transformed: \(n = \frac{m}{M}\)

\(t\) 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 dendrite of lead acetate (0.5 Molar 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. Table 1 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 20 sec.

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Branch Length for Branch (pixel)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>76.7</td>
</tr>
<tr>
<td>40</td>
<td>210</td>
</tr>
<tr>
<td>60</td>
<td>262</td>
</tr>
<tr>
<td>80</td>
<td>314</td>
</tr>
<tr>
<td>100</td>
<td>380</td>
</tr>
<tr>
<td>120</td>
<td>422</td>
</tr>
<tr>
<td>140</td>
<td>554</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Sec)</th>
<th>Branch length in mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>1.08</td>
</tr>
<tr>
<td>40</td>
<td>2.97</td>
</tr>
<tr>
<td>60</td>
<td>3.7</td>
</tr>
<tr>
<td>80</td>
<td>4.43</td>
</tr>
<tr>
<td>100</td>
<td>5.36</td>
</tr>
<tr>
<td>120</td>
<td>5.96</td>
</tr>
<tr>
<td>140</td>
<td>7.81</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time Step</th>
<th>Velocity of the branch in mm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>0.054084</td>
</tr>
<tr>
<td>40</td>
<td>0.148491</td>
</tr>
<tr>
<td>60</td>
<td>0.185006</td>
</tr>
<tr>
<td>80</td>
<td>0.221616</td>
</tr>
<tr>
<td>100</td>
<td>0.268111</td>
</tr>
<tr>
<td>120</td>
<td>0.297955</td>
</tr>
<tr>
<td>140</td>
<td>0.390576</td>
</tr>
</tbody>
</table>
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 electrodeposited 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 140 sec 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.

3. 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.

REFERENCES:
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