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Organised by
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[Faculty of Science]
Gramonnati Mandal's, Arts, Commerce, Science College, Narayangaon,
Tal- Junnar Dist- Pune, Maharashtra, India

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Green Approach is a sustainable way for designing and development of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment. The purpose of the conference is to assess the current state of the art in green chemistry and discuss the role of chemical research and science policy in advancing global environmental protection and sustainable development. The present two days' National Level Conference intends to provide a common platform for scientist, academician, researchers & industrialist about recent advancement & developments in Green technique in Environment & Chemical Science. The GAECS-2017 is a sincere effort to enrich and correlate the Green research activities & their applicability in all branches of science like Chemistry, Physics, Zoology, Botany, Mathematics, Biotechnology, Environmental Science, etc. The GAECS-2017 will provide an opportunity to exchange ideas & identify the prior areas of the future research in green technique for benefit of society & industry. We have arranged various interactive sessions of distinguished scientists & resource persons to guide the participants.

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Measurements of Glass Transition Temperature of Na-Borophosphate Glassesby Thermal Analysis

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ABSTRACT

Glasses of the series of xNa2O - (100-x) B2O3 (x=25, 30, 35, 40, 45,..) and 30Na2O-(70-x) B2O3-xP2O5 (x= 15, 20, 25, 30, 35) have been prepared by standard melt-quench technique. The glass samples were characterized using X-ray diffraction (XRD), thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) techniques. The X-ray diffraction pattern shows that all the samples no sharp Bragg's peak, but only a broad diffuse hump around low angle region. The amorphous phase of the prepared glass samples was confirmed from their XRD, TGA and DTA profiles.

Keywords : Glass ; Thermal Analysis, Annealed Glass, X-Ray Diffraction, Melt Quenching.

I. INTRODUCTION

Research in glass gained much interest now-a-days due to the increasing applications in engineering and technological fields.Glasses have been most widely used to make metal-ceramic seals because they can be modified to have a very close match of thermal expansion with metal materials. Except that, the glass seals show good result along with thermal and environmental stability [1-5].The glass transition temperature(Tg)[6-11]of a sample is an important parameter that determines its stability during storage. While Tg can be measured by a variety of methods, it is a time consuming procedure, especially if the sample is to be kept at subzero temperatures, in anhydrous conditions, or if sampling a portion of the specimen for analysis is cumbersome.

The glass transition is described to be the reversible change in amorphous materials between a hard, brittle state into a rubbery molten state. Materials which are capable of going through a glass transition are named as glass. Glass transition temperature is a metastable transition. Below this temperature, the material is specified to be a glass it means is typically hard and brittle; above, it is first a super cooled liquid i.e. a rubber like viscous liquid, and finally liquid [12].Pure boron trioxide (B_2O_3) is a very good glass former, covalently bonded, with interesting physicochemical properties.The Mixed Glass Former Glasses is improved thermal, chemical and mechanical properties, these glasses are significant candidates for improved solid electrolytes in next generation batteries [13].

II. MATERIALS AND METHODS

Glass Preparation

The glass samples were prepared with thefollowing chemical compositions *xNa_2O - (100-x) B_2O_3 (x=25, 30, 35, 40, 45) and $30Na_2O$-(70-x) B_2O_3-xP_2O_5 (x= 15, 220, 25, 30, 35)*. The chemicals used $NaNO_3$, H_3BO_3, $(NH_4)_2HPO_4$, are of analar grade.The appropriate chemicals were weighed andmixed thoroughly. These chemicals were thoroughly mixed and ground for 30-40 min in a mortar pastel and then the batches of (30g) was melted in alumina crucible using muffle furnace for 4-5 hrs at temperature -1000°C. When the melt was thoroughly homogenized and attained desirable viscosity it was poured either onto metal plate or into graphite moulds. The prepared glass was the annealed at appropriate temperatures (between 300 and 400°C) for 2 hrs and stored in desiccators prior to evaluation.At the end of the annealing process the glasses were allowed to cool down naturally to room temperature. The obtained glasses were confirmed bubble-free, homogeneous and transparent, in a circular glass disc shape with dimension of 10 mm diameter and 6 mm thickness.

X-ray Diffraction

In general, the glassy nature of the obtained glass could be confirmed by crystallographic and thermal analysis. Prepared glass samples were characterized by X-ray diffraction technique to check for possible crystallinity of glasses using X-ray diffractometer (Model. RigakuMiniflex II Desktop) with Cu-Kα radiation the XRD patterns were recorded in the 2θ=(20-80^o)with scanning rate 1^0/mint.

Thermal Analysis

In thermal study, Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on a Shimadzu DTG 60 simultaneous instrument from 0.00 to 800^{o}C. The thermal analysis of the very finely polished (powder) glass samples was done using Dilatometer (Model Shimadzu DTG 60 TGA-DTA). The heating rate was kept to 40^{o}C/min for all measurements. The properties like glass transition temperature, crystallization temperature were determined by using this technique. The glass transition temperatures (T_g) were taken as the inflection point of the endothermic changeof the calorimetric signal. Crystallization onset temperatures (T_c) were specified as the beginning of the reaction where the crystallization first starts and peak temperatures represent the maximum value of the exothermic.

III. RESULTS AND DISCUSSION:

XRD Analysis

The X-ray diffraction patterns of all the Sodium borateand Sodium borophosphateglass samples show no sharp peaks, indicating the absence of crystalline nature. This is clear indication of amorphous nature of glasses.

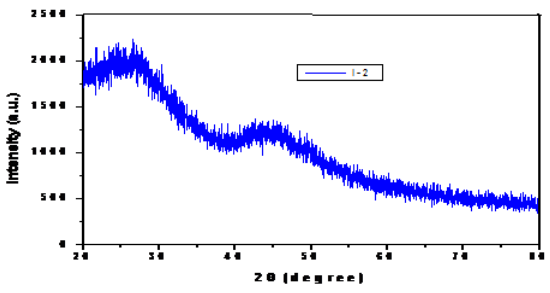

Figure 1. XRD profile for typical sample I-2 (X=20%).

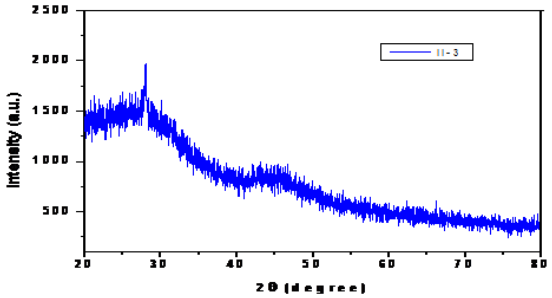

Figure 2. XRD profile for typical sample II-3 (X=25%).

TGA-DTA Analysis

The characteristic temperatures of the obtained glass were determined by TGA-DTA curves that were obtained for the as quenched glasses corresponding to the compositions x=30%, 35% of Na_2O and x=15%, 25% of $P_2O_5$are shown in figures respectively.

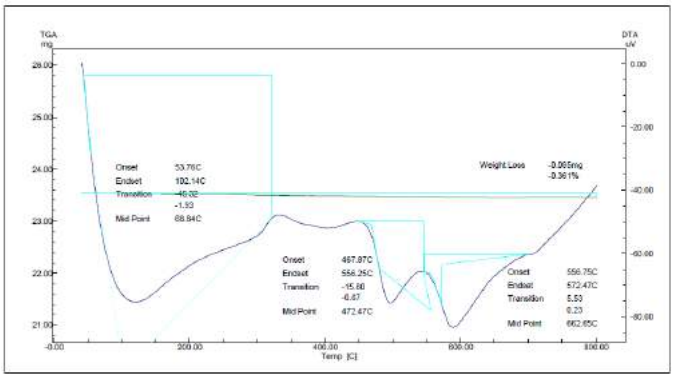

Figure 3. TGA-DTA curve and characteristic temperature determined for the compositions x=30% of Na_2O glass at heating rate of 40^{o}C/min.

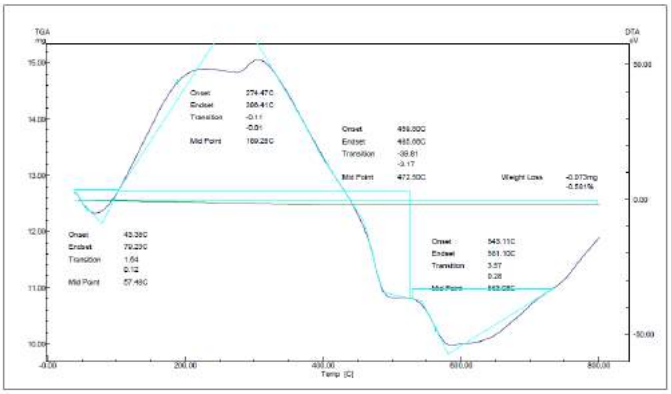

Figure 4. TGA-DTA curve and characteristic temperature determined for the Compositions x=35% of Na_2O glass at heating rate of 40^{o}C/min.

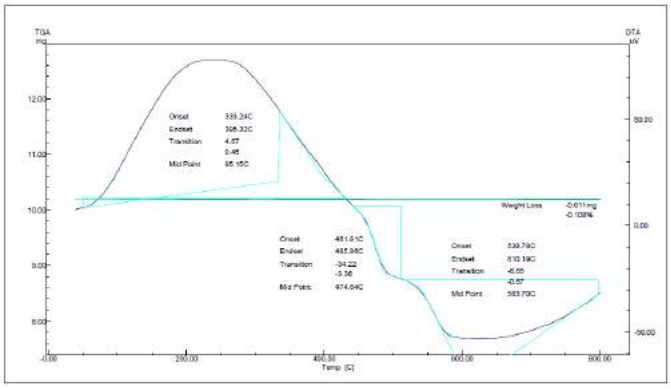

Figure 5. TGA-DTA curve and characteristic temperature determined for the Compositions x=15% of P_2O_5 glass at heating rate of 40^{o}C /min.

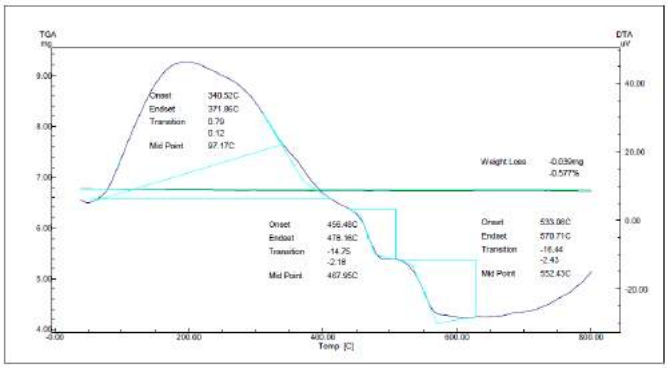

Figure 6. TGA-DTA curve and characteristic temperature determined for the Compositions x=25% of P_2O_5 glass at heating rate of 40^{o}C/min.

The glass transition temperatures (T_g) and crystallization temperature (T_c) of the Sodium borateand Sodium borophosphateglass samples are listed in table 1 and 2 respectively.

Table.1. Transition temperatures of sodium borate glass System indicated by TGA - DTA curves.

Sr. No.	Glass Code	Mole % Na_2O	T_g (^{o}C)	T_c (^{o}C)
1	I-2	30	472.47	556.75
2	I-3	35	472.50	543.11

Table 2. Transition temperatures of sodium borophosphate glass System indicated by TGA - DTA curves.

Sr. No.	Glass Code	Mole %P_2O_5	T_g (^{o}C)	T_c (^{o}C)
1	II-1	15	447.64	538.78
2	II-3	25	467.95	533.08

From table 1 it is observed that slight change with increasing the Na_2O content. It is due to the change in network structure; the material becomes soft. From table 2 it indicates that the T_g increase with increasing the P_2O_5 content. It may be due to the change in network structure (the material become soft) of the sodium borophosphate glass samples. It confirms that larger changes in glass structure occur.

IV. CONCLUSIONS

In the present investigation sodium borateand sodium borophosphateglass sampleswere prepared by conventional melt quench method.The amorphous phase of the prepared glass samples was confirmed from their XRD.Although glass is a very common material, its increasing technicality for special applications and issues linked with its worldwide scale manufacturing requires state of the art analytic tools. Apart from the glass transition temperature, which corresponds to the softening of the glass, TGA- DTA can become a key technique to study melting, crystallization and other phase transitions. Further, the increasing behavior of $T_g$indicates increasing the strength and thermal stability of the investigated glass systems with the increasing of Na_2O and P_2O_5 content in sodium borate and sodium borophosphate glasses.

V. ACKNOWLEDGEMENTS

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Y^{3+} Doped $Ni_{0.4}$ $Mg_{0.4}$ $Cd_{0.2}$ $Fe_{2-y}O_4$ Spinels Nanoferrite : Structural, Morphological, and Electrical Properties

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ABSTRACT

Structural, morphological, and electrical properties were investigated for Y3+ doped Ni0.4 Mg0.4 Cd0.2 Fe2-y O4 spinel nanoferrite (where y = 0.025 to 0.125) obtained by sol-gel techniques. Nanoscale samples were carried out at low temperature and cost effective method with analytical grade metal nitrate. Citric acid was used as a fuel. The prepared powder were sintered at 400 oC and characterized by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDAX) for structural property andscanning electron microscopy (SEM), transmission electron microscopy (TEM) for morphological studies. Ferrite formation was found to quite sensitive. The particle size was determined using Scherer's formula and it found that it decreases with increase in Y3+content. Also DC resistivity increases with increasing Y3+content and electrical conductivity increases with temperature increases. These results may be applicable for promising area such as high frequency electrical devices.

Keywords : Spinel Ferrite, Sol-Gel Autocombustion Method, Morphological Properties, Electrical Properties

I. INTRODUCTION

The spinel ferrites are interesting materials owing to their wide range of applications in modern science and technology.They have recently attracted considerable research interest on their structural, magnetic and electrical properties [1]. The physical properties such as increase in DC resistivity, low dielectric losses and magnetization characteristics are due to the substitution of tetrahedral cations in the parent crystal structure. The structural variation in the host lattice can be occurred due to proper choice and composition of trivalent cations such as Al^{3+}, Y^{3+}, $Cr^{3+}$and La^{3+}) to replace Fe^{3+} in the parent lattice of cobalt ferrite [2]. Magnetic properties of ferrites depend on their chemical composition, preparation method, sintering time and temperature [3]. The sol-gel method is used for the synthesis of Nickel substituted cobalt ferrite nanoparticles. The result proves that with increase in nickel content magnetic saturation decreases [4]. The sol-gel method is a good combination of combustion and chemical gel process. The advantage of sol-gel method is a good stoichiometric control and results in ultra-fine nanoparticles [5].Infrared spectroscopy (IR) is one of the most powerful techniques, which offers possibility of chemical identification. One of the advantages of IR over other methods for structural analysis is that, it provides useful information about the structure of a molecule rapidly and also without cumbersome evaluation methods. The technique is based upon the simple fact that a chemical substance shows marked selective adsorption in the infrared region. Various bands obtained in IR spectra are corresponding to the characteristic functional groups and bonds present in the chemical substance. The absorption bands in the IR spectra split on the basis of different cations present on tetrahedral (A) and octahedral [B] sites of spinel ferrites [6–8].Nickel ferrites are stable, relatively inexpensive and easily manufactured and have wide applications in electronics and communication industries owing to their interesting magnetic and electrical properties. The coercivity was decreased by increasing Cd content due to the decrease of magneto crystalline anisotropy constant of the samples [9]. Yttrium doped cobalt ferrite was prepared with different concentrations to identify the crystallite size with respect to the yttrium concentration, temperature and changes in the structural and electrical properties and reported that the resistance of the nanostructured yttrium doped cobalt ferrites nanopowder was analysed. The resistance was increased by the addition of yttrium to cobalt ferrites [10].

The present work investigation on the synthesis of nanosize Y^{3+} material substituted in Ni-Mg-Cd

nanocrystalline ferrites by sol-gel autocombustion techniques and characterized by XRD, EDAX, FTIR, SEM and TEM. It reports the consequent changes on their structural, optical, morphological and electrical properties.

II. MATERIAL AND METHOD

The Y^{3+} doped in Ni-Mg-Cd ferrite powders were synthesized by sol-gel auto combustion method at low temperatures for different compositions of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ (where y = 0.025, 0.050, 0.075, 0.100 and 0.125). The AR grade nitrate of Merck company (purity of 99%) are used in the experiments such as Yttrium nitrate ($Y(NO_3).6H_2O$), Nickel nitrate ($Ni(NO_3)\cdot 6H_2O$), Magnesium nitrate ($Mg(NO_3)\cdot 6H_2O$), Cadmium nitrate ($Cd(NO_3)\cdot 6H_2O$), Ferric nitrate ($Fe(NO_3)_3.9H_2O$). These nitrates and citric acid are using stoichiometric ratio proportion to obtain the final product and the citric acid ($C_6H_8O_7$) is used as a fuel in the ratio 1:3. The proportion of each reagent was defined according to its respective molar amounts [11]. All chemicals are dissolved in distilled water and were stirred till to obtain the homogeneous solution. To maintain pH equal to 7 by adding drop by drop ammonium hydroxide (NH_4OH) during the stirring process. This solution was stirred continuously with 80 $^{\circ}$C for about 4-5 hours to obtain sol. After 4-5 hours, gel converts into ash and ash convert into powder. Finally get fine powder of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ferrite nanoparticles after auto combustion. Powder was sintered at 400 $^{\circ}$C for 2 hours.

The general chemical reaction for the synthesis of sample can be presented as;

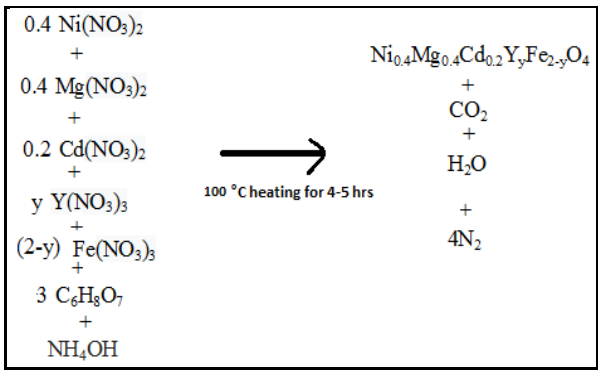

Figure 1. Structural properties of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ by XRD

Various analytical tools like X-ray diffraction (XRD), Energy dispersive x-ray spectroscopy (EDAX), Fourier transformation infrared (FTIR), Scanning electron microscopy (SEM), and Transmission electron microscopy (TEM) were used for the characterization and evaluation of properties. The structural characterization was done using XRD analysis. The X-ray diffractometer with Cu-Kα radiation of wavelength 1.5405 A^0 at 40 kV performed a scanning from 20 to 80 degree at a step size of 0.02 degree per second for each prepared sample and determined crystal structure, lattice parameter and crystallite size. The microstructure investigations were carried out on the fracture surfaces of the samples using thermal field emission scanning electron microscope (SEM, JSM-7600F) equipped with an energy dispersive x-ray spectroscopy (EDAX).The optical characteristics was studied using Fourier Transformation Infrared (FT-IR) of Bruker 3000 Hyperion microscope with vertex 80 single point detector performing images resolution ranging between 7500 to 450 cm^{-1}. The particle morphology was studied using Scanning electron microscopy (SEM) of JEOL JSM-7600F combines two proven technologies operating at 0.1 to 30 kV with high resolution and Transmission electron microscopy (TEM) of PHILIPS CM-200 operating at 20-200 kV with resolution 2.4 A^0. The temperature dependence of DC resistivity of samples was recorded at different temperature 200 ^{0}C and 300 ^{0}C with USB computer interface through SES-CAMM module using electrometer (TPX-600C having resolution 1 pA to 100 nA) in two probe method. Further investigations of the electrical properties are under way to elucidate the effective role of inter particle interactions in these samples.

III. RESULTS AND DISCUSSION

3.1 Structural Studies

a) XRD analysis : The resulting powder $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ (where y = 0.025, 0.050, 0.075, 0.100 and 0.125) nanocrystals were characterized by XRD pattern. The XRD pattern of sintered Y^{3+} doped the nickel-magnesium-cadmium ferrite nanocrystals as shown in figure-2. Obtained XRD pattern and crystalline phases were identified and it conforms the formation of a homogeneous well-defined spinal cubic structure with put any impurity. The broad peaks in the XRD pattern

indicate a fine particle nature of the particles. The particle size was determined using Scherer's formula,

$$t = \frac{0.9\,\lambda}{\beta Cos\theta}$$

Where, λ = wavelength of X-ray used, θ = peak position and β = FWHM of the peak θ and it is corrected for instrumental broadening. The average particle sizes of nanoparticles are given in Table-1. The particle size decreases as the concentration of Y^{3+} increases. Lattice parameter obtained for prepared sample is ranging between 1.9228 to 2.1300 A^0. The deviation in lattice parameter can be attributed to the cations rearrangement in the nanosize prepared ferrites. Value of lattice constant for Ni-Mg-Cd doped Yttrium ferrite shows the expansion of unit cell with rare earth doping when compared with pure Yttrium ferrite. This is expected due to substitution of large ionic radius of Y^{3+} ions (0.9 A^0) with small ionic radius Fe^{3+} ions (0.645 A^0). This result in Y^{3+} substituted ferrites to have higher thermal stability relative to Ni-Mg-Cd ferrite.

Table 1. The particle size of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ by XRD

Composition y	Average grain size (t) nm	Lattice constant (a) A^o
0.025	23.092	8.3597
0.050	24.352	8.3716
0.075	20.534	8.3603
0.100	21.984	8.3585
0.125	17.02	8.3624

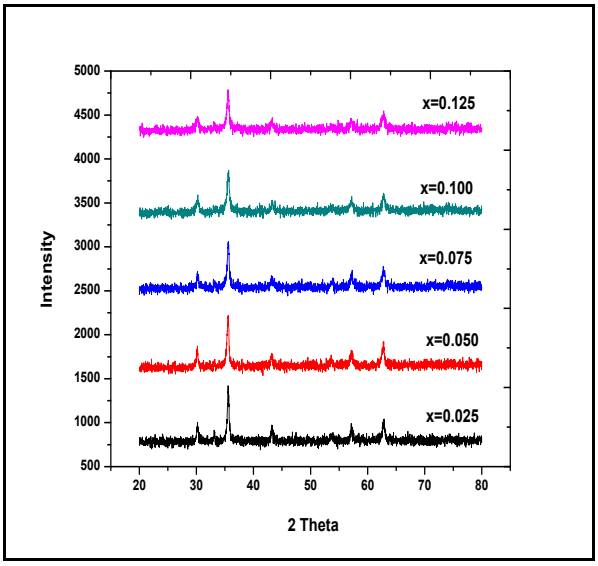

Figure 2. Structural properties of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ by XRD

b) EDAX analysis: The typical EDAX spectra taken from the ferrite grain and grain boundary of a typical sample $Ni_{0.4}$ $Mg_{0.4}$ $Cd_{0.2}$ $Y_{0.125}Fe_{1.875}O_4$to know the chemical constituents present in the materials and it reveals that the ferrite grain contain amount of Y^{3+} supporting indirectly the entering of yttrium ions into the sub lattice of ferrites. The EDAX spectrum shows the content of Y^{3+} is less than that of its normal composition due to segregation of yttrium ions into the grain boundaries and evaporation at high temperature. Also it is found that grain sizes of the samples decreases with increasing in doping of Y^{3+} ions because more cations vacancies, closed pores exist and grain boundary movement when large amount of Y^{3+} ions exist in the samples.

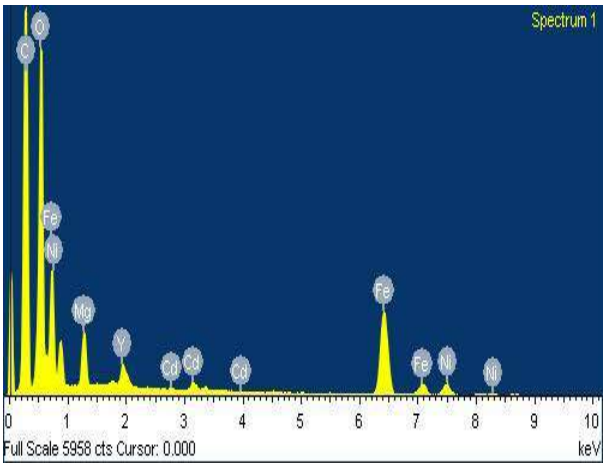

Figure 3. Structural properties of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_{0.125}Fe_{1.875}O_4$ by EDAX

3.2 Morphological Studies:

a) SEM analysis: The SEM images of Ni-Mg-Cd nanocrystalline ferrites by sol-gel auto combustion method as shown in figure-4. The SEM image of the prepared $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_{0.075}Fe_{1.925}O_4$ sample is composed of nanocrystals and shows the distribution of nanoparticles. The calculated ferrite gain sizes of the corresponding Yttrium doped Ni-Mg-Cd ferrite samples from these graphs are presented in table1. It is observed that the grain sizes of the ferrites in the samples decreases with increase in doping of Y^{3+} ions that indicates increase in grain size is not liquid-phase sintering. The melting point of Y^{3+} is 1522 ^{0}C which is much larger than the sintering temperature (400 ^{0}C) of the ferrites.

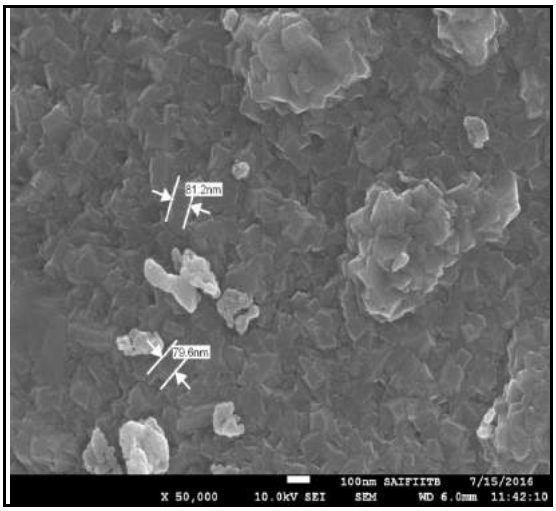

Figure 4. Morphology of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_{0.075}Fe_{1.925}O_4$by SEM

b) TEM analysis: The particle size was estimated using TEM analysis. The reduction in particle size with rare earth doping is evident from TEM images. Average particle sizes measured are given in table 1. Figure 5(a) and (b) show the TEM images of$Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$nanoferrite by using sol-gel autocombustion method. The most of nanoparticles are in spherical shape and agglomerated due to the tendency of nanoparticles.

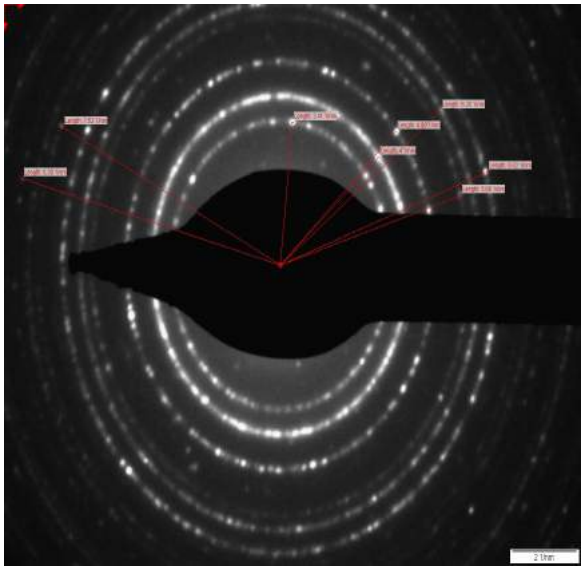

Figure 5(a). Morphology of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_{0.100}Fe_{1.900}O_4$ by TEM

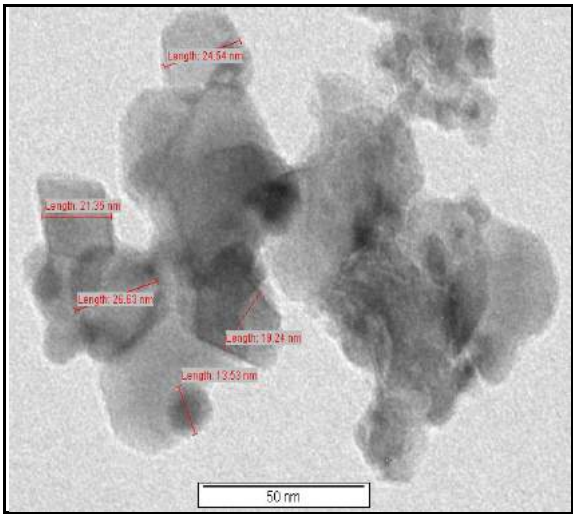

Figure 5(b). Particle size using morphology of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_{0.100}Fe_{1.900}O_4$ by TEM

3.3 Electrical studies:

Table 2. The resistivity and conductivity of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$

Composition	Resistivity (ρ) (ohm-m)		Conductivity (σ) (mho)	
	at 200 °C	at 300 °C	at 200 °C	at 300 °C
y=0.025	212746.14	4660288.79	5.1221 x 10^{-6}	2.1457 x 10^{-7}
y=0.050	1251638.44	244406.46	7.8677 x 10^{-7}	4.0915 x 10^{-6}

y=0.075	2122939.87	300018.62	4.7008 x 10^{-7}	3.3331 x 10^{-6}
y=0.100	914634.77	104424.91	1.2796 x 10^{-6}	9.5763 x 10^{-6}
y=0.125	3292097.63	256715.18	3.4270 x 10^{-7}	3.8954 x 10^{-6}

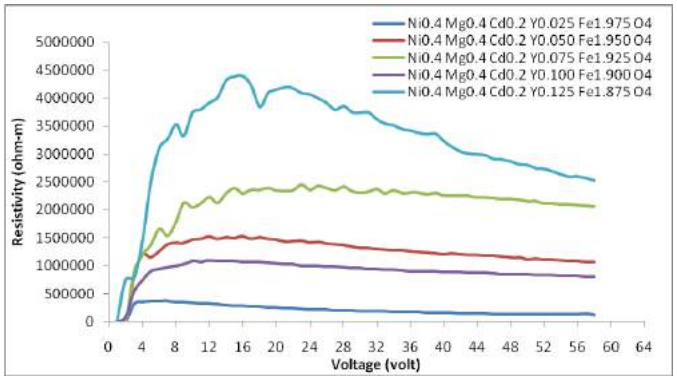

Figure 6(a). Electrical behaviour of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ at 200 °C

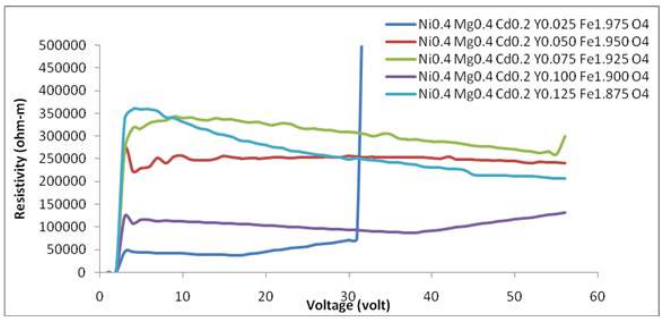

Figure 6(b): Electrical behaviour of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ at 300 °C

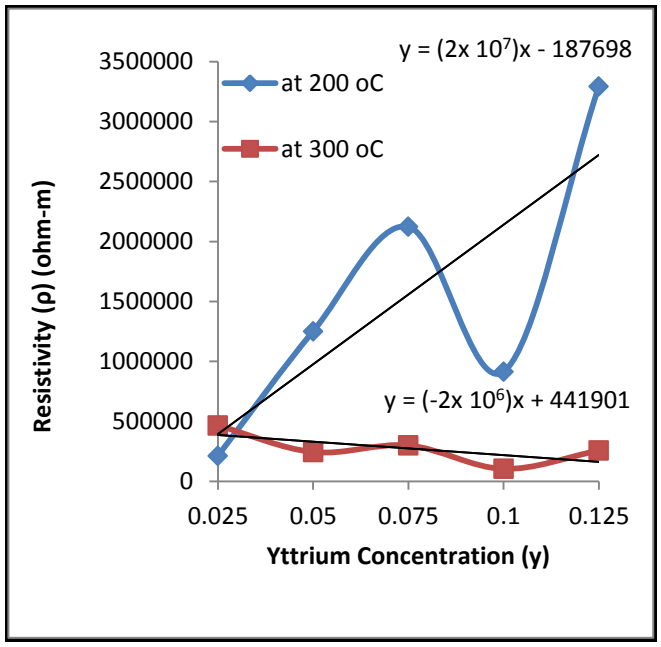

Figure 6(c). Variation of resistivity of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ spinal ferrite with yttrium content (y)

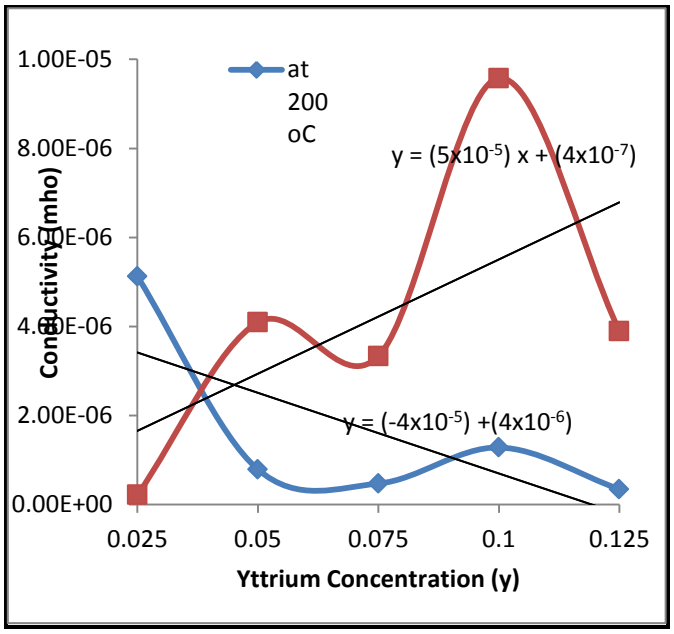

Figure 6(d). Variation of DC conductivity of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ spinal ferrite with yttrium content (y)

Changes inresistivity and DC conductivity of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ spinal ferrite with yttrium content (y) is shows in figure 6 (c) and (d). Actually conductivity in ferrites are collectivelly contributed by electron hopping between Fe^{2+} and Fe^{3+} ions and holes hopping between Y^{2+} and Y^{3+} ions and depends on availability of charge

carriers with mobility. Hence increase in conductivity explains increase in hopping pairs.

IV. CONCLUSIONS

Yttrium doped $Ni_{0.4}Mg_{0.4}Cd_{0.2}Fe_{2-y}O_4$ (where y = 0.025 to 0.125)powder have been successfully synthesized using sol-gel method. The formation of the ferrite powders has been confirmed by XRD, EDAX, SEM and TEM. The XRD pattern shows that nanoparticles decreases with the increase in Y^{3+} content and lattice parameter is ranging between **8.3585** to **8.3716**A^0 and average grain size ranging between 17 to 24.3 nm which will give great effect on it electric properties. It is also observed that the most of nanoparticles are in cubical shape and agglomerated due to the tendency of nanoparticles. The optical property of prepared samples was also investigated and shows the characteristic bond of spinel structure. The electrical property indicates that conductivity increases with the increase in temperature. It results the doping of Y^{3+} in Ni-Mg-Cd nanoferrite produces consequent changes on their structural, morphological, electrical properties and it applicable for high frequency electrical devices.

V. ACKNOWLEDGEMENTS

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Survey of Medicinal Plants in Gadchiroli District of Maharashtra State

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ABSTRACT

The Gadchiroli district consists of 11299 km of the forest lands making a home for a variety of gum plants, oil seeds, medicinal plants, flowers and fooding material, etc. the forest contain so many species. Some of them are comes under vulnerable (VU), and under lower risk (LR). The survey was crried out in the 2014-15. In this paperthe medicinal plants which are said by VAIDU of tribal caste (Madia, Gond, pardhan , Orav) are represented by their botanical names.

Keywords : LR, VU, Medicinal Plants

I. INTRODUCTION

For some disease we use the medicine from medicinal plants. But in the Gadchirolidistrict the major tribal peoples use medicine from medicine plants, for example tree like Butea monosperma (Palas), Holarrhena pubescens (pandarkuda), and Herb like Andrographis paniculata (Bhuilimb). The major focous is given on the medicinal plants found in the Gadchiroli District.

II. Collection of Material

For the collection of material there are 04 sevral tours organize from the Sept 2015 to July- 2016. The lacation of Gadchiroli district is south-East in the corner of Maharashtra. The Gadchiroli district was sorroundedby Chandrapur district in West, Gondia district in north, Chhattisgadh state in East and Telengana state in South. The Gadachiroli district lies between 19^0 31' and 19^0 45' N latitude and 80^0 5' and 80^0 45' E longitude.

III. Methodology

During the survey first I contact with the local villagers for which the medicinal plants used by them to cure. Some time I was go with the local people in forest. Due to only 04 visits the few medicinal plants are o be collected. The collected medicinal plants are verified by using standard literature.

Observation: the following is the list of plants with their family name, botanical name and local name.

Sr. No.	Family	Botanical name	Local name
01	Acanthaceae	**Andrographis paniculata**	Bhuililb
		Lepidagathis cristana	Kateri zendu
02	Amaranthaceae	**Achyranthes aspera**	Aghada
03	Anacardiaceae	**Buchanania cochinchinensis**	Char
		Mangifera indica	Ambha
		Semecarpus anacardium	Biba
04	Arecaceae	**Phoenix sylvestris**	Shindi
05	Lamiaceae	**Ocimum sanctum**	Tulsi
06	Zinziberaceae	**Costus specious**	Harduli
07	Sapotaceae	**Madhuca longifolia**	Mahua
08	Poaceae	**Dendrocalamus sritictus**	Bamboo
09	Pedaliaceae	**Sesamim orientale**	Til
10	Oxalidaceae	**Biophytum candolleanum**	Lajalu
11	Moraceae	**Ficus religiosa**	Pimpal
12	Asteraceae	**Chrysanthemum indicium**	Shewanti
13	Aloeaceae	**Aloe barbadensis**	Korphad

14	Caesalpinaceae	**Tamirindus indica**	Chinch
15	Cucurbitaceae	**Trichosanthus anguina**	Indrawan
16	Ebenaceae	**Diospyrus melanoxylon**	Tendu
17	Fabaceae	**Butea monosperma**	Palas
18	Lamiaceae	**Tectona grandis**	Sag

IV. Result And Discussion

The study was improving the knowledge of medicinal plants. These plants are used for many diseases like skin disease, cough, toothache, headache, fever, etc. by using their any part in the form of paste or making power.

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Synthesis and characterization of Zinc Maleate Dihydrate and its thermal decomposition by the study of direct Current Electrical Conductivity

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ABSTRACT

The possibility of using direct current electric conductivity measurement to study the solid state reactions involved in the preparation zinc oxide from zinc (II) maleate hydrated have been analyzed respectively. The study has been carried out in normal atmosphere. The steps corresponding to dehydration are well resolved in region from room temperature to 260 oC. The final product of decomposition in normal atmosphere was found to be ZnO from zinc maleate. The conductivity measurement was supplemented with the data obtained by chemical analysis; thermal analysis (TGA and DTG) and IR spectroscopy analysis.

Keywords : Thermal decomposition; Electric conductivity; Solid State; Maleate

I. INTRODUCTION

The decomposition characteristics of manganese, Iron, Cobalt, Zinc and Copper oxalates in the air and nitrogen atmospheres and reported a shift to lower temperature when oxygen is present for iron, manganese and cobalt oxalates but not for zinc and copper oxalates. The thermal, spectral and magnetic studies of compound of copper and zinc carboxylates have also been studied. nickel, copper and zinc with maleic acid was studied using thermo-gravimetry TG and differential thermal analysis DTA [1-2] .Thermal analysis of transition metal carboxylates [5] has been subject of recent interest due to technological importance[3].The maleates are of practical importance because of their use as coatings with specific properties, efficient catalysts and are also of medicinal significance. Dielectric characteristics of organo-metallic crystals are of increasing importance as the field of solid state electronics continues to expand rapidly. For these applications the properties of most concern are the dielectric constant, loss tangent and a.c. conductivity [4].

New devices and applications are continually increasing the frequency range and the range of environmental conditions, particularly temperature, that are of practical interest. The frequency dependent conductivity and dielectric constant provide important information on the ionic or electronic transport mechanism. It gives an insight into the structure of the materials since the localized electronic states within the material are created due to the presence of disorder in the atomic configuration and/or the composition. The structure of MHMH crystal was studied by various investigators [5, 6].

The oxidative behavior of different oxalates was better understood from the study of temperature variation of d.c.electrical conductivity measurements (7).

Using the electrical conductivity techniques in the study of solid state decomposition reactions of different metal (II) carboxylates [8-10] has been carried out. Report the thermal decomposition of copper (II) oxalate monohydrate and Zinc (II) oxalate dihydrate have been studied using two-probe d.c.electrical conductivity measurements to study the progress of reaction. This study has been supplemented with TGA, DTG and DTA, X-ray diffraction and Infrared spectroscopy.

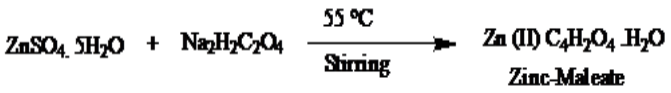
Use of measurement of direct current electric conductivity as probe for the study of progress of thermal decomposition of feO_2O_4. $2H_2O$ in normal atmosphere and other atmosphere (11). This compound initially is an insulator and final and intermediate products during decomposition are semiconducting in nature. It would therefore profitable to use technique direct current of electric conductivity to investigate the

path of thermal decomposition of metal to the dicarboxylates. In present work systematic preparation of zinc maleate done and by studying progress of thermal decomposition respective Zinc (II) maleate by using direct current electric conductivity measurements.

II. Experimental

A) Preparation of zinc (II) maleate diydrates

Zinc maleate was prepared by mixing equal volume (250 ml) and of equimolar (0.05 M) solution of zinc sulphate pentahydrate and sodium maleate at 55°C under vigorous stirring. The white crystallization zinc maleates ($Zn\ H_2C_4O_4$) was obtained then filtered and washed with cold water till the solid free from impurities i.e. sodium maleate. It was then washed with ethanol to speed up drying. Then it was air dried at ambient temperature.



Chemical analysis carried out by volumetric method (By EDTA method). The elemental analysis of carbon and hydrogen were done by micro analytical technique. Results are summarized in table no. (I). the IR spectroscopy was recorded in the region 400-4000 cm^{-} on Perkin –Elmer-337 spectrophotometer, using nujol mull using KBr windows. The frequency bands are summarized in table No (II). Magnetic susceptibility measurement done at 22±1°C on faraday balance using 7000 G. magnetic field. Thermogravimetric analysis curve were recorded using a "PERKIN-Elmer" thermal analysis instruments (Delta series TGA 7). Direct measurement of resistant did by using Philips G.M. 600g ohm-meter.

III. OBSERVATIONS

Table 1. Analytical data of Zinc (II) maleate dihydrate (Zn (II) $C_4H_2O_4$, Molecular weight =215.37)

Elemental Analysis							**Magnetic moment µB.M.**
Carbon %		**Hydrogen %**		**Zinc %**		M.P.	
Required	**Found**	**Required**	**found**	**Required**	**Found**		
22.28	22.20	2.78	2.69	31.58	30.34	355° C >	**0 (Diamagnetic)**

Table 2. Spectral analysis Infrared spectral bands and their probable assignment taken under Nujol-mull.

Zinc maleate dihydrate	**Assignment**
3450 Cm-	Asymmetric -O-H
1450 Cm-	Symmetric C-O
1573 Cm-	Asymmetric C-O
1300 Cm-	Symmetric C=O
1010 Cm-	C-H wagging
850 Cm-	C-C Deformation
670 Cm-	HOH
460 Cm-	Asymmetric Zn-O(M-O)

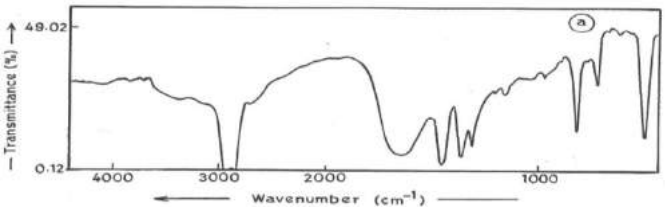


Figure 1. IR Spectra of Zinc (II) maleate dehydrate

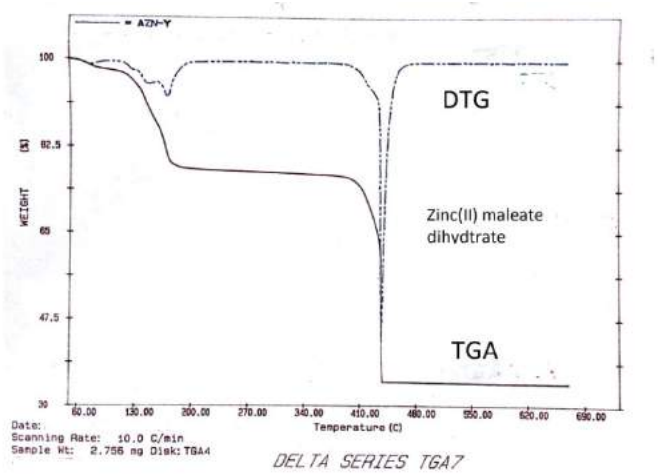


Figure 2. DTG and TGA spectra of Zinc (II) maleate

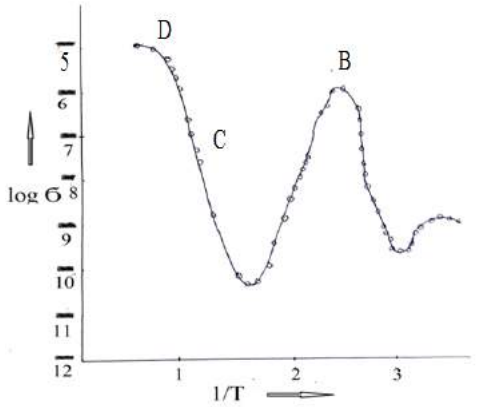


Figure 3. Graph log Ϭ Vs 1/T

IV. Results and discussion

Analytical data of Zn (II) maleate dihydrate synthesized have a water of crystallization as shown in Table No. I. These results are in accordance with physico- chemical data given in table No. (I). The thermal analysis and direct current electrical conductivity measurements confirmed the presence of water of hydration for these compounds under normal atmosphere. These results are also further supplemented by IR spectroscopy method by all above data it is confirmed that the compound have following polymeric octahedral structure.

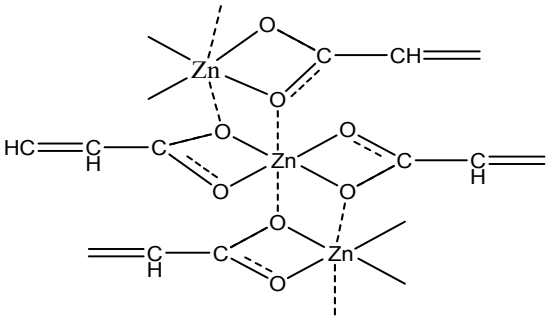


Figure 4. structure of Zinc (II) Maleate

Magnetic measurement suggests that the metal ion has octahedral environment. By studying IR spectrum compound show broad band at 3420 cm^- due to coordinated hydroxyl group (-OH) stretching, abroad band at 1600 cm^- due to υ asymmetric (C=O) and bands at 1460 cm^- and 1370 cm^- due to υ symmetric (C=O) of coordinated carboxylate groups (12). Metal- oxygen band of compound indicates a six coordinate environment for metal ions. Electrothermal analysis of compound by temperature variation of direct current electrical conductivity (log Ϭ Vs 1/T).The TGA curve showed a clear dehydration step corresponding to loss two water molecule from 60-180^oC with plateau upto 360 ^oC. This stage is supported by the presence of a broad endothermic peak at 150^oC on DTG curve. The plot of (log Ϭ Vs 1/T) showed a clear peak at 180 ^oC corresponding to dehydration step region B. The decomposition step would be seen on the DTG curve at 430 ^oC .The TGA curve at 430 showed weight loss from 360 ^oC to 460 ^oC until sample crystallized to mainly Zno. The plots (log Ϭ Vs 1/T) show steep increase in Ϭ at 330-570 ^oC (region C) and then remain constant above this temperature (region D). The region C may be corresponding to anhydrous $ZnC_4H_2O_4$ & ZnO. In region D the sample showed mainly Zno formation; the sample was white and had an electrical conductivity value of about 10^{-5} ohm^-cm^{-1}.When reaction has been carried out in normal atmosphere; gaseous product evolved during decomposition may affect solid state reaction. A complete dehydration of this maleate has been observed in TGA, DTG and (log Ϭ Vs 1/T) curves. The reaction are presented as follows-

$$Zn(II)\ C_4H_2O_4.\ nH_2O \longrightarrow Zn\ (II)C_4H_2O_4 + n\ H_2O\uparrow$$

$$2\ Zn\ (II)C_4H_2O_4 \longrightarrow Zn\ (II)C_4H_2O_4 + ZnO + C_2H_2\uparrow + CO\uparrow + CO_2\uparrow$$

$$ZnO + Zn\ (II)C_4H_2O_4 \longrightarrow 2ZnO + C_2H_2\uparrow + CO\uparrow + CO_2\uparrow$$

V. CONCLUSION

The IR spectral study shows that Zn (II) maleates hydrate are bidented link to metal atom. The spin only magnetic moment value for compound shows that complex is high spin with SP^3d^2 hybridization. IR spectra and magnetic moment suggest that the zinc (II) maleate were polymeric with octahedral structure. Dehydration took place in normal atmosphere indicated

by TGA and DTG curves. The step corresponding to same dehydration would be indicated by (log Ϭ Vs 1/T).

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Synthesis, Characterization and Evaluation of Antifungal and Antibacterial Activities of Some Quinazoline Derivatives

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ABSTRACT

Present work includes synthesis of 2-{[2-(piperazin-1-yl)quinazolin-4-yl]amino}ethan-1-ol (IV) , N2, N4-di p-tolylquinazoline-2,4- diamine (V) and N2, N4-bis(4-chlorophenyl)quinazoline-2,4-diamine (VI) which are quinazoline derivatives and out of these three quinazoline derivatives N2, N4-bis(4-chlorophenyl)quinazoline-2,4-diamine (VI) have shown "antifungal activity" against fungus "Aspergillus flavus" and "antibacterial activity" against bacteria "Pseudomonas". At first 2- amino benzoic acid react with urea at temperature 130 ºC to 140ºC to gives Quinazolin-2,4-diol (I) which on further reaction with phosphorus oxychloride at 150 ºC for 24 hr. to gives second product 2,4-dichloroquinazoline (II). Then 2-4-dichloroquinazoline (II) reacts with 2-aminoethan-1-ol and piperazine to gives 2-{[2-(piperazin-1-yl)quinazolin-4-yl]amino}ethan-1-ol (IV) and when p-toluidine react with 2-4-dichloroquinazoline (II) to gives N2, N4-di p-tolylquinazoline-2,4- diamine (V) and again this 2,4-dichloroquinazoline (II) react with p-chloroanline to gives N2, N4-bis(4-chlorophenyl) quinazoline-2,4-diamine (VI) which characterized by I. R., 1HNMR and 13CNMR.

Keywords : Quinazoline Derivative, Antifungal Activity, Antibacterial Activity, N2, N4-Di P-Tolylquinazoline-2, 4-Diamine, N2, N4-Bis (4-Chlorophenyl) Quinazoline-2, 4-Diamine, Quinazolin-2, 4-Diol, 2,4--Dichloroquinazoline

I. INTRODUCTION

Quinazoline is N-containing heterocyclic compound, till date many researcher have synthesized many derivatives of Quinazoline and all these derivatives have shown different pharmacological activities like anti-bacterial [3], antimicrobial [4], anti-inflammation [6], antifungal [8], anti-hypertension [10], anti-oxidation [12] analgesia [13], anticonvulsant [14], antimalarial [15], anti-tumor [16], anti-tuberculosis [17], anti-HIV activity [18] etc. Medicinal chemists synthesized a variety of quinazoline compounds with different biological activities by installing various active groups to the quinazoline moiety using developing synthetic methods. And the potential applications of the quinazoline derivatives in fields of biology, pesticides and medicine have also been explored. This process involved the construction of a starting general structure with a planar heterocyclic ring (quinazolineorpyrido [2, 3-d] pyrimidine ring), selected as the central fragment that can act as a scaffold to carry two functionalized branches at positions 2 and 4, which are equivalent or different with the aim of evaluating the possible influence of the symmetry/asymmetry on the target activity. We have synthesized derivatives of Quinazoline which are 2-{[2-(piperazin-1-yl)quinazolin-4-yl]amino}ethan-1-ol (IV) , N^2, N^4-di p-tolylquinazoline-2,4- diamine (V) and N^2, N^4-bis(4-chlorophenyl)quinazoline-2,4-diamine (VI) In first derivative that is 2-{[2-(piperazin-1-yl)quinazolin-4-yl]amino}ethan-1-ol (IV) we have substituted second and fourth position of quinazoline by piperazine and aminoethan-1-ol respectively while in second derivative that is N^2, N^4-di p-tolylquinazoline-2,4- diamine (V) by p-toluidine and in third derivative N^2, N^4-bis(4-chlorophenyl)quinazoline-2,4-diamine (VI) by p-chloroaniline. For synthesis of Quinazoline derivatives we have used piperazine, aminoethan-1-ol, p-toluidine and p-chloroaniline because individually they shows important pharmacological and other activities therefore at the time of synthesis we expected that after synthesis of these quinazoline derivatives they will be show some pharmacological activities and after evaluation of biological activities of these synthesized derivatives of quinazoline, result is that N^2, N^4-bis(4-

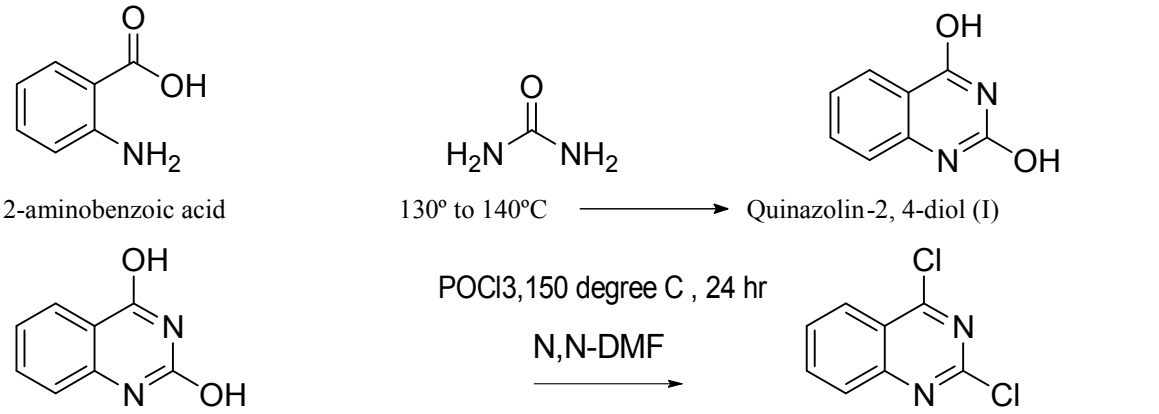
chlorophenyl)quinazoline-2,4-diamine (VI) have shown "antifungal activity" against fungus "Aspergillus flavus" and "antibacterial activity" against bacteria " Pseudomonas".

II. RESULT AND DISCUSSION

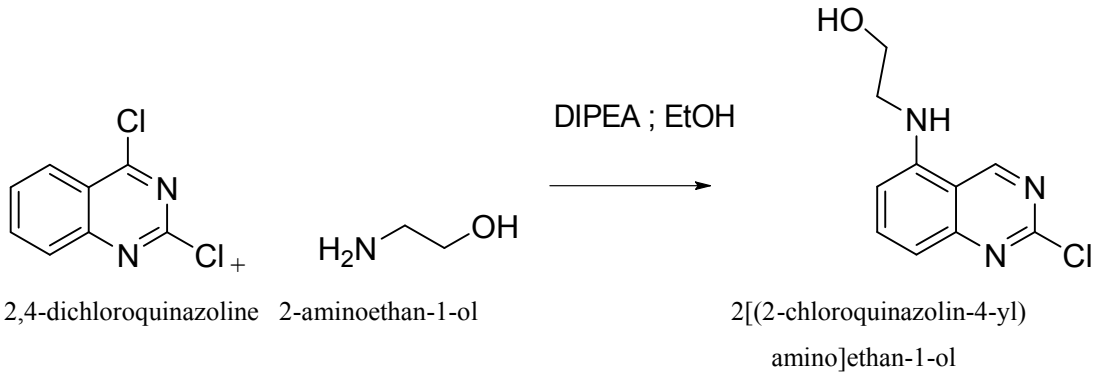
Target molecules which synthesized are 2-{[2-(piperazin-1-yl)quinazolin-4-yl]amino}ethan-1-ol (IV), N^2, N^4 - di p-tolylquinazoline-2,4- diamine (V) and N^2, N^4-bis(4-chlorophenyl)quinazoline-2,4-diamine (VI). At first 2- amino benzoic acid react with urea at temperature 130 ºC to 140ºC to gives Quinazolin-2,4-diol (I) which on further reaction with phosphorus oxychloride at 150 ºC for 24 hr. to gives second product 2,4-dichloroquinazoline (II). Then 2-4-dichloroquinazoline (II) reacts with aminoethan-1-ol and piperazine to gives 2-{[2-(piperazin-1-yl)quinazolin-4-yl]amino}ethan-1-ol (IV) and when p-toluidine react with 2-4-dichloroquinazoline (II) to gives N^2, N^4-di p-tolylquinazoline-2,4- diamine (V) and again this 2,4-dichloroquinazoline (II) react with p-chloroanline to gives N^2, N^4-bis(4-chlorophenyl) quinazoline-2,4-diamine (VI) which characterized by I. R., ^{1}HNMR and ^{13}CNMR. Out of these derivatives of quinazoline N^2, N^4-bis(4-chlorophenyl)quinazoline-2,4-diamine (VI) have shown "antifungal activity" against fungus "Aspergillus flavus" and "antibacterial activity" against bacteria " Pseudomonas".

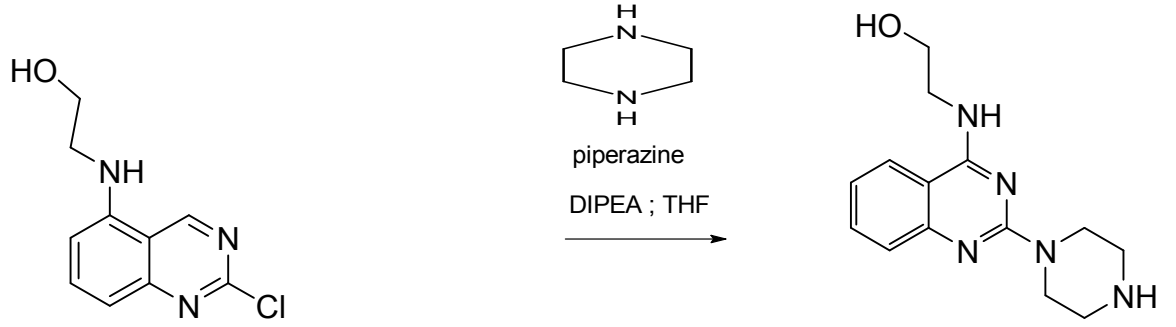
Present trends are to synthesize a large variety of quinazoline compounds with different biological activities by installing various active groups to the quinazoline moiety using developing synthetic methods therefore we have introduced piperazine, aminoethan-1-ol, p-toluidine and p-chloroaniline groups at second and fouth position of quinazoline because all these four groups have important pharmacological and other activities and have synthesized derivatives of quinazoline and tested for antifungal and antibacterial activities and we have got successful result according to our expectation.

Scheme 1.

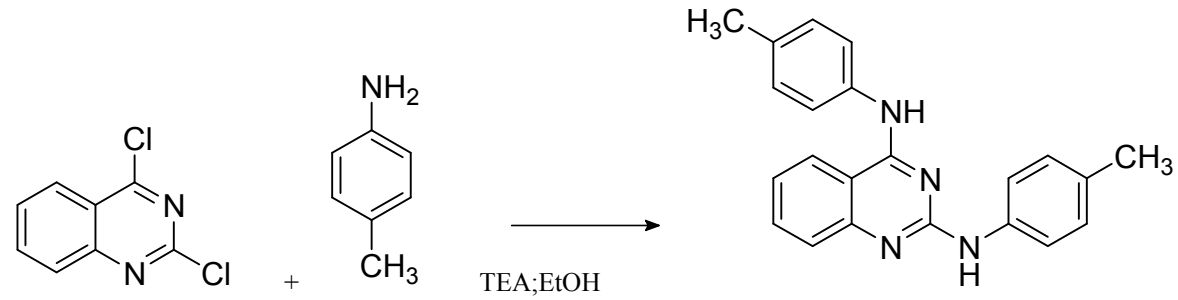


Scheme – II

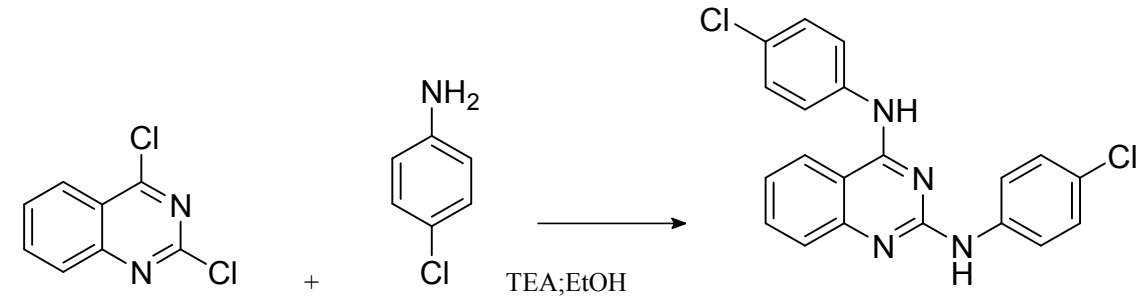




2[(2-chloroquinazolin-4-yl)amino]ethan-1-ol 2-{[2-piperazin-1-yl)quinazolin-4-yl] amino}ethan-1-ol **Scheme – III**



2,4-dichlorouinazoline P-toluidine 70ºC , 5 hr N^2,N^4-di p-tolylquinazoline-2,4- diamine (V)



2,4-dichloroquinazoline P-chloroaniline 70ºC , 5 hr N^2, N^4-bis(4-chlorophenyl)quinazoline-2,4-diamine(VI)

III. EXPERIMENTAL

Anthranilic acid, Urea, phosphorus oxychloride, N, N-dimethyl formamide, Triethyl amine, diisopropyl ethyl amine, 2-aminoethan-1-ol, piperazine, p-toluidine,P-Chloroaniline, ethanol obtained from local dealer. . Analytical TLC was performed on Silica plates- GF254 (Merck) with visualization by UV or in iodine. Melting points were determined by using thiels tube. ^{1}H-NMR (in CDCl3 / DMSO-d6) spectra were recorded using Bruker -400 with TMS as internal standard. ^{13}C were recorded by using DMSO solvent. All the chemicals used were of Laboratory grade.

Synthesis and characterization of Quinazolin-2, 4-diol (I) [25] : A mixture of Anthranilic acid (50g, 0.36 mol) and urea (109 g, 1.82 mol) in a round bottom flask equipped with mechanical stirrer was heated without solvent at 135 to 140ºC using an air condenser for 3h. The melted reaction mixture was poured into sodium hydroxide (1000 mL, 1N) solution and any insoluble material removed by filtration. The mixture was then acidified with HCl (2 N), to yield 2,4-dihydroxy quinazoline as a white precipitate which was collected by filtration and dried. Yield 70%; m. p. >250ºC.

IR max cm^{-1}: 3428 (OH, broad), 3079 (Ar C-H), 1604 (C=N), **^{1}H NMR (DMSO-d^6) δ ppm**: 7.56 (t, 2H, Ar-H), 7.98 (d, 1H, Ar-H), 9.19 (s, 1H, Ar-H), 7.17 (t, 1H), 9.16 (1H, S), **^{13} CNMR (DMSO-d^6) (δ/ppm)**: 121.11 (Ar C-H), 115.39 (Ar C-H), 142.59 (Ar C-H), 135.02 (Ar C-H),

163.98 (Ar C-OH), 155.69 (Ar C-OH), 108.35 (Ar C), 151.2 (Ar C)

Synthesis and characterization of 2, 4-dichloroquinazoline (II) [20] : A mixture quinazolin-2, 4-diol (6.0 milimole), POCl3 (5 ml) and N, N-DMF (catalytic amount) was stirred and heated for 150°C under reflux for 24 h. The solvents were removed under vacuum then cold water (0°C, 25 ml) and chloroform (25 ml) were added. The organic layer was washed with water (3X20 ml) and dried over anhydrous sodium sulfate. The solvent was removed under vacuum and compound obtained used for further analysis.

IR max cm^{-1}: 755 (C-Cl), 3029 (Ar C-H), 1625 (C=N), **^{1}H NMR (CDCl3-d^{1}) δ ppm**: 7.18 (m, IH), 7.61 (m, 2H), 7.87 (d, I H), **^{13}C NMR (CDCl3-d^{1}) (δ/ppm)**: 115.35 (Ar C), 122.33 (Ar C), 126.96 (Ar C), 134.97 (Ar C), 14.90 (Ar C), 150.31 (Ar C), 162.85 (Ar C)

Synthesis[20] and characterization of 2-[2-chloroquinazolin-4-yl) amino] ethan-1-ol (III) : Taken mixture of 1 eq. of 2, 4-dichloroquinazoline & 1.2 eq. of 2-aminoethan-1-ol in 100 ml two necked round bottom flask with appropriate requirement. Added to it (for 1 g sample required 10 ml ethanol) ethanol & DIPEA (3 eq.) at 0ºC then stir for 6 hr. The progress of reaction checked by TLC. After completion of reaction, distilled out it completely then added dichloromethane to it & washed with water. The Organic layer dried over sodium sulphate & concentrated to obtain off white solid. The obtained off white solid purified by hexane, dried it, weighed it & used for further analysis & reaction.

^{1}H NMR (CDCl3-d1) δ ppm : 3.66 (1 H, s), 3.61 (2H, t), 3.58 (2H, t), 8.25 (1 H, s), 8.28 (1H, d), 7.78 (1 H, t), 7.59(1H, t), 7.80 (1H, d).
^{13}C NMR (CDCl3-d1) (δ/ppm) : 161.73 (Ar C), 157.4 (Ar C), 150.65 (Ar C), 134.00(Ar CH), 127.01 (Ar CH), 126.43(Ar CH), 114.09 (Ar C-), 59.22 (aliphatic CH_2), 44.07 (aliphatic CH_2)

IV. Synthesis of 2-{[2-(piperazin-1-yl)quinazolin-4-yl] amino} ethan-1-ol (IV)
Taken mixture of 1 eq. of 2-[(2-Chloroquinazoline-4-yl) amino] ethan-1-ol & piperazine (1.2 eq.) in 100 ml two necked round bottom flask as per requirement. Added to it THF & DIPEA at 0ºC & then reaction mixture heated at 80ºC for 16 hr. The progress of reaction was checked by TLC. After completion of reaction diluted it with ethyl acetate & washed with water. The organic layer dried over sodium sulphate & concentrated to obtain white solid which is purified by hexane washing. Dried it, washed it & used for further analysis & reaction.
^{1}HNMR (400MHz, DMSO-d1) δ ppm: 5.04 (1H, s), 1.05 (1H, s), 8.11 (1H, s), 2.99 (4H, t), 2.88 (4H, t), 7.50 (1H, d), 7.30 (1H, m), 7.29 (1H, m), 7.08 (1H, t), 3.67 (2H, t), 3.56 (2H, t)
^{13}C NMR (CDCl3-d1) (δ/ppm): 160.12 (quinazoline C), 160.04 (quinazoline C), 158.53 (quinazoline C), 110.8 (quinazoline C), 125.05 (quinazoline CH), 132.31 (quinazoline CH), 132.4 (quinazoline CH), 123.04 (quinazoline CH), 59.17 (aliphatic CH_2), 43.59 (aliphatic CH_2), 43.00 (aliphatic CH_2), 41.93(aliphatic CH_2)

Synthesis and characterization of N^2,N^4-di p-tolylquinazoline-2,4- diamine (V) [20] : A mixture of 5 (5.0 mmol), the respective Toluidine (12 mmol), equimolecular amounts of triethylamine, and ethanol (15 mL) was heated at 70ºC for 5 h with stirring. The solvent was removed under vacuum and chloroform was added in solution and extracted with water. Product precipitated out in water layer because it is insoluble in water as well as in chloroform. Water layer washed with chloroform and filtered. Obtained water insoluble product dried, purified and characterized by using IR, ^{1}HNMR and ^{13}CNMR
IR max cm^{-1}: 3300 (-NH), 1616 (-C=N), **^{1}H NMR (DMSO-d6) δ ppm** : 7.99 (1H, s), 8.51(1H, d), 7.84 (2H, d), 7.62 (1H, d), 6.27 (1H, s), 7.58 (2H, d), 7.52(2H, d), 7.43 (2H, d) 7.38 (2H, d), 2.5 (6H, s), **^{13}C NMR (DMSO-d6) (δ/ppm)**: 46.33(aliphatic C), 103.06 (quinazoline C), 115.05 (quinazoline C), 125.12 (Ar C), 126.71 (quinazoline C), 129.67 (quinazoline C), 137.06 (quinazoline C), 174.68 (Ar C), 180.18 (Ar C), 180.99 (quinazoline C), 182.77 (quinazoline C), 183.04 (quinazoline C), 188.31 (quinazoline C)

Synthesis and characterization of N^2, N^4-bis(4-chlorophenyl)quinazoline-2,4-diamine (VI) [20] : A mixture of 5 (5.0 mmol), the respective p-chloroaniline (12 mmol), equimolecular amounts of triethylamine, and ethanol (15 mL) was heated at 70ºC for 5 h with stirring. The solvent was removed under vacuum and chloroform was added in solution and extracted with water. Product

precipitate out in water layer because it is insoluble in water as well as chloroform. Water layer washed with chloroform and filter. Obtained water insoluble product dried, purified and characterized by using IR, ^{1}HNMR and ^{13}CNMR

IR max cm^{-1}: 750 (C-Cl), 3015(Ar C-H), 1615 (C=N), 3360 (-NH), **^{1}HNMR (400MHz, DMSO-d1) δ ppm :** 8.03 (1 H, d), 8.17 (2H, t), 8.01 (2H, d), 7.66 (1 H, t), 7.62 (2H, d), 7.49 (1 H, s), 7.25 (1H, s), 7.08 (2H, d), 6.60 (2H, d), **^{13}C NMR (CDCl3-d1) (δ/ppm)**: 109.56 (quinazoline CH), 116.26 (quinazoline CH), 119.5 (Ar-C), 121.99 (quinazoline CH), 124.22 (quinazoline CH), 125.44 (Ar-CH), 126.40 (Ar-C), 127.92(Ar-C), 129.12 (Ar- CH), 128.99 (Ar-C), 130.51 (quinaoline-C), 131.57 (quinazoline-C), 134.53 (quinazoline-C)

Antifungal studies :

The newly synthesized compounds were screened and tested for their antifungal activity against "Aspergillus flavus" in DMSO solvent by well plate method. Sterile N.A. and P.D.A. plates were inoculated with Aspergillus flavus and make well with sterile cork borer. And then loaded 20 microliter of compound N^2, N^4-bis(4-chlorophenyl)quinazoline-2,4-diamine (VI) solution (0.01 g in 1 ml DMSO solvent) then this plate was dried by placing in an incubator at 37°C for 1 hr., prepared each well was labeled. The temperature was controlled and maintained at 37°C for 24 hr. The Inhibition zone were measured and compared with the controls. Zone diameter: 4 mm.

Antibacterial :

The newly prepared compounds were screened for their "antibacterial activity" against "Psedomonas aerogenosa" in DMSO by well plate method. Sterile N.A. and P.D.A. plates were inoculated with "Psedomonas aerogenosa". Made a well with sterile cork borer. Loaded 20 microlitre of compound N^2, N^4-bis(4-chlorophenyl)quinazoline-2,4-diamine (VI) solution (0.01 g in 10 ml DMSO solvent) then this plate was dried by placing in an incubator at 37°C for 1 hr, wells were made and each well was labeled. A control was also prepared in and maintained at 37°C for 1 day. Inhibition zone were measured and compared with the controls.

Zone diameter : 2 mm

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IV. CONCLUSION

We have synthesized 2-{[2-(piperazin-1-yl)quinazolin-4-yl]amino}ethan-1-ol (IV) , N^2, N^4-di p-tolylquinazoline-2,4- diamine (V) and N^2, N^4-bis(4-chlorophenyl)quinazoline-2,4-diamine (VI) and out of these quinazoline derivatives N^2, N^4-bis(4-chlorophenyl)quinazoline-2,4-diamine (VI) have shown "antifungal activity" against fungus "Aspergillus flavus" and "antibacterial activity" against bacteria " Pseudomonas" and all these compounds will be tested for various biological activities like anti-cancer, anti-inflammation, anti-bacterial, analgesia, anti-virus, anti-cytotoxic, anti-spasm, anti-tuberculosis, anti-oxidation, antimalarial, anti-hypertension, anti-obesity, anti-psychotic, anti-diabetes, etc.

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Si-Fe Catalyzed Biginelli Reaction : A Versatile Method for the Synthesis of Dihydropyrimidinones

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ABSTRACT

Dihydropyrimidinones were prepared involving Biginelli reaction of various aldehydes, urea/thiourea and ethyl acetoacetate in the presence of a heterogeneous Si-Fe catalyst.
Keywords : Biginelli Reaction, Multicomponent Reactions, Si-Fe Catalyst, Dihydropyrimidinone.

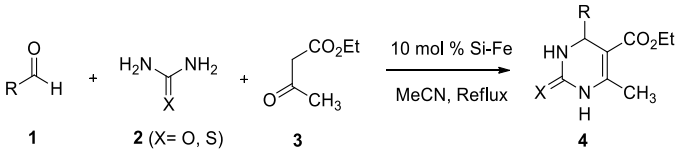
I. INTRODUCTION

Acid catalyst Biginelli reaction is a versatile route for the synthesis of dihydroprimidinones.[1-3] It is very useful intermediate having biological activity e.g. calcium channel blocker, antihypertensive, α-antagonist, antibacterial, antiviral antitumor, anti-inflammatory and HIV agents.[4-5] The several reports are available for the synthesis of dihydropyrimidinone by using acid catalyst like Conc. HCl, $BF_3.(OEt)_2$, Clay, $InCl_3$, $LaCl_3$, Lanthanide triflate, H_2SO_4, ceric ammonium nitrate, $Mn(OAc)_3$, ion-exchange resin, 1-*n*-buryl-3-methyl imidazolium tetra fluoroborate, $BiCl_3$, $LiClO_4$, $InBr_3$, $FeCl_3$, $ZnCl_4$, $Cu(OTf)_2$, $Bi(OTf)_3$, LiBr, ytterbium triflate, NH_4Cl, $MgBr_2$ and other reagents have been used for this transformation.[6-25] Due to their wide range of activity and importance, a simple and high yielding one-pot approach for the synthesis of dihydropyrimidinones is highly desirable.

Heterogeneous systems have tremendous advantages over homogeneous ones and through heterogenizing the catalysts of the reagents certain practical limitations of homogeneous systems can be eliminated. One of the most attractive advantages of heterogeneous systems is the easy separation and facile recovery of the solid catalyst from the products for recycling without tedious experimental workup. A simple, efficient and environment friendly, one-pot synthesis of dihydroprimidinones by direct condensation of aromatic aldehyde with acetoacetate esters and urea was undertaken using catalytic amount of Si-Fe complex.

II. RESULTS AND DISCUSSIONS

In continuation with our efforts to develop the new methods for the synthesis of bioactive organic compounds,[26] we have developed a new method for the synthesis of dihydropyrimidinone derivatives using heterogeneous Si-Fe catalyst in acetonitrile (**Scheme 1**). Si-Fe catalyst is prepared by using reported procedure in literature.[27] The reaction of benzaldehyde **1**, urea/thiourea **2** and acetoacetate **3** has been carried out in the presence of Si-Fe as a catalyst.



Scheme 1. Synthesis of dihydropyrimidinone derivatives

The generality of this method was examined by the reaction of several substituted aldehyde, acetoacetate and urea/thiourea using Si-Fe catalyzed in acetonitrile. The results are shown in **Table 1**. We have carried out similar reactions with various aldehydes **1** (1 mmol) with acetoacetate (1 mmol) and urea/thiourea (1.5 mmol) in the presence of Si-Fe catalyst (10 mol %). All the products obtained were confirmed by spectroscopic methods such as IR, ^1H NMR comparing with reported in literature.

Table 1. Si-Fe catalyzed synthesis of dihydropyrimidinone derivatives.

Entry	R	X	Time (hr)	Yield (%)
4a	Ph	O	18	90
4b	CH_3	O	16	88
4c	CH_3-CH_2	O	18	85
4d	CH_3-CH_2-CH_2	O	18	90
4e	4-(NO_2)-C_6H_4	O	18	80
4f	4-(Cl)-C_6H_4	O	20	85
4g	Ph-CH=CH	O	18	90
4h	3,4-di-(OMe)C_6H_3	O	18	88
4i	2-furyl	O	20	80
4j	5-methyl-2-furyl	O	20	95
4k	CH_3	S	20	80
4l	4-(Cl)-C_6H_4	S	20	82
4m	Ph-CH=CH	S	24	80

Reaction condition: **1** (a-m) (1 mmol), **2** (1 mmol), **3** (1.5 mmol), Si-Fe catalyst (10 mol%) in acetonitrile.

Aldehydes containing electron-donating or electron-withdrawing functional groups at different positions but it did not show any remarkable differences in the yields of product and reaction time. It was observed that the reaction of aromatic aldehydes with urea is very fast as compared to thiourea. The role of Si-Fe catalyst has been proposed to activate the aldehyde by binding the oxygen atom of aldehyde with transition metal Fe. Along with this we recovered the catalyst and reused for further reactions.

III. EXPERIMENTAL

General procedure for the synthesis of 3,4-dihydropyrimidinones: A solution of aldehyde (1.0 mmol), ethyl acetoacetate (156 mg, 1.2 mmol) and urea (72 mg, 1.2 mmol) in acetonitrile (6 ml) was heated under reflux conditions in the presence of Si-Fe catalyst (10% w/w) for 16-24h. The progress of the reaction was monitored by TLC. The reaction mixture was then poured on crushed ice and the solid product obtained was filtered and washed with ice-cold water. To recover the catalyst from the product, the mixture was treated with hot ethanol and filtered. The residue, being the catalyst, was dried and reused for the next run without noticeable effect on the product yield. The filtrate on concentration afforded the product, which was found to be sufficiently pure. The products obtained were characterized by spectral (NMR and IR) data and by comparison with those of authentic samples.

5-Ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (Entry 4a): White solid; **MP**: 206-208^oC; **IR** (neat) ν_{max}: 3327, 3214, 1695, 1663 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 1.08 (t, *J* = 7.2 Hz, 3H), 2.33 (s, 3H), 3.92 (q, *J* = 7.2 Hz, 2H), 5.22 (d, *J* = 2.8 Hz, 1H), 7.20-7.43 (m, 5H), 7.90 (s, 1H), 9.50 (s, 1H).

5-Ethoxycarbonyl-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1*H*)-one (Entry 4e): White solid; **MP**: 210-212^oC; **IR** (neat) ν_{max}: 3233, 1743, 1630 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 1.16 (t, *J* = 7.2 Hz, 3H), 2.34 (s, 3H), 4.06 (q, *J* = 7.2 Hz, 2H), 5.46 (d, *J* = 2.8 Hz, 1H), 6.51 (s, 1H), 7.49 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 8.8 Hz, 2H), 8.39 (s, 1H).

5-Ethoxycarbonyl-6-methyl-4-(4-chlorophenyl)-3, 4-dihydropyrimidin-2(1*H*)-one (Entry 4f): White solid; **MP**: 214-216^oC; **IR** (neat) ν_{max}: 3227, 1719, 1615 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 1.20 (t, *J* = 7.2 Hz, 3H), 2.37 (s, 3H), 4.11 (q, *J* = 7.2 Hz, 2H), 5.40 (d, *J* = 2.8 Hz, 1H), 5.79 (s, 1H), 7.23-7.232 (m, 4H), 7.98 (s, 1H).

IV. CONCLUSION

We disclose here a simple, clean, atom-efficient, synthesis of dihydropyrimidinones using Si-Fe as catalysts. A simple experimental procedure, relatively fast reaction rates and excellent yields are the key advantages of our protocol. Most significantly, efficiency, and cost-effectiveness will make this procedure useful to academia as well as industry.

V. Acknowledgements

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Theoretical Validation of Medicinal Properties of Ginger

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ABSTRACT

Molecular property and bio-activity scores of ten essential oil constituents present in Ocimum sanctum leaves were predicted using molinspiration software. For all the essential oil compounds, miLog P values were found to be <5 for compound 1-7 indicated their good permeability across the cell membrane and compound 8-10 shows miLog P values > 5 this shows these compounds were not easily permeable across the cell membrane. TPSA in the range of 0.00 -66.76 (well below 160Å2) and n violations= 1 or 0, molecular mass <500, n rotb < 5 [10], N0 of hydrogen bond donors ≤ 5 (the sum of OHs and NHs), No of hydrogen bond acceptor ≤ 10 (The sum of Os and Ns) were observed for these compounds. This indicate that these compounds were found to obey Lipinski's rule and can easily bind to receptor and were taken further for the calculation of bioactivity score by calculating the activity score of GPCR ligand, ion channel modulator, nuclear receptor ligand, kinase inhibitor, protease inhibitor and enzyme inhibitor.

Keywords: Molinspiration, Ocimum Sanctum, Bioactivity Score, Lipinski's Rule

I. INTRODUCTION

Zingiber officinale Roscoe (Zingiberaceae) known as adrak or ginger, is significant plant with numerous ethnomedicinal and dietary application. It is a rhizomatous perennial herb reaching up to 90 cm in height. Therhizomes are aromatic, thick lobed, white to yellowish-brown, unevenly branched, annulated and dense with smooth surface. It is initially originate in tropical Asia and now cultivated as a commercial crop in India, China, Australia, America, Africa as well as South East Asia. Ginger is cultivated in tropical and subtropical regions. It is grown by vegetative [1]. Ginger is planted during April-may and harvested about 7-8 months(December-January) after planting when the leaves turn yellow and steadily shrivel. They are washed properly and then dried to improve colour [2]. It is extensively utilized worldwide as a spice, flavoring agent and herbal remedy. In different traditional systems it is taken to cure a variety of diseases such as nausea, vomiting, asthma, palpitation, inflammation, dyspepsia, loss of appetite, constipation, digestion and pain [3,4]. It has been used in both fresh and dried forms for the treatment of cough, rheumatism, asthma, stroke, diabetes[5] and gastrointestinal cancer[6]. Chemical analysis of ginger shows that it contains over 400 different compounds. The major constituents in ginger rhizomes are carbohydrates (50-70%), lipids(3-8%), terpenes and phenolic compounds[7]. Terpene components of ginger include zingiberene, β-bisabolene, α-faresene, β-sesquiphellandrene and α-curcumene, while phenolic compounds include gingerol, paradols and shogaol. These gingerols (23-25%) and shogaol (18-25%) are found in higher quantity than others. Besides these amino acids, raw fiber, ash, protein, phytosterols, vitamins (e.g. nicotinic acid and vitamin A) and minerals are also present [8,9]. The aromatic constituents include zingiberene and bisabolene, while the pungent constituents are known as gingerols and shogaols[10]. Other ginerol- or shogaol related compounds (1-10%), which have been reported in ginger rhizome, include 6-paradol, 1-dehydrogingerdione, 6-gingerdione and 10-gingerdione, 4-gingerdiol, 6-gingerdiol, 8-gingerdiol and diarylheptanoids[11, 12]. The characteristic odour and flavour of ginger are due to mixture of volatile oils like shogaols and gingerols[13]. Because of remarkable biological activities of this plant, our aim to predict the molecular properties and to evaluate the bioactivity scores using molinspiration [14-16].

II. MATERIALS AND METHODS

Structures of all the ten compounds reported from Ginger were taken from the literature and their structures

were drawn using online molinspiration software (www.molinspiration.com) [14] for calculation of molecular properties (Log P, Total polar surface area, number of hydrogen bond donors and acceptors, molecular weight, number of atoms, number of rotatable bonds etc.) and prediction of bioactivity score for drug targets (GPCR ligands, kinase inhibitors, ion channel modulators, enzymes and nuclear receptors). The bioactivity score and drug likeness properties of the all the ten compounds were compared.

Prediction of bio-activity

1. Molecular properties of nine alkoxy derivative of Naringenin were calculated using molinspiration and the values were given in Table 1.
2. Bio-activity scores of the nine alkoxy towards GPCR ligand, ion channel modulator, nuclear receptor ligand, kinase inhibitor, protease inhibitor and enzyme inhibitors were given in Table 2.

Lipinski's Rule:

Lipinski's rule of five commonly known as the Pfizer's rule of five or simply the Rule of five is a regulation of thumb to estimate drug likeness or to indentify a chemical compound with a certain pharmacological or biological activity has properties that would make it a likely orally active drug in man. The principle was designed by Christopher A. Lipinski in 1997. The rule expresses molecular properties vital for a drug's pharmacokinetics in the human body, including their absorption, distribution, metabolism and elimination (ADME) Components of the Lipinski's rule [5, 6].

Lipinski's rule states:

- ✓ Not more than 5 hydrogen bond donors (nitrogen or oxygen atoms with one or more hydrogen atoms)
- ✓ Not more than 10 hydrogen bond acceptors (nitrogen or oxygen atoms)
- ✓ A molecular weight less than 500
- ✓ An octanol-water partition coefficient log P not greater than 5
- ✓ No more than one number of violation

Molinspiration

Molinspiration, web based software was used to obtain parameter such as MiLogP, TPSA, drug likeness. MiLogP, is estimated by the methodology developed by Molinspiration as a sum of fragment based contributions and correction factors. MiLog P parameter is applied to check good permeability across the cell membrane. TPSA is related to the hydrogen bonding potential of the compound. Computation of volume developed at Molinspiration is based on group contributors. Number of rotatable bonds measures molecular flexibility. It is a very good descriptor of absorption and bioavailability of drugs. Through drug likeness data's of a particle, it can be checked molecular properties and structure feature with regard to known drugs.

Bioactivity score

Bioactivity of the drug can be found out by estimating the activity score of GPCR ligand, ion channel modulator, nuclear receptor ligand, kinase inhibitor, protease inhibitor, enzyme inhibitor. All the parameters were determined with the aid of software Molinspiration drug-likeness score online (www.molinspiration.com). Calculated drug likeness score of each compound and compared with the specific bodily process of each compound.For organic molecules the probability is if the bioactivity score is (>0), then it is active, if (-5.0-0.0) then moderately active, if (< -5.0) then inactive.

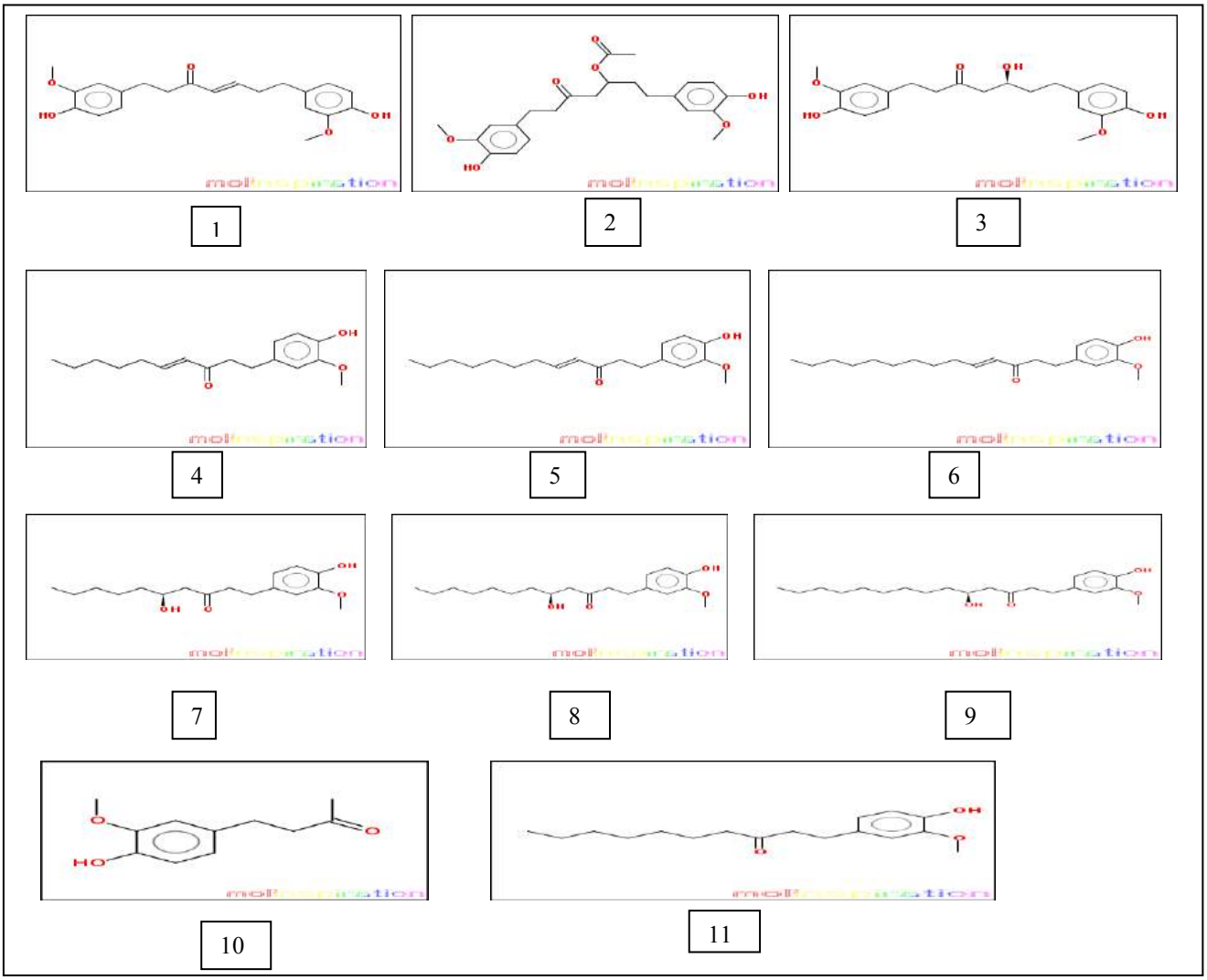

Figure 1

Table 1. Calculation of Molecular properties rttttt

S.N	Compound	miLogP	TPSA	natoms	MW	nON	noHNH	nviolations	nrobt	Volume
1	1	3.32	76.00	26	356.42	5	2	0	9	336.19
2	2	3.13	102.30	30	416.47	7	2	0	12	386.93
3	3	2.43	96.22	27	374.43	6	3	0	10	350.42
4	4	4.35	46.53	20	276.38	3	1	0	9	281.38
5	5	5.36	46.53	22	304.43	3	1	1	11	314.98
6	6	6.37	46.53	24	332.48	3	1	1	13	348.59
7	7	3.22	66.76	21	294.39	4	2	0	10	295.61
8	8	4.23	66.76	23	322.44	4	2	0	12	329.21
9	9	5.24	66.76	25	350.50	4	2	1	14	362.82
10	10	1.52	46.53	14	194.23	3	1	0	4	186.75
11	11	4.60	46.53	20	278.39	3	1	0	10	287.57

Table 2. Bioactivity score

S.No	Compound	GPCR Ligand	Ion channel modulator	Kinase inhibitor	Nuclear receptor ligand	Protease inhibitor	Enzyme inhibitor
1	1	0.13	0.06	-0.25	0.23	0.09	0.23
2	2	0.12	0.06	-0.30	0.13	0.16	0.26
3	3	0.18	0.08	-0.19	0.19	0.21	0.31
4	4	0.06	0.01	-0.50	0.20	-0.05	0.29
5	5	0.11	0.01	-0.39	0.26	0.03	0.27
6	6	0.13	0.01	-0.34	0.26	0.07	0.25
7	7	0.16	0.04	-0.33	0.20	0.15	0.38
8	8	0.18	0.03	-0.27	0.23	0.20	0.34
9	9	0.18	0.03	-0.24	0.22	0.21	0.32
10	10	-0.58	-0.18	-1.15	-0.59	-0.72	-0.07
11	11	-0.01	-0.04	-0.47	0.08	-0.09	0.18

III. RESULTS AND DISCUSSION

a. Molecular property of the Chalcones:

The ten oil constituents obeyed the Lipinski's rule of five and showed good drug likeness scores. MiLog P values of these oily compounds were found to be < 5 (1.07-4.60 for compounds 1 to 4, 7 to 8, 10-11) indicated their good permeability across the cell membrane. All the derivatives were found to have TPSA will be below 160Å^2 (100.13), molecular weight < 500, No. of hydrogen bond donors ≤ 5, No. of hydrogen acceptor ≤ 10, n-violations 0, number of rotatable flexible bonds >5.

b. Bioactivity scores of the components of Ginger:

The bioactivity scores of the ten compounds have shown the following observations.

1. GPCR Ligand: Among the ten compounds were found to be moderately active (≤ 0) and compound no 3, 8 and 9 shows highly active (≥ 0) towards GPCR ligands.
2. Ion channel modulator: Among the ten compounds compound 3 were found to be highly active (≥0). The remaining compounds were to be moderately active (≤ 0).
3. Kinase inhibitor: All ten compounds were found to be inactive (≤ 0) towards Kinase inhibitor.
4. Nuclear receptor ligand: Among the ten compounds, compound no 5-6 were found to be highly active (≥ 0) towards Nuclear receptor ligand. The remaining compounds were to be moderately active (≤ 0).
5. Protease inhibitor: Among the ten compounds, compound no 8- 9 were found to be highly active (≥ 0) towards Protease inhibitor. The remaining compounds were to be moderately active (≤ 0).
6. Enzyme inhibitor: Among the ten compounds, compound no 7-9 were found to be highly active (≥ 0) towards Enzyme inhibitor. The remaining compounds were to be moderately active (≤ 0).

IV. Conclusion

In conclusion, eleven compound show highly active to moderate bioactivity score. All compounds obey Lipinski's rule for Drug Likeness activity of the molecules.

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Miraculous Properties of Lohabhasma Proven by Modern Techniques

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ABSTRACT

Ayurvedic system of medicine includes an important class of drugs of mineral origin under which there is as subclass known as ayurvedicbhasmas. These are derived from metals like gold, silver, copper, iron, lead, supreme medicines due to their extraordinary medicinal properties. However, according to the modern science, heavy metals referred above are difficult to absorb at cellular levels and therefore are toxic and harmful to human bodies. As against this according toayurved, all these elements, after ayurvedic processes of bhasmikarananot only lose their toxicity but miraculous medicinal properties are induced when they are transformed into what is called as bhasma state. In an attempt to elucidate the exact nature of this bhasma state, we found that a genuine ayuvidicbhasma possesses two characteristics (i) extremelytiny particle size, tending to nano level of the order of 20-90 nm and (ii) attachment of an organic components to these nanosizedbhasma particles. These findings are expected to be useful to throw light on the medicinal potential of ayurvedicbhasma.

Keywords : Ayurvedic System , Bhasma, E-DAX, XRD

I. INTRODUCTION

Ayurved firstly introduced the concept of "Bhasma" in its medicinal system. Originally, ayurvedic system of medicine was mostly restricted to medicinal plants (vanaushadhi) and to, some extent to animal products such as cowurine, cowdung, cowmilk, honey etc. Later on metal-based bhasmas were introduced and subsequently they constituted the most important class of drugs of mineral origin.

The art and sciene of ayurvedicbhasmas in general and metal-based bhasmas in particular is the subject of "ayurved rasashastra" ,which is an extremely important and interesting branch of ayurved. The origin, history, developments in ayurvedrasashastra is itself an attractive and promising area for research especially for chemists. Research in this subject will be also relevant and encouraging in coming years because ayurved and ayurvedic medicines will receive more and more appreciation and importance all over the world. Metal-based ayurvidic drugs being the superior drugs as compared to all other classes of drugs, there is an excellent opportunity to rejuvenate this original art with the help of modern scientific developments. The present work is an attempt from this point of view.

II. SYNTHESIS AND CHARACTERIZATION OF METALLICBHASMAS

Synthesis of Metallic Bhasmas.

Preparation of bhasma is an elaborate process involving shodhana, marana and bhasmikarana. The classical texts of Ayurveda prescribe in detail these processes. Metals are first purified through a process called shodhana, during which the metal is repeatedly heated and then cooled in herbal extracts. This is fillowed by bhasmikarana where, the shodhit metal is repeatedly triturated with herbs (bhavana) and calcinated in closed earthen crucibles in a pit, by buringcowdung cakes (a Process called puta), to obtain bhasma. The size of pit, the number of cowdung cakes to be used to obtain a specific temperature and duration of heating are specified in detail in standard ayurvedic texts. This process is repeated as many times as prescribed in classical texts for each preparation. Thus we have dashaputa (10 cycles), shataputa (100 cycles), Sahastraputa (1000 cycles) etc. to ensure that the bhasma is properly prepared. To confirm the formation of a genuine bhasma a set of tests are also specified (Ayurvedic Formulary of India, 2003).

Though bhasma preparations are widely used in ayurved, practically noting is known as to what happens to the metal when it is subjected to bhavana with herbs and subsequent calcinations processes. The traditional texts also don't throw any light on the changes undergone by a metal during the obove processes.

The synthesis of an ayurvedicbhasma generally involves three major steps given below and illustrated in following flow sheet Ayurvedic purification of the metal (shuddhi).

a. Destruction of metallic state (marana).
b. Conversion of crude product into bhasma state (bhasmikarana).

Synthesis of Lohabhasma as a representative example

There are numerous methods reported in literature for the synthesis of lohabhasma which is an ancient and famous iron based ayurvedic preparation. Out of these following three methods are selected for the present work.

1.1 Method Using Plant (Kanchnar) Material

In this method the general purification was first done by the standard method. For special purification trifala extract was prepared in cowurine and the above processed iron powder was heated to red heat and then dipped in this extract successively seven times. The process of marana was done in the juice of kanchnar (bauhinia variegate). For this purpose the purified iron powder was mixed with this plant juice in a mortar and the mixture was triturated till a homogenous paste is formed. This paste was transformed to closed crucible system and then subjected to gaja-puta.

The process of bhasmikarana was also done in the same way as that for marana but here the trituration for plant juice followed by gaja-puta was repeated seven times.

1.2 Method Using cow-urine

In this method the first operation was identical with that described for general purification.For special purification, the above processed iron powder (500g) was heated and dipped in freshly collected cow-urine. This operation of heating and dipping the hot iron powder in cow urine was repeated seven times.

After special purification, the iron powder was taken in a mortar and mixed with cowurine and the mixture was triturated for six hours keeping it in viscous state. This mixture was kept overnight for interaction to complete the destruction of metallic state (marana).
Finally for bhasmikarana, the above iron powder is mixed with cow-urine in a mortar and triturated till a homogenous paste is obtained. The paste is transferred to closed crucible system and subjected to gaja-puta. Total seven gaja-puta are given

Finally for bhasmikarana, the above iron powder is mixed with lemon juice in a mortar and triturated till a homogenous paste is obtained. The paste is transferred to closed crucible system and subjected to gaja-puta. Total six gaja-puta are given.

III. Characterization and particle size Determination

Chemical Composition by E-DAX

The quantitative determination of the elemental constituents of the two lohabhasma samples to establish their chemical composition was done through EDAX model Inc

Mahwah NJ USA. The E-DAX patterns are shown in figure 1.1 and the result of analysis is shown in table 1.1

Table 1.1. Chemical Composition by E-DAX

Method	C	O	Fe	Al	Si	Cr	K	S	Ca
Method I	30.40	28.07	35.60	0.40	1.02	—	0.15	0.58	1.91
Method II	36.93	28.30	29.14	—	0.77	3.43	1.17	0.26	—

1.3 Phase analysis by XRD and partile size determination

The investigations were done to examine the crystalline modifications of iron oxides. The XRD patterns were recorded on Phillips X-pert Pro Powder diffratometer in the diffraction range (10.90)2. Debye Scherrer equation was used to calculate mean crystallite size.

The XRD patterns with relevant details are shown in Fig. 2.2 while the results of phase analysis and particle size determination are shown in Table 2

Table 2.2. components identified through XRD

Sr. No.	Method	Major Constituent	Solid State Nature	Crystallite Size
1.	Method I	Hamatite	Microcrystalline	39.7 nm
2.	Method II	Fe2O3	Mostly Amorhous	23.5 nm

Evidence for organic component [14]

The significant percentage of carbon identified by E-DAX and the nature of the IR spectra of lohabhasma (as well as for metallic bhasmas obtained from other metals) give some indications in favour of the presence of organic components associated with lohabhasma particles. However, since EDAX is unable to detect the presence of hydrogen and solid state IR spectra show poor resolution, some confirmatory evidence to support the presence of such organic component is necessary. For this purpose samples of lohabhasma(method II) were refluxedon pure toluene for 12 hour for three successive times and the soluble part was isolated. The IR spectra as well as electronic spectra (200-700 nm) in spectroscopic chloroform are then recorded)Tjese spectra gave confirmatory evidence for the presence of organic components. The exact nature of this component is under investigation at present.

IV. Conclusions

According to the ayurvedic principals, metals as well as non-metals alone, cannot exhibit extraordinary medicinal properties in their inorganic from. Therefore, pure metal oxides; sulfides; silicates; carbonates or phosphates are not known to possess significant medicinal properties and also they are not assimiable to human bodies. But when they are transformed info their bhasma state miraculous medicinal properties are claimed to be induced in them. Two major factors seem to be responsible for induction of tremendous medicinal potential in the bhasma state. These may be (a) extremely tiny size tending to nanolevel (10-90 nm) of the bhasma particles and (b) organic component imparted to these tiny bhasma particles.

In the present work, encouraging experimental evidence is obtained in favour of both these factors. Similar results and evidence is obtained in metallic

bhasmas derived from copper, gold, tin and zinc. These result and evidences are expected to be useful to throw some light on the nature of ayurvedicbhasmas and their claimed extraordinary medicinal properties.

V. Acknowledgement:

Im very much thankful to Dr. B.A Kulkarni ,Dr. RajendraKankaruya and MrudulaWadekar for cooperation to me for doing this work.

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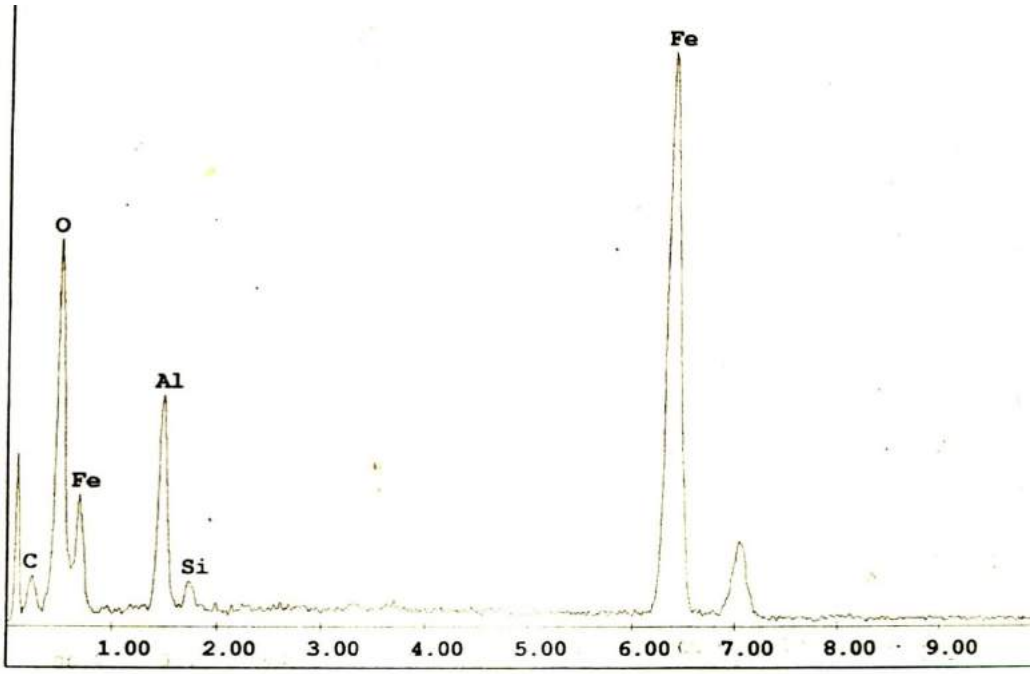
E-DAX ANALYSIS

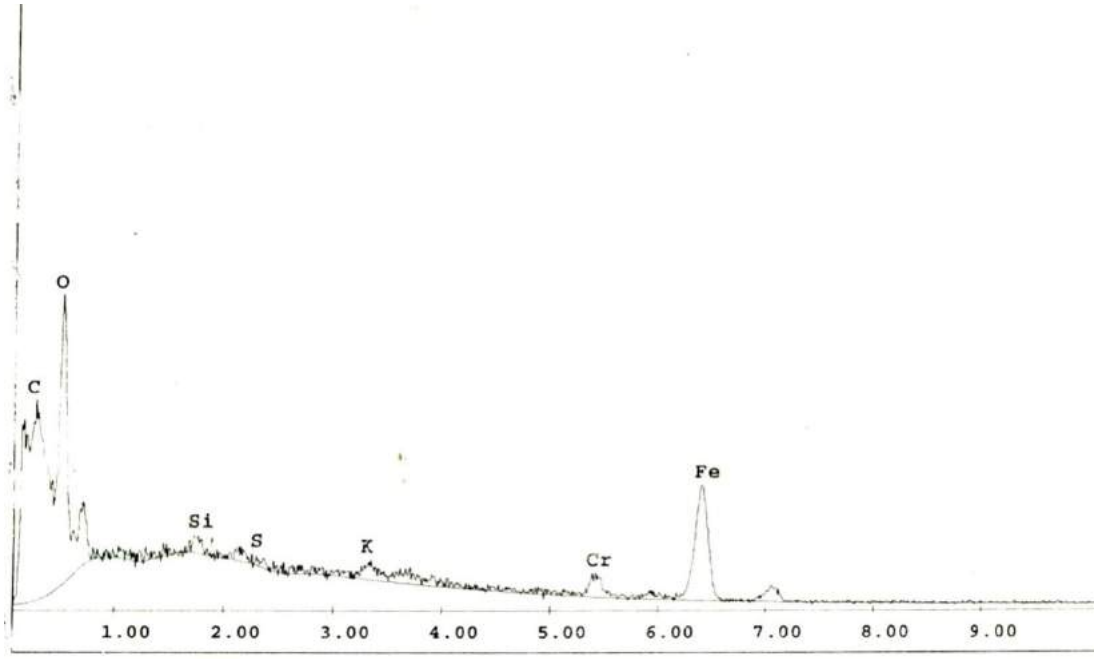
Figure No. : 3.6.1 Loha – 01



Element	Wt %
CK	12.95
OK	24.66
AlK	9.86
SiK	1.01
FeK	51.52

Loha - 02

Figure No. : 3.6.2



Element	Wt%
C K	36.93
O K	28.30
Si K	0.77
S K	0.26
KK	1.17
Cr K	3.43
Fe K	29.14
Total	100.00

XRD PATTERNS OF SYNTHESIZED *LOHABHASMA*

Figure No.: 3.7.1

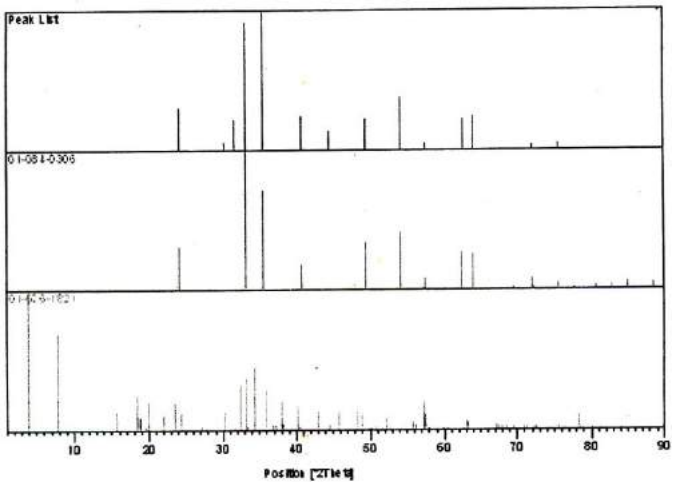
XRD patterns of

Loha-01

Anchor Scan Parameters :

Sample Identification	:	694
Comment	:	Fe203 RGS R1 100108
Measurement Date / Time	:	1/10/2008 1:52:08 PM
Raw Data Origin	:	XRD measurement (*.XRDML)
Scan Axis	:	Gonio
Start Position [^{0}2Th]	:	10.0100
End Position [^{0}2Th]	:	79.9900
Step Size [^{0}2Th]	:	0.0200
Scan Step Time [s]	:	1.0000
Scan Type	:	Continuous
Offset [^{0}2Th]	:	0.0000
Divergence Slit Type	:	Fixed
Divergence Slit Size [^{0}]	:	0.8709
Specimen Length [mm]	:	10.00
Receiving Slit Size [mm]	:	0.1000
Measurement Temperature [^{0}C]	:	25.00
Anode Material	:	Cu
Generator Settings	:	40kV. 30mA
Goniometer Radius [mm]	:	240.00
Dist. Focus-Diverg. Slit [mm]	:	100.00
Incident Beam Monochromator	:	No
Spinning	:	No

Graphics :



Name and Formula		
Reference Code	:	01-076-1821
ICSD Name	:	Iron Oxide
Empirical Formula	:	Fe_2O_3
Chemical Formula	:	Fe_2O_3
Crystallographic Parameters		
Crystal System	:	Hexagonal
Space Group	:	P3
Space Group Number	:	143
a (Å)	:	5.5600
b (Å)	:	5.5600
c (Å)	:	22.5500
Alpha (º)	:	90.0000
Beta (º)	:	90.0000
Gamma (º)	:	120.0000
Calculated density	:	2.63
Volume of cell	:	603.71
Z	:	6.00
RIR	:	2.08

Name and Formula		
Reference Code	:	01-084-0306
ICSD Name	:	Iron Oxide
Empirical Formula	:	Fe_2O_3
Chemical Formula	:	Fe_2O_3
Crystallographic Parameters		
Crystal System	:	Rhombohedral
Space Group	:	R-3c
Space Group Number	:	167
a (Å)	:	5.0347
b (Å)	:	5.0347
c (Å)	:	13.7473
Alpha (º)	:	90.0000
Beta (º)	:	90.0000
Gamma (º)	:	120.0000
Calculated density	:	5.27
Volume of cell	:	301.78
Z	:	6.00
RIR	:	3.27

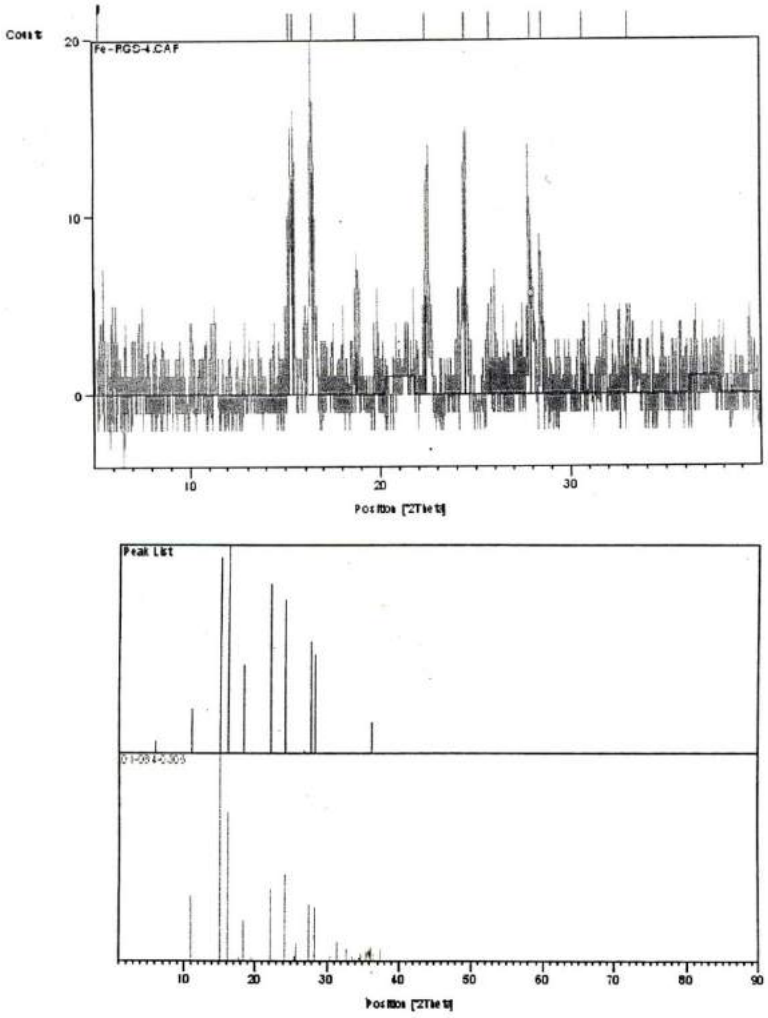
Figure No. : 3.7.2
XRD patterns of
Loha-02

Anchor Scan Parameters :

Sample Identification	:	654
Comment	:	Fe-RGS-4, Pyro 18/06/07
Comment	:	CuCeO2, 75,2%, 160C
Measurement Date / Time	:	6/18/2007 3:42:12 PM
Raw Data Origin	:	XRD measurement (*.XRDML)
Scan Axis	:	Gonio
Start Position [02Th]	:	5.0100
End Position [02Th]	:	39.9900
Step Size [02Th]	:	0.0200
Scan Step Time [s]	:	1.0000
Scan Type	:	Continuous
Offset [02Th]	:	0.0000
Divergence Slit Type	:	Fixed
Divergence Slit Size [0]	:	0.8709
Specimen Length [mm]	:	10.00
Receiving Slit Size [mm]	:	0.1000
Measurement Temperature [0C]	:	25.00

Anode Material	:	Mo
Generator Settings	:	40kV. 30mA
Goniometer Radius [mm]	:	240.00
Dist. Focus-Diverg. Slit [mm]	:	100.00
Incident Beam Monochromator	:	No
Spinning	:	No

Graphics :



Name and Formula		
Reference Code	:	01-084-0311
ICSD Name	:	Iron Oxide
Empirical Formula	:	Fe_2O_3
Chemical Formula	:	Fe_2O_3
Crystallographic Parameters		
Crystal System	:	Rhombohedral
Space Group	:	R-3c
Space Group Number	:	167
a (Å)	:	5.0016
b (Å)	:	5.0016
c (Å)	:	13.6202
Alpha (º)	:	90.0000
Beta (º)	:	90.0000
Gamma (º)	:	120.0000
Calculated density	:	5.39
Volume of cell	:	295.07
Z	:	6.00
RIR	:	3.28

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Antimicrobial Activity and Phytochemical Analysis of Carica Papaya Leaves, Root Extracts

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ABSTRACT

The leaves and roots of Caricapapaya were screened for its antimicrobial and phytochemical activities. The solvents used for the leaves and root extraction were benzene, acetone, aqueous. The extract was tested against infectious disease causing bacterial such asEscherichia coli, Pseudomonas aerginosa, staphylococcus aureus using the well diffusion method. The benzene, acetone extract of leaves of Carica papaya inhibition against all the test microbe ranging from 11mm to 13mm diameter inhibitory zone. The acetone and aqueous extract of root of Carica papaya inhibition against all the test microbe ranging from varying zone of inhibition of the growth of tested organism than benzene, acetone, aqueous, phytochemical properties of leaves and roots of Carica papaya obtain from, benzene, acetone, aqueous extract were investigated. The result confirmed that the presence of antibacterial activity and phytochemical in the shade dried extract of Carica papayaagainst the human pathogenic organisms.
Keyword: Carica Papaya Extract, Phytochemicals, Antimicrobial Activity.

I. INTRODUCTION

Medicinal plants have been identified and used throughout human history. Plants have the ability to synthesize a wide variety of chemical compounds that are used to perform important biological functions, and to defend against attack from predators such as insects, fungi and herbivorousmammals. At least 12,000 such compounds have been isolated so far; a number estimated to be less than 10% of the total (1) Chemical compounds in plants mediate their effects on the human body through processes identical to those already well understood for the chemical compounds in conventional drugs; thus herbal medicines do not differ greatly from conventional drugs in terms of how they work. This enables herbal medicines to be as effective as conventional medicines, but also gives them the same potential to cause harmful side effects (2).

Caricapapaya is one of the medicinal plants available on the earth; *Caricapapaya* belonging to family*caricaceae* is commonly known as papaya in English, papita in Hindi and erandakarkati in Sanskrit. [3, 4] Papaya is a powerhouse of nutrients and is available throughout the year. It is a rich source of threes powerful antioxidant vitamin C, vitamin A and vitamin E; the minerals, magnesium and potassium; the B vitamin pantothenic acid and folate and fiber. In addition to all this, it contains a digestive enzyme papaintha effectively treats causes of trauma, allergies and sports injuries. All the nutrients of papaya as a whole improve cardiovascular system, protect against heart diseases, heart attacks, strokes and prevent colon cancer. The fruit is an excellent source of beta carotene that prevents damage caused by free radicals that may cause some forms of cancer. It is reported that it helps in the prevention of diabetic heart disease. Papaya lowers high cholesterol levels as it is a good source of fiber.[5]

II. MATERIALS AND METHODS

A. COLLECTION OF PLANT MATERIAL

Collection of plant material the leaves, roots of *Carica papaya* were done from the area around pachore, Madhya Pradesh. The whole plant and parts were done by Phytochemical extraction and screening.

B. EXTRACTION OF PLANT

The leaves of *Carica papaya* were allowed to dry in shade for week and then grounded into fine powder in mixer grinder. 10 gm of dried powder was subjected to

soxhlet extraction with 200 ml of solvents starting from Benzene, followed by extraction with other solvents Benzene and Acetone and pure distilled water in separate ways. Soxhlet process was allowed to carry out till the complete exhaustion of sample material use for extraction with the maintenance of temperature below the boiling points of the solvents used. The extract in crystalline/slurry form which were suitably diluted and used for preliminary phytochemical analysis and studies of their antimicrobial activity.

The twigs of the roots of *Carica papaya* were washed and allowed to dry in shade for a week and then grounded into fine powder in mixer grinder. Similar as the extraction for leaves, 10 grams of dried powder of roots was subjected to soxhlet extraction with 200 ml of solvents starting from Benzene, followed by extraction with other solvents Acetone, and pure distilled water in separate ways. Soxhlet process was allowed to carry out till the complete exhaustion of sample material use for extraction with the maintenance of temperature below the boiling points of the solvents used. The extract in crystalline/slurry form which were suitably diluted and used for preliminary phytochemical analysis and studies of their antimicrobial activity.

C. PHYTOCHEMICAL ANALYSIS OF THE EXTRACT

A small portion of the extracts were subjected to the phytochemical test using Harbourne's(1983) methods to test for alkaloids, tannis, saponins, flavonoids, glycosides, steroids, phenolic compound, amino acids.[6]

Test for alkaloids: About 0.2 g extract warmed with 2% H2SO4 for two minutes, filtered and few drops of Dragendorff's reagent added orange red precipitate indicates the presence of alkaloids. And or filtrates were treated with Wagner's reagent (Iodine in Potassium Iodide). Formation of brown/reddish precipitate indicates the presence of alkaloids.

Test for glycosides: The extracts hydrolyzed with HCl solutions and neutralized with NaOH solutions. A few drops of Fehling solution A and B were added. Red precipitate indicates the presence of glycoside. Another test use was Benedict's test, in which the filtrates were treated with Benedict's reagent and heated gently. Orange red precipitate indicates the presence of reducing sugars.

Test for tannins: Small quantity of extracts mixed with water, heated, filtered and ferric chloride added. A dark green solution indicates the presence of tannins.

Test for saponins: About 0.2g of the extracts shaken with 5ml of distilled water and then heated to boil frothing (appearance of creamy mix of small bubbles) shows the presence of saponins.

Test for flavonoids: Extract of about 0.2 g of the extracts shaken with 5ml of distilled water and then a few drops of 10% lead acetate solution is added. A yellow or dirty white precipitate shows the presence of flavonoids.

D. CULTURE MEDIA AND INOCULUM PREPARATION

Nutrient agar broth cultures of the pure culture isolates of *Staphylococcus aureus, E. coli and Pseudomonas aeruginosa* were prepared by transferring a loop of culture into sterile nutrient broth and incubated at 37^{o}C for 48hours. A loop full was taken from these broths and seeded onto sterile nutrient agar plates through sterile cotton swab to develop diffused heavy lawn culture.

E. ANTIMICROBIAL ACTIVITY

The well diffusion method was used to determine the antibacterial activity of the extracts prepared from the*Carica papaya* leaves and roots using standard procedure. In this method, first the test bacteria broth of bacteria is used to inoculate on the nutrient agar plates with the help of sterile cotton swabs to develop the lawn culture. Then to these plates 6 mm diameter well are punched in agar plates pre-inoculated with test microorganisms Undiluted overnight broth cultures should never be used as an inoculum. Routine direct application of suitably diluted extracts is poured into the well. The plates were incubated at 37oC for 24 hr. and then examined for clear zones of inhibition. Sterile water was used as control. [7]

III. RESULT AND DISCUSSION

PHYTOCHEMICAL ANALYSIS OF BIOACTIVE COMPOUND IN DIFFERENT SOLVENTS EXTRACTS OF CARICA PAPAYA

The plant leaves extracts in different solvent were screened for the presence of various bioactive phytochemical compounds. The acetone leaves extract ofcarica papaya were found in alkaloids, glycosides, saponins, flavonoids, amino acids and phenolic compounds although tannins, and steroids are absent. The benzene leaves extract ofcarica papaya were found in alkaloids, glycosides, saponins, flavonoids, amino acids although tannins, phenolic compound and steroids are absent. The aqueous leaves extract of carica papaya were found in tannins, saponins, phenolic compound and steroids although alkaloids, glycosides, flavonoids, amino acids are absent. The aqueousroot extractof caricapapyawere found in alkaloids, tannins, saponins, flavonoids, phenolic, steroids althoughglycosides and amino acid are absent. The actone root extract ofcarica papaya were found in alkaloids, tannins glycosides, saponins, phenolic although flavonoids, amino acids, steroidsare absent. The benzene root extract ofcarica papaya were found in alkaloids, glycosides, saponins, flavonoids, steroids although tannins, amino acids, phenolic compound are absent. This were documented in table 1 and 2.

Table 1. phytochemical analysis of *Carica papaya* extracts from Leaves.

S.N.	Constituents	Benzene extract	Acetone extract	Aqueous extract
1	Alkaloids	+	+	-
2	Tannins	-	-	+
3	Glycosides	+	+	-
4	Saponins	+	+	+
5	flavonoids	+	+	-
6	Amino acids	+	+	-
7	Phenolic compound	-	+	+
8	steroids	-	-	+

[(+) means present, (-) means absent]

Table 2. Phytochemical analysis of Carica papaya extract from roots.

S.N.	Constituents	Benzene extract	Acetone extract	Aqueous extract
1	Alkaloids	+	+	+
2	Tannins	-	+	+
3	Glycosides	+	+	-
4	Saponins	+	+	+
5	Flavonoids	+	-	+
6	Amino acids	-	-	-
7	Phenolic	-	+	+
8	Steroids	+	-	+

ANTIMICROBIAL ACTIVITY OF DIFFERENT ORGANIC SOLVENT EXTRACTS OF CARICA PAPAYA

Antimicrobial activity of different solvents extract of *Carica papaya* is shown in table that the benzene, acetone extract of leaves of Carica *papaya*impart sufficient inhibitory actions against the test microbe ranging from 7 mm to 13 mm diameter inhibitory zones. And put of the aqueous extract only limitedinhibition was observe.

The acetone and aqueous extracts of *Carica papaya* impart sufficient inhibitory action against the test microbe ranging from 10 to 16 mm diameter inhibitory zones. The acetone extract of root has maximum zone of inhibition against the *Staphylococcus aureus* the common Gram positive pathogenic microorganism and this is the maximum inhibitory potential out of the all extracts viz. leaves and roots. And benzene extract of root only inhibition zone observe is against of Escherichia *coli*. The result of antibacterial activity is shown in table 3 and 4 and figure 1 and 2.

Table 3. Result of the antimicrobial activity of leaf extracts of Carica papaya

S.N.	Test microbes	Zone of Inhibition due to *carica papaya* Leaf extract 1mg/ml (in mm)		
		Benzene extract	Acetone extract	Aqueous extract
1.	*Staphylococcus aureus*	7	13	Nil
2.	*Escherichia coli*	11	10	3
3.	*Pseudomonas aeruginosa*	7	9	5

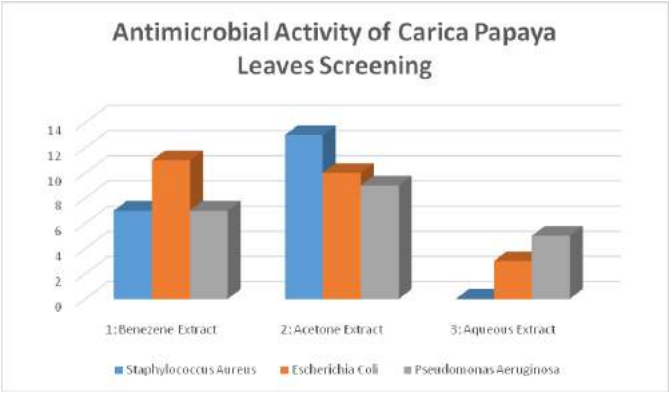

Figure 1. Graphical representation of Antimicrobial Activity of Carica papaya leaves of extract to three test species.

Table 4. Result of the antimicrobial activity of root extracts of Carica papaya

S.N.	Test microbes	Zone of Inhibition due to Carica papaya Root extract 1mg/ml (in mm)		
		Benzene extract	Acetone extract	Aqueous extract
1.	*Staphylococcus aureus*	Nil	16	14
2.	*Escherichia coli*	10	12	11
3.	*Pseudomonas aeruginosa*	Nil	10	12

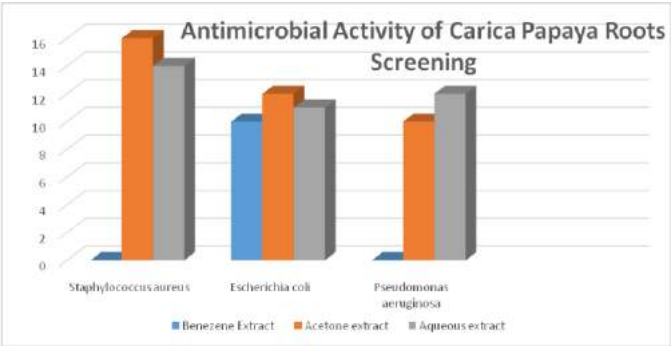

Figure 2. Graphical representation of Antimicrobial Activity of Carica papaya roots of extract to three test species.

IV. CONCLUSION

The phytochemical analysis revealed the bioactive compounds which are responsible for the in vitro antimicrobial of Carica papaya our all bacterial strains in all extracts could be benzene, acetone, aqueous extract of various parts of Caricapapaya might be exploited as a natural drug for the treatment of several infectious diseases caused by these organisms and could be useful in understanding the relations between traditional cures and current medications.

Our results showed that in present work that extracts obtained leaves of the plant Carica papaya using various solvent are rich sources of potent phytochemicals especially the leaves extract and has inhibitory effects on the experimental microbes. From previous studies and the current work, it is clear that the plants is rich source of alkaloids, glycosides, tannins, saponins, flavonoids, steroids, phlobatannis. These bioactive complex phytochemicals can be used for the development of potent drugs, medicines or antimicrobial agents that can be used for various purpose for human welfare upon further extensive and systematic studies.

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A simple, convenient Grape Juice Catalyzed Synthesis of Dihydropyrimidinone/thione by Grindstone Technique : A Green chemistry Approach

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ABSTRACT

Multicomponent reactions (MCRs) are chemical reactions in which three or more compounds react to form a single product. In the present work Biginelli reaction was accomplished just by grinding equimolar quantities of ethyl acetoacetate, Urea/thiourea and aryl aldehyde with grape juice as a catalyst for 15 to 20 minutes at ambient condition. The crude product was recrystallized by ethanol. This protocol is a greener approach for organic transformations, thus facilitating efficient synthesis of bioactive compounds in environmentally benign way with shorter reaction time, mild reaction conditions, and easy workup with excellent yield of the product.

Keywords : Green Chemistry, Grape Juice, Multicomponent Reaction, Grindstone Technique.

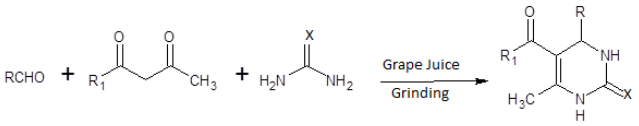
I. INTRODUCTION

The concept of "Green Chemistry"[1] has been widely adopted to meet the fundamental scientific challenges of protecting human health and environment while simultaneously achieving commercial viability. One of the thrust areas for achieving this target is to explore aqueous reaction medium for accomplishing the desired chemical transformation and eliminating the use of organic solvents.[2] Multicomponent reactions (MCRs) can provide products with diversity needed in the discovery of new compounds using simple and nonhazardous process[3-5]. Multicomponent reactions have been successfully adopted by the chemists for the synthesis of a large library of biologically active molecules. The multicomponent reactions (MCR's) are one of the most important protocols in organic synthesis and medicinal chemistry[6].These unique characteristics of the multicomponent reaction have attracted the attention of organic chemists. Moreover, higher selectivity is usually observed and the products can be easily isolated with good chemical purity by simple filtration avoiding more time consumption and tedious extractive workup. Recently great attention has been diverted towards cyclic and acyclic nitrogen containing heterocyclic compounds in pharmaceuticals as well as for medicinal purposes. Heterocyclic molecules are of biological interest due to their potential physical and chemical properties.[7] 3,4-Dihydropyrimidin-2(1H)-ones and thiones derivative have attracted increasing interest owing to their therapeutic and pharmaceutical properties, such as antiviral, antibacterial, anti-inflammatory and anti-tumour activities.[8-10]

Designing and development of non-hazardous synthetic methodologies for various organic transformations is one of the latest challenges to the organic chemists. Importance is now given for the development of environmental friendly and economic processes. Recent trends in organic synthesis utilize a non-conventional green techniques such as ultrasound (sonochemistry), microwave irradiation, grinding and by using ionic liquids which have also been proved to have many advantages[11]. Development of non- polluting, ecofriendly non-hazardous synthetic methodologies for organic reactions is one of the latest challenges to the

organic chemists. Even less hazardous byproducts are not desirable because of the growing concern for the environment. Lots of attempts are being made not only to quantify the greenness of a chemical process but also to consider factors such as product yield, the price of reaction components, safety in handling chemicals, hardware demands, energy consumptions and ease of product workup and purification. Grindstone technique has been considered as a clean and useful protocol in organic synthesis over the last few decades. In this technique, reaction occurs through generation of local heat by grinding the solid reactants using mortar and pestle. Reactions are initiated by grinding, with the small amount of energy through friction. The grinding reactions are simple to handle, reduce pollution, comparatively cheaper to operate and may be regarded as more economical and ecological [12-14].

The role of naturally available fruit juice in organic synthesis has attracted the interest of chemists, particularly from the view of green chemistry. In literature, a number of organic reactions using natural catalysts such as clay [15-16], natural phosphates [17-19], animal bone [20] and various fruit juices are reported. Due to acidic nature aqueous fruit juice like lemon [21-26], pineapple [27-28], coconut [29], *Acacia concinna*[30], *Sapindustrifolistus*[31] and *Tamarindusindica*[32] fruit has been found to be a suitable replacement for various homogeneous acid catalysts. In recent years, organic research is mainly focused on the development of greener and eco-friendly processes which involve in the use of alternative reaction media to replace toxic and expensive catalysts or volatile and hazardous solvents like benzene, toluene and methanol, commonly used in organic synthesis. Nowadays, many organic transformations have been carried out in water [33-35]. Water is unique solvent because it is readily available, inexpensive, nontoxic, safer and environmentally benign. The use of water as a reaction medium is not only inexpensive and environmentally benign but also provides completely different reactivity. [36] The applications of an aqueous extract of different fruit juice have witnessed a rapid development. This growing interest in fruit juice is mainly because of its biocatalysts, environmentally benign character, cost effectiveness. Fruit juice is also naturally occurring which was used as a biocatalysts in organic synthesis.In the present work Biginelli reaction was accomplished just by grinding equimolar quantities of ethyl acetoacetate, Urea/thiourea and aryl aldehyde with grape juice (pH 3.0 - 3.5)as a catalyst for 10 to 15 minutes at ambient condition. The crude product was recrystallized by ethanol. Tis protocol is a greener approach for organic transformations, thus facilitating efficient synthesis of bioactive compounds in environmentally benign way with shorter reaction time, mild reaction conditions, and easy workup with excellent yield of the product.



Scheme 1:Synthesis of dihydropyrimidone/ thioneWhere, X= S,O.

II. MATERIALS AND METHODS

All melting points were measured in open capillary and are uncorrected. The products were characterized by IR spectra, 1H NMR. IR spectra were recorded on Perkin–Elmer FT-IR-1710 Instrument. 1H NMR was recorded onBrukerMSL-300 instrument using TMS as an internal standard. All reagents were purchased from Merck and Loba and used without further purification.

Experimental:

Preparation of aqueous extract of grape juice (Vitisamurensis):The seed less grapes were purchased from the local market and the (10 g) was crushed in water (50 mL) by grinder, and it was centrifuged using micro centrifuge (REMI RM-12C). The clear portion of the aqueous extract of the grapes was used as catalyst for thereaction.

General method for series of dihydropyrimidinone / thiones (DHPMs) derivatives:

The mixture of 10 mmol of aldehyde, 10 mmol of ethyl acetoacetate, 10 mmol of urea / thiourea and 5 ml grapejuice was grinded using mortar pestle at room temperature with monitoring by TLC. Then the reaction mixture washed with water and was filtered, the crystalline solid recovered by crystallization with ethanol. Its identity was confirmed by IR and NMR and its melting point. This procedure is followed for the synthesis of all the dihydropyrimidinones / thiones.

III. RESULTS AND DISCUSSION

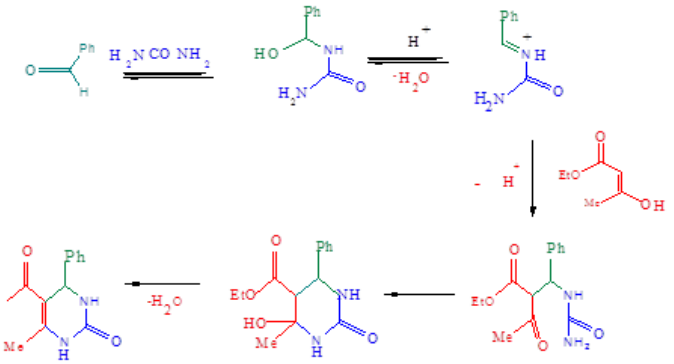
The synthesis of dihydropyrimidinones/thiones (DHPMs) derivatives which was accomplished by Biginelli reaction between substituted aryl aldehydes, ethyl acetoacetate and urea/thiourea (Scheme1) using natural and biocatalyst, which is an efficient and environmentally friendly catalyst. The results are presented in table1.The probable mechanism of the reaction is depicted in scheme 2. The reaction was accompanied having green chemistry approach, shorter reaction time, mild reaction conditions and easy workup procedure along with excellent yield. As compared to other catalyst reported in the literature[37 -39]this is a mild and highly selective transformation and synthesis in a facile and environmentally friendly manner. Moreover, fruits are inexpensive and easily available in the market, the extracted juice can be easily used as catalyst in the organic transformations.

Table 1: Grape juice catalyzed synthesis of 3, 4-dihydropyrimidin-2 (1H)-ones and thiones just by grinding at ambient condition

Sr.No	R	R_1	X	Yield (%)	M.P (^{o} C) Observed	M.P (^{o} C) Reported
1.	H	OEt	O	96	202-203	(201-203)[40]
2.	4-OMe	OEt	O	93	201-203	(199-201)[40]
3.	3-NO_2	OEt	O	92	228-230	(230) [41]
4.	2-OH	OEt	O	85	200-202	(200-202) [42]
5.	4-OH	OEt	O	92	225-226	(226-228)[43]
6.	H	OEt	S	90	208-210	(210-212)[44]
7.	4-OMe	OEt	S	85	136-138	(137-139)[45]
8.	4-Cl	OEt	S	86	182-184	(180-182)[46]
9.	2-OH	OEt	S	81	188-190	(183-185)[47]
10.	2-Cl	OEt	S	90	202-204	(205-206)[48]

The structures of the products were confirmed by comparing their M.P. /B.P. and spectral data with authentic samples.

The mechanism of the reaction is depicted in scheme 2grape juice plays a complex role in accelerating the coupling reaction and thus promotes the formation of products (Scheme 2).



Scheme 2: A probable mechanism for the reaction\

IV. CONCLUSION

This is a convenient and facile one pot synthesis ofdihydropyrimidinone and thioneswith a greener approach for organic transformations, thus facilitating efficient synthesis of bioactive compounds in environmentally benign way with shorter reaction time, mild reaction conditions, easy workup,less expensive with excellent yield of the product.

V. ACKNOWLEDGEMENTS

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Persistence of Organic Pollutants in Ground Water Around Kurkumbh Industrial Area (Daund) from Pune District, (MS) INDIA

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ABSTRACT

The global distribution of persistence of organic pollutants (POPs) has become one of the main environmental problems in the last decade. The environmental exposure to persistent of organic pollutants (POPs) become emerging risk factor for contribution of the knowledge of atmospheric transport and persistent organic pollutants (POPs) in remote area. Such persistent of organic pollutants (POPs) which includes chlorinated pesticides were determined in water sample collected around Kurkumbh industrial area during Pre-monsoon and post monsoon 2014. Concentration of total presticides ranges from 0.02 to 0.07 ng/L and 6.39 to 149.4 ng/L. The rate of percolation of pesticides and polycyclic aromatic hydrocarbons (PAHs) were high at site second as compare to site first from study area because of high slope of area. The organic pesticides like Hexachlorocyclohexane (HCH) as a-HCH, b-HCH, y-HCH, Heptachlor, Dieldrin, Aldrin Total pesticides (TP), Total cyclodiene (TC), Heptachloroepoxide (HCP) Dichloridiphenyl Trichloro ethane (DDT) and organic pollutants like Naphthalene, Phenathane, Pyrene, Toulene were studied. The concentration of organic pesticides and (PAHs) were bellow the detection limit in the study area.
Keywords: Chlorinated pesticides, (PAHs) and organic pollutant water around Kurkumbh industrial area.

I. INTRODUCTION

Persistance is the ability of substance to remain without change in the environment for a long period of time. It is the potential of this substance to travels hundreds to thousands kilometers away from its original sources. It causes damage or death to living organism. Some of them may cause cancer immunological and reproduction defects. They also disturb the nervous and respiratory system, affects the level of liver enzymes[1]. The POPs are bioaccumulation in living organism by capture it either directly from the environment and are indirectly from their food supply. The PCBs, DDT, PAHS may be responsible for occurrence of the breast cancer. Kurkumbh is considered as semi closed water body affected mainly from loading unloadind operation[2]. POPs have a wide range of industrial anthrpogenic and agriculture applications. They include pesticides such as DDT (dichlorodiphency / trichloroethane) and lindane (Y-HCH) in addition to petroleum hydrocarbons which are organic chemicals composed of fused benzene rings formed during incomplete combustion of coal, oil, petrol and wood. The soil is polluted by these substances primarily as use of pesticides application in agriculture. Another soil pollution sources may be also the over irrigation. Some pesticide is soluble in water which causes pollution of soil as well as ground water. Number of industrial sources such as power stations heating station as well as household furnaces transport and use of agricultural spray[3]. Evaporation of water or soil surfaces causes air pollution. Hence POPs concentration in atmosphere is increases gradually which are harmful to human being and any other living organism. To overcome these analytical problems, pesticides should be pre-concentrated as large possible to enable detection by the instruments[4].

POPs are synthetic organic compounds which are widely spread on land and in aquatic environment. There are commonly considered the most persistent anthropogenic organic compounds introduced in to the environment. Some of these are highly toxic and have a wide range of chronic effects including endocrine description mutagenicity and carcinogenicity. Furthermore POPs are chemically stable and therefore not easily degraded in the environment or in organism. They are lipophilic and

accumulate in the food chain[5]. Organo-chlorine pesticides are synthetic compounds that are chemically stable and hydrophobic. They include Dichlorodiphenyl Trichloro ethane (DDT). The Pesticides used in agriculture as an insecticide. This pesticide such as BHC (Hexachlorocyclohexane), chlordane and aldrin are other chlorinated pesticides use in agricultural. It is generally agreed that, the pollution around Kurkumbh industrial area has reached a critical level[6]. River runoff (Bhima) has the direct effect of reducing the salinity of the water. Untreated domestic waste water with agricultural and industrial wastes is still release through a number of drainages along the coastal area of study. The orgonochlorines pesticides actas never poisons and are highly toxic to fish because of their chemical structure and their persistence. The health hazard posed by these compounds has been studied extensively by several authors. The Kurkumbh are big industrial area which discharge industrial waste water in ground as well as on the surface (Fig. 5). The Bhima River is longest river nearby the area. Peoples are used river water for irrigation. The over irrigation used of insecticides, pesticides, fertilizers polluted the ground water[7-8]. There were various organic pollutants are percolated in ground water which causes harmful effects on living organism[9].

The organic pollutants cause harmful effects on human being, plant and living organism. The building blocks of living organisms are organic compounds which contain carbons and hydrogen[10]. However human have learnt to manufacture organic compounds that are extremely difficult to breakdown and as a result have become widely dispersed throughout the environment. These chemicals re-termed persistent organic pollutants (POPs) and are extremely resistant to nature break down processes and therefore are stable and long-lived. Most do not occurred in nature built are created through artificial process[11].

Once released (POPs) in to the environment many persist few years even decodes therefore even if production of all (POPs) ceased today. They would contain to pollute the environment for many years to come. Many POPs are also highly toxic and built up in the fatty tissues of animals and humans. In order to understand more clearly the behavior of these pollutants on a global scale and to prepare the future environmental policies; a baseline study is aimed to determine the occurrence of POPs in water of around Kurkumbh industrial area[12].

II. Material and Methods

Ten ground water samples were collected 5 km away from (site 1) Kurkumbh industrial area during (May, 2014). However another ten water samples are collected 10 km away from (site 2), during January 2014 (Fig. 2, 3a3b, 4a and 4b). According to slope and grading pattern (Fig. 1, 6a and 6b). The studied areas were represented by four sector, western sector, southern sector and northern sector. Water samples were extracted in the field and stored at 4^0c and transported to the laboratory for PAHs analysis using well established techniques[13]. The result measured in water samples using UV, Spectrophotometer (Sequoia-Tummer model 450) at 360 mm recitation and 415 mm emission. A calibration wave was determined by analyzing five separate concentration (0.5, 1, 2, 1 and 6 mg/L) of chrysene using h-hexane as the solvent. Clamp up and fractionation was performed prior to gas chromatograph / flame ionization detector and electron capture detector (GC/FID/ECD)[14].

The 1st ml of the extracted volume was passed through the silica column prepared by slurry packing 20 ml (10 gm) of silica followed by 10 ml (10 ml) of alumina and finally 1 gm of anhydrous sodium sulphate. Elution was performed using 40 ml of hexane/dichloromethane (90:10) followed by 20 ml of hexane/dichloromethane (50:50) which combined contain PAHs. Finally eluted samples were concentrated under a gentle stream of purified nitrogen to about 0.2 ml prior to be injected into GC/FID for pesticides analysis[15]. All samples were analyzed by a Hewlett Packard 5890 series II GC gas chromatography equipped with a flame ionization detector (FID) and electron capture detector. For hydrocarbon analysis the instrument was operated in split less mode (3ml split less injection) with the injection Dieldrin, DDT, to control the analytical reliability and assure recovery efficiency and accuracy of the results. Four analysis were conducted on organo-chlorine compounds[16].

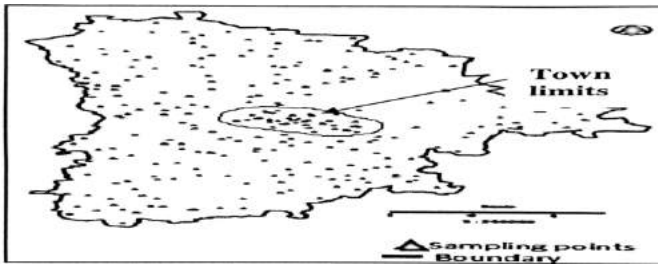

Figure 1. Location map of the study area.

Figure 2. Agricultural field and irrigation type around study area.

Figure 3(a). Source of irrigation around study area.

Figure 3(b). Source of irrigation around study area.

Figure 4(a). Dug well for around study area.

Figure 4(b). Dug well for around study area.

Figure 5. Chemical industry around study area.

Figure 6(a). First sampling site around study area.

Figure 6(b). Second sampling site around study area.

III. Result and discussion

Table (1 and 2) shows the residual concentration of organochlorine compounds determined in water samples collected from study areas. The data of Table (1 and 2) indicates that PP-DDT [2, 2, bis (P-Chloropheny)-1, 1, 1 trichlorothane] is the most dominant orgonochlorine compound during summer reason.The maximum concentration was 147.4 ng/L recorded DDT is generally used against a wide variety of agricultural and forest pests and pests including, vectors such as mosquito and test –test fly in the environment. DDT can be degraded by solar radiation or metabolized in organism Heptachlor is the common name for 1.4, 5, 6, 7, 8, 8- heptachloro 3a, 4, 7, 7a tetrahydro -4, 7-methane – 1H – indane. It is generally use as insecticides and also occurs technically as chlorodane. In the environment, degraded or metabolized and is more commonly found as its epoxide compared with a mean concentration of 0.151ng/L for all locations during summer from study area second[17].

Aldrin is an alicyclic chlorinated hydrocarbon and is rapidly converted to the epoxide form. Dieldrin. The presence of an average of 0.097 ng/L of aldrin with mean clue of 0.071 ng/L of dieldrin. Recorded at site second during summer season, part maintained at 29^0C and the detector maintained at 3^0C samples were analyzed on a fused silica capillary column HP-1 100% dimethyl polysiolane (30 m. length 0.32 mm i.d., 0.17 mm film thickness). The oven temperature was programmed from 60-29^0C changing at a rate of 3^0C min and maintained at 29^0C for 25 min. The carrier gas was nitrogen flowing at 1.2 ml /min. However HP-5 capillary column film thickness with Ni63 – electron capture detector (ECD) was used for pesticides analysis. The oven temperature was programmed from 9^0C – 14^0Cat rate of 5^0C / min maintained at 14^0C for 1 min then from 14^0C – 25^0C at rate of 3^0C /min maintained at 25^0C for 1 min then from 25^0C – 35^0C at rate of 2^0C /min and maintained at 30^0C for 1min the carrier gas was nitrogen flowing at 1.5 ml/min [18-19]. A stock solution containing the following PAHs was used for quantification of hydrocarbons naphthalene phenathrene, pyrene, Touluene by dilution to create a series of calibration standards of PAHs at 0.1, 0.25, 0.5, 0.75, 1.0, 2.0, 5.0 and 10 ng ml/L. The detection limit was approximately 0.01 ng /L for each PAH for analytical reliability and recovery efficiency of the results, six analyses were conducted on PAH reference material[20].

Orgonochlorine pesticides were quantified from individually resolved peak areas with corresponding peak areas of the external standards. They includes a, B and u. Hexachlorocyclohexanes, Heptachlor, Aldrin, heptachloroe epoxide It is declare that there is a renewal of Aldrin in water[21]. HCH (hexachlorocyclohexane) is a fully chlorinated alicyclic compound .The most common ismers are, a, B and u HCH they u isomer known as Lindane is one normally used as an agricultural pesticides. HCH is a responsibly stable compounds and only under alkaline condition decomposes to yield trichloro-benzane. It is considered as one of the less persistence organochlorine pesticides. A maximum of 0.25 ng/L of HCH was declared at the location second[22].

The data of tables I&II declared also that pesticides concentration were higher in study area second (10 km away) than study area first (10 km away). Total HCHs were the major pollutant followed by total DDTs, total cyclodines (TC) with an average calue of 0.063, 0.022 and 0.014ng/ L respectively in study area first[23].The average concentration of Nephthalene is 0.072 ng/L in side second than that of side first 0.298 ng/L. The order of concentration of phenanthrene pyrene and toluene from study area second is high than concentration of phenanthrene, pyrene and toluene from study area first because atmospheric fallorct (rain water) is the major source of pollution. Agricultural runoff river and discharge of industrial waste[24]. Form above observation it is that POPs construction recorded is more at site

second than site first n the study area. The residual polynuclear aromatic hydrocarbons Nephthalane, Phenathrene, pyrene and toluene were investigated in water of study area.

Table 1. Description sampling locations during May 2014

Sampling station	Sampling locations	Water Source	Soil Type	Crop
T1	10 Km. South from Industrial area Tal. Daund, Dist. Pune	Dug well	Black cotton	Sugar cane
T2	07 Km. West of Aalegaon Sugar factoryTal. Daund, Dist. Pune	Lift Irrigation from Bhima river	Black cotton	Paddy
T3	20 Km. West from Bank of Bhima river near Siddhatek.	Lift Irrigation from Bhima river	Alluvial	Cowpea
T4	05 Km. North from Industrial area Shindewadi Tal. Daund, Dist. Pune	Lift Irrigation from Bhima river	Black cotton	Pumpkin
T5	10Km. North from Industrial area jiregaon, Tal. Daund, Dist. Pune	Dug well	Black cotton	Ground nut
T6	15 Km. West from Industrial area, Malad, Tal. Daund, Dist. Pune	Dug well	Black cotton	Fenugreek
T7	02 Km. South from Industrial area, Pune Solapur highway	Lift Irrigation from Canal	Black cotton	Paddy

Table 2. Description sampling locations during January 2014

Sampling station	Sampling locations	Water Source	Soil Type	Crop
T1	10 Km. North from Industrial area Tal. Daund, Dist. Pune	Dug well	Black cotton	Sugar cane
T2	07 Km. East of Aalegaon Sugar factoryTal. Daund, Dist. Pune	Lift Irrigation from Bhima river	Black cotton	Sugar cane
T3	20 Km. East from Bank of Bhima river near Siddhatek.	Lift Irrigation from Bhima river	Alluvial	Sugar cane
T4	05 Km. South from Industrial area Shindewadi Tal. Daund, Dist. Pune	Dug well	Black cotton	Spinach
T5	10Km. South from Industrial area jiregaon, Tal. Daund, Dist. Pune	Dug well	Dark grey	Tomato
T6	15 Km. East from Industrial area, Malad, Tal. Daund, Dist. Pune	Dug well	Black cotton	Vegetables
T7	02 Km. North from Industrial area, Pune Solapur highway	Lift Irrigation from Canal	Black cotton	Sugar cane

Table 3. Concentration of (POPs) in ground water around Kurkumbh industrial area in May, 2014.

Organic pollutants	S1	S2	S3	S4	S5	S6	S7
Alpha-HCH	0.031	0.0012	0.0031	0.0099	0.0017	0.0011	0.0023
Beta-HCH	0.0068	0.0022	0.0068	0.0032	0.0019	0.0021	0.0012
Gama-HCH	0.0166	0.0013	0.0017	0.0011	0.0039	0.0012	0.0011
Naphthalene	0.0544	0.0048	0.0116	0.0139	0.0075	0.0044	0.0046
Heptachlor	0.0027	ND	0.0027	0.0063	0.0097	ND	0.0018
Aldrin	0.0024	0.022	0.0024	ND	0.0018	ND	0.0014
HCP	0.0003	0.0003	0.0028	ND	0.0027	ND	ND
Dieldrin	0.0003	ND	0.0026	ND	0.0035	0.0009	0.0229
TC	0.0057	0.0223	0.0105	0.0063	0.0177	0.0009	0.0061
Phenathrene	0.0013	0.0002	0.0013	ND	0.0084	0.0018	0.0079
Pyrene	0.0052	0.0083	0.0052	ND	0.0055	0.003	ND
PP-DDT	0.0019	ND	0.0019	0.0022	0.0025	0.0085	ND
Toulene	0.0083	0.0085	0.0083	0.0022	0.0164	0.0127	0.0099
Tp	0.0684	0.0156	0.0304	0.0224	0.0415	0.018	0.0207

TP: Total pesticides, **TC:** Total cyclodines, **HCP:** Heptachlorepoxide, **ND:** Not detected

Table 4. Concentration of (POPs) in ground water around Kurkumbh industrial area January 2014.

Organic pollutants	S1	S2	S3	S4	S5	S6	S7
Alpha-HCH	0.17	0.097	0.02	0.35	0.24	0.09	0.27
Beta-HCH	0.04	0.19	0.02	0.04	0.03	.001	0.02
Gama-HCH	0.01	0.25	0.01	0.0	0.02	0.01	0.01
Naphthalene	0.023	0.023	0.023	46	029	0.11	0.29
Heptachlor	0.13	0.44	0.08	0.2	0.07	0.03	0.12
Aldrin	0.07	0.32	0.04	0.16	0.05	0.04	0.05
HCP	0.17	0.49	0.04	0.22	0.05	0.06	0.04
Dieldrin	0.04	0.23	0.03	0.11	0.03	0.03	0.02
TC	0.42	0.42	0.2	0.69	0.2	0.15	0.23
Phenathrene	0.09	0.71	0.07	0.31	0.06	0.05	0.07
Pyrene	0.16	0.64	0.14	0.31	0.08	0.04	0.16
PP-DDT	69.79	147.4	58.83	14.97	54.5	6.0	78.99
Toulene	70.0	148.7	59.0	15.59	54.64	6.13	79.22
Tp	70.69	149.4	59.46	16.75	55.17	6.39	79.73

TP: Total pesticides, **TC:** Total cyclodines, **HCP:** Heptachlorepoxide, **ND:** Not detected

IV. Conclusion

The present study declared that the concentration of POPs from side second is more than concentrations of POPs from side first. Since rate of persistence of organic pollutants is high from higher slope area to lower slope area. The total average concentration of some POPs, a-HCH, B-HCH, u-HCS Nepthalane, Aldrin, Dieldrin TC, phenathrene pyrene HCP is bellow the admissible environment level but the POPs, P.P-DDT, toluene and total pesticides were above the permissible limit. The maximum levels of toxic substances, recommended for the protection of aquatic biota has been published. The environmental quality objectives set by European community is 10ng/l. of P-P DDT and for HCH isomers at 20ng/L. for Heptachlor. 10-100ng/L. Thus land based activities mainly agricultural and industrial wastes are the major sources of POPs pollution around study area.

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One Pot Synthesis of 6,7-Diimino imidazolo[2,3-b]pyrimido[5,6-e] pyrimido[2,3-b][1,3]benzothiazole Derivatives

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ABSTRACT

We have reported the synthesis of 6,7-Diimino imidazolo[2,3-b]pyrimido[5,6-e]pyrimido[2,3-b][1,3]benzothiazole derivatives by condensing 3-Cyano-4-imino-2-methylthio-4H-pyrimido[1,2-a]benzimidazole with 2-Amino benzothiazole derivatives in presence of N,N'-dimethyl formamide and anhydrous potassium carbonate as a catalyst under reflux condition. The structures of all newly synthesized cyclic compounds were confirmed on the basis of spectral analysis, IR, 1H NMR and Mass spectral properties.

Keywords : Benzothiazole, Pyrimido, DMF, Potassium Carbonate, Spectral Properties.

I. INTRODUCTION

Benzothiazole derivatives are significant class of fused heterocycles due to their extensive range of pharmacological potential, in addition to this its value in the synthesis of drug molecules and natural products. It shows anti-inflammatory[1], analgesic[2], antioxidant[3], antidiabetics[4], antimicrobial[5], antituberculosis[6], vasodilator[7], antitumor[8], antiproliferative[9], anticancer activity[10]. These things inspire us to synthesize some pyrimido-benzothiazole derivatives.

II. Material and Methods

All the chemicals used in present works are from analytical grade and used without further purification. Melting points of the products were determined in open capillary tubes on an electrothermal melting point apparatus and were uncorrected. All these reactions were monitored by TLC. IR spectra were recorded on Shimadzu FT-IR spectrophotometer, ^{1}HNMR spectra were obtained on Bruker avance spectrophotometer 500 MHz in DMSO-d6 using TMS as an internal standard. Mass spectrums were analyzed on GC-MS spectrometer using the ESI 70 eVtechnique.

III. General Procedure

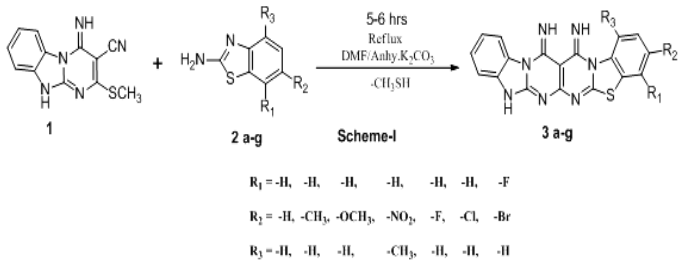
Synthesis of 6,7-Diiminoimidazolo[2,3-*b*]pyrimido[5,6-*e*]pyrimido[2,3-*b*][1,3] benzothiazole and their substituted derivatives (3B.40a-g).

The parent compound (**1**) (0.001 mol) and 2-Amino benzothiazole derivatives such as 2-amino benzothiazole **(2a)**, 2-amino-6-methylbenzothiazole **(2b)**, 2-amino-6-methoxy benzothiazole **(2c)**, 2-amino-4-methyl-6-nitrobenzothiazole **(2d)**, 2-amino-6-fluoro benzothiazole **(2e)**, 2-amino-6-chlorobenzothiazole **(2f)** and 2-amino-6-bromo-4-fluoro benzothiazole **(2g)** (0.001 mol) in 15 ml of DMF and anhydrous K_2CO_3 (10 mg) were refluxed for 5-6 hours. Reaction content cooled at room temperature and mixed with ice cold water then separated solid was filtered, rinse with water and recrystallized using DMF-ethanol mixture to give pure **(3a-g)** respectively.

IV. Result and Discussion

In the present research, we reported one pot synthesis of 6,7-diimino imidazolo[2,3-*b*]pyrimido[5,6-*e*]pyrimido[2,3-*b*][1,3]benzothiazole and their

substituted derivatives **(3a-g).** The reaction started with 3-cyano-4-imino-2-methylthio-4*H*-pyrimido[1,2-*a*]benzimidazole **(2)** were condensed with dissimilar substituted benzothiazoles in presence of refluxing N,N'-dimethyl formamide and anhydrous potassium carbonate to accomplish corresponding target compounds **(3a-g)** shown in scheme-I.



The reaction started with an initial attack of amino group of benzothiazoles on carbon attached to -SCH_3 group resulting in loss of the thiomethyl group in the form of methyl mercaptan. Resulting secondary amine polarizes on to nitrile carbon to give cyclized compounds

The structures of all newly synthesized cyclic compounds **(3Ba-g)** were confirmed on the basis of spectral analysis, IR, ^{1}H NMR and Mass spectral data**.** IR spectra of compounds showed the presence of absorption bands between 3400-3436 cm^{-1} which can be assigned to (=NH stretch). The ^{1}H NMR showed a singlet at δ 3.81 and δ 8.6 which can be assigned to (-NH & =NH) proton. Mass spectra of compounds exhibited the molecular ion peaks which correspond to their molecular weights.

6,7-Diiminoimidazolo[2,3-*b*]pyrimido[5,6 *e*]pyrimido[2,3-*b*][1,3]benzothiazole (3B.40a)
IR:

1577-1662 cm^{-1} (Ar C=C stretch), 3436 cm^{-1} (=NH stretch), **^{1}H NMR** : (500 MHz, DMSO) δ : 3.81 (s, 1H, Ar C-NH), 7.3-8.4 (m, 8H, Ar-H), 8.6 - 9.3 (s, 1H, two =NH) ppm, **Mass:*m/z***=358 (M+1).

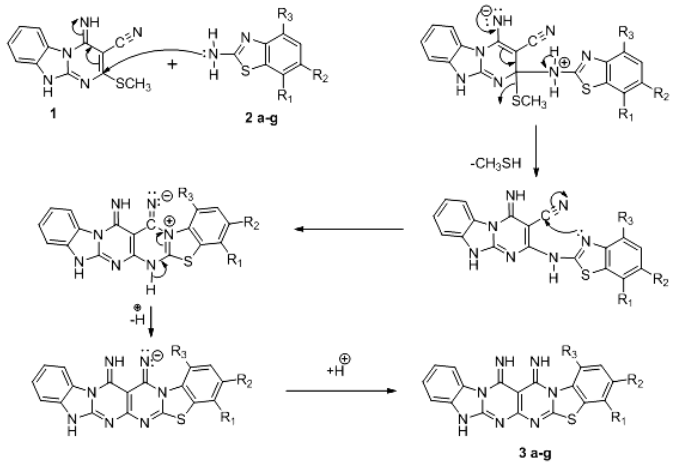
6,7-Diimino–2-methoxy-imidazolo[2,3-*b*] pyrimido [5,6-*e*] pyrimido [2,3-*b*][1,3] benzothiazole (3B.40c)
IR:

1454-1650 cm^{-1} (Ar, stretch), 3460 cm^{-1} (=NH stretch) **^{1}H NMR**: (500 MHz, DMSO) δ: 3.7 (s, 3H, -OCH_3), 3.81(s,1H, NH),7.0 - 8.5 (m, 7H, Ar-H), 8.6, 9.3 (s,1H, two =NH)ppm, **Mass: *m/z***=388 (M+1).

Table 1. Physico-chemical properties of synthesized compounds (3a-g).

Sr. No	Comp.code	Color	M.F.	M. W.	M.P.(^{0} C)	Yield (%)
1.	3a	Yellow	$C_{18}H_{11}N_7S$	357	316-318	80
2.	3b	Brown	$C_{19}H_{13}N_7S$	371	325-327	72
3.	3c	Yellow	$C_{19}H_{13}N_7OS$	387	314-317	70
4.	3d	Yellow	$C_{19}H_{12}N_8O_2S$	416	322-324	65
5.	3e	Yellow	$C_{18}H_{10}FN_7S$	375	312-315	68
6.	3f	Brown	$C_{18}H_{10}ClN_7S$	391	321-323	73
7.	3g	Brown	$C_{18}H_9BrFN_7S$	454	318-320	78

Plausible mechanism of compound (3a-g) (Scheme-I).



V. Conclusion

In the present work we have synthesized 6,7-diimino imidazolo[2,3-*b*]pyrimido[5,6-*e*]pyrimido[2,3-*b*][1,3]benzothiazole and their substituted derivatives **(3a-g)** in good yields. We have used inorganic base potassium carbonate as a catalyst for transformation instead of many other organic bases due to its distinctive features and DMF as refluxing solvent. We have achieved this synthesis in single step rather than multiple steps with minimum reaction time.

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Physico-Chemical cum Biological Characteristics & Water Quality Index (WQI) of Dimbhe Dam in Pune District, Maharashtra State, India

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ABSTRACT

The present work is aimed at assessing the water quality index (WQI) for the surface water of Dimbhe Dam near Near Shinoli, village of Taluka Ambegaon, District Pune, Maharashtra State, India. Surface water samples were collected at three sampling points, S1 upstream of village Shinoli, S2 near village Shinoli, and S3 downstream of village Shinoli,. The samples are subjected for comprehensive physical, chemical and biological analysis. For calculating the WQI, the following 14 parameters have been considered: pH, Total Dissolved Solids, Total Hardness, Calcium, Magnesium, Chloride, Nitrate, Sulphate, DO, BOD, Alkalinity, Sodium, Potassium and Fluoride. The high value of WQI has been found to be mainly from the higher values of TDS, Hardness, BOD and Nitrate. The analysis reveals that the surface water of the area needs some degree of treatment before consumption, and it also needs to be protected from the perils of contamination.

Keywords: Surface Water, Water Quality Standards, Water Quality Characteristics, Water Quality Index.

I. INTRODUCTION

Surface water is used for domestic, industrial, water supply and irrigation all over the world. In the last few decades, there has been a tremendous increase in the demand for fresh water due to rapid growth of population and the accelerated pace of industrialization. Human health is threatened by most of the agricultural development activities particularly in relation to excessive use of fertilizers[1]. According to World Health Organization (WHO), about 80% of all the diseases in human beings are caused by water[2]. Water Quality Index (WQI) is one of the most effective tools to communicate information on the quality of water to citizens. The formulation and use of indices has been strongly advocated by agencies responsible for water supply and control of water pollution[3]. Although any environmental impact could be either beneficial or adverse, in environmental analysis, impacts are historically considered only to be of adverse type caused by our developmental activities. Impacts can be generally categorized as primary, secondary or tertiary. Primary impacts are those caused directly by project inputs such as loss of forests, or changing of a river regime due to the construction of a dam. As such primary impacts can be attributed directly to a project activity. They are usually easy to measure. Secondary impacts are those caused by project outputs such as water flow regulation and channelization. In other words, they are indirectly attributed to the project activity. If one of the project outputs is availability of irrigation water, secondary impacts could be more severe than primary impacts and unfortunately, often more difficult to predict and measure[4]. Secondary impacts in turn may lead to tertiary impacts. It should be noted that the distinction between primary, secondary and tertiary impacts could often be arbitrary. Various types of water related activities can cause beneficial or adverse impacts on the environment, water channelization, flood land alteration and changes in land use patterns. Water quality is a very important consideration for all water development projects as it affects all aspects of water use-for humans, for animals, for crops and even for industry. All natural waters containing soluble inorganic ions are mainly from the weathering of soil and rock minerals. The weathering products of the rock minerals are released and transported by the action of water. Hence the nature and concentration of an ion in water depends upon the nature of rock mineral, its solubility and its resistance to weathering in fresh water or carbonated water (due to dissolution of atmospheric carbon dioxide in rain water) climate and local topography. Apart from these major causes, solubility of minerals in influenced by pH, particularly of iron and manganese hydroxides that decreases and aluminium hydroxide, which increase with the increase of pH. In recent years continuous

growth in pollution, rapid industrialization and accompanying technologies involving waste disposal has endangered the very existence of human race[5-7]. Eventually the rate of clearance of forests for the purpose of different land uses is far higher than the methods that are implemented for a forestation. Among the different types of pollution, water pollution is one of the major causes, which creates immense public health hazards. Therefore, regional variations in surface water quality can be determined only by sampling water at sites intended to give representative coverage of the various conditions of occurrence. Partial analysis to determine the concentrations of the principal chemical constituents in water may provide sufficient data for many investigations and modeling studies. The present study highlights the WQI Model of surface water in Dimbhe Dam. Further, the information obtained from the study will be useful for local people, environmental departments, public health departments etc. The main objectives of the study are Physical, Chemical and Biological analysis of surface water samples and application of Water Quality Index (WQI) model. Water quality index is created to give the Physico-Chemical cum Biological Characteristics & Water Quality Index (WQI) of Dimbhe Dam

II. Materials and Methods

The study area, Dimbhe Dam. is located 95 kilometers away from District Pune, Maharashtra state, India. Figure.1 shows the location map of Dimbhe Dam The Ambegaon taluka lies at Latitude of N: 18^0.23" and Longitude is E: 73^0.91'', can be to closest from Pune-Bangalore Hwy, Maharashtra, India. Minimum temperature is 15^o C and during peak summer it shoots up to 47^o C. Surface water samples were collected from Dimbhe Dam for two kilometer length of flow, three sampling points were selected. S1 upstream of village Shinoli, S2 near village Shinoli, and S3 downstream of village Shinoli,. The water samples were collected for every three days in the morning at 08:00 to 10:00 am for a period of 2 months successively during April 2011 to May 2011. Two and half liters of water samples were collected in white colored plastic containers and were transferred to the laboratory at the earliest. Collected samples were subjected to chemical analysis while temperature and pH were determined in field. The water samples were then analyzed for following parameters: TDS, pH, TH, Ca, Mg, Cl, SO4, NO_3 , BOD, Na, K, F, HCO_3 and DO using standard procedures of analysis recommended by APHA and compared with WHO and BIS.8-10 Water Quality Index (WQI) for Dimbhe Dam Water quality affects the quality of drinking water and the capacity of the surface water to support wildlife and healthy ecosystems. Water quality can be degraded by many different stressors in the watershed, including poor development practices and sprawl, poor storm water management, destruction of wetlands, runoff from agricultural area, and point source pollution. Water quality indices aim at giving a single value to the water quality of a source. One can then compare different samples for quality on the basis of the index value of each sample. For computing water quality index three steps are followed. In the first step, each of the 14 parameters has been assigned a weight (wi) according to its relative importance in the overall quality of water for drinking purposes. The maximum weight of 5 has been assigned to the parameter nitrate due to its major importance in water quality assessment. Magnesium has been given weight of 2 as magnesium by itself may not be harmful. In the second step, relative weight (Wi) is computed from the following equation:

$$Wi = wi \; 1i \; n \; wi = \sum \text{ ---------- (1)}$$

Where (Wi) is the relative weight, (wi) is the weight of each parameter and „n" is the number of parameters. In the third step, a quality rating scale (Qi) for each parameter is assigned by dividing its concentration in each water sample by its respective standard according to the guidelines laid down in the BIS and the result is multiplied by 100.3

$$Wi=wi/\Sigma wi \text{ ……. (1)}$$

$$Qi = (Ci /Si) *100 \text{ ---------- (2)}$$

Where, Qi is the quality rating, Ci is the concentration of each chemical parameter in each water sample in mg/L, except pH, and Si is the BIS (Bureau of Indian standards) water standard for each chemical parameter in mg/l according to the guidelines of the BIS-10500-1991. For computing the WQI, the Sub Index (SI) is first determined for each chemical parameter, which is then used to determine the WQI as per the following equation

$$SIi = Wi*Qi \text{ ---------- (3)}$$

$$\Sigma WQI = \Sigma Si \text{ ---------- (4)}$$

SIi is the sub index of I th parameter, Qi is the rating based on concentration of ith parameter and n is the number of parameter. The computed WQI values are classified into five types “excellent water”, “good water”, “poor water” “very poor water”, “water unsuitable for drinking” as shown in Table 1.

Table 1. Water quality classification based on WQI value WQI value

WQI value	Water quality
<50	excellent
50 – 100	good water
100-200	poor water
200-300	Very good water
>300	very poor water

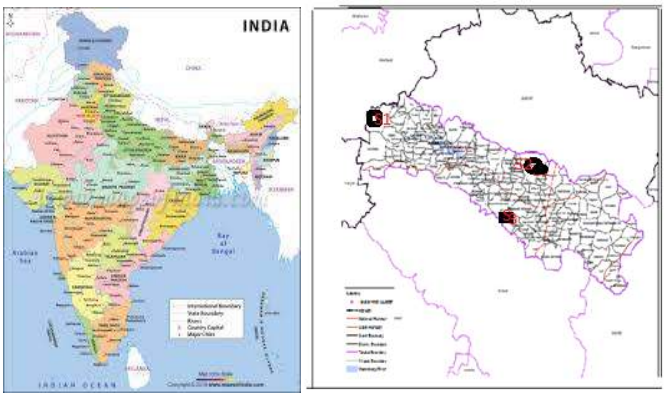

Figure 1. Showing the Sampling sites at Dimbhe Dam in Pune District

III. RESULTS AND DISCUSSIONS

The pH values of the samples varied between 6.30 to 7.90 at sampling point (upstream), 7.42 to 8.14 at sampling point (near village) and 7.20 to 8.05 at sampling point (downstream). It is observed that the pH of the surface water was slightly alkaline and only minor fluctuation in pH was recorded. The pH levels were within the limits set by the WHO and BIS. The permissible total dissolved salts for drinking water is 500 mg/L. In the absence of potable water source the permissible limit is up to 2000 mg/L. It is found from the analysis; all the water samples are within the maximum limit of 2000 mg/L. The range of TDS levels in the study area is 780.30 mg/L to 1020.0 mg/L at sampling point (upstream), 832.10 mg/L to 1160.30 mg/L at sampling point (near village) and 805.70 mg/L to 988.0 mg/L at sampling point (downstream). High values of TDS in surface water are generally not harmful to human beings but high concentration of these may affect persons who are suffering from kidney and heart diseases also water containing high solids may cause laxative or constipation effects. Natural hardness of water depends upon the geological nature of the drainage basin and mineral levels in natural water. The total hardness ranged between 630.90 mg/L to 800.40 mg/L at sampling point (upstream), 694.0 mg/L to 840.0 mg/L at sampling point (near village) and 647.0 mg/L to 791.70 mg/L at sampling point (downstream). Hardness is little more in this river water, a separate Geochemical/Hydro geochemical analysis is a must to arrive at the hardness nature of this river water. The magnesium hardness exceeds in all the samples, it ranges from 100.70 mg/L to 179.0 mg/L at sampling point (upstream), 86.0 mg/L to 160.0 mg/L at sampling point (near village) and 131.48 mg/L to 246.70 mg/L at sampling point (downstream). There are no known cases of magnesium poisoning. At large oral doses of magnesium may cause vomiting and diarrhea. High doses of magnesium in medicine and food supplements may cause muscle slackening, nerve problems, depressions and personality changes. The chloride content increases normally as the mineral content increases. The chloride level ranged between 34.50 mg/L to 153.10 mg/L at sampling point (upstream), Physico-Chemical cum Biological Characteristics & Water Quality Index (WQI) of Dimbhe Dam in… 13 90.0 mg/L to 274.0 mg/L at sampling point (near village) and 94.60 mg/L to 170.80 mg/L at sampling point (downstream). Here it is observed that the chloride concentration in the samples fall well within the permissible limit. The total alkalinity of the water samples was below the permissible and desirable criteria for domestic water supply. The observed alkalinity was due to methyl orange alkalinity since phenolphthalein alkalinities were zero in all the water sampling points. Consequently, the water samples are not polluted with respect to alkalinity. Dissolved Oxygen present in drinking water adds taste and it is highly fluctuating factor in water. In this study dissolved oxygen content varied in a limited range of 5.91 mg/L to 8.97 mg/L at sampling point (upstream), 1.45 mg/L to 8.14 mg/L at sampling point (near village) and 5.23 mg/L to 5.92 mg/L at sampling point (downstream). The Biological

Oxygen Demand (BOD) gives an idea of the quantity of biodegradable organic matter present in an aquatic system which is subjected to aerobic decomposition by microbes. Accordingly it provides a direct measurement of the state of pollution. The concentration of BOD ranged from 3.21 mg/L to 8.88 mg/L at sampling point (upstream), 0.77 mg/L to 7.5 mg/L at sampling point (near village) and 1.47 mg/L to 4.12 mg/L at sampling point (downstream). The concentration of fluoride in drinking water is critical considering health problems related to teeth and bones. High fluoride concentration causes dental fluorosis and skeletal fluorosis, whereas the absence or low concentration fluoride concentration (< 0.5 mgL-1) cause tooth decay. The recommended desirable limit of fluoride is 1 mg/L. In present study area, fluoride content in all sampling points is well within the permissible standards. The sulphate and nitrate concentrations of all three sampling points are well within the permissible standards. The MPN index values at all the sampling stations are high; this shows that water is not fit for drinking[8-9]. The data of all sampling points are presented in Table 2, 3 & 4.

Table 2. Normal Statistics of Water Quality Parameters of Surface Water at sampling point S1 (Upstream)

Sl. No	Parameters	Minimum	Maximum	Mean	S.D	C.V
1	Temp^{0}C	20.20	28.10	23.70	2.0	0.082
2	pH	6.35	8.0	7.20	0.5	0.058
3	TDS mg/L	780.0	1025.0	910.0	58.0	0.062
4	TH mg/L	630.80	800.0	730.90	51.60	0.071
5	Ca mg/L	513.30	681.0	599.9	49.35	0.081
6	Mg mg/L	100.75	180.0	132.5	21.35	0.162
7	Cl mg/L	35.0	153.0	130.50	25.75	0.198
8	F mg/L	0.15	0.50	0.4	0.08	0.251
9	So4 mg/L	20.50	35.0	25.50	4.75	0.185
10	NO_3 mg/L	16.85	18.70	17.95	0.60	0.032
11	Na mg/L	110.0	120.0	115.80	2.50	0.020
12	K mg/L	17.80	24.90	20.88	1.60	0.080
13	HCO_3 mg/L	60.75	89.05	78.65	9.15	0.115
14	DO mg/L	6.0	8.90	7.5	0.1	0.132
15	BOD mg/L	3.25	8.80	5.6	1.8	0.310
16	MPN mg/L	3.5	64.10	15.0	13.0	0.86

Table 3. Normal series of water quality parameters of surface water at sampling point S2 (near Village)

Sl. No	Parameters	Minimum	Maximum	Mean	S.D	C.V
1	Temp^{0}C	20.10	28.5	23.74	2.0	0.082
2	pH	7.40	8.14	7.80	0.2	0.028
3	TDS mg/L	832.0	1160.25	968.0	82.50	0.084
4	TH mg/L	694.5	840.1	766.14	28.95	0.035
5	Ca mg/L	540.5	680.1	648.80	29.90	0.045
6	Mg mg/L	85.9	159.5	116.30	17.65	0.150
7	Cl mg/L	90.1	274.1	186.7	51.85	0.275
8	F mg/L	0.10	0.86	0.6	0.20	0.400
9	So4 mg/L	31.9	167.8	89.90	37.75	0.40
10	NO_3 mg/L	27.59	40.0	32.80	3.15	0.095
11	Na mg/L	100.1	300.1	199.0	54.75	0.275
12	K mg/L	20.1	40.0	31.45	5.80	0.85
13	HCO_3 mg/L	99.99	220.2	149.20	33.80	0.225
14	DO mg/L	1.44	8.15	5.8	1.60	0.275
15	BOD mg/L	0.75	7.6	3.9	2.20	0.600
16	MPN mg/L	7.0	120.5	34.50	32.0	1.0

Table 4. Normal series of water quality parameters of surface water at sampling point S3 (Downstream)

Sl. No	Parameters	Minimum	Maximum	Mean	S.D	C.V
1	Temp^{0}C	20.10	28.5	23.75	2.0	0.084
2	pH	6.99	8.0	7.6	0.21	0.030
3	TDS mg/L	805.75	989.0	893.20	52.65	0.05
4	TH mg/L	648.0	790.90	735.90	33.60	0.050
5	Ca mg/L	510.5	545.5	528.85	10.0	0.015
6	Mg mg/L	131.35	250.	207.30	29.55	0.145
7	Cl mg/L	95.0	170.81	146.0	17.20	0.115
8	F mg/L	0.26	0.5	0.4	0.060	0.176
9	So4 mg/L	30.5	39.5	33.20	2.5	0.142
10	NO_3 mg/L	20.45	30.81	26.0	3.6	0.086
11	Na mg/L	85.21	110.0	95.85	8.2	0.185
12	K mg/L	19.20	35025	23.41	4.42	0.052
13	HCO_3 mg/L	85.0	100.0	92.20	4.8	0.036
14	DO mg/L	5.25	6.0	5.6	0.21	0.33
15	BOD mg/L	1.45	4.15	2.5	0.8	0.30
16	MPN mg/L	6.9	120.5	35.0	32.0	0.930

Table 5. Relative weight of chemical parameters at sampling point S1 (Upstream)

Sl. No	Parameters	Indian Standard	Weight (W1)	Relative weight	Quality rating (Qi)	Sub Index (Sli)
1	pH	6.5-8.5	3	00.068	84.58	5.7
2	TDS	500-2000	4	0.090	45.50	4.0
3	TH	300-600	3	0.068	121.82	8.2
4	Calcium	75-200	3	0.068	299.45	20.3
5	Magnesium	30-100	2	0.045	132.0	5.9
6	Sodium	300-600	2	0.045	16.54	0.7
7	Potassium	15-20	2	0.045	83.52	3.7
8	Alkalinity	200-600	2	0.045	13.11	0.5
9	DO	4-8	2	0.045	92.76	4.4
10	BOD	0-30	3	0.068	18.42	1.2
11	Chloride	250-100	4	0.090	13.5	1.1
12	Sulphate	200-400	4	0.090	6.37	0.5
13	fluoride	1-1.5	5	0.113	21.0	2.3
14	Nitrate	45-100	5	0.113	17.90	2.0
			∑wi=44	∑WI=0.99	∑Qi=966.50	∑Sli=61.0

Table 6. Relative weight of chemical parameters at sampling point S2 (Near Village)

Sl. No	Parameters	Indian Standard	Weight (W1)	Relative weight	Quality rating (Qi)	Sub Index (Sli)
1	pH	6.5-8.5	3	00.068	91.6	601
2	TDS	500-2000	4	0.090	48.30	4.2
3	TH	300-600	3	0.068	127.65	8.7
4	Calcium	75-200	3	0.068	324.5	22.0
5	Magnesium	30-100	2	0.045	116.30	5.2
6	Sodium	300-600	2	0.045	28.40	1.2
7	Potassium	15-20	2	0.045	125.80	5.6
8	Alkalinity	200-600	2	0.045	24.85	1.1
9	DO	4-8	2	0.045	21.75	3.2
10	BOD	0-30	3	0.068	26.5	1.8
11	Chloride	250-100	4	0.090	18.8	1.6

12	Sulphate	200-400	4	0.090	27.8	2.0
13	fluoride	1-1.5	5	0.113	73.9	4.0
14	Nitrate	45-100	5	0.113	32.8	3.7
			∑wi=44	∑WI=0.99	∑Qi=1085	∑Sli=71.80

The WQI of all samples taken were calculated according to the procedure explained above and are presented in Table 5, 6 and 7. The results obtained from this study revealed that WQI of Bhima river water is "good water" for all the three sampling points. The computed WQI was 61.09 in upstream of village Hipparga, 71.83 near village Hipparga and 62.60 in downstream of village Hipparga. All WQI values are between, 50-100 as per Table 1.

Table 7. Relative weight of chemical parameters at sampling point S3 (Downstream)

Sl. No	Parameters	Indian Standard	Weight (W1)	Relative weight	Quality rating (Qi)	Sub Index (Sli)
1	pH	6.5-8.5	3	00.068	88.90	6.0
2	TDS	500-2000	4	0.090	44.60	4.0
3	TH	300-600	3	0.068	122.60	8.3
4	Calcium	75-200	3	0.068	264.5	17.9
5	Magnesium	30-100	2	0.045	17.40	9.3
6	Sodium	300-600	2	0.045	13.70	0.6
7	Potassium	15-20	2	0.045	93.65	4.2
8	Alkalinity	200-600	2	0.045	15.35	0.7
9	DO	4-8	2	0.045	71.10	3.2
10	BOD	0-30	3	0.068	8.2	0.5
11	Chloride	250-100	4	0.090	14.60	1.3
12	Sulphate	200-400	4	0.090	8.30	0.7
13	fluoride	1-1.5	5	0.113	23.20	2.6
14	Nitrate	45-100	5	0.113	26.0	2.9
			∑wi=44	∑WI=0.99	∑Qi=1002	∑Sli=62.58

IV. Conclusion

After the careful study of analysis, interpretation and discussions of the numerical data it is revealed that water is hard in all the sampling points. The concentration of fluoride is well within the permissible limit. The concentration of Total dissolved solids in all sampling points is well within the permissible limit. The Water Quality Index (WQI) falls in the Good range at all the sampling points. Application of water quality index (WQI) in this study has been found useful in assessing the overall quality of water. This method appears to be more systematic and gives comparative evaluation of the water quality of sampling stations. The sulphate and nitrate concentrations of all three sampling points are well within the permissible standards. The BOD at all the three sampling points is higher, the reason might be anthropogenic, as villagers are in vicinity of river, activities viz., cloth washing, cattle rearing, bathing and even grey water of villagers also adding up in the river. From the MPN-Index, water is not suitable for drinking purpose. Hence water may be contaminated by airborne or anthropogenic activities. The analysis reveals that the surface water of the area needs some degree of treatment before consumption and it also needs to be protected from the perils of contamination.

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Synthesis and Characterization of SomeBiologically Potent 2-(2-butyl-4-chloro-1H-imidazol-5-yl)-4H-chromen-4-onederivatives.

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ABSTRACT

In the present investigation, a series of novel chromone derivatives containing imidazole moiety has been synthesized. The condensation of 2-butyl-4-chloro-1H-imidazole-5-carbaldehyde with various substituted o-hydroxy acetophenones in the presence of 40% KOH in PEG- 400 gives the chalcones. Oxidative cyclisation of chalcones withcatalytic amount of iodine in the presence of DMSO gives chromones. Chalcones and Chromones were obtained in satisfactory yield.The structure of intermediate and titled compounds was confirmed by spectral tools.
Keywords: Chalcones, Chromones, O-Hydroxyacetophenones, Imidazole, PEG-400

I. INTRODUCTION

Owing to interesting chemistry and various bioactivities, heterocycles are of prime importance for synthetic and medicinal chemists. Extensive studies are being carried out for designing potential pharmaceuticals. Chalcones are α,β-unsaturated carbonyl compounds and are used as intermediates for the synthesis of various heterocyclic compounds. Chalcones are well known precursor for the synthesis of various biologically important heterocycles[1-4].Chalcones belong to flavanoid family displayed an impressive array of biological activities[5].Chalcones exhibits different biological activities such as anti-inflammatory, anti-invasive, antimalarial, antitumor, anti-diabetic, cytotoxic and chemoprotective[6-10]etc.Imidazole is a part of essential amino acid histidine, biotin, and alkaloids. Recently, certain imidazole based compounds were reported to possess antimicrobial activities[11,12]. It is alsoreported that, imidazole derivatives are gained synthetic interest in recent yearsdue to their broad spectrum of biological properties[13-16].

By the synthetic point of view chromones are important in thesynthesis of the variety of heterocyclic compounds. Naturally, chromones are mostly in theform of 2-phenyl chromones called as iso-flavones those arefound in fruits and vegetables[17,18].In the plant kingdom, Chromone-4-ones, a class of naturally occurring compound, are widely distributed.Chromones and other related ring systems have plenty ofinteresting biological activities. Literature survey displayed thatchromone compounds possess various physiological andbiological properties and thus found use in medicine[19].Chromone compounds have considerable interest in the pastdecades[20]. A series of sulfonamide chromones areinhibitors of carbonic anhydrase, show in vitro antibacterialand antifungal activity[21-22]. Duringthe last decades the 5-hydroxy-2-styrilchromone were derivedfrom the green algae [chrysophaeum] against leukemia cells.Chromones substituted at 2-position has been shown to possessvarious activities. Few of the chromones have potentialantirhythmic activity such as HIV-integrase inhibition[23].Few of them showed anti-cancer, anti-tumour, anti-ulceractivities[24-25]. Synthesis of flavones (Chromones) and theirderivatives has considerable attention due to their significantbiocidal and pharmaceutical effects.

A synthesis is termed ideal if it relies on use of a green solventsuch as water, supercritical CO_2 or low-boiling liquid polymerssuch as polyethylene glycols(PEG's). Recently PEG-400 emerged as analternative green solvent with unique properties such as thermalstability, commercial availability, nonvolatility, miscibility witha number of organic solvents, and recyclability[26]. PEGs overcome the toxiceffects of solvents on the

environment. Therefore, we prepare chalconesusing KOH in PEG-400 as green solvent.

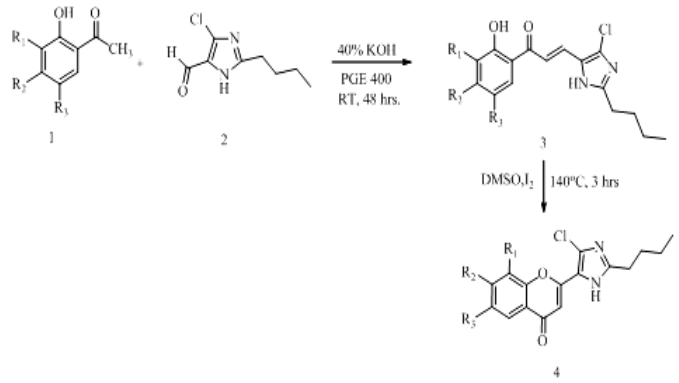
II. Methods & Material

All melting points were recorded in an open capillary tube in liquid paraffin bath and are uncorrected (Table-1). The purity and the progress of the reaction were routinely monitored by TLC. The product was purified by recrystallization technique.

IR spectra were recorded on Perkin-Elmer FTIR spectrum-2 with ATR-single Refl. ZnSe technology. ^{1}HNMR spectra were recorded on BRUKER-ADVANCE II 400 MH_z spectrometer in $CDCl_3$ and DMSO-d_6 as solvent and TMS as internal standard. Peak values are shown in δ ppm. Mass spectra were obtained by Finnegan mass spectrometer. TLC was performed on pre-coated silica-gel plates and was observed under UV light. All the synthesized compounds gave satisfactory elemental analysis.

In the present investigation a series of novel chromones derivatives containing imidazole moiety has been synthesized. The precursor,i.e. substituted *o*-hydroxy acetophenones, were prepared by fries rearrangement[27].The condensation of *o*-hydroxy acetophenones (**1**) with 2-butyl-4-chloro-1*H*-imidazole-5-carbaldehyde (**2**) in presence of 40% KOH in PEG-400 as a green reaction medium gives the chalcones (**3**). Oxidative cyclization of chalcones with catalytic amount of iodine in presence of DMSO gives chromones (**4**).

The structure of synthesized compound was confirmed by spectral analysis.Outline of synthesis of 2-(2-butyl-4-chloro-1*H*-imidazol-5-yl)-4*H*-chromen-4-one is summarized in Scheme 1.



Scheme 1

General Procedure for Synthesis of Chalcones (3a-3f):

Equimolar amount of substituted *o*-hydroxy acetophenones and 2-butyl-4-chloro-1*H*-imidazole-5-carbaldehyde were taken in 100 ml RB flask with minimum amount of PEG-400. To this mixture KOH solution (40%) was added drop wise and stirred for 1 hr. Progresses of reaction were monitored by TLC. After completion of the reaction, the mixtures were poured into crushed ice and acidify with conc. HCl. Solid thus obtained were separated by filtration and recrystallized from proper solvent to get chalcones (**3**).

3a: IRcm^{-1}:3557.3 (O-H stretching), 3133.9 (N-H stretching), 2960, 2930 (CH_3 stretching), 1635.38 (conjugated C=O group), 1554 (aromatic ring), 648, 782 (C-Cl bond stretching). ^{1}H NMR:0.85 δ (t, 3H, 7.28 Hz), 1.34 δ (m, 2H, 7 Hz), 1.8 δ (quintet, 2H, 7.4 Hz), 2.73 δ (t, 2H, 7.4 Hz), 2.23 δ (s, 3H)7.82 δ (d, 1H,16 Hz), 6.90 δ (d, 1H,16 Hz), 7.51 δ (d, 2H,8 Hz), 7.28 δ (t, 1H,8 Hz), 11.40 δ(s, 1H, O-H proton), 12.76 δ (s, 1H, N-H proton).MS: M+1 as m/z= 319.1.

Synthesis of 2-(2-butyl-4-chloro-1H-imidazol-5-yl)-4H-chromen-4-one (4a-4f):

Chalcone **(3)** was dissolved in 5ml DMSO. To this reaction mixture catalytic amount of I_2 was added. Contents were heated at 140 ^{o}C for 3 hours. Then the reaction mixture were poured over crushed ice containing 3-4 gm sodium thiosulphate to eliminate the unreacted I_2. The solid thus obtained was washed with cold water. The product obtained was recrystallized from alcohol to afford pure chromone **(4).**

4a: IRcm^{-1}:3139.8 (-N-H stretching), 3101-2872.4 (-CH_3 stretching), 1618.28(conjugated C=O group), 1544-1573.85 (aromatic C-H stretching), 629.32-817.04 (C-Cl stretching), 1034.07(C-O stretching). ^{1}H NMR: 0.91 δ (t, 3H, 7 Hz), 1.35 δ (m, 2H,7 Hz), 1.67 δ (quintet, 2H,7 Hz), 2.67 δ (t, 2H,7 Hz), 2.40 δ (s, 1H), 6.69 δ (s, 1H), 7.48 δ (d,1H,7.4 Hz), 7.56 δ (d, 1H, 7.4Hz), 7.79 δ (s, 1H), 12.96 δ (s, 1H), MS: M+1 as m/z= 317.1

III. Results and Discussion

The Claisen-Schmidt condensation is an important C-C bond formation for the synthesis of Chalcones. It is generally carried out by the using strong bases such as NaOH or KOH in polar solvents (MeOH or DMF). In present study, PEG-400 is used as a recyclable reaction solvent to obtain 1,3-diaryl-2-propen-1-ones with good to excellent yields[28].

First, we attempted condensation of various substituted*o*-hydroxy acetophenone with 2-butyl-4-chloro-5-formyl-imidazole using PEG-400 as a reaction solvent under alkaline condition. The reaction was completed within 1 h and the corresponding product was obtained upto 95% yield. The purity of the compounds waschecked by thin layer chromatography and structures of the synthesized products wereconfirmed by their spectral analysis.

Chalcone **3a** shows characteristic band at 1635 cm^{-1}indicats the presence of α, β- unsaturated >C=O group (Fig. 1).^{1}H NMR spectra of chalcone **3a** showed characteristic doublet signals at 7.82δdue to olefinic proton αH, J≈15.98Hz and 6.90 δ due to olefinic proton βH, J≈15.98Hz indicating the trans geometry.The phenolicproton (2'-OH) was observed as a singlet at 11.40 δdue to hydrogen bondingwith the adjacent carbonyl group(Figure 2). Mass spectra of compound **3a** satisfies molecular formula frommolecular ion peaks. Also it confirms the isotopic abundances of –Cl as 3:1 (Figure 3).

IR spectra of chromone showed characteristic bands at 1618.28 cm^{-1}due >C=O stretching vibrations. Lowering of normal >C=O frequency was observed due tothe presence of -C=C stretching in chromones(Fig. 4). ^{1}H NMR spectra of the compounds showedcharacteristic singlet signals at 6.69δ due to olefinicprotons. The –NH proton was observed as a singlet at 12.96δ, while other aromatic and aliphatic protons were foundat expected regions(Fig. 5). The mass spectra of compounds **4a** showed molecular ion peakscorresponding to their molecular formula. Besides the molecular ion peak [M+], thecompounds showed [M+1] (isotopic abundances), which confirmed the presence ofhalogen groups in respective compounds. The base peak was seen at m/z 317(Figure 6).

Table 1. The physical constants of prepared compounds (3a-f) and (4a-f)

Compound	Substituent			M. P.(°C)	Yield (%)
	R_1	R_2	R_3		
3a	H	H	CH_3	264	93
3b	H	CH_3	H	194	90
3c	H	CH_3	Cl	178	92
3d	H	H	Cl	218	95
3e	H	Cl	H	224	91
3f	Cl	H	Cl	186	94
4a	H	H	CH_3	282	74
4b	H	CH_3	H	228	70
4c	H	CH_3	Cl	192	72
4d	H	H	Cl	236	81
4e	H	Cl	H	232	75
4f	Cl	H	Cl	192	78

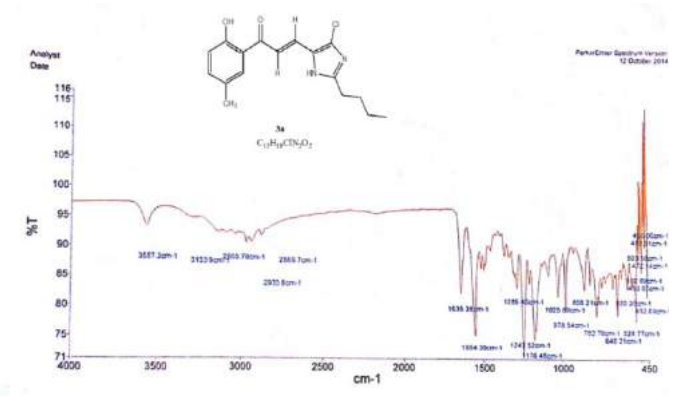


Figure 1. IR Spectra of compound **3a**

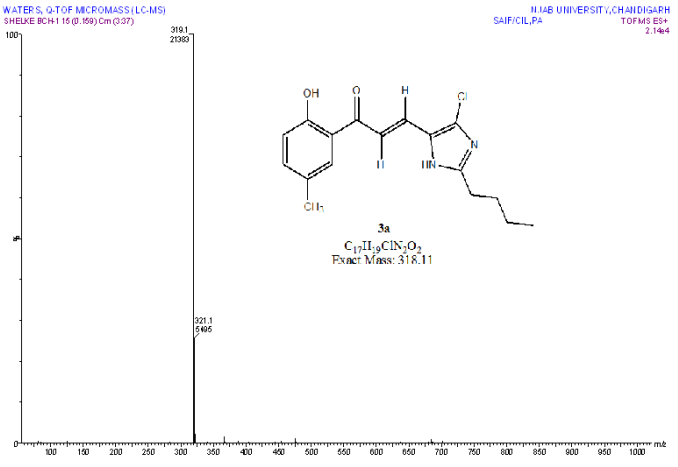


Figure 2. Mass Spectra of compound**3a**

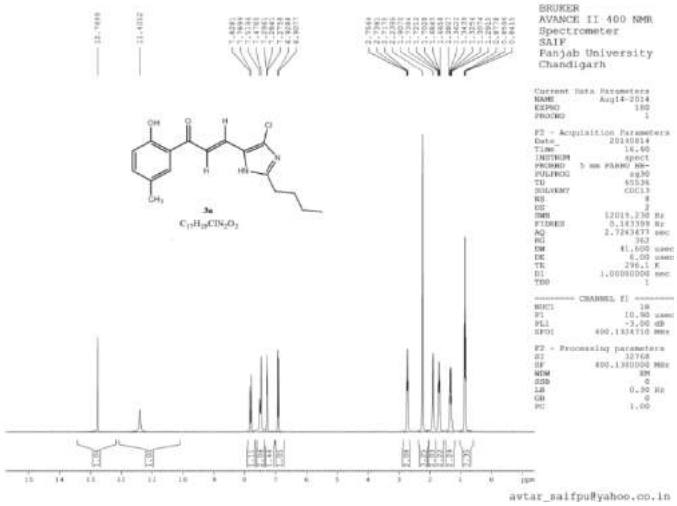


Figure 3. ^{1}H NMR of compound **3a**

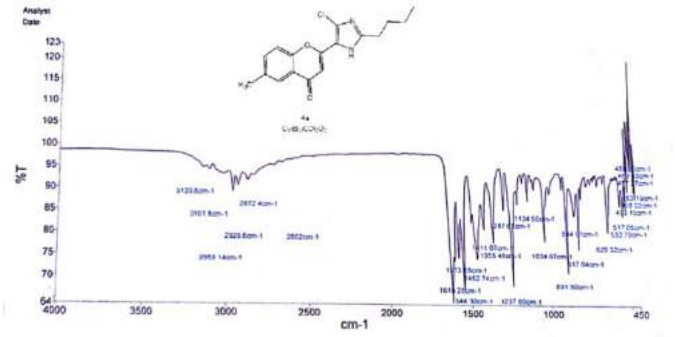


Figure 4. IR Spectra of compound **4a**

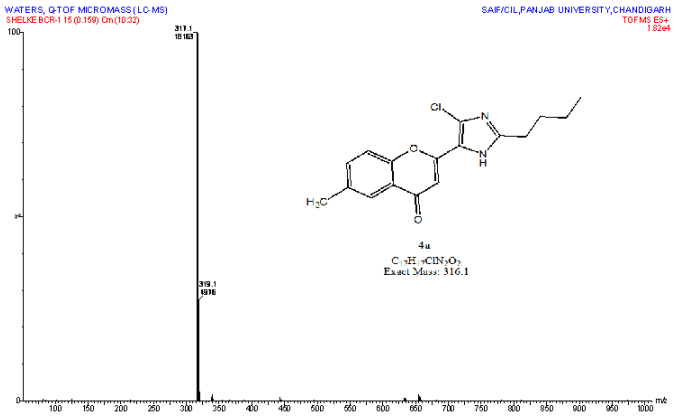


Figure 5. Mass Spectra of compound **4a**

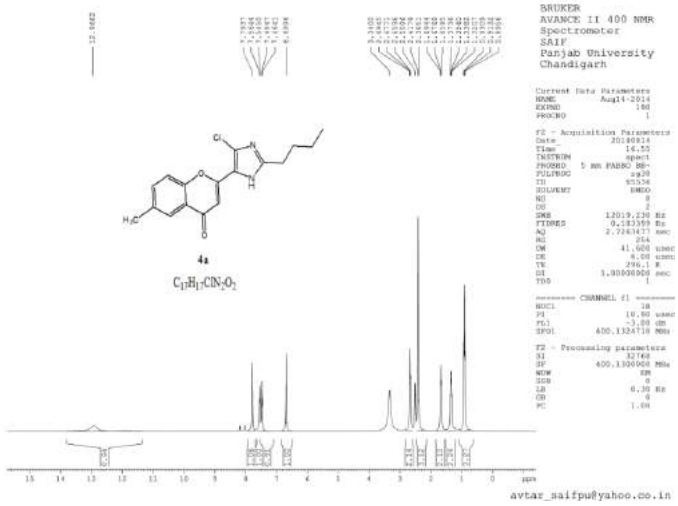


Figure 6. ^{1}H NMR of compound **4a**

IV. Conclusion

The present investigation reports the synthesis of 2-(2-butyl-4-chloro-1H-imidazol-5-yl)-4H-chromen-4-one derivatives by oxidative cyclisation of chalcones with catalytic amount of iodine in the presence of DMSO.The structures of synthesized chromone derivatives were established by the satisfactoryspectral analysis.

V. Acknowledgement

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Synthesis and Antimicrobial Screening of Metal Complexes of 1-(5-Chloro-2-Hydroxyphenyl)-3-(2,4-Dichlorophenyl) Propane-1,3-Dione

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ABSTRACT

1-(5-Chloro-2-Hydroxyphenyl)-3-(2,4-Dichlorophenyl) Propane-1,3-Dione and its metal complexes have been synthesized by conventional method. The diketone is offered by employing Baker- Venkatraman rearrangement. The synthesized compounds were confirmed by the spectroscopic analysis such as UV, IR , 1H-NMR, 13C-NMR, mass, elemental analysis, magnetic susceptibility, XRD and evaluated for antibacterial screening.

Keywords: Baker-Venkatraman rearrangement, metal complexes, XRD, thermal study.

I. INTRODUCTION

β-diketones and relative derivatives are considered as a class of very important ligands in the growth of coordination Chemistry. The Chemistry of 1,3-diketones has attracted the attention of scientists for almost century[1]. Due to the presence of two oxygen donor atoms and facile keto-enol tautomerism[2], they easily coordinate with metal ions after deprotonating the enolic hydrogen atom and provides stable metal complexes. They have been used as ligands for coordination of transition metals and have been investigated for use as potential antiviral agents[3]. Those are important class of organic compounds frequently encountered in synthetic chemistry[4-6]. As a result of their usability, the biological transformation of these compounds have recently arised interest[7-8]. 1,3-diketones have gained a lot of interest due their importance as good ligands[9], for the chelation with metals, as intermediate in the synthesis of core heterocycles such as pyrazole[10], flavones[11], isoxazole[12], triazole[13], benzodiazepine[14] and pyrimidine[15]. Those have pharmacological activities like antioxidant[10], prophylactic antitumor[16], systematic insecticidal[17] and antibacterial[18]. Recently, it is known that they have the important pharmacophores for the HIV-integrase(1N) inhibitors[19]. It has been used as anti-sunscreen agent[20].

Owing to β-diketones having such varying pharmacological activities, we were interested to synthesize a novel β-diketone and its transition metal complexes

II. Experimental

Synthesis of 2-acetyl-4-chlorophenyl 2,4-dichloro benzoate (A):

To The mixture of 5-chloro-2-hydroxyacetophenone and 2,4-dichlorobenzoic acid, a dry pyridine and POCl3 were added dropwise with constant stirring at 0C. Then the reaction mixture was stirred for about 7-8 hours. After completion of the reaction, the reaction mixture was poured into 100ml 1M HCl containing 50 gm of crushed ice and solid obtained was filtered and washed with 10 ml of water. It was recrystallized from ethnol, filtered and dried. Yield: 80%.

Synthesis of 1-(5-chloro-2-hydroxyphenyl)-3-(2,4-dichlorophenyl) propane-1,3-dione (B):

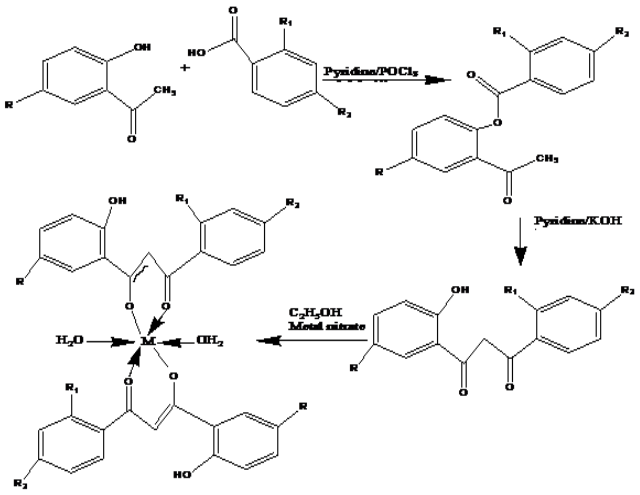
Compound (A) was dissolved in dry pyridine. To this powdered KOH was added and the reaction mixture was stirred for about 3-4 hours. After completion of the reaction, the reaction mixture was poured on ice cold water and acidified with conc. HCl. The yellow solid was filtered off and crystallized from absolute ethanol to obtain pure product. Yield: 80%.

FT-IR: (KBR) cm^{-1}: 3001.96 (OH), 1680.26 (C=O), 1480.18 (Ar C=C). 1H-NMR (300 MHz, CDCl3-d6);

δ=6.8(s, 1H, =CH-), 7.1 (s, 1H, Ar-H), 7.4-7.7 (m, 5H, Ar-H), 11.9 (s. 1H, OH), 15.1 (s, 1H, Enolic-OH), 13C-NMR (300MHz, CDCl3); δ=187.3 (s, C-1, C=O), 94.1 (s, C-2, -CH=), 185.6 (d, C-3), 115.2 (s, C-1'), 160.4 (s, C-2'), 119.2 (d, C-3'), 129.5 (d, C-4'), 125.5 (s, C-5'), 128.3 (d, C-6'), 135.2 (s, C-1"), 136.5 (d, C-2"), 131.5 (d, C-3"), 141.3 (s, C-4"), 127.2 (s, C-5"), 132.6 (s, C-6"). UV/Vis (DMSO)nm: 370,415. EC-MS: 344.91 (M+1).

Bis-(diketonato) Fe(III) complex:

The mixture of (3.43gm, 0.01 mol) of compound B and (4.04 gm, 0.01 mol) of anhydrous Fe(III) nitrate and 20 ml of anhydrous ethanol were added and refluxed for about 8-9 hrs. The brown solid which precipitated was washed with boiling ethanol and recrystallised from ethyl acetate to give brownish crystals of Fe(III) β-diketonate. Yield: 85%.



L: R=Cl, R1=Cl, R2=Cl
M= Cu, Ni, Co, Cr, Fe. In all these cases water of coordination is present.

Scheme 1. Synthesis of ligand and metal complexes.

III. Results and discussion

2-acetyl-4-chlorophenyl 2,4-dichloro benzoate was prepared by the esterification of 5-chloro, 2-hydroxyacetophenone with 2,4-dichlorobenzoic acid in the presence of POCl3. 2-acetyl-4-chlorophenyl 2,4-dichlorobenzoate undergoes Baker-Venkatraman transformation to offered pale yellow needle of ligand (B). The negative test for ester confirms the absence of ester group. The structure was further confirmed by spectral analysis.

The ^{1}H-NMR spectra gives characteristic peak at δ15.1 which corresponds to enolic proton and at δ11.9 which is due to phenolic proton adjacent to the carbonyl group. It confirms the formation of β-diketone. The compound in enolic form is more stable than that of ketonic one. The complex of synthesized compound(B) gives browened coloured Fe(III) in high yield. The structure was then confirmed by spectral analysis.

The C=O bond in complexes of shifted to lower frequency as compared to that of free ligand which indicates the coordination of metal atom with the carbonyl group of diketone[21].

Similarly, other metal complexes were prepared by the same method. The ligand and its metal complexes are quite stable. All the complexes are insoluble in water but soluble in DMSO and DMF. The complexes are non-electrolytic in nature[22].

Table 1. Molar conductivity, magnetic and Infrared spectral data of synthesized compounds.

Compound	Meff(BM)	Molar Conductance	IR (cm^{-1})				
			ν(C=O)	ν(C-O)	ν(-OH)	ν(M-O)	ν(OH) Coordinated H2O Molecule
Ligand			1680	1480	3001	--	---
Cu(II) complex	2.12	29.40	1657	1501	3016	527	3255
Ni(II) complex	2.73	54.22	1655	1505	3017	505	3258
Co(II) Complex	4.45	35.45	1666	1522	3020	505	3248
Cr(III) Complex	3.82	37.23	1663	1518	3018	520	3244
Fe(III) Complex6.11	6.11	61.65	1656	1523	3015	512	3260

IV. Powder X-ray diffraction analysis

The X-ray diffractograms of the complexes were scanned in the range 5-85º at a wavelength of 1.543ÅA. The diffractograms and associated data depict the 2θ values for each peak, the relative intensity and inter-plannar spacing (d-values). The X-ray diffraction pattern of these complexes with respect to major peaks of relative intensity greater than 10% were indexed using a computer programme[23]. This indexing method also yields Miller indices (hkl), the unit cell parameters and the unit cell volume. The unit cell of Cu(II) complex yielded values of lattice constant: a=21.543 Å, b=8.532Å and C= 7.592 Å and a unit cell volume V=1395.4 $Å^3$. The unit cell of the Co(II) complex yielded values of lattice constant: a=14.511, b=5.130 and c=13.087 and a unit cell volume V=974.29. In concurrence with these cell parameters conditions such as a≠b≠c and α=γ≠β required for a monoclinic sample were tested and found to be satisfactory. Hence, it can be concluded that the Cu(II) and Co(II) complexes were monoclinic crystal systems. The experimental density values of the complexes were determined using the specific gravity method[24] and found tobe 3.24 g cm^{-3}, 4.83 g cm^{-3} for the Cu(II) and Co(II) complexes respectively. Comparison of experimental and theoretical density values shows good agreement within the limits of experimental error[25].

V. Thermo Gravimetric Analysis

Cu (II) complex:

The simultaneous TG/DTA analysis of a representative metal complex of Cu (II) was studied from ambient temperature to 1000°C in nitrogen atmosphere using α-Al_2O_3 as reference. The thermogram curve of Cu(II) complex shows weight loss 8.11% (cal. 8.20) in the temperature range 190-215^{0}C and sharp endotherm at 195^{0}C which clearly indicate a removal of two coordinated water molecules**[26]**.

The anhydrous complex first showed decomposition from 265-570^{0}C with a 20.16% (cal. 20.50) mass loss and a broad exothermic peak with 390^{0}C in the DTA which may be attributed to the removal of the non-coordinated part of the ligand. The second step of the decomposition from 580-865^{0}C with a mass loss of 55.10% (cal. 51.79) corresponded to the decomposition of the coordinated part of the ligand. A broad endotherm in DTA was observed for this. The mass of final residue corresponds to stable CuO, 17.95% (17.10) which is in agreement with earlier workers**[27]**.

VI. Antimicrobial Screening

Antimicrobial screening[28] of prepared compounds were tested against bacteria as Staphylococcus aureus and Bacillus subtilis (Gram +ve); Escherichia coli (Gram –ve) and against fungi, Aspergillus niger and Fusarium Oxysporum by Kirby Baur's disc diffusion technique using dimethyl sulfoxide as a solvent. The streptomycin was used as reference in case of antibacterial and antifungal activity. A uniform suspension of test organism of 24 hrs old cultures was prepared in test tube containing sterile saline solution. A sterile nutrient agar was then added in each of the petri plates. The plates were related to ensure the uniform mixing of the micro organism in the agar medium which was then allowed to solidify. Sterile Whatmann filter paper disc were dipped in the solution of each compound and placed on the labeled plates. The DMSO was used as a control of the solvent. The streptomycin was used as a standard compound for comparison. Plates were kept in refrigerator for half an hour for diffusion and then incubated at 37◦C for 24hrs. After incubation the inhibitory zones around the discs were measured in terms of mm.The observed data of antimicrobial activity of compounds and the standard drugs are given in table.

Table 2. Antimicrobial activity of synthesized compounds

Copound No.	Conc. (ppm)	Antibacterial activity (inhibition in mm)			Antifungal activity	
		Bacillus subtilis	E. coli	Staphylococcus aureus	Aspergillus niger	Fusarium oxyporum

Ligand		12	11	9	9	8
Cu -B	100	16	14	10	17	10
Ni-B	100	13	13	12	18	11
Co-B	100	12	15	14	13	16
Cr-B	100	14	12	10	10	13
Fe-B	100	12	11	11	11	12

VII. CONCLUSION

In the present work Ligand and its transition metal complexes were synthesized and their structures elucidated on the basis of spectral analysis. ^{1}H-NMR and ^{13}C-NMR spectra revealed that the prepared diketone possess charecterestic peaks due to the presence of enolic proton (enol form of β-diketone) and phenolic proton adjacent to carbonyl group. These synthesized compounds were screened for in vitro antibacterial and antifungal activity and found to be promising candidates as new antibacterial and antifungal agents.

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Cr Doped TiO2 Catalystin Photocatalytic Degradation of Jakofix Red Dye (HE7B)

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ABSTRACT

Pigment / dye manufacturing industries are one of the highly polluting industries generating large volumes of high strength of waste water with disobedient properties. Different process covering anaerobic, aerobic as well as physico-chemical methods have been employed to treat this coloured effluent. The intense colour of the effluent leads to acute ecological problem when released untreated in to environment. Thedecolourisationor deterioration of effluent is known to be very challenging task. In this paper degradation of industrial dyein terms of colour, was studied by usingCr doped TiO2 photo catalyst. The Cr doped TiO2 nanoparticles were prepared by a using Chromium and titanium peroxide gel method with Titanium Isopropoxide as a precursor. The physico-chemical characteristics of the Chromium–titania catalysts of concentration range 0.5 to 5% (w/v) were determined using the methods of Brunauer-Emmett-Teller adsorption, X-ray diffraction, FE-SEM, FT-IR,and UV visible spectroscopy (DRS).The Cr-TiO2 catalystshowed a photo-degradation of dye for all concentration i.e. 0.5 to 5% (wt %).The maximum photocatalytic degradation (90%) ofwas observed for Jakofix red dye (HE 7B)at 0.5% Cr-TiO2sol gel catalyst, as compared to pure TiO2.

Keywords: BET, Colour, Dye, Effluent, Photocatalyst, and TiO2.

I. INTRODUCTION

Effluent originating from any dye/ pigment manufacturing industries contain large amount of dark coloured wastewater called coloured effluent. This effluent is the unwanted residual liquid waste to dispose because of acidic / basic pH, dark colour, unpleasant odour and high percentage of organic and inorganic matter.Dark colour of effluent is due to the presence of dye / pigment content. It decreases sunlight penetration in rivers and lakes which in turn decrease both photosynthetic activity and dissolved oxygen concentration affecting aquatic life. So the disposal of this effluent is one of the critical environmental issues.

Photocatalytic degradation of organic contaminants using TiO_2 photocatalyst is being widely studied as a relatively new technique for pollution abatement due to its desirable properties, such as non-toxicity, wide band gap, and stability in acidic as well as basic media [1-3]. However, the wide band gap of TiO_2 only absorbs light of wavelength less than 400 nm in the UV region, which restricts its applications in the presence of UV irradiation. For widespread applications, a TiO_2-based catalyst effective in visible radiation or for solar light needs to be developed as a future generation photocatalytic material. TiO_2 absorbs only 5% energy of the solar spectrum and hence numerous studies have been performed to extend the photo-response and photo catalytic activity by modifying its surface structure, surface properties and composition to shift its absorption in visible region so as to improve its photocatalytic activity in visible/solar light [4-6]. The surface modification by doping with metal ions and organic polymers has been proven to be an efficient route to improve the photo catalytic activity of TiO_2 [7–10].

Anpo et al. have studied the doping of TiO_2 with transition metals such as V, Cr and Fe by three different methods: sol–gel, co-precipitation and ion implantation techniques [11–14]. The higher photocatalytic activity of Chromium doped TiO_2 prepared by ion implantation was correlated to deep incorporation of Chromium into titanium oxide lattice due to bombardment of highly

energetic vanadium ions on TiO_2 targets. Generally titania powder is used for photocatalytic degradation of pollutants in aqueous solution using a photocatalytic reactor. The used catalyst is recovered by filtration for its recycle; this is quite a cumbersome process because of the very fine nature of the powder.

Thin films of titania as an active photocatalyst would be an attractive alternative to overcome the catalysts separation problems. In an attempt to modify the optical properties of TiO_2, we were successful in improving the photocatalytic activity of TiO_2 in sunlight by doping titania thin films with Fe and Au, which shifted its absorption into visible region [15–17]. In continuation of our earlier efforts, thin films of Chromium doped titania were deposited by simple dip coating techniques using vanadium and titanium peroxide gel on various glass substrates. These films have been characterized by using various techniques to determine their structural properties. Most of the dyes and poisonous metals are used in the textile industries are stable to light and are non-biodegradable.[18] In order to reduce the risk of environmental pollution from such waste, it is necessary to treat them to before discharging it receiving in the environment [19]. Photocatalytic degradation Methylene blue dye by photochemical reactor was studied by Suryawanshi etal [20] and dye and removal of chromium from waste water was studied by Shrivastava [21]

Semiconductor photocatalysis is one technique that has great potential to control organic as well as inorganic contaminants. Hence, its degradation prior to discharge is essential for the environmental safety. Though, the various effective physical and chemical methods such as ozonation, flocculation and activated carbon adsorption etc. have been attempted for the removal of colour.

In this paper, the Cr–TiO_2 catalyst was prepared by the sol– gel method. The samples were characterized by XRD, FE-SEM, FT-IRand UV–Vis absorption spectrum. The photocatalytic activity of solgel Chromium doped TiO_2 for the degradation of Jakofix red dye (HE 7B) has been studied and results are reported here.

II. Methods & Material

2.1 Catalyst Preparation:

A series of chromium–titania catalyst with Chromium content varying from 0.5,1,2,3,4 & 5 wt% were prepared by sol–gel technique using Chromium Nitrates and Titanium Isopropoxide astitanium precursors, respectively. In a typical synthesis of 1 wt% Chromium–titania catalyst, 4.028 g of Titanium Isopropoxide (Sigma-Aldrich make) was hydrolysed with 30 mL of MilliQ water (conductivity is <10 Ohm). To this, 20 mL of 30% aqueous hydrogen peroxide (Merck make) was added to get a transparent orange sol of titanium peroxide. Chromium Nitrate (76.9 mg, Merck make) was suspended in 20mL of MilliQ water; 3 mL of 30% aqueous hydrogen peroxide was added to it to get a clear green colored peroxochromic acid solution. This peroxochromic acid solution was added to the titanium peroxide solution and a transparent green yellow viscous gel was formed. To obtain the powder sample, we dried the Chromium–titania peroxide gel at ambient temperature and then heated it in ahot air oven at 110^0C and further calcined it at 400^0C under inert air flow using a muffle furnace. The heating / cooling rate was 5^0C/min, with a5 hour dwell time at the selected temperature. PureTiO_2 was also prepared similarly by the sol–gel technique using peroxide precursor for comparison.

2.2. Catalyst characterization:

2.2.1 X-ray diffraction and UV–Visible Spectroscopy:
The powder X-ray diffraction analysis of the powdered samples was carried out using a Rigaku X-ray diffractometer (Model DMAX IIIVC). The data was collected in the 2 thetarange, 20–80 with a step size of 0.028 and counting time of 15 second at each step. The diffuse reflectance UV–vis spectra were recorded in the range 200–800 nm with 0.5 nm spectral bandwidth in air at ambient temperature by using a Shimadzu instrument (UV 3600) spectrophotometer.

2.2.2FE-SEM & BET:

The surface morphology of the samples was studied using FESEM (SEM, XL-20 Philips). The particle morphology of the Cr–TiO2 photo catalyst was tested using a Hitachi H-800 transmission electron microscope (TEM). The BET, Porosity was checkedbyMicromeritics Gemini VII 2140 instrument.

2.2.3Element analysis by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

The Cr concentration in prepared catalyst was measured by ICP-MS instrument. The catalyst was tested by using Agilent make 7700 model with Mass Hunter Software.

2.3. Photocatalytic activity

For photocatalytic degradation of Jakofix red dye (HE 7B), the powder sample of Cr-TiO_2 wereused as photocatalyst. The catalyst powder 15 mg were taken in to a 250 mL glass beaker containing solution of 50mL dyehaving concentration 250 ppm. For degradation of dye,all the beaker werekept in sunlight for four to five hr. The degradation of dyewas checked at different time interval by using UV–Visible spectrophotometer.

III. Result & Discussion

3.1 Sol gel behaviour of Cr-TiO_2Sol:

When titanium Isopropoxide was hydrolysed and the resulting hydroxide was further reacted with hydrogen peroxide, a yellow solution was obtained after a vigorous exothermic reaction. The temperature of reaction was controlled by cooling the reaction mixture by jacketed cooled water or ice water till get transparent yellow solution. The Chromium nitrate solution was slowly added to this solution, a slightly greenish yellow solution was obtained. When this solution was kept for few hours, the thickness of solution was increased and transparent viscous gel was formed. The addition of Chromium concentration varies from 0.5%, 1%, 2%, 3%, 4% & 5% respectively. The non-gelatinous precipitate was obtained above the concentration of 4%. The sol gel behaviour of Cr-TiO_2 sol containing different concentrations of Chromium Nitrate (0.5-5 wt %) has been studied. The results showed similar behaviour, hence only sol containing 1% Cr-TiO_2 has been studied in detail as a characteristic example.

3.2 Optical Properties of Cr-TiO_2 powder.

The calibrated UV-3600 spectrophotometer was used in scanning mode at 200-400 nm range for measurement of absorbance of powder samples.The optical absorption of the powder sample calcined at 400^0C in UV–Visible range is shown in Figure 3.

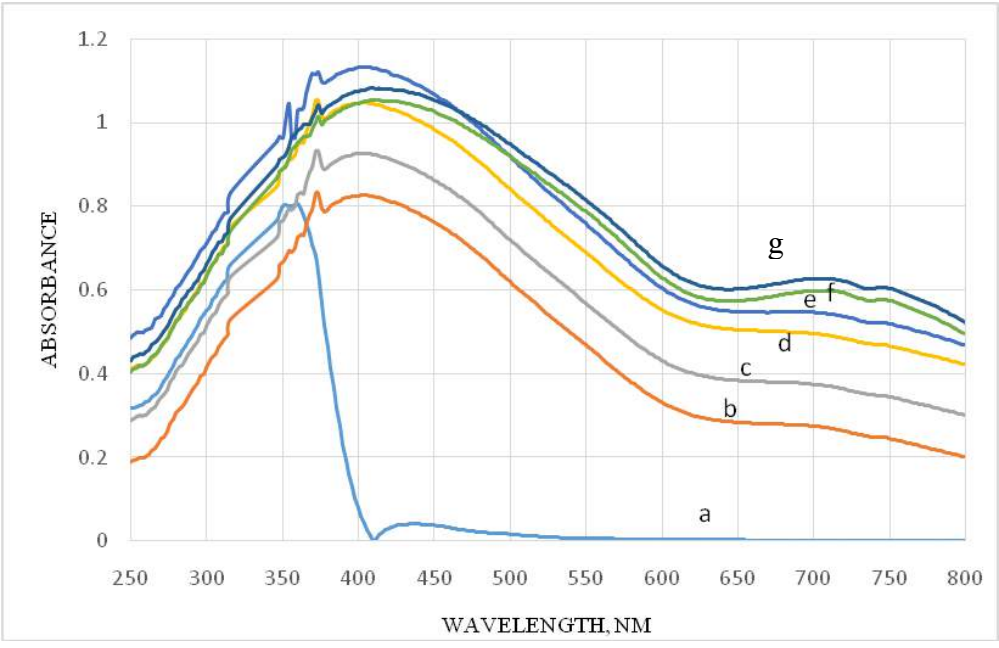
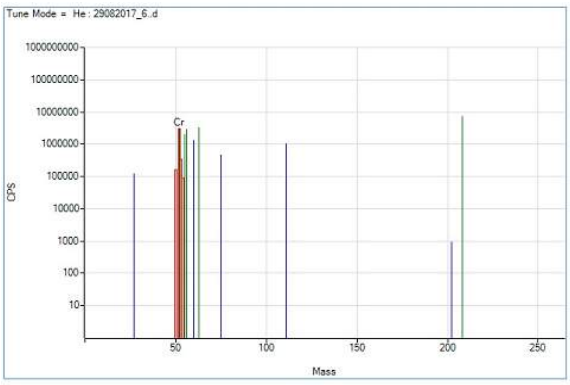


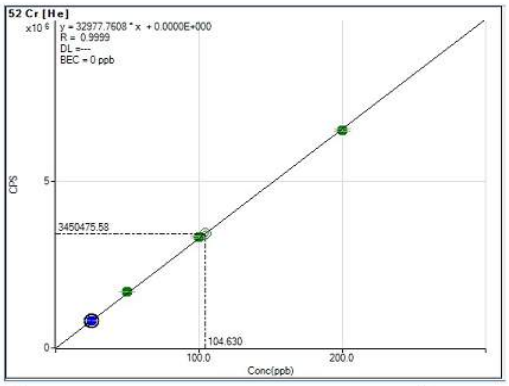
Figure1. DRS spectra of powder samples (a) TiO_2, (b) 0.5% Cr-TiO_2, (c)1.0% Cr-TiO_2, (d) 2% Cr-TiO_2, (e) 3.0% Cr-TiO_2, (f)4.0% Cr-TiO_2, (g) 5.0% Cr-TiO_2.

The pure TiO_2 curve (a) shows an absorption edge at around 360 nm, (the absorption edge is for bulk anatase TiO_2). It may be attributed to the smaller particle dimensions of TiO_2 (2–10 nm) in powder catalyst. The curve 'b' in figure represents the UV-Visible spectra of 0.5%Cr-TiO_2 which show absorption above 385 nm. In case of 1%, 2%, 3%, 4% and 5% Cr-TiO_2 (curves c, d, e, f and 'g') the absorption has been shifted further towards the visible side i.e. at 400 and 430 nm respectively. In all these samples, the wavelength shifting to visible regionmay be recognised to the incorporation of Chromium into the TiO_2, since the extent of shift to visible region is dependent on the concentration of Crin TiO_2.

Estimation of Cr by ICP-MS:

The calibrated ICP-MS (7700 model), Agilent make instrument was used for determination of chromium content.The catalyst powder sample were digested in Conc. Nitric acid (Merck make) solution for 1 hr. after cooling the solution dilute 250 ml with Milli Q water (conductivity is <10 Ohm). The linearity graph was plotted for 25 to 200 ppb concentration (Multistandard Element, Merck make)and resultant correlation coefficient of slope is 0.9999. The % RSD for this linear solution is not more than 1.2 indicate the less deviation in Cr estimation and performance of instrument (b)





Calibration

Level	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		25.000	25.284	833808.74		P	0.2
2		50.000	51.322	1692493.0		A	0.6
3		100.00	101.326	3341507.7		A	1.2
4		200.00	198.971	6561614.4		A	1.1

a b

Table 1. The concentration of Cr content in powder catalyst are mentioned.

Catalyst	Conc. of Chromium, %
TiO_2	ND
0.5% Cr_TiO_2	0.4999
1.0% Cr_TiO_2	0.9998
2.0% Cr_TiO_2	1.9997
3.0% Cr_TiO_2	2.9989
4.0% Cr_TiO_2	3.9987
5.0% Cr_TiO_2	4.9985

FT-IR spectra of Cr-TiO_2Catalyst:

The FT-IR of Perkin Elmer make with UATR technique instrument was used for measuring spectra of metal doped TiO_2 catalyst. The FT-IR spectra of pure TiO_2 and Cr-TiO_2 calcined at 400^0C are given in Figure 3.

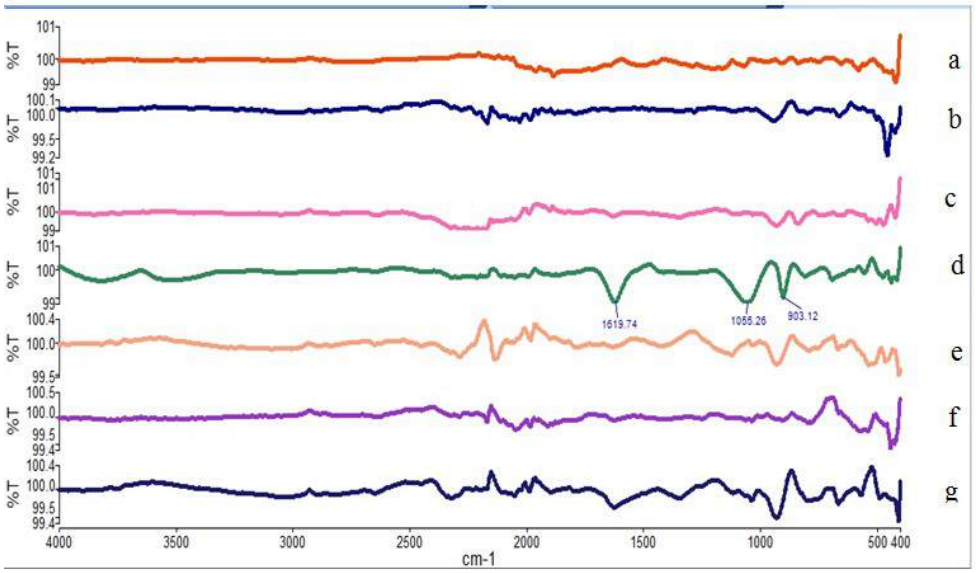


Figure 3. FT-IR spectra of (a) TiO2, (b) 0.5% Cr-TiO_2, (c) 1.0% Cr-TiO_2, (d) 2% Cr-TiO_2, (e) 3.0% Cr-TiO_2, (f) 4.0% Cr-TiO_2, (g) 5.0% Cr-TiO_2. Calcined at 400^0C

Each calcined catalyst sample was scan in the range of 4000 to 450cm-1. There are characteristic wide peaks in the region of 2000–500cm−1, which are related to the bending vibration of the Ti–O bonds. A new absorption at 1619, 1055 & 903cm−1 seen in the Cr–TiO_2sample but these peaks are absent in TiO_2 sample.

3.4 Crystallization behaviour of Cr-TiO_2 catalyst.

XRD data information

The gel was allowed to dry in at ambient temperature and used for the XRD analysis. The dried gel was calcined at 400^0C; results showed good agreement with the calculated values based on the chromium and titanium weighed during the preparation. The XRD patterns of air dried 1 % Cr-TiO_2 gel and of the gels calcined at 200, 300, 400,500 and 600^0C for 5hr are shown in Figure 4 (curves (a–e). As expected, the XRD pattern of as prepared sample (curve (a) shows the amorphous nature of air dried Cr-TiO_2 gel.

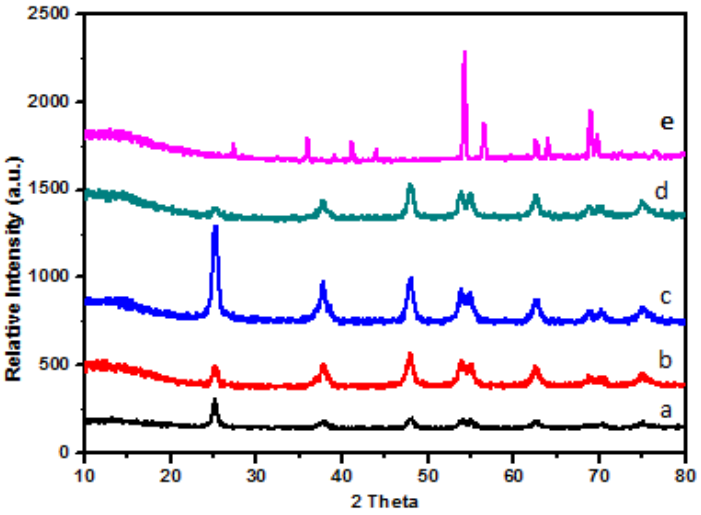


Figure 4. XRD pattern of 1% Cr-TiO_2 as prepared and calcined at (a) 200, (b) 300, (c) 400, (d) 500 and (e) 600^0C.

The sample heated at 200^0C (curve a) showed weak and broad peaks indicating the amorphous nature of the air dried gel. Curve (b) (sample calcined at 300^0C) shows a slight increase in the intensity of peaks corresponding to anatase TiO_2, indicating the beginning of crystallization of Cr-TiO_2 at this temperature. Further increase in calcination temperature to 400^0C curve (c) showed an increase in the intensity of the characteristic peaks of anatase phase, suggesting the further growth of anatase phase. The samples calcined at 400^0C showed peaks of fully grown anatase phase. Conversion of anatase to rutile phase with sharp peak was observed at 500^0C (d) & 600^0C (e)

The surface area and porosity of Chromium content have been studied by measuring surface areas and porosity of Cr-TiO_2 samples containing 0.5–5% Chromium by Micromeritics Instrument. The results of BET surface area, porosity are summarized in Table 2.

Catalyst	Surface Area, m^2/gm	Porosity, %
TiO_2	72.59	46.70
0.5% Cr_TiO_2	88.02	48.72
1.0% Cr_TiO_2	95.04	46.10
2.0% Cr_TiO_2	99.84	56.36
3.0% Cr_TiO_2	109.07	52.50
4.0% Cr_TiO_2	129.85	59.87
5.0% Cr_TiO_2	105.21	62.16

Table 2. BET, Porosity data of TiO_2 and Cr-TiO_2 catalyst.

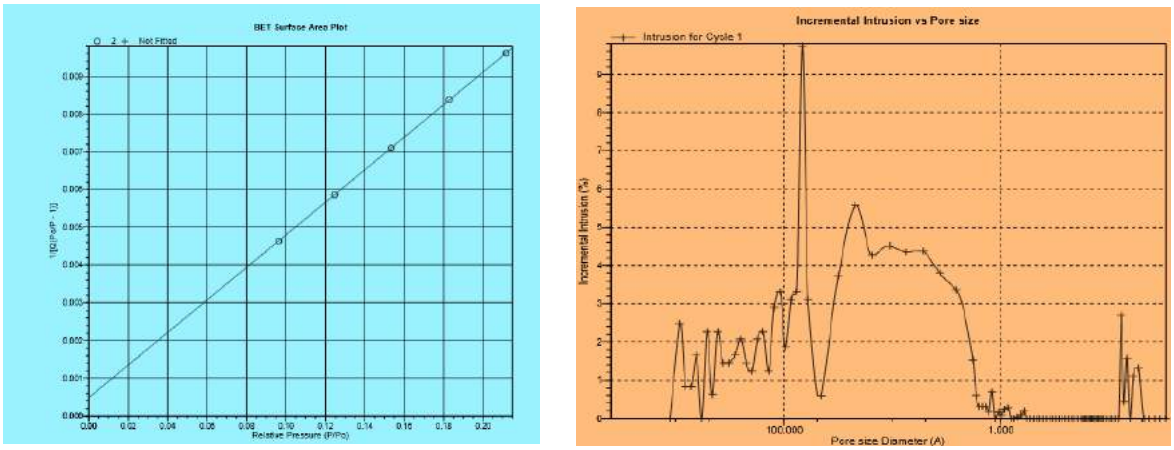


Figure 5. Graphical representation of 1% Cr-TiO_2 catalyst for Brunauer-Emmett-Teller (BET) & porosity

For BET surface area and Porosity measurement, sample was dried along with degassed with the help of UHP grade nitrogen gas at 110^0C for 2 hr. BET surface area was measured by using liquid nitrogen. The porosity of sample was measured as per ASTM method (D2484-07) i.e. by Mercury Intrusion Porosimetry technique.

The surface are of pure TiO_2 gel was 72.59 m^2/g; this increased to 129.85 m^2/g when Chromium loading was increased from 0.5 to 4%. The increase of surface area may be ascribed to the formation of homogeneous gel with increase in Chromium content. In this Cr-TiO_2 system, when chromium peroxide sol is added to titanium peroxide solution, below 4% Crcontent it forms a homogeneous greenish gel but as the Chromium content was further increased beyond 4%, the gel characteristics change and a non-homogeneous gel with agglomerated flocks was formed leading to decrease in surface area.

3.5 Surface Morphology of powder.

The surface morphology/microstructure of the powder samples wasanalysed by FE-SEM showed that, the powder have sphere-shaped granules. A granular texture with spherical or spheroidal shaped particles and particle agglomerates were observed on the surface.

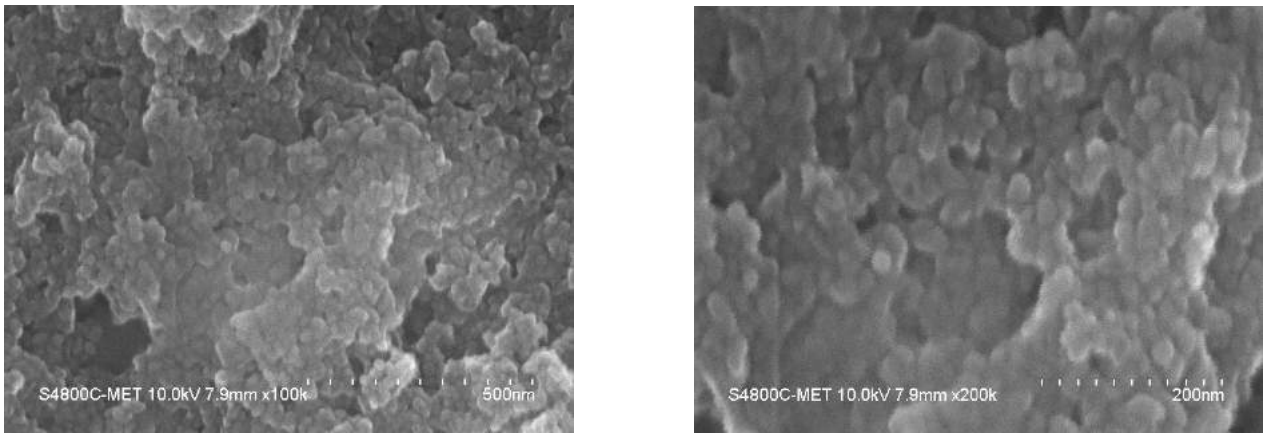


Figure 6. FE-SEM images of Cr.TiO_2.

3.6 Photo catalytic degradation of Jakofix red (HE 7B) dye.

Photocatalytic activity of Cr-TiO_2 thin film catalyst was tested for degradation of Jakofix red dye (HE 7B) (200 ppm solution) under solar radiation using Cr-TiO_2 powder. The change in the concentration of colour in the samples irradiated for different time intervals under solar radiation was monitored using UV–Visible spectrometer (200-800 nm) and compared with the blank which was kept in sunlight under identical experimental conditions. Typical UV spectra of the Jakofix red dye (HE 7B) solution in the presence of 0.5% Cr-TiO_2 catalysts, before and after solar light irradiation at different time intervals are presented in Figure 7.

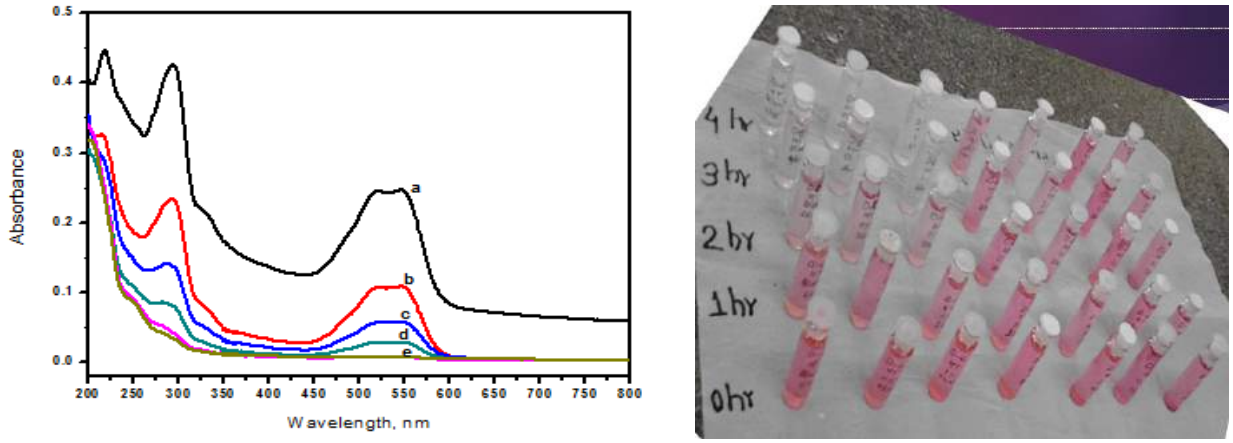


Figure 7. UV–vis spectra of Jakofix Red Dye (HE 7B) solution after irradiation with sunlight for (a) 0 h, (b) 1 h,(c)
2 h, (d) 3 h, (e) 4 h in presence of 0.5 % Cr-TiO_2 catalyst

The 99% degradation of Jakofix red dye (HE 7B) was observed in 3.5 hr. at 0.5 % Cr-TiO_2 catalyst. The degradation under sunlight was observed at UV & visible region.

IV. Conclusion

Chromium doped Titania powder catalyst prepared by simple sol–geltechnique for photocatalytic degradation of Jakofix red dye (HE 7B) in sunlight. Among the catalysts investigated Cr-TiO_2 catalyst containing 0.5% Chromium was found to be the most active catalyst for degradation of dye colour. The Cr-TiO_2 catalyst was found to be quite active for the degradation of dye from aqueous solution, which shows the potential of this catalyst for the removal of organic contaminants from industrial polluted water.Semiconductor photocatalysis is one of very simple, economical technique that has great potential to reduce organic as well as inorganic contaminants. Hence, its degradation prior to discharge is essential for the environmental safety.

V. Acknowledgement

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Poultry Production and the Environmental Issues in India - A Review

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ABSTRACT

Over the past two decades, Indian poultry sector has grown many folds. And it has raised number of environmental concerns. The direct consequences of this industry are that it produces large amount of waste. It causes serious environmental issues . This paper analyses the environmental impacts arising from intensive poultry production in India. The paper also presents technical options to mitigate the environmental issues raised by poultry industry.

Keywords : Poultry Production, GDP, Diseases, Pathogens

I. INTRODUCTION

Over last recent decades the poultry industry has made tremendous growth in India . By the survey made by experts it is revealed that the poultry industry in India grows two folds in every four years. Telangana, Andhra Pradesh , Karnataka, Tamilnadu, Maharashtra , Gujarat and Punjab states are the major producers of poultry products. The poultry industry contributes about 2% growth in GDP. In earlier days poultry was not considered as an industry but now a days it is come out as not only a small scale industry but a large scale industry. Indian poultry provides jobs to the thousands of peoples. The poultry industry also supports farming in India by many aspects. Though the poultry industry in India contributing Indian economy, it has raised some serious environmental issues.

Chicken manure is the major byproduct of poultry which is mainly used as the organic fertilizer in India. It is rich in nitrogen and phosphorous. Of all the animal manure , poultry manure has highest amount of nitrogen, phosphorus and potassium. chicken manure can be pelletized and this product may have additional phosphorus. , potassium and nitrogen.

Fresh chicken manure contains 0. 8% potassius, 0. 4% phosphorus and about 1 %nitrogen. Though this manure is come out as a good fertilizer it has raised major environmental issues. Excessive levels of nitrogen in the environment leads to a cascade to a effects including(Erisman et. al. 2001)

- ✓ Decreased species diversity, due to nitrogen deposition related to ammonia and nitrous oxide emission.
- ✓ Pollution of ground water due to nitrate leaching from agricultural soils and nonagricultural soils.

II. POLLUTION

Chicken manure creates an unpleasant odour. You can smell it from Miles away. So the peoples residing nearby poultry houses may have to face some health problems. It gets washed into waterways and pollutes our rivers and streams. Some environmentalists has claimed that poultry industry is polluting our streams and rivers.

III. ISSUES AT PRODUCTION UNIT

The peoples near the vicinity of poultry farms are facing major problems caused by poultry . Though manure is the main source of pollution, there are also other effective things which causes pollution. These are dead birds, fly's, dust, rodents, pests and feathers. The manureodorattracts files , rodents and pests that creates local nuisances and carry disease. The odor emissions from poultry farms adversely affects the life of people livingin the vicinity. The farm odor is mainly emitted from the manure and storage facilities. The odor is mainly composed of ammonia(NH_3), volatile organic compounds, and hydrogen sulphide(H_2S). Of the several compounds causing odor, ammonia is the major contributor. Ammonia gas has pungent smell and can

cause irritation. Exposure to ammonia for long period may cause serious health problems.

Odor is a local issue , which depends on populations neighboring the farm. Odor problems are generally concentrated within 500-600 meters. The emission of odor mostly depends on the manure storage, temperature, humidity and frequency of cleaning.

Flies are the second major issue caused by poultry manure. It has been found that flies population at farm level is about 85 times more than average flies population. Not only they cause nuisance, flies and mosquitoes can transmit diseases like typhoid, malaria, cholera, dysentery, dengue and fever.

Rats and pests are the third major issue at poultry farm. They can also transmit disease. Pesticides used to control pests can also cause pollution of ground water and surface water.

IV. ARSENIC

Arsenic is added to the chicken feed to make chicken fatter. Arsenic is one of the harmful ingredients in chicken litter. Chicken litter contains arsenic, which may lead heart diseases, diabetes and decline in mental functioning.

V. COPPER AND ZINC

In excess copper and zinc become toxic.

VI. DRUG RESIDUES

Antimicrobials are administered in poultry as growth promoters, to increase the feed efficiency or to kill the bacteria. But research has shown that at about 75 % of antimicrobial agents are excreted back into the environment. The resent evidences reveled that interactions between bacteria and antimicrobial in environment may cause antimicrobial-resistant strains.

VII. PATHOGENS

Food and water diseases are another major issues associated with manure management . Pathogens are mostly transmitted through untreated animal waste . Poultry manure also contains some pathogens which may affect soil and water sources. Parasites such as cryptosporidium and Giardia spp. can spread frommanure to water supplies and can remain viable in the environment for long periods of time(Bowman et. al. , 2000).

VIII. OPTIONS TO MITIGATE THE ENVIRONMENTAL ISSUES

Following are some important options by which environmental issues can be minimized.

1) Disposal of poultry litter far from the production unit.
2) Recycling of poultry litter.
3) Synthesis of organic fertilizers from manure.
4) Construction of environmentally controlled poultry houses.
5) Use of less antimicrobials.

IX. CONCLUSION

The paper has focused on Indian poultry industry and its impacts on environment. The paper captures most of the issues associated with poultry industry and pollution caused by poultry. The paper has also indicates the options to mitigate the problems.

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Cu (MeCN) 4BF4 Catalyzed Addition of 2-Pyridylzinc Bromide to Acid Chlorides

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ABSTRACT

The 2-pyridylzinc bromide was easily prepared via the direct insertion of active zinc into the corresponding bromopyridines. The subsequent addition reaction of the resulting 2-pyridyl zinc bromide to aryl acid chloride was catalyzed by several copper (I) complex catalyst. we have prepared benzoyl derivatives of pyridine using tetrakis acetonitrile copper (I) tetrafluroborate as efficient catalyst under mild condition.

Keyword : Highly Active Zinc Metal, 2-Pyridylzinc Bromide, Acid Chloride , Copper(I) Complex.

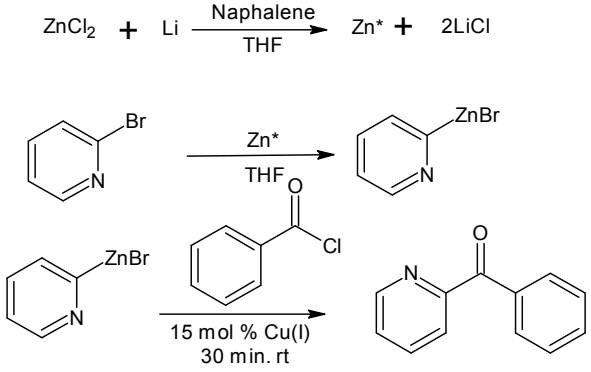
I. INTRODUCTION

Organozinc reagents are most useful organometallic reagent for organic transformation and occupied unique position in synthetic organometallic chemistry due to large number of functional group tolerance and easy formation and transmetalation.[1-6] The organozinc halides are undergo transmetalation by number of transition metal salt or complex such as copper, palladium and nickel etc.[7-12] They are undergo major pathway for carbon-carbon bond formation as conjugate addition to α, β unsaturated carbonyl compounds, cross coupling,[14] addition to acetylene and nuclephilic displacement of halides, sulphonates, allylic acetates.[15] The remarkable advantage offered by reagent is built up polyfunctional molecules without protection and deprotection.[21-22]

Pyridine ring system is widely distributed in nature in the form of pyridine derivatives and many important alkaloids. A numbers of pyridine derivatives have been used in pharmaceutical, agrochemical, medicinal chemistry and in material chemistry[23-27] The 2-pyridyl derivatives have been prepared using the Suzuki, Still, Grignard and Negishi coupling reaction catalyzed by transition metal.[28-34] The reike zinc metal is easily prepared by reduction of anhydrous zinc chloride using lithium in the presence of a catalytic amount of naphthalene in THF at room temperaure.[35] The resulting active zinc is highly reactive metal and readily undergoes oxidative addition with with 2-bromopyridine.[36]

II. RESULT AND DISCUSSION

We have prepared active zinc metal by reduction of zinc chloride using lithium naphthalenide known as rieke zinc. This is the highest active form of zinc used for oxidative insertion in 2-bromopyridine after 1 hr reflux condition. LiCl in THF not only solubilize the benzylic zinc halide but also assist the zinc insertion into 2-bromopyridine . The 2-bromopyidinezinc bromide was added to various acid chlorides at room temperature in presence of different copper (I) complex as catalyst i.e. catalyst screening. We have observed that $Cu(MeCN)_4BF_4$ found to be best catalyst for this addition reaction. Among the product 1a,2a,3a and 4a from table number 2 are form without catalyst in moderate yield[37] but use of catalyst enhance the yield.

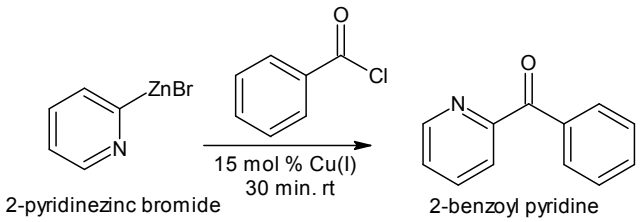


Scheme 1. Synthesis of 2-benzoyl pyridine derivatives.

Table 1. Different copper(I) catalyst screening

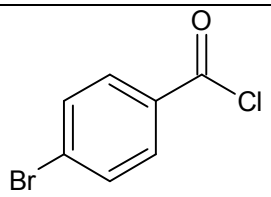
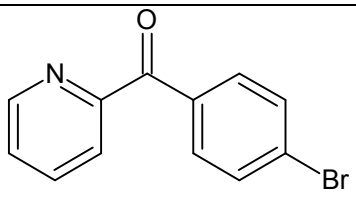
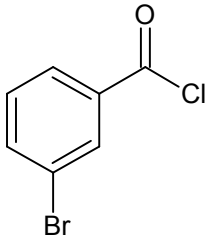
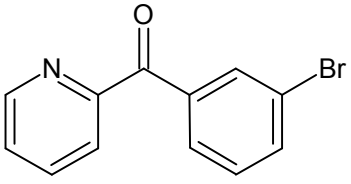
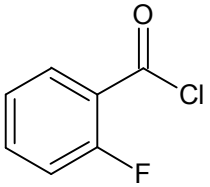
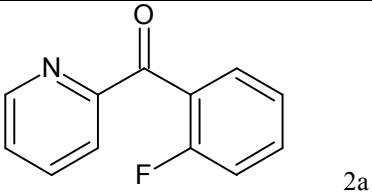
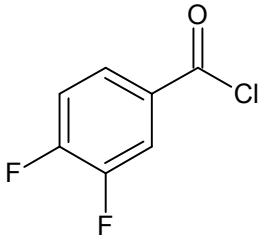
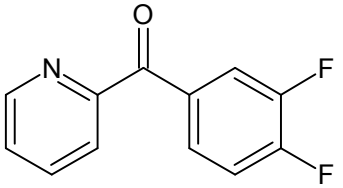
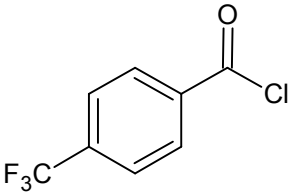
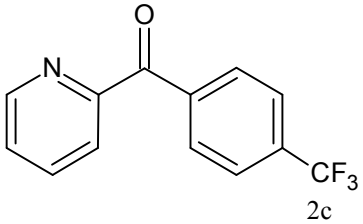
Sr. No.	Copper (I) Catalyst	% Yield
1	without catalyst	42 %
2	$Cu(MeCN)_4BF_4$	88 %
3	$Cu(MeCN)_2F_3CSO_3$	57%
4	$Cu(MeCN)_4ClO_4$	61%
5	$Cu(MeCN)_4NO_3$	58%
6	$Cu(MeCN)_4\ PF_6$	48%

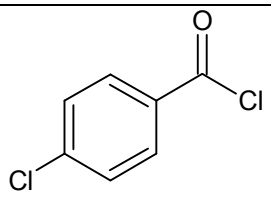
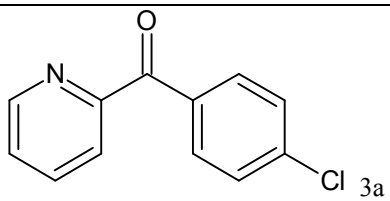
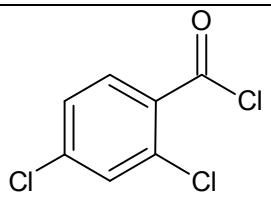
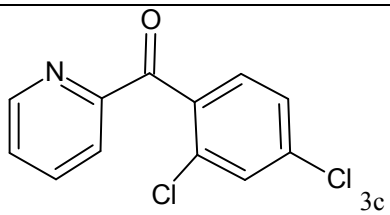
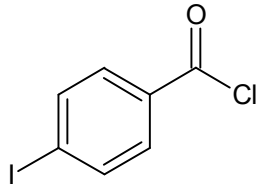
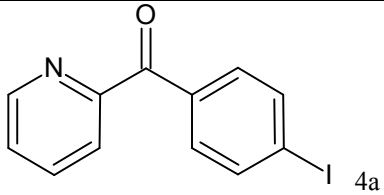
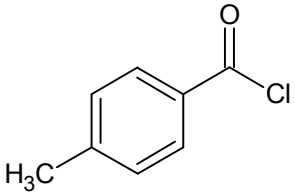
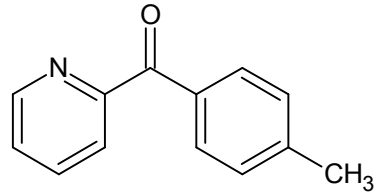
All the products are purified by column chromatography and yield was reported. They are known derivatives and confirm by melting point. The product was analyzed by IR, ^{1}HNMR and ^{13}CNMR The copper (I) catalyzed nucleophilic addition of 2-pyridinezinc bromide to acid chloride is an important reaction constitute a C-C bond formation and ketone functional group synthesis. The 2-benzoyl pyridine derivatives has tremendous potential in organic transformation i.e. versatile precursor in organic synthesis.



2-pyridinezinc bromide 2-benzoyl pyridine

Table 2. Synhesis of 2- benzoyl pyridine using tetrakis acetonirile copper (I) tetrafluroborate as catalyst

Entry	Acid chloride	Product	Yield	M. P. ^{0}C
1		 1a	68%	45-47^{0}C
2		 1b	74%	120-122^{0}C
3		 2a	85%	liq.
4		 2b	78%	105-107^{0}C
5		 2c	72%	115-117^{0}C

6		 3a	56%	65-67^{0}C
7		 3c	69%	120-125^{0}C
8		 4a	52%	liq.
09		 5a	82%	liq.

III. CONCLUSION

We have introduced **tetrakis** acetonitrile copper (I) tetrafluroborate as efficient catalyzes addition of 2-pyridylzinc bromide to acid chloride under mild condition.

Experimental Section

Precaution

1) Strictly anhydrous condition was maintained.
2) All glassware dried overnight 150^{0}C before use.
3) All solvents were dried as per Vogel's practical book procedure.

Typical procedure for preparation of copper (I) catalyst

4g (0.028 mole) cuprous oxide mixed with 80 ml acetonitrile in RBF suspension was observed. 113 mmole acid was added slowly with constant stirring at room temp.exotherm observed. The reaction mixture was keep at 50^{0}C for 30 min then filtered removing any unreacted copper (I) oxide. The colorless clear solution was then cooled at -10^{0}C in a freezer and left overnight. A white colored crystal settle at the bottom of RBF which was separated by filtration washed with diethyl ether under nitrogen atmosphere. Then the copper salt was recrystallised and store in acetonitrile. All the copper salts were confirmed by melting point. [38-44]

Typical procedure for preparation of reike zinc metal

One 50 ml two neck RBF was equipped with rubber septa, stopper and magnetic bar flush by nitrogen. A small amount freshly cut of lithium 0.05g (7.204 mmole), naphthalene 0.1 g (0.7813 mmole) and 5 ml dry THF was charged by syringe clear solution was observed. The mixture was stirred at room temp. colorless solution changes to dark green.

Second 50 ml two neck RBF was equipped with rubber septa, stopper and magnetic bar flush by nitrogen. Anhydrous Zinc chloride 0.5g (3.724mmole) was charged and 5ml dry THF added by syringe clear solution obtained. The zinc chloride solution was added to above dark green solution by syringe through septum. The mixture was stirred for 1 hr black-grey colored zinc metal observed in RBF. The weight of zinc metal

generated after reduction was 0.210 gram i.e.0.003211 mole.

Typical procedure for preparation of 2-pyridinezinc bromide and addition to acid chloride.

Anhydrous LiCl (2 equivalent) was dissolved in 2 ml dry THF and charged zinc metal (2.5 equivalent) solution by syringe. 2-pyidine bromide (1 equivalent) was dissolved in 2ml dry THF add to zinc metal solution and slowly allow to raise temp. reflux for 1 hr zinc insertion takes place. organozinc reagent formation confirm by TLC i.e. consumption of 2-bromopyridine. Again organozinc reagent containing solution cool to room temperature then substituted benzoyl chloride (1.1 eq.) was dissolved in 2 ml dry THF added by syringe and solid catalyst 15 mol %. The temperature of reaction mixture was stired at room temperature for 30 min. Add 30 ml saturated ammonium chloride solution stir reaction mixture for 1 hr at rt and heat the reaction mixture to evaporate THF completely. The product was extracted in ethyl acetate wash by aq. $NaHCO_3$ and water dried organic layer over sodium sulphate. The product was purified using column chromatography and yield was reported.

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An Efficient and Green Synthesis of 1, 5-Benzodiazepines

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ABSTRACT

An efficient and green synthesis of 1, 5-Benzodiazepines is reported under neutral conditions. The ammonium chloride catalyzed condensation of o-phenylenediamine with several ketones in methanol at room temperature furnished corresponding 1, 5-benzodiazopines.

Keywords: 1, 5-Benzodiazepines, O-Phenylenediamine, Ketones, Green Chemistry, Neutral Conditions.

I. INTRODUCTION

Benzodiazepines are a class of agents that work on the central nervous system, acting selectively on gamma-aminobutyric acid-A (GABA-A) receptors in the brain. It enhances response to the inhibitory neurotransmitter GABA, by opening GABA-activated chloride channels and allowing chloride ions to enter the neuron, making the neuron negatively charged and resistant to excitation.[1] Benzodiazepines are similar in pharmacological action but have different potencies and some benzodiazepine work better in treatment of particular conditions. They are used as sedatives, hypnotics, anxiolytics, anticonvulsants, analgesic, antidepressants, hypnotic, antiinflammatory and muscle relaxant agents.[2-6] In particular, 1, 5-benzodiazepines are useful precursors for the synthesis of fused ring benzodiazepine derivatives such as triazolo, oxadiazolo, oxazino, furano benzodiazepines. More recently their use has been extended to various diseases such as cancer, viral infections (non-nucleoside inhibitors of HIV-1 reverse transcriptase) and cardiovascular diseases.[7-13]

Due to the wide range of biological activity, the benzodiazepine nucleus has attracted many investigators to synthesize and screen their analogues for all possible biological activities.[14] However, the most commonly employed methods involve the cyclocondensation of 1, 2–diamines with α, β-unsaturated ketones, β-haloketones, alkynes.[15] Literature survey reveals the various catalysts and routes for the synthesis of these compounds by condensation reaction of *o*-phenylenediamine with α, β-unsaturated carbonyl compounds in the presence of protic organic and inorganic acids catalysts.[16] However, majority of methods reported in literature have several limitations such as high temperature, long reaction time, use of expensive reagents, low yields of products, high catalyst loading, corrosive reagents, strongly acidic conditions and further purification of products. Therefore, the need of development of an efficient method for the preparation of 1, 5-benzodiazepines is of prime importance.[17]

II. Results and Discussion

In continuation with our work in development of new methods for synthesis of heterocyclic compounds,[18] herewith we are reporting an efficient and green protocol for the synthesis of 1, 5-benzodiazepines from *o*-phenylenediamine (10 mmol) and various ketones (20 mmol) in presence of NH_4Cl (20 mol%) in methanol (**Scheme 1**). Ammonium chloride has been used as green catalyst in various condensation reactions.[19] Initially, we performed the reaction between *o*-phenylenediamine (10 mmol) and acetone (20 mmol) and NH_4Cl (50 mol%) in ethanol to afford moderate to good yield. To improve the reaction condition, we performed the same reaction in different solvents (**Table 1**).

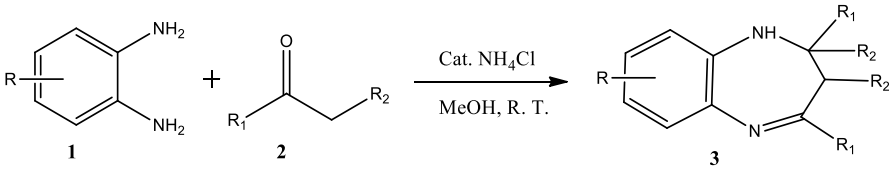
Table 1: Effect of solvent on synthesis of 1, 5-benzodiazepine.

S. N.	Solvents	Time (hr)	Yield (%)
1	Ethanol	3	95

2	THF	4	85
3	Iso-propanol	2.5	92
4	DCM	3.5	90
5	Methanol	2	98
6	Ethyl acetate	4.5	88
7	Acetonitrile	5	89
8	Toluene	6	70

It has been observed that the better solvent for the reaction is methanol. Also, we have optimized the catalyst by performing reactions at different mol%. The 20 mol % of NH_4Cl is sufficient for better results. The scope of present invention checked by performing reactions between various substituted *o*-phenylenediamines (10 mmol) and ketones (20 mmol) in presence of NH_4Cl (20 mol%) in methanol (**Scheme 1 & 2**). All the reactions furnished the corresponding 1, 5-benzodiazepines with 70-98% yields (**Table 2**). The progress of reaction was monitored by TLC. After completion of reaction, the solid product obtained was filtered and recrystallized by using ethanol. The analytical and spectral data of obtained compounds is matching with the reported in literature.

Scheme 1



Scheme 2

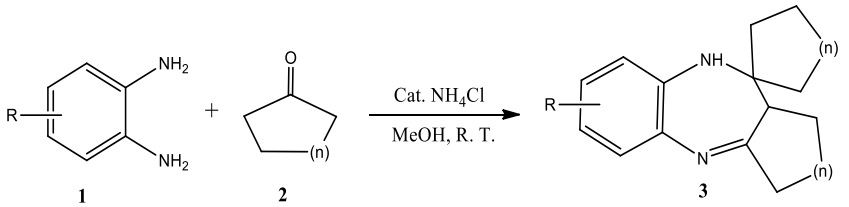
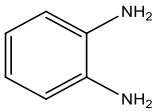
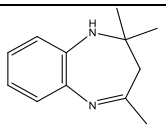
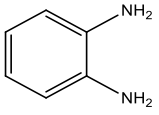
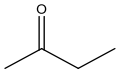
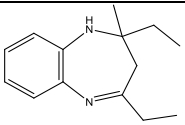
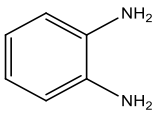
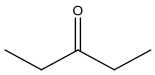
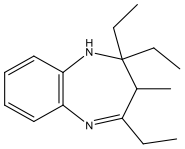
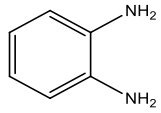
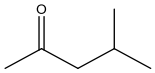
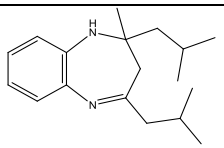
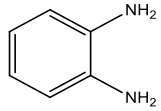
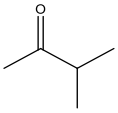
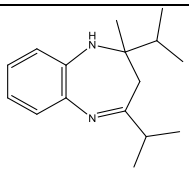
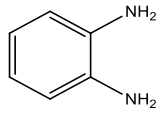
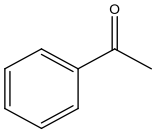
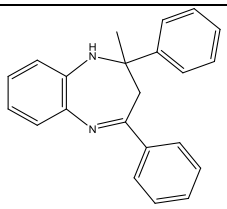
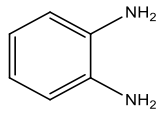
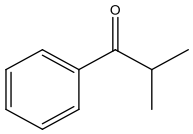
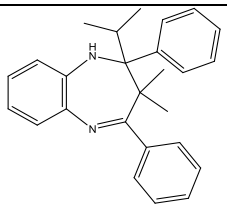
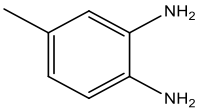
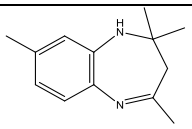
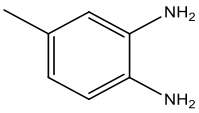
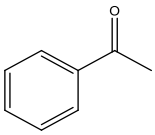
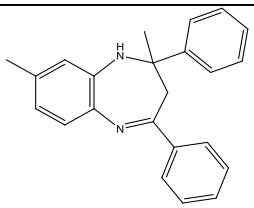
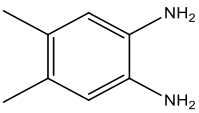
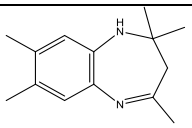
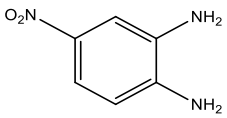
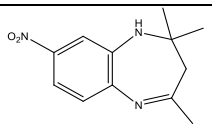
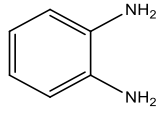
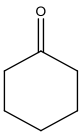
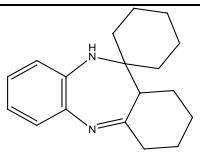
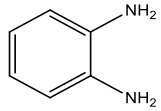
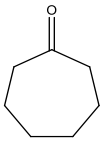
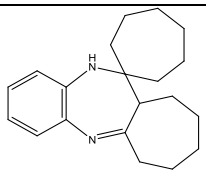
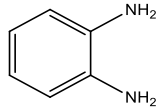
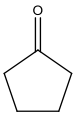
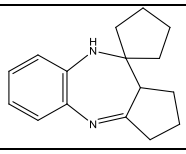
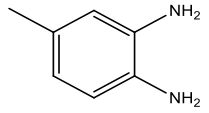
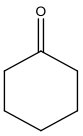
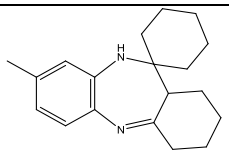
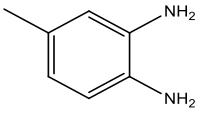
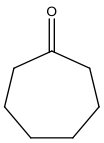
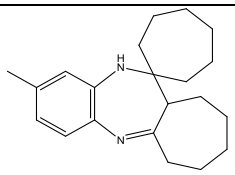


Table 2. Ammonium chloride catalyzed synthesis of 1, 5-benzodiazepines

S. N.	O-Phenylenediamine (1)	Ketones (2)	1, 5-Benzodiazepines (3)	Time (h)	Yield (%)	MP (^oC, Obs.)	MP (^oC, Lit.)
1				2	98	119-121	120-122
2				2.5	85	138-140	138-139
3				3	82	141-143	142-144

4				4	78	119-121	118-120
5				5	75	117-119	118-120
6				3.5	85	148-150	150-152
7				5.5	82	119-121	121-122
8				3	84	125-127	127-128
9				4.5	79	90-92	92-93
10				6	87	110-112	112-114
11				5.5	82	111-113	113-114
12				4.5	72	135-137	136-137
13				5.5	70	134-136	135-136
14				6	80	135-137	136-138

15				6.5	72	122-124	124-125
16				3.5	75	136-136	138-139

III. Experimental

All chemicals were purchased from commercial suppliers and used without further purification. All solvents were treated according to the standard procedure. The progress of the reactions was monitored by TLC. ^{1}H NMR (400 MHz) and ^{13}C(100 MHz) spectra were recorded with tetramethylsilane as the internal standard.

General procedure for 1, 5-benzodiazepines.

A mixture of *o*-phenylenediamine (10 mmol), Ketone (20 mmol) and ammonium chloride (20 mol%) in methanol (10 ml) was taken in a round bottom flask. The reaction mixture was stirred at room temperature for an appropriate time as mentioned in Table 2. After completion of reaction (monitored by TLC) solvent was evaporated under reduced pressure. The reaction mixture was extracted by ethyl acetate. The organic layer was dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure. The crude product was purified by recrystallization by using ethanol to furnish the corresponding 1, 5-benzodiazepines with 70-98% yields.

2, 2, 4-Trimethyl-2, 3-dihydro-1H-benzo[b][1, 4]diazepine (Entry 1): Pale yellow solid; **MP**: 119-121^{o}C [lit. 120-122^{o}C]; **IR** ($CHCl_3$) ν_{max}: 3345, 2109, 1630, 1456, 1246, 1051, 945, 713 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 1.35 (s, 6H), 2.23 (s, 2H), 2.37 (s, 3H), 2.99 (bs, 1H), 6.73-6.75 (m, 1H), 6.98-7.01 (m, 2H), 7.13-7.15 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 29.9, 30.5, 45.1, 68.4, 121.8, 122.1, 125.5, 126.9, 137.9, 140.8, 172.4.

IV. Conclusion

In conclusion, we have reported an efficient and green protocol for synthesis of various substituted 1, 5 benzodiazepines from *o*-phenylenediamine and ketones in presence of catalytic amount of NH_4Cl in methanol under neutral conditions. The present protocol has several advantages over earlier reported. This will be alternative and highly useful method for preparation of substituted 1, 5 benzodiazepines.

V. Conflicts of interest

There are no conflicts of interest to declare.

VI. Acknowledgements

PSP gratefully acknowledge the financial support of CSIR New Delhi.

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Recent Developments of Caesalpinia Decapetala

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ABSTRACT

Caesalpinia decapetala (Roth) Alston is classified under the family capsalpiniacae. The plant is found all over the world and warmer part of India. It is originally from India and Malaysia. It is climbing shrub with prickly braches. Young branches are densely covered by tiny brownish or golden colour hairs with sharp recovered thorns. Older stem is thick with large thorns. The leaves are bippinnate, alternatively arranged and have a pair of small leafy stipules at their base. The flowers are usually yellow or pale yellow in colour. The fruits are flattered pod, oblong with small beak at one end. Each pod contains 4-9 rounded seeds. Roots, stem, bark, flowers and seeds of plant showed medicinal properties. Hence the plant can act as a herbal medicine. Caselpinia decapetala shows anti-TMV, anti-anaphylactic, anti-oxidant, anti-cancer, anti-diarrheal, anti-microbial, anti-pyretic, anti-inflammatory, anti-diabetic activities. It also shows analgesic acute toxicity in mice and contraceptive activity in female hamsters. Terpenoids, carbohydrates, flavonoids , resins, alkaloids, proteins, sterols, fats, oils, phenols, tannins, glycosides and diterpenoids are found out in Caesalpinina decapetala by phytochemical screening.

Keywords : Anti-Oxidant, Caesalpinia Decapetala, Anthelminitic, Female Hamster, Diterpeniod, Cassane.

I. INTRODUCTION

Plants have been used for treatment of diseases from time immemorial and were still principle form of medicine in the most developed centuries till about 70 years back. Till the end of 20th century every village and rural community had a wealth of herbal folk which is seen even today. The herbs were used for common health problems applied as lotions or even mixed with fat and rubbed as ointment. Herbal medicines are effective against different therapies. Herbal medicines are safe and more reliable has increased the interest in these medicines. Digestive problems, cardio vascular disorders, metabolic problems, liver disorder and disorders of central nervous system can be cured by different part of plant. Western drugs are made up from plant extracts. The standard of the medicine, the safety and effectiveness is to be assured to make the safe use of the traditional herbal plants. Phytochemicals are the chemicals secreted by plants are important because they protect plants as well as human being from various diseases.

Out of 300000 species of the plants only 5% species have been studied scientifically for their medicinal uses. India has 45000 diverse groups of species spread over 16 different agro climatic zones, 10 vegetation zones, 25 biotic provinces, 426 habitats of specific species. Besides this, there are up to 18000 flowing plants, 2500 algae, 23000 fungi, 1600 types of lichen and 1800 varieties of bryophytes. Out of these 15000-20000 are of medicinal value. But only 7000 to 7500 plants are used for medicinal purposes. Researchers found that developing countries depend upon herbal plants to cure disease where there is lack of hospital facility. All the parts of plants namely root, stem, bark, leaves, flowers and seeds are used as herbal medicine. It is commonly known as crested fever nut. In Ayurveda, *Caesalpinia decapetala* is used as anti-inflammatory, anti-malarial, anti-histamine, anti-asthma, anti-aging agent and anti-pyretic properties. It is also used to cure diseases like skin diseases, medicinal paste for treating poisonous snake bite, treating liver stagnation type reflux oesophagities, treating ecthyma and headache, for rabies, treating hyperosteogeny. Different parts of it are used to prepared Chinese medicines.

Synonyms:

- Latin Name :Caesalpinia decaapetala (Roth) Alston
- Marathi Name: Chillar, Chillhari, Chillati.
- English Name: Mysore thorn, Shoofly Black Bonduc.
- Sanskrit Name: Kantaki Karanja
- Hindi Name: Ralan, Alia, Arlu, Kingan.
- Gujrati Name: Kirmich Chilar
- Urdu Name: Kander Relan
- Kannada Name:Gajalige, Hotasige, Hunnula, Kurudu, Gejjuga, Kurutugajjika
- Malayalam Name: Inna

Geographical Distribution:

Caesalpinia decapetala (Roth) Alston is a climbing shrub and is widely distributed around the world. It is found out throughout warmer parts of India, Myanmar, China, Japan. It is introduced in the tropical regions of India, Korea, Thailand, Laos, Vietnam, Malaysia, Philippines. All the parts root, bark, leaves, flowers and seeds are used as herbal medicines.

II. Morphology Characters

Caesalpinia decapetala is originally from Asia and Malaysia. It is a large sprawling shrub (growing up to 7m) with prickly branches; it can climb on large tree up to 20m high. Young branches are densely covered by tiny brownish or golden colour hairs having sharp thorns. Older stem is thick with large thorns. The leaves are bipinnate, alternately arranged and have a pair of small leafy stipules at their base. The stipules are 4-20 mm long, egg shaped in outline with broad end at base but taper to a point. The leaves are borne on stalk 3-8 cm long. Each stalk has 4-10 pair of branchlets called pinnae. Each branchlets has 8-12 pairs of leaflet called pinnules. The leaflets are 7-20 mm long and 2-8 mm wide. They are oblong or abovate form outer side and narrower end toward base. The flowers are usually pale yellow or yellow in colour sometimes whitish. It has five petals with 10-15 mm long, five sepals with 9-10 mm long, ten stamens with 10-16 mm long and a style with 15-20 mm long topped with a cup-shaped stigma. Four petals are circular in shape but upper petal is smaller and narrower than the others. The flower are borne on stalks 15-25 mm long and arranged in erect position. The fruits are flattened, pods, oblong with small beak at one end. These woody pods are 6-10 cm long and 25mm wide with hairs and turns from green to brown as they mature. After maturity they split to release 4-9 rounded seeds. These seeds are 6-10 mm in diameter with brown to black in colour. The seeds get scattered after breaking of pods. The seed surface is smooth, outer coating of seed is too thick and hard hence it required several months to years for its germination.

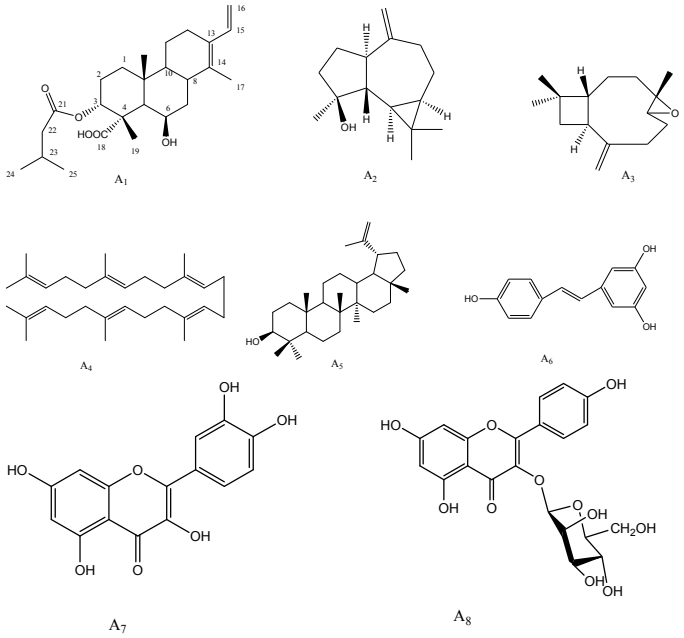
III. Traditional and Modern Uses

Herbal plants are used for medical purposes long back in India. They play important role in illness as well as in maintaining health. It has medicinal properties like anti-inflammatory[1], anti-oxidant, anti-histamine, anti-skin aging agent, anti-asthma-COPD herbal composition, anti-pyretic analgesic, anti microbial, anti-diarrheal[2], anti- cancer, anti-hyperalycemic[3], anti-diabetic. Caesalpinia decapetala plant is used to cure diseases like skin, diabetic, bacterial, pyretic, diarrhea, asthma and malaria. Root extract of C. decapetala is used to treat sexually transmitted infections[4]. Bark is poisons and used as fish poisoning. Fruit extract shows inhibitory effect against candida abbicans[5]. It is used to prevent cold and treat bronchitis. Used in eye drop for treating tranchoma caused by Chalmydia trachomatis in Chinese medicine[6]. In Chinese medicinal pest for treating poisonous shake bite[7]. Leaves of C. decapetala mixed with essential oil which shows antibacterial activity[8]. Used for treating blood stasis type closed bone fracture[9]. Used in Chinese medicine lotion for treating ecthyma with headache[10]. It is used in Chinese medicine for treating scaled and burn[11]. For treating hyperlipemia caused by excessive uptake of meal[12]. This plant is used in Chinese medicine for treating rabies[13]. It has been used in treatment of jaundice, stomach disorder and biliousness. The leaves and roots are used as purgative and emmenagogue[14]. It shows anti fertility activity[15].

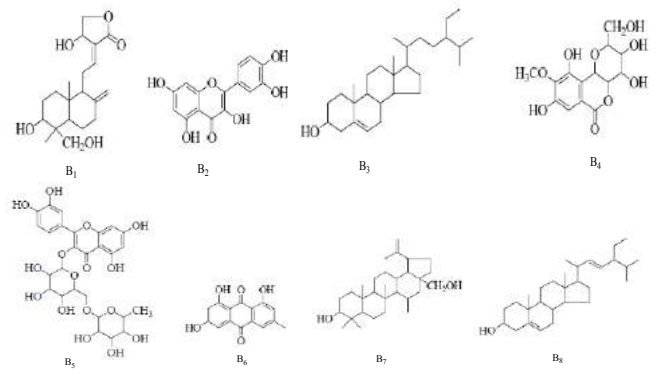
IV. Phytochemical Investigation

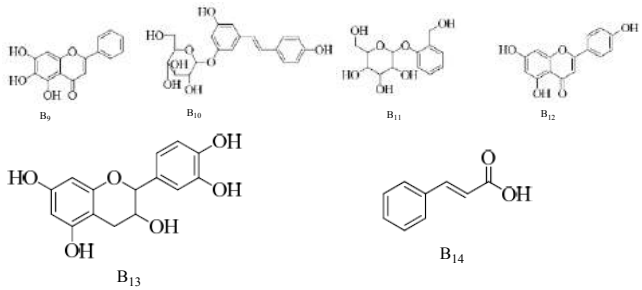
Caesalpinia decapetala (Roth) Alston is a medicinal plant. In Vietnam it is used as traditional medicine as an anti-inflammatory and immunomodulatory. The genus caesalpinia contains cassane diterpeniod in it. From the leaves of C. decapetala eight known compound are isolated namely A_1) spathulenol, A_2) 4,5 epoxy-8(14)-caryophylene,A_3) squalene, A_4) lupeol,A_5) trans-

resveratrol, A_6) quercetin, A_7) astragalin and A_8) stigmasterol. Along with these compound new cassane diterpenoid, caesaldecan is isolated and its structure is find out. Structures of compounds are given below.



Fourteen known compounds were isolated using column chromatography and physical identification was performed by physical and spectral analysis. Most of compounds were isolated from roots of Caesalpinia decapetala. The biological activities of compounds were also evaluated by 3 – (4, 5 dimethythiazol-2-yl) - 2, 5 – diphenyl tetrazolium bromide (MTT) and 2, 2-diphenyl -1- picrylhydrazyl (DPPH) assays. Emodin(B_6), baicalein (B_9) and apigenin (B_{12}) shows antitumor activity against the MGC – 803 cell line. Quercetin(B_2), rutin (B_5), baicalein(B_9) and epicatechin (B_{13}) shows stronger DPPH scavenging activity. Andrographolide(B_1), bergenin (B_4), betulin(B_7), polydatin(B_{10}), salicin(B_{11}) are isolated by first time. The compounds were identified by ^{1}H- NMR and ^{13}C-NMR spectroscopy. The structures of compounds are as follows.





Out of fourteen compounds two terpenoids (B_1, B_7), five flavones (B_2, B_5, B_9, B_{12} & B_{13}), two sterols (B_3, B_8), one isocoumarin (B_4), one anthraquinone (B_6), two polyphenols(B_{10}, B_{11}). All compounds except B_3, B_8, B_{13} and B_{14}, were isolated from the roots of Caesalpinia decapetala[21].

V. Pharmacological Activities

Anti Diabetic Activity [3]:

Insulin or hypoglycaemic agents can be used to treat diabetes mellitus. Diabetes can be treated by herbal and natural products which are safe and widely being evaluated for their therapeutic and safety potential[16]. Natural products are rich source of different effective drugs. Substances derived from plant origin have show activity in treating non-insulin dependent diabetes mellitus (NIDDM) [17]. *Caesalpinia decapetala* has been locally claimed to be effective as anti diabetic and even effective in diabetic wound healing. Aqueous ethanol extract of leaves and whole plant was given to alloxan-induced diabetic rabbit orally. 300 mg/kg and 500 mg/kg oral extract doses were able to reduce average blood glucose level from 250.6 mg/dL to 204.2 mg/dL and 188 mg/dl respectively during 14 days. Total cholesterol, triglyceride and low density lipoprotein (LDL) level increased significantly while high density lipoprotein (HDL) decreased in diabetic rabbits.

Hypercholesterolemia and hypertriglyceridemia Activity [3]:

Both of above have been found in alloxan- induced diabetic rabbits[18]. Aqueous methanol of extract of wood and pericarp of *C. decapetala* is given to the rabbits orally. The extract decreases the total cholesterol and triglycerides level in diabetic rabbit. *C. decapetala* treatment significantly decreased the elevated levels of SGPT and SGOT levels in diabetic groups. It showed

that *C. decapetala* reduce the risk of liver failure. The plants also decrease the elevated levels of serum urea and serum creatinine which showed that this may act as crucial trigger for kidney to revert to their metabolic homeostasis. Thus *C. decapetala* protect the activity of liver and kidney. Anti-diabetic activity of plant is due to presence of polyphenol, flavonoids, tannines in it.

Analgesic Activity:

The activities were studied by hot plate method and acetic acid-induced writhing response to albino mice. Acetic acid causes severe abdominal pain and contraction (writhing). The activity was evaluated by reduction in the number of writhing and compares it with control group. 0.2 ml 3% acetic acid was injected in the abdominal cavity via intra peritoneal injection to Swiss albino mice having weight between 20-30 g. Aqueous methanolic and n-hexane extract of C. decapetala were given to the mice and writhing were measure with time. The extract was given orally of 100 mg/kg dose.

For evaluating the analgesic effect of aqueous methanolic and n-hexane extract of C. decapetala the hot plate method analgesia meter was used. Writhing gets reduced in both methods. It shows that C. decapetala having analgesic property. It may be due to presence of phenols, tannins, oils, flavonoides and glycosides.

Anti-Inflammatory activity[1]:

Anti-inflammatory activity was studied by using aqueous methanolic and n-hexane extract of C. decapetala to the Swiss albino mice. 0.1 ml carrageenan in 0.9% normal saline increases paw circumference which is indication of inflammation. By giving extract dose of C. decapetala, paw circumference get reduced. It shows the anti-inflammatory activity of C. Decapetala[19].

Anti-pyretic Activity [1]:

Anti- pyretic activity was studied by using aqueous extract of methanol and n-hexane of C. decapetala. Initially temperature of Swiss albino mice was increased by giving yeast-induced pyrexia. Then extract of plant and aspirin was treated with animals. It decreases the rectal temperature. It shows the anti-pyretic activity of C. decapetala plant.

Acute Toxicity in mice [1]:

The animals were given extract of C. decapetala in n-hexane and methanol with doses of 500, 1000, 1500 and 2000 mg/kg body weight and normal saline and measured the mortality for 2 days. Their body weight was monitored per day for one week. There is no change in weight and behaviours of animals. No animal was died during study. Hence the plant C. decapetala is non-toxic to mice.

Anti-Microbial Activity [2]:

The ethanol extract of C. decapetala leaves shows anti microbial activity. 150 and 300 mg/kg dose of plant extract was given to the Wistar albino rat which inhabits the growth of Staphylococcus aurous, Bacillus subtilis, Escherichia coli and kliebsiella pneurnoniae. Anti-microbial activity was performed against gram positive and gram negative bacteria strains. Carbohydrate, tannin, flavonoids and glycosides present in C. decapetala could be responsible for anti-microbial activity.

Anti-Diarrheal Activity [2]:

Castor oil induced diarrhoea

The Wistar albino rats weighing 150-200 gm were administrated vehicle orally, 1 mg/kg loperamide orally, 150 mg/kg and 300 mg/kg of ethanolic extract of leaves orally for four groups respectively. After 30 mins 1 ml castor oil is given orally to each group. The number of frequency and weight of diarrhoea were measured for six hours[20]. Ethanol extract of C. decapetala leaves reduced the frequency of defecation, weight of wet stools was observed in extract treated group compare to other groups. Thus the leave of C. decapetala could be used for treatment of various gastrointestinal diseases in folk medicine. Anti-diarrhoeal property is due to presence of tannins and flavonoids. These compounds will precipitate proteins and reduces the peristaltic movement as well as intestinal secretions.

Anti-cancer Activity:

Fourteen known compounds were isolated from C. decapetala by column chromatography. Biological activities of these compounds were evaluated by 3-(4,5-dimethythiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) assays. Out of fourteen compounds emodin, baicalein and apigenin show anti tumour activity against the

human gastric carcinoma cell line MGC-803. MTT assay is widely used method for the detection of cell survival and growth. The inhibitory percentage of cells was treated with 20 μmol/L of each compound for 72 hrs. Baicalein had the best anticancer activity with an inhibition rate of 75.7% at a concentration of 20 μmol/L while apigenin had the best anticancer activity with an inhibition rate of 34.1% at a concentration of 5 μmol/L. In previous studies it was found that emodin could increase the Reactive Oxygen Species (ROS) levels of cells and increase the apoptosis-inducing effect. It enhances the drug's cancer cell killing activity.

Anti-oxidant Activity [21]:

Out of fourteen compounds isolated from C. decapetala (Roth) Alston, quercetin, rutin, baicalein and epicatchin showed stronger DPPH scavenging activity compared with ascorbic acid. The DPPH assay is used to examine the antioxidant activity of compound. It has tendency to isolate pure compounds to act as hydrogen atom donors. The antioxidant activity of antioxidant standard was assessed on the basis radical scavenging effect of the stable DPPH free radical. All compounds dissolved in ethanol with Vc as positive control. It was found that rutin had high DPPH scavenging activity with the rate of 75.8 % at 5 μmol/L while baicalein had high antioxidant activity with the scavenging rate at 93.4% at 20 μmol/L. The compound with more phenolic hydroxyl groups having high DPPH scavenging capacity. Quercetin, rutin, baicalein and epicatchin belong to flavonoids which have good antioxidant properties. Roots of C. decapetala are used for anti-cancer and anti-oxidant properties.

Anti-Tobacco Mosaic Virus (TMV) Activity [22]:

From NMR spectroscopic data analysis and the time - dependant density functional theory calculation *C. decapetala* plant contains three new and ten known diterpenoids. Most of the diterpenoids shows anti-TMV activity.

Contraceptive activity in Female hamsters[23]:

The ethanolic extract of the aerial parts of *C. decapetala* was prepared. It is given orally for 1-8 days post- coitum at 500 mg/kg dose. It shows significant contraceptive activity in female hamsters.

Anti-anaphylactic activity[23]:

Caesaljapin, a cassane triterpenoid isolated from the roots of *C. decapetala* showed inhibitory activity against the anaphylactic contraction in taenia coli of guinea-pigs sensitized by anti-egg albumin rabbit IgE.

VI. Conclusion

Caesalpinia decapetala is widely distributed all over the world. In India it is found in warmer regions. Each part of this plant shows medicinal application. Hence it can act as herbal medicine. It has many pharmacological applications. Still there is lot of scope for further research. This plant shows Anti-pyretic Activity [1], Acute Toxicity in mice [1],Anti-Microbial Activity [2],Anti-Diarrheal Activity [2],Anti-cancer Activity,Anti-oxidant Activity [21],Anti-Tobacco Mosaic Virus (TMV) Activity [22],Contraceptive activity in Female hamsters[23] and Anti-anaphylactic activity[23].

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Studies on the General Parameters from Soil Sample in Shrirampur Tehashil. Dist : Ahmednagar, (M.S.), India

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ABSTRACT

In ten soil samples of cultivating area in Ahmednagar District of Maharashtra, general parameters along with physico-chemical parameters have been studied. All the soil series are free from salinity hazards. Most of the soil samples contain excess general parameters like carbon, boron, sulphur, phosphorous, potassium, nitrogen, molybdenum, fluoride, calcium.

Keywords : Soil Quality, Physico-Chemical Parameters, Parameters.

I. INTRODUCTION

In many parts on India, surface as well as soil has been used extensively for various purposes viz. agriculture etc. Sometimes soil is not suitable for healthy plants growth and other purposes because of chemical and biological contamination. Different are essential for the healthy growth of plants, these elements are grouped into macro and micronutrients. The deficiency or excess of these parameters such as Carbon, boron, sulphur, phosphorous, potassium, nitrogen, molybdenum, fluoride, calcium may produce synergetic and antagonistic effects on the plant growth and crop yields. Soil is the most important component of the earth. About 3.50% of ground area found on the earth is in the farms and hill. Now pollution is major problem in developing countries. The soil from manmade activities such as house hold appliances, industrial processes, high use of pesticides and fertilizers creates water pollution as well as soil pollution problems. One of the most serious threats faced today by mankind is the pollution of our environment. In fact, most of the devolopement countries have already realized that the very existence of life on the earth may be endangered if suitable steps are not taken for the control and abatement of air, soil and water pollution. Knowledge about the soil quality would help to decide the treatment, which should be given to soil for different purposes[1-3]. Hence, many people and many foreigners visit at this village, which is responsible for creates pollution. At Kamalpur, Gujarwadi, Belapur, Umabergoan, Wangi budruk , matapur, wangi khurd, kadit budruk, kadit khurd and nimbgaon khairi. sugarcane, wheat, sorghum, soyabean, onion are cultivated as main crops but from last few years the crop yields per acre are found to be decreasing in many parts of the Kamalpur, Gujarwadi , Belapur , Umabergoan , Wangi budruk, matapur, wangi khurd, kadit budruk, kadit khurd and nimbgaon khairi area. The present study deals with the measurements of the pH, electrical conductance and estimation of available carbon, boron, sulphur, phosphorous, potassium, nitrogen, molybdenum, fluoride, calcium in different soil samples[4-5].

II. Experimental

Soil samples were collected from ten villages studied on the bank of Kamalpur, Gujarwadi , Belapur , Umabergoan , Wangi budruk matapur, wangi khurd, kadit budruk, kadit khurd and nimbgaon khairi area in Shrirampur tehashil Ahmednagar district. The collection of soil samples and brings to laboratory for analysis according to standard method prescribed in APHA[6]. The pH and electrical conductivity of the soil were determined with 1:2 soil water suspension carbon, boron, sulphur, phosphorus, potassium, nitrogen, molybdenum, fluoride, calcium were estimated for different soils using different methods. All the chemicals used were of AR grade.

III. Result and discussion

The moderate range of pH is 7.8 to 8.5. The soil with pH greater than 8.5 is called as sodic soil. In our sample series only two samples are sodic in nature and remaining soil series are free from solidicity hazards. The increase in pH due to high content of bi-carbonate and carbonate. The electrical conductivity in the range of 0.980 to 1.120 ds/m. conductivity is a measure of total conductance of the ionized substances. The mobility of the ions, valences, actual and relative concentrations affects conductivity. The organic carbon is in the range 0.20 mg/kg to 0.80 mg/kg., which is depends upon the pH of humic substances. The boron content was 1.39 to 1.46 mg/kg and depends on the different factors like pH, soil texture, organic matter, light and moisture, calcium etc are known to influence the availability of boron in soil. Boron affects the metabolism and transport of carbohydrates in plants. Boron deficiency like calcium affects the growing points of roots, shoots and young leaves. Sulphur found in the range 19.0 to 21.5 mg/kg. It is moderate range and useful for the plant growth[7-8]. The exact moderate value of sulphur is 20 mg/kg. the amount of phossphorous, potassium, nitrogen, molybdenum, fluoride and calcium are found in the moderate range shown in table no. 1.

Table 1. Concentration of physico-chemical parameters

Sr. No	pH	EC ds/m	% organic carbon	Boron mg/kg	Sulphur mg/kg	Phosphorous mg/kg	Potassium mg/kg	Nitrogen mg/kg	Molybdenum mg/kg	Fluoride mg/kg	Calcium mg/kg
1	8.0	0.980	0.30	1.46	21.0	8.5	101	255	0.30	0.8	7.5
2	8.4	0.990	0.20	1.45	20.0	7.0	107	260	0.20	0.9	7.50
3	8.5	1.000	0.75	1.44	20.5	8.0	110	250	0.25	0.8	7.60
4	8.7	1.100	0.28	1.42	21.5	7.5	105	265	0.25	0.9	7.85
5	8.9	0.990	0.35	1.41	19.5	8.5	112	210	0.20	0.8	7.90
6	7.8	0.980	0.80	1.39	19.0	7.5	105	265	0.30	0.75	8.00
7	8.1	1.120	0.55	1.40	21.0	7.3	107	255	0.30	0.9	8.25
8	8.2	1.110	0.60	1.42	20.0	9.2	106	260	0.20	0.8	8.50
9	8.3	0.990	0.45	1.43	20.5	7.2	104	265	0.25	0.7	9.00
10	8.7	0.980	0.50	1.39	19..5	8.0	101	260	0.25	0.7	9.25

IV. Conclusion

The study of evaluation of soil fertility status revealed that the soils from study area are alkaline nature. The EC values from 0.980 to 1.120 ds/m. the slightly increases shoes downstream part of Godavari river, which is due to low flushing rate and sluggish ground water movement. This leads to salinity and sodicity in the area. The organic carbon content is found to be varied from 0.20 to 0.80. The boron content 1.39 to 1.46 mg/kg, is useful for transport of carbohydrates in plants. Its deficiencies affect on roots, shoots and leaves.

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Synthesis, Spectral Characterization, Molecular Docking, Antimicrobial And Antioxidant Evaluation Of Pharmacophores 1, 3-Diones with Their Transition Metal Complexes

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ABSTRACT

Three series of 1, 3-diones 4(LA- LC) and their transition metal (II) complexes 5LA (a-e), 5LB (a-e) and 5LC (a-e) have been synthesized, spectroscopically characterized and their in vitro efficacies were evaluated. Bidentate ligands were derived from substituted aromatic acids and substituted ortho hydroxy acetophenone under ultrasound irradiation methods at low temperature. The simple substitution reactions between the metal nitrate and ligands yielded the titled complexes. However, in situ procedure gives high yield with formation of single products as evident by TLC. Elemental analysis, IR, 1H and 13C-NMR , Masss pectra, UV-Vis., magnetic susceptibility and conductance measurements were done to characterize the ligands and their metal complexes [where, M= Mn (II), Fe (III), Co (II), Ni (II) and Cu (II)]. All the evidences suggested that the complexes have octahedral geometry. The stoichiometry of the complexes was found to be 1:2 (metal: ligand). The conductivity data show that the complexes are non-electrolyte in nature. The antioxidants activity of the ligands and their metal (II) complexes have been carried out using DPPH free radical scavenging activity and found to be most effective. The antibacterial and antifungal activity of the ligands and their complexes have been carried out and on the basis the molecular docking studyagainst the peptide deformylase of the most effective complexes has been reported.

Keywords: 1, 3-diones, Metal complexes, Antimicrobial, Antioxidants and Molecular docking.

I. INTRODUCTION

The coordination chemistry of transition metal (II) complexes with 1, 3-diones as ligands is of current interest because they can provide new materials with useful properties such as antifungal, antibacterial, anticancer [1,2], antisecticidal [3], antioxidant [4], potential prophylactic antitumor activity [5,6], magnetic exchange [7,8], electrical conductivity [9]. The biological importance of metal (II) complexes is that they are sometimes highly effective than the free ligands [10]. Metal complexes containing pyridine and derivatives have aroused considerable interest in view of their industrial and biological importance [11, 12]. They have also been found to be active against influenza and have been suggested as possible pesticides and fungicides. Their activity has been thought to be ability to chelate trade metals [13, 15].

Recently, applications of these transition metal complexes in the design and development of synthetic restriction enzymes, new drugs and stereo selective probes of nucleic acids structure have been explored extensively [16]. Transition metal complexes offer two peculiar advantages as DNA-binding agents [17] and functionality of the binding agent [18] these characteristics have promoted metal complexes used in a wide range of applications [19].

In continuation of our interest in the functionalized 1, 3-diones and their metal (II) complexes, we, herein report the synthesis, spectral characterization, antimicrobial, antioxidants studies of a bidentate ligands containing O, O pharmacophores. The molecular docking study of ligands and their metal complexes has been reported [20-21]. The antibacterial and antifungal activities of ligands and their metal (II) complexes observed that, metal complexes showed highest activity than the free ligands.

II. Experimental

2.1 Materials and Methods

All chemicals used were of the analytical grade. *Ortho* hydroxyacetophenone and 4-nitrobenzoic acid were SD fine products and used as supplied. The UV-Vis spectra of the ligands and their complexes were recorded on Shimadzu UV-1800 Spectrophotometer. IR spectra were recorded on Shimadzu FT-IR-4100 spectrometer using KBr pallets. ^{1}H-NMR spectra of the ligand was recorded using a Bruker DRX-500 MHz NMR spectrometer. Mass spectra were taken on a Macro Mass spectrometer.

2.2 Synthesis of 2-acetylphenyl benzoate3(a-c):

To the reaction mixture of substituted *ortho* hydroxy acetophenone (1.70 g, 0.01 mol) and substituted benzoic acid (1.66 g, 0.01 mol), a dry pyridine (5mL) and $POCl_3$ (1mL) were added drop wise maintaining temperature 0 ^{0}C.Then the reaction mixture was irradiated for about 2-3h under ultrasound. After completion of the reaction (monitored by TLC), the mixture was poured into 100ml 1M HCl containing 50 gm crushed ice with vigorous stirring. The crimson colored solid (ester) was obtained which was filtered and washed several times with ice-cold methanol. It was crystallized with distilled ethanol.

2.3 Synthesis of Ligands 4(L_A-L_C)

2.3.1 Synthesis of 1-(2-hydroxyphenyl)-3-(4-nitrophenyl) propane-1, 3-dione 4(L_A):

A Compound (**3a)** was dissolved in 15 ml dry pyridine. To this mixture, powdered KOH was irradiated for about 1-2 h. Then it was poured over crushed ice and acidified with conc. HCl. The resulting solid **4(L_A)**was recrystallized from ethanol (Yield: 82%); m.p.132 ^{0}C.)^{1}H-NMR, 14.80δ (s, 1H, enolic -OH), 11.87δ (s, 1H, Phenolic –OH) 7.49δ (s, 1H, =C-H ethylene), 6.54-7.98δ (m, 8H, Ar-H); IR (KBr) ν_{max}/cm^{-1}; 1735 (ν (C=O) ketonic), 1199 (ν (C-O) enolic), 3099 (ν (-OH) intramolecular H-bonding in Phenolic). UV/Vis. (DMSO) nm: 399, 340. MS *m/e*: 285.06

2.3.2 Synthesisof1-(5-bromo-2-hydroxyphenyl)-3-(4-fluorophenyl) propane-1, 3-dione 4(L_B):

A Compound containing (**3b)** 3.18 g, 0.01 mol) was dissolved in 15 mL dry pyridine. To this mixture, powdered KOH (1.12 g, 0.02 mol) was irradiated for about 1-2 hrs. Then it was poured over crushed ice and acidified with concentrated hydrochloric acid. The resulting solid **4(L_B)**was recrystallized from ethanol (Yield: 80%);m.p.:172^{0}C. ^{1}H-NMR (500 MHz, $CDCl_3$-d_6); δ /ppm = 15.56 (s, 1H, enolic -OH), 12.02 (s, 1H, Phenolic –OH), 7.55 (s, 1H, =C-H ethylene), 6.72-8.02 (m, 7H, Ar-H). ^{13}C-NMR (500 MHz, $CDCl_3$) δ/ppm = 194.17 (C=O), 177.35 (C-O enolic), 91.85 (=C-H ethylene).IR (KBr) ν_{max}/cm^{-1}; 1744 (ν(C=O) ketonic), 1178 (ν (C-O) enolic), 3109 (ν (-OH) intramolecular H-bonding in Phenolic). UV/Vis. (DMSO) nm: 371, 256. MS *m/z*: 337.98.

2.3.3 Synthesis of 1-(2-hydroxyphenyl)-3-(4-t-butylphenyl) propane-1, 3-dione4(L_C):

A Compound(**3c)**was dissolved in 15 ml dry pyridine. To this mixture, powdered KOH was irradiated for about 1-2 h. Then it was poured over crushed ice and acidified with conc. HCl. The resulting solid **4(L_C)** was recrystallized from ethanol (Yield: 82%); m.p.122 ^{0}C.)^{1}H-NMR, 11.35δ (s, 1H, Phenolic –OH) 7.99δ (s, 1H, =C-H ethylene), 6.98-8.09δ (m, 8H, Ar-H), 1.31δ (s, 9H, t-butyl group);IR (KBr) ν_{max}/cm^{-1}; 1688 (ν (C=O) ketonic), 1235 (ν (C-O) enolic), 3025 (ν (-OH) intramolecular H-bonding in Phenolic). UV/Vis. (DMSO) nm: 369, 256.

2.4 Synthesis of metal complexes

The metal complexes were prepared by the hot solution of the appropriate metal nitrate (10 mmol) in ethanol (25ml) to the hot solution of the ligands **4(L_A-L_C)** (10 mmol) in the same solvent. The resulting mixture was irradiated for about 1h under ultrasound whereupon the complex precipitated. They were collected by filtration, washed thoroughly with ethanol and dried in vacuum.

2.4.1Ana. Calcd. for5L_A (a-e):

(Yield: 80-85%) IR (KBr) ν_{max}/cm^{-1}; 1680-1665 (ν(C=O) ketonic), 1203-1209 (ν(C-O) enolic), 3072 (ν (-OH) intramolecular H-bonding in Phenolic), 3435-3462 (ν (-OH) in H_2O molecules) 450-465 (ν (M-O bond in complex);UV/Vis. (DMSO) nm: 271 ($\pi \rightarrow \pi^*$),398 (LMCT) , 672-674 (d-d transition).

2.4.2 Ana. Calcd. for5L_B (a-e):

(Yield: 80-82%) IR (KBr) ν_{max}/cm^{-1}; 1649-1645 (ν (C=O) ketonic), 1143-1149 (ν (C-O) enolic), 3072-3030 (ν (-OH) intramolecular H-bonding in Phenolic), 3464-

3367 (ν (-OH) in H_2O molecules) 526-513(ν(M-O bond in complex); UV/Vis. (DMSO) nm: 271(π→ π*),398(LMCT) , 670-674 (d-d transition)

2.4.3 Ana. Calcd. for$5L_C$ (a-e) :

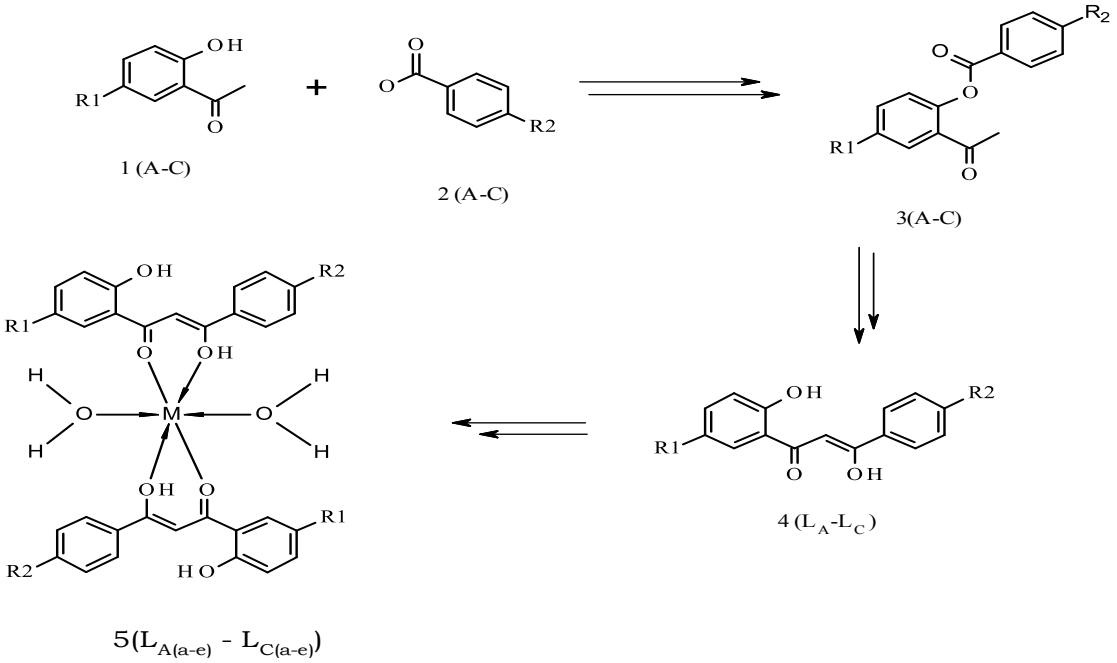
(Yield: 82-87%) IR (KBr) ν_{max}/cm^{-1}; 1590-1631 (ν(C=O) ketonic), 1126-1198 (ν(C-O) enolic), 2957-3009 (ν (-OH) intramolecular H-bonding in Phenolic), 550-565 (ν (M-O bond in complex); UV/Vis. (DMSO) nm: 256-267 (π→ π*),369-376

III. Results and discussion

1, 3-diones was prepared by the esterification of substituted 2-hydroxy acetophenones **1(A-C)** with substituted aromatic acid **2(A-C)** in presence of $POCl_3$ (Scheme 1) to afford **3(A-C**) which upon subsequent treatment with KOH afforded yellow solid **4(L_A-L_C).** All the complexes **5L_A (a-e), 5L_B (a-e)** and **5L_C (a-e)**were colored solids, air stable and soluble in polar solvents like DMF and DMSO. The elemental analysis show 1:2 (metal: ligand) stoichiometry for all the complexes. The structures of the compounds were characterized by spectral analysis. The magnetic measurement studies showed that the complexes **5(a-e)** have octahedral geometry.[22] All complexes showed higher antibacterial activity than the free ligands. Antioxidants results were more effective.

3.1 Synthesis of 1, 3-diones

Scheme: I



Reaction Conditions: i) $POCl_3$ / Py / Ultrasound irradiations

ii) KOH / Py / Ultrasound irradiations

Compounds	R_1	R_2
4 (L_A)	-H	$-NO_2$
4 (L_B)	-Br	-F
4 (L_C)	-H	-t butyl

M:

a Mn (II)
b Fe (II)
c Co (II)
d Ni (II)
e Cu (II)

3.2 Conventional and ultrasound irradiation techniques

Table 1. Physical Characterization and ultrasonic study of ligands and their metal complexes.

Ligands/Complexes	Mol.Wt.	M.P./decomp. Temp (^{0}C)	Conventional		Ultrasound Irradiation [a]	
			Time (min)	Yield (%)	Time (min)	Yield (%)
$4L_A$	285.25	132	370	70	120	82
$5L_A$(a)	659.46	272	280	72	90	80
$5L_A$(b)	660.36	324	280	68	90	84
$5L_A$(c)	663.45	268	280	70	90	85
$5L_A$(d)	663.21	213	280	**73**	90	**83**
$5L_A$(e)	668.06	239	280	**74**	90	**85**
$4L_B$	337.14	172	370	68	120	80
$5L_B$(a)	763.23	≥300	280	72	90	82
$5L_B$(b)	764.14	≥300	280	68	90	80
$5L_B$(c)	767.23	≥300	280	70	90	85
$5L_B$(d)	766.99	≥300	280	**71**	90	**84**
$5L_B$(e)	771.84	≥300	280	**74**	90	**86**
$4L_C$	296.36	122	370	70	120	82
$5L_C$(a)	681.67	267	280	67	90	80
$5L_C$(b)	682.58	291	280	65	90	84
$5L_C$(c)	685.22	287	280	69	90	79
$5L_C$(d)	685.43	292	280	**70**	90	**85**
$5L_C$(e)	690.28	266	280	**72**	90	**87**

[a] Ultrasound irradiation method has improved yields than the conventional method

The reactions under ultrasound irradiation assisted organic synthesis is an efficient and eco-friendly synthetic strategy for improve yields and increases selectivity. The result shows that the metal complexes of Ni (II) and Cu (II) have highest yields than the others metal (II) complexes.

3.3Magnetic measurements

The magnetic measurements of complexes were measured at room temperature. The observed magnetic moment value of **(5a)** complex is 5.86 BM, **(5b)** complex is 6.33 BM, **(5c)** complex is 4.26 BM, **(5d)** complex is 2.50 BM, and **(5e)** complex is 2.12 BM. The magnetic measurement studies showed that the all complexes have octahedral geometry.[23-26]

3.4 Spectroscopic analysis

The ^{1}H-NMR spectrum of the compound **4(L_A-L_C)** exhibited a singlet at δ 15.56 and 14.80 ppm due to enolic proton a singlet at δ 12.02, 11.87 and 11.87 ppm due to phenolic proton adjacent to the carbonyl group and a singlet at δ 7.55, 7.49 and 7.99ppm respectively showed ethylene proton indicate that keto- enol form in 1,3-diketone is more stable. The characteristics infrared spectral assignment of ligand **4(L_A-L_C)** and their metal complexes **5(a-e)** the presence of broad band at 3030-3072cm^{-1} exhibited intramolecular hydrogen bonding due to –OH group. All the above evidences were further supported by the emergence of new bands at 513-526 cm^{-1} due to metal-oxygen vibrations. These new bands observed in the spectra of the transition metal complexes and not in ligands.

3.5 Antioxidants Activities

An aliquot of 0.5 ml of sample solution (0.2, 0.4, 0.6, 0.8, 1 mg/ml) was combined with 5 ml reagent solution (0.6 M sulfuric acid, 28 mM sodium phosphate and 4 mM ammonium molybdate). The tubes were capped and incubated in a boiling water bath at 95^{0}C for 90 min. After the samples had cooled to room temperature, the absorbance of the aqueous solution of each was measured at 695 nm against blank in Spectronic 20 visible spectrophotometer. A typical blank solution contained 5 ml of reagent solution and the appropriate volume of the same solvent (methanol) used for the sample and it was incubated under same conditions. For samples antioxidant capacity is expressed as equivalents

of ascorbic acid and butyrate hydroxy toluene (BHT) as a reference standard. The ligands **4(L_A), 4(L_B) and 4(L_C)** shows that higher antioxidants capacity than the corresponding metal (II) complexes in terms of IC50.

3.6 Antibacterial and antifungal activities

The present paper is focused on the newly synthesized ligands **4(L_A), 4(L_B)** and **4(L_C)** and their metal (II) complexes **5L_A (a-e), 5L_B (a-e)** and **5L_C (a-e)** as possible antibacterial and antifungal agents. The minimum inhibitory concentrations (MICs, mg/mL^{-1}) of tested compounds against certain bacteria and fungi are shown in table 2. A series of synthesized compounds were prepared and tested for their in vitro antimicrobial activity against the four strains of bacteria (gram +ve, gram –ve), and one strain of fungi (*Candida Albicans*). Four compounds of the obtained series **5L_A (b), 5L_A (d), 5L_B (b)** and **5L_C (e)** showed excellent antibacterial activity against *Escherichia coli* and *Pseudomonas aeruginosa.* The compounds **5L_A (c), 5L_A (d), 5L_B (a), 5L_B (b), 5L_C (a)**and**5L_C (c)**showed that high activity against *Staphylococcus aureus* and *Bacillus Subtilis* as compared to the standard drug *Ciprofloxacin.* The compounds **5L_A (b), 5L_B (b), 5L_B (e),** and**5L_C (a)** showed excellent antifungal activity against *C. Albicans*as compared to the standard drug *Fluconazole*. The compounds were added in nutrient broth medium with bacterium and incubated on a rotary shaker at 37 °C for 24 h at 150 rpm. The percentage growth was calculated by the following equation.[27]

$$\% \text{ Growth} = (\text{OD at 600nm sample} / \text{OD at 600 nm control}) \times 100$$

Table 2. Antimicrobial and Antioxidants activity of compounds. Minimum inhibitory concentrations (mcg/mL^{-1})

Ligands/ Complexes	Antibacterial Activity				Antifungal Activity	Antioxidant Activity
	B. Subtilis **(NICM 2063)**	***S.Aureus*** **(NICM 2079)**	***P.Aeruginosa*** **(NICM 2200)**	***E.Coli*** **(NICM 2065)**	***C. Albicans***	**IC 50**
$4L_A$	197.2	124.4	163.6	156.2	184.2	95.2
$5L_A$(a)	79.6	128.0	99.0	45.4	162.2	40.11
$5L_A$(b)	74.8	135.5	101.0	62.3	162.2	46.35
$5L_A$(c)	57.2	151.0	65.0	89.5	148.0	79.47
$5L_A$(d)	106.4	97.7	110.0	77.4	55.0	21.25
$5L_A$(e)	123.3	79.6	76.0	102.4	104.2	78.49
$4L_B$	143.1	178.1	191.3	187.5	164.9	108.3
$5L_B$(a)	181.4	85.4	69.6	56.1	42.8	10.76
$5L_B$(b)	188.7	82.7	120.4	41.1	164.3	19.47
$5L_B$(c)	135.3	74.1	93.9	105.8	*	28.45
$5L_B$(d)	49.4	108.7	72.6	*	158.4	93.47
$5L_B$(e)	44.8	119.1	59.8	*	179.6	88.91
$4L_C$	166.1	147.9	109.1	102.5	174.2	129.2
$5L_C$(a)	120.4	61.3	43.5	65.1	187.2	*
$5L_C$(b)	105.9	90.6	45.4	84.4	146.6	17.74
$5L_C$(c)	92.9	158.6	89.3	56.8	*	92.54
$5L_C$(d)	76.5	109.3	*	168.2	141.3	*
$5L_C$(e)	94.1	117.2	175.3	39.4	94.2	74.64
Ciprofloxacin	50.0	25.0	50.0	25.0		
Fluconazole					50.0	
BHT						16.50
Ascorbic acid						12.80

*No activity reported up to 200 mcg /mL

IV. Conclusion

The functionalized 1, 3-diones **4(L_A), 4(L_B)** and **4(L_C)** and their metal (II) complexes **5L_A (a-e), 5L_B (a-e)** and **5L_C (a-e)** were characterized by spectral and elemental analysis. All the evidences suggested that the complexes have octahedral geometry. The stoichiometry of the complexes was found to be 1:2 (metal: ligand). The conductivity data show that the complexes are non-electrolyte in nature. The synthesized compounds were studied theoretically for prediction of bioactivity and verified experimentally. All the compounds were screened for antimicrobial and antioxidant activity. The compounds **5L_A (b), 5L_A (c), 5L_A (d), 5L_B (a), 5L_B (b), 5L_C (a)** and **5L_C (e)** were found to be potent antibacterial and antifungal agents comparable with *ciprofloxacin*. The newly synthesized compounds **4(L_A), 4(L_B) and 4(L_C)** were also shown to have the promising antioxidant activity. Molecular docking study corroborates the experimental antimicrobial activity specifically against E. coli. In the docking studies against E. coli peptide deformylase enzyme, the importance of ligand complex's access to deeper binding pocket is revealed. It can be also concluded from docking studies that the presence of electronegative substituent's like bromo, fluoro enhances the antimicrobial activity. On the basis of hypothesis based on Petra, it is found that, these compounds could form the highly interesting combined two or more pharmacophores sites in one molecule. Thus, it is concluded that the compounds were found to possess a broad range of hydrophilic and lipophilic characters; hence indication of favorable bioavailability based on drug likeness [29, 30].It is predicted that most of these compounds could be used without risk of toxicity as diverse antibacterial and antioxidant agents.

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Regio-Selective Nitration of Phenols Using Phosphorus Based Ionic Liquids

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ABSTRACT

Highly regio-selective mono nitration of phenols is accomplished using hydrated ferric nitrate as nitrating agent in phosphorous based ionic liquids in particular phosphonium ionic liquids viz, trihexyl (tetradecyl) phosphoniumtetrafluoroborate (PIL-1) and trihexyl (tetradecyl) phosphonium chloride (PIL-2) as the solvents. Trihexyl (tetradecyl) phosphoniumtetrafluroborate (PIL-1) is found to be more suitable even though the nitration rate was low. The higher rate of nitration in case of trihexyl (tetradecyl) phosphonium chloride PIL-2 may be due to high acidity. In particular, excellent paraselectivities were observed for the unsubstituted, orthoand metasubstituted phenols. The quantitative conversion was observed during all reactions making this methodology attractive for synthetic and commercial utility.

Keywords : Phosphonium Ionic Liquids, Nitration, Phenols: Regio-Selective

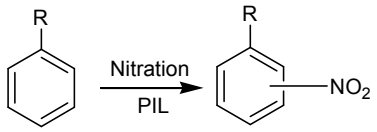
I. INTRODUCTION

Nitration is a unit process[1] of great industrial importance generating commercially valuable intermediates and there is a great need for regio-selective pollution free processes. Usually, nitration reactions are not selective and are the cause of environmental concerns regarding the disposal of large excesses of mixed acids employed in these processes. Thus, the utility of the existing processes[2,3]are generally low. A variety of nitrating agents, including concentrated nitric acid, $Yb(OTf)_3$, and $Hf(OTf)_4$ in conjunction with HNO_3,[4] mixture of nitric acid with sulfuric acid, acetic anhydride, acetic acid, phosphoric acid, peroxynitrite (ONOO-),[5] nitrogen oxides,[6] and several metal nitrates[7] have been employed.

Nitration of phenols lacks position selectivity for para isomer.[8]various metal nitrates and supported metal nitrates are reported to effect para selectivity. The nitrating effect of various metal nitrates in the nitration of phenols was also studied for position selectivity of nitration.[9] Ferric nitrate in chloroform and chromium nitrate gave higher para selectivity. Ionic liquids like ([emim]OTf and [emim][CF_3COO]-) were found to be promising solvents in nitration of aromatics.[10] Good yields were observed for both activating and deactivating substrates. The use of 1,3-di-n-butylimidazolium tetrafluroborate, [bbim]BF_4, as a new room temperature ionic liquid in nitration of phenols with ferric nitrate at ambient conditions has been reported.[11] Nitration of various aromatic compounds using [bmim]BF_4, [bm_2im][$N(Tf)_2$] and [bmpy][NTf_2] at 25°C were also studied using acyl nitrate generated in situ.[12] They observed that in activated system there was little difference between the ionic liquid and the molecular solvent. Dinitration of various aromatic compounds was reported using dilute nitric acid as nitrating agent in presence of 1-decyl-3-methylimidazolium trifluoromethanesulfonate and 1-butyl-3-methyl imidazoliumtrifluoromethane sulfonate.[13]

Recently, a new class of ionic liquids, known as phosphonium ionic liquids (PILs), where phosphorus acts as a cation, and differ from the imidazolium ionic liquids, has been introduced in organic reactions.[14] Phosphorous based ionic liquids are also found to be suitable solvents for electrophilic reactions such as sulfonation and nitration.1[5]

This communication describes for the first time the regioselective mono nitration of phenols with hydrated ferric nitrate using trihexyl (tetradecyl) phosphoniumtetrafluroborate (PIL-1) and trihexyl (tetradecyl) phosphonium chloride (PIL-2) as the room temperature ionic liquid as shown in the **Scheme 1.**



o-, p- directing = F, Cl, Br, I, CH_3, OCH_3, OH
m-directing = COOR, COOH, NO_2, CCl_3

Scheme 1. Nitration of phenols with ferric nitrate in PILs

II. Results and discussion

The results are summarized in Table 1 and 2. The reaction mixtures were homogeneous during nitration in both the ionic liquids and the reactions were monitored by TLC. All the reactions went to complete conversion at 30 °C for all substituted phenols in both PIL-1 and PIL-2 except for nitro and acetyl substituted phenols in PIL-1 where conversion was carried out at 60 °C. Addition of ferric nitrate in ionic liquids was mild exothermic process hence addition of ferric nitrate was done maintaining temperature at 30 °C. PIL-2 could be recovered by filtering the crude reaction product through silica gel.[16]It could be used at least 2 times for nitration of phenol. During nitration of *o*-carbomethoxyphenol and *p*-carbomethoxyphenol in PIL-2 the carbomethoxy group partially hydrolyzed to yield corresponding carboxylic acids in 5- 6% yield. This may be due to the presence of HCl in PIL-2. The nitration of phenols in PIL-2 required less hours than it required for reactions in PIL-1. However, it was more than that of [bbim][BF_4].[8a]

Table 1. Nitration of phenols using trihexyl (tetradecyl) phosphoniumtetrafluroborate (PIL1)

S. No.	Substrate	Time	Conversion	Yields %		
				Ortho	Para	others
1	H	3.0 h	quantitative	18	75	7
2	*o*-Cl	2.5 h	quantitative	15	76	9
3	*o*-OCH_3	4.0 h	quantitative	14	72	14
4	*o*-$COCH_3$	3.0 h	>90%	---	82	18
5	*o*-NO_2	6.0 h	>90%	---	83	17
6	*o*-$COOCH_3$	5.0 h	quantitative	---	83	17
7	*m*-CH_3	3.0 h	quantitative	11	73	16
8	*p*-Cl	3.0 h	quantitative	91	---	9
9	*p*-CH_3	3.0 h	quantitative	86	---	14
10	*p*-$COCH_3$	2.5 h	>90%	83	---	17
11	*p*-NO_2	6.0 h	>90%	82	---	18
12	*p*-$COOCH_3$	5.0 h	quantitative	82	---	18
13	*p*-OCH_3	4.0 h	quantitative	79	---	19

As is evident from Table 1 and Table 2, though in both ionic liquids regioselectivity of ortho and para isomers were same, the ratios of *ortho: para* were different. In PIL-1, phenol,*ortho* and *meta* substituted phenols afforded the p-nitrophenols in very high selectivity and isolated yields were 72–83%. In PIL-2, in all reactions *ortho* and *meta* substituted phenols afforded 71-80% p-nitrophenols. In case of phenol, ortho selectivity was much more in PIL-2 as comparison with PIL-1. In both ionic liquids para substituted phenols afforded very high selectivity and isolated yields were 79–91% in PIL-1 and 82-97% in PIL-2. Regioselectivity of nitration of phenols was comparable with [bbim][BF4].[8a] All of the isolated nitrophenols are known compounds and were characterized by their spectral data.[17] Neither the *m*-isomer nor the dinitrated products could be detected. After recovering of the mono nitro products, the rest of the reaction mass could only be isolated as a mixture difficult to resolve and separate into individual components by chromatographic techniques for their identification. In all probability these constitute a complex mixture of polymeric/oxidized products designated as others in the **Tables 1** and**Table 2** to account for the mass balance.

Table 2. Nitration of phenols using trihexyl (tetradecyl) phosphonium chloride (PIL-2)

S. No.	Substrate	Time	Conversion	Yields %		
				Ortho	Para	others
1	H	1.5 h	quantitative	42	58	---
2	*o*-Cl	2.5 h	quantitative	11.01	80	9
3	*o*-OCH_3	5.0 h	quantitative	9	73	18
4	*o*-$COCH_3$	6.0 h	quantitative	---	75	25
5	*o*-NO_2	4.0 h	quantitative	---	78	22
6	*o*-$COOCH_3$	4.0 h	quantitative	---	78	22
7	*m*-CH_3	2.5 h	quantitative	14.3	71	14.7
8	*p*-Cl	2.5 h	quantitative	92	---	8
9	*p*-CH_3	2.5 h	quantitative	97	---	3
10	*p*-$COCH_3$	3.0 h	quantitative	87	---	13
11	*p*-NO_2	4.0 h	quantitative	87	---	13
12	*p*-$COOCH_3$	3.5 h	quantitative	82	---	18
13	*p*-OCH_3	5.0 h	quantitative	82	---	18

Representative procedure for the preparation of nitrates:

To a solution of phenol (Entry 1) (1.92 g, 20 mmol) in trihexyl (tetradecyl) phosphoniumtetrafluroborate (PIL-1) (5.0 g), $Fe(NO_3)_3.9H_2O$ (4.85 g, 12 mmol) was added in single lot and was stirred vigorously at 30 °C under nitrogen atmosphere. Reaction was monitored by TLC. After completion of reaction (absence of starting phenol), reaction mixture was extracted with n-hexane (3 X 20 ml). Organic layer was washed with brine (10 ml), dried over sodium sulphate and the solvent evaporated under reduced pressure. Crude product was chromatographed over silica gel to isolate first PIL in hexane and then *o*-nitrophenol (0.5 g, 18%) and *p*-nitrophenol (2.08 g, 74.8%). Melting points of all the nitrophenols are compared with melting points reported in literature.

III. Conclusion

In conclusion, the mono nitration of phenols with ferric nitrate has been achieved with high regio-selectivities in excellent isolated yields using both PIL-1 and PIL-2 as solvent. Trihexyl (tetradecyl) phosphoniumtetrafluroborate (PIL-1) was found to be more suitable even though the nitration rate was low. The higher rate of nitration in case of trihexyl (tetradecyl) phosphonium chloride (PIL-2) may be due to high acidity In particular, excellent *para*selectivities were observed for the unsubstituted, *o*- and *m*-substituted phenols. The quantitative conversion was observed during all reactions making this methodology attractive for synthetic and commercial utility.

IV. Acknowledgment

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Dilution Effect on the Thermodynamic Parameters of some Transition Metal Salt by Viscosity Method

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ABSTRACT

The physical properties such as densities, specific viscosities of CaCl2, MnCl2 and NiCl2 at different concentration in the range (1x10-2 M to 6x10-4 M) in aqueous medium at temperature 299K, 305K and 311K are reported. The experimental data shows, the effect of concentration of solute on viscosity in aqueous medium which gives idea about the molecular interactions present in different solutions. Appreciable molecular interactions have been observed between the Chloride salt of Ca2+, Mn2+ & Ni2+ and water. The thermodynamic parameters ΔG, ΔS and ΔH for the dissolution of CaCl2, MnCl2 and NiCl2 were calculated from values of viscosity and densities at different temperatures such as 299K, 305K and 311K in aqueous medium. The experimental data gives the idea about effect of temperature on the molecular interaction and structural changes in solute.

Keywords : Specific Viscosity, Density, Thermodynamic Parameters, Thermodynamic Parameters ΔG, ΔS and ΔH, Chloride Salt of Ca2+, Mn2+ & Ni2+.

I. INTRODUCTION

Physicochemical and thermodynamic investigations play an important role in understanding the nature and the extent of the patterns of molecular aggregation that exist in liquid mixtures and their sensitivities to variations in composition and the molecular structure of the pure components[1] .Since most of the biochemical processes occur in aqueous media, the studies on the thermodynamic and transport properties of drugs in the aqueous phase provide useful information in pharmaceutical and medicinal chemistry[2].

The solute-solvent molecular interaction and their temperature dependence play an important role in the understanding of nature of solute. Viscometric properties provide valuable clues for solute–solvent interactions in the solution phase. Such results can be helpful in predicting the absorption of metal salt and transport of metal across the biological membranes.

Therefore, it may be interesting to investigate variation of their properties with temperature for understanding the mechanism of some transition metal salt such as $CaCl_2$, $MnCl_2$ and $NiCl_2$. The detailed literature survey reveals that thermodynamic and transport properties of the above mentioned chloride salt of metal in aqueous medium are scarce. This prompted us to investigate the thermodynamic and transport properties of three significant metal salt in aqueous solutions at different temperature.

Ca^{2+}, Mn^{2+} & Ni^{2+} has a variety of biological roles in enzymology, cell membrane/wall structure, muscle cell physiology, and nucleic acid structure. Ca^{2+}, Mn^{2+} & Ni^{2+} are an essential co-factor in many enzymes, including DNAse, some restriction enzymes, and Ribonuclease-H. $CaCl_2$, $MnCl_2$ and $NiCl_2$ are widely used to supply the Ca^{2+}, Mn^{2+} & Ni^{2+} ion in various molecular biology applications, including PCR reactions[3,4].

The present work represents the continuation of a systematic investigation of the viscometric properties of some transition metal salt of chloride in aqueous medium at various temperatures. Viscosity is one of the important physical property owned by the liquid. Shearing effect in the liquid is responsible for the viscous nature of the liquid which is nothing but the movement of liquid layers over each other.

The study of molecular interaction of an electrolyte in aqueous medium by viscometrically plays an important role[1,2]. Many researcher study the biologically important $CaCl_2$, $MnCl_2$ and $NiCl_2$ at different temperature[1,2,3] . The Jones-Doles equation [1] helps to evaluate the observed viscosity concentration dependence of dilute electrolyte solutions.

II. Material and Method

The chemicals $CaCl_2$, $MnCl_2$ and $NiCl_2$ of AR grade were used. The densities of pure solvent and solutions of various concentrations were measured at different temperature using a precalibrated bicapilary pycnometer. All the weighings 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 Ostwald viscometer (± 0.1% $Kgm^{-1}s^{-1}$). The flow time of solutions were measured by using digital clock of racer company having error (±0.01sec).

III. Result and Discussion

In the present investigation, the relative viscosity of $CaCl_2$, $MnCl_2$ and $NiCl_2$ solutions decreases with decrease in concentration of solutions. The increase in viscosity with increase in concentration may be ascribed to the increase in the interactions of solute-solvent. The increasing order of relative viscosity for a solution of $CaCl_2$, $MnCl_2$ and $NiCl_2$ is $Ni^{2+}>Ca^{2+}>Mn^{2+}$ at all temperature which are consider for study. The relation between viscosity ($\eta_{sp}/\sqrt{C}$) and concentration of solution ($\sqrt{C}$) represented by plotting the graph (Figure1-3). The plotted graphs prove the validity of Jones-Dole equation for all systems by giving linear straight line. The values of Jones-Dole coefficients especially β -coefficients are the slope of graph ($\eta_{sp}/\sqrt{C}$) Vs ($\sqrt{C}$) while the values of Falkenhagen coefficient i.e. A-Coefficient are the intercept of graph of ($\eta_{sp}/\sqrt{C}$) Vs ($\sqrt{C}$). The order or disorder introduced by solute in solvent is measured by the values of β coefficient which shows either positive or negative values. β coefficient is in turn measures the effective hydrodynamic volume of solute, which accounts for the ion-solvent interaction.

In this work, the values of β -coefficients for all systems are negative at all temperature. It is apparent from table-4 that, β -coefficient is found to be negative for all system and is measure the effective thermodynamic volume of solute which accounts for solute-solvent interaction. It is known as a measure of disorder introduced by a solute in to the solvent. From data of table-4, it is conclude that, the order of Falkenhagen coefficient (A) are $Ni^{2+}>Ca^{2+}>Mn^{2+}$.

From Table 1, 2 & 3 the value of relative viscosity and density decreases for all system as the concentration of solution decreases. Polar nature of metal ion is depend upon its electropositivity and size of ion. Hence, metal ion having more polar character shows high value of relative viscosity. The order of decreasing the relative viscosity all metal ion at all temperature (299K, 305K & 311K) are as $Ni^{2+}>Ca^{2+}>Mn^{2+}$ and density of solution change in the order of $Ni^{2+}>Mn^{2+}> Ca^{2+}$.

As the temperature increases the value of relative viscosity and density decreases shown in table-1, 2 & 3. Due to increase in temperature the interaction between solute-solute and solute-solvent decreases. The thermodynamic parameter such as free energy change(ΔG), enthalpy change(ΔH) and entropy change (ΔS) of different $CaCl_2$, $MnCl_2$ and $NiCl_2$ metal salt are calculated by plotting graph between 1/T Vrs logη_r for a concentration of 0.01M at three temperature are shown in (Figure4-6). Thermodynamic parameters are mentioned in table-4, indicate variation of metal ion with water. The negative value free energy change (ΔG) shows interaction is feasible in all cases. Enthalpy change (ΔH) interpreted that interaction of metal ion and water solvent are spontaneous and exothermic and positive value of entropy change (ΔS) interpreted that, randomness of solute molecule in solvent increases i.e. there is dissociation of solute molecule in aqueous medium.

IV. Calculation

To determine the relative and specific viscosity, in the different concentration of $CaCl_2$, $MnCl_2$ and $NiCl_2$ solutions were prepared and there viscosities are measured with help of the following mathematical relation

$(\eta_r)=(ds \times ts/dw \times tw)\times \eta_w$ 1

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

From the calculated values of relative viscosities (η_r) and the temperature (T), the graph between log (η_r) vs 1/T are plotted.

The relative viscosities of $CaCl_2$, $MnCl_2$ and $NiCl_2$ solutions at different concentration at 299K, 305K & 311K are presented in table no. 1, 2, & 3 respectively. The viscosity data have been analyzed by Jones –Dole equation.

$$(\eta_r - 1)/\sqrt{C} = \eta_{sp}/\sqrt{C} = A + B\sqrt{C} \text{ ---------- } 3$$

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

The Falkenhagen coefficient (A) measures the solute-solute interation while Jones-Dole coefficient (B) measures the solute-solvent interaction.

The thermodynamic parameters i.e. free energy change(ΔG), enthalpy change(ΔH) and entropy change (ΔS) are determined by using following relation,

$$\Delta G = -2.303 \times R \times \text{slope} \quad \ldots 4$$

$$\log \eta_{r1} - \log \eta_{r2} = (\Delta H/2.303) \times (1/T1 - 1/T2) \quad \ldots 5$$

$$\Delta S = (\Delta G - \Delta H)/T \quad \ldots 6$$

Table 1. Densities (d) gm/cc and relative viscosities (η_r) of Chloride salt of Ca^{2+}, Mn^{2+} & Ni^{2+} at different concentration in aqueous solvent at 299K.

Conc. mole/lit	$CaCl_2$		$MnCl_2$		$NiCl_2$	
	Density (d) (Kgm^{-3})	Rel. Viscosity η_r	Density (d) (Kgm^{-3})	Rel. Viscosity η_r	Density (d) (Kgm^{-3})	Rel. Viscosity η_r
0.01	0.9974	2.5223	0.9998	1.7552	1.0052	2.6786
0.005	0.9927	2.1992	0.9964	1.6139	0.9998	2.4234
0.0025	0.9877	1.9094	0.9925	1.4727	0.9965	2.1347
0.00125	0.9848	1.6774	0.9902	1.3555	0.9931	1.8576
0.000625	0.9837	1.4905	0.9805	1.2602	0.9908	1.6359

Table 2. Densities (d) gm/cc and relative viscosities (η_r) of Chloride salt of Ca^{2+}, Mn^{2+} & Ni^{2+} at different concentration in aqueous solvent at 306K.

Conc. mole/lit	$CaCl_2$		$MnCl_2$		$NiCl_2$	
	Density (d) (Kgm^{-3})	Rel. Viscosity η_r	Density (d) (Kgm^{-3})	Rel. Viscosity η_r	Density (d) (Kgm^{-3})	Rel. Viscosity η_r
0.01	0.9937	2.3837	0.9937	1.5247	1.0002	2.4966
0.005	0.9855	2.1404	0.9902	1.4016	0.9985	2.3305
0.0025	0.9815	1.9408	0.9886	1.3032	0.9962	2.1421
0.00125	0.9795	1.7463	0.9856	1.2247	0.9925	1.9197
0.000625	0.9771	1.5626	0.9815	1.1666	0.9885	1.7090

Table 3. Densities (d) gm/cc and relative viscosities (η_r) of Chloride salt of Ca^{2+}, Mn^{2+} & Ni^{2+} at different concentration in aqueous solvent at 311K.

Conc. mole/lit	$CaCl_2$		$MnCl_2$		$NiCl_2$	
	Density (d) (Kgm^{-3})	Rel. Viscosity η_r	Density (d) (Kgm^{-3})	Rel. Viscosity η_r	Density (d) (Kgm^{-3})	Rel. Viscosity η_r
0.01	0.9899	2.2706	0.9905	1.3410	0.9985	2.3462
0.005	0.9839	2.0367	0.9882	1.2937	0.9954	2.1719
0.0025	0.9812	1.8115	0.9861	1.2357	0.9923	1.9652
0.00125	0.9796	1.6222	0.9835	1.1775	0.9911	1.7521
0.000625	0.9762	1.4636	0.9812	1.1308	0.9895	1.5722

The value of A = Falkenhagen coefficient, B= Jones-Dole coefficient is calculated by ploting the graph between of √ C V/S ŋsp/√C of Chloride salt of Ca^{2+}, Mn^{2+} & Ni^{2+} at 299K, 306K & 311K.

Table-4

Temp in K	$CaCl_2$		$MnCl_2$		$NiCl_2$	
	A	B (Lit/mol)	A	B (Lit/mol)	A	B (Lit/mol)
299	6.6964	-5.9494	3.600	-3.829	8.972	-11.579
305	7.9317	-11.746	2.227	-1.851	10.210	-17.946
311	6.4256	-7.7740	1.861	-2.456	8.143	-12.541

Figure 1. Plot of √ C Vs $\eta_{sp}/\sqrt{C}$ for $CaCl_2$, $MnCl_2$ and $NiCl_2$ at 26°C

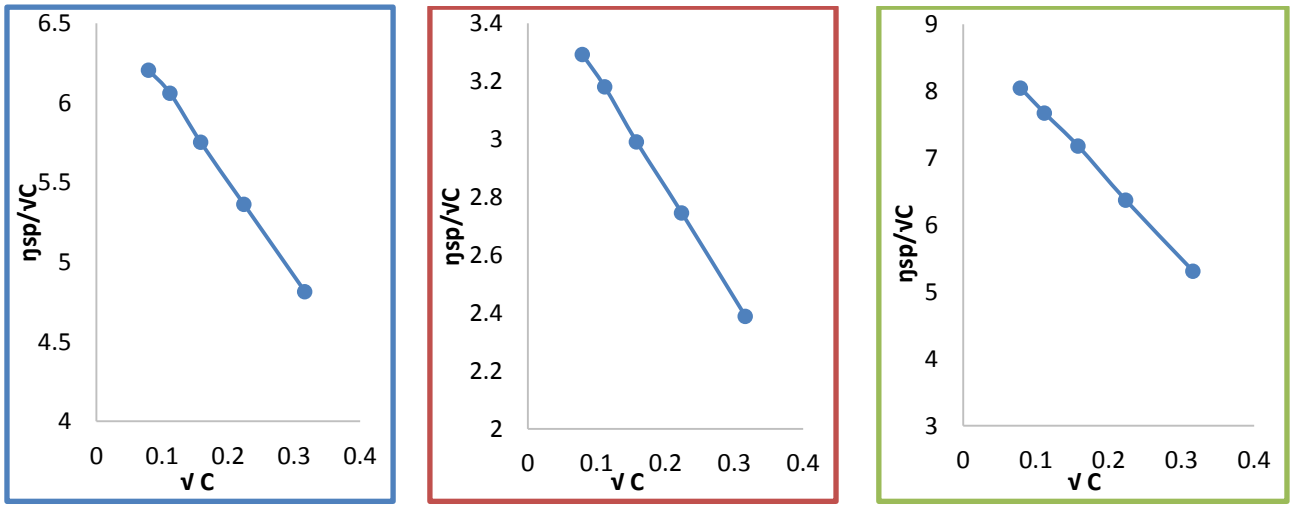

Figure 2. Plot of √ C Vs $\eta_{sp}/\sqrt{C}$ for $CaCl_2$, $MnCl_2$ and $NiCl_2$ at 32°C

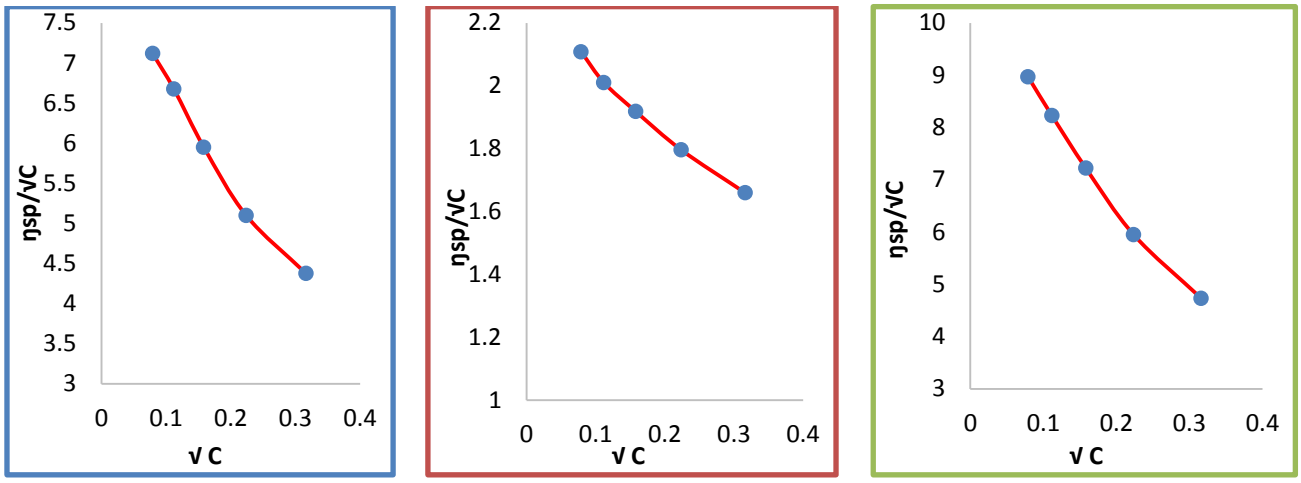

Figure 3. Plot of √ C Vs $\eta_{sp}/\sqrt{C}$ for $CaCl_2$, $MnCl_2$ and $NiCl_2$ at 38°C

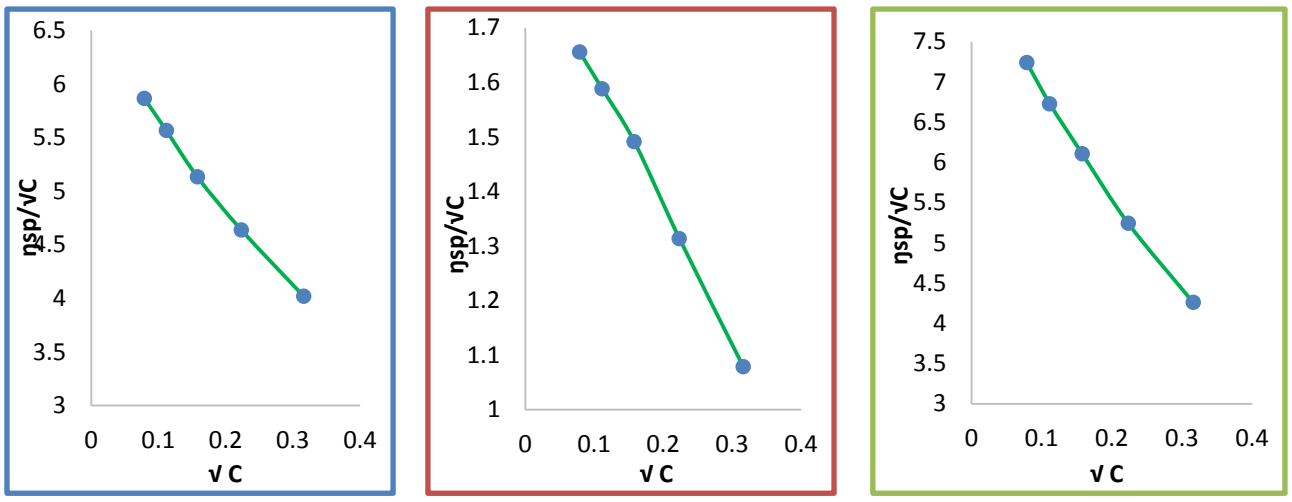

Table 5. Densities (d) gm/cc Relative and relative viscosities (ŋr) of Chloride salt of Ca^{2+}, Mn^{2+} & Ni^{2+} 0.01M concentration in aqueous medium at 299K, 306K & 311K.

Temp. in K	$CaCl_2$		$MnCl_2$		$NiCl_2$	
	Density (d) (Kgm^{-3})	Rel. Viscosity η_r	Density (d) (Kgm^{-3})	Rel. Viscosity η_r	Density (d) (Kgm^{-3})	Rel. Viscosity η_r
299	0.9974	2.5223	0.9998	1.7552	1.0052	2.6786
306	0.9937	2.3837	0.9937	1.5247	1.0002	2.4966
311	0.9899	2.2706	0.9905	1.3410	0.9985	2.3462

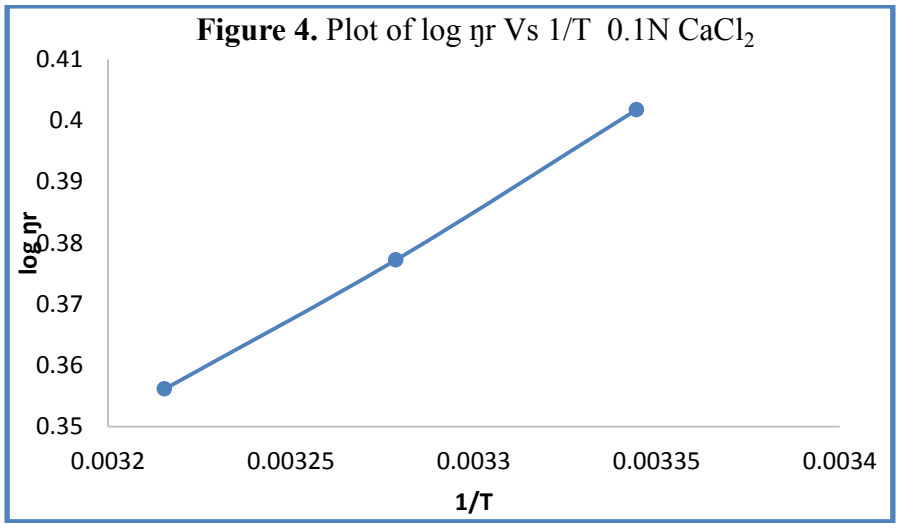

Figure 4. Plot of log ŋr Vs 1/T 0.1N $CaCl_2$

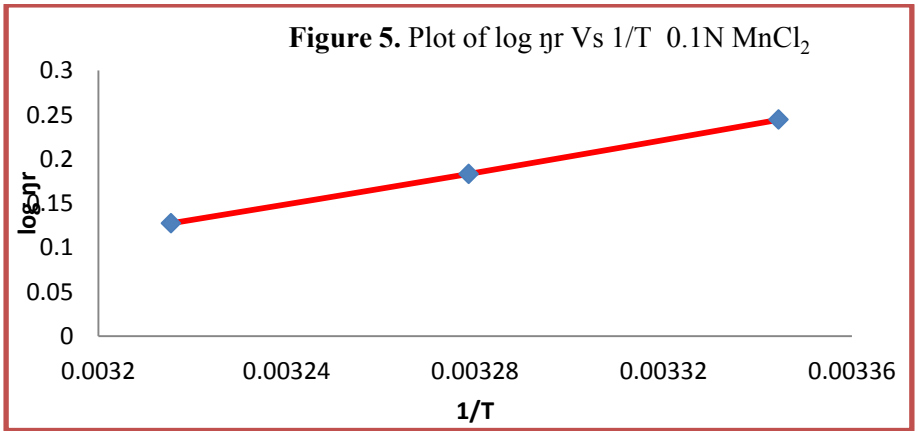

Figure 5. Plot of log ŋr Vs 1/T 0.1N $MnCl_2$

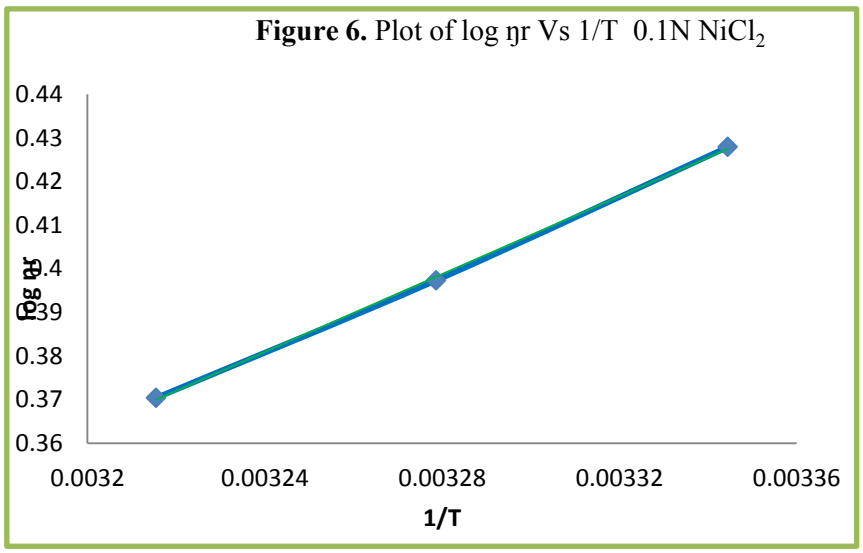

Figure 6. Plot of log ŋr Vs 1/T 0.1N $NiCl_2$

Table 4. Values of Thermodynamic Parameters for temperature difference **299K – 306K**

System	ΔG (J mol^{-1} K^{-1})	ΔH (J mol^{-1} K^{-1})	ΔS (J mol^{-1} K^{-1})
$CaCl_2$	-6676712	-6774.69	21446.74
$MnCl_2$	-5397550	-17343.30	17299.70
$NiCl_2$	-2657042	-8535.87	8516.09

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Synthesis, Anti-Tubercular and Antimicrobial Screening of 2-aryl/benzyl-2'-Benzyl-4'-Methyl-4,5'-Bithiazole Derivatives

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ABSTRACT

A small focused library of 2-aryl/benzyl-2'-benzyl-4'-methyl-4,5'-bithiazole derivatives, **7a-ag** has been efficiently synthesized. The chemical structure of the newly synthesized compounds was determined by analytical and spectral methods. The title compounds were screened for inhibitory activity against *Mycobacterium smegmatis* MC^2 155 strain while the antimicrobial properties were investigated against *Bacillus subtilis, Staphylococcus aureus, Escherichia coli, Proteus vulgaris, Saccharomyces cerevisiae* and *Candida albicans.* Most of the synthesized compounds showed moderate antitubercular activity while some compounds showed good antibacterial activity against *B. subtilis.* This study provides valuable directions to our ongoing endeavour of rationally designing more potent antimycobacterial agent.

Keywords: Bisthiazoles, *Mycobacterium Smegmatis*, Antibacterial Activity.

I. INTRODUCTION

Tuberculosis, a contagious disease, is now coexisting with human immunodeficiency virus (HIV) and is responsible for high mortality worldwide [1-2]. The last major clinical advance in tuberculosis chemotherapy was the introduction of Rifampicin in 1968 [3]. The unusual cell wall barrier, ability to remain dormant and emergence of multidrug (MDR) as well as extensively drug resistant (XDR) Mtb strains, demands the development of library of novel entities having various biodynamic heteryl scaffolds and active pharmacophores for treatment of TB [4-5].

Thiazole and its derivatives are important structure in medicinal chemistry that could provide a rich spectrum of biological activities [6-26]. Bithiazoles and directly linked polyazoles containing compounds are the backbone of bioactive natural products and thiopeptide antibiotics [27-28]. Bisthiazoles (cystothiazoles A-F), isolated from the myxobacterium culture broth of *Cystobacter fuscus*, has demonstrated potent antifungal activity against the phytopathogenic fungus *Phytopathora capsici* [29-30]. Large numbers of bisthiazoles have been synthesized by several research groups and screened for their biological activities [31-37].

Bis-1,3-azole scaffolds linked by different chain length and connectivity points between the rings, are present in numerous natural products with broad spectrum of biological activities [38-40]. Representative examples include Bengazoles, containing an uncommon [2,5'] bioxazole system [41-43], Cystothiazole A, with a [2,4']-bithiazole system [44], Largazole containing a [2,4'] thiazoline thiazole system [45], Leucamide A with a [2,4'] oxazole-thiazole system [46] and cyclic peptides containing 1,3-azoles as Venturamide A [47]. 2'-Alkyl/aryl-2-aryl-4-methyl-4',5- bithiazolyls showed anti-inflammatory activity [48] and thiazole linked with other azoles have exhibited anti-tubercular activity [49-50]. We have reported the clubbed 4,5'-bisthiazole derivatives as potential anti-tubercular and antibacterial agent [51]. By considering the importance of bisthiazole derivatives and as part of search for compounds as candidates for antitubercular drugs employing molecular simplification, in this present work we described the synthesis of 2-aryl/benzyl-2'-benzyl-4'-methyl-4,5'-bithiazole derivatives, **7a-ag** as potential antimycobacterial agents.

II. METHODS AND MATERIAL

EXPERIMENTAL

All the reactions were monitored and purity of the products was checked by thin-layer chromatography (TLC). TLC was performed on Merck 60 F-254 silica gel plates with visualization by UV light. Melting points were determined in capillary tubes in silicon oil bath using a Veego melting point apparatus and are uncorrected. ^{1}H (300 MHz) NMR and ^{13}C (75 MHz) NMR spectra were recorded on Varian mercury XL-300 and BRUKER AVANCE II 400 NMR spectrometer (Bruker Instruments Inc., Billerica, MA, USA) at either 400-MHz (^{1}H NMR) and100-MHz (^{13}C NMR) spectrometer instruments. Chemical shifts are reported from internal tetramethylsilane standard and are given in δ units. Infrared spectra were taken on Shimadzu FTIR (KBr) (Shimadzu Corporation, Kyoto, Japan) – 408 in KBr. The LC-MS spectra were recorded on a Shimadzu 2010 LC-MS. Column chromatography was performed on silica gel (100–200 mesh) supplied by Acme Chemical Co. (Mumbai, Maharashtra, India). The chemicals and solvents used were laboratory grade and were purified as per literature methods.

Synthesis of 3-bromopentane-2,4-dione (2)

A mixture of acetylacetone (10 mmol) and p-toluenesulfonic acid (5 mmol) in DCM (50 mL) was stirred at 0 ºC for 10 minutes, followed by NBS (10 mmol). The reaction mixture was further stirred for 6-8 hour (TLC). The reaction was quenched by sodium bicarbonate solution and stirred for 10 minutes. The aqueous layer was extracted with DCM and combined organic layers was washed with water, dried with sodium sulphate and distilled under vacuum. The product isolated was used for second step without purification.

Synthesis of 1-(2-substitutedbenzyl-4-methylthiazol-5-yl)ethanone (4a):

A mixture of benzylthioamide (6.62 mmol) and of 3-bromopentane-2,4-dione, (6.62 mmol) was refluxed in ethanol. After completion of reaction (TLC), solvent was removed under reduced pressure and the residue was dissolved in ethyl acetate. Organic layer was extracted with sodium bicarbonate and then water. Organic layer was dried over sodium sulphate and distilled under vacuum. The product obtained was purified by column chromatography using hexane: ethyl acetate (9:1) as eluent.

Synthesis of 2-bromo-1-(4-methyl-2-(4-benzyl)thiazol-5yl)ethanone (5a):

A mixture of 1-(4-methyl-2-benzylthiazol-5-yl)ethanone (10 mmol) and pTSA (5 mmol) in DCM (50 mL) was stirred at 0 ºC for 10 minutes, then Br_2 (10 mmol) in DCM (20 mL) was added dropwise in reaction mixture. The reaction mixture was further stirred for further 12 hours at room temperature (TLC). After completion of the reaction, sodium bicarbonate solution was added in reaction mixture and stirred for 10 minutes. The aqueous layer was extracted with DCM and combined organic layer was washed with water, dried with sodium sulphate and distilled under vacuum.

General method for the synthesis 2-aryl/benzyl-2'-benzyl-4'-methyl-4,5'-bithiazole derivatives (7a-ag):

A mixture of 2-bromo-1-(2-(4-phenyl)-4-methyl thiazol-5yl)ethanone (1 mmol) and substituted thioamide (1.1 mmol) was refluxed in dry ethanol (15 mL). The reaction was monitored on TLC. After completion of the reaction; reaction mixture was poured in ice water and extracted with ethyl acetate. The organic layer was washed with sodium bicarbonate and water. The solvent was dried over sodium sulphate and removed under vacuum. The product was purified by crystallization from ethanol.

2'-benzyl-4'-methyl-2-phenyl-4,5'-bithiazole (7a):

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.63 (s, 3H, CH_3), 4.35 (s, 2H, CH_2), 7.20 (s, 1H, thiazole-H), 7.31-7.44 (m, 8H, Ar-H), 7.92-7.95 (m, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.0, 38.9, 114.3, 126.2, 127.7, 128.5, 129.1, 129.7, 130.4, 130.8, 132.5, 133.8, 147.5, 148.4, 165.1, 168.3; LC-MS, m/z: 349.1 $(M+H)^+$.

2'-benzyl-2-(4-bromophenyl)-4'-methyl-4,5'-bithiazole (7b):

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.58 (s, 3H, CH_3), 4.22 (s, 2H, CH_2), 7.12 (s, 1H, thiazole-H), 7.24-7.28 (m, 5H, Ar-H), 7.45 (d, J = 8.00Hz, 2H, Ar-H), 7.72 (d, J=8.00Hz, 2H, Ar-H); ^{13}CNMR(75MHz,$CDCl_3$): δ 17.0, 38.9, 114.3, 123.1, 126.2, 127.7, 128.7, 129.1, 129.7, 132.2, 132.5, 135.4, 147.5, 148.4, 165.1, 168.9; LC-MS, m/z:427.0 $(M+H)^+$, m/z:429.0 $(M+H+2)^+$.

2'-benzyl-2-(3-chlorophenyl)-4'-methyl-4,5'-bithiazole (**7c**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.63 (s, 3H, CH_3), 4.35 (s, 2H, CH_2),7.20 (s,1H, thiazole-H), 7.24 -7.28 (m, 5H, Ar-H,), 7.30-7.49 (m, 4H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.1, 39.8, 114.2,124.7, 126.5, 127.5, 128.5, 129.0, 130.2, 131.3, 131.6, 134.7, 135.1, 137.7, 148.6, 148.7, 166.0, 168.6; LC-MS, m/z:383.0 $(M+H)^+$, m/z: 385.0 $(M+H+2)^+$.

2'-benzyl-2-(4-chlorophenyl)-4'-methyl-4,5'-bithiazole (**7d**):
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.58 (s, 3H, CH_3), 4.22(s,2H, , CH_2)7.21(s, 1H, thiazole-H) 7.24-7.28 (m, 5H, Ar-H,), 7.33 (d, J = 8.00Hz, 2H, Ar-H), 7.42(d, J = 8.00Hz, 2H, Ar-H); ^{13}C NMR (75MHz, $CDCl_3$): δ 17.3, 39.8, 114.0, 116.1, 126.4, 127.6, 128.5, 129.2, 130.2, 131.8, 136.1, 144.2, 152.4, 163.1, 168.1, 168.9; LC-MS, m/z:383.0 $(M+H)^+$, m/z:385.0 $(M+H+2)^+$.

2-benzyl-5-(2-(3-chloro-4-fluorophenyl)thiazol-4-yl)-4-methylthiazole (**7e**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.59 (s, 3H, CH_3), 4.22 (s, 2H, CH_2), 7.12-7.30 (m, 7H, Ar-H, thiazole-H), 7.77-7.80 (m, 1H, Ar-H), 7.99-8.02 (m, 1H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.3, 39.6, 114.1, 117.0, 122.0, 126.4, 128.3, 129.0, 129.3, 130.3, 130.7, 133.4, 135.4, 148.1, 148.5, 159.4, 164.9, 167.6;LC-MS, m/z: 401.0 $(M+H)^+$,m/z:403.0 $(M+H+2)^+$.

2'-benzyl-2-(4-fluorophenyl)-4'-methyl-4,5'-bithiazole (**7f**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.66 (s, 3H, CH_3), 4.28 (s, 2H, CH_2), 7.10 (t, J = 9.0Hz, 2H, Ar-H), 7.17 (s, 1H, thiazole-H) 7.31-7.36 (m, 5H, Ar-H, thiazole-H), 7.90-7.94 (m, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.3, 40.2, 114.0, 115.6, 116.1, 116.8, 125.9, 128.6, 129.1, 129.6, 136.4, 144.2, 152.2, 162.9, 168.2, 168.9; LC-MS, m/z: 367.1 $(M+H)^+$.

2'-benzyl-4'-methyl-2-(p-tolyl)-4,5'-bithiazole (**7g**): ^{1}H NMR (400 MHz, $CDCl_3$):
δ 2.36 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 4.28 (s, 2H, CH_2),7.10 (s, 1H, thiazole-H) 7.08-7.35 (m, 9 H, Ar-H); ^{13}C NMR (100MHz, $CDCl_3$): δ 17.2, 21.5, 39.8, 113.3, 126.5, 127.2, 127.3, 128.8, 129.0, 129.1, 129.6, 130.5, 140.6, 148.1, 148.5, 167.9, 168.2; LC-MS, m/z: 363.1 $(M+H)^+$.

2,2'-dibenzyl-4'-methyl-4,5'-bithiazole (**7h**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.59 (s, 3H, CH_3), 4.37 (s, 2H, CH_2), 4.30 (s, 2H, CH_2), 7.08 (s, 1H, thiazole H),7.28-7.35 (m, 10H, Ar-H); ^{13}C NMR (100MHz, $CDCl_3$): δ 17.2, 39.8, 40.4, 114.1, 115.4, 125.4, 125.8, 128.2, 128.6, 129.1, 129.6, 136.2, 136.6, 143.1, 152.2, 167.6, 168.1; LC-MS, m/z: 363.1 $(M+H)^+$.

2'-benzyl-2-(4-chlorobenzyl)-4'-methyl-4,5'-bithiazole (**7i**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.60 (s, 3H, CH_3), 4.27 (s, 2H, CH_2), 4.28 (s, 2H, CH_2), 7.10 (s, 1H, thiazole-H), 7.23-7.35 (m, 9H, Ar-H); ^{13}CNMR (100MHz, $CDCl_3$): δ 17.1, 39.6, 40.1, 114.1, 115.6, 125.8, 128.4, 128.9, 129.2, 130.6, 134.2, 136.1, 136.8, 143.2, 152.1, 167.8, 168.4; LC-MS, m/z: 397.1 $(M+H)^+$, m/z: 399.1 $(M+H+2)^+$.

2'-benzyl-2-(3-fluorobenzyl)-4'-methyl-4,5'-bithiazole (**7j**):
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.58 (s, 3H, CH_3), 4.26 (s, 2H, CH_2), 4.29 (s, 2H, CH_2), 7.10 (s, 1H, thiazole-H), 6.00-7.14 (m, 9H,Ar-H);^{13}C NMR (100 MHz, $CDCl_3$): δ 17.1, 39.8, 40.1, 114.1, 115.6, 116.8, 124.4, 127.2, 127.5, 128.8, 129.0, 129.3, 131.2, 137.8, 147.2, 148.4, 161.1, 168.2, 168.9; LC-MS, m/z: 381.1 $(M+H)^+$.

2'-benzyl-2-(4-fluorobenzyl)-4'-methyl-4,5'-bithiazole (**7k**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.58 (s, 3H, CH_3), 4.25 (s, 2H, CH_2), 4.26 (s, 2H, CH_2), 6.99 (t, J = 8.8Hz, 2H, Ar-H), 7.08 (s, 1H, thiazole-H), 7.24-7.38 (m, 7H, Ar-H); ^{13}C NMR (100 MHz,$CDCl_3$): 17.1, 39.8, 40.2, 114.1, 115.2, 115.8, 125.8, 128.8, 129.2, 130.8, 131.8, 136.4, 143.2, 152.2, 160.1, 167.7, 168.2; LC-MS, m/z: 381.1$(M+H)^+$.

2'-(4-chlorobenzyl)-4'-methyl-2-phenyl-4,5'-bithiazole (**7l**):
^{1}H NMR (300 MHz,$CDCl_3$): δ 2.68 (s, 3H, CH_3), 4.29 (s, 2H, CH_2), 7.14-7.31 (m, 6H, Ar-H, thiazole-H), 7.41 (d, J = 7.2Hz, 2H, Ar-H), 7.85-7.90 (m, 2H, Ar-H);^{13}C NMR (75 MHz, $CDCl_3$): δ 16.5, 38.7, 115.0, 126.2, 128.4, 129.2, 129.8, 130.3, 130.9, 131.2, 133.4, 134.0, 147.7, 148.2, 167.6, 169.1; LC-MS, m/z: 383.0 $(M+H)^+$,m/z: 385.0 $(M+H+2)^+$.

2-(4-bromophenyl)-2'-(4-chlorobenzyl)-4'-methyl-4,5'-bithiazole (**7m**):
^{1}H NMR (300 MHz, $CDCl_3$): 2.69 (s, 3H, CH_3), 4.29 (s, 2H, CH_2), 7.28-7.35 (m, 5H, Ar-H, thiazole-H), 7.57 (d, J = 8Hz, 2H, Ar-H), 7.83 (d, J = 8Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.2, 38.8,114.4, 126.3, 128.5, 129.0, 129.7, 130.2, 130.8, 131.3, 132.9, 135.4, 147.7, 148.0, 166.8, 168.3; LC-MS, m/z: 460.9 $(M+H)^+$, m/z: 462.9 $(M+H+2)^+$.

2'-(4-chlorobenzyl)-2-(3-chlorophenyl)-4'-methyl-4,5'-bithiazole (**7n**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.78 (s, 3H, CH_3), 4.52 (s, 2H, CH_2), 7.26-7.50 (m, 7H, Ar-H, thiazole-H), 7.77-7.80 (m, 1H, Ar-H),7.96-7.97 (m, 1H, Ar-H); ^{13}CNMR (100 MHz, $CDCl_3$): δ 17.1, 38.3, 114.2, 115.8, 125.6, 126.9, 128.4, 128.9, 130.2, 130.8, 131.2, 134.2, 134.8, 135.1, 144.0, 151.9, 168.0, 168.8; LC-MS, m/z: 417.0 $(M+H)^+$, m/z: 419.0 $(M+H+2)^+$.

2'-(4-chlorobenzyl)-2-(4-chlorophenyl)-4'-methyl-4,5'-bithiazole (**7o**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.66 (s, 3H, CH_3), 4.26 (s, 2H, CH_2), 7.22-7.32 (m, 5H, Ar-H, thiazole-H), 7.41 (d, J = 8Hz, 2H, Ar-H), 7.88 (d, J = 8Hz, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.0, 38.6, 114.0, 116.0, 128.2, 128.8, 129.2, 130.0, 131.2, 131.8, 133.9, 134.4, 144.2, 151.9, 167.9, 168.8; LC-MS, m/z: 417.0 $(M+H)^+$, m/z: 419.0 $(M+H+2)^+$.

2-(3-chloro-4-fluorophenyl)-2'-(4-chlorobenzyl)-4'-methyl-4,5' bisthiazole (**7p**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.65 (s, 3H, CH_3), 4.26 (s, 2H, CH_2), 7.16-7.34 (m, 6H, Ar-H, thiazole-H), 7.77-7.80 (m, 1H, Ar-H), 7.99-8.02 (m, 1H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.2, 39.0, 114.2, 117.3, 122.0, 126.4, 128.3, 129.0, 130.3, 130.7, 132.8, 133.4, 135.4, 148.4, 148.8, 159.5, 165.0, 167.7;LC-MS, m/z: 435.0 $(M+H)^+$,m/z:437.0 $(M+H+2)^+$.

2'-(4-chlorobenzyl)-2-(4-fluorophenyl)-4'-methyl-4,5'-bithiazole (**7q**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.65 (s, 3H, CH_3), 4.25 (s, 2H, CH_2), 7.10 (t, J = 8.4Hz, 2H, Ar-H), 7.20 (s, 1H, thiazole-H), 7.24-7.41 (m, 4H, Ar-H), 7.91-7.95 (m, 2H, Ar-H);^{13}C NMR (100MHz, $CDCl_3$): δ 17.2, 38.8, 114.0, 116.0, 116.4, 128.6, 129.1, 129.8, 130.6, 131.4, 134.6, 144.0, 152.0, 163.0, 168.2, 168.8; LC-MS, m/z: 401.0 $(M+H)^+$, m/z: 403.0 $(M+H+2)^+$.

2'-(4-chlorobenzyl)-4'-methyl-2-(p-tolyl)-4,5'-bithiazole (**7r**):
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 4.20 (s, 2H, CH_2), 7.01 (s, 1H, thiazole-H), 7.00-7.38 (m, 8H, Ar-H); ^{13}C NMR (75MHz, $CDCl_3$): δ 17.0, 21.5, 38.8, 113.8, 115.8, 127.2, 128.8, 129.6, 130.2, 130.8, 131.6, 133.8, 138.4, 144.2, 152.0, 167.9, 168.8; LC-MS, m/z: 397.1 $(M+H)^+$, m/z: 399.1 $(M+H+2)^+$.

2-benzyl-2'-(4-chlorobenzyl)-4'-methyl-4,5'-bithiazole (**7s**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.58 (s, 3H, CH_3), 4.24 (s, 2H, CH_2), 4.30 (s, 2H, CH_2), 7.01 (s, 1H, thiazole-H), 7.25-7.40 (m, 9H, Ar-H);^{13}C NMR (100 MHz, $CDCl_3$): δ 17.2,39.6, 40.4, 114.4, 115.6, 126.2, 128.1, 128.8, 129.2, 130.3, 131.4, 134.4, 136.2, 143.2, 152.0, 167.9, 168.1; LC-MS, m/z: 397.1 $(M+H)^+$, m/z: 399.1 $(M+H+2)^+$.

2,2'-bis(4-chlorobenzyl)-4'-methyl-4,5'-bithiazole (**7t**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.58 (s, 3H, CH_3), 4.23 (s, 2H, CH_2), 4.26 (s, 2H, CH_2), 7.11 (s, 1H, thiazole-H),7.22-7.32 (m, 8H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.1, 38.8, 39.0, 114.2, 127.2, 128.3, 128.8, 129.0, 130.4, 133.1, 133.2, 135.9, 136.2, 147.2, 148.5, 136.3, 169.6; LC-MS, m/z: 431.0 $(M+H)^+$, m/z: 433.0 $(M+H+2)^+$.

2'-(4-chlorobenzyl)-2-(3-fluorobenzyl)-4'-methyl-4,5'-bithiazole (**7u**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.58 (s, 3H, CH_3), 4.24 (s, 2H, CH_2),4.30 (s, 2H, CH_2), 7.01 (s, 1H, thiazole-H), 6.77-7.15 (m, 8H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.1, 38.6, 38.8, 112.6, 114.2, 115.4, 116.2, 124.8, 128.8, 130.1, 130.8, 131.4, 134.4, 138.1, 142.9, 152.0, 163.1, 167.9, 168.2; LC-MS, m/z: 415.0 $(M+H)^+$, m/z: 417.0 $(M+H+2)^+$.

2'-(4-chlorobenzyl)-2-(4-fluorobenzyl)-4'-methyl-4,5'-bithiazole (**7v**):
^{1}H NMR (400 MHz, $CDCl_3$): 2.58 (s, 3H, CH_3), 4.24 (s, 2H, CH_2), 4.27 (s, 2H, CH_2), 6.99-7.04 (m, 2H, Ar-H), 7.11 (s, 1H, thiazole-H), 7.25-7.31 (m, 6H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.2, 32.6, 38.8, 114.2,

115.4, 115.8, 128.8, 130.2, 130.8, 131.1, 131.9, 134.6, 142.9, 152.1, 160.1, 167.6, 168.2; LC-MS, m/z: 415.0 $(M+H)^+$, m/z: 417.0 $(M+H+2)^+$.

2'-(4-fluorobenzyl)-4'-methyl-2-phenyl-4,5'-bithiazole (**7w**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.63 (s, 3H, CH_3), 4.24 (s, 2H, CH_2), 6.93-6.99 (m, 2H, Ar-H), 7.10-7.43 (m, 6H, Ar-H, thiazole-H), 7.86-7.11 (m, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.9, 38.6, 113.9, 115.7, 126.6, 128.6, 128.9, 130.4, 130.7, 131.4, 133.3, 147.9, 158.6, 162.0, 167.9, 168.4; LC-MS, m/z: 367.1 $(M+H)^+$.

2-(4-bromophenyl)-2'-(4-fluorobenzyl)-4'-methyl-4,5'-bithiazole (**7x**):
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.64 (s, 3H, CH_3), 4.27 (s, 2H, CH_2), 6.94-7.00 (t, J = 9.1Hz, 2H, Ar-H), 7.11-7.42 (m, 5H, Ar-H, thiazole-H), 7.48 (d, J = 8.4Hz, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.0, 38.8, 114.0, 115.8, 126.7, 128.7, 129.1, 129.9, 130.5, 131.2, 132.6, 148.0, 148.2, 162.5, 167.7, 168.6; LC-MS, m/z:445.0 $(M+H)^+$,m/z: 447.0 $(M+H+2)^+$

2-(3-chlorophenyl)-2'-(4-fluorobenzyl)-4'-methyl-4,5'-bithiazole (**7y**):
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.76 (s, 3H, CH_3), 4.89 (s, 2H, CH_2), 7.11-7.22 (t, J = 9.1Hz, 2H, Ar-H), 7.48 (s, 1H, Thiazole-H) 7.73-7.86 (m, 4H, Ar-H), 7.88 (d, J = 8.2Hz, 2H, Ar-H); ^{13}C NMR (75MHz, $CDCl_3$): δ 17.2, 38.9, 114.0, 115.9, 124.7, 127.1, 128.1, 128.7, 130.7, 132.3, 133.5, 148.4, 148.8, 158.6, 160.8, 163.2, 166.4, 168.2; LC-MS, m/z: 401.0 $(M+H)^+$, m/z: 403.0 $(M+H+2)^+$.

2-(4-chlorophenyl)-2'-(4-fluorobenzyl)-4'-methyl-4,5'-bithiazole (**7z**):
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.65 (s, 3H, CH_3), 4.26 (s, 2H, CH_2), 7.11 (t, J = 9.1Hz, 2H, Ar-H), 7.41 (s, 1H, thiazole-H), 7.44-7.55 (m, 4H, Ar-H), 7.82 (d, J = 8.4Hz, 2H, Ar-H);^{13}C NMR (75 MHz, $CDCl_3$): δ 17.0, 38.6, 114.0, 115.2, 116.0, 128.8, 129.6, 130.8, 131.2, 132.0, 134.4, 144.0, 152.0, 159.9, 167.8, 168.6; LC-MS, m/z: 401.0 $(M+H)^+$, m/z: 403.0 $(M+H+2)^+$.

2-(3-chloro-4-fluorophenyl)-2'-(4-fluorobenzyl)-4'-methyl-4,5'-bithiazole (**7aa**):
^{1}H NMR (400 MHz, DMSO-d_6): δ 2.59 (s, 3H, CH_3), 4.20 (s, 2H, CH_2), 7.10-7.26 (m, 5H, Ar-H, thiazole-H), 7.94- 7.99 (m, 3H, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 17.2, 38.9, 114.1, 115.7, 117.1, 126.7, 128.8, 130.4, 130.7, 132.7, 133.5, 134.2, 148.5, 148.9, 159.5, 160.9, 165.0, 168.2; LC-MS, m/z: 419.0 $(M+H)^+$,m/z: 421.0 $(M+H+2)^+$.

2'-(4-fluorobenzyl)-2-(4-fluorophenyl)-4'-methyl-4,5'-bithiazole (**7ab**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.66 (s, 3H, CH_3), 4.26 (s, 2H, CH_2), 7.00-7.05 (m, 2H, Ar-H), 7.11 (t, J = 8.4Hz, 2H, Ar-H), 7.20 (s, 1H, thiazole-H), 7.30-7.33 (m, 2H, Ar-H), 7.91-7.95 (m, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.2, 38.9, 113.6, 115.6, 115.9, 127.1, 128.5, 129.5, 130.6, 133.5, 148.2, 148.7, 160.8, 162.8, 166.4, 168.1; LC-MS, m/z: 385.1 $(M+H)^+$.

2'-(4-fluorobenzyl)-4'-methyl-2-(p-tolyl)-4,5'-bithiazole (**7ac**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H, CH_3), 2.67 (s, 3H, CH_3), 4.26 (s, 2H, CH_2), 7.0-7.05 (m, 2H, Ar-H), 7.17 (s, 1H, thiazole-H), 7.22 (d, J = 8.2 Hz, 2H, Ar-H), 7.29-7.33 (m, 2H, Ar-H), 7.84 (d, J = 8.2 Hz, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.1, 21.5, 38.9, 113.5, 115.5, 126.5, 127.4, 129.6, 130.2, 130.8, 131.8, 133.6, 148.0, 148.6, 162.0, 167.8, 167.9; LC-MS, m/z: 381.1 $(M+H)^+$.

2-benzyl-2'-(4-fluorobenzyl)-4'-methyl-4,5'-bithiazole (**7ad**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.67 (s, 3H, CH_3), 4.31 (s, 2H, CH_2), 4.33 (s, 2H, CH_2), 7.00-7.20 (m, 6H, Ar-H, thiazole-H), 7.31-7.40 (m, 4H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.2, 38.8, 39.2, 113.8, 114.9, 115.4, 126.0, 128.8, 129.2, 130.6, 132.0, 136.2, 143.2, 151.9, 160.0, 167.6, 168.2; LC-MS, m/z: 381.1 $(M+H)^+$.

2-(4-chlorobenzyl)-2'-(4-fluorobenzyl)-4'-methyl-4,5'-bithiazole (**7ae**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.68 (s, 3H, CH_3), 4.34 (s, 2H, CH_2), 4.36 (s, 2H, CH_2), 7.08-7.12 (m, 4H, Ar-H), 7.20 (s, 1H, thiazole-H), 7.31-7.40 (m, 4H, Ar-H);^{13}C NMR (100 MHz, $CDCl_3$): δ 17.3, 39.8, 40.2, 114.2, 115.1, 115.8, 128.6, 129.9, 130.4, 131.1, 132.0, 134.4, 143.0, 152.0, 160.0, 167.8, 168.0; LC-MS, m/z: 415.0 $(M+H)^+$, m/z: 417.0 $(M+H+2)^+$.

2-(3-fluorobenzyl)-2'-(4-fluorobenzyl)-4'-methyl-4,5'-bithiazole (**7af**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.71 (s, 3H, CH_3), 4.36 (s, 2H, CH_2), 4.47 (s, 2H, CH_2), 7.11-7.24 (m, 5H, Ar-H, thiazole-H), 7.37-7.43 (m, 4H, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 17.1, 32.6, 38.8, 114.2, 115.5, 124.4, 127.2, 128.6, 129.3, 130.6, 131.3, 133.5, 147.1, 148.4, 161.0, 162.2,163.3, 167.9, 169.6; LC-MS, m/z: 399.1 $(M+H)^+$.

2,2'-bis(4-fluorobenzyl)-4'-methyl-4,5'-bithiazole (**7ag**):
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.70 (s, 3H, CH_3), 4.34 (s, 2H, CH_2), 4.36 (s, 2H, CH_2), 6.85-7.04 (m, 8H, Ar-H), 7.20 (s, 1H, thiazole-H); ^{13}C NMR (100MHz, DMSO-d_6): δ 17.2, 38.6, 38.8, 114.0, 114.9, 115.2, 115.6, 130.2, 130.6, 131.2,131.6, 142.9, 151.9, 159.9, 160.1, 167.4, 167.9; LC-MS, m/z: 399.1 $(M+H)^+$.

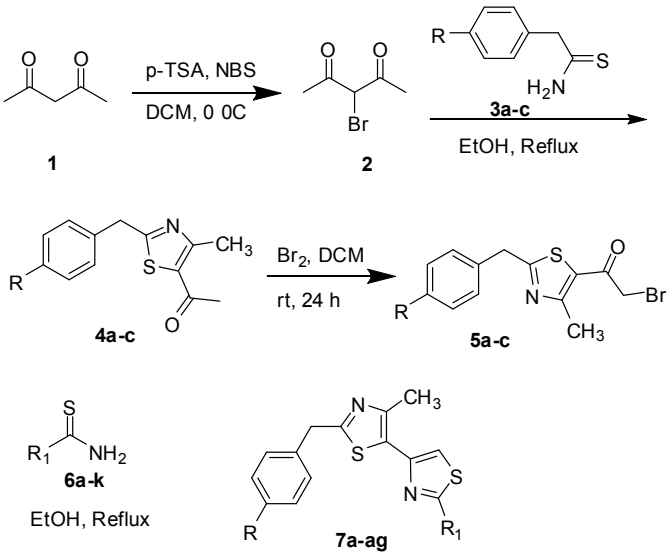
Anti-tubercular activity:
The synthesized compounds were screened for their antitubercular activity against *M. smegmatis* MC^2 155 strain. The series of compounds were obtained in 10 mM stock concentrations. Further, each compound was diluted with the required 100% (v/v) DMSO to achieve a working concentration of 1.5 mM. The inoculum for the assay was prepared by reviving aglycerol stock in Middlebrook 7H9 broth supplemented with 0.1%Tween 80 and 0.5% glycerol. At the time of inoculation, 10% ADS was added to the media and the culture was incubated in ashaker incubator at 37 °C and 200 rpm. The O.D. of the inoculums reached to 0.8-1 approximately, a secondary inoculum was inoculated and subsequently incubated. This was incubated overnight till the O.D. of the inoculum reached 0.4 approx., following which the inoculum was diluted 1:1000 times. In a 96 well microtiter plate, a 2 µL aliquot of the 1.5 mM dilution of compound was added to each well in triplicate, to which 98 µL of inoculum dilution was added, making the final concentration of compound 30 µM. To each plate, a set of controls was added to better ascertain the activity of the compounds. These included DMSO, which was taken as a growth control, and media control (Blank) and Rifampicin and Isoniazid, which were taken as positive controls of inhibition of *M. smegmatis*. After the completion of the period of 32 h, the absorbance of the inoculum in wells was measured at 600 nm using a Multi Mode Reader. Absorbance is considered directly proportional to the increase in growth of bacteria. Thus, it gives a measure of the growth of bacteria in each well. Percentage inhibition was determined against DMSO.

Antimicrobial activity:
The *in vitro* antimicrobial activities of all the synthesized compounds were done by the disc diffusion method [56-57]. All the strains were obtained from National Chemical Laboratory, Pune, India. All cultures were maintained at 4ºC over nutrient agar slants throughout the experiment. The cultures were incubated overnight at 37ºC in nutrient broth before using for antimicrobial activity. Five hundred microliters of overnight old bacterial / fungal suspension was spread over the nutrient agar plates using a sterile cotton swab in order to get a uniform microbial growth. The synthesized compounds were dissolved in DMSO. Under aseptic conditions, empty sterilized discs (Whatman no. 5, 6mm diameter) were impregnated with different concentrations (25µg/disc, 50 µg/disc, 75 µg/disc, 100 µg/disc) of respective synthesized compounds and placed on the agar surface. Paper disc moistened with aqueous DMSO was placed on seeded petri-plates as a vehicle control. The plates were left for 30 min. at room temperature to allow the diffusion of synthesized compounds and then incubated at 37 ºC for 24 h. The antimicrobial activity was evaluated by measuring the zone of inhibition against the test of microorganism. All experiments were carried out in triplicates.

III. RESULTS AND DISCUSSION

A series of 2-aryl/benzyl-2'-benzyl-4'-methyl-4,5'-bisthiazole derivatives, **7a-ag** were synthesized according to Scheme 1. Acetyl acetone **1** on reaction with p-toluene sulphonic acid and NBS in DCM gave 3-bromopentane-2,4-dione, **2** which on cyclocondensation with benzyl thioamide, **3a-c** in dry ethanol gave 1-(2-benzyl-4-methyl-thiazol-5-yl) ethanone, **4a-c**. Compounds **4a-c** on bromination with bromine and p-toluene sulphonic acid as catalyst in DCM at room temperature resulted in the formation of 1-(2-benzyl-4-methyl-thiazol-5-yl)-2-bromo-ethanone, **5a-c** which on

further cyclocondensation with aryl/benzyl thioamide, **6a-k** furnished 2-aryl/benzyl-2'-benzyl-4'- methyl 4,5'-bisthiazole derivatives, **7a-ag**. The physical data and yield of synthesized compounds **7a-ag** are reported in Table 1.



Scheme 1. Synthetic route of compounds**7a-ag**

The structure of the title compounds, **7a-ag** was confirmed by IR, NMR and MS. As a representative analysis of compound **7ac**, the IR (KBr) spectrum showed C=C/C=N absorption bands at 1629-1475 cm^{-1}. The ^{1}H NMR spectrum of compound **7ac** displayed three singlet in aliphatic region at δ 2.39 (CH_3) δ 2.67 (CH_3), δ 4.26 (CH_2) and a singlet in aromatic region at δ 7.17 (thiazole CH). A triplet at δ 7.02 and multiplate at δ 7.29-7.33 were attributed to protons of fluoro substituted phenyl ring, while doublets at δ 7.22 and δ 7.84 corresponds to protons of methyl substituted phenyl ring. The ^{13}C NMR spectrum of compound **7ac** revealed the two signal of methyl carbon at δ 17.1, 21.5 and a signal at δ 38.9 attributed to methylene carbon. Aromatic carbons showed typical fluoro-coupling [$\underline{C}_1$-F, δ 164.0, 160.5 (^{1}J = 250 Hz), $\underline{C}_2$-F δ 115.7, 115.4 (^{2}J = 22 Hz), $\underline{C}_3$-F δ 127.5, 127.4 (^{3}J = 8 Hz)]. Structure of compound **7ac** was further confirmed by molecular ion peak at *m*/*z* 381.1 $(M+H)^{+}$. Structures of all the derivatives were ascertained similarly.

IV. Antitubercular activity

The synthesized compounds (**7a-ag**) were screened for their antitubercular activity against *Mycobacterium smegmatis*, which is a fast growing non-pathogenic strain to assess the activity of the compounds in primary screening. The literature revealed that *M. smegmatis* based screens show 100% specificity and 78% sensitivity in comparison to MDR *Mycobacterium tuberculosis* [52-55]. The percentage inhibition was determined against DMSO. Rifampicin and isoniazid were used as reference drugs. The results of antitubercular activity are reported in **Table 1**.

The *in vitro* antitubercular activity against *M. smegmatis,* revealed that compounds **7d**, **7r**, **7s** and **7ac** exhibited moderate activity at 30 μM concentration. The preliminary structure activity relationship study revealed that replacement of hydrogen atom of phenyl ring A and B (**Figure 1**) by substituent groups like Br, Cl, F and CH_3 affects the antitubercular activity.

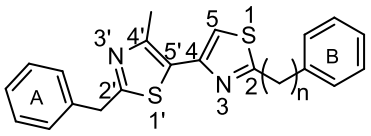


Figure 1

Further it was also noted that among the compounds **7a-g**, with un-substituted benzyl ring A and substituted phenyl ring B, only compound **7d** showed moderate activity. Compounds **7h-k** with substituted benzyl ring B were found to be less active. Among the compounds **7l-r** with 4-chloro substituted benzyl ring A and substituted phenyl ring B, compound **7r** showed moderate activity.

Table 1. Antitubercular activity of synthesized compounds **7a-ag**

Comp.	R	R^1	Yield (%)	MP (°C)	*M.smegmatis*[a]
7a	H	C_6H_5	58	94	13.764
7b	H	4-Br C_6H_4	60	116-118	8.648
7c	H	3-Cl C_6H_4	58	93-94	13.886
7d	H	4-Cl C_6H_4	60	106-108	32.4
7e	H	3-Cl,4-F C_6H_3	62	135-136	-
7f	H	4-F- C_6H_4	60	97-99	16.443
7g	H	4-CH_3-C_6H_4	62	48-50	12.911
7h	H	$C_6H_5CH_2$	60	60-62	7.065
7i	H	4-Cl-$C_6H_4CH_2$	65	82-84	7.552
7j	H	3-F-$C_6H_4CH_2$	62	78-80	-
7k	H	4-F-$C_6H_5CH_2$	62	78-80	4.141

7l	4-Cl	C_6H_5	65	88-90	21.924
7m	4-Cl	4-Br C_6H_4	62	101-103	4.385
7n	4-Cl	3-Cl C_6H_4	65	130-132	-
7o	4-Cl	4-Cl C_6H_4	66	52-54	-
7p	4-Cl	3-Cl,4-F C_6H_3	62	148-150	-
7q	4-Cl	4-F-C_6H_4	65	118-120	-
7r	4-Cl	4-CH_3-C_6H_4	60	136-138	32.034
7s	4-Cl	$C_6H_5CH_2$	70	75-77	38.49
7t	4-Cl	4-Cl-$C_6H_4CH_2$	62	78-80	22.655
7u	4-Cl	3-F-$C_6H_4CH_2$	60	48-50	14.251
7v	4-Cl	4-F-$C_6H_4CH_2$	66	82	11.084
7w	4-F	C_6H_5	60	104	16.797
7x	4-F	4-Br C_6H_4	65	109-110	13.281
7y	4-F	3-Cl C_6H_4	64	116-118	13.281
7z	4-F	4-Cl C_6H_4	66	118-120	8.333
7aa	4-F	3-Cl,4-F C_6H_3	58	104-106	5.078
7ab	4-F	4-F- C_6H_4	60	112-114	13.151
7ac	4-F	4-CH_3-C_6H_4	70	96	38.347
7ad	4-F	$C_6H_5CH_2$	60	98-100	24.609
7ae	4-F	4-Cl-$C_6H_4CH_2$	60	52-54	24.479
7af	4-F	3-F-$C_6H_4CH_2$	65	84	11.719
7ag	4-F	4-F-$C_6H_4CH_2$	66	94-96	13.021
Rifampicin					98
Isoniazid					97

a: % inhibition; - : Not active

Compounds **7s-v** with substituted benzyl ring B, compound **7s** showed moderate activity. Among the compounds **7w-ac**, with 4-fluoro substituted benzyl ring A and substituted phenyl ring B, compound **7ac** exhibited moderate activity. Compounds **7ad-ag** with substituted benzyl ring B, were found less active. It was notable that, chloro or fluoro substituents on ring A and 4-methyl substituted phenyl ring B showed moderate antitubercular activity.

V. Antimicrobial activity

The *in vitro* antimicrobial activity of all the synthesized compounds was done by the disc diffusion method. The antibacterial studies were against the standard Gram-negative bacteria, *Escherichia coli* (NCIM 2576), *Proteus vulgaris* (NCIM 2813) and Gram-positive bacteria, *Bacillus subtilis* (NCIM 2162), *Staphylococcus aureus* (NCIM 2602), while the antifungal activity was against the *Saccharomyces cerevisiae* (NCIM 3045) and *Candida albicans* (NCIM 3100). Amoxycillin and ciprofloxacin served as positive controls for antibacterial whereas fluconazole served as positive control for antifungal activity. The *in vitro* preliminary screening values (zone of inhibition) against microorganisms tested are summarized in **Table 2**.

Careful analysis of the antibacterial results presented in **Table 2**, provides some lead molecules with good antibacterial activity. Among the compounds **7a-ag** tested, it was observed that all the synthesized compounds showed moderate to good activity against *S. aureus* and *B. subtilis*, whereas most of the derivatives showed moderate activity against *E. coli* and *P. vulgaris.*

Table 2. Antimicrobial screening of compounds **7a-ag** (zone of inhibition in mm)

Comp.	Antibacterial activity				Antifungal actiity	
	E. coli	*P. vulgaris*	*S. aureus*	*B. subtilis*	*S. cerevisiae*	*C. albicans*
7a	7	7	10	10	22	16
7b	7	8	7	9	-	7
7c	7	8	7	9	-	7
7d	7	9	7	10	-	8
7e	7	9	11	8	-	-
7f	7	9	8	11	-	7
7g	7	8	7	7	-	7
7h	7	9	7	7	-	8
7i	9	9	10	18	-	9
7j	10	10	11	10	7	8
7k	10	9	11	13	-	7
7l	8	8	10	13	14	8
7m	7	7	7	10	-	9
7n	7	8	7	8	10	9
7o	7	8	7	8	-	10
7p	7	8	7	16	-	8
7q	7	8	7	10	-	7
7r	7	9	8	9	-	7
7s	7	9	9	9	-	10
7t	8	10	10	10	-	7

7u	9	10	10	12	-	-
7v	9	9	9	14	-	7
7w	-	-	8	10	-	-
7x	-	-	7	7	-	7
7y	7	8	8	8	7	7
7z	8	7	7	10	-	10
7aa	7	7	9	8	7	-
7ab	7	7	7	9	-	-
7ac	7	8	7	9	7	8
7ad	-	-	7	8	-	8
7ae	9	10	10	11	-	8
7af	10	11	9	10	-	7
7ag	10	11	10	11	7	-
Amox.	24	40	42	28	NA	NA
Cipro.	27	31	28	26	NA	NA
Fluco.	NA	NA	NA	NA	14	17

Amox: Amoxycillin (100 µg/disc), Cipro: Ciprofloxacin (100 µg/disc), Fluco: Fluconazole (25 µg/disc) were used as reference; synthesized compounds (100 µg/disc);
NA = Not Applicable; (-) = Inactive.

It was worthwhile to note that compounds **7i-k** with un-substituted benzyl ring A and chloro and fluoro substituted benzyl ring B exhibited moderate activity against all the tested strains. The activity was retained for 4-chloro substituted benzyl ring A and chloro and fluoro substituted benzyl ring B as in compounds **7t-u** and 4-fluoro substituted benzyl ring A and chloro and fluoro substituted benzyl ring B as in compounds **7ae-ag**. The results of antifungal activity revealed that most of the synthesized compounds were able to produce moderate inhibitory activity against *C. albicans*. It was noteworthy that un-substituted benzyl ring A and un-substituted phenyl ring B in compound **7a**, showed good activity comparable to the standard drug fluconazole against *S. cerevisiae* and *C. albicans*.

VI. CONCLUSION

In the present study, we have detailed the synthesis and biological screening of bisthiazole derivatives. It can be concluded that, most of the synthesized compounds with Cl and F substituent on benzyl and 4-methyl substituent on phenyl ring showed moderate antitubercular activity. Most of the synthesized compounds exhibited good antimicrobial activity towards most of the tested species. Thus, these results warrant the need for synthesis of similar libraries with other substituents to ascertain the trend described in this work.

VII. REFERENCES

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Role of Gibberellic Acid, Leaf Extract of Azadirachtaindica and Pongamiapinnata on Growth and Productivity of Garlic

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ABSTRACT

A pot experiment was carried out to evaluate the effects of foliar application of four different concentrations of GA3 and leaf extract of Azadirachtaindica and Pongamiapinnata on garlic plants. An experiment was carried out with three replications. The growth characteristics e.g. root length, shoot length; number of leaves, fresh weight and dry weight, growth and vigour index etc. were studied. The biochemical contents like chlorophyll a, b and total chlorophylls as well as relative water content contents were studied. The four different concentrations of GA3 were made in absolute alcohol and the dilutions were made in distilled water. For the foliar spray 25 ppm, 50ppm, 75ppm and 100 ppm concentrations of GA3 was used at an interval of 7 days each. The leaf extract of Azadirachtaindica and Pongamiapinnatawas made by crushing 10 g leaves in 100 ml of distilled water and stored in refrigerator separately. The six sets of garlic plants were made with six plants in each set. Among each set of six plants three plants were used as control and three as replicates. The leaves of all the three replicates were sprayed with 25, 50, 75 and 100 ppm of GA3, leaf extract of Azadirachtaindica and Pongamiapinnatarespectively. The first treatment was given after completing the growth for 40 days and the subsequent sprays were given after every seven days. All the plants were watered after every six days. The foliar spray was applied for five times and the plants were used to study the growth parameters after 120 days. Leaf extracts showed comparatively better results than GA3.

Keywords : Gibberellic Acid, Garlic, Azadirachta, Pongamia, Yield

I. INTRODUCTION

Garlic (*Allium sativum* L.) belongs to family Liliaceae and it is an important bulb vegetable due to its medicinal and nutritional values[1]. Garlic is a bulbous plant closely related to the onion. Garlic is produced commercially for its composite bulb, which consists of several individual bulblets, known as 'cloves.' These individual bulblets are enclosed in a membranous bag that is whitish or purplish in color. In its fresh form, garlic is usually sold as a composite bulb. Garlic is noted for its pungent odor, which is caused by organic sulphur compounds. These compounds reportedly possess antibacterial properties, which have played a role in folk medicine from time immemorial. The major use of garlic is as a flavoring in cooking. In addition to use in its fresh form, garlic is also processed into numerous dehydrated products and may be pureed or frozen. A portion of each year's production is also used as seed garlic for planting future crops.

Plant growth regulators like Gibberellic acid to boost crop growth and yield [2]. It also has stimulating effects on most morphological, physiological and biochemical aspects of plant growth have additive impacts on overall growth and development of plants[3]. Application of GA_3 at full bloom increases plant growth and vigour including fruit size [4].

The leaves of the plants of *Azadirachtaindica* A. Juss. and *Pongamiapinnata* L. are traditionally being used as medicines, antiseptic, pesticides, insecticides and biofertilizers. The leaves contain minerals and nutrients [5]. The leaves of neem plant contain azadirachtin, meliacin, gedunin, salanin, nimbin, valassin etc. The leaf extract is best environmental friendly and a pesticide as well as the source of phosphate fertilizers [6].

At present research work the prominence has given to evaluate the utility of different concentrations of GA_3 and leaf extract of *Azadirachtaindica* A. Juss., and *Pongamiapinnata* L. on growth, vigour, biochemical

content and yield of *A. sativum* (Garlic) plants in pot experiment.

II. METHODSANDMATERIAL

The garlic cloves were planted in plastic bags of 30 cm diameter. The bags were filled with the soil and sand with the ratio of 3:1. Each bag was filled with 4 kg of soil and sand mixture. Total six sets with control plants were prepared with three replicates each. The bags were placed in Botanical garden under natural conditions. From each set of six bags three bags were treated with foliar spray (experimental) and three were maintained as control. The cloves were grown as seedlings after 8-10 days. The seedlings kept in the bags for the growth. After six weeks i.e. 42 days of normal growth the first foliar spray was initiated in all the experimental plants. The experimental plants of all the four sets of GA_3 were sprayed with 25, 50, 75 and 100 ppm of GA_3 respectively and fifth and sixth set was sprayed with the leaf extract of *Azadirachtaindica* and *Pongamiapinnata* respectively. The leaves were sprayed after every seven days for four weeks and watered after every six days. The foliar spray was given for five times and after 120 days the garlic plants were analyzed for study of growth parameters and biochemical contents.

Stock solution of Gibberellic acid was made in absolute alcohol and the different dilutions were made in distilled water and stored at refrigerator for further use. The fresh leaves of *Azadirachtaindica* and *Pongamiapinnata* were collected and washed thoroughly after drying the leaves with blotting paper; the leaves were weighed 10 g and grinded in 100 ml of distilled water. The grinding was carried out by using blender and the leaf extract was stored separately in refrigerator for further use.

Leaf length and root length was measured by using measurement tape and germination percentage were calculated by counting the number of seeds grown and number of seedlings germinated the growth and vigour index (GVI) of all the plants was calculated by using formula. As there is no true shoot in onion we have considered here leaf length as shoot length. By using the formula of[7], [8], [9]. GVI = shoot length x Root length x germination percentage.

Number of leaves was directly counted and recorded. Fresh weight of garlic cloves were recorded by using electric balance. Dry weight of garlic cloves (bulblets) were recorded after placing them in incubator at 50°C for 96 hours.

The amount of chlorophyll a; chlorophyll b and total chlorophylls was determined by Arnon's method, [10]. Chlorophyll extract was prepared from fresh leaves (100 mg) of garlic by grinding in a pre chilled mortar and pestle, together with 10 ml of ice cold 80% acetone. The homogenate was centrifuged at 3000 rpm for 2 minutes in cooling centrifuge. The supernatant was saved and pellet was re-extracted twice with 5 ml of 80% acetone. All the supernatants were pooled and saved.

The absorbance of the extract was recorded at 663 nm, 645 nm and the concentration of chlorophyll a, chlorophyll b and total chlorophyll was calculated using Arnon's equations as follows.

Chl. a = (12.7 × A663-2.69 × A645) × 10 /mg leaf weight
Chl. b = (22.9 × A645-4.61 × A663) × 10 /mg leaf weight
Total Chl. = (20.2 × A 645-8.02 × A 663) × 100 /mg leaf weight

The relative water contents were studied by Barr and Weatherley, method[11]. For this the leaves were sliced in to 5-10 cm^2 pieces and then weighed immediately to record fresh weight. Leaf sample was floated in deionized water in Petri dish for 4 hours at normal room temperature and light. After 4 hours, the sample was taken out from water, and surface water was removed and again weighed to obtain fully turgid weight. Sample was dried in an oven at 80°C for 24 hours weighed again. It is calculated using following formula.

$$\text{RWC (\%)} = \frac{(\text{Fresh wt.} - \text{dry wt.})}{(\text{turgid wt.} - \text{dry wt.})} \times 100$$

III. RESULTS AND DISCUSSION

After the growth of 120 days the growth parameters like number of leaves, length of leaves and length of roots of the garlic plants was recorded. The number of leaves was recorded more in the garlic plants which were sprayed with Gibberellic acid and leaf extracts than the

control plants in all the sets. The minimum number of leaves recorded was ranging in between 8 and 9 in control plants. The maximum number of leaves (11) was recorded in plants sprayed with leaf extract of *Pongamiapinnata.* It was recorded 11 and 10 in plants sprayed with 100 ppm GA3 and leaf extract of *Azadirachtaindica*respectively. Other treated plants showed 5 to 9 leaves. The application of the foliar nutrition and GA_3 on garlic leaves increased their metabolism and this has resulted in increased number of leaves in all the replicates as compared to control plants (Table 1).

The root as well as leaf length was recorded more in all the experimental plants as compared to control plants. The increased concentrations of GA_3 had positive response on the root and leaf length. At 25 ppm concentration of GA_3 the root and leaf length was minimum whereas the plants sprayed with the extract of *Pongamiapinnata* showed maximum.

At all the concentrations of GA_3 the root and leaf length was recorded more than control plants. Germination percentage of all the sets was cent percent. The growth and vigour index of all replicates was recorded more than the control plants. Our results corroborate with the results recorded by Mislevy*et al.,*[12],Harrington *et al.,* [13]Tanimoto[14], Maske*et al.,*[15],Awan and Alizai[16],Lee [17], Sarkar *et al.,*[18].

Table 1. Effect of different concentrations of GA3 and leaf extracts *Azadirachtaindica* and *Pongamiapinnata*on number of leaves, leaf length and root length of onion plant after 110 days.

Garlic	Root length (cm)	No. of leaves	leaf length (cm)	GVI
Control	2.00	6	23.00	4600
GA 25 ppm	2.50	9	26.50	6625
Control	2.25	5	22.75	5119
GA 50 ppm	2.75	9	27.25	7494
Control	2.00	5	23.75	4750
GA 75 ppm	2.75	9	27.50	7563
Control	2.00	6	23.00	4600
GA 100 ppm	2.75	11	28.00	7700
Control	2.00	6	24.75	4950
Pongamiapinnata	3.25	11	27.50	8938
Control	2.25	6	23.25	5231
Azadirachtaindica	3.00	10	27.75	8325

The foliar spray of leaf extract of *Pongamiapinnata*and *Azadirachtaindica*also showed positive response on root and leaf length. The root and leaf length of treated garlic plants was more than control plants. The growth response of garlic plants sprayed with extract of *Pongamiapinnata* was more as compared to *Azadirachtaindica.* The effect of leaf extract of *Pongamiapinnata*was same as in plants treated with GA3.

Gibberellic acid has stimulating effect on all the physiological and biochemical aspects of plant growth and has additive impacts on overall growth and development of plants. It is a most important growth hormone which regulates plant growth Mikitzel, [19],(EL-Naggar*et al.,*[20].

The growth and vigour index of all the foliar sprayed plants was more than control plants (Table 1). The highest GVI was recorded in foliar sprayed plants of *Pongamiapinnata* and*Azadirachtaindica.* This enhancement in the GVI was resulted due to increased cell division and cell elongation. Similar results were obtained by Kothule*et al.,*[21],Yadav and Abha-Tikkoo[22],Behairy and Rizk[23],El-Sayed et *al.,*[24], Alexopoulos*et al.,*[25]. The leaf extract of *Pongamiapinnata* and *Azadirachtaindica* has high nutrient contents and if sprayed on leaves they give jump start to the growth of plants.

The chlorophyll content of garlic leaves were analyzed after 75 days from fresh leaves by Arnon's, (1949) method. The amount of chlorophyll a was recorded minimum in control plants of all the sets (Figure 1). It was recorded highest in plants sprayed with 100 ppm of GA3 and the plants sprayed with leaf extract of *Pongamiapinnata*. The plants sprayed with leaf extract of*Azadirachtaindica* also recorded higher amount of chlorophyll a. The results were similar for the chlorophyll b and total chlorophylls. The increased amount of the chlorophyll a, b and total chlorophylls might have resulted due to the GA3 in first four sets and nutrient contents of leaves of *Pongamiapinnata* and *Azadirachtaindica*in last two sets.

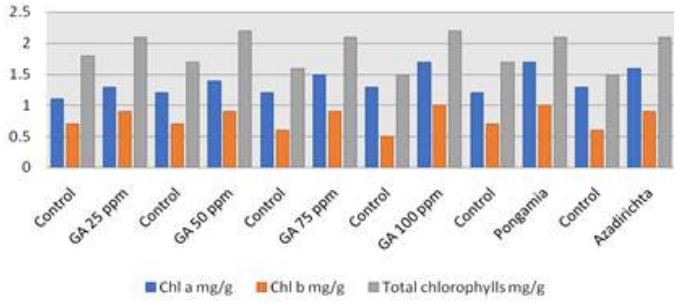

Figure 1. Effect of different concentrations of GA3 and leaf extracts of *Azadirachtaindica* and *Pongamiapinnata*on chlorophyll content of garlic leaves after 75 days.

Application of GA3 increases absorption potential and assimilation of mineral nutrients during vegetative growth stage (Shah andSamiullah, 2006). It is possible that GA3 had the potential to accelerate the nutrients partitioning towards cells and active growth sites and concomitantly increases those nutrients absorption via increased root potential, and finally intensifies minerals and their related bio-molecules accumulation in shoots especially new leaves and apical shoots passing active growth and development. GA3 links with chlorophyll biosynthesis in leaves and hence showed positive effects on plants chlorophyll content. Our results are in agreement with the results of Shah andSamiullah[26], Reda *et al.,*[27].

The relative water content (RWC) in garlic leaves were recorded after growth of 75 days. The RWC from leaves was recorded more in all plants which were applied foliar sprays than control plants (Figure 2). The increased cell division, cell size and cell number was due to GA3 and availability of nutrients in the leaves of *Azadirachtaindica* and *Pongamiapinnata* increased the metabolism of the plant. Increased contents of chlorophylls in the leaves enhanced the photosynthetic efficiency of the plants which resulted in increased growth and vigour. Foliar nutrients were absorbed by the leaves of onion plants and utilized well and hence the RWC in all the plants which were applied foliar sprays was more than control plants. Garcia and Hanway, [28];Brantly, [29] obtained the similar results.

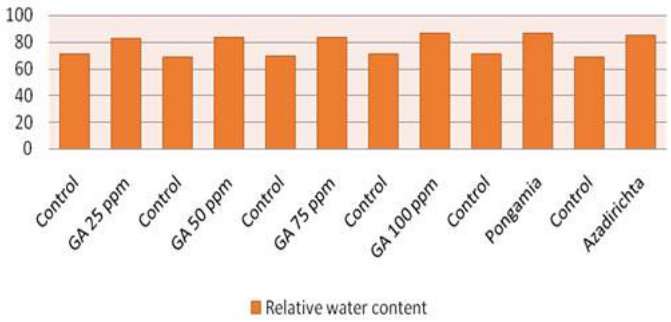

Figure 2. Effect of different concentrations of GA3 and leaf extract of *Azadirachtaindica* and *Pongamiapinnata*on relative water content (RWC) of garlic leaves after 75 days.

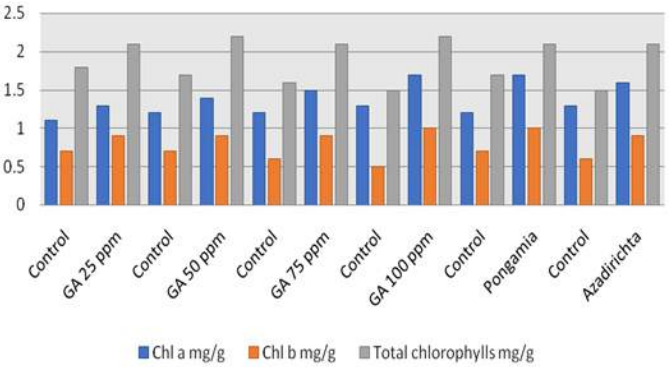

Figure 3. Effect of different concentrations of GA3 and leaf extract of *Azadirachtaindica* and *Pongamiapinnata*on fresh weight and dry weight of non tunicated bulb of garlic.

The fresh weight as well as dry weight of garlic bulblets after 110 days was more in all the experimental plants than control plants of onion (Figure 3). The GA3 speeds up the nutrients partitioning towards cells and active growth sites and along with increases nutrient absorption and finally reinforce minerals absorption and their related bio-molecules accretion in leaves and apical shoots passing active growth and development. The root length, leaf length and growth vigour index was enhanced in all the experimental plants. The increased leaf length leads to increased surface area of leaves and this resulted in more absorption of nutrients and higher photosynthetic efficiency. Due to this the root length of the plants was recorded more in all the experimental plants. Root and leaf length collectively had improved response of plants with respect to chlorophyll content, photosynthetic efficiency, relative water content etc. Hence the fresh weight of the plants was more in all the experimental plants as compared to the control plants.

Our results are in line with the findings of Amal *et al.,*[30], Bideshki*et al.,*[31].

IV. CONCLUSIONS

The present research work showed the role of GA3 and leaf extracts of *Pongamiapinnata*and *Azadirachtaindica* in the growth of the garlic plants was positive. The optimum concentration of GA3 for the growth of onion was 100 ppm. The foliar nutrition of the *Pongamiapinnata* (10 g / 100 ml) influenced the growth of garlic plants similar to 100 ppm GA3. The results of the foliar spray of leaf extract of *Azadirachtaindica* were also superior to the results of 75 ppm GA3. Among the results of leaf extract foliar sprays of *Pongamiapinnata*showed better results than leaf extract of *Azadirachtaindica.*

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Preliminary Studies on Medicinal Plants With Anthelminthic Properties Used by Goat Owners In Sangamner and Akole Tehsil, India

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ABSTRACT

Goat farming is the major livestock industry in and around Sangamner and Akole Tehsil. Amongst the various diseases of goat, gastrointestinal parasitism is one of the major health problems in these animals. 1. The traditional use of medicinal plants for the helminth infection of goat is the most common practice used by the tribal people of this region. The study reveals survey of those medicinal plant species, traditionally used as anthelmintic and may need scientific validation for efficacy 2, 5 ,.6 .The study is based on well-structured questionnaire and detailed interviews and discussions with goat owners of this region and recorded 26 plant species which are claimed as anthelminthic in various preparations and forms. The plants reported in this study will further help in the evaluation of in vitro and in vivo anthelminthic activity and set a platform for pharmacological studies.

Key words: Livestock, Medicinal Plants, Helminth Infection, Anthelminthic.

I. INTRODUCTION

Sangamner and Akole Tehsil are situated in Ahmednagar district, Maharashtra state, India. It is surrounded by Sahyadri mountain ranges of Western Ghats. It is surrounded with beautiful hills and valleys having the highest peak of Kalsubai in Maharashtra. The hilly region of these areas is rich in large varieties of medicinal plants. The tribal people living in these areas are mainly Thakar, Bhil, koli. They mostly depend on agriculture and livestock industry. Since olden days the tribal people use the medicinal plants and there products for the treatment of diseases of human and their domestic animals. Goat farming is one of the most established livestock industries in the study areas. Goat farming is possible for marginal farmers or unemployed, landless poor people as its initial investment are very low. The advantages of Goat farming is more as compared to the agro business. Goat can efficiently survive on available shrubs and trees. Due to good products such as milk, meat leather many people prefers goat farming in the Ahmednagar District. In the study area, different types of goat farming such as large scale, small scale, mixed, individual etc. is observed. Not only poor farmers but rich landlords also domesticate the goats.

Gastrointestinal parasite infection causes loss of the goat owner. It includes infection of helminth parasites like tapeworm, roundworm etc. It causes irreversible damage and even death of the animal. The typical signs of helminth infection in goat are loss of weight, less milk, rough hair coat, anemia, female become less productive, fever, fast breathing, Bottle jaw, coughing (*Lynn Pezzanite et.al.)* with the help of these symptoms tribal people identify the infection of gastrointestinal parasite.

In study area the tribal people use the different medicinal plants and their product for de-worming the parasites for them and their domesticated animals like sheep goat. Though there are pharmaceutical drugs available in the market for their domestic animals, but they still rely on their traditional formulations used by their ancestors. So seeking the need to do the survey of those medicinal plant species, traditionally used as anthelmintic and need scientific validation for efficacy, the authors did the survey of medicinal plants used by these goat farmers for deworming, based on well-structured questionnaire and detailed interviews and discussions with goat owners of this region.

II. Materials and Method

The present study was carried out through field surveys in the year 2016 in Sangamner and Akole region. The data was collected by questionnaire method and interview. Interviews and discussions were done with

the goat owners and tribal people. Interviews were taken in the local Marathi language and the information was collected from the local elder experienced goat owners, even the elderly ladies of the house. Individual interview was carefully analyzed and information was collected about the vernacular name of the plant, methods of preparation of the extract and its way of administration. Data was also collected by herbalists for identification of medicinal plants used as anthelminthic in folklore. For the correct identification of the medicinal plant species, the interviews were conducted on the field so as to get the plants confirmed. The fresh plants and plant parts were collected and identified. Information was also collected from the book known a Vansapati Bacl written by prakash kale Vanaushadhi gurndarsh by shankar dajishawshri. The plants species were authenticated by the botanist of Sangamner College.

III. Results and Discussion

The present survey done during the year 2016 in the study area resulted in the identification of variety of plant species used in folklore as anthelmintic in goat farming. The list of anthelmintic plants used are represented in Table 1.

Table 1. List of the plant used by tribal people for de-worming as per survey

Sr. No.	Common Name	Scientific Name	Family	Plant Parts used for deworming	Targeted animal
1)	Babbul	*Acacia arebica*	Fabaceae	Fruit, bark	Goat, man
2)	Shisham	*Dalbergia sissoo*	Fabaceae	Leaf extract, seed	Goat, cow
3)	Gorakh chinch	*Adansonia digitata*	Malvaceae	Dry bark fruit powder	Goat
4)	Wild Carrot	*Daucus carota*	Apiaceae	Root	Goat, man
5)	Papya	*Carica Papaya*	Caricaceae	Fruit	Man
6)	Tarwad	*Cassia auriculata*	Fabaceae	Stembark Flower bud	Man, goat
7)	Sabza	*Ocimum basilicum*	Lamiaceae	Seed	Goat, man
8)	Khajkhujli	*Aquadulce Claudia*		Bristles on fruit	Cow, man, goat
9)	Ajwain	*Trachyspermum ammi*	Apiaceae	Leaf extract	Cow, goat, man
10)	Onion	*Allium cepa*		Juice	Man, goat
11)	Mint	*Mentha aquatica*		Leaf juice	Man, goat
12)	Horsebean (kalith)	*Dolichous biflorus*	Leguminosae	Seed boil in water	Man, goat, cow
13)	Tamarind	*Tamarindus indica*		Fruit juice	Goat

14)	Pomogranate	*Punica granatum*		Root peels	Goat, man
15)	Mango	*Mangifer indica*		Seed powder	Goat, man
16)	Caster	*Ricinus communis*		Leaf juice	Goat, man
17)	Supari	*Areca cateucha*	Palmae	Seed powder	Got, man, hen
18)	Pumkin	*Cucurbita*	Cucurbitaceae	Fruit	Man
19)	Aloevera	Aloe vera	Liliacae	Leaf juice	Man, goat
20)	Sagargota	Bonduc nut	Caesalpincae	Leaf extract	Goat, cow
21)	Baniyan	Moraceae Ficus		Aerial root tip	Man, goat
22)	Garlic	Allium sativum		Root juice	Man
23)	Kath	Acacia catechu	Leguminosae	Bark extract	Goat
24)	Yeltur	Leucaena leucocephale		Leaf juice	Goat
25)	Parijatak	Nyctanthes arbortristis		Leaf extract	Man, goat
26)	Biba	Semecrapus anacadium		fruit	Man, goat, cow

IV. CONCLUSION

As per the survey carried on goat owners, it was found that **10%** of the large scale goat owners used injections and chemical drugs for deworming. 80% of the large-scale goat owners used both medicines as well as plants for de-worming. 20% small scale goat owner used only plant medicine for de-worming. 40% goat owner trust on plant medicine. 60% trust on chemical medicine only for de-worming. The observations show 50% of the goat owners (small scale) are not aware about the side effect of chemical drugs. But 100% of the large-scale goat owners are well known about side effects of chemical drugs.

- ✓ Small scale consists of 5 to 10 goats, large scale consists of 10 to 50 goats.
- ✓ Mix type include Cow, Goat and Sheep.

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Evaluation of Biological Activities of Chick Egg White on Water Pollutant Bacteria

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ABSTRACT

Water pollution is a major global problem which requires ongoing evaluation and revision of water resource policy at all levels. It has been suggested that water pollution is the leading worldwide cause of deaths and diseases, and that it accounts for the deaths of more than 14,000 people daily.That is why, inhibition of this pollution using natural and easily available resources is the intrinsic aim of the current study. Industrial methods have been developed for its economic recovery from egg whites, and the deproteinized egg whites have been approved for food use in Europe and recently in the United States. Therefore, the current study aimed at evaluation antimicrobial activity of Chick egg white and partial purified lysozyme. The experimental designs in the current work has been carried out with several aspects of antimicrobial activity of egg white and partially purified lysozyme. Interestingly, lysozyme showed articulate inhibition activity on gram positive bacteria. Results relevant to egg white are assorted with the earlier literature of not getting inhibition zone on gram negative bacteria. At the same time, the same concept should also be applied at the industrial level to amplify the research being carried out. The future prospects of the present study would be dragged to advanced aspects in molecular evidences with respect to the genes involved in bacteria which are being inhibited by the egg white.

Keywords : Water Pollution, Egg White, Lysozyme, Antibacterial Activity.

I. INTRODUCTION

Water pollution refers to the presence of components that decrease the quality of fresh or marine water (Gale 2009). Pollution of water is the presence of some foreign organic, inorganic, biological, radiological or physical substances in the water. These substances contaminate water by degrading its quality which may cause health hazard or decrease the utility of water. Water pollution is a major global problem which requires ongoing evaluation and revision of water resource policy at all levels. It has been suggested that water pollution is the leading worldwide cause of deaths and diseases, and that it accounts for the deaths of more than 14,000 people daily. An estimated 580 people in India die of water pollution related illness every day. About 90 percent of the water in the cities of China is polluted. As of 2007, half a billion Chinese had no access to safe drinking water (Kahn, Joseph; Yardley, Jim 2009). In addition to the acute problems of water pollution in developing countries, developed countries also continue to struggle with pollution problems. For example, in the most recent national report on waterquality in the United States, 44 percent of assessed stream miles, 64 percent of assessed lake acres, and 30 percent of assessed bays and estuarine square miles were classified as polluted. The head of China's national development agency said in 2007 that one quarter the length of China's seven main rivers were so poisoned the water harmed the skin (Wachman, Richard, 2009). That is why, inhibition of this pollution using natural and easily available resources is the intrinsic aim of the current study.

Egg white mainly consists of water (88%) and protein (11%), with the remainder consisting of carbohydrates, ash, and trace amounts of lipids (1%). Ovalbumin (54%), ovotransferrin (12%), ovomucoid (11%), lysozyme (3.5%), and ovomucin (3.5%) are considered as the main proteins and avidin (0.05%), cystatin (0.05%), ovomacroglobulin (0.5%), ovoflavoprotein (0.8%), ovoglycoprotein (1.0%), and ovoinhibitor (1.5%) are the minor proteins found in egg white (Kovacs-Nolan et al., 2005). Egg white, therefore has been considered as the antimicrobial agent in the current study. Lysozyme is one of the most thoroughly investigated of all proteins and was the very first protein subjected to X-ray structural analysis. As implied by its name, it is an enzyme, one found in other animal tissues and secretions

as well. It cleaves specific bonds in specific polysaccharides, ones that constitute the cell walls of many bacteria. Lysozyme thus has antibacterial activity, and provides an embryo with a measure of protection against infection during its developmental phases (Klaus Roth). Antimicrobial mechanisms of lysozyme, is the degradation of the glycosidic (1-4) ß-linkage between the N-acetylglucosamine and the N-acetylmuramic acid of the peptidoglycan layer in the bacterial cell walls (muramidase activity). The peptidoglycan is a strong, woven mesh that maintains the cell's shape and allows the diffusion of solutes and other type of molecules via large openings in the mesh. The cell wall determines the shape of the cell and protects cells from osmotic lysis. Without a wall or when it is attacked by lysozyme or other antimicrobial agents, the cell would swell and burst. Bacteria that are susceptible to the enzymatic action of lysozyme are not lysed when they are in an osmotically balanced medium. Cell death occurs by the lytic action of lysozyme on peptidoglycan only when in low-osmotic-strength media, or when the rate of the synthesis and polymerization process for new peptidoglycan formation is slower than the lysozyme catalyzed degradation (N. Guyotet, al. 2013). Such a lysozyme mechanism is unfortunately, limited to certain Gram-positive bacteria. The peptidoglycan of some Gram-positive bacteria is indeed resistant to hydrolysis by lysozyme because of chemical modifications (N. Guyotet, al. 2013).Adham M. Abdou (2013) suggested that the name lysozyme was originally used to describe an enzyme which had lytic action against bacterial cells. Lysozyme is one of the oldest egg components to be utilized commercially after it was discovered by Alexander Fleming in 1922. L. Hughey and E. A. Johnson (1987) concluded that lysozyme is an important component in the prevention of bacterial growth in foods of animal origin such as hen eggs and milk . The enzyme may also have applications as a preservative in foods that do not naturally possess it. It is attractive as a food preservative because it is specific for bacterial cell walls and harmless to humans. Industrial methods have been developed for its economic recovery from egg whites, and the deproteinized egg whites have been approved for food use in Europe and recently in the United States.

Therefore, the current study aimed at evaluation antimicrobial activity of Chick egg white and partial purified lysozyme.

II. MATERIALS AND METHODS

Sample preparation:

Water sample

Polluted water sample were collected from Mula-Mutha River, Pune (Maharashtra, India).

Egg white

Eggs were obtained from the shop near NowrosjeeWadia College, Pune.

Eggs were hand broken and the egg white was manually separated from the whole egg (N.Guyotet al.2013)

Isolation of microorganism shows antimicrobial activity.

Nutrient agar medium were prepared, autoclaved and poured in the petri dish and allowed to settle. 150 µl of polluted water sample were poured on petri plates and spread by using spreader. 5mm diameter well was made by using borer in the middle of petri plates. 200µl of egg white were poured in the well and sealed with parafilm properly. The petri plates were leaved at room temperature for 2 hours to allow the diffusion of egg white. The plates were incubated at 37^0C temperature for 24 hours. After incubation the colony which shows antimicrobial activity was isolated and maintained in nutrient agar slant. Above Procedure were carried out for 2 to 3 times to obtain pure culture of bacteria (Seham Abdel‐Shafi et al. 2016).

Partial purification of lysozyme.

For the partial purification of lysozyme, egg whites, carefully separated from the egg yolks, were diluted 3- or 3.3-fold with 0.05 M NaCl solution. To precipitate the egg white proteins other than lysozyme, the pH of this mixture was set to 4.0 by carefully adding several drops of 1N acetic acid and it was diluted with an equal volume of 40% ethanol. After 6 hours incubation at room temperature in the presence of ethanol, the mixtures were centrifuged at 15,000 x g for 15 min at 4 °C; then the precipitates were discarded. The supernatant were collected and stored in refrigerator (SeyhunGEMiLi et al. 2007).

Antimicrobial activity of egg white and partial purified lysozyme

Nutrient agar medium were prepared, autoclaved and poured in the petri dish and allowed to settle. 150 µl of pure bacterial culture were poured on petri plates and spread by using spreader. 5mm diameter well was made in middle of petri plate. Partially purified lysozyme and egg white were poured in well. Petri plates were sealed with parafilm properly and leaved at room temperature for 2 hours to allow the diffusion of egg white. The plates were incubated at 37^0C temperature for 24 hours. The radius of zone of inhibition was measured in mm (Seham Abdel‐ Shafi et al. 2016).

III. RESULT AND DISCUSSION

Isolation of microorganism shows antimicrobial activity

In the present study, on nutrient agar petri plate 2 to 3 types of colonies were observed, among them 8 mm zone of inhibition was formed by inhibition of one microorganism. The zone was not clear because there was growth of bacteria which was not inhibited by the egg white. SompongThammasirirak et al., (2008) concluded that the egg white was not active against the Gram-positive bacteria. The bacteria which showed the zone of inhibition, was isolated and separately tested against egg white to confirm the isolation of purecolonies. Isolated bacteria was gram positive. 12mm zone of inhibition of isolated bacteria against egg white was observed. The bacteria was identifies by Gram's staining. The bacteria were Gram-positive. The bacteria were rod shaped and violet in color. The positively charged crystal violet pass through the cell wall and cell membrane and binds to negatively charged components inside the cell. Addition of negatively charged iodine (in the mordant) binds to the positively charged dye and forms a large Crystal violet (hexamethyl-para-rosaniline chloride) interacts with aqueous KI-I2 via a simple anion exchange to produce a chemical precipitate. The small chloride anion is replaced by the bulkier iodide, and the complex thus formed becomes insoluble in water. During decolorization, alcohol dissolves the lipid present in the outer membrane of Gram negative bacteria and it leaches the dye-iodine complex out of the cell. A thin layer of peptidoglycan does not offer much resistance either. The dye-iodine complexes are washed from the Gram negative cell along with the outer membrane. Hence Gram negative cells readily get decolorized. On the other hand Gram positive cells become dehydrated from the ethanol treatment, closing the pores as the cell wall shrinks during dehydration. The dyeiodine complex gets trapped inside the thick peptidoglycan layer and does not get decolorized (ShridharRao, 2014).

Partial purification of lysozyme

The partial purification of lysozyme by ethanol precipitation was applied by SeyhunGemili et al. (2007). Lysozyme was partially purified from egg white and confirmed by testing against microorganisms. 14mm zone of inhibition was observed. During the incubation period, the fluctuations also occurred in the protein contents and changes in both activity and protein content were similar up to the sixth hour of incubation in the presence of 40% ethanol. Thus, it seems that these fluctuations are due to the change in lysozyme and other proteins' solubility in the extract during incubation. The further increase to 8 h of incubation at the 40% ethanol concentration precipitated particularly non-lysozyme proteins and this increased the specific enzyme activity considerably (SeyhunGemili et al. 2007).

Antibacterial activities of egg white and partially purified lysozyme

Antibacterial activities were carried out against Gram-positive bacteria.12mm zone of inhibition of egg white and 14 mm zone of inhibition of partial purified lysozyme was observed. S.Gomathi et al.(2015) tested Quail egg white against Micrococcus Luteus. They observed 12mm zone of inhibition of Purified Quail egg white Lysozyme and 18mm zone of inhibition of standard lysozyme. Lysozyme is a hydrolase that cleaves the glycosidic bond between N-acetylemuramic and N-acetylglucosamineheteropolymer of the peptidoglycan, the components of the bacterial cell wall (SompongThammasirirak et al., 2008). These enzymes are strongly active against Gram-positive bacteria bus inactive against Gram-negatve bacteria (SompongThammasirirak et al., 2008).EdySusanto et al (2014) concluded that antimicrobial activity of lysozyme can be converted into active against gram-negative bacteria through genetic hydrophobic peptide C terminal

to lysozyme. Bakteriolitic lysozyme activity against gram-negative bacteria through the destruction of the function of the phosphate groups of phospholipids with lipopolysaccharide in the outer V. membrane of gramnegative bacteria. The research results prove that egg white lysozyme thermal modification can increase the antibacterial spectrum mainly on gram-negative bacteria *E.coli*.RenataCegielska-Radziejewska et al,(2003) concluded that, investigations indicated a possibility to extend the range of lysozyme activity using thermal and chemical-thermal modification. It was observed that lysozyme concentration in the solution subjected to thermal modification, the pH value of the solution, the temperature and time of modification had a significant effect on the content of the forming polymers. The time of oxidation influenced also the amounts of polymers in the case of the chemical-thermal modification. The investigation indicated also a possibility to extend the range of lysozyme activity to include Gram-negative bacteria, i.e. Escherichia coli. Modification of lysozyme by the membrane technique also broadened the spectrum of enzyme antibacterial action especially against Pseudomonas fluorescens and Proteus mirabilis bacteria. It may be stated that increased antibacterial activity against Gram–negative bacteria is not connected with a decrease in the activity of modified lysozyme preparations against Gram-positive bacteria. Studies showed that the applied lysozyme preparations showed a varying activity, depending on the type of bacteria. *C. glutamicum, X. oryzae, S. flexneri, and S. cerevisiae,* including *E. coli*, were influenced by the lysosome treatment, except for S. albus. In the case of S. albus, the antimicrobial effect was lower than the other species. This suggests that the lysosomal activity against some strains forming bacteria.

IV. CONCLUSION

The present work has been focused on the antimicrobial activity of egg white and the lysozyme as it would channelize the indirect control of water pollution. The study has been more emphasized upon the lysosomal antimicrobial activity which has been articulately proved via experimental designs. Further, the study concludes that egg white being an easy source for purified lysozyme should be worked upon at laboratory level in various aspects. This is because very meager work has been carried out on egg white as an antimicrobial agent. At the same time, the same concept should also be applied at the industrial level to amplify the research being carried out. The future prospects of the present study would be dragged to advanced aspects in molecular evidences with respect to the genes involved in bacteria which are being inhibited by the egg white. The identification of wide range of inhibiting bacteria by lysozyme is also to be carried out. The specificity of inhibition activity on gram positive bacteria is also an intrinsic issue to be concerned which has to be investigated further.

FIGURES:

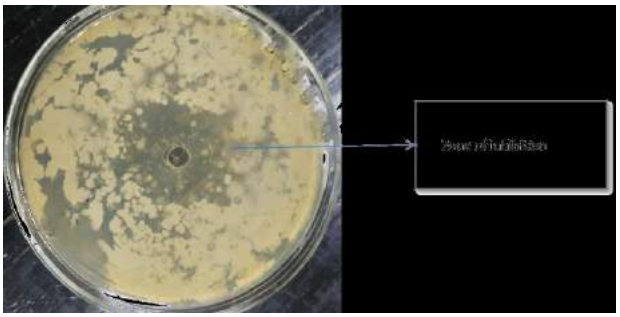

Figure 1. Zone of inhibition of water sample

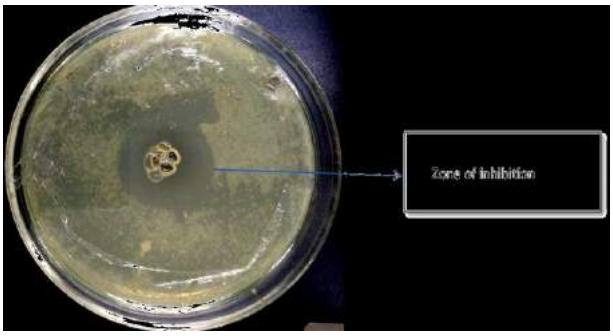

Figure 2. Zone of inhibition of isolated bacteria

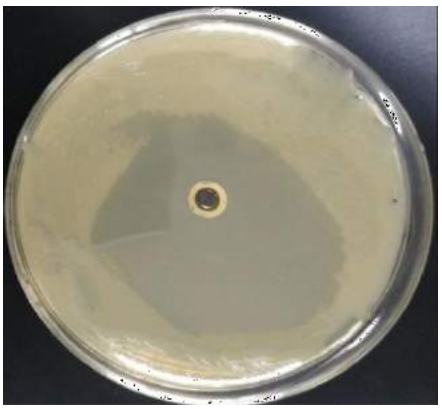

Figure 3. Lysozyme zone of inhibition.

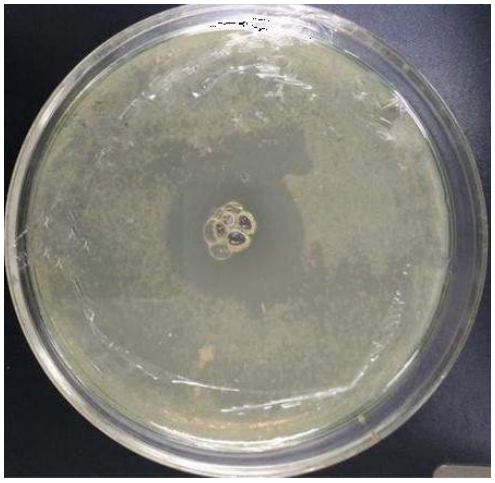

Figure 4. Egg white zone of inhibition.

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Study of Various Bio-products Used as Pesticides and Fertilizers in Agricultural Practices - A Review

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ABSTRACT

Large amount of chemical fertilizers and pesticides are used to fulfill the demand of population which leads in to the different types of pollution. Tremendous use of chemical fertilizers and pesticides shows adverse effect on the health of human and animals. It also decreases the fertility of soil. Though the quantity of agricultural product is increased but the quality of agricultural products is getting down which directly affects the export value. In modern era farmers are turning towards the organic farming rather than the inorganic farming because they are aware about the side effect of chemical pesticides and fertilizers. The present study focuses on the use of bio-products as a pesticides and fertilizers to conserve the health of soil, farmer and environment.

Keywords : Bio-Products, Chemical Fertilizers and Pesticides

I. INTRODUCTION

To fulfill the demand of basic needs of exploited population farmers use chemical fertilizers and pesticides. Nowadays farming is the main business of rural people for economy. Lack of organic fertilizers and pesticides and also to get the more income in less time there is no option to use the chemical fertilizers and pesticides. The overuse of these chemical fertilizers and pesticides leads to water pollution, soil pollution and air pollution[1,2]. Due to continuous used of these chemicals insect or pests developed their resistance power against chemical insecticides. To overcome these problems different chemical fertilizer and pesticides companies launch the new and deadly poisonous inorganic insecticides. The drawback of these chemicals is that these pesticides and fertilizers leave their residue in soil and also in plant products and because of this lots of health related problems in human and domestic animals arise[2]. It also affects the export of the agricultural products. These chemicals also destroy the flora and fauna of the soil[1,2,3]. To overcome these problems it is the time to come back towards organic farming Hence different workshops, seminars and research works are organized having the aim to develop and use different organic pesticides and fertilizers. Not only researcher but also some farmers developed their own techniques to formulate different bio products as pesticides and fertilizers. Now it is essential to use bio products to increase the fertility of soil, pest control, and quality of crop yield, economical condition of poor farmer and also to control the pollution. The present review focuses on the use of bio-products as a pesticides and fertilizers to conserve the health of soil, farmer and environment.

II. METHODOLOGY

1. Information is collected from literature, different articles and research papers.
2. Discussion and interview with farmers who uses bio-products for farming.
3. Own farming practices.

III. DISSCUSSION

All the available bio-products used by farmers are presented in following tables

A. Bio-products used as pesticides

i) Plant Origin bio-products

Sr. No.	Name of bio-product	Source	Uses
1	Neem leaf extract	Neem(Azadirachta indica) tree	To control caterpillars, grasshoppers, bettles and mites
2	Neem seed oil	Neem(Azadirachta indica) tree	It used as a insecticides To control nematodes
3	Neem dry leaves	Neem(Azadirachta indica) tree	To control store grain pest
4	Dry leaf extract	Neem(Azadirachta indica) tree	As a Fumigant to control household pest
5	Neem bark and root extract	Neem(Azadirachta indica) tree	To control fleas and sucking pest in rice
6	Dry leaves	Garlic	To control store grain pest
7	Leaf extract	Garlic	To control root knot nematodes in tomato
8	Leaf powder of gram seed	Gram seed	To control the pulse beetle
9	Tobacco leaf powder	Tobacco plant	Leaf eating bugs and beetles, spiders and mites To control larvae pest
11	Nilgiri seed and leaf extract	Nilgiri tree	Used against Jassids, Aphids, Scales
12	Chilli powder	Red chilli plant	To control different pest, fruit borer, leaf eating caterpillar brinjal fruit and shoot borer
13	Lemon oil	Lemon fruit	To kill aphids, mites, fire ants, paper wasps and house crickets
14	Wood ash	Any tree	Use around the bottom of crop to control aphids Used as a insect repellant in chilli and tomato crops Use for preservation of seed
15	Dhatura plant extract	Dhatura plant	Use to control thrips, aphids, termites
16	Rui (calatropis gigantia) leaf extract	Rui plant	To control termites
17	Leaf extract	Lantana camera	Beetle and leaf minor
18	Peel extract	Orange fruit	As a insect repellent like mealy bugs, slugs, aphids, fleas, mites, fire ants, paper wasps
19	Dashparni arc	Different leafs	To control all type of insect, pest and caterpillar

ii) Animal Origin bio-products as pesticides

Sr. No.	Name of bio-product	Source	Uses
1	Vermiwash	Earthworm	Antibacterial, antifungal
2	Fish oil	Fish	Insect repellant
3	Human urine	Human	Herbicides
4	Cow urine	Cow	Fungicides Insecticides

B) Bio-products used as fertilizers

i) Plant Origin bio-products

Sr. No.	Name of bio-product	Source	Uses
1	Seed cake	Neem seed	Increased rate of photosynthesis Used as fertilizer and control the growth of harmful bacteria Increased the water holding capacity Maintain the nutrient value and fertility of soil
2	Drumstick leaves	Drumsteak (Moringa oleifera)	Growth stimulation of different crops
3	Tag	Whole plant of tag (Crotalaria juncea)	Used as fertilizer and weed controller
4	Slurry	Different grains	Used as fertilizer

ii) Animal origin bio-products used as fertilizer

Sr. No.	Name of bio-product	Source	Uses
1	Vermicompost	Earthworm (Eisenia fetida)	Used as fertilizer
2	Fish waste	All type of fish	As a fertilizer
3	Cow dung and cow urine	Cow	Used in preparation of different slurry
4	Mixture of milk egg and jaguar	Cow, Hen,	Used as a fertilizers
5	Cow urine	Cow	Growth stimulant antimicrobial agent
6	Jivaamrut		Growth stimulant Control the different pests

IV. OBSERVATIONS

1. Fish oil, Neem seed cake are readily available in market.
2. Different formulation such as Jivamrut, slury is available in market as well as farmers can easily prepare it for their own use.
3. Many vermiculture units (small scale and large scale) are maintained by the farmers.
4. Formulation of different useful bacteria are available in market.
5. Different plant extracts are freshly prepared and used by farmers.
6. Bio-products suppliers easily supply different bio-products as per demand at the village level.

V. CONCLUSIONS

All above bio-products are frequently used by farmers in Maharashtra

All these bio-products are beneficial, biodegradable and do not show any adverse effect on human and environmental health. Regular and excess use of these products is not harmful at certain level. All these products are easily available, economical and eco-friendly. Use of bio-products helps in improving soil fertility, and also helps to improve quality, quantity and nutrient value of the crop yield. Economical value of this crop yield is also high. Because of this economical condition of farmer will be better and it helps to reduce the suicide of farmers.

VI. Acknowledgment

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Effect of Gloriosa Superba Root Extract on Development of Chick Embryo

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ABSTRACT

Gloriosa superba has been widely used for several medicinal purposes in Indian traditional medicine system. It is traditionally used for the treatment of gout, chronic ulcers, haemorrhoids, cancer, and leprosy and also for inducing labour pains etc. The seed and tubers of this plant contain cholchine as major constituent. The purpose of study is to evaluate the effect of Gloriosa superba root extract on development of chick embryo. The Soxhelt aqueous extract of tuber was extracted using methanol. The effect of different concentration of tuber extract was carried out on eggs. The effect of extract was found that it stops development of chick embryo. Gloriosa superba showed abortifacient and oxytocic activity activity due to the presence of colchicines.

Keywords: Abortificient ; Gloriosa superba; Oxytocic activity

I. INTRODUCTION

In traditional medicinal culture thousand of references are available for the use of plants for the problems related to reproduction. Traditionally used herbs have great importantance in modern world because of their efficacy, safety and minimal side effect on the human health as compared to chemically synthesized medicines. Gloriosa *superba* Linn. (Family-Liliaceae) is a flowering plant commonly known as flame lily, fire lily, climbing lily. It is semi-woody, climbing using tendrils on bushes[1]. The plant has great importance in Ayurveda and is used in inflammations[12], anthelmintic[5], gout, rheumatoid arthritis, gonorrhea and relieving fever[2]. Root extract are used to cure leprosy, ulcer, piles, skin diseases and show anti-dote property against snake bite. It is also used as abortifacient[4] and extract of tuber are applied topically during childbirth for reducing labor pains[6][10]. The leaf powder is extensively used to overcome jaundice and head lice[10][7][8]. The anti-microbial[9], antibacterial[11] properties of tuber of the plant are reported[8].

Literature study show that a plant seed and root are great sorce of colchicine and colchicoside. Colchicine is a powerful antimitotic agent that blocks or suppresses cell division by inhibiting mitosis, the division of a cell's nucleus. These phytochemical constituents are responsible for the plant's abortifacient and oxytocic activities[16][17]. Considering traditional importance of Gloriosa *superba*, the aim of study was to investigate the effect of root extract of Gloriosa *superba* on embryonic development of chick egg.

II. MATERIAL AND METHODS

Collection and authentication of the plant material

The tuber of the healthy plant Gloriosa *superba* was collected from Mordara, Pemgiri, Sangamner (Maharashtra). The plant material was taxonomically identified with the help of available literature.

Preparation of extract

Freshly collected tubers were washed with distilled water. The cleaned tubers were subsequently dried under sunshade to remove moisture completely and powdered by using mechanical grinder.The powdered plant material was extracted using methanol with Soxhlet apparatus for 18 h. The extract was concentrated by evaporating on water bath and dried to obtain a dark brown semi-solid mass.

Phytochemical screening

Identification of the phytochemical was carried out on the plant extract to find out the presence of alkaloids, steroids, proteins and glycosides by using specific reagents[18].

Experiment

Chick Embryos: The chick embryos are easily available in large numbers hence chick embryo has been used to observe the teratological studies, because the post-blastula chick embryo and the mammalian embryo are similar, and thus the chick embryo is a good model for studying vertebrate embryonic development. All aspects of animal care compiled with the ethical guidelines and technical requirements were approved by the Institutional Animal Ethics Committee (IAEC) and Institutional Review Board (IRB).

Eighteen (18 nos.) fertile, pathogen free eggs incubated at 35˚C for 48 hrs. and 75% relative humidity until the embryos reached stage ten of development according to Hamburger and Hamilton [12]. All the eggs were labelled and divided into three groups consisting of six eggs per group. The Group one (G1)- Normal (uninjected) eggs, Group two (G2)- Injected with physiological saline, Group three (G3)- injected with the 5 mm root extract of Gloriosa *superba* and 5 mm physiological saline

Dosage of root extract of Gloriosa *superba*

Dosage was prepared by diluting 0.5 gm root extract of Gloriosa *superba* in 1 ml physiological saline(50 % solution).

Method of injection

Eggs were wiped with 70% alcohol and labelled on the outer shell. A hole was made on the blunt pole of the egg with a sharp and thick needle under aseptic condition. Using a sterile needle and a syringe, 0.5 ml dosage of 50% solution of root extract in saline was injected to the corresponding groups of eggs. The gap created in the eggs was sealed.

All eggs were kept in incubator for 48 hrs.

Observations

In each group, to determine the development of the chick embryos, the eggs were removed from the incubator after 48 hrs. The egg shell was opened to see the embryo. All the chick embryos were transferred to a petri dish by the careful sterile dissection.

On observation it is revealed that embryos from G1 and G2 shows development and embryo from G3 showed no development. **(Table 1) (figure 1)**

Table 1. Experimental design of chick embryos

Sr. No.	Groups	Observation
G1	Normal group	Normal Development
G2	Group injected with physiological saline	Normal Development
G3	Group injected with dilute root extract of Gloriosa *superba* in physiological saline	No Development

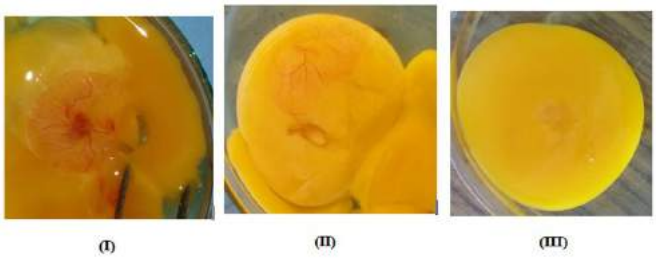

Figure 1. (I) chick embryo of Normal group, (II) chick embryo injected with physiological saline, (III) injected with dilute root extract of Gloriosa *superba* in physiological saline

III. Conclusion

The experiment indicates that due to the injection of root extract, there is no further growth seen in chick embryo. It gives scientific evidence for the traditional use of Gloriosa *superba* as a abortifacient.

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Diversity of Butterflies of Pune City

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ABSTRACT

Insects are the most fascinating creatures on the planet earth. They are specialized pollinators, hunters, parasites and predators forming basis for most of the terrestrial ecosystems. Among insects the butterflies are most charismatic ones. Their size ranges from the tiny jewels like blues, to the gorgeous birdwings with a wing-span as great as eight inches. Their glowing colours and delicate glittering movements catch and charm our eyes. No wonder then that they were willingly collected and studied by early naturalists.

Keywords: Butterflies, Organic Matter, Entomological Pins, Insect Box

I. INTRODUCTION

Gardens are discrete patches of human- managed habitat that are common in many urban areas. Man-made gardens and parks are inhibited by a variety of insects and other organisms. Insects play an important role in nutrient cycle, Organic matter decomposition, Pollination and soil aeration in urban ecosystem. Some insects visit park and gardens for nectar or other resources, while some reproduce and spend most of their lifespan in the gardens. Thus there has been a rising research to show the potential of small scattered habitats like domestic gardens, community gardens, green roofs and parks to support rich biodiversity, even in heavily populated urban areas. (Saha and Gaikwad, 2014).

Butterflies are commonly referred to as "insects of the sun" with their eye catching color and delicate charisma. They have been admired for centuries for their physical beauty and behavioral display (Arya and Chaudhari, 2014). Among the insects, butterflies occupy a vital position in the ecosystem and their occurrence and diversity are considered as good indicators of the health of any given terrestrial biotope. Butterflies are also good indicators of environmental changes as they are sensitive to habitat degradation and climate change (Kunte, 2000). The butterflies have fascinated peoples of all age group. That is why these are considered as the "fluttering jewels of nature" (Illustrated Encyclopedia of Wildlife). The order Lepidoptera is the second largest order in the animal kingdom, coming under the class Insecta. The word Lepidoptera means `Scale wings`(Greek; Lepis- scale; Pteron-wing).

Butterflies are taxonomically well studied group of insects and receive reasonable amount of attention throughout world not only by the entomologists but also by laymen. Presently, butterflies are classified into two superfamilies, of which Hesperioidea has all the skippers, While Papilionoidea includes the rest, the 'true' butterflies. Hesperioidea consist of a single family of Hespeiidae, whereas papilionoidea has four families: Papilionidae(Swallowtails), Pieridae (White & Yellows), Nymphalidae (Brush- footed butterflies) and Lycaenidae(Blues). Out of about 25,000 species of butterflies recorded from all over the world, 1501 are from India (Gay et al., 1992). From which 321 are Skippers, 107 Swallowtails, 109 White and Yellows, 521 Brush footed butterflies and 443 Blues (Kehimkar). Pune, being one of the most urbanized, congested and polluted city, has been taken as the study site.PMC has already developed 111 big and small gardens and parks measuring upto 475 acres [Corbet PS., 1999]. The body of an adult butterfly is composed of the head and 13 segments, which are not obvious. Broadly, the insect's body is divided into head, thorax and abdomen.

Lifespan, Butterflies as adult are short-lived insects. Small butterflies like some Blues may live only for a few weeks, while large butterflies like the Swallowtails

and some Nymphalids or Brush-footed butterflies may live for as long as eight months. Otherwise most butterflies live up to two to four weeks, if they not attacked or eaten by predators. Sometimes, ecological factors such as temperature, availability of food and suitability of habitat have an impact on the lifespan of an adult butterfly. Polymorphism is a unique variation that occurs within a species. In this kind of variation, two or more forms of the same species occur at the same time in the same area. The female of Common Mormon occurs in three forms, one of which mimics the Common Rose, while the second form mimics the Crimson Rose, and the female of the third form resembles the male. Some butterfly shows Seasonal variation, with two forms, the dry season form and the wet season form. The common evening brown is recognized by a series of eye spots on the wing border during the monsoon, while in the summer it is almost invisible among the leaves due to its mottled brown colour without the eyespot.

II. METHODS AND MATERIAL

Following equipment were used during present investigation. Insects

Collecting Net:

Samples were collected with insect collecting net or sweep net. It has a handle, a wire ring and cloth bag. The handle is about 2 feet long made up of wood or metal but light and strong. The handle at one end has a steel or iron wire ring. The wire ring is 30-35 cm in diameter. The bag is either of muslin cloth or fine nylon net. The bag is 2 or 2 1/2 times as deep as the diameter of ring i.e. 60 cm to 75 cm. The edge or bag is made up of cloth-like canvas. The strong cloth is folded around the ring to form home. Sweeping of flowers and other plants with side - wise motion of insect net helps in the collection of larger number of insects than up and down sweep.

Insect Packets:

Insect packets made up of butter paper were used to store the pithed butterflies during field collection. Size: 10×5 cm.

Entomological Pins:

Insects were held on entomological pins to facilitate their morpho-taxonomic. The pins are hard made up of non–corrosive metals (nickel etc) with sharp edge and small head with size: No 2 with 40×0.38 mm and No 3 with 41×0.42 mm. The pins were inserted vertically into the thorax body of butterflies.

Insect Spreading Board:

It is an insect spreading board for spreading the insects in desired position. It is made from the fine fiber wood. The base of the board is 4" X 12" x ¾". These are two tap pieces of soft wood or cork on the upper side of the board which inclined towards centre. Out of 2 pieces one piece is fixed and another piece is movably articulated. In between the 2 pieces is an adjustable channel to accumulate the body of insects. The insect pin is passed through the body of insect & fixed in the channel. The thin paper strips are used to press the wings of insects on the spreading board. Then the specimens are allowed to remain in this position for 15 days or till they dry.

Insect Box:

Specimens were kept in insect box for presentation of pinned dried specimens. The box is made up of plywood with variable sizes but convenient in handling. The top of the box is made up of glass. The bottom of the box is covered with a thermacoal. The box is treated with saturated solution of naphthalene in benzene. Naphthalene balls are kept in corners if box to protect the dried insects from pest.

The present study was conducted during the period from August 2015 to February 2016. The study areas were monitored in every month during the study period with 10-15 days with minimum of 2 to 3 hours per day. The random method of sampling was used to collect the butterflies. The collections were done in four seasons comprising monsoon, and post monsoon. The collections were done in warm but not too hot condition especially in the morning from 7 am to 11 pm which is a peak time for butterfly activity and evening 4pm to 5.30 pm. The butterflies are very delicate in nature and hence their handling is also done with extreme care. Butterflies were collected by using aerial nets. The net consist of a strong, light handle with a length of 1m and at its end a 13'' diameter ring is attached which is joined by the nylon cloth bag of 33''depth. The long handle allows the net to be used as far away from body as possible, making

sweeping over hanging bushes easier and extends the area of individual sweep.

The soft bodied butterflies were gently removed from the bottom of the bag, after it becomes enclosed in the bag by a rapid twist of the handle. The butterflies are killed by pressing the thorax region gently by the hands. Since immediate pinning is not possible, these butterflies are kept in a piece of paper with wings folded and then edges of the paper are folded over to lock it inside. The butterflies are pinned through the centre of thorax or a little behind, between bases of the forewings on a piece of thermocoal. It is then kept in insect box. The insect boxes are made of good quality wood and serve the purpose of keeping the collection away from moisture. It is also provided with a glass top to facilitate observation. Naphthalene balls are kept inside the box to prevent insect pest and fungal attack. On both the wings, a piece of paper strip is pinned so as to spread the wings. The collection was done on sunny days continuously for one year. The collected specimen was identified by following standard literature (Kehimkar 2008)

Species Diversity Analysis:

The present diversity study on species of 5 families of butterflies from gardens and park of Pune municipal corporation enumerated a total of 655 examples pertaining to 65 species distributed over 48 genera and belonging to 14 subfamilies. Among these Five families, Nymphalidae is more species rich and dominant one with 23 species pertaining to 15 genera. Family Lycaenidae with 20 species under 17 genera, family Pieridae consists of 12 species to 9 genera followed by family Papilionidae having 6 species to 3 genera and family Hesperiidae shows very poor diversity.

Two diversity indices were calculated with the help of PAST software version, 2.17C. Simpson's diversity index and Shannon-Weiner index were taken under consideration to analyze the diversity.

G1: Savitribai phule University, pune; G2: Empress garden; G3: Sarus baug; G4: Deshpande garden; G5: Sant gajanan maharaj garden; G6: Peshve park; G7: Bund garden; G8: Parvati; G9: Sambhaji garden, G10: Botanical garden modern college, G11: Kamala Nehru park; G12: Shaniwar wada; G13: Tathavade garden; G14: Thorat garden; G15: Dhondiba sutar park.

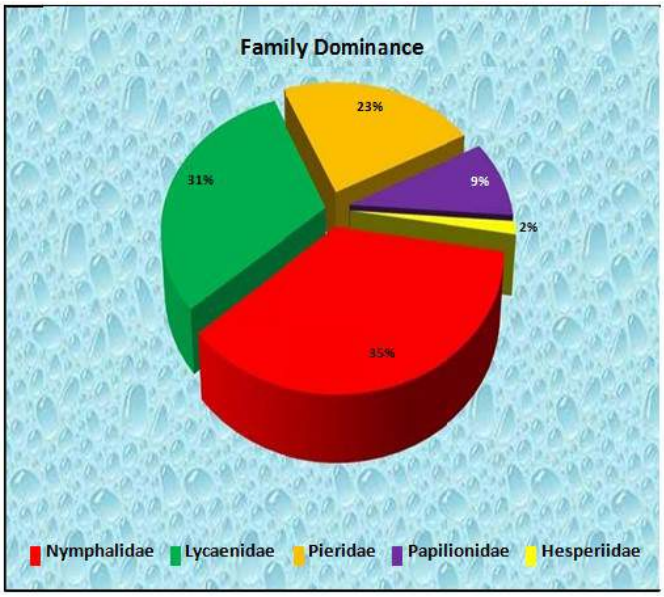

Figure 1. Family Dominance

Following graph shows the percentage wise family abundance as, A total number of 5 families have been studied from the collection sites. Family Nymphalidae was the most abundant with a total number of 23 species belonging to 195 individuals making a 35% of the total number. This is followed by family Lycaenidae with a tot l number of 20 species belonging to 171 individuals constituting a total of 31%. Then the Family Pieridae with a total number of 15 species including 210 individual consisting a total of 23%, family Papilionidae having a total number of 6 species belonging to 77 individual making a 9% .

The following graph shows the abundance and diversity of species in different localities as, The most diverse study site was Savitribai phule university, pune shows rich diversity of 56 species pertaining to 154 number of individuals followed by Empress garden represented by 50 species belonging to 88 number of individuals, Saras baug having 43 species pertaining to 64 number of individual. And Tathavade garden shows very less diversity consisting number of 14 species distributed to 15 individuals followed by Thorat garden shown number of 12 species consisting15 number of individual and Dhondiba Sutar Park also shows very less diversity with 11 species belonging to 14 numbers of individuals.

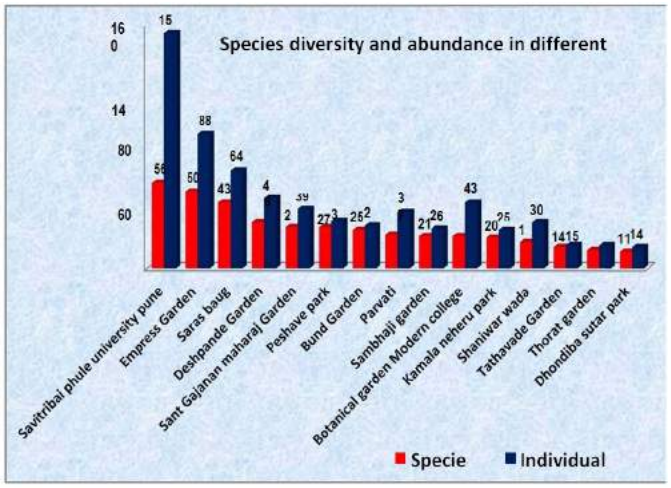

Figure 2 : Species diversity and abundance in different localities

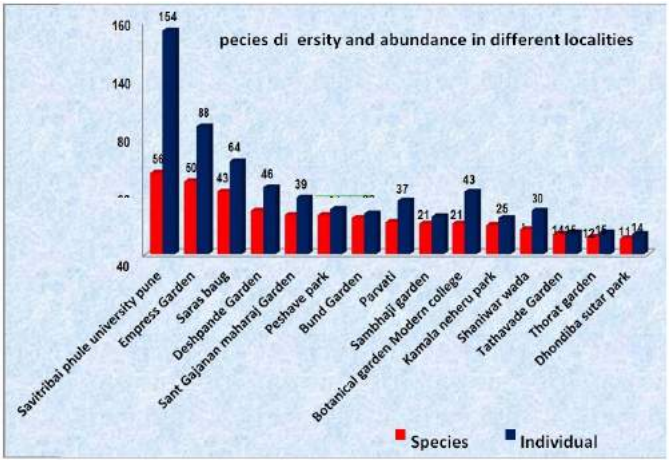

Figure 3: Locality wise species Diversity

The following graph shows the locality wise species diversity. The highest number of species (56 species) was observed in the Savitribai Phule University, pune, Empress garden and also from saras baug. The lowest number of species were recorded in Thorat garden, Dhondiba Sutar park, Shaniwar Wada and each of these localities recorded for species. Locality like Deshpande garden, Sant Gajanan Maharaj garden, Peshve park, Bund garden and Parvati recorded a medium number of species like 5 and 8 respectively.

Locality wise species Diversity

The species Eurema hecabe was the most abundant one with a total of 68 individuals recorded this is followed by the species Junonia lemonias with a total of 50 individuals and also the species Pachliopta aristolochiae includes 32 number of individuals. And also some species having very least number of individuals like, species Papilio helenus pertaining to very few number of 3 individual species, While the Byblia ilithyia with very poor individuals followed by the species Ixias mariannae with 1 individual recorded.

Biodiversity indices in the 15 Parks and Gardens of study area:

The biodiversity indices in the 15 sampling sites (Table: 2) indicates that most of the sampling sites were found to have moderate diversity. Among the 15 parks and gardens, site G1 (Savitribai phule university, Pune) records highest species diversity as well as abundance followed by site G2 (Empress garden) and site G3 (Saras baug). However, site G13, and G14 records lowest number of species diversity and site G15 having the very least number of individuals.

Table 2 : Biodiversity indices in the 15 sampling sites

Collection	No of	Individuals	Simpson_1-D	Shannon_H
G1	56	154	0.9577	3.631
G2	5-	88	0.9675	3.683
G3	43	64	0.9688	3.627
G4	3-	46	0.949	3.208
G5	27	39	0.952	3.175
G6	27	31	0.9594	3.255
G7	25	28	0.9688	3.184
G8	22	37	0.935	2.932
G9	21	26	0.9467	2.992
G1-	21	43	0.9313	2.847
G11	2-	25	0.9376	2.9
G12	17	3-	0.9022	2.606
G13	14	15	0.9244	2.616
G14	12	15	0.8978	2.396
G15	11	14	0.8878	2.396

Discussion:

In 2014 S. Ankalgi and M. Jadesh recorded family Nymphalidae to be the most diverse from Ankalga village (Gulbarga District) Karnataka. Similarly the diversity stydy carried by H. A. Dhamke et al. in 2013 from Haveli and Maval Tahasil of pune District, Pune, Maharashtra. Their result also shows the family

Nymphalidae was the most dominant from this region. And also in 2014 P. Kumar and A. G. Murugesan recorded the relative abundance was high for family Nymphalidae among all other families. The present study also adheres earlier work of similar time by Ankalgi and jadesh (2014), Dhamke et al (2013) also P. Kumar (2014).

The composition of species of individual families shows similar results obtained by Kunte (2001), Arun (2002), Manoj et al. (2004), Kunte (2001), Kunte (2009), Singh (2010), Alagumurugan et al. (2011), Menasagi Jyoti B. (2011), Nimbalkar et al. (2011), S Amala et al. (2011), Karve, et al. (2013), Abdul Hammed (2013), Kumar Ashok. (2013), Sharma et al. (2014), Arya et al. (2014), Bara Atanu et al. (2014), Kumar P. (2014), Sahu Usha et al. (2014), Prabakaran S. et al. (2014), Kumar Ashok. (2014), Aishwarya et al. (2014), Ravindra. (2014) and Shiva Rama Krishna et al. (2014), Naikwadi et al. (2015), Naikwadi et al. (2016).

III. CONCLUSION

Butterflies are most efficient pollinators as well as some species are agricultural pests; hence are of economic importance. The gardens and parks are important as regards of maintaining diversity of insect population in urban habitats moreover keeps the pollution under control. The present work represents an account on diversity of butterflies from parks and gardens of Pune City. The occurrence of butterflies depends on various factors like presence of indigenous flowering plants, levels of anthropogenic annoyance and garden management practices. Present work depicted the study from 15 gardens and parks of the city. Further exploration will unquestionably add to species number qualitatively as well as quantitatively.The present endeavor depicts the study of total 655 examples pertaining to 65 species distributed over 48 genera and belonging to 14 subfamilies under 5 families from 15 parks and gardens of Pune municipal corporation. Among 5 families studied, family Nymphalidae is found to be dominant with respect to species quantity and quality, the genus Junonia is the largest with 6 species. A species like Eurema hecabe, Euploea core and Catopsila pomona they are most divers among all species studied. Further study on seasonal basis will definitely add one more dimension to the study.

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Effect of Heavy Metals on Antioxidant Enzyme of Fresh Water Major Carp Catla Catlafrom Mula Dam Ahmednagar

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ABSTRACT

Accidental industrial spills may lead to a high concentration of toxic metals in the aquatic environment which may leadto acute and chronic toxicity. Of all aquatic species, fish are particularly sensitive towaterborne contamination and are recognized as bioindicators for water quality monitoring. Thepresent study was planned to enumerate the accumulation of heavy metals like Fe, Cu, Ni and Zn in various tissues of fish like muscles,gills,liver, and kidneys). Level of these metals in different organs of fish were determined by Atomic Absorption Spectrophotometer (AAS).Total proteins and levels of antioxidant enzymes, Thiobarbituric acid reactive substance (TBARS), Superoxide dismutase (SOD) andCatalase(CAT) in the tissuesof the Indian major carps were measured.
Key words: Oxidative stress, Pollutants, heavy metal, antioxidant enzymes, Catla catla, Mula dam.

I. INTRODUCTION

Heavy metals are the metals or metalloid of the environmental concern.The term heavy metaloriginates with reference to the harmful effects of various elements like iron, copper, nickel, and zinc.Heavy metals have been reported to have a significant influence on all life forms mostly aquatic fauna. Heavy metals have been reported to affect aquatic animals like fish and indirectly pose a threat to human life. Heavy metals arrive in to the aquatic ecosystem through natural as well as anthropogenic sources, including industrial and domestic sewage, storm, run-off, leaching from landfills/dumpsites and atmospheric deposits (Forstner et al, 1983). The increasing concentration of heavy metals in the tissues of fish leads to biomagnifications in the successive tropic levels of food chain. Several studies have been carried out to examine the contamination of fish by various heavy metals.

Fish makes up a major part of the human diet due to their high protein contents and less saturated fat value (Sivaperumal et al.,2007; Raychaudary et al., 2008; Raouf et al .,2009 ; Yilmaz et al., 2009,Bhattacharya et al .,2010). Fish makes up major forms of the aquatic fauna and are considered as the best bio-indicator of heavy metal pollution in aquatic systems (Alinnor et al., 2010). Fresh water bodies are being continuously contaminated with heavy metals released from various sources (Adnano 1986). When compared with other toxicant, heavy metals are considered to be unrelenting components of the aquatic habitats. Heavy metals are omnipresent, soluble in water, easily transported by water and are usually easily consumed by aquatic biota (Mendel et al., 2005). The study of bio-accumulation of heavy metal in the living tissues of aquatic animals is a significant method to monitor the pollutionlevel of waterbodiesandat the same time can prove to be helpful method to study the biological role of heavy metals present at an increased level in fish and other aquatic organisms (Ahmad et al .,2010).

II. Materials and Methods

Study area:

Mula Dam is located 19º20'to 19º35' N latitude & 74º25' to 74º25' to 74º36 E latitude. The dam was artificially built across the Mula river in 1971 and contains natural water and capacity of dam is 26 TMC. It experiences an average rain fall 58 cm. Maximum depth being 67.97 m. The physiography of basin is semi agricultural &semi-arid with cultivated top soil bank(A J Dhembare,2011).

Experimental Animal:
The fresh water major carp *Catla catla*was collected from mula dam by fishermen using multifilament, nylon

gill net of mesh sizes ranging from 30 mm. After collection, samples were kept in ice pack and brought to the laboratory on the same day and then frozen at -20ºC until dissection, according to standard FAO methods.

Heavy Metal Analysis:

One gram of muscle, liver, kidney and gill racers from each sample was dissected for analysis. The dissected samples were transferred to a Teflon beaker and digested in an acid solution to prepare the sample for heavy metal analysis (Kenstar closed vessel microwave digestion) using the microwave digestion program. The samples were digested with 5 ml of nitric acid (65%). After complete digestion the samples were cooled down to room temperature and diluted to 25 ml with double distilled water. All the digested samples were analyzed for metals like Fe, Cu, Ni and Zn using Atomic Absorption Spectrophotometer (Perkin-Elmer AA 700). The instrument was calibrated with standard solutions prepared from commercially available chemicals procured from Merck, Germany (Kingston, Jassie et al., 1988).

Result:

The concentration of heavy metals and enzymatic biomarkers determined from different tissues of *Catla catla* is tabulated as follows.

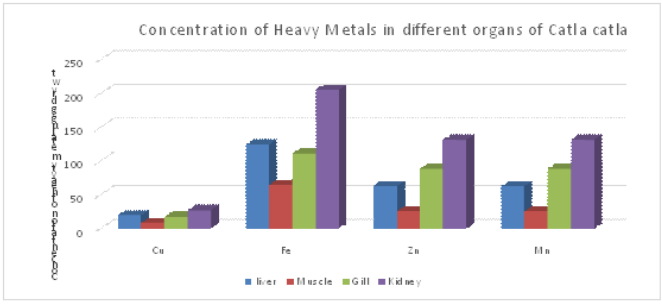
Table 1. Concentration of heavy metals in different tissues of *Catla catla*

Organs	**µg/g dry weight**			
	Cu	**Fe**	**Zn**	**Mn**
Liver	19.77±2.711	124.3±47.98	62.79±10.21	62.79±10.21
Muscle	8.37±1.29	64.58±5.24	25.66±7.05	25.67±7.05
Gill	17.5±4.49	111.04±28.47	88.66±33.52	88.66±33.52
Kidney	2.48±4.37	205.25±55.26	131.7±52.18	131.75±52.19

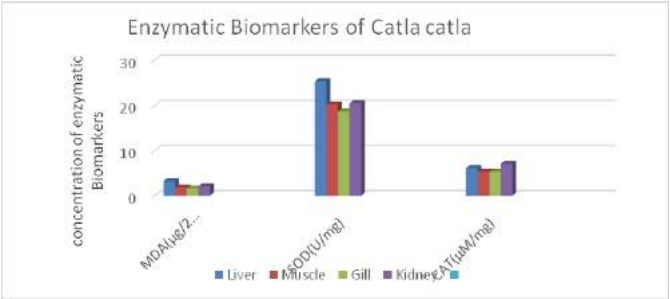
Table 2. Enzymatic Biomarkers of *Catla catla*from Mula dam.

Organs	MDA (µg/25mg)	SOD (U/mg)	CAT (µM/ mg)
Liver	2.34±0.0844	27.44 ±.0977	5.30±0.1562
Muscle	1.23±0.0393	26.16±0.6472	5.70±0.4856
Gill	1.10±0.0659	21.76±0.4985	5.10±0.0880
Kidney	1.58±0.0723	19.12±0.6674	6.64±0.3527

Graphic representation of heavy metal and enzymatic biomarkers of *Catla catla:*



Graph 1. Heavy metal concentration in various tissues of *catla catla*



Graph 2. Enzymatic Biomarkers of *Catla catla.*

III. Conclusion

The toxic effects of heavy metals in fish have been demonstrated in the present study. It is richly clear that metals induce an early response in the fish as proved by alterations both at structural and functional levels of different tissues include enzymatic and genetic effects, thereby affecting the innate immune system of exposed fish or increasing susceptibility to multiple types of diseases.

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Micro-Rainwater Harvesting : Low-Cost Technology (Jalkund) for New Livelihood of Rural Farmers in Western Ghat of Maharashtra

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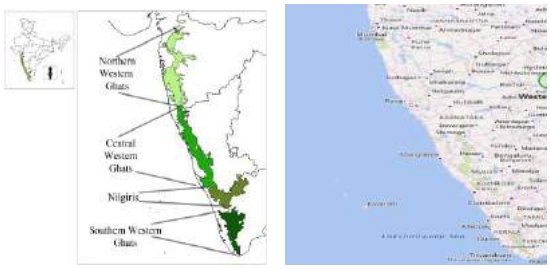
ABSTRACT

Western Ghats, known for its high precipitation rate, suffers from water scarcity during post-rainy season. In the absence of major and medium irrigation potential/facilities, the alternative method is to explore minor irrigation potential through effective water-conservation measures. A low-cost rainwater harvesting structure called Jalkund of varying capacity (6000-30,000 l of water) developed for the hilltops, useful in water management. Farmers may have option for the capacity according to their water requirement for the crop intended to be cultivated and also for diversified use of stored water in various farm activities like crop, livestock and fish production during post-rainy season (stress period). The Jalkund was made up of clay and cow-dung plastering followed by 3-5 cm cushioning with dry pine leaf, laying down of 250 µm LDPE black agrifilm and covering with 5-8 cm bamboo thatch. The study revealed that the cost/l of stored water was Rs 0.14 during the first year considering Rs 4205 of total cost which came down to Rs 0.046/lit. of stored water during the third year owing to negligible maintenance cost. Using stored water economically in various farm activities is the most acceptable and profitable one particularly to those in the hilltops, who are the worst sufferers due to water scarcity. This economically viable and easily adoptable technology needs to be popularized among farmers.

Keywords : Micro-Rainwater Harvesting, Jalkund, Hilltops, Bamboo Thatch.

I. INTRODUCTION

Western Ghats–Physiographic view
Satellite image



The western region of India comprising five states, viz. Gujarat, Maharashtra, Goa, Karnataka, Kerala and Tamil Nadu has spread along west coast of India. The region is characterized by different terrain, wide variation in slope and altitude land tenure systems and cultivation practices. The agriculture is the region is mostly rainfed and monocroped. Economic development of this region is highly dependent on the judicious use of its natural resources mainly soil and water. Crop productivity through efficient water management and suitable agronomic practices enhances the rural economy, quality of life and creates more job opportunities through developing of agro industry. Maharashtra is located in the north centre of Peninsular India. It links the north to the south and the plains of India to the southern peninsula. The state is bound on west by Arabian Sea, on north-west by Gujarat, on north by Madhya Pradesh, on southeast by Andhra Pradesh and on south by Karnataka and Goa. It is the third largest state in terms of area in the country. Physiographical regions of this state are divided into three natural divisions - the coastal strip (the Konkan), the Sahyadri or the Western Ghat and the plateau. Konkan consists undulating low lands. North Konkan has the vast hinterlands. The average height of Sahyadri is 1,200 meters. The slopes of the Sahyadri gently descending towards the east and south-east directions. Tapi, Godavari, Bhima and Krishna are the main rivers of the state. Maharashtra receives its rainfall mainly from south-west monsoon. The rainfall in state varies considerably. There is heavy rainfall in the coastal region, scanty rains in rain shadow areas in the central part and moderate rains in eastern parts of the state.

II. Water resources and potentiality

Water is considered to be the key input for augment agricultural production all over the world. The annual average range of rain fall of the region is 2000 mm, accounting from one of the country's total water of 420 Mha m. it can till date utilize only 0.85 Mha m of water [3]. The remaining more than 41.0 Mha m water is loss annually particularly due to its major portion being hilly. Though the region receives high rain fall, lack of appropriate rain management conditions coupled with lack of suitable rain and water conservation measures lead to severe water scarcity, particularly during post monsoon season and effect crop productivity. June to October duration is water surplus period while November to May is mainly categorized under water deficient period.

III. Necessity of micro rain water harvesting

Rain water harvesting has tremendous potential of being an irrigation water resource for domestic as well as agricultural purposes for the resource poor farmers in this vulnerable environment. One of the major constraints for water harvesting structure in the hilly region is high seepage loss from storage tanks. As soil is coarse textured and lower strata are seepage losses are high seepage loss is reported to be 300- 400 l/m^2 wetted area per day[7]. Gradual siltation clogging of soil pores has resulted in the development of layers of low hydraulic conductivity. Konkan region is having low altitude (valley), mid altitude and high altitude (upland terrace)[1]. In the valley, collection of runoff water in micro water harvesting structures (ponds) having reasonably large catchment area has been proved successful, provided due attention is given to check seepage loss. In case of upland terrace at the hilltop ,where land available for constructing a pond is less with limited catchment area and there is scarcity of water during off season as most of the rain water goes waste by runoff through terrace land, In this area construction of low cost micro rain water harvesting structure is the right option. If subsistent farmers of this region invest in micro rain water harvesting structure with suitable lining material which completely check seepage loss, this can increase productivity .They can diversify their farming by growing cash crops and rearing of live stock (poultry, dairy, piggery and fisheries). Micro rain water harvesting structure called Jalkund for hilltops has been developed. Cost of preparation, water loss lounge, lining material used water productivity; size and capacity are delt with. An account of this technology is discussed in this paper.

IV. About Jalkund

Site is selected on hilltop and excavation of kund is completed before the onset of monsoon. The bed and sites of kund are leveled to avoid damage to the lining material. Spraying of endosulfan on the surface of inner walls and bottom. Apply aluminiun phosphide 1 tablet per live hole around 5 meter of kund done before lining process. The inner walls were properly plastered with mixture of cow dung and clay in the ratio 5:1. After plastering 3to5 cm thick cushion of dry leaves to avoid any kind of damage to the lining material is done. This is followed by lying down of 250µmLDPE black agri-film. Seepage loss was completely checked. Jalkund was covered by thatch (5to8 cm thick) made of locally available bamboo and grass .Use of neem also help to reduce evaporation during off season.

V. Water loss Seepage

There was no seepage loss of water from poly- lined Jalkund of all sizes (6000-30000l) except from a 40000 l capacity where the joint of LDPE agri- film Jalkund, had opened probably due to more water load during heavy rains. During the rainy season water load in the big sized Jalkund also damaged the bottom of the embankment.

Evaporation:

The evaporation rate of water was maximum in February (9.2mm/day) and minimum (1.8mm/day) in October in the control Jalkund[7]. Use of neem oil as anti evaporates on the water surface and Jalkund covered with thatch were found effective to minimize evaporation. It was recorded that application of neem oil (10 ml/sq.m) on the water surface after each watering reduced 43.25% evaporation rate whereas use of thatch reduced up to 80% in comparison to the control water (without neem oil or thatch)[7,8] the size was restricted from 6000 to 30000 lit. with respective dimensions of 3m X 2m X 1m, 3m X 2m X 1.5m, 4m X 3m X 1m, 4m X 3m X 1.5m and 5m X 4m X 1.5m. the size of lining material of the

corresponding dimension was 6m X 4m, 7m X 6m, 8m X 7m and 9m X 8m respectively.

VI. Low preparation and maintenance cost

The cost per lit. harvested water, which was calculated on the basis of aging ,duration of lined LDPE agri-film, to expenditure under different materials and capacity of Jalkund is given in Table 1.It was observed that during the first year ,cost/l of stored water was Rs.0.14,conside the total expenditure of Rs.4205 for preparing a 30,000 capacity Jalkund .At end of the third year ,the cost came down to Rs.0.046/l of stored water, owing to negligible maintenance cost during the second and third year (Table 1).

Table 1. Cost of making Jalkund (capacity 30,000 *lit*)

Particulars	Unit price	Cost in Rs.
Digging expenses	30/m^3	900
Plastering with clay	2.50/m^2	120
Cushing with dry leaves	2.50/m^2	120
Lining with LDPE agri film (250µm)	40/m^2	2880
Thatching	2/m^2	60
Fencing	2/m	75
Insecticide	-	50
Total	-	4205
Cost/lit stored water for First year	-	0.14
Cost /lit stored water for Second year	-	nil
Cost /lit stored water for Third year	-	nil
Average cost/ lit stored water	-	0.046

VII. Capacity

Farmers have the option to go in for size and capacity of the Jalkund according to the water requirement for clay intended to be cultivated. Preparation cost is reflected accordingly. However considering the seepage loss due to unavailability of water during November to April, most of the hill areas remain barren. Stored water from the Jalkund was used for irrigation. Siphon technique was used for supplying water to the plant through a polypipe. Medical plants (Alpina galanga, local name: kulanjan) are grown all along the periphery of the Jalkund increase farm income as a whole. This does not require direct water in for growth as they require soil moisture is maintained throughout the periphery of the Jalkund. The rhizome of the plant yield essential oil contains methyl cinnamate, cineole and oleoresin used to for rheumatism, bronchitis and carminative, and having high medicinal value for pharmaceutical/ clinical industries[1].

Livestock and fish production

The stored water in the Jalkund could partly be used for crop production and partly for livestock and fish production or integration of both livestock and fish. Use of stored for the dual purpose of crop production and live stock are fish production was a complementary system, where none of the enter pries was practiced at the cost of the other as far as water use was concerned. Various options of farmer choice were tested for diversification and economic use of stored water in the Jalkund. Farmers can opt for this farming system according to resources available with them.

Pig based activity:

based on three years on study at the research farm, per unit water requirement of rabbi crop and piglet has been standardize, which envisaged that 30000lit of stored water could support 2000 plant plant in 250sq. m area and five piglets for 200 days during dry the spell period (November to April) of the year.

Poultry based activity:

based on per unit water requirement, 30000lit of stored water can support 200 plant plants in 250 sq.m area along with 50 poultry birds for 200 days during water stress period (November to April) of the year.

Fish and duck based activity:

The stored water in Jalkund could be partly used for crop production and partly for integration of fish cum-duck culture where Azolla is used as a feed for fish production (figure 5). In duck fish integration the duck

variety selected was the Indian runner which was found to survive well in the mid hill conditions. Excreta of duck reared in the Jalkund were also used as a fish feed. The water was used for vegetable production during December to February, an fish and duck live together in the Jalkund during the whole post rainy season without affecting water supply to the vegetable crops. The fish culture was with grass carp, Ctenopharyngodonidella and golden hybrid tilapia. These two species were selected considering their compatibility in the culture system, utilization of unwanted weeds and Azolla for raising grass carp and the effective utilization of decomposed feed materials and fecal matter of grass carp by golden hybrid tilapia. Grass carp was stocked@1 no./sq.m and golden hybrid tilapia @3 no. /m. Golden hybrid tilapia being a natural breeder, bred in the pond during the culture period and the young ones were allowed to grow even after the harvest of main stock (table size fish)in November. The study revealed that apart from meeting water requirement of rabi crops , 30000lit of water could support 1000 fish seedling of one month age ,25 fishes five months age and two ducks. By doing so, the water quality of stored water not only improved, but also income had increased.

Impact analysis based on economics:

It was observed that with 30000lit of stored water in Jalkund ,farmers can opt for three complementary diversified farm activities, viz (i)crop production and duck cum fish culture ,(ii)crop production and pig rearing (iii)crop production and poultry rearing .However ,selection and adoption of a particular farm activity depends on resources available with them to bear initial expenditure and preferential food habit ,and the income should also improve their standard of living .Economical analysis of each activity was made with the aim to select ,recommend a profitable activity for farmers, which they should adopt for properly utilizing stored water in Jalkund as well as for maintaining their livelihood. Details of economic analysis are presented in Table 3. Expenditure on seedling, feed cage and maintenance was also included in the analysis. Water requirement 90 days(December to February) for plant and 200 days (November to April) for fish was considered the analysis. Since the Jalkund is usually field directly with rain water during may-October, water during this period was not included in the calculations.Call market price of each input was also taken into consideration. If a farmer utilizes 30000 liter of water each system will be as follows:

1. Plant-pig based activity:

Water Application to for @11/days and for pig 101 days has been standardized based on this ,it was estimated that to grow 200 plant 18000 liter of water was needed for 90 days, while 10000 was needed for pig rearing for 200 days. The rest 200 could be used for miscelleous purposes.

Table 3: Economic analysis

Farming Activity	**Total Water Requirement**			**Expenditure(Rs)**				**Income**			**Profit**	**Cost**
Plant - pig	**Plant**	**Pig**	**Misc. use**	**Plant**	**Pig**	**Jalkund**	**Total**	**Plant**	**Pig**	**Total**		
	18000	10000	2000	Hybrid seed-500	Piglets-5000	Making-4205	14,205	3700	20000	23700	9495	1.67
				Other inputs-250	Feed-4000	Polypipe-250						
Plant poultry	18000	5000	7000	Hybrid seed-500	Chicks-750	Making-4205	10955	3700	15000 (egg)	18700 (egg)	7745 (egg)	1.71 (egg)
				Other inputs-250	Feed-5000	Polypipe-250						
		12000 (meat)	15700 (meat)	4745 (meat)	1.43 (meat)							
Plant-Duck Fish	18000	-	-	Hybrid seed-500	Ducklings-30	Making-4205	5835	3700	1600 (egg)	8800	2965	1.51
				Other inputs-250	Fish seed-100	Polypipe-250			2000 (mature fish)			
					Feed-500							

Plant-poultry based activity:

Water requirement poultry @500 ml/day for 200 days has been standard and total 5000 L of water was needed for 200 days

Plant fish duck based activity:

a Jalkund of 30000 L capacity can support 200 Plant plants,two ducks and about 1000 finger-lings,where 18000L of water was needed for Plant. The rest 12000 L was utilized by duck and fish for survival during the stress period. In this case, 12000 L of water was not considered as actual consumption perse, unlike other live stock. Therefore calculation of water requirement per unit was not done for fish and duck. Since the kund was small, maintenance cost, including water treatment was negligible and was not considered in the calculations. Though the total Expenditure incurred in this system was much less, net profit and B:C ratio was also less(Rs 2965 and 1.51 respectively) compared to pig and poultry based activities

If net profit and B:

C ratio of all 3 systems are compared, it is clear that Plant –Pig based Activity provided 22.6 and 220% higher profit than poultry and Fish-Duck based activity respectively[1].

Future plan

1. A sanitization programme in each state is necessary to disseminate and popularize the proven technology among farmers of western Ghat regions. In the context, linkage is needed among the research instituted, financial institutes, state departments and farm to channelize the technology from the technology producing center to farmers. Having successfully implemented the technology the farmers at 25 locations in each state where 2 Jalkund of 30000 L capacity, about 1.2 hectares rainwater may be stored in the region, which otherwise goes waste. It is also estimated that with 1.2 hectares water, 100 hectare area may be covered along with region of 2000 piglets or 20000 poultry birds and 800 ducks.
2. The technology may open options for farmers who can afford a green house, polyhouse for cultivation of vegetables/flowers/medicines/medicinal plants/orchids. Not only for fetching higher market value during off seasons, also for providing employment opportunities to run youth.
3. Usually at the hilltop, area available with farmers is cultivated and their homes are situated with cultivated field. Therefore to store water in Jalkund for longer periods during off season, collection may be linked up wherever possible.

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Antibacterial Potential of Tridax Procumbens L.

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ABSTRACT

In our present study, we carried out the antibacterial activity of plant *Tridax procumbens L.* which belongs to family asteraceae. The aim of the present work was to evaluate scientifically antibacterial potential of *Tridax Procumbens L.* Extract and its fractions. Extraction has been performed by Soxhlet apparatus with different solvents and then they get fractionated. Fractions of residue and filtrate evaluated for anti-bacterial activity by using agar-well diffusion method. Some of them fractions show remarkable activities against bacteria *Escherichia coli & Klebsiella.*
Keywords: Tridax Procumbens L, Klebsiella, Escherichia coli & Klebsella

I. INTRODUCTION

Increase of resistance to antibiotics by bacterial pathogens is a growing problem in both developed and developing countries [2]. Therefore it is required to overcome this problem by different way such as controlling the use of antibiotics, to develop research to better understanding of the genetic mechanism of resistance and to continue study to develop new drugs either synthetic or natural [3]. We know that the herbal plants are the valuable source of natural products for maintaining human health [4]. Plants are used medicinally in different countries and are a source of many potent and powerful drugs. Medicinal plants represent a rich source of antimicrobial agent [5]. Different parts of plants, herbs and spices have been used for many years for the prevention of infection. The use of plants with known antimicrobial properties can be of great significance in treatment of infections [6]. *Tridax Procumbens L.* is a plant used for its medicinal propery as a therapeutic agent with no side effects. It has been reported that the plant *Tridax Procumbens L.* have various pharmacological effects like hepatoprotective, mosquito repellant activity, leishmanicidal, immunomodulatory effect, wound healing activity and antiprotozoal effects [7,8,9,10]. The aim of the present work carried out was to evaluate scientifically the traditional use of *Tridax procumbens* as antibacterial potential. The present work aims at assessing the antibacterial property of *Tridax procumbens L.* plant extract through scientific study and to substantiate its medicinal use for infectious diseases.

II. EXPERIMENTAL

Plant collection and Preparation:

The plant *Tridax Procumbens L.* was collected from Awasari forest, Tal-Ambegaon, Dist- Pune, Maharashtra, India. The plant was identified from Botanical survey of India, Pune. A botanical specimen is preserved for further reference. The plant was dried under shade for 8-10 days. Immediately after drying, it was powdered using an electric mixer- grinder and sieved through a BSS mesh No. 85 sieve. The powdered sample was stored in airtight plastic container at room temperature for further analysis.

Extraction of Plant Sample:

Accurately weighed 20gm of the powder extracted by using a Soxhlet apparatus with mixture of methanol and water (500 ml) in volume ratio 4:1. The extract was cooled and filtered through whatman filter paper 41 and was used for further Fractionation process. The obtained residue also fractionated.

Fractionation of Residue: The residue was extracted with 125CC of (5 x 25 CC) of ethyl acetate and filtered it. The residue obtained after filtration comprised plant fibers. 0.05 gm separated fibers was weighed and transferred to 5 ml of ether and filtered through Whatman filter paper No.1. It was referred as Sample **I.**

The filtrate obtained from above process was evaporated to dryness on a water bath maintained at 45 C +- 5 ^{0}C after evaporation of ethyl acetate the beaker was allowed to cool at room temp in dessicator. It consists of fats and waxes. 0.05 gm of separated fats and waxes was weighed and transferred to 5 ml of ethyl acetate and filtered through Whatman filter paper No.1. It was referred as Sample **II**.

Fractionation of Extract:

The extract obtained was evaporated to approximately 1/10th its volume by heating in a water bath maintained at a temperature less than 70^{0}C. It was acidified with 2M H_2SO_4. The acidified filtrate was extracted using 150 ml (3 x 50 ml) chloroform in a separating funnel. The aqueous and the chloroform layers were thus separated. The aqueous Layer obtained was basified to pH=10 with 2M NaOH. It was further extracted with 120 ml (2 x 60 ml) chloroform: methanol in volume ratio 3:1 followed by extraction with 40 ml (2 x 20 ml) chloroform in a separating funnel. The aqueous Basic layer was evaporated to dryness on a water bath. After evaporation of the solvent the beaker was allowed to cool at room temp in a dessicator. It consists of quaternary alkaloids and N oxides. 0.05 gm separated alkaloids was weighed and transferred to 5 ml of Water and filtered through Whatman filter paper No.1. It was referred as Sample

The chloroform layer obtained from above extraction was evaporated to dryness on a water bath maintained at 45 ^{0}C. After evaporation of chloroform it was allowed to cool at room temp in dessicator. It consists of terpenoids. 0.05 gm of separated terpenoids was weighed and transferred to 5 ml of chloroform and filtered through Whatman filter paper No.1. It was referred as Sample **IV**.

The organic layer (Chloroform and methanol) was evaporated on a water bath at 45 ^{0}C. After evaporation of solvent it was allowed to cool at room temperature in a desiccator. After cooling the 0.05 gm of residue was weighed and transferred to 5 ml of Chloroform and methanol in volume ratio 3:1. The chloroform and Methanol extract was then collected and filtered through Whatman filter paper No.1 at room temperature. It was referred as Sample **V**.

The resulting Fractions (sample) were used to study antibacterial potential.

Sample	Solvent	Solvent extract	Weight in gm	Volume in ml
I	Ether(residue)	Fibers	0.05	5
II	Ethyl acetate	Fats & waxes	0.05	5
III	Water(filtrate)	Quaternary alkaloids & N-oxides	0.05	5
IV	Chloroform	Terpenoids & Phenolics	0.05	5
V	Chloroform & Methanol (3:1)	Alkaloids	0.05	5

Table 1 : Fractions of residue & Extract of Plant *Tridax Procumbens L.* for Antibacterial activity.

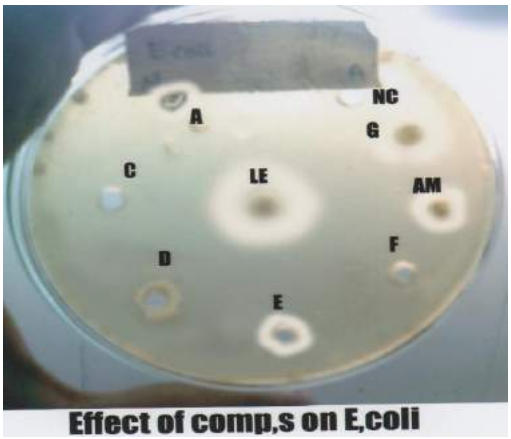
Evaluation for antibacterial Activities:

Evaluation for the antibacterial activities were carried out against bacterial strains *Escherichia coli & Klebsella* by the agar well diffusion assay using Nutrient Agar plates. The microbial work was carried out in aseptic area. The additions of the extract, medium and microbial culture was done as per standard procedure. The tubes were then inoculated with 0.05 ml of the standardized culture. The tubes were incubated at temp 37^{o}C for 24 hrs and observed for the turbidity produced. The test procedure was repeated to check the reproducibility of the result. The lowest concentration that can inhibit the growth is the Minimum Inhibitory Concentration. 40 µl of the sample was added to each well. The zones of inhibition produced by the extracts were compared with the standard Levofloxacin, Amoxycyline, Gentamycin.

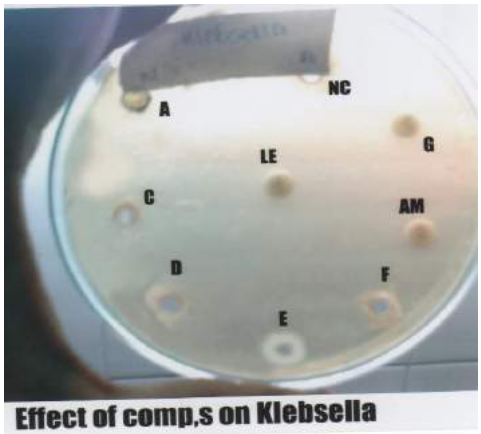
LF:Levofloxacin, **AM**: Amoxycyline, **G**: Gentamycin

Table 2: Antibacterial Activities of *Tridax Procumbens L Powder* Extracts.

Sr. No.	Sample	Bacteria	
		E.coli	*Klebsiella*
1	I	10	--
2	II	--	10
3	III	--	--
4	IV	10	10
5	V	12	--
6	LF	16	20
7	AM	10	10
8	G	--	12



Effect of comp.s on E.coli



Effect of comp.s on Klebsella

III. RESULTS AND DISCUSSION

The results of the present study observed that the extract and fractions prepared from the plant Tridax procumbens had inhibitory activity against some bacterial strains. Ethyl acetate fraction of residue (Fats & waxes) and Chloroform fraction of filtrate (Terpenoids & Phenolics) shows antibacterial activity against bacterial pathogens for Klebsiella. Ether fraction of residue (Fibers), Chloroform fraction of filtrate (Terpenoids & Phenolics) and Chloroform & Methanol (3:1) fraction of filtrate (Alkaloids) are biologically active against E. coli pathogen. As per given in table 2, aqueous fraction of filtrate (Quaternary alkaloids & N-oxides) does not show remarkable activities.

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Computational Methods of Drug Designing and Docking studies of Synthesized Derivatives of 5-substiuted-1,3,4-Thidiazole-2-amine

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ABSTRACT

A series of 2, 5-disubstitiuted 1,3,4-thidiazole derivatives were synthesized and screened their antimicrobial activities in silico as well as in vitro. In this research article main emphasis on the computational docking methods, with empirical scoring functions are used to predict binding affinities and ligand orientations inside the binding sites of proteins. Topoisomerase targets are widely used as antibacterial activity as per literature review study. In silico and in vitro studies of synthesized derivatives have comparative similar results which can be explained on molecular docking studies and structure activity relationship (SAR). Urea moiety enhances the pharmacological significance of derivatives. It has promoted research work to new direction considering all the factors such as binding sites, TPSA values, Log10P IC50 values and binding energies of the molecules.

Keywords: 2,5-Disubstitiuted 1,3,4-Thidiazole, Computational Docking Methods, SAR, Pharmacological Significance, In Silico, In Vitro

I. INTRODUCTION

James Black famously stated in 2000 that "the best way to discover a new drug is to start with an old one" [1]. Synthesis of novel molecules seems to be creativity of organic chemist. Now a day's researchers have been interested to synthesize analogues of known, proven drugs available in the market. For this Structure based drug discovery (SBDD) is a proven strategy for the rational development of small molecules of therapeutic interest without necessitating its synthesis at the preliminary stages. These are effective beta-lactamase inhibitors and potent ampicillin and cefazolin potentiators against both Gram-positive and Gram-negative beta-lactamase producing bacteria [2]. In this research article synthesized derivatives of 1,3,4-thidiazole in which disubstituted urea moiety acts as bridge between pharmacophore 1,3,4-thidiazole and another selected biologically active molecule. Synthetically and pharmacologically 1,3,4-thidiazole series of compounds have been recognized as a unique class of small compounds with a wide range of applications. 1,3,4-thidiazole derivative which has connecting urea moiety have been shown to be highly effective against various therapeutic activities, such as potent inhibitors of interleukin-8, anthelmintics, antimalarial, anti-HIV, diuretic, analgesic, antibacterial, antifungal, antimicrobial, algaecidal or antiperiphytic agents[3–6]. Literature survey reveals that N,N′-Disubstituted ureas, amides and carbamates are reported as new powerful and stable inhibitors of soluble epoxide hydrolase (SEHs), both in vivo and in vitro[7]. They were determined to be useful for the treatment of hypertension, Raynaud syndrome, respiratory distress syndrome, inflammation, diabetic complications, arthritis and renal type of diseases [8]. A urease is an enzyme that decomposes urea to ammonia and carbonic acid and provides nitrogen to an organism [9-10]. On the other hand, bacterial ureases cause different pharmacological problems, ranging from the development of infectious stones, pathogenesis of encephalopathy, pyelonephritis, urinary catheter encrustation and hepatic coma to peptic ulceration[11–14].

Despite the wealth of structural information, the role of SBDD has been limited to suggest the analogues of existing leads and to post-rationalize the bioactivity data. Therefore, in this work, molecular docking is the primary computational method chosen for the identification of potential target specific ligands (lead generation), synthesis and biological evaluation were

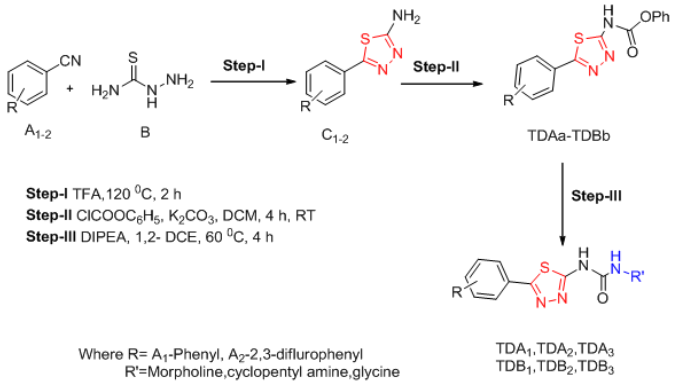
carried out in pursuit of designing some potential novel antimicrobial compounds carrying 1,3,4-Thiadiazoles ring as core nucleus.

II. EXPERIMENTAL

Methodology: Computational methods:
Software and program Schrodinger's maestro visualization program v9.6 [15] is utilized to visualize the receptors, ligand structures, hydrogen bonding network, to calculate length of the bonds and to render images. Chemsktech was used to draw the ligand compounds. Autodock 4.0 [16] is the primary docking program used in this work for the semi-flexible docking studies. Preparation of the ligands and protein receptors in pdbqt file and determination of the grid box size were carried out using Auto-Dock Tools version 1.5.6. Molinspiration, Orissis property explorer program was used to study the ADMET properties of the compounds. The crystal structure of the Topoisomerase IV (PDB ID: 3FV5) was obtained from the Protein Data Bank (PDB) [17]. The crystal structure contained many missing atoms which were supplemented by the repair commands module of AutoDock. Before docking, the protein crystal structure was cleaned by removing the water molecules. H-atoms were added to these target proteins for correct ionization and tautomeric states of amino acid residues. The modified structure so obtained was used for the semi-flexible dockings. The ligand molecules were drawn using chemsketch software. The energy of the ligand molecule and receptors were minimized in Steepest Descent and Conjugate Gradient methods using Accelrys Discovery Studio (Version 4.0, Accelrys Software Inc.) [18]. The minimization methods were carried out with CHARMM force field [19]. Semi-flexible docking Autodock Version 4.0 is used to predict binding pose with associated energy along with the IC_{50} value prediction of the compounds with drug target Topoisomerase IV (PDB ID: 3FV5) for anti-bacterial activity . Protocol followed for carrying out the docking studies using Autodock.

Chemistry:

General Scheme:



III. RESULTS AND DISCUSSION

Docking Studies of Synthesized Derivatives:
The binding energy of synthesized derivatives -4.40 to -6.84 Kcal/mol with critical interactions with residues hydrophobic interactions ALA A:86, GLU A:82, LEU A:89, HIS A:79, LEU A:94, ARG A:93, ILE A:90, SER A:117, VAL A:118, LEU A:91 with a half maximal inhibitory concentration (IC_{50}) value in between 1.97 to 50.0 micro molar. As per the docking study the best compound of docking interactions with Topoisomerase IV (PDB ID: 3FV5) for anti-bacterial activity is depicted below:

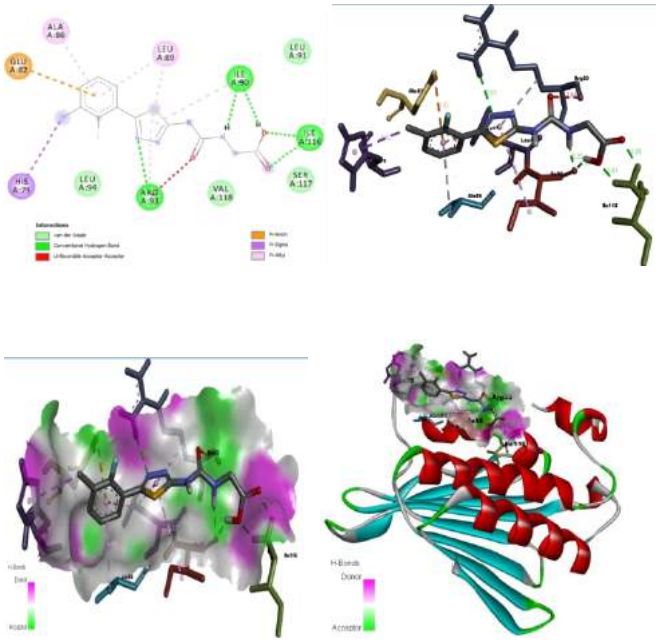


Figure 1. a) represents 2D interactions b) represents 3D interactions c,d) represents surface area interactions with Topoisomerase IV.

All the derivatives of 2, 5-disubstitiuted 1, 3,4-thidiazole were studied in this research work. They have shown to be successfully docking inside the active site of Topoisomerase IV (PDB ID: 3FV5) domain for anti-bacterial activity with a binding energy in a range of -4.40 to -6.84 Kcal/mol. The docking results with some of the FDA approved drug (Cefazoline) was identified and compared with docking studied synthesized derivatives. They are showing better binding energies than these controls.

IV. CONCLUSION

The present investigated derivatives of 2, 5-disubstitiuted 1, 3,4-thidiazole offers the possibility of appropriate additional modifications that could give rise to lead structures with enhanced inhibitory activity and selectivity towards the drug receptor target like Topoisomerase IV. The knowledge gained through this present study could be of high value for computational screening understanding the molecular interaction basis between ligand and receptor.

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Master Gas Chromatographical Identification of Condom Lubricants

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ABSTRACT

In most of the cases of sexual assault, scientists are in search of biological evidences like blood, skin, hair, saliva, urine, semen for DNA analysis. The uses of condoms in sexual assault cases were now increasing to avoid leaving the biological traces in the crime scene. In these cases, finding of the condom lubricant traces from victims can play a vital role in sexual assault cases. It has been found that gas chromatography gives an important method of such identifications. Gas chromatography was one of the important analytical tools used in majority of forensic laboratories. In present study condoms were referred to forensic science laboratories from police station was used to analyze these lubricants. The finding shows that majority of condom lubricants used were polydimethylsiloxane (PDMS). The Gas chromatograph spectra database of lubricants can be used to provide associative evidences between victim and sexual assailants.

Keywords: Gas chromatography, Condom lubricant and victim.

I. INTRODUCTION

In cases of sexual assaults, it is often found that the physical evidences from the victim are used for DNA analysis to obtain some evidences. Recently due to increasing public awareness, the offender often wore a condom to avoid the proof of biological evidences at the crime scene [1-6]. A vaginal swab may be taken from the victim to examine the condom lubricants even though the small amount of the lubricants can be found for analysis purpose [4, 7]. By analyzing the condom lubricants, one can obtain the valuable intelligence information between the victim and the suspect. Such trace evidences associated with the use of a condom can originate from the condom or additional use of lubricants. The components of the lubricants or additives used on condoms available in different brands are considerably different [5]. Condoms are manufactured from several materials, primarily synthetic polymers and sheep caecum. But the majority of condoms are made from latex rubber, which has the chemical structure *cis*-1,4-polyisoprene [8,9]. The major components can be used as the lubricants on condoms, such as polydimethylsiloxane (PDMS), polyethylene glycol (PEG), polypylene glycol (PG), and glycerin, though PDMS is far more common [5,10]. Some type of condoms may contain additives that give the lubricant formula with specific desired properties, such as its color, flavors, and perfumes [5, 10, 11]. In this study, we found that the oil lubricants and non-spermicidal condoms. Previous researches had used several techniques to detect lubricants on condoms, such as FTIR, high performance liquid chromatography (HPLC), NMR spectroscopy, Matrix-assisted laser desorption or Ionization-time of flight-mass spectrometry (MALDITOF- MS), Capillary electrophoresis, PyGC-MS, GCMS, and Raman spectroscopy [12]. Maynard et al. provided that the extraction and analytical protocol for lubricant analysis purpose from cotton swab. They showed that the infrared spectra may reveal the major type of the lubricants. For further discrimination of the lubricants or confirmatory identification test, PyGC-MS, fluorescence microscopy and fluorescence spectroscopy can be used as one of the technique [1]. Condom lubricants have been analyzed by using capillary electrophoresis (CE) by Burger et al. They showed that CE can detect and discriminate condom lubricants; however this instrument is not much common in forensic science laboratories. The limitation of this technique is that CE cannot identify lubricant residues correctly after lubricant 34 Forensic Science Journal 2012; Vol. 11, No. 1 recovery from the skin and cloth surfaces taken after 30min [5]. Lee et al. showed that NMR is a method capable of distinguishing between sexual lubricants used

in condoms by the different manufacturers. They developed the flow chart for differentiation of condoms using NMR method that could be easily implemented in any forensic laboratories [8]. However, the sample preparation and analysis time for NMR is time more and time consuming. NMR analytical method may not ideal for trace detection purpose [10]. In Hollenbeck et al.'s research, LC/ESI-MS, nano ESI-MS and MALDI-FTMS have been shown to be capable for identifying the traces of the spermicide nonoxynol-9 from internal vaginal swabs taken postcoitus, and in an actual evidence sample [13]. Spencer et al. had clearly shown that MALDI-TOF-MS is ideal for detecting condom lubricants and additives, especially the trace evidences were condom and personal lubricant residues and their mixtures with biological fluids. This research also used ATR-IR spectra to find the additives to the lubricant formula that were either undetectable or poorly detected in the mass spectrometer. ATR-IR provided valuable information about the additives found in PDMS-based lubricants. The present task showed that Infrared spectroscopy can used to support and clarify the MALDI data [10]. In recent year, gas chromatograph becomes the most popular instrument in the forensic science laboratory. Gas chromatographic analysis is the standard method for routine screening of swabs recovered from the sexual assault with respect to lubricants identification [2, 3, 12, 14]. Blackledge et al. had developed a protocol for the recovery of latex condom lubricants traces and their identification. FTIR was used to identify the PDMS and nonoxynol-9. They also used the desorption chemical ionization mass spectrometry (DCI-MS) to compare the PDMS from the different manufactures, the amount of sample size can reduced to 20mg of the material. PDMS tend to remain in the vaginal vault and had been successfully recovered and identified up to 24 hours after sexual intercourse [2,3]. In another Blackledge's research, they measured the viscosity by using Fourier selfdeconvolution (FSD) method to resolve overlapping IR spectral bands. They were successful in determining the average chain length of different PDMS polymers. FTIR with FSD could also be used as a preliminary screening procedure to identify PDMS traces and to determine the approximate viscosity [14]. Raman spectroscopy is a one of the complementary technique of FTIR. Coyle and Anwar have shown that Raman spectroscopy is an excellent tool for the screening of swabs for condom lubricants prior to DNA analysis. They found the majority of condoms were PDMS lubricants on the UK market [15]. Forensic scientists prefer using nondestructive methods of analyzing trace evidences rather than using destructive methods. Image documentation spectroscopy is a spectroscopic technique used for the nondestructive identification of molecular species, including polymer. In the forensic laboratory, trace evidences such as explosives, fibers, paints, pigments, drugs, inks, gunshot residues and forgeries and fakes can be analyzed by Image documentation. Gas chromatogram technique in the forensic science is sensitive enough for to detect the traces of the condom lubricants in extracts from cotton swabs. The purpose of present investigation is to use Gas chromatogram analyzing the condom lubricants associated with crime exhibits. Hopefully, the Gas chromatogram and image documentation database of the condom lubricants can give the information and spectral comparison for the forensic laboratories.

Chemicals and Reagents:

The chemicals Ether, used for analysis was HPLC grade and milli Q ultra pure water is used.

Preparation of sample Solution:

Cotton swabbing of condom was recovered from suspected accuse and recovered from crime scene were taken and extracted with 10ml of ether and further extract were concentrated to 1ml and injected on gas chromatogram for analysis.

II. Methods and Material

Instrumentation:

Gas chromatography

(A) The Gas liquid chromatography (DANI MASTER Gas Chromatograph) coupled with FID

(B) Operating Conditions: The following operating parameters were used

Column (Capillary): Dani–DN-5 MS capillary column (5% phenyl) - 95% Methyl polysiloxane Film thickness is 0.25µm, max temperature used 350ºC Non polar bonded and cross-linked, inertness low bleeding and of Good thermal stability

Column Material: The Capillary Length of 30mm, O.D 0.25mm, I.D. 0.25mm

Carrier Gas : Nitrogen, with flow rate 30ml/min.

Fuel : Hydrogen, flow rate 35ml/ min.

Air : Flow rate 350ml/min.

Split flow : 1:50

(C) Programming

A. Oven initial Temperature used is 240°C.
B. hold for 2 min
C. Heating Rate is 20°C
D. Oven final Temperature is 280°C
E. Injector Temperature is 280°C
F. Detector Temperature is 285°C

Image documentation : Make – Aetron

III. Results and discussions

Identification of Condom Lubricants by using the DANI master gas chromatograph technique, were done by using the samples prepared as per sample preparation were injected on gas chromatogram. The modular design of DANI master gas chromatograph components allows easy changing any GC configurations. Three injections units and three detectors units were mounted simultaneously. Dani selective detectors specifically eliminate the matrix interferences while providing the maximum sensitivity. The detectors data acquisition rate used is up to 300Hz for a better reproducibility and accuracy of chromatographic results. The Gas sampling valves, auxiliary ovens, switching valves and other optional devices make DANI MASTER Gas Chromatography as the most suitable gas chromatograph for the development of complex analytical systems in a wide range of applications. DANI MASTER GC can be connected to DDS CLARITY work station through a local area network (LAN). Dedicated turnkey systems are the added value of all DANI instruments. DANI MASTER GC coupled with DANI HSS 86.50 Head space sampler and DANI TD Thermal desorber, covers a wide range of applications for the environmental, chemical petrochemical pharmaceutical, food and beverages.

On condoms three types of lubricants were found and are polydimethyl siloxane (PDMS) polyethylene glycol (PEG) and glycerin, the majority condom lubricants were PDMS-based lubricants. Figure 1shows gas chromatogram of condom seized from accuses. Figure 2 shows gas chromatogram of condom seized from accuses. Even though some of the condoms indicated special favors, scents and colors, gas chromatogram can indicates the differences between them. If we overlay the gas of we can definitely conclude weather these are of same or not. However, gas chromatogram is a good and sensitive tool to detect the very minar amount of evidences.

Methods Applied for Detection of semen in condom are Classified as: [16]

1. Physical Examination
2. Chemical Examination
3. Microscopic Examination

Physical Examination
This includes the visual Examination. To naked eye seminal stains generally appear translucent or opaque spots, at times with yellowish tint and darker border depending on colour and thickness of substrata, which, if absorbent, also acquire stiffness due to dried semen. On good substrata seminal stains may appear to be fluorescent under the ultraviolet light.

Chemical examination:PH = 7.4 Alkaline.
The tests used to detect Seminal Stains are:

1. Florence Test
2. Barberio Test
3. Acid Phosphatase Test

MICROSCOPIC EXAMINATION:

The Microscopic detection of the seminal stains is based on morphology of spermatozoa. All above methods were applied for the detection of semen stain. It gives positive presence of semen in condom found at crime scene. Individualization of semen stains with help of Absorption elution method and cross over the electrophoresis technique.

Table remaining

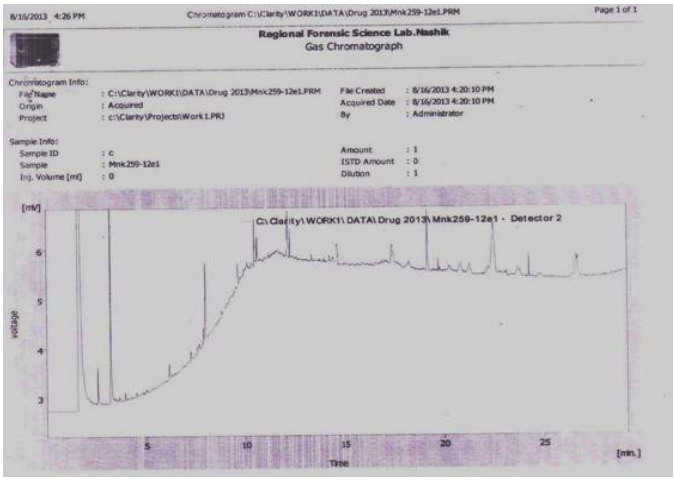

Figure 1. Gas chromatogram of condom seized from accuses.

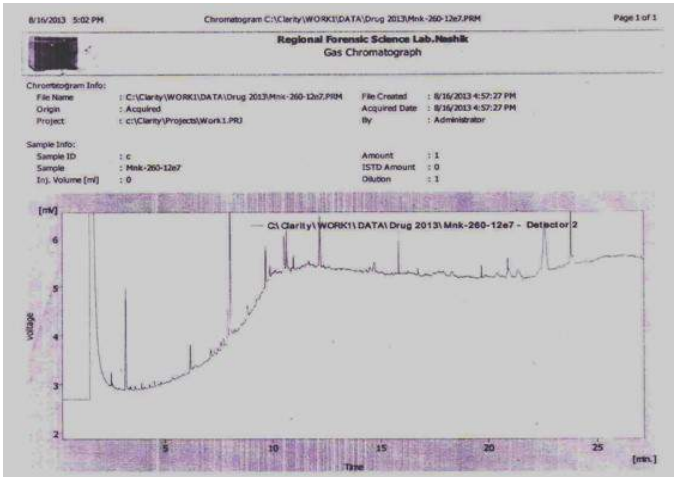

Figure 2. Gas chromatogram of condom seized from crime scene.

Figure 3. Spectrum taken on image documentation in top visible and trans visible mode.

Figure 4. Spectrum taken on image documentation in top visible and trans ultra violet mode

Figure 5. Spectrum taken on image documentation in top UV and trans ultra violet mode.

IV. Conclusions

Condom lubricants have very good gas chromatogram and they can be identified with the help of gas chromatography. The Gas chromatogram is available in most of the forensic laboratories but it may not be sufficient to distinguish the polymers having the similar structures. Image documentation has shown that it is the most useful technique to analyze condoms as well as trace evidences collected for analysis in the forensic laboratories. This preliminary study gives a basis for further research to develop other good techniques for classification of condom lubricants in future.

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Polyethylene Glycol (PEG-400): As Green Reaction Media for Rapid Synthesis of Preparation of Isoxazolinederivatives and Its Antimicrobial Screening

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ABSTRACT

We wish to describe an efficient and rapid synthesis of isoxazolines by the reaction of substituted pyrazol-5-one were condensed with hydroxylamine hydrochloride in presence of clay (pH =12.5) and PEG-400 as a green reaction media. Herein, we report the conventional condensation method of substituted pyrazol-5-one with hydroxylamine hydrochloride in PEG-400 as reaction solvent at mild reaction condition. Structures of the synthesized compounds were confirmed by the spectral analysis. Furthermore, all the synthesized compounds were evaluated for their antimicrobial screening against several pathogenic representatives, these newly synthesized compounds were screened for their antimicrobial activity against bacterial strain Escherichia coli (MTCC-443), Bacillus subtilis (MTCC-441), Staphylococcus aureus (MTCC-96) and Salmonella typhi. (MTCC-98). The antifungal activity was evaluated against Aspergillus niger (MTCC-1781), Aspergillus flavus (MTCC-3008), Candida albicans (MTCC-227) and Penicillium chrysogenum (MTCC-160).The result revealed that most of the compounds showed good to moderate Antimicrobial screening. The major advantages of this protocol are it gives excellent yields of products, work up procedure and isolation is easier, Procedure is green and environmentally benign, shorter reaction times.
Keywords : Pyrazolone, Isoxazoline, PEG-400, Clay(pH =12.5) andAntimicrobial activity.

I. INTRODUCTION

Isoxazoline derivatives are useful as intermediates in the organic synthesis, polymers, pharmacologically active materials, dyes and pesticides.They are possessing fungicidal, antimicrobial, bactericidal and mutagenic activities.Isoxazolines possess various biological and pharmacological activities. In addition, they find application as dyestuffs, auxiliaries in fiber finishes, dropping dye in the electroluminescence device and in liquid crystalline mixture. Isoxazolines are biologically active, synthetically useful and important heterocycles having wide role in medicinal chemistry.Synthesis of novel isoxazoline derivatives remains a main focus of medicinal chemist, due to their diverse pharmacological activity. Isoxazoline derivatives have been reported to possessantibacterial[1],antifungal[2,3]anti-inflammatory[4], anticonvulsant[5], analgesic[6]andantiviral[7]activity.

Much research has been carried out with the aim to finding therapeutic values of isoxazolines moiety since their discovery. A large number of substituted isoxazoline derivativesare prepared and tested for variety of biological activities. Such as antimicrobial activity[8, 9]and hypolipemics[10].

Keeping these therapeutic interest and biological observations of isoxazolines in mind and in continuation of our research work on the synthesis of biologically active heterocyclic compounds [11-12], it was planned to synthesize some new series of isoxazolines derivatives.

II. Experimental Section

Melting points were determined by an open capillary method and are uncorrected. The chemicals and solvents used are of 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 methods for the synthesis of Isoxazolines:

A mixture of substituted pyrazol-5-one (0.001 mmol) and hydroxylamine hydrochloride (0.0015 mmol) was heated in (pH =12.5) and PEG-400 as a reaction media for 2-3 hrs. After completion of the reaction (checked by TLC), the contents were poured into ice-cold water. Solid get separated was filtered and washed by distilled water 20x2 mL, wet solid dried at 60-65°C, recrystallized from absolute ethanol to get pure isoxazolines . Aqueous MLR distilled under reduced pressure at 65-70°C to recover Poly (ethylene) glycol (PEG-400), which is reusable up to second recycle for same reaction. The structures of isoxazolines were confirmed by spectral analysis (IR, ^{1}H NMR and MS).

Spectral data of selected compounds:

1.3-(2-butyl-4-chloro-1H-imidazol-5-yl)-4-methyl-6-phenyl-3a,6-dihydro-3H-pyrazolo[3,4-] isoxazole(IIIa)

IR (KBr): 3300, 3188, 2926, 1616, 1564, 820, 690 cm^{-1}.^{1}H NMR (DMSO-d_6) : δ 0.93 (t, 3H, -CH_3), 1.33 (m, 2H, -CH_2), 1.66 (m, 2H, -CH_2), 2.13 (s, 3H, -CH_3), 2.68 (t, 2H, -CH_2), 3.45-360 (dd, 1H, H_a), 4.4-4.6 (dd, 1H, H_b),7.2-7.9 (m, 5H, Ar- H), 8.3 (s, 1H, -NH, D_2O exchangeable)ppm.Mass (m/z) [% rel. intensity]: 357[M^+ ion], 272[10], 254[45], 209[15], 183[18], 167[25],139[57], 111[30], 92[15], 77 [100], 65[40], 51[50].

2.3-(3-(4-chlorophenyl)-1-phenyl-1H-pyrazol-4yl)-4-methyl-6-phenyl-3a,6-dihydro-3H-pyrazolo[3,4-c]isoxazole(IIIc).

IR (KBr) : 3442, 3057, 2956, 1599, 1492, 748, 690 cm^{-1}.^{1}H NMR (DMSO-d_6) : δ 2.25 (t, 3H, -CH_3), 3.2-3.3 (dd, 1H, H_a) 4.45-4.6 (dd, 1H, H_b), 7.10-8.00 (m, 14H, Ar- H + s, (pyrazol ring)ppm.

Mass (m/z)[% rel. intensity]: 453[M^+ ion],407[8], 274[35], 231[10], 168[12], 155[100], 147[12], 119[20], 91[12], 76[12], 63[10].

3.4-methyl-3-(3-(4-nitrophenyl)-1-phenyl-1H-pyrazol-4-yl)-6-phenyl-3a,6-dihydro-3H-pyrazolo [3,4-c]isoxazole(IIId).

IR (KBr: 3404, 3300, 2926, 1616, 1564, 839,690 cm^{-1}.^{1}H NMR (DMSO-d_6):δ 2.20 (t, 3H, -CH_3), 3.23-3.36 (dd, 1H, H_a), 4.50-4.66 (dd, 1H, H_b), 6.90-8.22 (m, 14H, Ar-H+ s, 1H, (pyrazol ring)ppm.Mass (m/z) [% rel. intensity]: 464[M^+ ion], 415[35], 359[34], 323[40], 282[26], 280[30],249[55], 232[10], 212[15], 185[18], 171[50], 92 [100],65[48], 43[40].

Table 1. physicoanalytical data ofSynthesized of Isoxazoline derivatives.

Entry	Product No.	Mol. Formula	Yield %	M. P. (°C)
1	IIIa	$C_{18}H_{20}ClN_5O$	88	138-140
2	IIIb	$C_{15}H_{14}N_4OS$	90	119-121
3	IIIc	$C_{26}H_{20}ClN_5O$	86	154-156
4	IIId	$C_{26}H_{20}N_6O_3$	88	156-158
5	IIIe	$C_{17}H_{13}ClIN_3O_2$	92	120-122
6	IIIf	$C_{18}H_{16}IN_3O_3$	90	113-115
7	IIIg	$C_{17}H_{15}N_3O_2$	84	102-104
8	IIIh	$C_{17}H_{14}ClN_3O$	86	92-94
9	IIIi	$C_{17}H_{14}FN_3O$	88	90-92
10	IIIj	$C_{19}H_{20}N_4O$	86	96-98

General Mechanism:

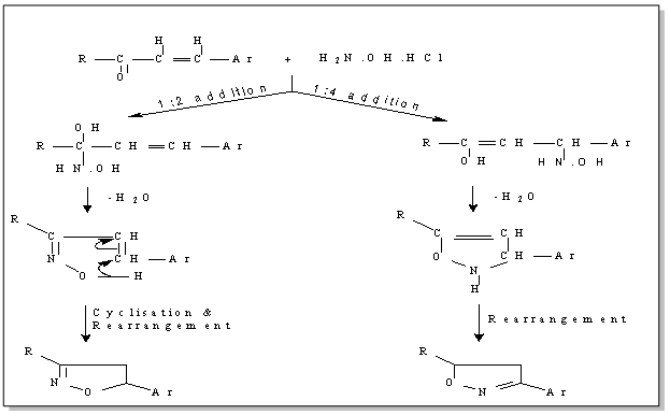
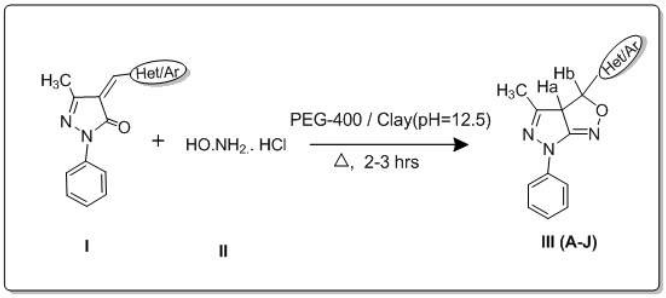


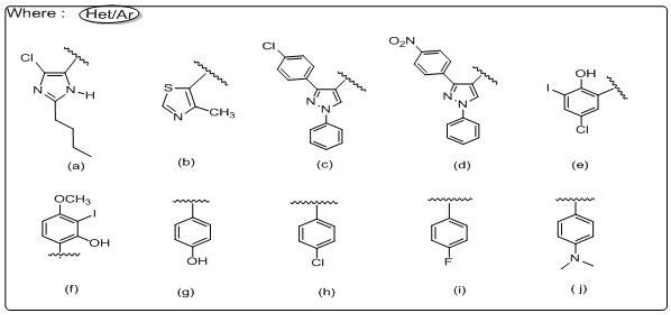
Table 2. Effect of solvent on the reaction of 3-(2-butyl-4-chloro-1H-imidazol-5-yl)-4-methyl-6-phenyl-3a,6-dihydro-3H-pyrazolo[3,4-c]isoxazole(IIIa)

Entry	Solvent	Time (h)	Yield (%)
1	EtOH	6	68
2	THF	6	75
3	Dioxane	4	74
4	Acetonitrile	5	67
5	PEG-400	130(min)	86

Reaction Scheme:



Synthesis of isoxazolines from Pyrazol-5-ones with hydroxylamine hydrochloride:



Antimicrobial Screening:

The antimicrobial activities of the synthesized compounds **III(a-j)**were determined by agarwell diffusion method[13].The compounds were evaluated for antibacterial activity against*Escherichia coli (MTCC-443)*, *Bacillus subtilis(MTCC-441), Staphylococcus aureus(MTCC-96)*and *Salmonella typhi. (MTCC-98)* The antifungal activity was evaluated against *Aspergillusniger*(MTCC-1781), *Aspergillus flavus (MTCC-3008), Candida albicans(MTCC-227)* and *Penicilliumchrysogenum(MTCC160)* were procured from Institute of Microbial technology (IMTech),Chandigarh, India. The antibiotic penicillin (25µg/mL) was used as reference drug forantibacterial and *Nystatin* (25µg/mL) used as antifungal activities. Dimethyl sulphoxide (1%, DMSO) was used a control without compound.

The culture strains of bacteria were maintained on nutrient agar slant at 37±0.5 °C for 24hrs. Theantibacterial activity was evaluated using nutrient agar plate seeded with 0.1 mL of respectivebacterial culture strain suspension prepared in sterile saline (0.85%) of 105 CFU/mL dilutions.The wells of 6 mm diameter were filled with 0.1 mL of compound solution of concentration 25to 150µg/mL separately for each bacterial strain. All the plates were incubated at 37±0.5 °C for24 hrs. Zone of inhibition of compounds in mm were noted and minimum inhibitoryconcentrations (MICs) were noted. The results of antibacterial studies are given in Table 2. For antifungal activity, all the culture strains of fungi maintained on potato dextrose agar (PDA)slant at 27±0.2 °C for 24-48 hrs, till sporulation. Spore of strains were transferred in to 5 mL ofsterile distilled water containing 1% Tween-80 (to suspend the spore properly). The spores were counted by haemocytometer (106 CFU/mL). Sterile PDA plate was prepared containing 2% agar;0.1 mL of each fungal spore suspension was spread on each plate and incubated at 27±0.2 °C for12 hrs. After incubation well prepared using sterile cork borer and each agar well was filled with0.1 mL of compound solution at concentration 25 - 150 µg/mL. The plates were kept inrefrigerator for 20 minutes for diffusion and then incubated at 27±0.2 °C for 24-28 hrs. Afterincubation, zone of inhibition of compounds were measured in mm along with standard andminimum inhibitory concentrations (MICs) were noted. The results of antifungal studies aregiven in Table 3.

Table 3. Antibacterial activity of synthesized compounds III(a-j)

Product	*Escherichia coli(MTCC-443),*	*Bacillus subtilis(MTCC-441),*	*Staphylococcus aureus(MTCC-96)*	*Salmonella typhi. (MTCC-98)*
IIIa	22(25)	16(25)	16(25)	16(25)
IIIb	18(25)	15(25)	18(25)	14(25)
IIIc	20(25)	16(25)	28(50)	16(25)
IIId	18(50)	17(25)	26(50)	22(50)
IIIe	22(50)	11(50)	11(50)	30(50)
IIIf	19(50)	15(50)	10(50)	30(50)
IIIg	29(50)	12(50)	25(50)	18(50)
IIIh	16(50)	18(50)	14(50)	----
IIIi	20(50)	------	16(50)	32(50)
IIIj	26(50)	14(50)	-----	18(50)
Reference-1	24(25)	18(25)	24(25)	18(25)

Table 4. Antifungal activity of synthesized compounds III(a-j)

Product	*Aspergillus niger*(MTCC-1781)	*Aspergillus flavus (MTCC-3008)*	*Candida albicans (MTCC-227)*	*Penicillium chrysogenum(MTCC160)*
IIIa	20(25)	17(25)	16(25)	16(25)
IIIb	19(25)	20(25)	17(25)	15(25)
IIIc	19(25)	22(25)	14(25)	14(25)
IIId	15(25)	14(25)	-----	17(25)
IIIe	18(50)	10(50)	20(50)	19(50)
IIIf	19(25)	19(25)	18(25)	14(25)
IIIg	14(50)	-----	15(50)	-----
IIIh	18(50)	14(50)	12(50)	16(50)
IIIi	14(50)	15(50)	------	15(50)
IIIj	15(50)	12(50)	18(50)	15(50)
Reference-2	20(25)	18(25)	22(25)	18(25)

Zone of inhibitions are expressed in mm, MIC values (mg/mL) are given in brackets. Reference-1=Penicilllin, Reference-2=Nystatin, -- MIC > 50 mg L –1, Solvents: DMSO, water

The examination of the data Table (3) and Table (4) reveals that majority of the compounds showed antibacterial and antifungal activity when compared with standard drug. The results of in vitro antibacterial activities of compounds III(a-j)against various bacterial strains are summarized in Table 3. It has been observed that some of compounds exhibited interesting antibacterial activity. In comparison with reference antibacterial, compounds IIIa, IIIb and IIIc shows good zone of inhibition against *Escherichia coli* as well as Compounds IIIa,IIIc and IIId were also displayed comparative activity against *Bacillus subtilis*. Compounds IIIa and IIIb display moderate to good activity against *Staphylococcus aureus*. IIIa and IIIc shows promising activity against *Salmonella typhi.*IIIh, IIIi, and IIIj display reduced activity against all tested bacteria.

Antifungal data in Table 4 revealed that compounds IIIa, IIIb, IIIc andIIIf showed good to moderate activity against *Aspergillus niger*. Compounds IIIa, IIIb, IIIf and IIIc were showed most promising activity compared to standard antifungal against *Aspergillus flavus*. Compounds IIIb and IIIf were showed good activity against *Candida albicans*. Only the compound IIIa,IIIb and IIId was showed stronger activity compared with standard drug against Penicillium chrysogenum. When structure activity relationships are concerned, the antimicrobial activity might be increased by the presence of halo (I, Br and Cl) groups as substituents position.

Considering the results obtained from antibacterial and antifungal activities, it is possible to say that most of the tested compounds showed good zone of inhibition against bacteria and fungi also the minimum inhibitory concentrations (MICs). Therefore, the present study is useful drugs in medicinal investigation against bacterial and fungal diseases.

III. Result and Discussion

In continuation of our work on the synthesis of some new bioactive heterocyclic compounds [14-15],herein we report new series of Isoxazoline derivatives by the condensation of pyrazol-5-onewith hydroxylamine hydrochloride using basic clay in polyethylene glycol (PEG-400) as a green reaction solvent**.**The reaction went to completion within 130 to150 minutes and corresponding product III**(a-j)** was obtained in 86-92% yield. In order to optimize the reaction conditions, we carried out the above reaction in different solvents such as ethanol, tetrahydrofuran, dioxane, acetonitrile and polyethylene glycol-400 (Table2). We found that polyethylene glycol-400 as an efficient reaction medium in terms of reaction time as well as yields (86-92%). Encouraged by the results, we turned our attention to variety of substituted isoxazoline derivatives. In all cases, the reaction proceeded efficiently in high yields at 60°C using PEG-400 as an alternative reaction solvent. Again these synthesized compounds were characterized by IR,NMR and Mass.The IR spectra showed characteristic absorption band at 1590-1620 cm^{-1} due to C=N stretching. Beside these bands 680–800 cm^{-1} due to C-Cl stretching,^{1}H NMR of the isoxazoline showed following type of peak which confirmed the formation of product and mass spectra confirmed representative molecular weight of the compound. These newly synthesized compounds were screened for their Antimicrobial screening, the results obtained from antibacterial and antifungal activities, it is possible to say that most of the tested compounds showed good zone of inhibition against bacteria and fungi also the minimum inhibitory concentrations (MICs).

IV. Conclusion

In conclusion, our protocol is a practical approach which uses of Clay(pH =12.5)) and PEG-400as a commercially

available, low-cost, easily available solvent. In most cases, the reaction proceededsmoothly to produce the correspondingderivatives. The reactionwas clean and the products were obtained in excellent yields without formation of anyside products.

V. Acknowledgements

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Perspectives on Virtual Animal Dissections as Alternatives : Green Approach to Biodiversity Conservation

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ABSTRACT

Students and researchers in life sciences using experimental animals for dissections, every year millions of experimental animals are used all over the world. The distress, pain and death experienced by animals during dissections have been one of the debating issues among researchers and conservation bodies for long time. Besides the major concern of animal ethics and environmental conservation there are various disadvantages of animal dissections such as habitat destruction, enormous degradation of biodiversity, massive ecological imbalance, natural calamities etc. animals obtained from natural habitat and purposely bred in facilities that profit from their sales also most of animals are target of animal dealers who makes money from stealing and selling. In concern with this the University Grants Commission has issued the Notification under 12(j) of UGC Act, 1956 (UGC guidelines –Point No.7.3.1, Page no.4) urging all the universities to stop the dissections of animals, accordingly animal dissection has to be replaced with animal dissections software for virtual dissections.

Key words: Animal ethics, Virtual dissections, Biodiversity Conservation, UGC.

I. INTRODUCTION

Most of the student of basic sciences , life sciences and medical sciences need to learn animal anatomy , histology and physiology by means of animal dissection, every year millions of experimental animals are used all over the world. The distress, pain and death experienced by animals during dissections have been one of the debating issues among researchers and conservation bodies for long time. Besides the major concern of animal ethics and environmental conservation there are various disadvantages of animal dissections such as habitat destruction, enormous degradation of biodiversity, massive ecological imbalance observed. Theory books provides only theoretical information's what about practical knowledge which gain through animal dissections but it has various problems which are solved by technology , various alternatives to animal dissections were proposed to overcome this. With the technology we have various 3D virtual programs as well as virtual models that can replace the experimental animals.

Most of the foreign and Indian universities had replaced the traditional methods of animal dissections and experimentations with alternatives of virtual dissections for the student of basic sciences, life sciences and medical sciences. Non animal dissections not only beneficial for biodiversity conservation but also ethical, eco -friendly and cost effective. Most of the educational stake holders are discovering a kinder way to teach and study life science by implementing non animal dissections and accepting virtual way of dissections.

II. Dissection Alternatives

There are hundreds of alternatives for educators and students to replace dissections by Virtual softwares, models, Videos CD- ROM, Videos, Charts and much more.

Students and researchers in life sciences and medical sciences developing their own ways of understanding anatomy with their cognitive and manual skills by using physical and virtual models ,videos, e-books and activity sets. In fact most of Medical colleges, Schools of basic sciences, Veterinary schools does not recommended dissections as part of curriculum but are using modern technology for the same.

III. Virtual / Computer models

Various alternative to animal dissections were proposed to overcome dissection problem, it also avoids the ethical procedures .A strategy of 3Rs (Reduction, Refinement and Replacement) is applied as the alternatives for animal dissections. Different virtual dissections, methods and alternative software are applied to implement this strategy most of the available alternatives with advantages and disadvantages are discussed in this review.

3.1 Examples of featured programs.

A) Digital frog: Total interactive frog dissection by means of Digital frog 2.5 including detailed anatomy, all major systems with more than seventy digital detailed screens it is good for video demonstrations.

B) V- Frog: It is world's first virtual reality based frog dissection software which is designed for life science education. By using simple PC a teacher and student can pick up dissecting instrument like scalpel and cut open the frog and easily study anatomy and physiology just like physical frog.

C) Cat dissection: CatWorks help students to perform exciting very accurate virtual cat dissection through the use of special buttons and cursors, student able to dissect nearly all areas of cat internal organization, movies also shows selected options of actual dissections along with voice descriptions of detailed procedures , it also include laboratory practices and comparative histology .

D) Emantras rat dissection: It is virtual rat dissection app is available for the iPad , it features vivid 3D images of the rats internal anatomy ,step by step descriptive instruction with procedures help to learn accurately.

E) Virtual Canine Anatomy : It is Developed by Colorado State University **,** it is an innovative program for student to learn canine anatomy with interactive photograph and description , it also magnify interesting structures .This program also includes a dissection guide which covers osteology , dentition anatomy etc.

G)Froguts Fetal pig : It combines detailed technology of dissection with computer technology to bring students an effective mean of learning anatomy .

Some other animal models are: *Earthworm,Fish,Cockroach,prawn,Scoliodon,Pigeon , Mussel,Crab,Grasshopper etc.*

3.2 Educational Grants: PETA can provide grant for software purchase.

IV. Online dissections programs and Alternative websites:

Following are major online dissection programs and websites

Anatomy in Clay® Learning System, Glencoe Interactive Dissections , Froguts, Kidwings ScienceWorks, Virtual Frog Dissection Kit, Virtual Pig Dissection (VPD), Earthworm serviceheb@gmail.com, Clam Dissection Virtual Mouse Necropsy, Cockroach Dissection ,The Virtual Pig Dissection Cow's Eye Interactive Frog Dissection Starfish Dissection CrayfishDissection , Sheep Brain Dissection: Squid Dissection Rat Dissection Guide I and II ,

Alternatives Databases:

NORINA (Norwegian Inventory of Audiovisuals): http://oslovet.veths.no/NORINA The NORINA database has information on over 3,000 computer programs, laser discs, films, slide series, 3-D models and classroom charts that can be used as alternatives or supplements to the use of animals in all levels of education.

V. Stakeholders involvement

There are hundreds of alternatives are available to replace dissections, biodiversity conservation in team work, whether you are Parent, Student, Researchers, Educators who concern with use of animal in education there are many things you can do for replacement of animals from dissections and conserving our valuable biodiversity.

VI. Conclusion

It is necessary to control and prevent the biodiversity disruption to conserve and maintain ecological balance by using appropriate alternative technology in place of animal dissection, because animal ethical issues are as important as human welfare, so more efforts needs to be taken for effective biodiversity conservation as we are thoroughly depends on animals but animals are not depends on us!

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Conflicts of interest statement:
The authors declare that there are no conflicts of interest.

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Potential Source of Antioxidants : Buchanania Lanzan Spreng

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ABSTRACT

The term 'antioxidant' referes to any molecule capabale of stabilizing or deactivating free radicals before they attack cells. Humans have evolved highly complex antioxidant systems (enzymic and nonenzymic), which work synergistically and in combination with each other to protect the cells and organ systems of the body against free radical damage. The antioxidants can be endogenous or obtained exogenously e.g., as a part of diet or as dietary supplements. Endogenous antioxidants play a crucial role in maintaining optimal cellular functions and thus systemic health and well-being. However, under conditions, which promote oxidative stress, endogenous antioxidants may not be sufficient and dietary antioxidants may be required to maintain optimal cellular functions. The most efficient enzymatic antioxidants involve glutathione peroxidase, catalase and superoxide dismutase (Mates et al 1999).

Keywords: Antioxidant, Drug Toxicity, Antioxidative Effect, Amny Spices, Buchanania Lanzan

I. INTRODUCTION

Investigations of natural antioxidants and bioactive compounds for the preservation of traditional medicines and use in treating certain human diseases have received much attention (Lin Y W et. al., 2010). Phenolic antioxidants can inhibit free radical formation and interrupt propagation of auto oxidation. Vitamin E and vitamin C are both effective in appropriate matrix. Plant extracts, generally used for their flavoring characteristics, often have strong H-donating activity thus making them extremely effective antioxidants. The antioxidant activity is most often due to phenolic acids, phenolic diterpenes, favonoids and volatile oils (Brewer M S et. al., 2011). Reactive oxygen species (ROS) effect oxidative damage to various biomolecules including proteins, lipids, lipoproteins and DNA (Farber JL et. al., 1994). This oxidative damage is a critical ethological factor implicated in several chronic human diseases including cardiovascular dysfunctions, atherosclerosis, inflammation, carcinogenesis, drug toxicity, neurodegenerative diseases and cancer. Recently, traditional medicine plants have received much attention as sources of biological active substances including antioxidants that might serve as leads for the development of novel drugs (Silvaa CG et. al., 2009).

Spices have been investigated for their antioxidant properties for last 50 years. As early as 1952, amny spices were examined and 32 spices were found to retard the oxidation. Many spices have been shown to impart an antioxidative effect in foods. Spices and herbs have been used for flavour, colour and aroma for more than 2000 years. Due to the tremendous phytochemicals, the spices have been used as preservatives in foods and beverages. The antioxidants in spices and herbs are very effective because they possess excellent antioxidant activity. The spices and herbs have been used as antioxidants as whole or ground spice/herb, extracts, encapsulated or as emulsions (Milda E.Embuscado, 2015). Several studies also showed that black pepper, clove, cinnamon and coriander exhibited antioxidant properties. In recent decades, a number of phenolic substances were isolated from a variety of spice sources, including phenolic acids (e.g., Gallic acid, Caffeic acid, etc), flavonoids (eg. quercetin, rutin, myricetin, luteolin, naringenin and silybin), phenolic diterpenes and volatile oils. Considering all these aspects relevant to spices and antioxidants, the current study has been formulated to investigate the treasure of antioxidants from *Buchanania lanzan* Spreng.

Buchanania lanzan, commonly called as Chironji (belongs to family Anacardiaceae), is an evergreen tree with a straight cylindrical trunk up to 15m height, commonly found in dry deciduous forest upto an altitude of 1200m and in the sub Himalayan tract up to 900m. This plant is reported to possess cardio tonic, astringent, antioxidant activity and is also used in treatment of skin diseases (Y. Dai, W. C. Ye et. al., 2002). The parts of the plant are used for the treatment of various disorders. The oil from the seeds is used to reduce the swelling of the neck (T. Horio and A. A. Gohar K Ye et. al., 1997). Antistress activity of the methanolic extract of *Buchanania lanzan* in-vivo in both normal and stress induced rats following a biochemical approach was evaluated (Kapoor et. al., 2011). The present work is therefore channelized towards the analysis of phenols and flavonoids found in *Buchanania lanzan.* Oxygen free damage induce damage due to peroxidation to bio-membranes and also to DNA, which leads to tissue damage, thus cause occurrence of a number of diseases. Antioxidants neutralize the effect of free radicals through different ways and may prevent the body from various diseases. Antioxidants may play vital role in the metabolic disorders. Indian stands with highest percentage of people with diabetes, hypertension and cardiovascular disorders among the world. This may be due to the life style, ethnicity and improper food habits. Hence, the search for effective, non-toxic natural compounds with anti-oxidative potentials has been identified in recent years. In this study, antioxidant activity of methanolic, ethanolic and aqueous extracts of *Buchanania lanzan* Spreng. was evaluated. Along with phenols and flavonoids, sterols and thiamine were also considered to be one of the perspectives of the study. Subsequently, the study is aimed at questing and analyzing the immense antioxidant properties of *Buchanania lanzan*.

II. MATERIALS AND METHODS

The plant material of *Buchanania lanzan* Spreng. was collected from Mumbai region where the plant has been naturally inhabited. The plant was identified and authenticated with the help of wealth of India and flora of Bombay presidency.

Preparation of plant extracts:
The plant part used for the analysis was fruit pulp of *Buchanania lanzan*. The slices of dried fruits of the plant were successively extracted using methanol, ethanol and aqueous separately. The collected extracts were concentrated by evaporation under room temperature and used for the study. They were further screened for the flavonoids, phenols, sterols and thiamine by using standard protocols.

Determination of total flavonoid content: spectrophotometric aluminium chloride method was used for determination of flavonoids (Ebrahimzadeh et al, 2009 b). Total flavonoid contents were calculated as quercetin from a calibration curve. The calibration curve was prepared by preparing quercetin solutions at concentrations 12.5 – 100 mg/ml.

Determination of total phenol content: Total phenol content was determined by Folin-Ciocalteau method (Nabavi et al, 2008b). Standard curve was prepared by 0, 50, 100, 150, 200, and 250 mg/ml solutions of gallic acid in methanol:water (50:50 v/v). Total phenol values are expressed in terms of gallic acid equivalent (GAE) [mg/g of dry mass], which is a common reference compound.

TLC method for flavonoids: Minute quantity of seeds are measured in 2M hydrochloric acid and heated at 100˚ C for 30-40 minutes. Extract is cooled, filtered and extracted with ethyl acetate. It may be re-extracted with a small volume of amyl alcohol. The amyl alcohol extract is concentrated to dryness, taken up in a few drops of 1% methanolic HCL and aliquots chromatographed one-dimensionally in Forestal solvent (Acetic acid-conc. HCL- water; 30:3:10).

TLC method for phenols: The thin layer chromatographic method was done for revealing the presence of different flavonoids in the plant material. Four different liquid phases have been used to prove the particular phenolic acids present. These moving phases involve: a. CHCL3: Acetic acid (9:1); b. Acetone: Toluene: Acetic acid (50:40:20); c. Benzene: methanol: acetic acid (79:14:7); CHCL3: methanol: H2O (65:45:12) (Nedime D UR UST et. al., 1999). 0.2M sodium acetate was used as an absorbent.

Extraction and isolation of phenols: 2M HCL was added to known amount of finely ground fruits and hydrolysed by heating for 1 hour. After filteration the aqueous acidic solution was extracted with ethyl acetate. Ethyl acetate extract was treated with 5% $NaHCO_3$. The organic acids in the aqueous phase were extracted with ethyl acetate again and p-hydroxybenzoic acid, caffeic acids and p-coumaric acid were isolated from this extract and there presence was observed in chromatogram.

Estimation of sterols: It was done by Liebermann-Burchard method (J.B. Harborne et al., 1973). In this reaction the Acetic anhydride in the Liberman – Burchard regent is reacted with the sterol in the sample which gives a Green colour, whose absorbance can be determined by UV-visible spectrophotometer. Total sterol contents were calculated as cholesterol from a calibration curve. Pipette out standard cholesterol solution as 0.5, 1.0, 1.5, 2.0, 2.5 ml in five test tubes whereas tube 6 was kept blank and marked as S1, S2, S3, S4, S5 and S6. Then, 2 ml of the Liberman-Burchard regent was added to all six tubes and final volume of 5ml was made equal in each test tube by adding chloroform**.** The test tubes were covered with carbon black paper and kept in dark for 15 minutes in ice bucket. Then taken base line on spectrophotometer with blank (S6) at λmax 640nm. The absorbances of all standards (six tubes) were determined on spectrophotometer and standard graph was plotted.

Reducing power determination: 1 ml of different concentrations of the extract fractions was mixed with potassium ferricyanide and 2.5 ml of phosphate buffer. The mixture was incubated at 50^0 C for 20 min. 2.5 ml TCA (10%) was added to it and centrifuged at 3000 rpm for 10 min. 2.5 ml of supernatant was taken and 2.5 ml wate and 0.5 ml $FeCl_3$ (0.1%) were added to it. The absorbance was measured at 700nm. Higher absorbance of the reaction mixture indicated higher reducing power.

III. RESULT AND DISCUSSION

Determination of total flavonoid content: The present investigation showed the values of total flavanol compound for aqueous, methanolic and ethanolic extract to be 60 ug/ml, 57ug/ml and 27ug/ml respectively. This indicates the efficiency of aqueous extract of *Buchanania lanzan*. Thus the concentration of flavonoids obtained is **Aqueous > Methanol > Ethanol**. Thus, *Buchanania lanzan* contain good amount of flavonoids which can be used as medicinal foods (John Bradley Morris, 2008) and thus proving its beneficence for human as potential nutraceutical. The concentration of flavonoids in plant extracts depends on the polarity of solvents used in the extract preparation (Min and Chun-Zhao, 2005).

TLC method for flavonoids: In *Buchanania lanzan,* **Apigenin (0.83)** flavonoid was detected.

Determination of total phenol content: Phenolics are ubiquitous secondary metabolites in plants and possess a wide range of therapeutic uses such as antioxidant, antimutagenic, anticarcinogenic and also decrease cardiovascular complications (Yen G., Duh P. 1993). Total phenols determination in current study showed 150ug/ml, 50ug/ml and 190ug/ml total phenols in aqueous, methanolic and ethanolic extracts respectively. Thus the concentration of flavonoids obtained is **Ethanol > aqueous > Methanol**.

TLC method for phenols: In present investigation, the phenolic compounds were identified by TLC method with four different solvent systems and two spraying agents. In *Buchanania lanzan*, three phenolic compounds were detected. p-OH benzoic acid was obtained in solvent system C and D with $FeCl_3$ reagent. p-Coumaric acid was obtained in system A and B with $FeCl_3$ reagent and Vanillic acid was obtained in solvent system A with Folin reagent. **This shows the abundance of p-OH benzoic acid and p-Coumaric acid in *Buchanania lanzan*.**

Estimation of sterols: The present investigation showed the ethanolic extract of *Buchanania lanzan* with maximum amount of sterols (105ug/ml) followed by methanolic extract (100 ug/ml) followed by aqueous extracts (35ug/ml). Thus the concentration of sterols obtained is **Ethanol > Methanol > Aqueous**.

Reducing power determination: Reducing capacity was determined with aqueous extract at different concentrations. In present work, the concentrations of phytoactive chemicals were found to be **Phenols > Flavonoids > Sterols. Interestingly sterols**

concentration was found to be highest in *Buchanania lanzan*.

IV. CONCLUSION

Considering the overview of present study, *Buchanania lanzan* showed presence of flavonoids, phenols, sterols which are the potential antioxidants. The present work also corroborates the justification of increase in concentrations proportionately rising with increase in reducing capacity. *Buchanania lanzan* is a rich source of phenolic compnds which have been linked to most of the pharmacological activities. Thus, the plant should be exploed further as alternative source of medicine. Further in vivo antioxidant activities and in different antioxidant mechanisms are needed. The spices screened for phytochemical constituents seems to have the potential to act as a source of useful drugs and also to improve health status of the consumers as a result of the presence of various compounds that are vital for good health.

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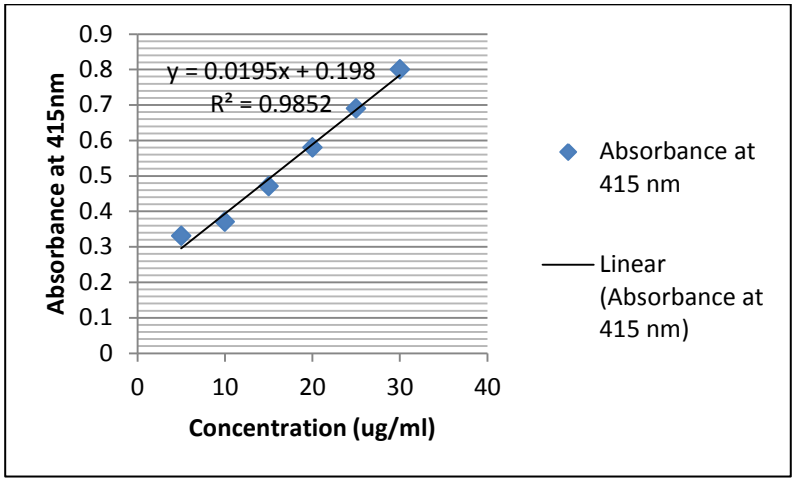
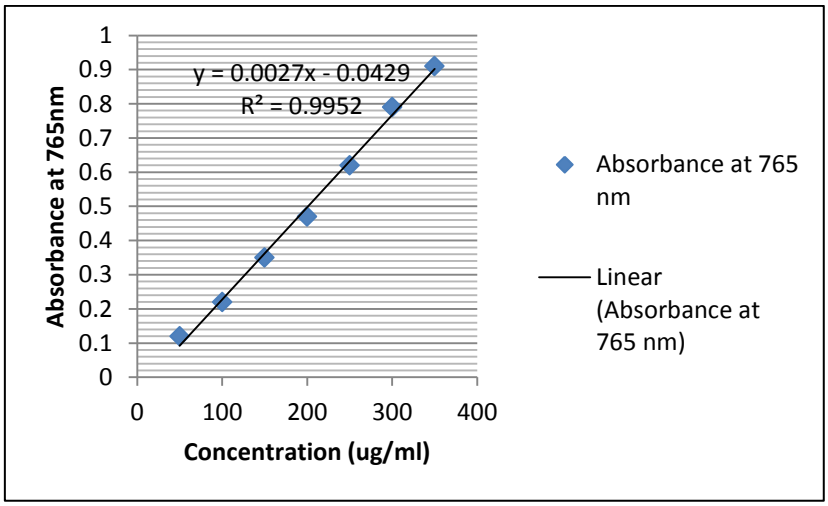
Tables and Graphical Representation:

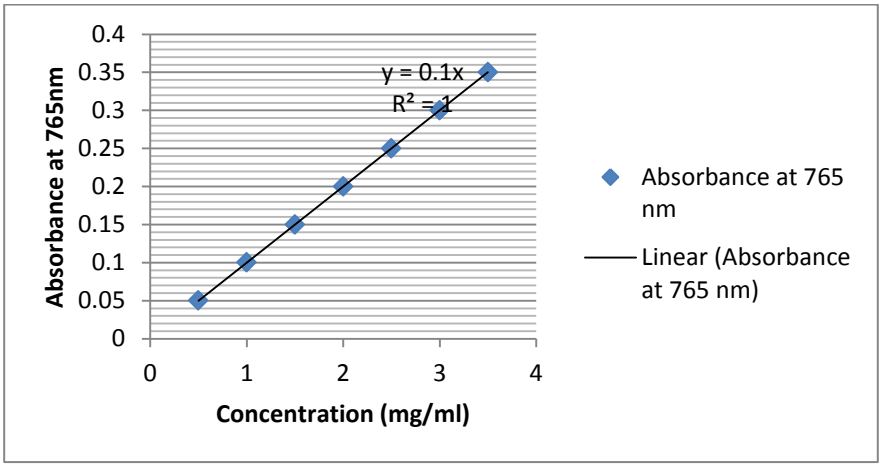
1. **Standard graph for Quercetin (Flavonoid)**:



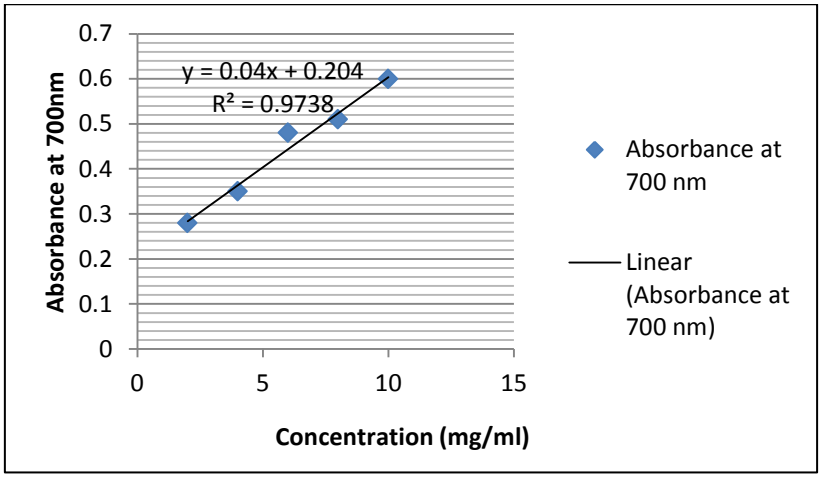
2. **Standard graph for Gallic acid (Phenol)**:



3. **Standard graph for Cholesterol (Sterol):**



4. Graph for reducing capacity:



5. Chromatographic results for Flavonoids:

SR. NO.	Flavonoids	Standard Rf Values	Rf values of flavonoids obtained
1	Apigenin	0.83	0.84

6. Total contents estimation:

Sr. no.	Extracts	Total Phenol content (ug/ml)	Total Flavonid content (ug/ml)	Total Sterol content (ug/ml)
1	Aqueous	150	60	35
2	Methanol	50	57	100
3	Ethanol	190	27	105

7. Chromatographic results for Phenols:

SR. NO.	Phenolic acids	Solvent systems and Rf values				Colours and spray reagent
		1	2	3	4	
1	P-Hydroxybenzoic acid	-	-	0.673	0.958	Yellow ($Fecl_3$)
2	P- Coumaric acid	0.51	0.905	-	-	Orange ($Fecl_3$)
3	Caffeic acid	-	0.851	-	-	Bluish grey ($Fecl_3$)
4	Vanillic Acid	0.82	-	-	-	Blue (Folin)

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Ifluence of Vam (Glomus Fasciculum) Inoculation on Protein Content Of Black Gram (Vigna Mungo (L.) Hepper)

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ABSTRACT

Result of experiments conducted on *Vigna mungo* (L.) Hepper. a legume crop to study the effect of VAM inoculation on protein content have been described in present research. The plants were grown in non sterilized and sterilized soil to obtain results of inoculated VAM, *Glomus fasciculatum* (Tha) Geared and Trap. along with native VAMs. Marked increase in protein content in VAM inoculated plants supplied with recommended phosphates in both sterilized and non sterilized soils were observed. There was visible increase in total grain Biomass per plant in VAM inoculated plants supplied with recommended phosphates in comparison with controlled set.

Keywords: VAM, Vigna mungo (L.) Hepper, Protein content

I. INTRODUCTION

During recent years VAM technology is getting increasing recognition as a potential Biofertilizer. Beneficial effects of VAM inoculation on trees, crops & ornamental plants at field condition are shown by various workers (Bagyaraj, *et.al.* 1979 and Bagyaraj, et.al. 1980) these studies indicate that plants shows response to inoculation with VAM with efficient strain of VA mycorrhiza.

The present paper aims at the effect of *Glomus fasciculatum* inoculation on protein content in *Vigna mungo* (L.) Hepper. Locally known as "UDAD" is valued for food. It is very popular in Punjabi cuisine, as used in dal makhani, In Bengal, it is used to prepare Biulir Dal and in Rajasthan it is used to prepare dal which is especially consumed with bati. In Maharashtra, especially in Satara district it used to make a curry called Udadach Ghuta. Black gram is also an coarse ingredient of papad a starter utilized all over India. Black gram is very nutritious as it contains high levels of protein (25g/100g), potassium (983 mg/100g), calcium (138 mg/100g), iron (7.57 mg/100g), niacin (1.447 mg/100g), Thiamine (0.273 mg/100g), and riboflavin (0.254 mg/100g), (USDA National Nutrient Database for Standard Reference)

II. Material and Method

Matured healthy seed of *Vigna mungo* (L.) Hepper were collect from Narayangaon, Taluka- Junnar, Dist- Pune, Maharashtra. Earthen pots with 25cm diameter and depth and with proper drainage were selected for planting filled with 3Kg of sterilized soil mixture containing Sand: Soil: FYM in 1:2:1 proportion. Pots were place in sunlight and watered till the capacity a day before planting. Further they were watered till the field capacity on alternate days for 60 days of growth. Phosphate was added at different levels as suggested in various treatments. In all there were six sets with six treatments in sterilized soil. The results were based on three replication of each treatment.

Treatments:

Set I UP00 (Control , un-inoculated, without phosphate & VAM)
Set II IP00 (VAM Inoculated, without phosphate)
Set III UP100 (VAM un-inoculated with 1gm phosphate per pot)
Set IV IP100 (VAM Inoculated with 1gm phosphate per pot)
Set V IP75 (VAM Inoculated with 0.75gm phosphate per pot)

Set VI IP50 (VAM Inoculated with 0.50gm phosphate per pot)

Same sets were made for non sterilized soil. Observations were recorded at the age of 60 days one plant from each replicate was harvested at the end of sixty days. Plants were removed carefully along with the roots. Roots were carefully and fixed with in F.A.A. for 24 hours and scrutinized for VAM colonization (Schenck and Perez, 1987) using following formula-

$$\%\, VAM\ colonization = \frac{Number\ of\ Mycorrhizal\ root\ segments}{Total\ no\ of\ root\ segments\ screened} \times 100$$

Extramatricular clamydospores produced by the VAM fungus in soil was estimated by wet sieving and decanting method (Gerdemann and Nicolson, 1963).further observation were recorded at flowering and fruiting period for reproductive parameters. Dry biomass of shoot and root was recorded after 60 days.

Protein was determined as per Lowry et al., (1951). The protein was measured by taking absorbance at 750 nm in the spectrophotometer. A standard curve was constructed on graph paper. From the standard curve coefficient was determined. Protein was determined by

$$\text{Concentration of protein} = \frac{R\ x\ co\ -\ eff.x\ V\ x\ D}{\text{F. Wt}}\text{mg/g}$$

Where,

R= Sample reading - blank reading,
Co-eff. = Calculated mean co-efficient,
V = Volume of the sample,
D = Dilution Factor,
F. Wt= Fresh weight of plant sample in g

III. Result and Discussion

The result of present investigation clearly indicates that *Vigna mungo* (L.) Hepper. responds well to the mycorrhizal inoculation under pot condition.

The total dry biomass was maximum in plants inoculated with VAM at 100 percent recommended phosphate and least in control in both sterilized and non sterilized soil. There was considerable increase in the biomass in inoculated plants as compared to control. Similar observations were reported by Wang, *et al.,* (1989) in *Phaseolus aureus.*

Plants showed double dry weight than control. Hayman and Mosse (1971) increased shoot dry weight in Onion and Coprosma. Bagyraj and Manjunath (1980) in Cotton, Cow pea and Finger millet. Bagyraj and Powell (1985) in Marigold.

Grain biomass was maximum in plants inoculated with VAM at 100 percent recommended phosphate 7.55gm in non sterilized soil and 8.45gm in sterilized soil. Increase in phosphate level was directly proportional to grain biomass. Following workers observed similar trend. Saif and Khan (1977) in Barley, Iqbal, et. al.(1980) in Rice, Costa, et. al.(1989) in Oat, Khadge et. al.(1992) in Sorgham and Bajra and Joseph et. al.(1997) in maize and pearl millet.

Protein content showed increase with increase in phosphate supplement and was recorded maximum in inoculated plants in both type of soils. Percent of protein content was higher in non sterilized soil than sterilized soil. Similar result was noted by Mesbaul *et al.,* (2015) Percentage of VAM colonization was higher in mycorrhizal plants with 50 percent recommended phosphate in sterilized and non sterilized soil. Similar observations were reported by Okon *et al.,* (1996) in *Gliricidia sepum* and *Senna siamea.* VAM with 50 percent recommended phosphate shows maximum number of Mycorrhizal spores in non sterilized soil. Clamydospores were not observed in uninoculated plants. This suggest that the number of infective propagules in the soil is low and the infectivity of native fungi lower than that of inoculant fungus. Further there is decrease in VAM colonization level at 100 percent recommended phosphate and higher soil phosphate levels. There is increase in VAM colonization level in nonsterilized soil inoculated with VAM also observed by Bagyraj and Manjunath (1980) in Cotton, Cowpea and Finger millet. Present investigation clearly indicates that *Vigna mungo* (L.) Hepper responds well to *Glomus fasciculatum*. VAM inoculation in combination with Phosphate at all levels increased Protein content and grain yield in both non sterilized and sterilized soil. Similar trend was observed by [Kanade A. M. and Bhosale R. S. (2010);(2013)a, (2013)b, (2013)c, (2013)d]

in *Elusine coracona, Dolichos lab-lab, Sida acuta and Casia tora.,* [Kanade A. M (2012)a, (2012)b, (2012)c] in *Sesbania grandiflora, Setaria italic and Punica indica;* Kanade, A.M. (2013) in *Spinaceae oleracea,* Kanade, A.M. (2014) in *Amaranthus blitum* and Kanade A. M (2015) in *Buchanania lanzan.*

Table 1: Growth performance of *Vigna mungo* (L.) Hepper in response to various levels of phosphate and VAM in non sterilized and sterilized soil.

Soil type	**Non sterilized**					
Set	I	II	III	IV	V	VI
Treatments	UP00	IP00	UP100	IP100	IP75	IP50
Parameters	*	*	*	*	*	*
Grain biomass /plant (gm)	7.0	7.45	7.50	7.55	7.43	7.40
Protein content (%)	25.2	25.5	25.8	25.9	25.4	25.3
% VAM Colonization	00	46	00	42	31	53
Spore count (Per 50 gm of soil)	00	16	00	29	33	38

Soil type	**Sterilized**					
Set	I	II	III	IV	V	VI
Treatments	UP00	IP00	UP100	IP100	IP75	IP50
Parameters	*	*	*	*	*	*
Grain biomass /plant (gm)	8.0	8.35	8.40	8.45	8.32	8.30
Protein content (%)	25.4	25.8	25.6	25.7	25.6	25.7
% VAM Colonization	00	13	00	62	30	40
Spore count (Per 50 gm of soil)	00	12	00	30	31	38

UP00 (Control , un-inoculated, without phosphate & VAM). **IP00** (VAM Inoculated, without phosphate). **UP100** (VAM un-inoculated with 1gm phosphate per pot). **IP100** (VAM Inoculated with 1gm phosphate per pot). **IP75** (VAM Inoculated with 0.75gm phosphate per pot). **IP50** (VAM Inoculated with 0.50gm phosphate per pot) Standard deviation (SD)

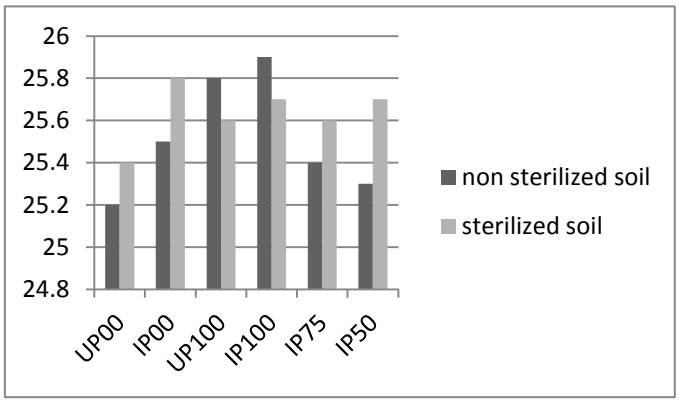

Figure 1. Influence of VAM on grain yield in sterilised and non sterilized soil at various levels of phosphates in *Vigna mungo* (L.) Hepper

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Study of Polyvinyl Chloride Composites Based on CaCO3 and Alkali Treated Coconut Fibers

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ABSTRACT

The present paper deals with mechanical and morphological study of polyvinyl chloride (PVC) hybrid-composites using CaCO3 as a filler and coconut fibers as a reinforcing material. A series of batches were compounded by using both, alkali-treated and untreated coconut fibers (1%, 3%, 5%, 7.5% to 10%) separately while the CaCO3 content was maintained uniform in all the formulations. The formulation was first dry blended and then compounded on a two-roll mill. The dry blended composition was then compression molded into sheets in the temperature range of 160-180°C. A study was done as per ASTM standards to evaluate tensile properties, impact strength, shore hardness, coefficient of friction, water absorption and using SEM. The mechanical properties keep on increasing till the coir content (treated and untreated) reaches 5% and then starts decreasing beyond 5%. Alkali treated fiber composites have shown superior properties to untreated ones. SEM study supports the fact that the alkali treated fiber reinforced composites are morphologically more uniform than untreated ones resulting in better properties.

Keywords: Polymer Composites, Natural Fiber Reinforcement, Polyvinyl Chloride Composite, Coconut Fibers.

I. INTRODUCTION

The past few decades have seen a great upsurge in research on polymer composites, as these materials can offer enhanced mechanical properties and low cost as compared to virgin polymers. This resurgence of interest is due to the increasing cost of plastics and also because of the environmental aspects of using renewable and biodegradable materials. The advantage of composite materials over conventional materials stems largely from their higher specific strength, stiffness and fatigue characteristics, which enables structural design to be more versatile. Work has been conducted on a wide variety of polymers, including thermoplastics, such as styrenics, polyolefins, etc. and thermosetting materials, such as epoxy resins and phenolics.

A wide research has been carried out on fiber reinforced polymer composites [1-7]. Flax fiber reinforced polyolefins are extensively used today in the automotive industry, but the fiber acts mainly as filler material in non-structural interior panels [8]. Natural fiber composites used for structural purposes do exist, but then usually with synthetic thermoset matrices which, of course, limit the environmental benefits [9]. Natural fibers such as jute, sisal, pineapple, abaca and coir have been studied as a reinforcement and filler in composites [10-12].

The use of inorganic fillers has been practiced for many decades in both elastomeric and plastic materials. It has been reported that simultaneous enhancement of toughness and stiffness can be achieved in polymer/rigid particle system, e.g. PVC/$CaCO_3$ [13] and HDPE/$CaCO_3$ [14-15]. To incorporate mineral filler into a polymer, coupling agent is generally used in order to improve the dispersion and bonding of the filler [14-15]. Use of nanoparticulate calcium carbonate to toughen the PVC/$CaCO_3$ has also been reported.

A strong fiber-matrix interface bond is critical for high mechanical properties of composites. A good interfacial bond is required for effective stress transfer from the matrix to the fiber whereby maximum utilization of the fiber strength in the composite is achieved [16]. There is a limited compatibility between the natural fibers and thermoplastic matrices due to their strong hydrophilic character; which can be improved by surface treatment or chemical modification of the natural fibers. Modification to the fiber also improves resistance to moisture induced degradation of the interface and the composite properties [17]. In addition, factors like

processing conditions/techniques have significant influence on the mechanical properties of fiber reinforced composites [18]. Jute has been treated with alkali, for the composite to have good bonding between the fiber and the resin matrix. A process known as mercerization has been commercialized for cotton fibers for superior reactivity with dyes [19]. Several authors have investigated the changes occurring in the fiber properties due to alkali treatment of jute [20-21]. Jute fibers have been treated with NaOH solution of concentration 1%, 8% for 48 h and 2% for 1 h and showed improvements in fiber properties [20, 22]. Similar treatments were attempted on isometric jute yarns and reported an improvement of 120% and 150% in the tensile strength and modulus respectively when treated with 25% NaOH solution for 20 min and 60% improvement in the jute/epoxy composite properties reinforced with these treated yarns. The improvements have been attributed to the greater reactivity of the treated fibers with the resin administering superior bonding [23-25]. Coir has also been tested as filler or reinforcement in different composite materials [26, 27].

There is a considerable attention in the research community as well as in industry on composite materials where coconut fiber is used as reinforcing filler. Growing attention is nowadays being paid to coconut fiber due to its low cost and availability. This is also due to a range of potential advantages of coconut fibers, such as low specific weight, low cost of production, easy processing, and good thermal and acoustic insulating properties. Over 50% of the coconut fiber produced annually throughout the world is consumed in the countries of origin [28]. Because of its hard-wearing quality, durability and other advantages; it is used for making a wide variety of floor furnishing materials, yarn, rope etc [29]. However, these traditional coir products consume only a small percentage of the potential total world production of coconut husk. Hence, research and development efforts have been underway to find new use areas for coir, including utilization of coir as reinforcement in polymer composites [30-32].

The main objective of the current work is to formulate a series of hybrid composites by varying the coir content in various formulations of PVC/coir/$CaCO_3$, with and without alkali treatment of coir and to study mechanical and morphological properties of the same.

II. METHODS AND MATERIAL

PVC resin (57 GE R01 suspension grade suitable for injection and compression molding in powder form obtained from Reliance Industries India Ltd.) was used as a polymer matrix. Calcium carbonate ($CaCO_3$), dioctyl phthalate (DOP), tri basic lead sulphate (TBLS), ethylene vinyl acetate polymer (EVA), low density polyethylene (LDPE), calcium stearate, titanium dioxide (TiO_2) were obtained from various commercial sources and were either used directly or after purification and /or drying as per the standard procedure. Coconut fibers (coir) were obtained from coconut husk and were either treated with alkali or used directly after drying.

Tensile properties were measured using dumb-bell shaped specimens on a tensile testing machine, Model No STS-248, India, according to ASTM D638M-91 procedure at 100% strain rate; the crosshead speed of 50 mm/min was maintained for testing. The values of tensile modulus were also determined at low strains. Optical extensometer was used to measure tensile modulus accurately. Izod impact strength values were evaluated on a Zwick Izod Impact tester (Digital), Model No: S102, Germany, according to ASTM D256 test procedure using notched samples. The average values of the mechanical properties and their standard deviations have been reported. All mechanical tests were performed at room temperature. A JEOL, JSM-6380 Scanning Electron Microscope (SEM) was used to evaluate the dispersion of reinforcing fibers and filler in the polymer matrix. The freshly cut plastic surface was used to take SEM micrograph. Coefficient of friction was determined by using inclined surface coefficient of friction (slide angle) tester as per TAPPI T815 standards.

A. Chemical Treatment of Coconut Fibers

The coconut fibers obtained from coconut husk were cleaned, dried and were cut into approximately 2 cm length. The fibers were soaked in excess of 5% aqueous alkali (NaOH) solution for 4h at room temperature. The treated (soaked) fibers were then removed from alkali solution and washed with distilled water to remove traces of alkali and dried at 60°C for 48 h before use [33].

B. Compounding and Processing

A series of formulations using PVC/$CaCO_3$/coir were prepared in the present investigation. Table 1 presents the detailed compositions of various batch formulations used in the present work. Compounding of PVC resin was done using various additives and

fillers in sigma mixer rotating at about 1500 rpm. The steps involved initial addition of processing aid and lead stabilizer to the polymer matrix and fillers. This was followed by addition of lubricants and dioctyl phthalate (DOP) after the mixture reached 80-85°C. The mixing was continued till the temperature reached 110-115°C. The mixture was cooled and previously dried coconut fibers (treated or untreated) were added and mixed uniformly for next 10 min. The mixture was then subjected to a two-roll mill and compounded at 80°C. The uniformly compounded material was then compression molded in the form of sheets in 160 - 180°C temperature range using a compression mold having 3.2 mm cavity. The sheets thus obtained were used for mechanical and morphological evaluation purpose.

TABLE 1: COMPOUNDING FORMULATIONS

Formulation *	PVC %	Fiber %	$CaCO_3$ %	EVA/LDPE %	TiO_2 %	TBLS %	Calcium Stearate %	DOP %
1	29.43	0	50	8.24	1	2.74	1.09	7.5
2	29.43	1	50	8.24	1	2.74	1.09	7.5
3	29.43	3	50	8.24	1	2.74	1.09	7.5
4	29.43	5	50	8.24	1	2.74	1.09	7.5
5	29.43	7.5	50	8.24	1	2.74	1.09	7.5
6	29.43	10	50	8.24	1	2.74	1.09	7.5

* Same formulation (1-6) was repeated for treated and untreated coconut fibers.

III. RESULTS AND DISCUSSIONS

The present work was intended to study the mechanical and morphological behavior of various formulations of PVC filled with $CaCO_3$ and coir. In the present system of PVC/coir/$CaCO_3$, the content of other additives viz. $CaCO_3$, EVA/LDPE, TBLS, DOP, TiO_2 and calcium stearate were kept constant. However, the coir content was varied from zero to 10 % of total formulation, as it was aimed to study the effect of reinforcing material content on composite properties. In the present study EVA/LDPE was used as processing aid, $CaCO_3$ as inorganic filler while calcium stearate was used as a lubricant. Tri basic lead sulphate (TBLS) was used as a stabilizer and DOP was used to plasticize the system. The role of TiO_2 was as a pigment.

It is known that coir fiber includes 5.25% water soluble compounds, 3.00% pectin and related compounds, 0.25% hemicellulose, 45.84% lignin, 43.44% cellulose and 2.22% ash. Cellulose fibers are generally lignocellulosic consisting of helically wound cellulose microfibrils in an amorphous matrix of lignin and hemicelluloses that run along the length of the fiber. When these fibers are treated with alkali, loss in weight was observed due to heavy dissolution of lignin and hemicellulose content and the strands became well separated and dispersed into microfibrils. The modulus of the jute fibers was found to be increased when treated. The tenacity at break point also increased while percentage breaking strain was reduced [33]. It was imperative that the fibers became stiff and brittle on account of its high strength and low extensibility. Similar increase in strength of jute fibers on alkali treatment has also been reported [20].

The study on the influence of lignin content on the mechanical behavior of jute found a gradual decrease in both the strength and stiffness of the fiber with lignin removal. The extensibility of the fiber was also found to follow the same trend [33]. Similar experiments, which were carried out on sugarcane fiber provided additional evidence of the significant contribution of lignin to fiber strength.

In the present work too, alkali treatment of coir fibers led to removal of lignin and hemicellulose matrix from the clumps of coconut fiber. The combined effect of alkali treatment and milling (on two roll mill) has led to the formation of separated micro and nanofibers. Similar

kinds of observations have been reported earlier [34]. The SEM study, in the present investigation exhibits separated microfibers in treated coir filled specimens as compared to that of untreated coir filled specimens where the fibers are intact. The coconut fibers were observed in the form of micro and nanofibers having lowest diameter around 50 nm as shown in Figure 5(a) for treated fibers while it was above 300 nm for untreated ones (Figure 5(b)).

A. **Mechanical Properties**

The present work was divided into two parts for the systematic study of composite materials. First part consisted of six samples where alkali treated coir was used while the other part i.e. part two involved use of untreated coir fibers. The study involved comparison of both, mechanical and morphological properties of treated as well as untreated coconut fiber filled composite materials. Fig. 1 represents tensile strength of the samples from both parts (i.e. treated and untreated coir fiber samples). It is seen that as the percentage of reinforcing filler (treated and untreated both) goes on increasing from 0 to 10 % the tensile strength also increases till filler content reaches 5% and then it starts declining, irrespective of treatment given to the fiber. Similar observations are recorded earlier [35]. However; treated fiber composites have shown higher values of tensile strength and modulus as compared to that of untreated ones for every formulation.

The impact strength of the specimens tested also follow similar trend as that of tensile properties. The impact strength also keeps on increasing till the coir content (treated and untreated) reaches 5% and starts decreasing beyond 5%. When compared, it was observed that the treated fiber composites exhibited higher impact property values as compared to that of untreated fibers for every formulation. This observation was very much similar to the tensile strength study where the similar trend is observed.

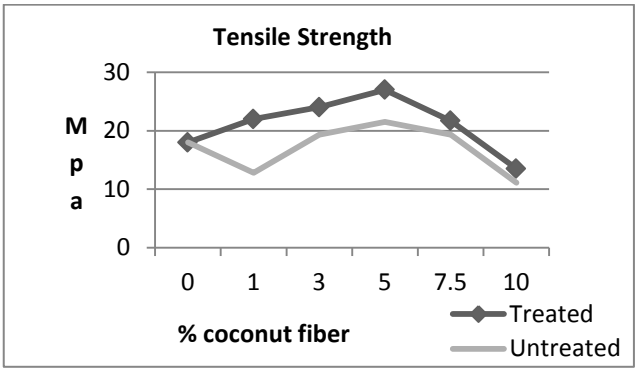


Figure 1. Tensile Strength versus % coconut fiber

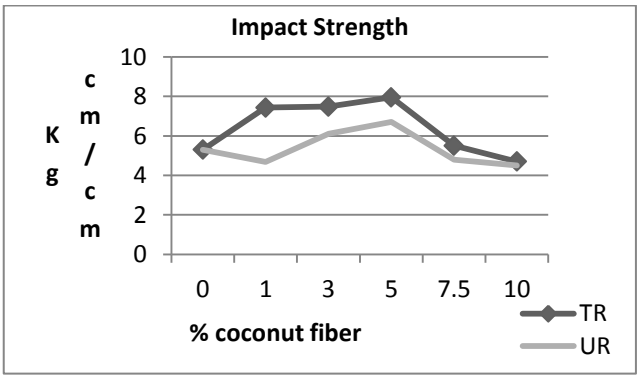


Figure 2. Impact Strength versus % coconut fiber

The above observations i.e. higher tensile and impact properties for treated fibers as compared to that of untreated ones and decline in properties after certain percentage (i.e. 5% in the present study) of reinforcing fibers can be interpreted based on following observations.

The improvement in mechanical properties of treated coir fibers can primarily be attributed to the superior bonding between the coir fibers and polymer matrix. This is because when coir is treated with alkali there is dissolution of hemicelluloses layer surrounding the fibers that leads to improved impregnation of fibers in polymer matrix and hence improved mechanical properties.

Another theory to support the improved mechanical properties of treated fiber composites can be explained as, when fibers are treated with alkali, the fiber strands become well separated and get dispersed due to dissolution of hemicelluloses and lignin to from micro and nanofibers. It is well established fact that lignin provides strength and stiffness to the microfibers in natural materials. The incorporation of these micro and nanofibers into PVC matrix in the present study is

associated with replacement of lignin (due to alkali treatment) with polymer matrix. That is the micro and nanofibrils are embedded in PVC matrix instead of lignin as observed in natural polymers. The PVC matrix, in absence of lignin, provides strength and stiffness to the composite material. In addition the treated fibers as such show improved properties due to increased crystallinity, tenacity and modulus than raw fibers. This explains for the increased mechanical properties of the treated fiber reinforced composite material.

There is initial decrease in values of mechanical properties in case of untreated fiber composites where as treated fiber composites show improvement in values. At low fiber volume fraction, a drastic decrease in tensile strength is usually observed. This has been explained with dilution of the matrix and introduction of flaws at the fiber ends where high stress concentrations occur, causing the bond between fiber and matrix to break. At high fiber volume fraction, the matrix is sufficiently restrained and the stress is more evenly distributed. This results in the reinforcement effect outweighing the dilution effect. As the volume fraction of fibers is increased to a higher level, the tensile properties gradually improve to give strength higher than that of the matrix. At very high fiber volume fraction, the strength again decreases due to insufficient matrix material. The decline in properties can also be due to a lack of fiber dispersion owing to the wide differences in polarity and also the strong intermolecular hydrogen bonding between the fibers at higher concentration. This lack of fiber dispersion can result in clumping and agglomeration of cellulosic fibers which will act as stress concentration points to initiate cracks during loading. This effect contributes to inferior mechanical properties at higher concentration of fibers.

The reinforcement caused by fibers in the thermoplastic matrix is governed by the parameters like fiber dispersion, fiber-matrix adhesion, fiber aspect ratio, fiber orientation, and fiber volume fraction.

Good dispersion is the one where fibers are separated from each other (i.e. there are no clumps and agglomerates), and each fiber is surrounded by the matrix (polymer). After alkali treatment the fibers get separated while the untreated fibers are in the form of clumps. These fiber-rich areas (i.e., clumps) lead to an inhomogeneous mixture and are susceptible to microcracking. Microcracks contribute to inferior mechanical properties of composites. Moreover the untreated, raw fibers have 'natural' matrix that is loosely held on the surface of the fiber. This loosely held matrix acts as a stress concentration point and lead to failure. This is indeed the case in the present work. That is, comparative study of treated and untreated fibers revealed the fact that the treated ones exhibit better properties as compared to that of untreated ones which is clearly seen in Figure 1 and 2.

B. Coefficient of Friction

The property, coefficient of friction, exhibited irregular trend in the present study irrespective of the treatment given to the fibers. The irregularity in the trend can be attributed to the uneven appearance of coir fibers on the surface which can be seen visually on the compression molded

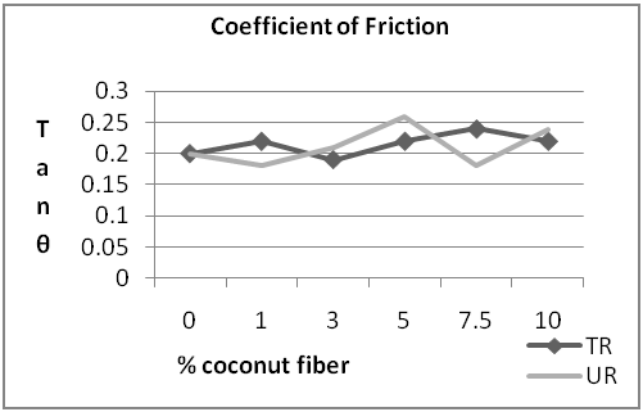


Figure 3. Coefficient of friction versus % coconut fiber

specimen. Though the filler is abrasive in nature, unevenness of appearance of fibers on the surface of the compression molded sheet might have lead to inconsistent contact with the friction surface, leading to irregular trend in as seen in Fig. 3. However, as a gross effect of filler content on coefficient of friction, the study suggests that there is a positive bias on the improvement of coefficient of friction.

C. Shore Hardness

Figure 4. represents a comparison of shore A hardness for all specimens. No definite trend was observed for the untreated samples. The polymer where highest (10%) untreated filler was used exhibited highest value of hardness. However, in case of treated fibers, the observation is in line with the earlier observations made

for tensile and impact properties. That is, after initial increase of hardness at 1% filler, it retains the hardness till 5% addition, from where it starts decreasing. Though there is no definite trend, the unfilled polymer (0% filler) shows lower shore A hardness as compared to that of filled polymers, irrespective of chemical treatment given to the fibers in general.

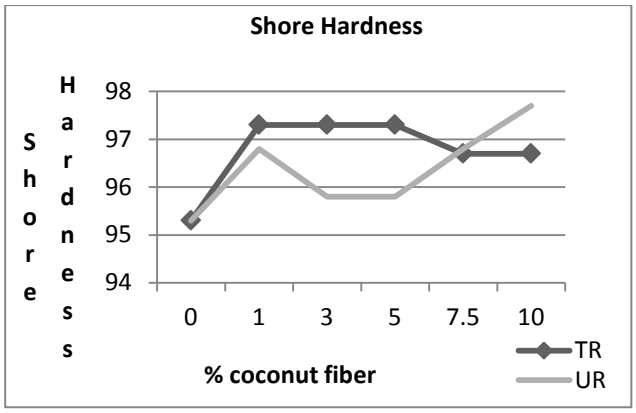


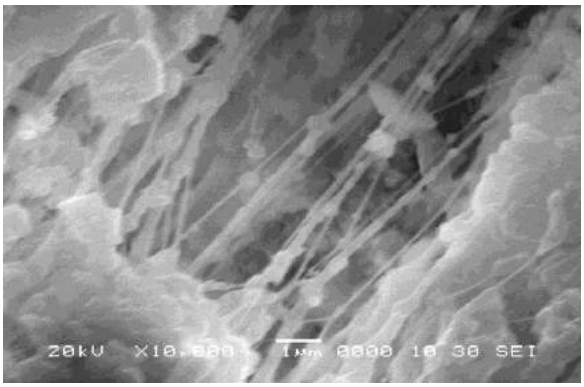
Figure 4. Shore hardness versus % coconut fiber

D. **Water Absorption**

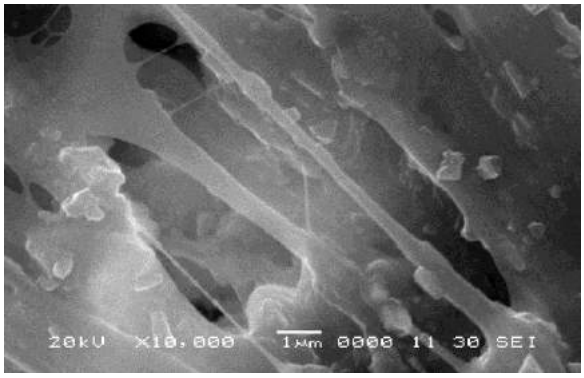
Preliminary experiments have shown that the composites with alkali treated fibers shows less water absorption in comparison to the untreated fiber composites, though water absorption increases with increasing percentage of fibers. Similar observations have been made in an earlier work where the study was conducted on effect of alkali treatment on water absorption of abaca fibers [35].

E. **Scanning Electron Microscopy**

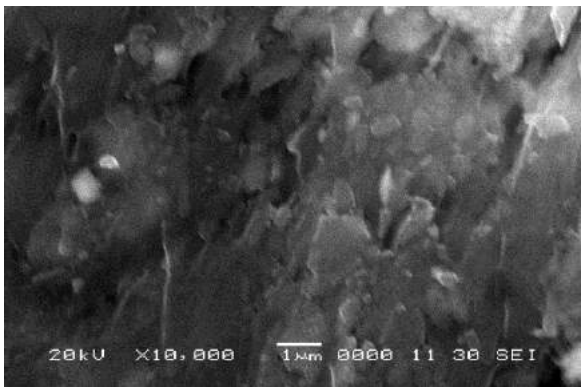
Morphological behavior of the composite was studied by scanning electron microscopy (SEM). Fig. 5 a, b,



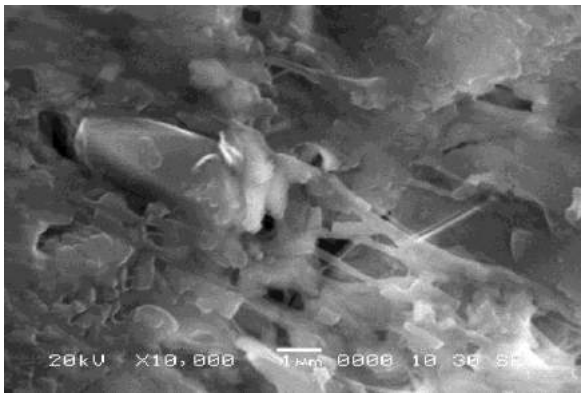
(a)



(b)



(c)



(d)

Figure 5. SEM of (a) alkali treated 10%, (b) untreated 10%,(c) alkali treated 5% and (d) untreated 5% coconut fibers

c, d represent scanning electron micrographs of the composite materials of alkali treated 10%, untreated 10%, alkali treated 5% and untreated 5% coir fibers respectively. The observations made by SEM supports the mechanical behavior observed in the present study as mentioned above. It was seen that, in general, there was improvement in mechanical properties of the reinforced composite samples. Moreover, alkali treated fibers lead to improved properties than that of untreated ones. When compared, Fig. 5a-d, it is clearly seen that the coir fibers in untreated samples (Fig. 5: b,d) are in clusters

where as the treated ones (Fig. 5: a,c) show finely separated fibers (microfibrils). In addition the SEM observation also supports the behavior that above 5% coir fibers the mechanical properties start deteriorating. As it is clearly seen that when the fiber loading is 5% (Fig. 5: c, d) the fibers can scarcely be seen in SEM indicating it is well impregnated in polymer matrix where as 10% loading samples (Fig. 5: a, b) in polymer show abundance of fibers. Also the higher fraction of fibers in polymer led to non uniform distribution of fibers in polymer matrix leading to voids whereas at lower loading percentage the fiber-polymer matrix compatibility is quite uniform with less voids as seen in SEM. The presence of voids in polymer composite leads to stress concentration points leading to failure of composites as observed in the present study whereas the samples with fiber loading till 5% have shown increase in mechanical properties.

TABLE 2: COMPARISON OF PROPERTIES OF TREATED AND UNTREATED COCONUT FIBER FILLED COMPOSITE MATERIAL

Property	Sample	0 %	1 %	3 %	5 %	7.5 %	10 %
Tensile strength (Mpa)	Treated	18	22	24	27	21.68	13.54
	Untreated	18	12.81	19.34	21.45	19.31	11.14
Impact strength (Kg cm/cm)	Treated	5.3	7.43	7.48	7.95	5.5	4.7
	Untreated	5.3	4.68	6.10	6.7	4.8	4.5
Shore hardness ASTM D 1706-61	Treated	95.33	97.33	97.33	97.33	96.66	96.66
	Untreated	95.33	96.83	95.83	95.83	96.83	97.66
Coefficient of friction	Treated	0.2004	0.2156	0.1943	0.2229	0.2376	0.2216
	Untreated	0.2004	0.1763	0.2125	0.2555	0.1793	0.2370
Water absorption %	Treated	0	0.007	0.016	0.026	0.063	0.094
	Untreated	0	0.031	0.032	0.034	0.065	0.099

IV. CONCLUSION

The present study revealed that both alkali treated and untreated coir fiber based composite have shown improvement in mechanical properties. The mechanical properties keep on increasing till the coir content (treated and untreated) reaches 5% and starts decreasing beyond 5%. Amongst the both, alkali treated fiber based composites have shown superior properties to untreated ones. This is attributed to superior bonding, microfibril formation in alkali treated coir fibers (due to alkali treatment and milling) and uniform impregnation of these coir micro fibrils in polymer matrix. SEM study supports the fact that the alkali treated fiber reinforced composites are morphologically more uniform to untreated ones.

V. ACKNOWLEDGEMENTS

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Synthesis and antimycobacterial evaluation of new 1-substituted benzyl-4-(1-phenyl-3-substituted phenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole Derivatives

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ABSTRACT

A new series of 1-substituted benzyl-4-(1-phenyl-3-substituted phenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole derivatives, 5a-k have been synthesized. The structure of the newly synthesized compounds was determined by spectral analysis. The title compounds were screened for their preliminary antitubercular activity against Mycobacterium tuberculosis H37Ra active and dormant (MTB, ATCC 25177) and antimicrobial activity against standard Gram-negative bacteria, Escherichia coli (NCIM 2576), Pseudomonas flurescence (NCIM 2059) and Gram-positive bacteria, Staphylococcus aureus (NCIM 2602), Bacillus subtilis (NCIM 2162). Most of the synthesized compounds reported moderate activity against M. tuberculosis H37Ra and Bacillus subtilis strains.

Keywords:1,2,3-Triazole,Pyrazole,Antitubercular Activity, Antibacterial Activity

I. INTRODUCTION

Mycobacterium tuberculosis (MTB) was one of the top 10 causes of death worldwide and was responsible for more deaths than HIV and malaria [1]. Due to emerging infectious diseases and the increasing number of multi-drug resistant microbial pathogens in the last decades, a need for new classes of antimicrobial agents is warranted. The increase in antibiotic resistance due to multiple factors has encouraged the search for new compounds which are active against multi-drug resistant pathogens.

The synthesis of motifs containing more than one heterocycle ring has received much attention in recent years. Triazole and its derivatives are important class of bioactive molecules. Among other heterocyclic derivatives, triazole compounds were reported as most promising candidates towards anti-TB activity [2-8]. They also exhibit significant pharmacological activities such as anti-microbial [9,10], anti-convulsant [11], anti-proliferative [12], anti-cancer [13], anti-malarial [14] β-lactamase inhibitors [15], fungicidal [16], insecticidal [17] and anti-viral activity [18].

Pyrazole and its derivatives are important structure in medicinal chemistry that could provide a rich spectrum of biological activities [19-28]. The structural diversity and biological importance of triazole and tpyrazole have made them attractive targets for synthesis. 1,2,3-Triazole and pyrazole rings present in the same molecule could be convenient models for investigation of their biological activity. Keeping in mind the biological significance of triazole and pyrazole derivatives, we report herein the synthesis 1-substituted benzyl-4-(1-phenyl-3-substituted phenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole derivatives, **5a-k** as antimycobacterial agents.

II. METHODS AND MATERIAL

All the reactions were monitored by thin-layer chromatography (TLC). TLC was performed on Merck 60 F-254 silica gel plates with visualization by UV light. Melting points were determined in capillary tubes in silicon oil bath using a Veego melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on BRUKER AVANCE II 500 NMR spectrometer (Bruker Instruments Inc., Billerica, MA,

USA) at either 500-MHz (^{1}H NMR) and 126-MHz (^{13}C NMR) spectrometer instruments. Chemical shifts are reported from internal tetramethylsilane standard and are given in δ units. Column chromatography was performed on silica gel (100–200 mesh) supplied by Acme Chemical Co. (Mumbai, Maharashtra, India).

General procedure for synthesis of 4-ethynyl-1,3-diphenyl-1H-pyrazole (3a)

To a ice cold solution of diethyl (1-diazo-2-oxopropyl)phosphonate (13 mmol) and K_2CO_3 (20 mmol) in dry methanol (20 mL), solution of 1,3-diphenyl-1H-pyrazole-4-carbaldehyde (**2a**) [29] (10 mmol) in methanol (20 mL) was added and reaction mixture was stirred at room temperature for 24 hours. After completion of the reaction (TLC), solvent was distilled under vacuum and residue was dissolved in water (50 mL) and reaction mass was extracted by ethyl acetate (3 x 25 mL). Organic layer was washed with brine, dried over sodium sulphate and evaporated on rotary evaporator. The crude product was purified by column chromatography using Ethyl acetate:hexane (2:8) as eluent gave 4-ethynyl-1,3-diphenyl-1H-pyrazole (**3a**), Yield 1.02 gm, 42 %).

General procedure for the synthesis of 1-benzyl-4-(1,3-diphenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole (5a)

A reaction mixture of 4-ethynyl-1,3-diphenyl-1H-pyrazole, **3a** (0.244 g, 1 mmole), benzylazide, **4a** (0.14 gm, 1 mmole), copper sulphate (0.040 gm, 0.25 mmole) and sodium ascorbate (0.050 gm, 0.22 mmole) in DMF:Water (6 mL, 3:1) was stirred overnight. After completion of reaction (TLC), the reaction mixture was quenched in water and extracted by ethyl acetate (3 x 15 mL). Organic layer was dried over sodium sulphate and evaporated on rotary evaporator. The crude product was purified by column chromatography (Ethyl acetate:hexane) furnished target compound 1-benzyl-4-(1,3-diphenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole (**5a**). Compounds **5b-k** was synthesized by similar procedure.

4-(1,3-diphenyl-1H-pyrazol-4-yl)-1-(4-methylbenzyl)-1H-1,2,3-triazole, **5a**: ^{1}H NMR (500 MHz, DMSO) δ 8.46 (s, 1H), 8.06-8.08 (m, 4H), 7.89-7.91 (m, 5H), 7.42-7.44 (m, 2H), 7.30-7.31 (m, 2H), 7.12-7.14 (m, 2H), 5.64 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 150.96, 147.07, 140.41, 133.99, 130.43, 130.36, 129.90, 129.88, 126.91, 126.88, 126.48, 125.87, 121.38, 115.99, 115.53, 113.63, 113.22, 52.93, 21.49; LCMS: 392.2 $(M+H)^+$.

1-benzyl-4-(3-(4-bromophenyl)-1-phenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole, **5b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.79 – 7.74 (m, 2H), 7.50 – 7.44 (m, 6H), 7.37 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.20 (m, 3H), 5.52 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.54, 140.38, 139.64, 134.65, 131.97, 131.65, 130.09, 129.55, 129.15, 128.82, 127.91, 127.19, 126.89, 122.59, 120.58, 119.07, 112.54, 54.20; LCMS: 456.1 $(M+H)^+$.

4-(3-(4-bromophenyl)-1-phenyl-1H-pyrazol-4-yl)-1-(4-fluorobenzyl)-1H-1,2,3-triazole, **5c:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.77 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.52 – 7.44 (m, 6H), 7.37 – 7.29 (m, 1H), 7.28 – 7.20 (m, 4H), 7.07 (t, *J* = 8.6 Hz, 2H), 5.49 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.87, 161.89, 149.55, 140.54, 139.63, 131.98, 131.68, 130.52, 130.50, 130.12, 129.83, 129.76, 129.56, 127.18, 126.93, 122.65, 120.34, 119.09, 116.24, 116.07, 112.45, 53.44; LCMS: 474.1 $(M+H)^+$.

4-(3-(4-bromophenyl)-1-phenyl-1H-pyrazol-4-yl)-1-(4-methylbenzyl)-1H-1,2,3-triazole, **5d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.70 – 7.65 (m, 2H), 7.43 – 7.36 (m, 6H), 7.25 – 7.21 (m, 1H), 7.12 – 7.08 (m, 3H), 7.06 (d, *J* = 8.1 Hz, 2H), 5.39 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.53, 140.26, 139.65, 138.79, 131.97, 131.62, 130.08, 129.80, 129.55, 128.00, 127.16, 126.87, 122.55, 120.53, 119.06, 112.58, 54.01, 21.21; LCMS: 470.1 $(M+H)^+$.

1-benzyl-4-(3-(4-fluorophenyl)-1-phenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole, **5e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.77 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.58 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.47 (dd, *J* = 8.4, 7.6 Hz, 2H), 7.36 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.23 (dd, *J* = 7.0, 2.4 Hz, 2H), 7.19 (s, 1H), 7.03 (t, *J* = 8.7 Hz, 2H), 5.51 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.89, 161.92, 149.78, 140.53, 139.69, 134.68, 130.37, 130.30, 129.54, 129.13, 129.10, 128.79, 127.89, 126.98, 126.80, 120.43, 119.04, 115.56, 115.39, 112.53, 54.17; LCMS: 396.4 $(M+H)^+$.

1-(4-fluorobenzyl)-4-(3-(4-fluorophenyl)-1-phenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole, **5f**: ^{1}H NMR (500 MHz,

$CDCl_3$) δ 8.42 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.56 (m, 2H), 7.47 (t, *J* = 7.9 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.23 (dd, *J* = 8.5, 5.2 Hz, 2H), 7.19 (s, 1H), 7.06 (t, *J* = 8.6 Hz, 4H), 5.48 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.92, 163.85, 161.95, 161.88, 149.77, 140.68, 139.66, 130.55, 130.52, 130.40, 130.33, 129.81, 129.75, 129.55, 129.13, 129.10, 126.98, 126.84, 120.19, 119.05, 116.22, 116.05, 115.58, 115.41, 112.44, 53.42; LCMS: 414.1 $(M+H)^+$.

1-(4-chlorobenzyl)-4-(3-(4-fluorophenyl)-1-phenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole, **5g**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.51 (dd, *J* = 8.1, 5.6 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.8 Hz, 3H), 7.16 – 7.06 (m, 3H), 6.99 (t, *J* = 8.6 Hz, 2H), 5.40 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.93, 161.96, 149.78, 140.72, 139.65, 134.86, 133.17, 130.40, 130.34, 129.55, 129.33, 129.21, 129.11, 129.09, 127.01, 126.85, 120.26, 119.05, 115.61, 115.44, 112.36, 53.42; LCMS: 430.1 $(M+H)^+$.

4-(3-(4-fluorophenyl)-1-phenyl-1H-pyrazol-4-yl)-1-(4-methylbenzyl)-1H-1,2,3-triazole, **5h**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.76 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.58 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.46 (dd, *J* = 8.4, 7.6 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.16 (t, *J* = 4.0 Hz, 3H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.03 (t, *J* = 8.8 Hz, 2H), 5.45 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.88, 161.91, 149.78, 140.41, 139.69, 138.75, 131.64, 130.37, 130.31, 129.76, 129.53, 129.14, 129.11, 127.96, 126.95, 126.77, 120.37, 119.07, 119.02, 115.53, 115.36, 112.59, 53.98, 21.16; LCMS: 410.2 $(M+H)^+$.

1-benzyl-4-(3-(4-methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole, **5i**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.77 (dd, *J* = 4.8, 3.8 Hz, 2H), 7.54 – 7.50 (m, 2H), 7.45 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.24 – 7.19 (m, 3H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.49 (s, 2H), 3.82 (s, 3H) ; LCMS: 408.2 $(M+H)^+$.

1-(4-fluorobenzyl)-4-(3-(4-methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole, **5j**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.72 – 7.68 (m, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.39 (dd, *J* = 8.5, 7.6 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.17 – 7.10 (m, 3H), 6.97 (t, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 5.38 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.75, 160.77, 158.78, 149.48, 139.92, 138.73, 129.61, 129.59, 128.78, 128.74, 128.67, 128.45, 125.63, 125.56, 124.40, 119.17, 117.93, 115.10, 114.93, 112.86, 111.35, 54.27, 52.30; LCMS: 426.1 $(M+H)^+$.

4-(3-(4-methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl)-1-(4-methylbenzyl)-1H-1,2,3-triazole, **5k**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.77 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.46 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.21 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.45 (s, 2H), 3.83 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.78, 150.51, 140.74, 139.81, 138.57, 131.78, 129.80, 129.71, 129.48, 127.87, 126.70, 126.55, 125.50, 120.35, 118.95, 113.90, 112.53, 55.31, 53.91, 21.16; LCMS: 422.2 $(M+H)^+$.

Antitubercular Activity

All the synthesized compounds were screened for their *in vitro* activity against dormant and active *M. tuberculosis* H37Ra (ATCC 25177) at 3 μg/mL. Activity against MTB was determined through the XTT reduction menadione assay (XRMA) reading absorbance at 470 nm as per the protocol described in literature [30-34]. Percentage inhibition was calculated using the following formula:

% inhibition = [(control–CMP) / (control–blank)] x 100

Where 'control' is the activity of mycobacteria without compounds, 'CMP' is the activity of mycobacteria in the presence of compounds and 'blank' is the activity of the culture medium without mycobacteria.

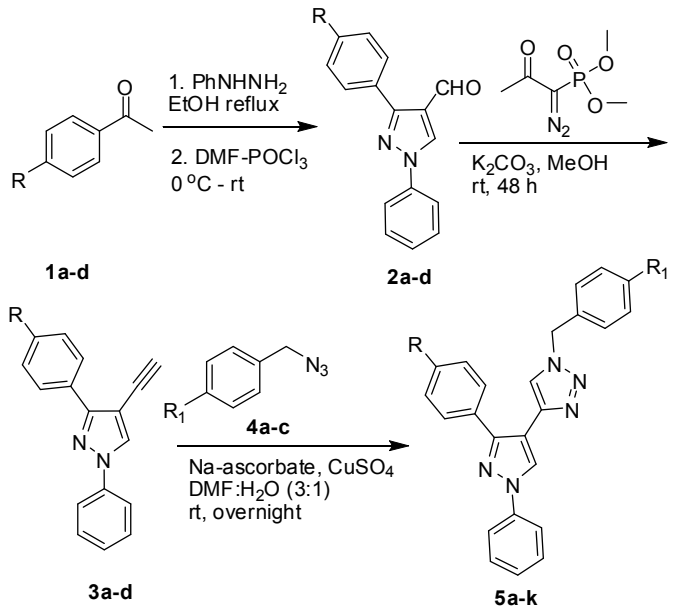
Antibacterial activity

All bacterial cultures were first grown in Luria Burtony media at 37 ºC at 180 rpm. Once the culture reaches 1 O.D., it is used for anti-bacterial assay. Bacterial strains *Escherichia coli* (NCIM 2576), *Pseudomonas flurescence*(NCIM 2059) as Gram-negative and *Staphylococcus aureus* (NCIM 2602), *Bacillus subtilis* (NCIM 2162) as Gram-positive were obtained from NCIM (NCL, Pune) and were grown in Luria Burtony medium from Hi Media, India. The assay was performed in 96 well plates after 8 hours and 12 hours for Gram negative and Gram positive bacteria, respectively. 0.1 % of 1 O.D. culture at 620 nm was used for screening

inoculated culture was added into each well of 96 well plate containing the compounds to be tested. Optical density for each plate was measured at 620 nm after 8 hours for Gram-negative bacteria and after 12 hours for Gram- positive bacteria.[34,35]

III. RESULTS AND DISCUSSION

A series of 1-benzyl-4-(1-phenyl-3-substituted phenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole derivatives, **5a-k** were synthesized according to Scheme 1. Substituted acetophenone **1a-d** on condensation reaction with phenyl hydrazine in ethanol gave corresponding phenyl hydrazone derivative, which on Vilsmeyer-Hack formylation reaction with dimethyl formaide and phosphorus oxychloride gave 1-phenyl-3-substituted phenyl-1H-pyrazole-4-carbaldehyde, **2a-d.** Aldehyde **2a-d** on reaction with diethyl (1-diazo-2-oxopropyl)phosphonate and K_2CO_3 in methanol (Ohira-Bestman reaction) gave 4-ethynyl-1-phenyl-3-substituted phenyl-1H-pyrazole, **3a-d**. Alkyne **3a-d** on click reaction with substituted benzyl azide, **4a-c** furnished target compounds 1-benzyl-4-(1-phenyl-3-substituted phenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole, **5a-k**. The physical constant and yields are predicted in **Table 1**



Scheme 1. Synthetic route of 1-benzyl-4-(1-phenyl-3-substituted phenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole derivatives, **5a-k**

Comp.	R	R_1	MP (°C)	Yield[a] (%)
5a	H	CH3	140-142	68
5b	Br	H	138-140	65
5c	Br	4-F	136-138	60
5d	Br	4-CH_3	154-156	70
5e	F	H	140-141	58
5f	F	4-F	142-144	59
5g	F	Cl	169-171	52
5h	CH3	F	152-153	67
5i	OMe	H	102-103	60
5j	OMe	4-F	118-120	66
5k	OMe	4- CH_3	120-121	66

[a]Yield after column purification

The structure of 1-benzyl-4-(1-phenyl-3-substituted phenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole compounds, **5a-k** was confirmed by NMR and mass. As a representative analysis of compound 4-(3-(4-methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl)-1-(4-methylbenzyl)-1H-1,2,3-triazole, **5i** the ^{1}H NMR spectrum of compound **5i** displayed three singlets in aliphatic region at δ 2.34 (CH_3), 3.83 (OCH_3) and 5.49 (Ar-CH_2-triazole). Two doublets at δ 6.88 and 7.52 were attributed to methoxy substituted phenyl ring, while multiplate at δ 7.27-7.31 and two double doublets δ 7.46 and 7.77 corresponds to protons of N-phenyl ring. Two doublets appeared at δ 7.12 and 7.16 corresponds to the protons of methyl substituted phenyl ring. Triazole and pyrazole protons were resonated as singlet at δ 7.21 and 8.43 respectively. The ^{13}C NMR spectrum of compound **51** showed three signals of aliphatic carbons at δ 21.16 (Ar-CH_3), 53.91 (Ar-CH_2-N) and 55.31 (Ar-OCH_3). Aromatic, triazole and pyrazole carbons showed signals from δ 112.53 to 159.72. Structure of compound **5i** was further confirmed by MS, molecular ion peak at *m*/*z* 422.20 $(M+H)^+$. Structures of all the derivatives were ascertained similarly.

Biological evaluation

The antitubercular activity for each synthesized compound was determined by measuring inhibition of growth against avirulent strain of *M. tuberculosis* H37Ra, dormant and active (MTB, ATCC 25177) in liquid medium. In a preliminary screening, the antimycobacterial activity of these compounds was assessed at 3 μg/mL concentration using first-line

antitubercular drug rifampicin as reference standard. *In vitro* activity studies against MTB were performed using the XRMA [30-34]. The antibacterial activity of synthesized compounds was determined against the standard Gram-negative bacteria, *E. coli* (NCIM 2576), *P. flurescence* (NCIM 2059) and Gram-positive bacteria, *S. aureus* (NCIM 2602), *B. subtilis* (NCIM 2162). Ampicillin served as positive control for antibacterial activity [34,35]. The *in vitro* preliminary screening values (% inhibition) against microorganism tested are summarized in **Table 2**.

Table 2. Antibacterial screening of compounds **5a-k** (% growth inhibition) at 3 µg/mL

Comp.	*S. aureus*	*B. subtilis*	*E. coli*	*P. flurescence*	*Dormant* H37Ra	Active H37Ra
5a	4.36	1.45	-	8.92	32.67	33.45
5b	13.95	41.42	-	5.81	34.1	47.5
5c	7.26	44.3	-	7.05	34.81	39.37
5d	19.27	27.59	-	-	37.07	46.53
5e	25.91	45.79	-	-	36.6	47.8
5f	-	50.36	-	7.13	26.72	30.88
5g	11.26	33.48	-	4.63	38.17	45.91
5h	24.68	-	-	-	36.86	51.14
5i	14.2	36.82	-	7.51	29.57	53
5j	10.86	25.71	-	3.1	43.49	44.32
5k	16.51	25.71	-	-	36.38	41.2
Amp	93.8	93.5	92.25	92.15		
Rifam[b]					96.4	97.88

a - indicates not active;
b - Rifampicin[b] 0.5 µg/mL concentration.

The *in vitro* antimycobacterial activity against *M. tuberculosis* H37Ra (dormant and active) *E. coli*, *P. flurescence*, *S. aureus* and *B. subtilis* revealed that most of the compounds reported moderate activity at 3 µg/mL against *M tuberculosis* and Gram positive bacterial strains. The preliminary structure activity relationship study revealed that replacement of hydrogen atom of phenyl ring A and B (**Figure 1**) by substituent groups like Br, F, OMe and CH_3 affects the activity.

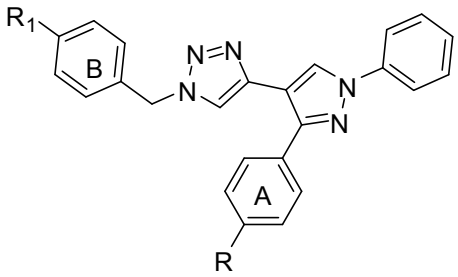


Figure 1. Compounds **5a-k**

Compound 5a (R = H, R_1 = CH_3) showed moderate activity against *M. tuberculosis* H37Ra dormant and active strains where as inactive against Gram +ve and Gram –ve bacterial strains. Among the compounds, **5b-d** with bromo substituted phenyl ring A and substituted phenyl ring B, compound **5b** (R_1= H) showed good activity against *M. tuberculosis* H37Ra active and *B. subtilis* and moderate activity against *M. tuberculosis* H37Ra dormant strain. Whereas, compound **5c** (R_1= F) showed good activity against *B. subtilis* and moderate activity against *M. tuberculosis* H37Ra dormant and active strains. Compound **5d** (R_1= CH_3) reported good activity against *M. tuberculosis* H37Ra active strain and moderate activity against *M. tuberculosis* H37Ra dormant and *B. subtilis* strains. Among the compounds, **5e-h** with 4-fluoro substituted phenyl ring A and substituted phenyl ring B, compound **5e** (R_1= H) showed good activity against *M. tuberculosis* H37Ra active and *B. subtilis* and moderate activity against *M. tuberculosis* H37Ra dormant and *S. aureus* strains. Compound **5f** (R_1= F) reported good activity against *B. subtilis* and moderate activity against both mycobacterial strains. Compound **5g** (R_1= Cl) showed good activity against *M. tuberculosis* H37Ra active strain and moderate activity against *M. tuberculosis* H37Ra dormant and *B. subtilis* strains. Compound **5h** reported good activity against *M. tuberculosis* H37Ra active strain and moderate activity against *M. tuberculosis* H37Ra dormant and *S. aureus* strains. Among the compounds, **5i-k** with 4-methoxy substituted phenyl ring A and substituted phenyl ring B, all compounds were reported good activity against *M. tuberculosis* H37Ra active strain. Compounds **5i** and **5k** showed moderate activity against *M. tuberculosis* H37Ra dormant and *B. subtilis* strains. Compound **5j** also reported good activity against *M. tuberculosis* H37Ra dormant strain and moderate activity against *B. Subtilis.*

Thus, it is concluded that compounds with R^1 = H, CH_3 and Cl, group showed good antibacterial activity against *M. tuberculosis* H37Ra active strain. compound with R = OMe and R^1 = H reported good activity against both *M. tuberculosis* H37Ra strains. It was worth to mention that all the synthesized compounds are less active against Gram –ve bacterial strains.

IV. CONCLUSION

In the present study, we have detailed the synthesis and primary biological screening of 1-substituted benzyl-4-(1-phenyl-3-substituted phenyl-1H-pyrazol-4-yl)-1H-1,2,3-triazole derivatives, **5a-k**. It can be concluded that, most of the synthesized compounds with Br, F and OMe substituted phenyl ring at 3-position of pyrazole and unsubstituted, 4-CH_3 and 4-Cl substituted benzyl ring at 1-position of 1,2,3-triazole showed good antitubercular activity against *M. tuberculosis* H37Ra active strain. Most of the synthesized compounds exhibited moderate to good antibacterial activity against *M. tuberculosis* H37Ra dormant *B. subtilis* strains. Thus, these results warrant the need for synthesis of similar libraries with other substituents to ascertain the trend described in this work.

V. Acknowledgments

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Pectin - Ethanolamine Graft Copolymer Hydrogel for Ointment and Transdermal Patches Consist of Tridax Procumbens L. Ethanol-Water Extract as Antiseptic and Antifungal Agent

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ABSTRACT

Currently research has been carried out for the development of transdermal drug delivery systems. Specific transdermal drug delivery system is chemically modified pectin based hydrogels. This modified gel is used to carry ethanol-water extract of Tridax procumbens L. as antiseptic, antifungal. Pectin forms gel with crosslinking agents like divalent or multivalent cations, glutaraldehyde etc. Transdermal patches and ointment with petroleum wax made from the cross-liked modified pectin gel and the leaf extract of plant in ethanol-water were loaded through diffusion method. In the current study an attempt has been made to improve the properties of the pectin gels by graft copolymerization with ethanolamine and the swelling properties were modified by varying concentration of crosslinking agent, glutaraldehyde and used for various biomedical applications,. Antiseptic and antifungal activity of loaded hydrogel were studied.

Keyword: Hydrogel, pectin modification, Tridax procumbens L. Transdermal patches, ointment.

I. INTRODUCTION

Hydrogels are three-dimensional hydrophilic polymer networks capable of imbibing large amounts of water, which have been widely used in the field of biomedicine and pharmacy [1-3], such as wound dressing, super-absorbents, drug delivery systems, etc Pectin is a complex heterogeneous polysaccharide found in primary cell wall of most plants, citrus and apple where it gives mechanical strength and flexibility due to it's interaction with other cell wall components.. The dominant structural feature of pectin is a linear chain of poly α 1-4 – galacturonic acids, with varying degree of methylation of carboxylic acid residues[4].

Pectins with low degree of methylation forms gel in presence of calcium ions whereas pectin with higher degree of methylation forms gel in acidic media with the addition of different sugars e.g., sucrose or glucose [5]. The carboxyl group of pectin is often esterified with methanol. Pectin can be classified in to high-methoxyl (>50% esterified) and low- methoxyl (<50%) pectins.The two classes have profoundly different gel forming properties [6].Typically, large concentration of sucrose (>55 wt %) are added to high-methoxyl pectins under acidified conditions (pH ~3.5) to induce gelation. Under these conditions, network formation occurs via hydrogen bonding between carboxyl or hydroxyl groups on adjacent chains and hydrophobic interactions between methyl ester groups [7-9]. It was reported that alkyl esters of pectin and pectic acid absorb bile acids, fat and cholesterol. The chemical modification of pectin (amidation, trans-eterification) is relatively easy and it modifies in a significant way physiochemical and biological properties of pectin.[3]. [10-12]. N- Alkyl pectinamides have some advantages in comparison with other alkylated derivatives of pectin. The amide bond is sufficiently resistant to hydrolysis by acids or alkali. The reaction yield of N- alkylamidees prepared by the reaction of pectin with aliphatic non branched amines are relatively high.

In this present study attempts have been made to chemically modify pectin with various concentrations of ethanolamine(1:1,1:2,1:3,1:4),this is further used for the preparation of hydrogels by crosslinking with Glutaraldehyde (GA) in acidic medium. The prepared hydrogels were characterized by FTIR, organic elemental analysis and x ray diffraction studies. Drug release studies, swelling behavior of the hydrogels have been also been done. Cytocompatibility studies of the

hydrogels have also carried out. Recommended treatments include the administration of ethanolic extract of *Tridax procumbens L*. which must be released at the infected sites, it is also useful to have dosage forms that are able to specifically release drugs, such as peptides, proteins, vermifunges and diagnostic agents .

II. MATERIALS AND METHODS

Pectin, methanol, salicylic acid and glutaraldehyde **(GA)** were obtained from Loba-Chemie Indoaustranal Co., Mumbai, India. Ethanolamine is obtained from SRL research laboratories, Mumbai, India. Hydrochloric acid 35% pure was obtained from Merck Limited, Mumbai, India. Double distilled water was used throughout the study. Commercial pectin was purified and converted in to H- form by washing with 0.1mol/1 HCl dissolved in the ethanol water mixture (1:1 v/v). Pectin subsequently was washed several times with ethanol water mixture fallowed by 96% ethanol until the chloride reaction was negative, and finally dried at 60^0C.

A. Synthesis of modified Pectin

The reaction has been done according to method of (Sinitsya et. al. 2000). The reaction was carried out in heterogeneous medium with methanol as a solvent. . Pectin powder (5 gram) was weighed in a well equipped 250 ml three necked flask and it was suspended in 50 ml methanol. An amount of 10 ml ethanolamine was get dissolved in a 50 ml methanol and the solution was added gradually in the flask under stirring. The reaction has been carried out at 25^o C temperature until 96 hours of continuous stirring. After completion of the reaction the product was obtained in the powder form by simple filtration method. The product obtained is converted in to acid forms by washing with 0.1M HCl in an ethanol-water mixture (1:1,v/v) to convert free carboxylic group in to protonated form. Finally the sample were washed several times with 40% (v/v) ethanol until it shows the negative reaction to chloride, then treated with 80% (v/v) ethanol, filtered and dried at 60^0C. This EAMP is used for the preparation of hydrogel membranes using glutaraldehyde(GA) as crosslinking agent.

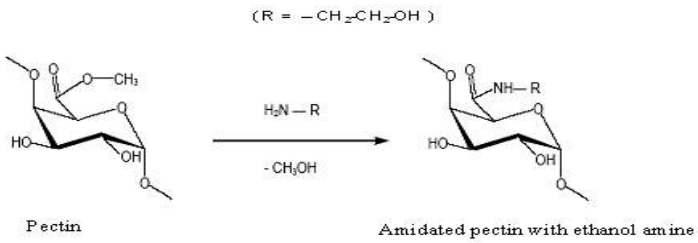


Figure 1. Amidation Reaction of Pectin with Ethanolamine (Sinitsya et. al)

B. Analysis of EAMP (Ethanolamine-Pectin copolymer) Samples

The degree of amidation (DA) the mass and molar yield of the reaction is calculated on the basis of organic elemental analysis results, according to the fallowing equations (Sinitsya et. al. 2000).

$$\frac{M_N}{M_C}\left[6+\frac{73}{100}+(K-1)\frac{M_N}{14}\right]\times 100$$

$$Y_m=\frac{M_N M_A}{14}$$

$$Y_n=\frac{DA}{73}\times 100$$

Where DA is the degree of amidation, Ym the mass yield of the reaction,i.e the relative mass of bonded amine (%) in reaction product, Yn the molar yield of the reaction i.e. the relative content of ester groups substituted by amine (%), M_N the nitrogen content (%) and M_C the carbon content (%), M_A the molar mass of amine(g mol^{-1}), 12 the carbon atomic mass (g mol^{-1}), 14 the nitrogen atomic mass (g mol^{-1}), 6 the sum of carbon in galacturonic unit, K the some carbons in amine molecule and 73 is the methylation degree(DM) of original pectin (%).

Sample	M_N (%)	Mc (%)	D_A (%)	D_M (%)	Y_M (%)	Y_N (%)
1	2.17	38.31	33	31	8.8	46

Table 1. Characterization of samples based on the results of Organic Elemental Analysis

C. Preparation of EAMP (Ethanolamine-Pectin copolymer) hydrogels crosslinked with GA (Glutaraldehyde)

The EAMP/GA hydrogel crosslinked with GA used in the study were fabricated using a casting/solvent evaporation technique. A stock viscous solution of EAMP in water (10% w/v) was prepared by dissolving 2g of EAMP in 20ml of distilled water and stirring for 2hrs at room temperature. To the dissolved EAMP solution 1ml of glutaraldehyde was added and each solution was acidified with 35% HCL solution. That solution was stirred for 30 min at room temperature to complete the crosslinking reaction. The thick crosslinked gel was finally obtained further sonicated to remove the trapped air bubbles and used for further study.

D. Swelling Study

The film was made from prepared gel by pouring it into shallow dishes (with diameter 8.5 cm) and dried in laminar flow air chamber at room temperature for 3 days. Finally, the crosslinked EAMP films were thoroughly rinsed with distilled water to remove residual GA. After drying in air, the crosslinked EAMP films (0.15 mm thickness) were cut into small disks (with diameter of ~9 mm) and used for swelling study. The swelling characteristics of test hydrogels were determined by immersing dried test samples to swell in 5 ml of a phosphate buffer solutions at pH 1.4, 5.4, 7.4, simulating gastrointestinal tract conditions [18,19] and 9.4 solutions for 24 hours. At specific time intervals, the samples were removed from the swelling medium and were carefully blotted with a piece of paper towel to absorb excess water on the surfaces. The % swelling (% Sw) of test samples were calculated from the following expression

$$\% Sw = (Ws - W_D) / W_D \quad X\ 100$$

Where `Ws' is the weight of the swollen test sample and `Wd' is the weight of the dried test sample. The sample, which had the best swelling characteristics, was subsequently selected for the salicylic acid release profile study.

E. Drug release profile of ETE (ethanolic extract of *Tridax procumbens L.*) from EAMP hydrogel

The drug release study was carried out by using prepared cellulose membrane. The crosslinked EAMP with 1ml of GA gel was used for the drug release study. In the preparation of the drug loaded [8,9] crosslinked hydrogel, EAMP first cross-linked with 1ml concentration of glutaraldehyde with continuous stirring for 30 min at room temperature. ethanolic extract of *Tridax procumbens L*. (ETE) as model drug incorporated in the cross linked hydrogel by diffusion method. The drug ETE dissolved in ethanol and the crosslinked EAMP hydrogel kept in the ethanol solution of drug for 5hrs then finally drug loaded hydrogel washed with distilled water to remove the drug adhered to the surface of hydrogel. The release study was carried out at 37^0C.

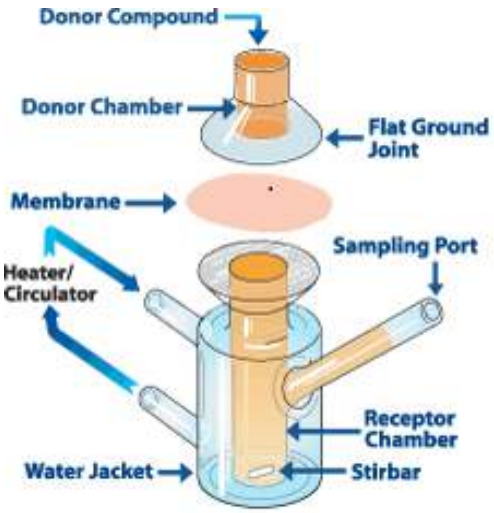


Figure 2. Frantz Diffusion Cell

F. MTT Assay

Mice were sacrificed and their spleens were removed aseptically. The cell suspension was prepared by loose potter and flushing. After centrifugation at 1000 rpm for 10 min at 250 c, erythrocytes were lysed by hypotonic solution and the cell pellets were washed twice with Dubelco minimum essential medium (DMEM). The cells were resuspended in DMEM medium and cell number were adjusted to 106 cell/ ml.

The viability of splenocytes was determined by the MTT dye technique. Hydrogel samples were cut in to 5 mm x 5mm dimensions and transferred in polystyrene petriplates. Samples were sterilized by pouring 70 % ethanol in petriplates and keeping the same under U V light in a laminar hood until the a alcohol evaporated. To the samples 20µl of of cell suspension was seeded and kept in the incubator (37o c for 1 hrs to allow the cells to adhere to the sample matrix. After cell adherence, 2mm of the DMEM medium was added to the each of the

precipitates and again incubated for 48 hrs for allowing cell proliferation. After 48 hrs of incubation, 200µl of MTT dye (4mg/ml) was added and the system as again incubated for 3 hours. After incubation the media from petriplates were discarded and 400µl of DMSO was added for the colour development. For control the cells were seeded in the petriplates. The colour was developed spectrophtometrically at 570 mm.The relative cell proliferation was measured by the fallowing formula;

$$Rp = A_{test} / A_{contrrol}$$

Where; Rp = relative cell proliferation ,
A_{test} = absorbance of the samples and
$A_{contrrol}$ = absorbance of the control.

In a similar manner, L929 cell suspension (106 cell/ml) was used to carry out the MTT assay. For blank, cells were directly seeded to the polystyrene petriplates (taken as controls) since polystyrene is a known biocompatible material.

G. Hemolysis Test

In the present work the hemolysis tests were carried out broadly on the basis of ASTM standard [19]. The test is mainly aimed at finding the extent of hemolysis caused in the presence of the sample prepared. The hemolysis percentage is defined as

$$\textbf{\% Hemolysis} = \{[OD_{test} - OD_{negetive}] / [OD_{Positive} - OD_{negetive}] \times 100$$

For this purpose goat's blood was collected in a beaker containing sodium citrate in the proportion of 3.8 g of sodium citrate per 100 ml of blood to avoid coagulation. The anti- coagulated blood was then diluted with N-saline in the proportion of 8:10. For checking the haemolysis 0.2 ml of diluted blood was added to 0.5 ml of 0.01N hydrochloric acid (HCl) followed by the dilution up to 10 ml and incubated for 60 min at 37 °C. The OD of the incubated solution was measured in an UV spectrometer at 545 nm wavelengths. Since HCl is known to cause large-scale rupture of RBC the OD count of this solution is taken as positive control referred to as $OD_{positive}$. Similarly, for negative control 0.2 ml of diluted blood was added to 10 ml of normal saline and again this was incubated for 60 min at 37 °C.

The OD of this solution is found again in an UV spectrometer at 545 nm wavelength and the OD is referred to as $OD_{negative}$. The reason for adding normal saline solution for negative control test is that this is known to cause the least RBC rupture. Having obtained the two standard OD, the OD of the material is obtained in similar lines. Sample having dimension of 5 mm X 5 mm was cut and was taken in a standard test tube containing N-saline and incubated at 37 °C for 30 min for providing temperature equilibrium. 0.2 ml of diluted blood was then added to the test tube, mixed gently and incubated for 60 min. OD of the sample is then obtained. This process is referred to as OD_{test}. The accepted norm is that if the haemolysis percentage is less than 10 the test material is taken as hemocompatible and if it is less than 5 the material is highly hemocompatible.

III. RESULTS & DISCUSSION

A. FTIR Characterization

The FTIR spectrum of EAMP hydrogel and pectin were taken in the range of 4000 – 400 cm^{-1} as KBr pellet and attenuated total reflectance (ATR for films) with the help of FTIR spectrophotometer (NEXUS – 870,Thermo Nicolet Corporation). Fig.1.A. has shown the FTIR spectra of the pure pectin. As the spectrum shown 3432 cm^{-1} due to –OH groups ,2921 cm^{-1} shows C-H stretching, 1758 cm^{-1} shows >C=O ester, 1020 cm^{-1} shown secondary alcohol(characteristic peak of -CH-OH in aliphatic cyclic alcohol C-O stretch). Fig 1 B shows the FTIR spectra of EAMP hydrogel.The carboxyl vibration region 1500-1900 cm-1 is most important for our analysis. The acid form of modified pectin has two important bands at 1674 cm-1 (amide I) and 1571cm-1 (amide II). The presence of these two bands and absence of intense carboxylate stretching bands indicates that the subsituents were bound to pectin chain by covalent amide bond, although we do not exclude the possibility that small amount of the amine salt might be found in the pectin.The conversion in to salt form lowers the carbonyl frequency and brings about the strong absorption band at 1605-1630 cm-1 belonging to the antisymmetric vibration of carboxylate anion. The intense carboxylate antisymmetric vibrations bands overlap with amide bands, which greatly complicate the analysis.

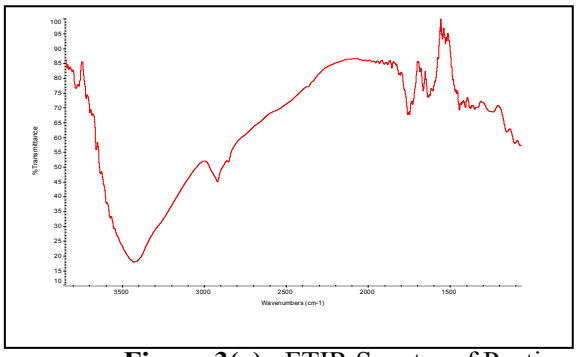


Figure 3(a). FTIR Spectra of Pectin

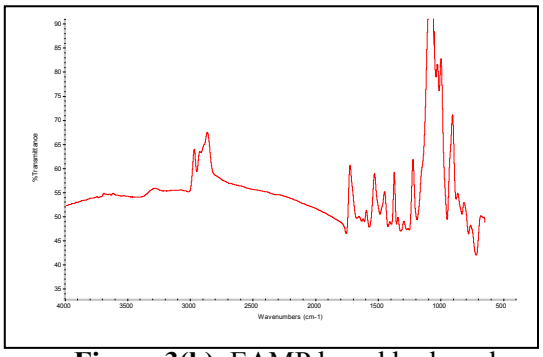


Figure 3(b). EAMP based hydrogel

Figure 3. (a), and (b) FTIR Spectra of Pectin and EAMP based hydrogel respectively.

B. X-Ray Diffraction study

XRD study of the pectin and EAMP done with XRD-PW 1700, Philips, USA. Ethanolic extract of *Tridax - procumbens L* using Cu K αradiation generated at 40 Kv and 40mA. The range of diffraction angle was 10°–70oThe Figure 2d, 2c shows XRD pattern of the pectin and EAMP respectively. In x-ray diffractogram of the EAMP there shown three intense peak at 46.17° - 2θ, 22° -2θ, 39.9 °- 2θ where as in the case of pectin peak appears at 2θ. This indicates that considerable increase in the crystallinity of the EAMP based hydrogel.

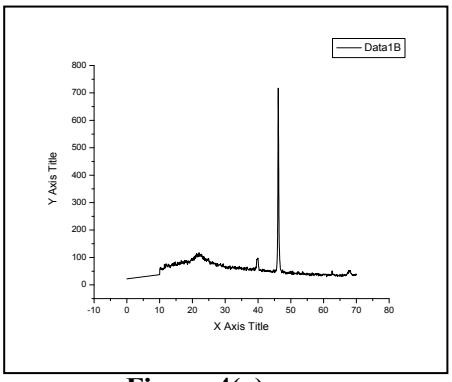


Figure 4(a)

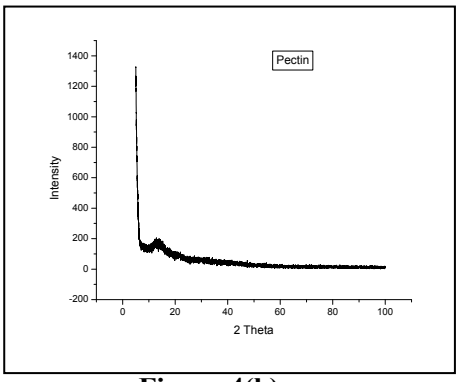


Figure 4(b)

Figure 4. (a) and (b) XRD patterns of pectin and EAMP based hydrogel resp.

C. Swelling Behavior

The EAMP was water soluble polymer so it required cross-linking by cross-linker. The EAMP hydrogel was cross-linked with 1ml of GA as a cross-linking agent respectively (acidified GA with HCl) were allow to swell in 5 ml of phosphate buffer solutions pH 1.4, 5.4, 7.4 and 9.4. The results indicates that GA crosslinked EAMP hydrogel swelled more significantly. (swelling 335%) at pH 7.4 due to a large swelling forces created by the electrostatic repulsion between the ionized acid groups as well as amide group.

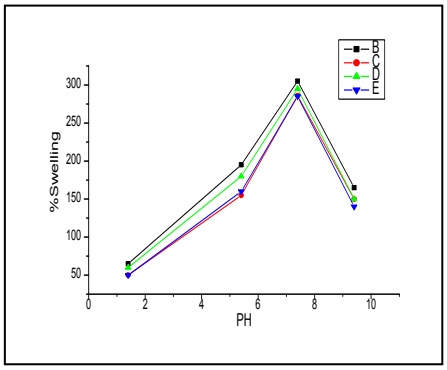
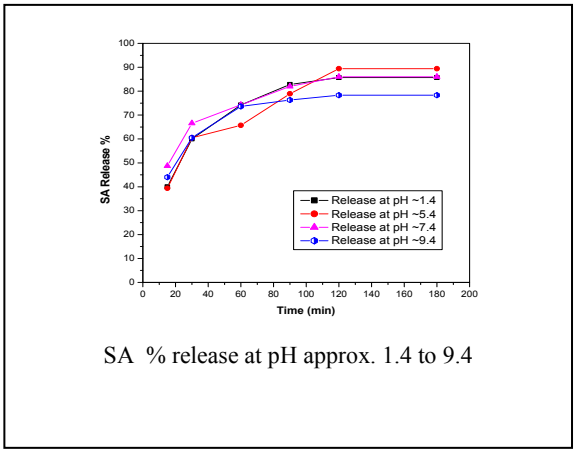


Figure 5. Swelling behavior of EAMP hydrogel (1:1, 1:2, 1:3, 1:4concentrations)

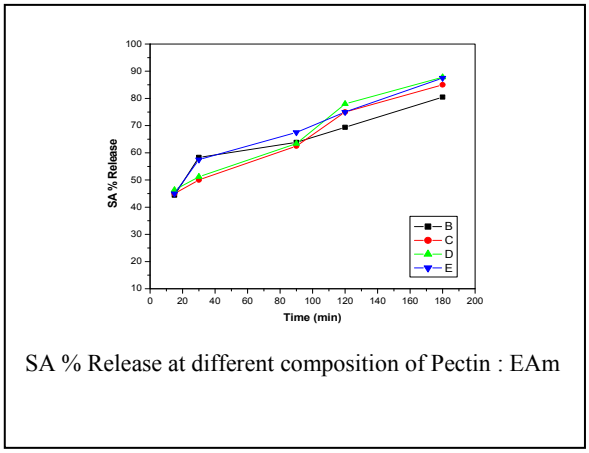
D. Drug Release Studies

The EAMP cross-linked with 1 ml of cross-linking agent (GA) which is further acididified with HCL showed more % swelling, so it was selected for drug release studies. Fig 3A and 3 B shows the ETE release profiles from the GA crosslinked EAMP hydrogel at deferent pH ~ 1.4, 5.4,7.4 ,9.4 and drug release behavior of hydrogels at different concentration(1:1,1:2,1:3 and 1:4) which is prepared by varying concentration of ethanolamine. It is evident from the graph 3, A at pH 5.4, the amount of ETE release increased significantly (approximately 89%) and at pH 7.4 the amount of ETE release is increases considerably (~85%) because the swelling of the hydrogel network increases at neutral pH. After 5 hrs of release at pH 7.4 the cumulative ETE release still maintained at approximately 85%. This due to some ETE molecules may be cross linked with hydrogel network directly by GA, and those cannot be released unless polymer matrices are degraded. Fig. 3. B. shows that release pattern of ETE increases considerably with increasing concentration of ethanolamine. It it is evident from the graph that ETE release is approximately 85% at concentration 1:2 1:3,1:4, and at 1:1, the release of ETE is relatively low (approximately 72%). Thus it clearly suggests our view that SA release increases with the increasing concentration of ethanolamine.



SA % release at pH approx. 1.4 to 9.4

Figure 6(a)



SA % Release at different composition of Pectin : EAm

Figure 6(b)

Figure 6. Drug release profile from the hydrogels,6 (a) drug release profile of EAMP hydrogel at defferent pH (1.4, 5.4, 7.4 and 9.4),6 (b) drug release profile of EAMP hydrogel at defferent concentrations (1:1, 1:2, 1:3 and 1:4).

E. Drug Release Kinetics from the Hydrogel

The release kinetics of the drug from hydrogels indicates that hydrogels of 1:1 and1:4 concentration both follows Higuchian kinetics, thus both are diffusion-controlled. The hydrogels which are prepared in 1:2 and 1:3 concentrations follows zero order release kinetics.

Diffusion systems may release drug following Higuchian or Fickian kinetics. The rate of release of a drug dispersed as a solid in an inert matrix has been described by Higuchi [32–34]. In this model, it is assumed that solid drug dissolves from the surface layer of the device first; when this layer becomes exhausted of the drug, the next layer begins to be depleted by dissolution and diffusion through the matrix to the external solution. In this fashion, the interface between the region containing dispersed drug and that containing dispersed drug moves into the interior as a front. For the purposes of data treatment the above model is depicted by the following equation;

M ¼ kt1=2

Where M is the mass of the drug released per unit area, k is a constant, so that a plot of amount of drug released versus the square root of time, t, should be linear if the release of the drug from the matrix is diffusion controlled. The release of drug from a diffusion system can also be described by Fick's first law of diffusion [35, 36]:

J ¼ _D

where J is the flux of drug across a membrane in the direction of decreasing concentration (amount/area-time), D is the diffusion coefficient of the drug in the membrane (area/time) and dCm/dx is the change in concentration of drug in the membrane over a distance x. Drug release pattern from Patches B and C also followed zero-order kinetics

indicating that the patches can be used for controlled drug delivery system. Fig, 7, Drug release kinetics from the EAMP hydrogels, Figure 7.(a),(b),(c) and (d).

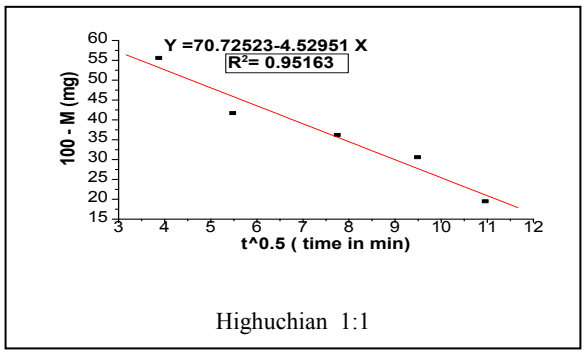


Figure 7(a). Drug release kinetics from the hydrogel (1:1)

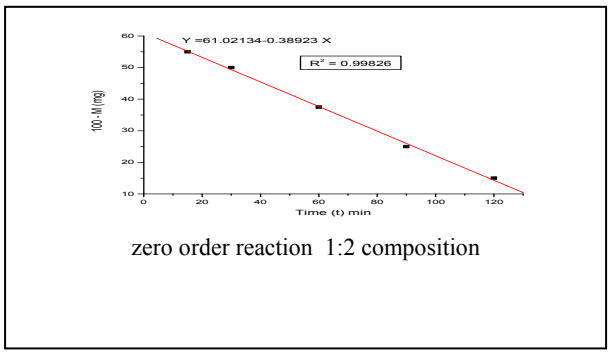


Figure 7(b). Drug release kinetics from the hydrogel (1:2)

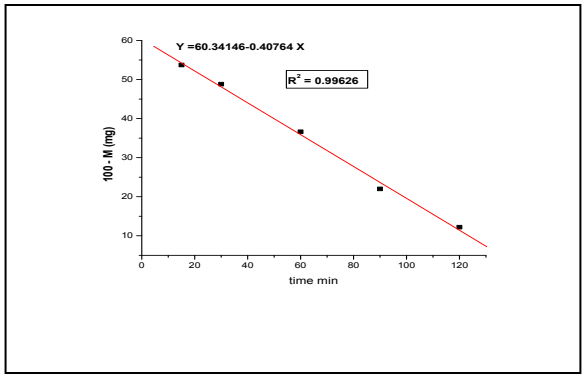


Figure 7(c). Drug release kinetics from the hydrogel (1:3)

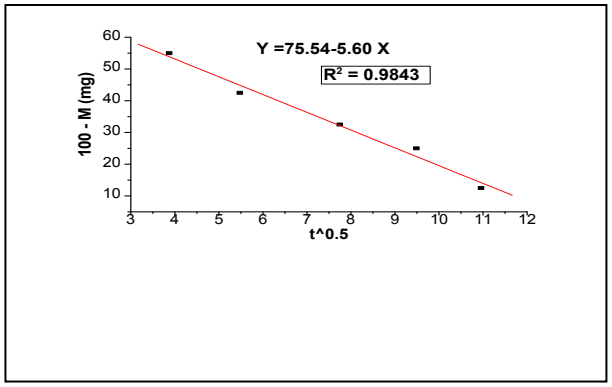


Figure 7(d). Drug release kinetics from the hydrogel (1:4)

F. Hemolysis Study

Hemocompatibility results of the EAMP hydrogels reveals that all the hydrogel samples have value less than 5, hence it clearly indicates that all the samples in defferent compositions (1:1, 1; 2, 1:3 and 1:4) are highly hemocompatible.

S.No.	Hydrogel compositions	OD of the sample	Hemolysis	Remarks
1	1:1	.0110	3.33	Highly hemocompatible
2	1:2	.0122	3.69	-
3	1:3	.0131	3.96	-
4	1:4	.0143	4.33	-

Table 2. Hemolysis result of EAMP Hydrogel in defferent concentrations (1:1, 1:2, 1:3, 1:4)

IV. CONCLUSION

In this work EAMP has been prepared by the amino de-alkoxylation (aminolysis) of pectin with various concentrations of ethanolamine. The structural changes in the modified pectin have been investigated using FTIR spectroscopy. Vibration bands of amide bands (amide I, amide II) and N- alkyl groups have been observed in FTIR spectra of EAMP and assigned. The data obtained were in good agreement with other analytical methods (organic elemental analysis). The amidation with primary amines permits various functional groups to be attached to pectin macromolecule, which influences the physical and chemical properties of pectin derivatives and their possible application. Crosslinking between pectin

macromolecule can occur when another part of amine radical carries such active groups like chlorine, oxyrane rings or other amino groups. Finally such bioactive molecules as protein, peptides, enzymes or drugs can be immobilized on the surface of pectin surface via amidation. We think that EAMP based hydrogel could be more interesting for colon targeted drug delivery systems.

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Facile Synthesis of 2-Substituted Benzimidazoles Using Waste Aluminium Foil

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ABSTRACT

Aromatic aldehydes and *o*-phenylenediamine in presence of waste aluminium foil synthesizes 2-Substituted benzimidazoles were synthesized in a one pot under microwave condition.at specific temperature it gives good yield and high selectivity.

Keywords: Benzimidazoles, *o*-Phenylenediamine, Aromatic aldehyde, FeCl3/Al2O3

I. INTRODUCTION

Benzimidazole is important hetrocycles in drug discovery 1 large variety of biological activity benzimidazole have 2-4.Benzimidazole nucleus exhibit wide spread occurrence and exhibit wide range of properties like HIV,RNA,influenza,HCMV,5 they have Bis benzimidazoles derivatives as mirror groove binding agent for DNA for antitumor activity 6 many times they are used for biological modelling of biological systems 7-8Benzimidazole are also important in organic synthesis for various reactions 9-10Therefore the benzimidazole is centre of attraction now adays.preparation of benzimidazoles has gained considerable attention in recent years 11-14. Despite their importance from pharmacological, industrial and synthetic points of view,comparatively few methods for the preparation of benzimidazoles have been reported inchapter 1. The most popular synthetic approaches generally involve the condensation ofan arylenediamine with a carbonyl equivalent 15. These includes the condensation of oaryldiaminesand aldehyde using air as the oxidant 16, the condensation of oaryldiamineswith carboxylic acids or their derivatives recently by PS-PPh3/CCl3CN 17 , thermal or acid promoted cyclization reactions 18 or the use of microwave irradiation 19-20 . In all these approaches, condensation of arylenediamines with aldehyde involves a two step procedure that includes the oxidative cyclodehydration of aniline Schiff'sbases, which often generated in situ. Various recent oxidative reagents, such as(bromodimethyl) sulphonium bromide 21, TiCl422, Sulphamic acid 23, Iodobenzenediacetate 24, H2O2-HCl 25, silica sulfuric acid 26, FeBr3 or Fe (NO3)3. 9H2O 27 Oxalicacid. 28 in dioxane solvent by air oxidation at 100 °C 29, Silica supported thionylchloride 30. Some solid-phase synthetic methods are explored in the synthesis ofbenzimidazole derivatives 31. A number of protocols that involves the condensation ofo-phenylenediamine with different substituted aldehydes in the presence of transitionmetal triflate salts such as Sc(OTf)3 or Yb(OTf)3 were reported 32-33 .

II. Experimental

All chemicals were from S.D. Fine chemicals suppliers and used without further purification. Melting points were uncorrected. 1H NMR spectra were recorded on a Bruker AVANCE 600 spectrometer using TMS as internal standard and DMSOas solvent.

III. Preparation of Catalyst

Waste aluminium foil collected, dried in oven at 50 ^{0}c crushed in pristle and mortar to fine powder. Obtained powder is dried at 60 0c in oven, and then stored in glass bottle.

General procedure for the Synthesis of 2-substituted benzimidazoles

O-Phenylenediamine (10 mmol) and aromatic aldehyde (10 mmol) were dissolved in DMF(2 mL) in a 25 ml conical flask, the waste aluminium foil (120 mg, 0.1 mmol,) was then added and the mixture sonicated at specific time at 25^{o}C for the specified time as indicated

in The progress of reaction was followed by TLC. After the completion of the reaction, the mixture was dissolved in dichloromethane, and the catalyst was removed by filtration and washed with dichloromethane. The solvent was evaporated under pressure to give the crude product, which was purified by column chromatography on silica gel and eluted with hexane and etylacetate. All of the compounds were studied by comparing their melting points references 2,14,17 and characterized by 1H NMR and mass spectra.

Sr. No	Aromatic group	Time (min)	. (%)Yield	MP (^{0}C)
1	C6H5	15	88	290
2	2-ClC6H4	15	90	134
3	3- ClC6H4	14	92	236
4	4- MeOC6H4	20	90	227
5	2- NO2C6H4rvation	12	94	250
6	3- NO 2C6H4	12	93	305
7	4- NO2C6H4	18	88	306
8	4-MeC6H5	14	85	266
9	4-Me2NC6H4	18	87	237
10	2-Furanyl	19	78	287

Spectral analysis

2-(4'-Methylphenyl)benzimidazole

Light yellow crystal. 1H NMR _: 10.53 (s, 1H), 8.27 (d, 2H, J = 8.1 Hz), 7.34
(s, 1H), 7.22 (s, 1H), 7.46 (d, 2H, J = 7.5 Hz), 7.20 (s, 2H), 2.38 (s, 3H) .

2-(2'-Furanylphenyl) benzimidazole

Light yellow crystal. 1H NMR _: 10.23 (s, 1H), 7.45 (d, 1H, J = 1.2 Hz), 7.57
(s, 2H), 7.59-7.32 (m, 3H), 6.73-6.44 (m, 1H).

IV. Results and Discussion

In order to get the best experimental condition, we have considered the reaction of *O-phenylenediamine*andBenzaldehyde in the presence of catalyst under sonication at ambient temperature reaction.This reaction gives higher yield with good purity.

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Cotton Dyeing with Natural Dye Extracted from Yellow Flowers of Caesalpinia pulcherima

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ABSTRACT

Flower waste is an easily available and replenishable source for natural dyes.The present study deals with the extraction of natural dye from flowers of Caesalpinia pulcherima using four different extraction methods.Various shades were obtained using four different mordents. The finding reveals thatCaesalpinia pulcherima yellow flowers are a good source of natural dye which will behelpful in textile industry for dying Cotton fabrics.

Keywords: Natural dye, Mordent.

I. INTRODUCTION

India has a rich biodiversity. It has approximately 4,90,000 plant species of which about 17500 are Angiosperms. More than 400 are domesticated crop species and almost an equal number aretheir wild relatives[1, 2].Hence plant is a huge source of natural product out of that natural dye is our product.The application of synthetic dye causes serious health hazards and influences adversely the eco-balance of nature[3]. On the other hand, natural dyes are eco-friendly; for example turmeric the brightest of naturally occurring yellow dyes is a powerful antiseptic which revitalizes the skin while indigo gives a cooling sensation[4]. Certain problems with the use of natural dyes in textile dying are color yield, complexibility of dying process, limited shades, blending problem and inadequate fastness properties[5, 6]. But these problems can be overcome by using chemicals called Mordents. Mordents are the metal salts which produce an affinity between the fabric and the dye[7, 8].Metal ions act as electron acceptor and form a complex with the dye molecule. Alum, Chrome, Stannous chloride, Copper sulphate, ferrous sulphate etc. is the commonly used mordants[6, 8, 9].

In the present work,dyeswere extracted from yellow colored flowers of *Caesalpinia pulcherima* using different extraction methods andapplied on cotton cloth in presence of different mordents. Different shades of dye were observed. The color fastness of the dye materials were also studied in this work.

Caesalpinia pulcherima is a species of flowering plant in the pea family, Fabaceae that is native to the tropics and subtropics of the Americas. It could be native to the West India but its exact origin is unknown due to widespread cultivation. It is a shrub growing about 3 m tall. In climates with little to no frosts, this plant will grow larger and is semi-evergreen freezing; plant will die back to the ground depending on cold, but will re-bound in mid to late spring. This species is more sensitive to cold than others; the leaves are bipinnate, 20-40 cm long, bearing 3-10 pairs of pinnae, each with 6-10 pairs of leaflets 15-25 mm long and 10-15 mm broad. The flowers are borne in racemes up to 20 cm long, each flower with five yellow, orange or red petals. The fruit is a 6-12 cm long. *Caesalpinia pulcherima* are common flowers in India [Figure 1][10]. The flower themselves are edible.

In the present study, yellowcolor flowers of *Caesalpinia pulcherima* were used for extraction of natural dye using different solvents. The dye has low affinity towards cotton and hence attempts were made to dye cotton fabrics in presence of different mordents giving different shades. Thus it has wide scope to be used as dye in textile industry for dying specially the cotton fabrics.

Figure 1. Plant of Caesalpinia pulcherima

II. MATERIALS

2.1 Plant Material

Fresh yellow color flowers of *Caesalpinia pulcherima* were collected in polythene bags from local area of Sangamner (District- Ahmednagar, Maharashtra, India).

2.2 Substrate

The 100% soft cotton fabric was used as substrate.

2.3 Chemicals

2% solutions of Alum($K_2SO_4.Al_2SO_4.24H_2O$), Copper sulphate ($CuSO_4.5H_2O$), Ferroussulphate ($FeSO_4.7H_2O$), Stannous chloride ($SnCl_2$) are used as Mordents and 95% Ethanol was used as solvent.

III. METHODS

3.1Extraction of dye from flower

Extraction of color dye was done by following four different methods.

1. **Aqueous Extraction Method**
   5 gm of fresh yellow color flowers of *Caesalpinia pulcherima* were boiled in 100 ml distilled water at 80 ^{0}C for 30 minutes. The filtrate is used for further study.

2. **Acidic Extraction Method**
   In acidic extraction method, 5 gm of fresh yellow color flowers of *Caesalpinia pulcherima* were treated with 100 ml 1% Hydrochloric acid solution and boiled at 80 ^{0}C for 30 minutes. The filtrate is used for further study.

3. **Alkaline Extraction Method**
   5 gm of fresh yellow color flowers of *Caesalpinia pulcherima* were boiled in 100 ml 1% Sodium hydroxide at 80 ^{0}C for 30 minutes.The filtrate is used for further study.

4. **Alcoholic Extraction Method**
   5 gm of fresh yellow color flowers of *Caesalpinia pulcherima* were boiled in 50% Ethanol for 30 minutes in water bath. Finally the filtrate is used for further study.

3.2Exhausting of cotton cloth

Cotton cloth used for dyeing were boiled in 10% NaOH solution for 20 minutes to remove starch and impurities in the cloths and then thoroughly washed with cold water.

3.3 Mordenting and Dyeing

Rectangular pieces of cotton cloth measuring 3 cm x 2 cm were treated with 25 ml 2% solutions of different mordents namely Alum, $CuSO_4$, $FeSO_4$ and $SnCl_2$ for 30 minutes. Then the above said pieces are allowed to drain and immediately soaked in different extracts.

3.4 Color Fastness to Washing[11-17]

Color fastness to washing is the ability to retain its color after washing. The rating of 1 to 5 was adopted to define fastness for I to V washing respectively Table 1.

Table1. Result for the method of extraction.

Mordent Method	Alum	$CuSO_4$	$SnCl_2$	$FeSO_4$
Aqueous extraction	Pale Yellow (I)	Yellow (III)	Pale Yellow (IV)	Dark Brown (III)
Acidic extraction	Gray (II)	Pale Yellow (III)	Pale Yellow (II)	Red (IV)
Alkaline extraction	Yellow (III)	Pale Brown (II)	Light Yellow (III)	Brown Red (III)
Alcoholic Extraction	Dark Brown (II)	Pale Brown (II)	Pale Brown (III)	Dark Brown (IV)

( ) - Indicates fastness to washing in the rating scale I to V

IV. RESULT AND DISCUSSION

Different color shades were observed from various extracts of *Caesalpinia pulcherima* red color flowers and the color intensities are showcased in Figure 2. The present work successfully produced the red, brown and yellow color shades. The color strength also depends

upon use of mordent. Mordents are the metal salts having tendency to coordinate with dye and fibre[18]. The aqueous extract gave the pale yellow, yellow, pale yellow and dark brown color shades with mordent such Alum, $CuSO_4$, $SnCl_2$ and $FeSO_4$respectively. Various shades like gray, pale yellow, pale yellow and red on cotton fabrics were obtained using acidic extract with Alum, $CuSO_4$, $SnCl_2$ and $FeSO_4$. The alkaline extract with Alum, $CuSO_4$, $SnCl_2$ and $FeSO_4$ give yellow, pale brown, light yellow and brown red color shades respectively. While the alcoholic extract gave dark brown, pale brown,pale brown and dark brown color shades in combination with mordents such as Alum, $CuSO_4$, $SnCl_2$ and $FeSO_4$respectively. The study revealed that the production of various natural color shades is possible from plant pigments. The present work suggests that utilization of flowers waste for isolation of natural color is an example of value addition to waste leading to an impact on the economic growth of the rural communities. This work is also helpful for small scale dyeing and printing industries in locality.

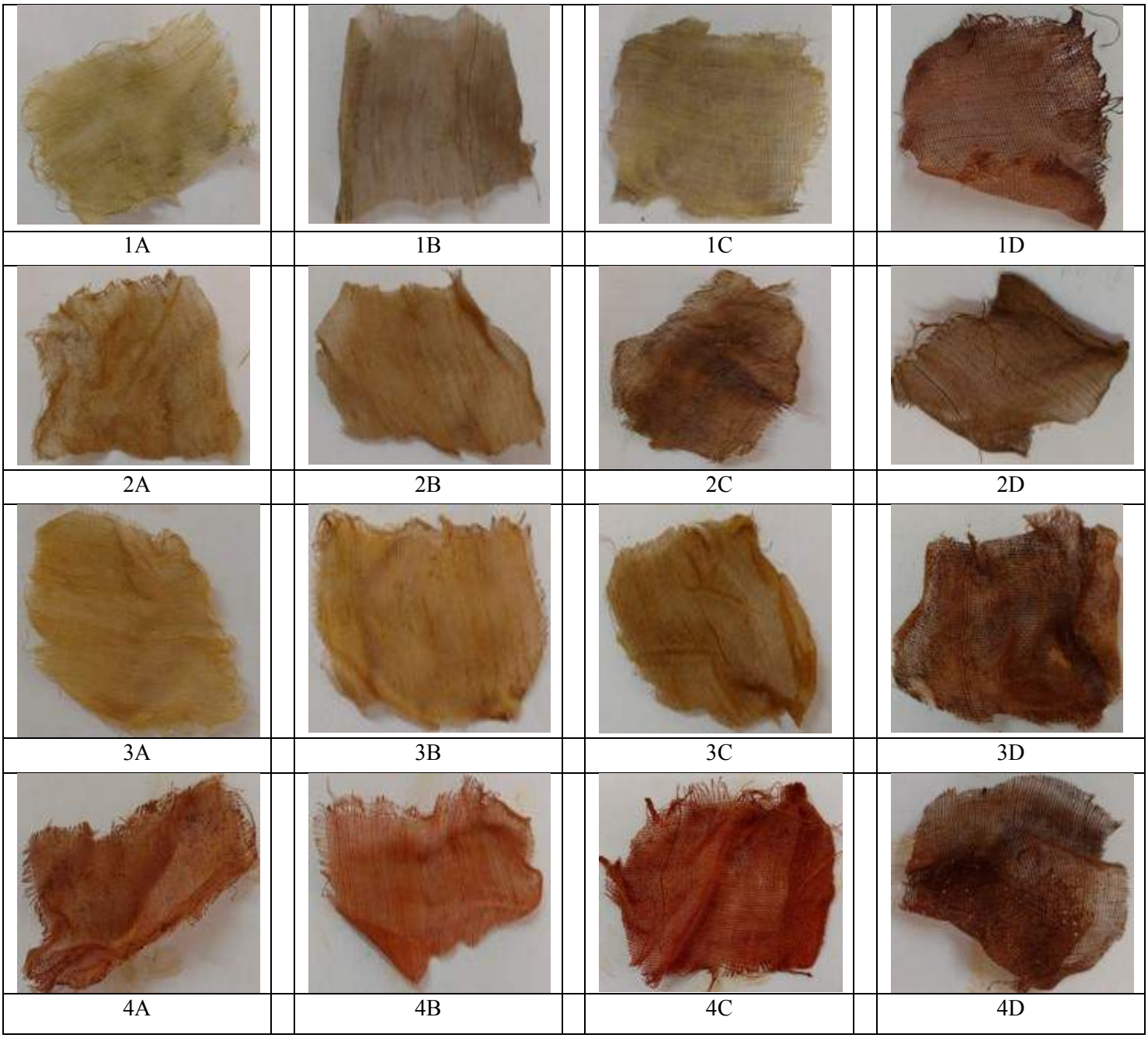

Figure 2. Color shades obtained on cotton fibersmordent with Alum (1), Copper sulphate (2), stannous chloride (3) and ferrous sulphate (4) using different extracts- Aqueous (A), Acidic (B), Alkaline (C) and Alcoholic (D)

V. CONCULSION

The natural dyes extracted from yellow flowers of *Caesalpinia pulcherima* are safe because these are non-toxic and biodegradable in nature. Thus results obtained from the present investigation rebuild that the extracts of flowers of *Caesalpinia pulcherima* show four different color shades like pale yellow,yellow,gray, dark brown, brown red, pale brown and red on cotton in presence of mordents like Alum ($K_2SO_4.Al_2SO_4.24H_2O$), Copper sulphate ($CuSO_4.5H_2O$), Ferrous sulphate ($FeSO_4.7H_2O$), Stannous chloride ($SnCl_2$) with good fastness property to washing.

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Synthesis & Characterization of Pectin - N-isopropyl acrylamide modified graft co-polymers for potential Applications

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ABSTRACT

Recently research is being carried out for the development of various copolymers, modified polymers for various potential applications like coatings, composite, paints, adhesives, drug delivery systems, hydrogel-based delivery devices can be used for oral, rectal, ocular, epidermal and subcutaneous application. tablet coatings, etc.[1] In this work we tried to improve the properties of the polysaccharide based polymers pectin, by graft copolymerization with N-isopropylacrylamide polymers using emulsion polymerization technique. The effect of various variables like initiator concentration, monomer concentration, temperature and time has been studied. The grafted copolymer was characterized by Fourier transform infrared spectroscopy (FT-IR), organic elemental analysis, differential scanning calorimetry (DSC) and X-ray diffraction (XRD). FT-IR studies indicated incorporation of amide group. Rheological behavior of pectin solution was compared with that of the grafted copolymer. The comparative rheological properties of pectin and grafted copolymer indicated change in the property of the product. Differential scanning calorimetry and XRD suggested formation of the grafted copolymer.

Keywords: Graft Copolymerization, Pectin, N-Isopropyl Acrylamide, Rheology, Differential Scanning Calorimetry.

I. INTRODUCTION

A graft copolymer is a system comprised of a backbone material to which a second polymer is attached at intervals along the chain to make them into synthesized modifications and synthesized polymer gel networks to form natural reforming different attractive properties like pH sensitivity, Thermo sensitivity, light sensitivity etc. This gives technological advances in various application and potential benefits. Pectin is one of the natural heterogeneous biocompatible, biodegradable, and abundant. polysaccharide containing linear chains of a-(1-4)-linked- D-galacturonic acid residues.[2]

In our study, we have grafted N-isopropyl acrylamide on pectin to improve its properties like gel strength, film forming ability, pH sensitive behavior, thermal sensitivity and to make it more shear stable so that it can finds its potent application. Pectin graft copolymer is modified natural polymeric materials that have a three-dimensional network structure and can swell considerably in aqueous medium without dissolution after crosslinking.[2]. Swelling behavior of hydrogel is control by cross-linking by varying concentration of cross-linking agent. The grafted copolymer(GP) was characterized by Fourier transform infrared spectroscopy (FT-IR), organic elemental analysis, differential scanning calorimetry (DSC) and X-ray diffraction (XRD). FT-IR studies indicated incorporation of amide group. Rheological behavior of pectin solution was compared with that of the grafted copolymer. The comparative rheological properties of pectin and grafted copolymer indicated change in the property of the product. Differential scanning calorimetry and XRD suggested formation of the grafted copolymer.

II. MATERIALS AND METHODS

A. MATERIALS

Pectin, methanol, and glutaraldehyde **(GA)** were obtained from Loba-Chemie Indoaustranal Co., Mumbai, India.

N-isopropyl acryl amide is obtained from SRL research laboratories, Mumbai, India. Hydrochloric acid 35%

pure was obtained from Merck Limited, Mumbai, India. Double distilled water was used throughout the study. Commercial pectin was purified and converted in to H-form by washing with 0.1mol/1 HCl dissolved in the ethanol water mixture (1:1 v/v). Pectin subsequently was washed several times with ethanol water mixture fallowed by 96% ethanol until the chloride reaction was negative, and finally dried at 60^0C.

B. METHODS

1. Synthesis of modified Pectinand Purification ofgraft-copolymer from homo-polymer(Poly-N-isopropylacrylamide)

The reaction has been done according to method of (Sinitsya et. al. 2000). The reaction was carried out in heterogeneous medium with methanol as a solvent. Pectin powder (3 gram) was weighed in a well equipped 250 ml three necked flask and it was suspended in 70 ml methanol. An amount of 10 ml N-isopropyl acrylamide was get dissolved in a 50 ml methanol and the solution was added gradually in the flask under stirring. The reaction has been carried out at 25^o C temperature until 48 hours of continuous stirring. After completion of the reaction the product was obtained in the powder form by simple filtration method. The product obtained is converted in to acid forms by washing with 0.1M HCl in an ethanol- water mixture (1:1,v/v) to convert free carboxylic group in to protonated form. Finally the sample were washed several times with 40% (v/v) ethanol until it shows the negative reaction to chloride, then treated with 80% (v/v) ethanol, filtered and dried at 60^0C. This Graft-copolymer (GP) is used for the preparation of hydrogel membranes using glutaraldehyde(GA) as crosslinking agent. Theprobable mechanismofthereaction isshowninFig.1.Theproduct waspurified byextracting thehomo-polymer of Poly-N-isopropyl acrylamide (that might be produced during the polymerization)from the crude product by washing with acetone-watermixture (30:70).The procedure was repeated10times.Thepuregraftpolymer(GP)soobtained wasfinallywashedwithpureacetone and wasallowedto dryinlaminar flowairdrierfor72hatroomtemperature.The percentage grafting (PG) and grafting efficiency (GE) were calculated according to following formula Table1.[3]

Table 1. Formula for calculation of percentage grafting (%PG) andgrafting efficiency (%GE)

$$GE\ \% = \frac{\text{Weight of the grafted side chain polymer}}{\text{Weight of the grafted side chain polymer} + \text{Homo-polymer}} \times 100$$

$$PG\ \% = \frac{\text{Weight of the grafted side co- polymer} - \text{Weight of pectin}}{\text{Weight of Pectin}} \times 100$$

2. Reaction Mechanism

Graft copolymers are synthesized by opening the monomer rings of polysaccharide backbone and grafting of N-isopropyl acrylamide onto the free radicals generated in emulsion. The opening imparts slight flexibility to the backbone. Moreover, the percentage of polysaccharide is small in comparison with the poly vinyl alcohol.The radical formation occurs by breaking of carbon- carbon bond and monomer polymerization reaction occurs.When the Ce^{+4} reacts with C_2 and C_3 carbon atom, it gives radical formation via breaking the C-C bond, immediately monomer adds to the radical and chain polymerization reaction occurs.[3] Probable reaction mechanism is given in Figure 1.[4]

3. Swelling behavior study of the GP hydrogels

Preparation of graft copolymer (GP) cross-linked with glutaraldehyde(GA) hydrogel and Swelling study

The GP/GA hydrogel cross-linked with different concentration of GA used in the study were fabricated using a casting/solvent evaporation technique.[5] A stock viscous solution of GP in water (10% w/v) was prepared by dissolving 2g of GP in 20ml of distilled water and stirring for 7hrs. at room temperature.To the dissolved GP solution 0.2, 0.4, 0.6, 0.8 ml of glutaraldehyde was added and each solution was acidified with a drop of HCL . Those solution was heated at 70^0C for 20 min to complete the crosslinking reaction.The thick cross-linked gel was finally obtained further sonicated to remove the trapped air bubbles and used for study.[6]

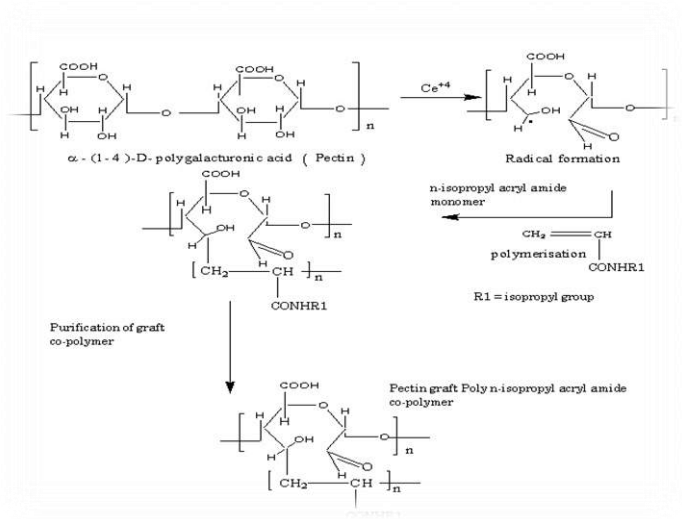

Figure 1. Probable Reaction Mechanism of polymerization Reaction

The film was made from prepared gel by pouring it into shallow dishes (with diameter 8.5 cm) and dried in laminar flow air chamber at room temperature for 3 days. Finally, the cross-linked GP films were thoroughly rinsed with distilled water to remove residual GA. After drying in air, the cross-linked GP films(0.15 mm thickness) were cut into small disks (with diameter of ~9 mm) and used for swelling study.The swelling characteristics of test hydrogels were determined by immersing dried test samples to swell in 5 ml of a phosphate buffer solutions at pH 1.4, 5.4, 7.4, simulating gastrointestinal tract conditions [7-9] and 9.4 solutions for 24 hours. At specific time intervals, the samples were removed from the swelling medium and were carefully blotted with a piece of paper towel to absorb excess water on the surfaces. The % swelling (% Sw) of test samples were calculated from the following expression.

$$\% Sw = (Ws - W_d) / W_d \times 100$$

Where `Ws' is the weight of the swollen test sample and `Wd' is the weight of the dried test sample. The sample, which had the best swelling characteristics, was subsequently selected for the salicylic acid release profile study.

4. Characterization

Characterization were done at outsourced laboratory. Pectin, N-isopropylacrylamide and GP were subjected to FTIR spectroscopy in the range of 4000-400 cm^{-1} as KBr pellets and the patches were subjected to Attenuated total reflectance (ATR) spectroscopy in the range of 4000-400 cm^{-1}. An FTIR spectrophotometer (NEXUS-870, Thermo Nicolet Corporation) was used for the study. The raw materials and the GP were subjected to X-ray diffraction (XRD-PW 1700, Philips, USA) using CuKα radiation generated at 40 kV and 40 mA; the range of diffraction angle was 10.00-100.00^0 2θ. A Netzsch DSC-200 PC Phox, Germany was used for studying the melting and crystallization behavior of the polymeric materials. The temperature and energy scales were calibrated with the standard procedures. The melting studies were performed in the temperature range of 25-200^{0}C at a heating rate of 10_C/min in N2 atmosphere. For the study of viscoelastic properties GP gel without cross-linked was subjected to Rheometer (Advance Rheometer AR 1000, TA Instrument, England.) with nip gap was 600μ.

III. RESULTS AND DISCUSSION

3.A. EffectofInitiator Concentration

It is evident from **Figure 2** that percentage-grafting increaseduptocertainlevelofinitiator concentrationand thendecreased.Themaximumpercentagegraftinghasbeen observedat[CAS]¼0.006molel^{-1}.Ithasbeenpresumed that up to the critical initiator concentration,the entire radicalproducedfromtheinitiatorareusedin producing growing monomer radicals as well as homo-polymer radicals.Afterthislimit,theradicalsaremostlyinvolved in recombinationandothertermination processesandhence decreaseinpercentagegraftingandgraftingefficiency.

3.B. EffectofReactionTime

The percentage grafting and grafting efficiencygraduallyincreasedwithtimeandthenleveledoff(Fig.3).This result may beattributedto the fact that the freeradical formed initially on the polymeric backbone contribute moreforgrafting reaction, whereaswithincreaseofsome of the free radicals and the macro radicals might be involvedinthehomo-polymerformation.**NAM**(N-isopropyl acrylamide).

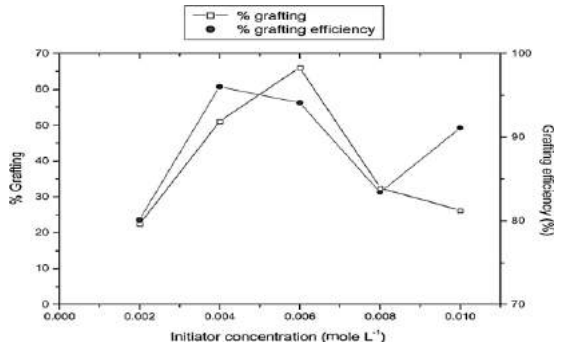

Figure 2. Effect of initiator concentration on percentage grafting of **NAM**(N-isopropyl acrylamide) on pectin; reaction conditions were pectin (2 g), acrylamide (0.440 mole l—1), time (150 min), and temperature (35oC).

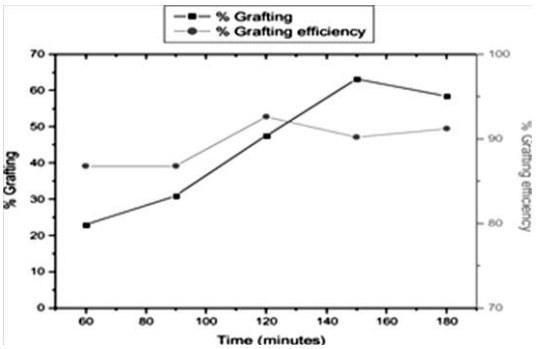

Figure 3.Effectofreaction timeonpercentage grafting ofNAMonpectin;reaction conditions werepectin (2g),acrylamide(0.440mole l^{-1}), CAS(0.006molel^{-1}),andtemperature(35^{o}C).

3.C. Effect of Monomer Concentration

Figure.5 shows that, with increase in monomer concentration the percentage grafting and grafting efficiency gradually increased and then decreased after a monomer concentration of 0.44 mole l—1. The decrease in grafting efficiency may be attributed to the participation of initiator radicals in graft copolymerization rather than homo polymerization. As the monomer concentration is increased, more monomer units are competing for the initiator radicals resulting in the increased rate of homo polymerization. Hence, there was decrease in percentage grafting and grafting efficiency.[9]

3.D. Effect of Reaction Temperature

It was observed that with increase in the temperature of grafting reaction, the percentage grafting and grafting efficiency increased up to certain level and then decreased (Fig. 6). It was established that more grafting sites would be created by frequent chain transfer of growing radicals to the backbone at higher temperature resulting in an increase in percent grafting and grafting efficiency. Further increase in temperature decreased the percentage grafting and grafting efficiency, this fact can be attributed to involvement of growing radicals in termination processes. Increase in temperature not only facilitated the chain transfer process, but also accelerated homo polymer formation thereby decreasing the grafting efficiency.[9-11]

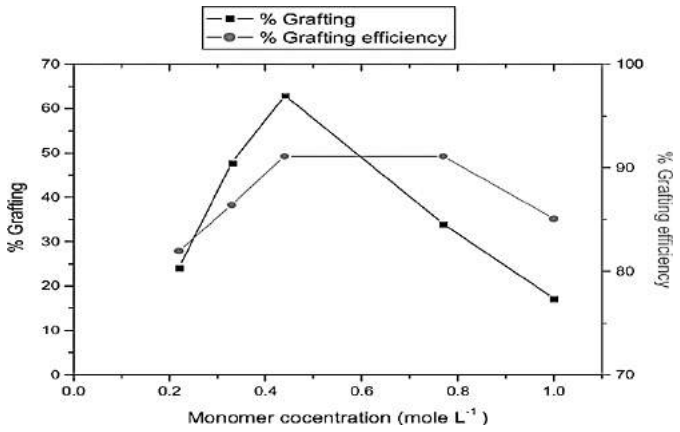

FIG. 6. Effect of reaction temperature on percentage grafting of NAM on pectin; reaction conditions were pectin (2 g), acrylamide (0.440 mole l^{-1}), CAS (0.006 mole l^{-1}), and time (150 min).

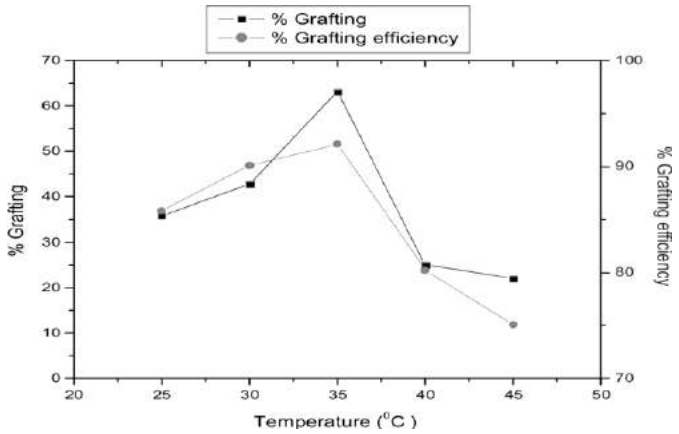

FIG. 5. Effect of monomer concentration on percentage grafting of NAM on pectin; reaction conditions were pectin (2 g), CAS (0.006 mole l^{-1}), Time (150 min) and temperature (35°C).

3.E. FTIR Characterization

The FTIR spectrum of GP and pectin were taken in the range of 4000 - 400 cm^{-1} as KBr pellet and Attenuated total reflectance (ATR) with the help of FTIR spectrophotometer (NEXUS - 870,Thermo Nicolet Corporation).

Figure 7.a. shown the FTIR spectra of the pure pectin. As the spectrum shown a broad band at 3415 cm^{-1} due to stretching frequency of the -OH groups. The band at 2913 cm^{-1} is due to -C-H stretching vibration. The presence of a strong absorption band at 1756 cm^{-1} due to >C=O stretching vibrations confirms the presence of -$COOCH_3$ group. The bands around 1441 cm^{-1} and 1342 cm^{-1} are assigned to -CH_2scissoring and -OH bending vibration, respectively. The band at 1023 cm^{-1} is due to -CH-O-CH- stretching. The broad band around 1150 cm^{-1} is due to characteristic peak of -CH-OH in aliphatic cyclic secondary alcohol C-O stretch.

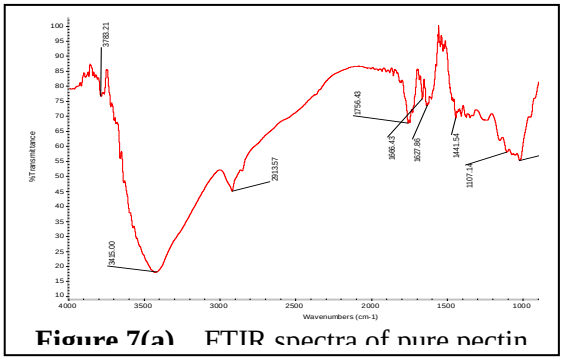

Figure 7(a) FTIR spectra of pure pectin

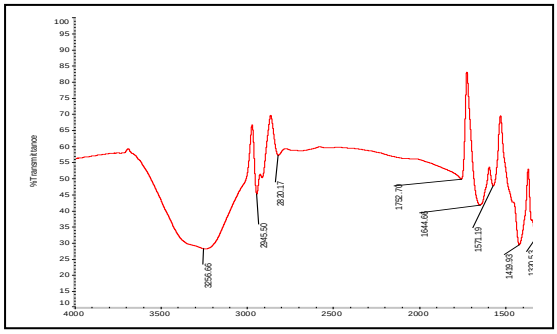

Figure 7b. shows FTIR spectra of graft copolymer (GP). presence of a broad absorption band around 3200 -3260 cm^{-1} is due to the overlap of -OH stretching band of pectin. The presence of a band at 1752 cm^{-1} is due to free acid groups (-COOH). The sharp band at 2937 cm^{-1} and 2910 cm^{-1} peaks observed due to C-H stretching frequency of -CH_2 groups. The band at 1419 cm^{-1} is due to -CH bend of -CH_2 group. The band at 1085 cm^{-1} shows -OH bending, 1041 cm^{-1} shown secondary alcohol(characteristic peak of -CH-OH in cyclic alcohol C-O stretch). The presence of all above bands in the graft copolymer gives strong evidence of grafting. Pectin FTIR shows1737 cm^{-1} C=O stretch of ester, acid or aldehyde, 1187 cm^{-1} C-O stretch ester, 2937 cm^{-1} -CH_2 - methylene stretch, 1449 cm^{-1} -CH_2 - methylene scissors deformation, 1085 cm^{-1} C-O stretch, and GP shows polymer backbone2829 cm^{-1} C-H stretch, 3200-3400 cm^{-1} OH stretch, 1409 cm^{-1}, 1571NH bends, 1321, 613 cm^{-1} NH deformation this spectra show formation of expected copolymer.

3.6. X-ray diffraction study (XRD)

The pectin sample was finely powdered and film sample of GP were subjected to X-ray diffraction (XRD-PW 1700, Philips, USA) using CuKα radiation generated at 40 kV and 40 mA; the range of diffraction angle was 10^o-100^o 2θ. The XRD patterns of pectin **(Figure 8a)** and GP **(Figure 8b)** revealed that the pectin peak was at ~20.10^o 2θ while that of pectin was ~13.58^o 2θ. The XRD patterns of the GP shown noisy with diffused peaks pattern revealed that the amorphous nature of graft copolymer and the crystalinity of the GP disrupt slightly because of the grafted backbone of poly n-isopropyl acryl amide. There had been a marked decrease in crystalinity of GP as compared to that of parent pectin.

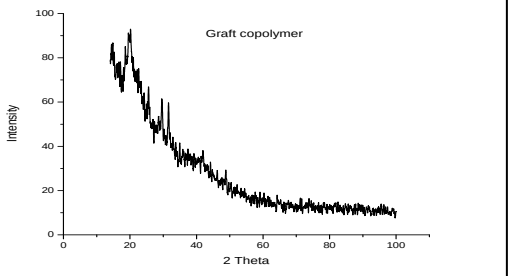

Fig.8a. Graft copolymer (GP)

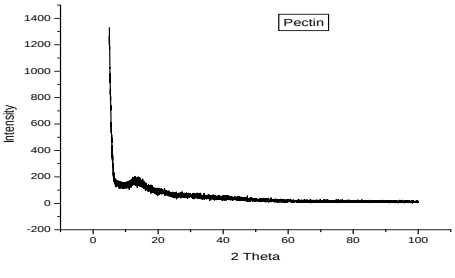

Fig.8b. Low methylated pure Pectin

3.G. Differential Scanning Calorimetry Characterizations (DSC)

In differential scanning calorimetry characterization. A 11.21 mg pectin and 7.13 mg GP sample was placed in a 100 µL aluminum pan, weighed on a microbalance and crimped with a lid containing a pinhole and placed in the DSC unit along with a similar pan as a reference. The sample was heated at a rate of 10 ◦C/min from -20 to 200^{0}C. Nitrogen was used as a purge gas with a flow rate of 50 mL/min.

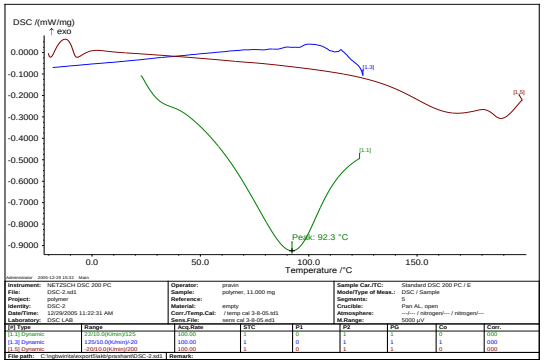

Figure 9(a). DSC of pectin

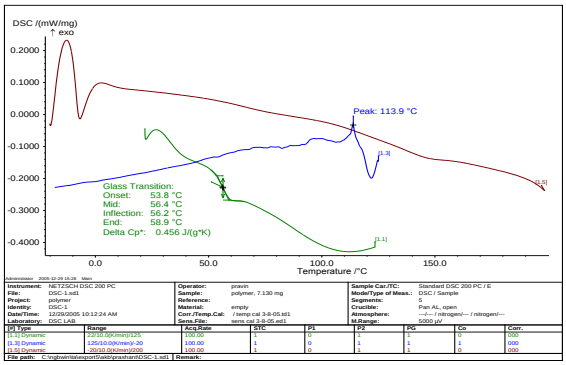

Figure 9 (b). DSC of GP

3.H. Swelling behavior of the GP cross-linked with 0.2, 0.4, 0.6, 0.8 ml of glutaraldehyde GA

The GP was water soluble co-polymer so it required cross-linking by cross-linking agent.[11-15] The GP hydrogel was cross-linked with different concentration of glutaraldehyde (GA),B, C, D, F (as shown in the **Fig.10.**) 0.2, 0.4, 0.6, 0.8 ml of GA cross-linking agent respectively (acidified GA with HCl, kept constant 0.05 ml) were allow to swell in 5 ml of phosphate buffer solutions having pH 1.4, 5.4, 7.4 and 9.4. The results indicates that GA cross-linked GP hydrogel swelled more significantly (swelling 190 %) at pH 7.4 due to a large swelling forces created by the electrostatic repulsion between the ionized acid groups -COO$^-$ as well as amide groups. Figure 11. showing effect of crosslinking density on swelling behavior of GP.

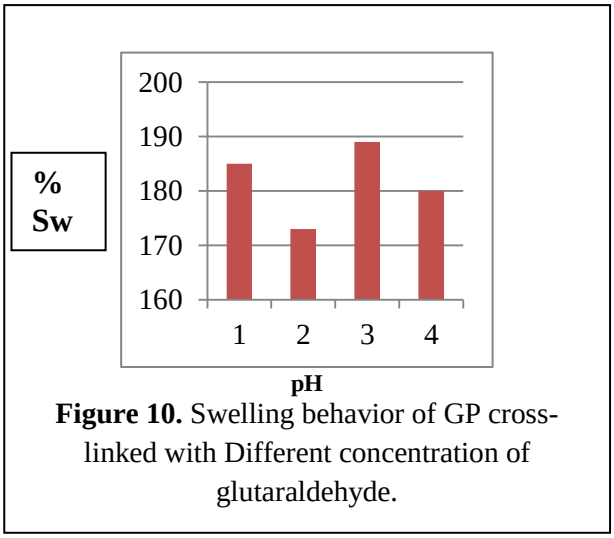

Figure 10. Swelling behavior of GP cross-linked with Different concentration of glutaraldehyde.

At pH 7.4, the carboxylic acid group on the GA cross-linked GP hydrogel became progressively ionized (-COO $^-$). By observing swelling behavior, it had shown that GP cross-linked hydrogel had pH dependent swelling behavior. The degree of swelling increased from pH 1.4 to 7.4 but in pH 9.4 swelling decreases again. The hydrogel swells maximum in the pH 7.4 .The swelling behavior also depends upon cross-linking density, as concentration of GA

increases % swelling decreases because greater extent of chemical cross-linking of the polymer chains that restricts the mobility of the polymer chains. Thus we can control % swelling by varying concentration of cross-linking agent.[11-15]

3. I. Rheological Study

Viscosities versus shear rate **(Figure 11(a).)** of the 5% polymer solution were plotted. The viscosity of the polymer solutions decreases with increase in shear rate. Similar results were are observed earlier[16-18] for carboxymethyl cellulose Rheological viscosity measurement study. Both the aqueous 5% solutions of GP and Pectin showed strong pseudo plastic behavior. It is evident from the viscosity versus shear rate curve **(Figure 11(a).)** that at shear rate of 11.56 the viscosity of the 5% GP solution is 45.93 poise, but with further increase in shear rate leads to regular decrease in viscosity of the GP solution, and the lowest viscosity of8.13 poise was observed at shear rate of 100. A similar pattern was observed in the case of 5% pectin solution **(Fig. 11b.)**, and the figure shows that at shear rate of11.56, the viscosity of pectin solution was 0.49 poise but as the shear rate increased up to 99.8 the viscosity of the solution decreased to 0.37 poise. Hence, it can be concluded from the results that at low and high shear rates the viscosity of the GP solution was higher than pectin solution and it can be suggested that grafted pectin solution was more shear stable than the native pectin. This is due to the grafting of longer polyacrylamide chain on pectin back- bone[19,20]. It can be attributed to the fact that, the graft copolymers having fewerbut longer branches are found to be more shear-stable than ungrafted polymers[21-22].

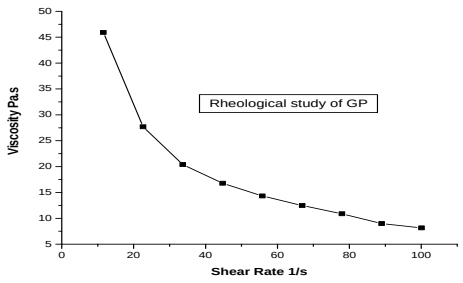

Figure 11(a). Viscosity versus shear rate curves of 5% GP solution.

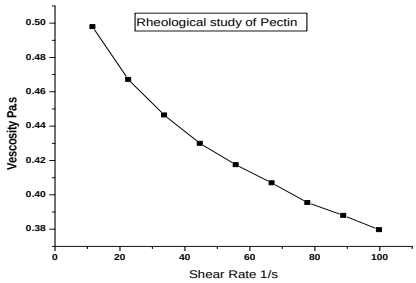

Figure 11(b). Viscosity versus shear rate curves of 5% pectin solution

3.J. Haemocompatibility Study

In the Haemocompatibility study we found Haemolysis of test sample is 36.36 % ; therefore we can assume that the GP had less haemolytic effect on the human red cell suspension. So that GP material is highly haemocompatible [25-27].

Table 2. Haemocompatibility observations and results.

OD of Negative control	OD of Positive control	OD of Test Sample	% Haemolysis and Result
0.04	**0.37**	**0.052**	**36.66 % Highly Haemocompatibility**

IV. CONCLUSIONS

The main objective in relation to this study was to graft - copolymer consist of N-isopropyl acrylamide on the pectin backbone by ceric ammonium sulphate as an initiator. . The impact of polymerization variables including initiator concentration, monomer concentration, reaction

time and temperature on grafting parameters was investigated. Study of FT-IR, elemental analysis, XRD, and DSC confirmed our view that the PAM side chain was grafted on the pectin backbone by graft copolymerization. Rheological study of the pectin and GP solution shows that the shear stability of pectin was improved after grafting. Further, it can be suggested that synthesized grafted pectin could be tried as a hydrogel for drug delivery systems and other various potent applications.

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Green Protocol For Synthesis Of 7 (1hbenzimidazol-2-Yl)-5-(Substituted Phenyl) Pyrido [2, 3-D] Pyrimidin-4-Amine

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ABSTRACT

Sequence of 7-(1H-benzimidazol-2-yl)-5-(substituted phenyl) pyrido [2, 3-d] pyrimidin-4-amine were synthesized by reacting substituted cyanopyridine derivatives with formamide, formic acid and dimethyl formamide using green approach. The synthesized compounds are studied for their spectral analysis. These compounds are studied for in vitro antioxidant activity by agar diffusion and DPPH methods, respectively. These compounds show better activity.
Keywords: Benzimidazole, Spectral Chacterisation, Antioxidant Activity.

I. INTRODUCTION

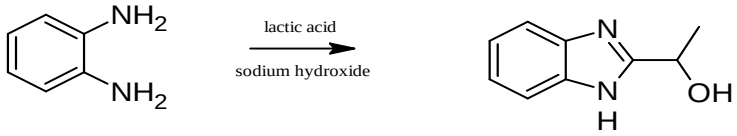
Most of the hetocyclic compounds having the pyridopyrimidine as basic nucleus having very intrusted pharmacological activities interesting pharmacological properties. One of them pyridopyrimidine derivatives has versatile biological activities like antiinflammatory[1], antifungal[2]anti-tumor[3] and antimicrobial[4]etc.Most of the Benzimidazole derivatives represent one of the most active of biological compounds. Many of them have very good biological activity such as antifungal[5], antibacterial [6] anticancer[7], Anthelmintic[8,-14]other vast biological activities.Selected of these compounds activitiesinclude ,antioxidant. Due to this immense importance we have planned for synthesis of these compounds.

Thesynthesis of 7-(1H-benzimidazol-2-yl)-5-(substituted phenyl) pyrido [2, 3-d] pyrimidin-4-amine. The antioxidant activity was performed by DPPH· method using ascorbic acid as standard.

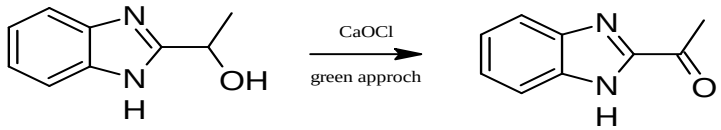
Green route used for the synthesis of these benzimidazole derivatives compounds **were** synthesized by reacting 2-amino-6-(1*H*-benzimidazol-2-yl)-4-(substituted phenyl) pyridine-3-carbonitrile with formamide, formic acid and dimethyl formamide in sonication method . 2-amino-6-(1*H*-benzimidazol-2-yl)-4-(substituted phenyl) pyridine-3- carbonitrile**(**was prepared by reaction between benzimidazole chalconein malanonitrile and ammonium acetate in ethanol medium under sonication method. Benzimidazole chalcone was prepared by reaction between 2-acetyl benzimidazole **in**potassium hydroxide in aromatic aldehydes in microwave method . 2-acetyl benzimidazole was prepared by reaction between 2-(α-hydroxyethyl) benzimidazole in potassium dichromate in sulphuric acid medium in Sonication .2-(α-hydroxyethyl) benzimidazole was prepared by reaction between o-phenylenediamine (**1**) and lactic acid in sodium hydroxide medium[11-12.]

Reaction Scheme

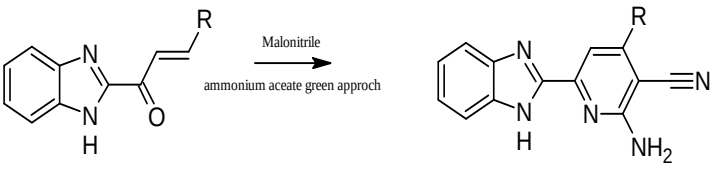
Step I



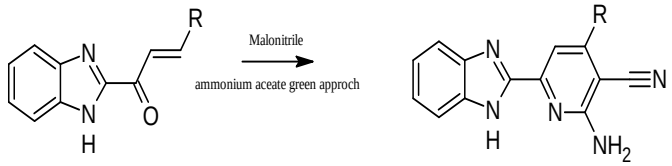
Step II



Step III



Step IV



Step V

II. EXPERIMENTAL

Melting points of the synthesized compounds were determined using Thiele'smethod were found uncorrected. The IR spectra of the synthesized using Automated IR spectra and frequencies were recorded in wave numbers (cm-1). The 1H NMR spectrawere recorded on Punjab university Chandigarh Chemical shifts (δ) are reported in parts per million (ppm) down field frominternal reference tetramethylsilane (TMS). Purity of the compounds was studied by thin layerchromatography.

Step I: Synthesis of 2-(α-hydroxyethyl) benzimdiazole:

A mixture of 10 mmol of o-phenylene diamine, lactic acid 30 mmol and ferrous sulphate 2 gm.were taken in conical flask and kept in microwave oven for specified time. Check progress of reaction using thin layer chromatography .after completion of reaction, Cool at room temperature. The completion of this reaction was monitored by TLC. The resulting solution was filtered and washed with water dried into vacuum and recrystallized from ethanol.

Step II: Synthesis of 2 – acetyl Benzimidazole:

To a solution of **(** 10 mole) in Dioxane (20ml), was added solid CaOCl2 (1.42gm, 10 mole) and the solution was sonicated at 40 ^{0}c for 2 - 4 hrs. During this period, the progress of the reaction was monitored on TLC for the disappearance of the starting material. No product formation was observed on TLC and starting material was recovered on processing the reaction mixture by filtration and evaporation of the filtrate.

Step III: Synthesis of Arylidene acetophenones

Derivatives: Sodium hydroxide pellets (0.02mmole) and compound from (10mmoles) were ground in a mortar to a fine powder at room temperature. To this 10mmoles of aromatic aldehyde is added and the mixture was at for sonication a few more minutes till the condensation was complete as shown by TLC. After completion of reaction pour product in crushed ice neutralized by dilute hydrochloric acid. The crude compound was recrystallized from a suitable organic solvent (acetic acid) to get the pure product. A single spot on the TLC plate confirmed the purity.

Step IV:Aldol condensation reaction:

10 mmole of compound from step III in dry conical flask to this add 10 mmole of the malanonitrile and 20 mmole of the ammonium acetate sonicate this mixture at 40 0c for 2 hours, check progress of reaction using thin layer chromatography, after completion of reaction pour reaction mixture over crushed ice to obtain the product. Purify the product using acetone as solvent.

Step V:7-(1hbenzimidazol-2-yl)-5-(substituted phenyl) pyrido [2, 3-d] pyrimidin-4-amine:

A mixture (10 mmol) from step IV , formamide (10 MMOLE), formic acid (10m mol) and dimethyl formamide (10 mol) were taken in 100 mL round bottom flask, sonicate for 6 h at 40^{o}C.The reaction completion was monitored through TLC and reaction medium was cooled, the product obtained was filtered and recrystallized with ethanol. The formation of 7-(1hbenzimidazol-2-yl)-5-(substituted phenyl) pyrido [2, 3-d] pyrimidin-4-amine is Confirmed by the difference in M.P. and Rfvalue.

Observation table 17-(1hbenzimidazol-2-yl)-5-(substituted phenyl) pyrido [2, 3-d] pyrimidin-4-aminederivatives

Sr.No.	Compound with aldehyde	Molecular weight	Melting point(0c)	% yield
1	C6H5	339	195	67
2	FC6H4	356	186	71
3	ClC6H5	372	170	70
4	OHC6H4	355	178	74
5	OCH3C6H4	369	170	75
6	N(CH3)2C6H4	381	165	76

Spectral Analysis
Compound 1

7-(1*H*-benzimidazol-2-yl)-5-phenylpyrido [2, 3-*d*] pyrimidin-4-amine (6a)

IR (υ, cm-1) 2460 (NH_2), 1869 (ArC-H), 1231 (C=N), 1209 (ArC=C).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm), 5.2 (s, 2H, -NH_2), 4.82 (s, 1H, -NH), 7.32-
7.428 (s, 5H, Ar-H), 7.26 -6.45 (s, 4H, Ar-H), 7.7 (m, 1H, -CH), 8.0 (s, 1H, Ar-H),

Spectral Analysis

Compound 4

IR (υ, cm-1), 3310 (NH_2), 2747 (ArC-H), 1611 (C=C), 1647 (-OH) .

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm), 3.74 (s, 2H, -NH_2), 4.70 (s, 1H, -NH), 5.72 (s,
1H, Ar-OH),6.81-7.97 (s ,4H, Ar-H), 7.77-8.05 (s, 4H, Ar-H), 7.57 (s, 1H, Ar-CH),

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Bio-derived Synthesis of Silver Nanoparticles using aqueous Honey and Turmeric Solution (HTS) and their Antimicrobial Activity

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ABSTRACT

Nowadays, Nanotechnologyis playing an important role as a multidisciplinary research concept to primary scientific field. It involves the synthesis of nano-material using different ways and having huge applications.Recently, the use of bio-derived products for the synthesis of nano sized material of interest is in vogue leading to modern nanobiotechnology. In present investigation, we have developed rapid and eco-friendly method for green synthesis of Silver nanoparticles using aqueous solution of honey and turmeric (HTS-AgNPs).The synthesized Silver nanoparticles were characterized by UV-Visible Spectroscopy, FTIR Spectroscopy, Zeta potential, Polydispersity Index and their antimicrobial activity.The present study suggests that the bio-derivedSilver nanoparticles are having particle size 2.4 nm and show moderate antimicrobial activity.

Keywords: HTS-AgNPs, Zeta potential, Polydispersity index.

I. INTRODUCTION

Metallic nanomaterials have gained tremendous interest over past few decades. Amongst these, Silver nano structures have attracted much attention especially due to its antimicrobial application[1]. The synthesis of Silver nanoparticles has been reported using various method including physical and chemical methods, electrochemical and photochemical reduction[2]. The main disadvantage of these synthetic methods is that they involve hectic procedure, use of hazardous chemicals and their yield is relatively very low. Therefore, there is a growing need to develop ecofriendly nanoparticles.

The powerful antioxidant action of honey has been attributed to its high content of phenolic compounds[3]. Honey has been used in the field of nanotechnology to develop cost-effective and environmentally benign synthesis of nanoparticles[4,5]. Honey is a sweet viscous fluid produced from bees and is mainly composed of carbohydrates, enzymes, vitamins, minerals and antioxidants[6]. The use of honey in the synthesis of Silver nanoparticles has been reported recently[5,7-9].Nguyen Thi Ngoan[10]synthesizedSilver nanoparticle-Curcumin conjugates for wound dressing.

In this paper, we have exploited the mixture of honey and turmeric powder (HTS) with sunlight irradiation for fast synthesis of Silver nanoparticles. The honey serves as both reducing and capping agent. Hence no other stabilizing agent was added.

II. MATERIALS AND MEHODS

2.1 Chemicals and Materials

A.R.grade Silver nitrate was used. Natural honey sample and turmeric were obtained from local area of Sangamner (district Ahmednagar, Maharashtra) and used in this study.

2.2 Synthesis of Silver Nanoparticles

For the reduction of Silver ions, 5mL of honey and 2 g of turmeric powder were boiled with 50mL distilled water. The resultant solution was filtered and saved for further analysis. 1mM $AgNO_3$ were mixed with HTS in 1:9.This reaction mixture was stirred and exposed to sunlight for 2 hrs for accelerative bio reduction of $AgNO_3$. The brownish colorindicated that the formation Silver nanoparticles.

2.3 Purification of Silver Nanoparticles.

The reduced Silver nanoparticles solution was centrifuged at 10000 rpm for 5 minutes. The residue was purified with distilled water.

III. Characterization of Silver Nanoparticles

3.1 UV-Visible Spectral Analysis

The reduction of Silver ions was monitored by visual inspection of the solution. The colorof the reaction mixture changes to dark brown color showing the formation of Silver nanoparticles (Figure 1). UV-Visible analysis was done by using Chemito Spectrophotometer UV-2100 in the wavelength range 400-800 nm.

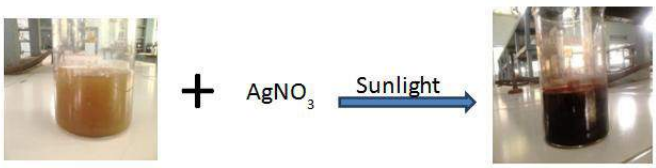

Figure 1. Synthesis of HTS-AgNPs

3.2 FT-IR Analysis

The characterization of functional groups on the surface of AgNPs was made by FT-IR(Bruker Alpha T) model and the spectra were scanned in the 4000cm^{-1}to 400 cm^{-1}range.

3.3Zeta Potential Study

The sample was dispersed in deionized water using ultrasonication.The solution was centrifuged for 15 min with 8000 rpm and the supernatant was collected. The supernatant was diluted for 4 to 5 times and then the particle distribution in light was studied in a computer controlled particle size analyzer. The zeta potential of dispersion is measured by applying an electric field across the dispersion. Particles within the dispersion with a zeta potential will migrate toward the electrode of opposite charge with a velocity proportional to the magnitude of the zeta potential. The particle size distribution is exhibited in terms of Span value which is obtained by using formula[11].

$$\text{Span value} = (D_{90} - D_{10}) / D_{50} \text{ X } 100$$

Where D_{90}, D_{50} and $D_{10}$are the calculated Mean Diameter at which 90,50 and 10% (cumulative %) of the nanoparticles are counted.

IV. ANTIMICROBIAL ACTIVITY

The bacterial strains used in this study were E.coli (ATCC 25922), Pseudomonas aeruginosa (ATCC 27853), Staphylococcus aureus (ATCC 25923) and Candida sp.

V. RESULT AND DISCUSSION

- **UV-Visible Spectroscopy**

Metallic nanoparticles display characteristic optical absorption spectra in the UV-Visible region called Surface Plasmon Resonance (SPR). Figure 2 shows UV-Visible spectra of synthesized Silver nanoparticles. Absorption spectra of Silver nanoparticles formed in the reaction mixture has a peak at 438 nm. The broadening of the peak at that wavelength is attributed to the formation of polydispersed Silver nanoparticles[12].

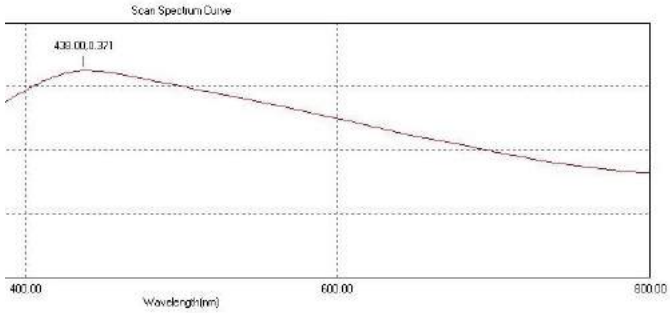

Figure 2. UV-Visible Spectra of synthesized HTS-AgNPs

- **FT-IR Spectroscopy**

FT-IR analysis has been employed to detect the biomolecules presented in HTS-AgNPs (Figure 3). The broad band appeared at 3225.76 cm^{-1}corresponds to the N-H stretching of 1^0, 2^0 amines and amides. The band appeared 1632.62 cm^{-1} belongs to –C=C- heterocyclic compounds e.g. alkaloid or flavones. Band at 2942.58 cm^{-1} appeared due to O-H stretching of carboxylic acids and bands at 1294.13 cm^{-1} and 1137.63 cm^{-1} belong to the
C-N stretching of aromatic and aliphatic amines respectively.

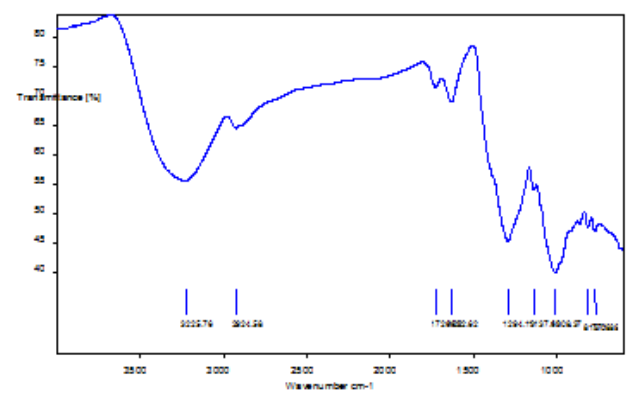

Figure 3. FT-IR of Synthesized Nanoparticles

- **Particle Size Distribution**

The average size and Polydispersity index of the synthesized Silver nanoparticles were determined by Horiba Particle Size Analyzer SZ-100 Ver-1.90 and the result was shown in Figure 4. The particle size of synthesized Silver nanoparticles was found to be 2.4 nm. It shows the average aggregate particle diameter 2097.7 nm and Polydispersity index 0.197.

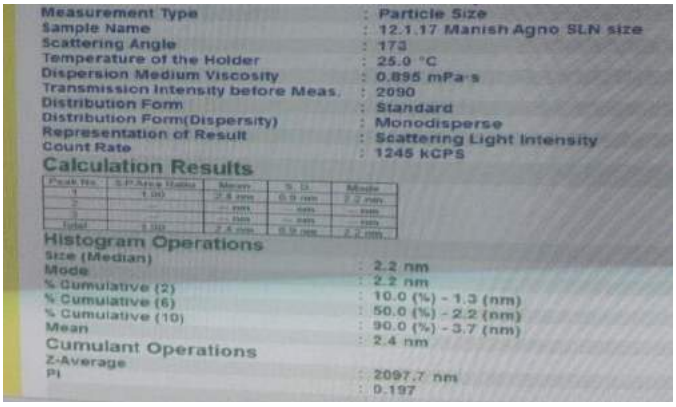

Figure 4. Polydispersity Index of HTS-AgNPs

- **Zeta Potential Analysis**

The stability of the Silver nanoparticles was determined using Zeta potential analysis (Table 1). The Zeta potential value was found to be -0.5 mV (Figure 5).

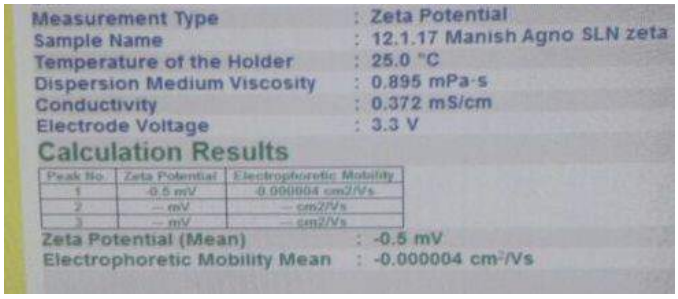

Figure 5. Zeta Potential of HTS-AgNPs

Table 1. Relationship between Zeta potential and the stability of the particles

Zeta potential(mV)	Stability behavior of the particles
From 0 to +.5	Rapid Coagulation or Flocculation
From 10 to +- 30	Incipient Instability
From 30 to +- 40	Moderate Stability
From 40 to +- 60	Good Stability
More than +- 61	Excellent Stability

- **Antimicrobial Activity**

The antimicrobial activity of synthesized Silver nanoparticles was carried out in the agar plate and the zone of inhibition bySilver nanoparticles and by Standard were compared. The zone of inhibition for different strains using saturated solution ofHTS-AgNPsin DMSO as compared with Gentamicin and Nystatin as Standards were summarized in Table 2.

Table 2 : Antimicrobial activity of synthesizedHTS-AgNPs

Bacteria / Compound	E.coli (ATCC 25922)	P.aeruginosa (ATCC 27853)	S.aureus (ATCC 25923)	Candida sp.
HTS-AgNPs	10 mm	17 mm	16 mm	-
Gentamicin	22 mm	27 mm	31 mm	-
Nystatin	-	-	-	22 mm

VI. CONCLUSION

The bio-directed synthesized Silver nanoparticles using the mixture of honey and turmeric powder provides ecofriendly, simple and cost effective method for synthesis of nanoparticles. The spectroscopic techniques like as UV-Visible spectroscopy and FT-IR. Polydispersity studies suggested that the HTS has played important role in the reduction of Silver to Silver nanoparticles and synthesized HTS-AgNPs has been show the rapid coagulation. The particles size of HTS-AgNPs from Zetapotential is about 2.4 nm. The moderatemicrobial activity against Pseudomonas aeruginosa, S.aureus and E.coli are shown by HTS-AgNPs.

VII. ACKNOWLEDGMENT

We are thankful to Principal Dr K.K.Deshmukh for providing the facilities and motivation.

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Study of Physico-chemical Parameters for Soil Quality of Agricultural Field Used in Villages of Nanded- Waghala Municipal Corporation, District : Nanded (Maharashtra), India

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ABSTRACT

The soil is the most important component of our farming. The type of soil is a major factor in determining what types of plant will grow in any area. Soil sampling is the most important step for any soil Analysis. Some important physicochemical parameters of agricultural soil sample near Godavari River from Nanded Taluka. Dist. Nanded, State Maharashtra were studied. Soil samples were collected from 12 representative locations from depths of 0 to 20 cm for physicochemical study. Some physicochemical parameters such as colour, moisture, pH, total organic carbon, Electrical Conductivity (EC), % of Nitrogen (N), % of Phosphorus (P_2O_5), % of Potassium (K_2O), TDS and different metals content were analyzed by using standard procedures. From this study it has been revealed that there is excessive dose of Potassium (K) & phosphorus (P) into the soil due to excessive use of chemical fertilizers. Similarly concentration of elements such as Mg, Ca etc. has also been seen higher than the normal range due to application of sewage water from river & poorer drainage conditions, which leads to increase in soil alkalinity. This study shows that variable concentrations of various parameters and irregular distributions of micronutrients is decreasing the quality of soil for use of agriculture crop formation mean while there is marked variation in nutrients and parameters of various sample point in different agricultural field. This knowledge will help to the people who are interested to work in agricultural field.

Keywords: Physiochemical parameters, Micronutrients, Soil, fertilizers, TDS, flame photometric method, Conductivity, etc.

I. INTRODUCTION

Soil is basic life support system which is a mixture of minerals, organic matter, liquids and myriad of micro and macro organisms that can support plant life & acts as important valuable resources of the nature. All living things are directly or indirectly dependent on soil for day to day needs and 95 % of the human food is derived from the earth soil. Soil has complex function which is beneficial to human and other living organism. It acts as a filter, buffer storage, transformation system and thus protects the global ecosystem against the adverse effects of environmental pollutants.

Study of Soil quality is the most important today. Soil quality is the capacity of a specific kind of soil to function within natural or managed ecosystem boundaries to sustain plant and animal productivity. Each plant species has its nutritive requirements differing from varying concentrations of micro and macro elements at different levels and concentrations (such as Pb, Cd, Fe, etc.) and the soil's physicochemical parameters such as moisture, pH, electrical conductivity (EC), organic carbon (OC), potassium, sodium, calcium and magnesium .Thus the agricultural chemist must know the importance of physicochemical parameters for soil management and plant growth [1-2]. The fertility of the soil depends on the concentration of N, P, K, organic and inorganic materials, conductivity, moisture content, specific gravity Nitrogen as a fertilizer [3-6]. The concentration of these physiochemical parameters affects the agricultural land positively or negatively depending on the levels or concentrations to which they are available.

Activities of human have caused massive loss of this soil organic carbon such as the use of fire on soil, tillage, drainage, grazing management expose, use of fertilizers, pesticides and sewage sludge etc…When the soil is

contaminated, it means that the whole environment is indirectly or directly polluted, This is because crop yield will be adversely affected by soil contamination. Additionally, excess uptake of atmospheric heavy metals emissions has been identified as a one of the reason of heavy metal contamination in vegetable crops. Vegetable growing areas which are situated near to the industries have high risk of contamination of high concentrations of heavy metals in vegetables. These Contaminants can adversely impact the health of living species when inhale or come in contact with contaminated soil. The excessive application of nitrogen, other organic fertilizers and inorganic fertilizers to these vegetables can accumulate high levels of nitrate, other anions as well as heavy metals. When untreated wastes are used in agricultural field, then there is risk of diseases like cholera, typhoid, dysentery, malaria, ulcers etc. Soils can be contaminated by many factors such as industrial activities, automotive emission, mining and repeated use of metal rich compounds including fertilizers, fungicides, untreated wastewater irrigation, and bio compounds. The effect of pH on heavy metal availability to plants has been reported by many researchers and it is accepted that, as pH decreases, the solubility of metals in the soil solution increases and, therefore, they become more readily available to plants [7].

In India, large quantities of chemical fertilizers are used which leads to increase productivity but decreases the quality of soil. Hence today its real time to analyze physicochemical parameters of soil, because with excess of chemical fertilizer exposure to the soil, it is difficult to control the worst effects of these harmful chemicals to the plants, human being and animals[8-9].

1.1 Survey & Background for Research:

Nanded is one of the agricultural favored side situated near the coast of River Godavari located in dist. -Nanded, State-Maharashtra, India. For commercial purpose, due to because of physical, chemical & geographical condition of this soil, Nanded is an eminent place for cultivation of wheat, jawar, pulses, sugarcane, vegetables and fruits etc. Now the river polluted with tremendous amounts of wastes from residence houses and industry. The contaminated water from this river is used for the irrigation for farming of wheat, jawar, pulses, sugarcane, vegetables. A survey around these coastal areas revealed that most solid and liquid wastes which contain some of the heavy metals (like Pb, Cd, Fe, etc.) are carelessly dumped on the open areas, and these may leach into the soil after rainfall and consequently pollute the soil. Hence, this affects significant effect on the soil and crops which cause the health problem to living species due to bioaccumulation of trace metals with time.

This draws the significant attention for me to study qualities of these lands, to determine the presence of heavy metals, radicals, hydrocarbon contents, etc. at different levels & concentration. The main aim of physicochemical parameters study of these collected soil samples from different villages is to analyze the quality of soil for agriculture purpose and scope of soil for future farming.

II. MATERIALS & METHODS

2.1 Study Areas:

Nanded is the one of the largest agricultural place in Maharashtra. The study area lies between latitude 19°16′N and longitude 77°31′E, and elevation between 366m. The study was conducted at selected sites of twelve different agricultural villages of Nanded, in district Nanded, state Maharashtra. (S_1-Taroda.bk, S_2-Pasadgaon,S_3-Sugaon Khurd,S_4-Babulgaon ,S_5-Kakandi, S_6-Rahati, S_7-Pimpalgaon Korka,S_8-Daryapur, S_9-Borgaon, S_{10}-Jannapuri, `S_{11}-Jaitapur, S_{12}-Jannapuri) which represent soils of that village.

2.2. Sample Collections:

All top quality soil samples were collected from agriculture side during summer season randomly at 0 to 20 cm depths from twelve selected agriculture areas with a soil auger and obtained a minimum volume of 0.5 kg of soil per sampling area. These collected sample were stored in sterilized zip lock as described by Arotupin et.al (2008)[10] .

2.3. Sample Pre-treatment & Preservation:

The soil samples were air dried for a period of one week. Then they are ground using mortar and pestle and passed through 2.0 mm sieved. Further the soil samples were kept in dry polythene packets for subsequent physical, chemical analysis.

2.4. Sample Analysis Methods:

A.R. grade chemicals and reagents from S. D. Fine and Merk chemicals, Bombay is used for analysis of physicochemical parameters. The soil samples were suspended in distilled water (1:4 w/v) and allowed to settle down particles for analysis of physicochemical parameters. Methods used for Estimation of these physiochemical Parameters were carried out with standard procedures [11-16].

Methods use for estimation of some physicochemical parameters is shown in Table 1.

Table 1. Methods Used for Estimation of Some Parameters

Sr. No.	Physiochemical Parameters	Methods
1	Colour	By Viewing Soil
2	Moisture	By Weighing
3	pH	pH metry
4	electrical conductivity (EC),	Conductometry
5	% organic carbon (OC)	Titration (Walkley and Black method using diphenylamine indicator)
6	Available Nitrate Nitrogen	Titration (alkaline permanganate method)
7	% Alkalinity	Titration
8	Total Dissolved Solid	TDS metry
9	Calcium	by EDTA titration & atomic absorption spectrophotometer
10	Magnesium	by EDTA titration & atomic absorption spectrophotometer
11	% Phosphorus	Bray's method
12	% Potassium	Flame photometric method

Analysis of these physiochemical parameters were carried out in the P.G. Laboratory of Department of Chemistry, Gramonnati Mandal's Arts, Commerce & Science College Narayangaon, Taluka Junnar, Dist.-Pune, MS, India.

III. Results and Discussion

Physicochemical parameters of twelve samples are summarized in Table 2.

Table 2. Physicochemical Parameters of Soil Samples

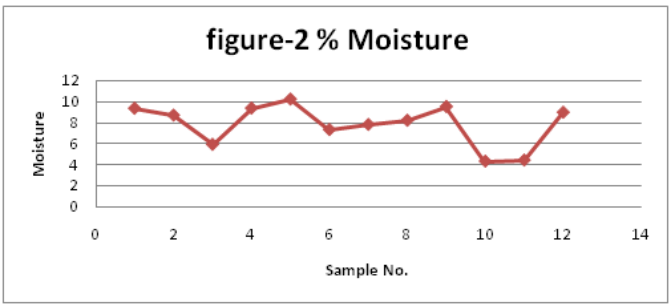
Sr. No.	Physiochemical Parameters	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}
1	Color	Faint Black	Faint Black	Faint Black	Dark Black	Dark Black	Faint Black	Faint Black	Dark Black	Dark Black	Faint Black	Faint Black	Dark Black
2	% Moisture	9.36	8.70	5.90	9.38	10.24	7.32	7.81	8.21	9.53	4.29	4.40	8.98
3	pH	7.72	7.92	7.45	7.78	7.45	7.26	7.10	7.55	6.94	7.35	7.12	7.65
4	electrical conductivity (EC),	0.18	0.26	0.22	0.14	0.23	0.19	0.11	0.09	0.16	0.11	0.15	0.14
5	% organic carbon	0.74	0.63	0.30	1.28	0.45	0.98	1.23	1.11	0.86	0.98	1.20	0.98

3.1 Colour:

The colour of the sample S_1, S_2, S_3, S_6, S_7, S_{10} and S_{11} are faint black, whereas colour of sample S_4, S_5, S_8, S_9 and S_{12} is dark black.

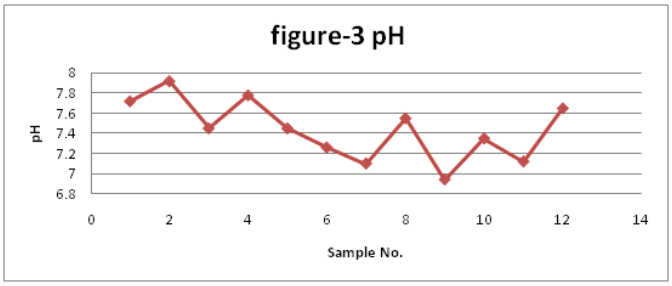
3.2 Moisture:

The moisture content value ranges from 4.29% to10.24%. It is clear from result that the sample S_5has highest moisture content than remaining eleven samples.



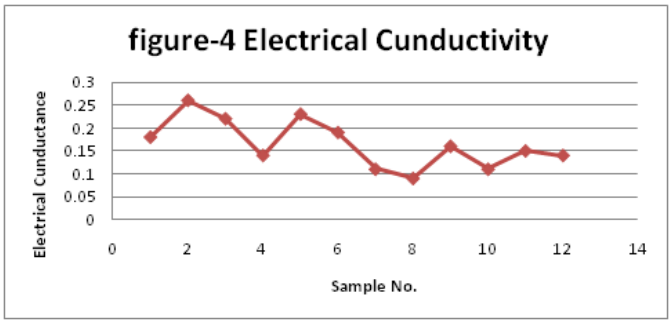
3.3 pH:

The pH of soil is one of the most important parameter which determines the capacity of soil. pH value expresses the acidity or alkalinity of the soil. It affects mineral, nutrient quality and much microorganism activity. All the pH values are less than 8.5 (table-2). The range for pH value for soil is -acidic. < 6.5, Normal alkaline -6.5-7.8, medium alkaline 7.8- 8.5, Alkali > 8.5.The pH values for above selected samples were observed in between the ranges from 6.94 to 7.92. The samples S_2 is very slightly high alkaline and remaining samples are in normal alkaline range.



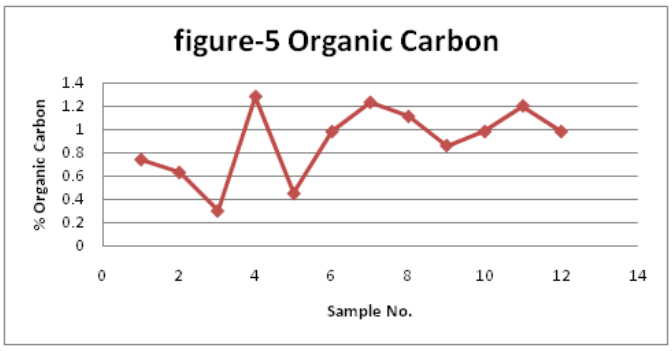
3.4 Electrical Conductivity:

The measurement of electrical conductivity gives a clear idea of soluble salt present in the soil. Conductivity depends upon the dilution of soil suspension. Standard value of Electrical conductivity in soil is - Normal < 0.8 dsm-1, critical for salt tolerant crops 1.6 -2.5 dsm-1, Injurious to most crops > 2.5 dsm-1.The conductivity values ranges from 0.09 µS to 0.26 µS . Conductivity of sample S_8 is less as compared to other remaining samples.



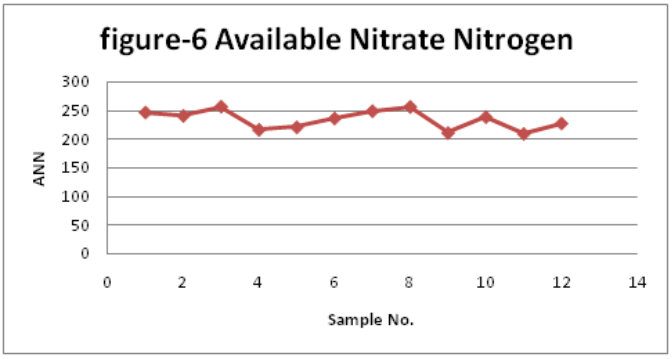
3.5 Organic Carbon:

Organic carbon is the index for nitrogen. The source of organic carbon in the cultivated soil included crop residue, animal manure, cover crops, green manure and organic fertilizer etc. Standard value of organic carbon value is - low < 0.50, medium 0.50- 0.75 and high > 0.75. Organic carbon values of selected samples ranges from 0.30% to 1.28%. Organic carbon of sample S_4 is high as compared to other remaining samples.



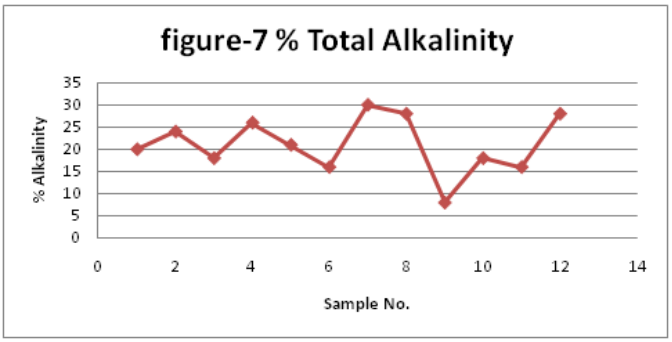
3.6 Available Nitrate Nitrogen:

Available nitrate nitrogen in the soil ranges from 208.6 Kg/hectare to 256.4 Kg/hectare. The soil sample S_3 has high nitrate nitrogen as compared to remaining collected samples.



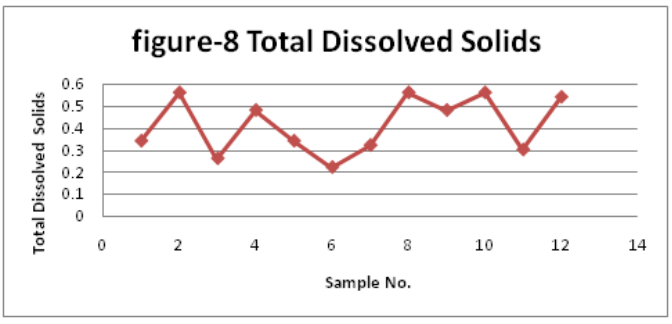
3.7 Alkalinity:

Alkalinity was observed in the ranges from 08% to 30%. Alkalinity of sample S_9 is less as compared to other collected samples.



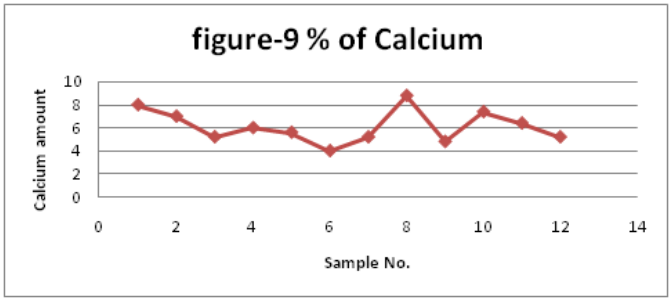
3.8 Total Dissolved Solid (TDS):

TDS values for soil samples ranges from 0.22 to 0.56. Soil sample S_6 has lowest TDS as compared to other remaining samples.



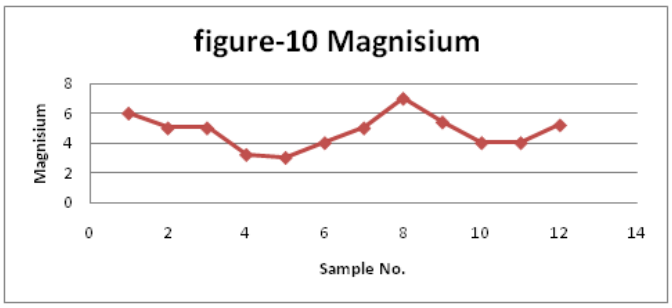
3.9 Calcium:

Calcium ranges from 4.0 ml/100gm to 8.8ml/100gm. Soil sample S_8 have high calcium content as compared to remaining analyzed samples.



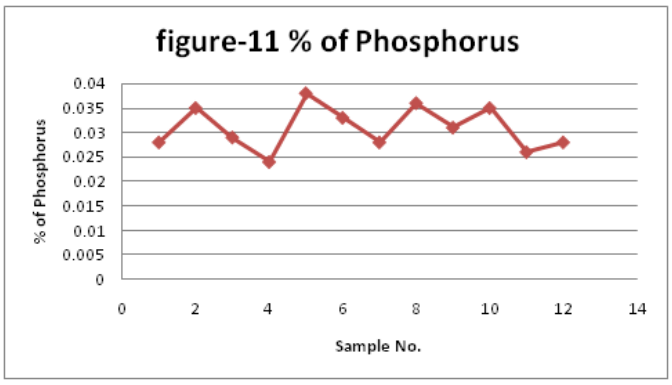
3.10 Magnesium:

In the form of Mg^{+2}, magnesium is available for plant. Magnesium content in the soil samples ranges from 3 ml/100gm to 7ml/100gm. Sample S_4 contains less amount of magnesium.



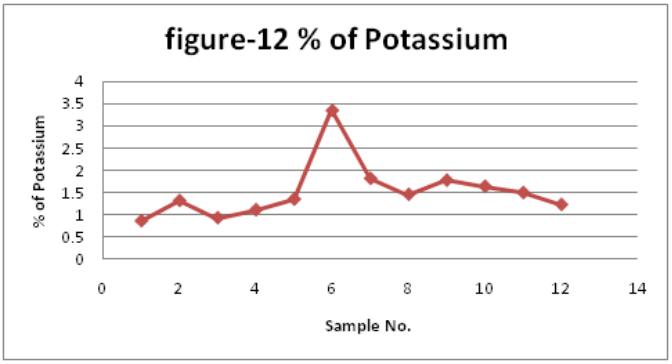
3.11 Phosphorus:

Phosphorus was found in the range of amount low, medium, high (table no.2). Inorganic orthophosphate plays an important role in aquatic ecosystem. Phosphorus is the most important micro nutrient. Phosphorus values for soil samples ranges from 0.024% to 0.038%. Soil sample S_5 has highest phosphorus amount as compared to other remaining samples.



3.12 Potassium:

Potassium is present in the form of K2O in soil. Although potassium present in small amount in soil sample, it plays an important role as micronutrient. The K is relatively abundant in the earth's crust; most of it is not accessible to plant. Potassium values for soil samples ranges from 1.23 to 3.36. Soil sample S_6 has highest potassium quantity as compared to other remaining samples.



IV. Conclusion

The research carried out on soil quality of twelve study areas in different villages in Nanded shows that the pH of soil samples was slightly alkaline , the level of organic carbon found to be very low, which is not helping the soil to function for agricultural use. The electrical conductivity and NPK values of all soil samples were found to be very less. Hence commercial fertilizers containing required essential elements needs to be added for proper growth and development of crop. Magnesium and calcium content in all soil samples are in high amount this is due to because of exposure to high metals contamination. The physiochemical parameters of soil should be protected by discouraging bush burning and grazing management which cause loss of soil organic carbon. When these are done, the quality of the soil will be improved, enhancing the agricultural use of it, on the other hand life of these areas will enjoy safe environment and healthy life.

V. Acknowledgments

VI.

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Antioxidant Effects of Melatonin and R-α-lipoic acid on Mimetically Aged Houseflies

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ABSTRACT

D-galactose (D-gal) has been widely used to induce mimetic aging in various animals. In the current study, we used Melatonin and R-α-lipoic acid to explore their antioxidant and anti-aging effect in D-gal induced mimetic aging in male Musca domestica. In this study, we finalized the doses of Melatonin and R-α-lipoic acid upon chronic administration (20 days). Our results confirmed that these antioxidant administrations significantly improved the ROS generated by decreasing the levels of AOPPs, and MDA levels in aging houseflies. Melatonin and R-α-lipoic acid administration elevated the activities of SOD and proteins levels which are suppressed by aging. Our results signify that both Melatonin and R-α-lipoic acid effectively alleviated oxidative stress and improved protein levels in D-Gal induced aged houseflies.

Keywords: Aging; D-galactose; oxidative stress; Musca domestica; Melatonin; R-α-lipoic acid

I. INTRODUCTION

Aging is the progressive accretion of alteration over time which is allied with or accountable for the increasing susceptibility to disease and death. D-Galactose (hereafter referred as D-Gal) accelerated aging models are found have tremendous similarity with normal aging models thus and extensively used for study of aging, for assessing various agents used for slowing down the effects of aging and related diseases.

Musca domestica L. 1758 is considered as excellent model system to explore longevity promoting qualities of neutraceutical extracts and phyto-constituents (Toroser and Sohal, 2005). This aging model might be valuable in spotting the role of efficient antioxidants and underlying mechanisms in retarding aging (Cui et al., 2004).

Melatonin (N-acetyl-5-methoxy-tryptamine, hereafter referred as MEL) is a main product secreted by the pineal gland using tryptophan. MEL has been reported to minimize the accretion of lipid per oxidation generated products. As it is not showing any pro-oxidant and lethal effects, this hormone is proved to possess a great radical scavenging property.

R-α-lipoic acid (hereafter referred as LA) is a naturally occurring component, essential for the function of different enzymes that take part in mitochondria's oxidative metabolism. Because of this property, LA is commonalty used in multivitamin preparations, anti-aging drug supplements, and also added in pet food (Shay et. al, 2009). LA is a potent biological antioxidant with a scavenging capacity for many reactive oxygen species (Scott, et. al, 1994; Packer et.al, 1995).

As till date there is no report on *M. domestica* oxidative stress during mimetic aging, the current study was conceded out to check the hypothesis that the oxidative stress elicited by the ingestion of D-Gal is associated with antioxidant defense.. The effect of MEL and LA acid supplementation on *M. domestica* aging is not so far studied. Therefore this is the first effort to study such effect. In current investigation the male houseflies were used to study whether D-Gal- induces oxidative stress and can it be minimized by the antioxidant properties of MEL and LA.

II. Materials and Methods

Based on our previous standardization experiments of MEL and LA supplementation; 1mM MEL and 0.5 mM LA were found to be most suitable to minimize the adverse effects of D-Gal on *M. domestica* life span i.e. these two doses significantly increased the life span of *M. domestica* when co-treated with D-Gal (unpublished

data). To ensure further and to confirm that whether these concentrations are actually minimizing the stress, we made following six experimental groups of houseflies which were randomly selected into six groups (n=4).

Group I: a Control group (C); houseflies were fed on 2% D-sucrose
Group II: a D-Gal model control group; houseflies were fed by 2% D-galactose
Group III: MEL group; houseflies were fed by 2% D-sucrose + 1mM melatonin
Group IV: LA group; houseflies were fed by 2% D-sucrose + 0.5 mM LA
Group V: a positive MEL group (D-Gal + MEL) where in addition to receiving D-Gal, the houseflies were supplemented with 1mM MEL
Group VI: a positive LA group (D-Gal + LA); in addition to receiving D- Gal, the houseflies were fed a diet supplemented with 0.5 mM LA

We used the technique reported by Aksu et al, (2014) was used with some modifications for standardization and dose selection experiment. Both male and female individuals (n=2, each) were kept in single experimental jar for 5 weeks under normal culture conditions i.e. 26 ± 1°C and 70% humidity. At the end of this period the experiment was concluded. During this phase, the houseflies enter in middle age. Only males were isolated and and used for further biochemical estimations. We discarded female houseflies as there might be probable role of estrogens as antioxidants (Altun et al., 2011). Each experiment was repeated thrice.

Gustatory assay:
Assessment of food intake by house fly was done by adding visible dye into diets, and after that gut redness was measured (Cui et al., 1998). Sulforhodamine B was used to detect the amount of food consumed by flies. Houseflies were starved for 24 hours on tissue paper soaked with distilled water. After starvation period, they were again transferred back on their respective experimental set. Food i.e. the drinking water was mixed with 2% sulforhodamine B. They were allowed to feed for 3 hours on the dye-mixed food. After 3 hours of feeding, flies were immobilized by placing on ice, and dissected. Their entire gut region of was dissected and homogenates were prepared using the 0.1 M phosphate buffer, pH 7.2. Absorbance of supernatant was measured at 540nm.

Biochemical Methods:
After 20 days of treatment male houseflies (n=10 per group) were exposed to -80 °C for 15 minutes and their heads were dissected. We used ice-cold 50 mM sodium phosphate buffer (pH 7.0) for homogenization of heads facilitated by sterilized motor driven tissue grinder (Genetix Biotech). Subsequently, the homogenates were subjected to centrifugation at 10,000 rpm for 10 minutes (0 °C) and the resultant supernatants were kept at -80 °C. These supernatants were used for further biochemical estimations.

Quantification of Advanced Oxidative Protein Products (AOPPs):
For this assay, the method reported by Hanasand et al., (2012) with some modifications was used for spectro-photometric analysis of AOPPs. The reaction mixture absorbance was instantly read at 340 nm. Concentrations of AOPP were determined using Chloramine Standard curve and calculated as µM / lit of chloramines-T equivalents.

Estimation of Thiobarbituric Acid Reacting Substances (TBARS):
The levels of lipid peroxidation was estimated by measuring the TBARS content as per the procedure of Ohkawa et al., (1979) with minor modifications.

Superoxide Dismutase Activity (Cu,Zn-SOD):**dismutase activity** (EC – Number 1.15.1.1) **assay**:
Cu,Zn-SOD (EC1.15.1.1) activity was measured by inhibition of formazon formation in the presence of enzyme (Beauchamp and Fridovich, 1971). The enzyme activity was calculated in terms of Units/mg of protein.

Quantification of total Protein:
Protein concentrations in all test samples were determined by using Bradford reagent (Bradford, 1976) with some modifications with bovine serum albumin (BSA) as a standard.

III. Results

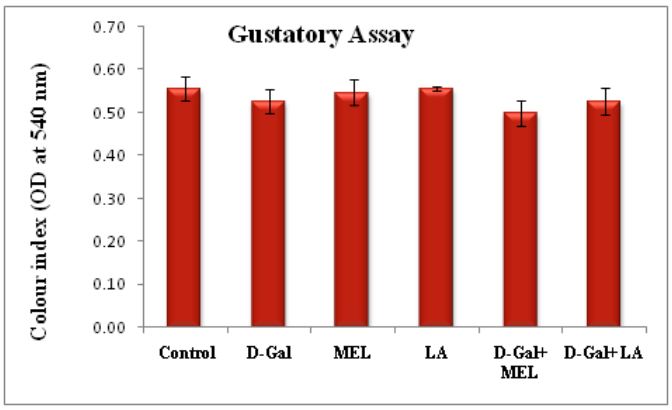

Figure 1. Gustatory (feeding) assay

Above figure shows that the all the six groups of houseflies did not show significant difference in their feeding assay (Figure 1). Thus the results obtained from the following experiments are not due to the alteration in the feeding behaviour of the houseflies, but it was due to the presence of the treatment compound itself.

Table 1. Effect of MEL and LA on D-gal-induced aging related parameters in male houseflies.

Treatment	AOPPs levels µM / lit of chloramines-T equivalents (% of control)	LPO nmoles MDA per gm of tissue (% of control)	Cu,Zn-SOD Units / mg of protein (% of control)	Total Protein mg / ml BSA (% of control)
Control	99.18 ± 13.86 (100)	0.178 ±0.05(100)	46.362±3.16(100)	0.109 ± 0.04 (100)
D-Gal	212.6 ±52.76 [a](214.36)	0.585 ±0.06a (328.65)	15.628±2.15 [a](33.71)	0.087 ± 0.018 [a](79.82)
MEL	97.44 ± 23.96 (98.92)	0.173 ± 0.03 (97.19)	45.86±3.12 (98.92)	0.103 ± 0.03 (94.50)
LA	108.2 ± 17.15 [b](109.09)	0.169 ± 0.04 [b](94.94)	46.212 ± 4.11 (99.68)	0.105 ± 0.023 (96.33)
D-Gal +MEL	144.2 ± 22.15 [c](145.39)	0.453± 0.06 [b,c] (254.49)	21.93 ±2.049 [c](47.30)	0.0927 ± 0.018 [a](85.05)
D-Gal +LA	120.9± 23.77 [c](121.89)	0.305 ±0.06 [c](171.35)	25.872 ±2.05 [b,c](55.80)	0.0979 ± 0.018 [a](89.82)

Values are mean ±S.E.M. [a]P<0.05 as compared to Control group;
[b]P<0.05 as compared to D-gal-treated group;
[c]P< .05 as compared to D-Gal +MEL and D-Gal +LA to D-gal group
(repeated measures one-way ANOVA followed by Tukey's test for multiple comparisons).

As shown in Table 1, compared to Control group houseflies, chronic administration of D-Gal significantly increased AOPP and MDA concentration, whereas resulted in depletion of superoxide dismutase, and total protein level (P <0.05).

As compared to control group, D -Gal group displayed a remarkable increase of AGEs levels (p< 0.001) (Table 4.4.) indicating elevation of *in vivo* oxidative stress in the brain of D-Gal-treated houseflies. Remarkably, Melatonin and LA could decrease brain AGEs levels when compared with D -Gal group, similarly D-Gal+MEL as well as D-Gal+LA group showed decreased AGEs levels (p< 0.05). However, no significant difference was found in two indexes between Control and MEL groups.

However, chronic co-treatment of both MEL and LA significantly relieved the oxidative damage which is shown by abridged AOPP and MDA levels and refurbishment of superoxide dismutase, and total protein level as than D-gal- group levels. Further, MEL and LA treatment by itself did not show any significant changes in oxidative stress parameters of Control group houseflies (Table 4.4). These results ensured and confirmed that these concentrations are actually safe for the individual experiments.

IV. Discussion

Based this we first tried to establish the mimetic aging in houseflies caused by D-Gal. MEL and LA doses were added in the drinking water and their effect on various physiological assays like feeding rate of houseflies was studied. Analyses of feeding rates were done by gustatory assay between repetitive trials of D-Sucrose fed houseflies shown no significant differences. Likewise, there was no significant difference observed between all replicates of D-galactose-fed as well as antioxidants (MEL and LA) fed houseflies tested. Hence, it was specified that any potential effect of D-Gal as well as antioxidants (MEL and LA) on houseflies would not be due to un-even feeding.

Lots of publications revealed that the mimetic aging induced by the chronic administration of D-Gal is linked with accretion of oxidative stress. Lessened activity of antioxidant enzymes and increase in LPO are biomarkers of oxidative stress (Cui et al., 2006; Hsieh et al., 2011). Oxidative stress performs a crucial role in the age-linked cognitive decline in neurodegenerative disease like Alzheimer's (Kumar and Gupta, 2003) and Parkinson (Kaur et al., 2011) as neuronal membranes easily get damaged by free radicals. MDA is an

imperative biomarker of oxidative damage under conditions of oxidative stress (Elia et al., 2002).

Thus, these findings clearly demonstrated that, D-Galactose induces oxidative stress in the males of *Musca domestica*. This stress can be reduced by Melatonin and R-α-lipoic acid. Thus, Melatonin as well R-α-lipoic acid acts as an efficient free radical scavenger by protecting tissues and also tries to prevent D-galactose induced oxidative stress. OS is also elevated in D-Galactose induced aging process in comparison to controls. Sucrose control in response to anti-oxidant treatment over the duration of study partially restored the antioxidant defense and decreased the extent of oxidative damage in D-Galactose induced aged houseflies. This study also necessitates the importance of antioxidant therapy in aging houseflies to alleviate oxidative damage caused. Thus, these could be effectively used in the treatment of aging related disorders owing to their anti-aging and antioxidant potential.

V. Conclusion

The present study thus concludes that, D-Galactose induces oxidative stress in *Musca domestica.* This stress can be reduced by Melatonin and R-α-lipoic acid. Thus, Melatonin as well R-α-lipoic acid acts as an efficient free radical scavenger by protecting tissues and also tries to prevent D-galactose induced oxidative stress. However, the long-term effects of unbiased and antioxidant- supplemented revival on various organ functions necessitates further study.

VI. Acknowledgement

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A New Protocol using Potassium Hydrogen Sulfate as the Promoter for An Efficient Synthesis of Functionalized Quinoxalines

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ABSTRACT

A simple, greener and highly efficient method for the synthesis of biologically important functionalized quinoxalines has beendeveloped employing KHSO4as a promoter in water. To the best of our knowledge this transformation isachieved for the first time using an organic catalyst. A small library of quinoxalineconjugates have been synthesized using this green chemistry oriented effective protocol.

Keywords: Green chemistry, KHSO4, medicinally important.

I. INTRODUCTION

Quinoxalines represent as important class of biologically active compounds that are known to have antimicrobial, [1, 2] as well as anticancer [3]. This scaffold is present in several anticancer agents such as XK469(**1**), chloroquinoxaline sulfonamide (**2**) and in some natural products like izumiphenazineC(**3)**and NCG555879-01 (**4)** (Fig. 1)[4,5] . It is also a part of various antibiotics such as actinoleutin,echinomycin andlevomycin which are known to inhibit the growth of Grampositive bacteria. Further, quinoxaline derivatives are also used in electroluminescent materials, organic semiconductors,dyes,cavitands, etc[6-12].

Owing to widespread applications of quinoxalines several synthetic methods for their preparation both in solution as well as in solid-phase have been developed. [13-17] Among them the condensation of 1,2-diamines with 2-hydroxy ketone and oxidative cyclization of a-hydroxy ketones with 1,2- diamines under various conditions are widely used.[18-24]

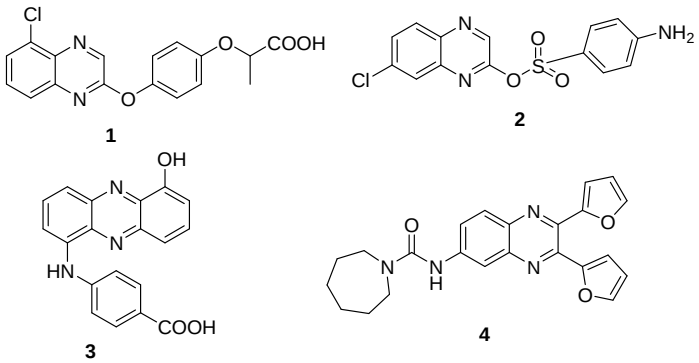
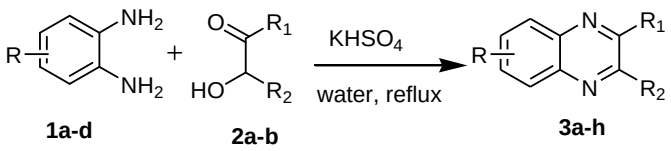


Figure 1. Biologically important quinoxalines.

Recent reports indicate the use of several catalysts such as Ru/C in the presence of b-Cyclodextin, manganese oxide octahedral molecular sieves (OMS-2), MnO_2, $RuCl_2(PPh3)_3$-TEMPO,KF/Al_2O_3, HgI_2 and Au-NPs for onepot synthesis of quinoxaline from a-hydroxy ketones.[25-31] However, they often suffer from one or more disadvantages such as long reaction time, use of costly and hazardous organic solvents, unsatisfactory product yields and harsh reaction conditions.On the other hand, organic catalysis is an emerging area of applied as well as core organic synthesis wherein small molecules are used to catalyze organic transformations. In continuation to our research towards the development of novel protocol for the organic transformations.[32,33] herein in this report we wish to introduce $KHSO_4$ as a mild and efficient catalyst [34] for the synthesis of substituted quinoxalines in high yields for the first time. The method is highly efficient and free from aforesaid drawbacks. The condensation reactionsofdiamine with

hydroxyketone proceeded smoothly at 60°C to afford the corresponding quinoxaline derivatives in high yields in shorter reaction times.



1a-d **2a-b** **3a-h**

Scheme 1. $KHSO_4$ catalyzed synthesis of quinoxalines

II. RESULTS AND DISCUSSION

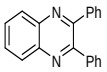
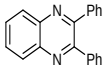
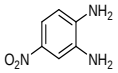
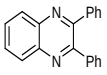
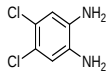
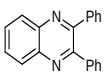
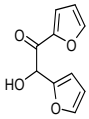
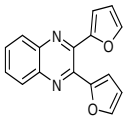
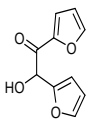
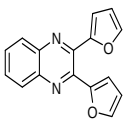
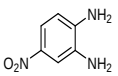
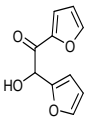
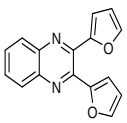
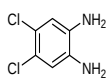
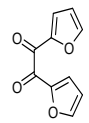
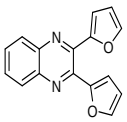
Chemistry In the beginning, a systematic study was carried out for the catalytic evaluation of Potassiumbisulfate ($KHSO_4$) towards the synthesis of quinoxalines. Initially a blank reaction was performed using benzoin and 1,2-diaminobenzene in water without any catalyst at room temperature and the completion of the reaction was monitored by TLC. It was observed that the reaction did not proceed even until 24 hours. Whereas the same reaction was executed in the presence of catalytic amounts of $KHSO_4$in water at room temperature and traces of the product were found (less than 5%). Later, this reaction was carried out under refuxing conditions and the desired transformation was observed furnishing the product in very good yield (Scheme 1). After obtaining the desired product, the amount of catalyst and the time required for the completion of reaction were evaluated. The reaction was performed using 5, 10, 20 and 30 mol% of the catalyst and was monitored for 2–8 hours. It was observed that 20 mol% of the catalyst loading provided maximum yield (87%) in 2 hours. While 5 and 10 mol% of the catalyst afforded 64% and 72% of the product even after refuxing the reaction for 8 hour and above. An additional increase of the catalyst loading to 30% did not improve the yield. On the contrary, the reaction slows down

Table 1. Condensation of benzoin and 1,2-diaminobenzene in waterat different catalyst ($KHSO_4$) concentrations.

Entry	catalyst (mole %)	Time (h)	yield (%) [a]
1	--	24	Nil
2	05	10	60
3	05	15	62
4	10	10	75
5	10	15	76
6	20	08	78
7	20	10	80
8	30	06	87
9	30	02	88

a = isolated yield

Table 2. $KHSO_4$ mediated synthesis of quinoxalines from hydroxy ketone with 1,2-diamines

Entry	Diamine	Hydoxyketone	Product	Time (h)	Yields[a] (%)
1				2	86
2				2	87
3				2.5	82
4				2	86
5				2	87
6				2	88
7				2	83
8				2	85

a = isolated yield

on adding more than 20 mol% of the catalyst (Table 1). With the optimized conditions in hand, the reaction was

performed with different set of substituents to explore the scope and generality of the present protocol. The quinoxaline derivatives were synthesized using two hydroxyl ketones namelybenzoin(**2a**) and furoin (**2b)** with varying 1,2-diamines(**1a-c**). Thediamines used possessed both ring activating as well as deactivatingsubstituents and the results of these observations aresummarized in Table 2. From the results it can be concludedthat the electronic factors of 1,2-diamine influences the progressof the reaction. Electron donating substituents such asmethyl (entry 2 and 6) provided excellent yields of the correspondingproducts.

In presence of weak ring deactivatinggroups such as dichloro (entry 4 and 8) thereaction progressed smoothly and the product was obtained ingood yields. This trend was also observed in the absence ofsubstituents on the diamine moiety. However, in case of ringdeactivating groups such as nitro (entry 3 and 7) the reactionwas slower and the yields were also comparable very lower.
In conclusion, we have successfully developed a simple, efficient and ecofriendlymethod for the synthesis of quinoxalines from 1,2-diamines and a hydoxyketones using cost-effective and readilyavailable catalyst $KHSO_4$. To the best of our knowledge thistransformation has not been reported with an inorganic catalyst.The advantages of this method over previous reports include itssimplicity of operation, cleaner reactions, higher yields, shorterreaction times and use of inexpensive catalyst. The mild reactioncondition makes this protocol an alternative procedureto the conventional acid or base-catalyzed processes for thesynthesis of quinoxalines and has practical applicability.Further, using this protocolsynthesis of library of quinoxaline–based conjugatesare under development for the medicinal chemistry driven drug synthesis.

III. CONCLUSION

In conclusion, we have successfully developed a simple, efficient and ecofriendlymethod for the synthesis of quinoxalines from 1,2-diamines and a diketones using cost-effective and readilyavailable catalyst $KHSO_4$. To the best of our knowledge thistransformation has not been reported with an inorganic catalyst.The advantages of this method over previous reports include itssimplicity of operation, cleaner reactions, higher yields, shorterreaction times and use of inexpensive catalyst. The mild reactioncondition makes this protocol an alternative procedureto the conventional acid or base-catalyzed processes for thesynthesis of quinoxalines and has practical applicability.Further, using this protocolsynthesis of library of quinoxaline–based conjugatesare under development for the medicinal chemistry driven drug synthesis.

IV. EXPERIMENTAL

3.1 General remarks

Melting points were determined with an electrothermalmeltingpoint apparatus and are uncorrected. Infrared (IR) spectra wererecorded on Perkin-Elmer model 683 or 1310 spectrometerswith sodium chloride optics. 1H NMR spectra were recorded onanAvance 300 MHz spectrometer (Bruker, Fallanden, Switzerland)and^{13}CNMR spectra were recorded on a UNITY 300 MHz(Varian, Switzerland). Chemical shifts (d) are reported in ppm,downfield from internal TMS standard. Mass spectra wererecorded using a quadruple ion trap mass spectrometer (Thermo Finnign, San Jose, CA, USA) equipped with an electrospray source.

3.2 Representative experimental procedure for the synthesis quinoxalines (3a–h)

In a 50 mL round bottom flask 1,2-diamine (1 mmol) and hydoxyketone (1 mmol) were taken in water (5 mL). Catalyticamount (30 mol%) of potassium hydrofgen sulfate ($KHSO_4$) was added and the reactionmixture was refluxed for 2 hours. The progress of the reactionwas monitored by TLC. After completion of the reaction, themixture was cooled to room temperature. The precipitated solidwas collected by filtration, washed with water and recrystallizedusing methanol.

2,3-Diphenylquinoxaline (3a)

Whitish solid; Mp: 125–126^{o}C; ^{1}HNMR (300 MHz $CDCl_3$): d 7.30–7.41 (m, 6H), 7.51–7.56 (m, 4H), 7.77–7.83 (m, 2H), 8.15–8.23 (m,2H); ^{13}C NMR (75 MHz $CDCl_3$): d 127.49, 128.10, 128.41, 129.00,129.31, 138.0, 140.34, 152.57; ESI-MS: m/z = 283 (M + H)+.

6-Methyl-2,3-diphenylquinoxaline (3b)

Brown white solid; Mp: 120–121^{o}C; ^{1}HNMR (300 MHz $CDCl_3$): d 2.6(s, 3H), 7.3 (d, J =6.8 Hz, 6H), 7.5 (d, J = 6.79 Hz, 4H), 7.6(dd, J = 1.51, 8.7 Hz, 1H), 7.9 (s, 1H), 8.0 (d, J = 8.49 Hz, 1H);^{13}C NMR (75 MHz $CDCl_3$): d 20.8,

126.8, 127.0, 127.5,127.6, 128.8, 131.1, 138.0, 138.4, 139.3, 140.0, 151.2,151.9; ESI-MS: m/z = 297 (M + H)+.

6-Nitro-2,3-diphenylquinoxaline (3c)

solid; Mp: 139–140°C; ^{1}HNMR (300 MHz $CDCl_3$): d 7.34–7.46 (m, 6H), 7.53–7.57 (m, 4H), 8.3 (d, J = 9.25 Hz, 1H), 8.5(dd, J = 2.45 & 9.25 Hz, 1H), 9.1 (d, J = 2.45 Hz, 1H); ^{13}C NMR(75 MHz $CDCl_3$): d 123.3, 125.6, 128.4, 129.6, 129.7,129.8, 129.8, 130.7, 138.0, 138.1, 139.9, 143.5, 147.8,155.6, 156.2; ESI-MS: m/z = 328 (M + H)+.

6,7-Dichloro-2,3-diphenylquinoxaline (3d)

Solid; Mp: 141–143 °C; ^{1}H NMR (300 MHz $CDCl_3$): d 7.3–7.4 (m, 6H), 7.50–7.54 (m, 4H), 8.3 (s, 2H); ^{13}C NMR (75 MHz$CDCl_3$): d 127.6, 128.6, 129.0, 133.4, 137.6, 139.1, 153.7;ESI-MS: m/z = 351 (M + H)+.

2,3-Di(furan-2-yl)quinoxaline (3e)

Solid; Mp: 134–135°C; ^{1}HNMR (300 MHz $CDCl_3$): d 6.5–6.6 (m, 2H), 6.6 (dd, J =0.56 & 3.58 Hz, 2H), 7.6 (dd, J = 0.56& 1.70 Hz, 2H), 7.7–7.8 (m, 2H), 8.11–8.17 (m, 2H); ^{13}C NMR(75 MHz $CDCl_3$): d 111.8, 112.9, 129.0, 130.3, 138.4,140.5, 142.5, 144.1; m/z = 263 (M + H)+.

2,3-Di(furan-2-yl)-6-methylquinoxaline (3f)

Solid; Mp: 123–124 °C; ^{1}H NMR (300 MHz $CDCl_3$): d 6.6 (d, J =16.42 Hz, 4H), 7.6 (t, J =8.87 Hz, 3H), 7.9 (s, 1H), 8.0 (d, J = 8.49 Hz, 1H); ^{13}C NMR (75 MHz $CDCl_3$): d 21.2, 111.3, 111.9, 112.2, 127.2, 127.8, 132.1, 138.3, 140.0, 140.4, 141.0, 141.8, 143.3, 143.4, 150.2; ESI-MS: m/z = 277 (M +H)+.

2,3-Di(furan-2-yl)-6-nitroquinoxaline (3g)

Solid; Mp: 152–154 °C; ^{1}H NMR (300 MHz $CDCl_3$): d 6.6–6.6 (m, 2H), 6.87 (dd, J = 3.58 & 16.80 Hz, 2H), 7.65 (dd, J = 0.94& 5.09 Hz, 2H), 8.2 (d, J = 9.253 Hz, 1H), 8.5 (dd, J = 2.45 & 9.253 Hz, 1H), 9.0 (d, J = 2.45 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): d 111.3, 111.4, 113.4, 114.3, 122.4, 123.9, 129.4,137.92, 141.8, 142.9, 143.4, 143.9, 144.4, 146.6, 148.9,150.0; ESI-MS: m/z = 308 (M + H)+.

6,7-Dichloro-2,3-di(furan-2-yl)quinoxaline (3h)

Solid; Mp: 135–137 °C; ^{1}H NMR (300 MHz $CDCl_3$): d 6.6–6.7 (m, 2H), 6.7 (d, J = 3.50 Hz, 2H), 7.6 (d, J = 1.06 Hz, 2H),8.2 (s, 2H); ^{13}C NMR (75 MHz $CDCl_3$): d 111.5, 113.2, 128.7,133.7, 138.4, 142.5, 143.9, 149.5; ESI-MS: m/z = 330 (M +H)+.

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Physico-Chemical Analysis of Ground Water Quality of Narayangaon Area Tal-JunnarDist- Pune Maharashtra

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ABSTRACT

The Bore wells underground water samples were collected from Narayangaon Area in summer and rainy seasons. These sixteen samples were collected from difference places nearby Narayangaon area for analysed their Physico-Chemical characteristics. The water quality were determined from eight area such as, (Warulwadi A1, Anandwadi A2, Kukadi ColonyA3, Thakarwadi A4, Gunjalwadi A5, Manjarwadi A6, Narayanwadi A7 andKhodad A8) In physico-chemical analysis various parameter were studied such as turbidity, alkalinity pH,TDS, COD, OD, sulphate, chloride hardness and temperature. These parameter are useful for determine quality of ground water. The result were compared with the drinking water guidelines of WHO.It was concluded that the water quality in the investigation area is found to be suitable for drinking only in few location.

Keywords: Ground Water, Physico- Chemical, Water Quality Parameters

I. INTRODUCTION

A multiplicity of water characteristics is encountered in nature. This is more significant from a chemical point of view than a physical perspective. Water plays an essential role in human life. An understanding of water chemistry is the bases of the knowledge of the multidimensional aspect of aquatic environmental chemistry which involves the composition, source, transportation and reactions of water[1].Ground water is main source of water for drinking and other purposes of people[2]. Regional, seasonal availability and quality of surface of water and ground water are all highly influenced for the environment, economic growth and development[3]. Water is one of main compound of ecosystem of all living organism and non- living organism therefore necessary that the quality of drinking water should be checked at regular time of interval because contaminated drinking water due to increased human population, industrialisation, use of fertilizer for agriculture purposes and man-made activity [4]. The existence of human society cannot be overemphasized by the importance of groundwater[5]. Vagaries of monsoon, increase in demand for domestic, agricultural and industrial purposes has reached an all-time high in recent decades due to reasons such as unreliable supplies from surface water by the dependability on ground water[6]. Ground water and surface water is main source of water. Urbanization, industrialization, fertilisation and growing population, the rate of discharge of pollutants into the environment which ultimately finds their way into these water bodies is higher than the rate of purification[7].Generally surface water is more polluted than ground water, hence the use of ground water such as borehole water as the major source of drinking water in many urban and rural areas. Unfortunately ground water can be polluted as various way such as fertilizer from agricultural, vehicle maintenance, sewage disposal and domestic waste. Water is mandatory for the functioning of biological system of entire living and non-living organisms the analysis of its physico chemical parameters such as turbidity, alkalinity PH,TDS, COD, OD, sulphate, chloride and hardness is very essential.

Here we reported the physicochemical analysis of bore wells drinking water of Narayangaon area. Narayangaon is situated in Pune district of Maharashtra. Bore wells water is usually utilize for Drinking and additional household functions in this area. Bore wells water pollution due to use excess of pesticides and fertilizers, lime, septic tank, refuse dump, etc. However, the main objectives of the study were as follows:

1) The aim of to evaluate water quality index.

2) Carried out the Physico-chemical analysis of bore wells drinking water.

II. Experimental Procedure

Material and methods: The Water Samples from borewell were collected in summer and rainy seasons from eight different stationsnearbyNarayangaon area in the morning hours between 10am to 12 am in Polythene bottle two times. The Water samples were immediately brought in to Laboratory for the Estimation of various Physico-chemical parameters like as turbidity, alkalinity PH,TDS, COD, OD, sulphate, chloride hardness and temperature and were estimated in the Laboratory as per methods given in "Guide Manual: Water and Waste Water Analysis" Central Pollution Control Board, Government of India.

Results and Discussion:

Physicochemical parameters of water samples from eight different places nearby Narayangaonarea during summer and rainy Seasons are presented in Table 1 and Table 2 respectively.

Observation Table 1. Physico-Chemical Parameters in Summer Season

Sr. No.	Parameter	Permissible limits as per WHO drinking water standards	A1	A2	A3	A4	A5	A6	A7	A8
1	Temperature in ^{0}C	30-40	29.5	27.6	28.7	28.2	29.3	28.6	28.5	29.1
2	P^H	6.5-8.5	8.07	8.05	8.4	7.5	7.7	8.1	8.3	8.06
3	TDS in mg/L	500-2000	1300	1250	1410	1220	700	830	1120	1020
4	Turbidity	1-5	2.5	2	0.5	3	2.4	3.5	3.4	4.5
5	Alkalinity(mg/L)	200-600	592	612	630	510	650	635	640	570
6	Calcium (mg/L)	75-200	64.45	55	69.23	65.48	58.69	63.52	62.36	70.35
7	Magnesium(mg/L)	30-100	75.66	66.78	68.10	69.10	67.58	59.63	64.96	72.10
8	Total hardness (mg/L)	200-600	440.12	496.45	450.94	448.56	455.23	467.89	447.23	480.15
9	Sulphate(mg/L)	200-400	65.13	62.20	68.44	59.44	67.36	61.89	70.12	65.33
10	Chloride(mg/L)	250-1000	102.23	96.36	132.50	98.96	85.56	97.89	96.14	89.44
11	Dissolved Oxygen(mg/L)	6	5.412	5.300	5.412	4.812	5.023	5.147	4.789	4.652
12	COD (mg/L)	----	5.124	4.986	5.187	4.583	4.843	4.921	4.521	4.256

Observation Table 2. Physico-Chemical Parameters in Rainy Season

Sr. No.	Parameter	Permissible limits as per WHO drinking water standards	A1	A2	A3	A4	A5	A6	A7	A8
1	Temperature in ^{0}C	30-40	28.4	26.7	27.5	27.3	28.3	27.2	27.4	28.3
2	P^H	6.5-8.5	7.8	7.03	7.2	7.1	6.9	7.09	7.63	7.52
3	TDS in mg/L	500-2000	1380	1350	1480	1340	900	950	1210	1150
4	Turbidity	1-5	4	4.5	6	5	5.6	2.3	4.1	3.6
5	Alkalinity(mg/L)	200-600	550	520	536	492	541	512	523	510
6	Calcium (mg/L)	75-200	66.13	62	70.52	68.23	60.56	65.12	64.56	72.36
7	Magnesium(mg/L)	30-100	80.23	70.66	76.64	72.86	68.22	67.41	68.44	76.56
8	Total hardness (mg/L)	200-600	520.23	514.36	534.66	563.44	542.54	563.45	591.23	524.31
9	Sulphate(mg/L)	200-400	67.56	64.12	75.13	74.12	70.54	69.77	76.64	68.64
10	Chloride(mg/L)	250-1000	106.31	100.63	135.36	102.56	101.54	110.20	100	105.11
11	Dissolved Oxygen(mg/L)	6	5.621	5.436	5.621	5.022	4.993	5.289	4.890	4.894
12	COD (mg/L)	----	5.432	5.269	5.397	4.987	4.798	4.998	4.654	4.623

Temperature

Temperature affects rate of photosynthesis and dissolved oxygen. The average temperature range was 27.6 to 29.5in summer and 26.7 to28.4 in rainy seasons for present analysis. During this investigation the temperature was found lower in rainy season than summer season. Temperature change depend on environmental condition.

pH

pH is an important parameter in water. The hydrogen ion concentration is represented by the pH value. pH value rang was 7.5 to 8.4 in summer and 6.9 to 7.8 in rainy seasons. The average value of summer and rainy shows alkaline nature of water. All the sample were in standard limit prescribed by WHO. All these samples were neither acidic nor more alkaline which may be suitable for consumption purpose. pH of water depend upon percentage of carbon dioxide, carbonate and bicarbonate. The partial pressure of carbon dioxide is much higher in ground water than earth's atmosphere. pH of ground water will rise when it expose to atmosphere due to carbon dioxide escape [8].

TDS

The concentration of all dissolved minerals in water means TDS. The range of TDS value was found in the investigation 700 to 1410 in summer and 900 to 1480 in rainy seasons. The study showed the higher value of TDS in rainy season than summer season. The average value of both seasons were in standard limit prescribed by WHO. The TDS value in rainy season increase due to ground water pollution. Residential and commercial area are polluted by the ground due to discharge of waste water. This waste material mix with rainy water were migrated in ground surface, down to the water[9].

Turbidity

A measure of the extent to which light is either absorbed or scattered by suspended material in water means turbidity of water. Turbidity range from 2 to 4.5 NTU in summer and 2.3 to 6NTU in rainy Season. In present study turbidity of ground water was higher in rainy season thansummer season. In rainy season mud material and dissolved clay were migrated in ground water and water becomes turbid. The average value of both seasons were in standard limit prescribed by WHO. Only area A3 and A5 were out of range in standard limit prescribed by WHO.

Alkalinity

A chemical measurement of water's ability to neutralize acid means alkalinity. The range of alkalinity from 510 to 640 mg/L in summer and 492 to550 mg/L in rainy seasons were found in present study. During this investigation the value of alkalinity was found higher in summer than rainy seasons. Area A2, A3, A5, A6 and A7 were out of range in standard limit prescribed by WHO. Carbonates, bicarbonates, silicates and hydroxyl ions causes alkalinity in water. Natural water contain more amount of dissolved carbon dioxide which is main source of alkalinity of water [8]. Total alkalinity had

higher in summer seasons was diluted in rainy water in rainy season [10].

Calcium

The mean value of calcium from 55 to 70.35 mg/L in summer and 60 to72.36 mg/L in rainy seasons were found in investigation. The values of Ca were higher in rainy season than summer season. The average value of both seasons were in standard limit prescribed by WHO. Higher values of calcium in rainy season due to run off municipal sewage, domestic waste and plant nutrients from surrounding of ponds [11].

Magnesium

The average values of magnesium were obtained from 59.63 to 75.66 mg/L in summer and 68.22 to 80.23 mg/L in rainy seasons. The average value of both seasons were in standard limit prescribed by WHO.

Total Hardness

The water hardness is usually due to many minerals dissolved in water. The average range of total hardness from 440.12 to 496.45 mg/L in summer and 520.23 to 591.23 mg/L in rainy seasons. The values of Hardness was higher in rainy season than summer season. The average value of both seasons were in standard limit prescribed by WHO. The organic substance and agricultural waste increases hardness [12].

Sulphate

The average range of sulphate from 59.44 to70.12 mg/L in summer and 64.12 to76.64 mg/L were found in investigation. The average values of sulphate was higher in rainyseason than summer season.The average value of both seasons were in standard limit prescribed by WHO.

Chloride

Chloride range from 100.6 to 135.36 mg/L in rainy season and 85.56 to 132.50 mg/L were found in investigation. The average values of chloride was higher in rainy season than summer season. The average value of both seasons were in standard limit prescribed by WHO. High percentage of chloride causes harmful effect on human being like as High blood pressure and salty taste.

Dissolved Oxygen

The average range of dissolved Oxygen from 4.652 to 5.412 mg/L in summer and 4.890 to 5.621mg/L in rainy seasons.

Chemical Oxygen Demand

The extent of chemical pollution mainly from industrial effluent is indicated by chemical oxygen demand [9]. The average values of chemical oxygen demand from 4.256 to 5.124 mg/L in summer and 4.623 to5.432 mg/L in rainy seasons. The present study showed higher values in rainy season than summer season.

III. CONCLUSION

In present investigation we describe the study of various Physico-chemical analysis of bore wells water like, temperature, pH, dissolved oxygen, total dissolved solids, chloride, total alkalinity, calcium magnesium hardness, sulphate and chemical oxygen demand. It was concluded that the water quality in the investigation area is found to be suitable for drinking only in few location. TDS, chloride, sulphate, calcium magnesium, and dissolved oxygen these are water quality parameters showed near permissible limit of WHO. The values of Alkalinity and turbidity showed beyond the permissible limits of WHO in some area. Required planning and implementation for drinking water contamination in study area.

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Review of air quality in Pune city

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ABSTRACT

Air Pollution is the condition in which air is contaminated by foreign substances, or the substances themselves. Air pollution consists of gaseous, liquid, or solid substances that, when present in sufficient concentration, for a sufficient time, and under certain conditions, tend to interfere with human comfort, health or welfare, and cause environmental damage. The most widespread pollutants include carbon monoxide, volatile organic compounds(VOCS), ozone, nitrogen dioxide(NOx), sulfur dioxide(SO2) and fine and coarse particles. These substances are used as indicators of air quality in cities. Air pollution causes a number of health problems that include respiratory diseases such as asthma and bronchitis, or increase the risk of respiratory problems. According to a study by Environment Status Report (ESR) in July 2010, air pollution in Pune has become a serious problem. The respiratory suspended particulate matter (PM10) in the air is more than the standard national level. About 93,000 commercial properties which include hotels, malls and hospitals emit 204 tons PM10 every year. The major cause of pollution in Pune is transport. Its emission has increased by 12.15% in the past three years. At present there are 31 National Ambient Air Quality Monitoring Stations (NAQMS) in Maharashtra .In Pune there are four which include Pimpari- Chinchwad, Bhosari, Nal Stop, Karve Road and Swarget. There is measurement of SO2,NOx and RSPM daily.

Keywords: Air pollution, asthma, bronchitis, VOCS, NOx, SO2, PM10, NAQMS, Pune.

I. INTRODUCTION

Air pollution is defined as the introduction of particulates, biological molecules, and many harmful substances into Earth's atmosphere, causing diseases, allergies, death to humans, damage to other living organisms such as animals and food crops, or the natural or built environment. Any substance which causes air pollution is called air pollutant. An air pollutant is a substance in the air that can have adverse effects on humans and the ecosystem. It can be solid particles, liquid droplets, or gases. A pollutant can be of natural origin or man-made.

According to the recent study held by WHO in 2016, about 34 Indian cities figured in the list of the 100 most polluted ones, and 22 Indian cities found their names among the top 50 most polluted cities in the world.A research conducted by the World Health Organization revealed that around 2.4 million people die every year because of air pollution. Every year, air pollution causes 527,700 fatalities in India.[1]In 2012, air pollution was linked with 1 out of every 8 deaths, globally – or around 7 million people. Around 600,000 of those were children under 5 years old, globally. Almost one million children die from pneumonia each year, more than half of which are directly related to air pollution.[2]

Pune city is located at 559 mtrs from the mean sea level. It is located between 18.32° North and 73.51° east. Pune city is located in the Deccan Plateau and is about 100 kms east from Konkani coast and at a distance of about 160 kms from Mumbai. It is located at the confluence of Mula-Mutha River. Out of the total area, 38.6% is residential area, 1.8% is commercial area, 9.5% is defense area, 11% is Industrial area, 9.7% is recreational area etc. The temperature of city ranges between Minimum 12°C & Maximum 37°C. The average rainfall recorded is 600 to 700 mm. The maximum rainfall is observed in June to September months. [3]

The Indian Institute of Topical Meteorology (IITM) has revealed that Pune's pollution level is over twice that of the prescribed national air quality standards. There are many reasons why pollution levels in the city is double the national standards as shown by the IITM. Vehicular

emission is one of the reasons, but the city also has a number of industrial pockets. There is a chemical industry zone in Sinhagad area along with other chemical factories in and around the city. So many industries are spread across Pune, which cannot be relocated. It is a known fact that Pune's public transport is not up to the mark and adds to it the traffic chaos and mismanagement on the city roads. The carbon rating is going to increase due to all these issues of vehicular emission.

II. Measurement of Air Pollution

Air Quality Index

Air Quality Index is a tool for effective communication of air quality status to people in terms, which are easy to understand. It transforms complex air quality data of various pollutants into a single number (index value), nomenclature and colour.

There are six AQI categories, namely Good, Satisfactory, Moderately polluted, Poor, Very Poor, and Severe. The proposed AQI will consider eight pollutants (PM_{10}, $PM_{2.5}$, NO_2, SO_2, CO, O_3, NH_3, and Pb) for which short-term (up to 24-hourly averaging period) National Ambient Air Quality Standards are prescribed.[10]

An **air quality index** (AQI) is a number used by government agencies to communicate to the public how polluted the air currently is or how polluted it is forecast to become. As the AQI increases, an increasingly large percentage of the population is likely to experience increasingly severe adverse health effects. Different countries have their own air quality indices, corresponding to different national air quality standards.

The Minister for Environment, Forests & Climate Change Shri Prakash Javadekar launched The National Air Quality Index (AQI) in New Delhi on 17 September 2014 under the Swachh Bharat Abhiyan. It is outlined as 'One Number- One Colour-One Description' for the common man to judge the air quality within his vicinity. Here is a table which includes values for SO_2,NOx, PM_{10} and $PM_{2.5}$.

Pollutant µg/m^3	**Time weighted Average 24 hours**	**Concentration in Ambient Air**	
		Industrial, Residential, Rural and Other Areas	**Ecologically Sensitive Area (notified by Central Government)**
Sulphur Dioxide (SO_2), µg/m^3	Annual	50- 80	20 -80
Nitrogen Dioxide (NO_2), µg/m^3	Annual	40- 80	30- 80
Particulate Matter (size less than 10 µm) or PM_{10} µg/m^3	Annual	60 -100	60- 100
Particulate Matter (size less than 2.5 µm) or $PM_{2.5}$ µg/m^3	Annual	40 -60	40 -60

Table 1. National Ambient Air Quality Standards
Source – Gazette of India 18Nov. 2009

Air Quality Index and health impacts.

The AQI values and corresponding ambient concentrations (health breakpoints) as well as associated likely health impacts for the identified eight pollutants are as follows.

0 - 50	Good	Air quality is considered satisfactory, and air pollution poses little or no risk
51 - 100	Moderate	Air quality is acceptable; however, for some pollutants there may be a moderate health concern for a very small number of people who are unusually sensitive to air pollution.
101-150	Unhealthy for Sensitive Groups	Members of sensitive groups may experience health effects. The general public is not likely to be affected.
151-200	Unhealthy	Everyone may begin to experience health effects; members of sensitive groups may experience more serious health effects
201-	Very	Health warnings of emergency

300	Unhealthy	conditions. The entire population is more likely to be affected.
300+	Hazardous	Health alert: everyone may experience more serious health effects

Source " Central Pollution Control Board ".
Retrieved 2 Jan. 2017.

Average emission of SO_2, NOx and R.S.P.M. in Pune (Karve Road)

Here is a data of SO2, NOx and RSPM measured at Karve Road station. It shows pollution level change for the years 2012,2013,2014,2015 and 2016.

Year	SO_2 (µg/m3)	NOx (µg/m3)	RSPM (µg/m3)
	Average	Average	Average
2012	19.09	45.05	64.48
2013	9.86	85.03	97.6
2014	14.85	NA	111
2015	34.35	65.13	146.48
2016	15.76	87.6	151.24
2017	28.15	48.89	

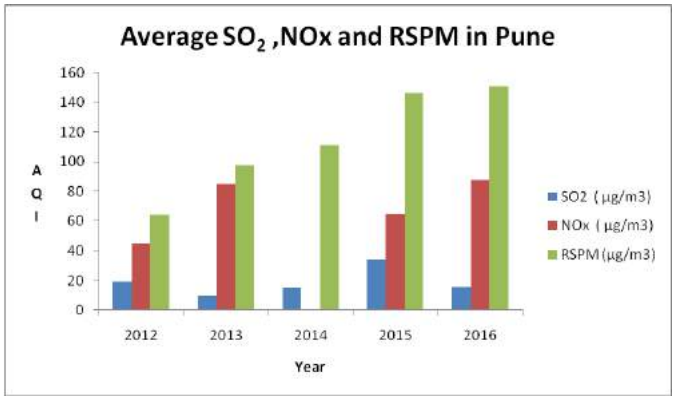

Figure 3. Average emission of SO_2, NOx and R.S.P.M. in Pune (Karve Road)

(Source- http://mpcb.gov.in/envtdata/demoPage1.php)
The measurement of SOx, NOx and RSPM in the five places recorded in October 2017 is given below.

Name of the Station	SOx	NOx	RSPM
Karve Road	27.14	48.78	76.07
Nal Stop	15	59.18	126
Swargate	21	61.22	93.56
Bhosari	17.33	53.22	100.78
Pimpari Chinchwad	16.15	54.04	104.46

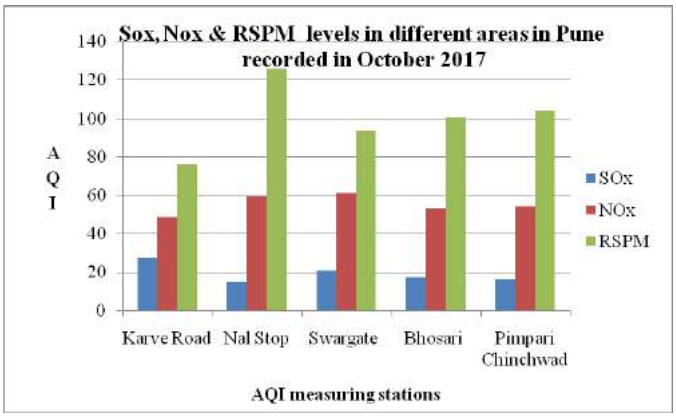

Figure 4. SOx, NOx and RSPM levels recorded in October 2017

(Source - http://mpcb.gov.in/envtdata/demoPage1.php)

III. Conclusion

It can be seen that SO_2 levels in the city are lower and NOx levels are much higher. They are really worry some. The main and serious concern is the respirable suspended particulate matter (RSPM).They are nearly twice the normal range. It is mainly affecting the health of residents in Pune.

The main cause of pollution in Pune is the vehicular emission. Pune has highest number of vehicles in the country. The air quality is fast deteriorating because of bad public transport. The only solution to the issue is that we need more efficient public transport, so that it discourages citizens to use private vehicles. Increasing the green cover in the city will not reduce particle pollution. We have to reduce vehicular emission, which is the biggest source of pollution in the cities. The industries have been reducing pollution because it is related to their profit margin. The more energy efficient they are all the more they will save. It is mainly the sheer number of vehicles on the city roads that is adding to the pollution. If our public transport is streamlined it will obviously discourage citizens from using private vehicles. By having a good metro rail and public bus network, the citizens will not only save time and money but also contribute to curbing pollution in the city.

The amount of RSPM is highest at Nal- Stop. this is due to huge number of vehicles on the road and less efficient public transportation. Bhosari and Pimpari Chinchwad areas is due to particulate emission from industrial processes in nearby MIDC. The higher RSPM at Swargate is due to the same reason as Nal-Stop.

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Clean and green synthesis of structurally diverse 4H-benzo[b]pyrans derivatives in water

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ABSTRACT

Magnesium sulphate has been reported as a cheap and readily available common desk reagent for the synthesis of highly functionalized 4H-benzo[b]pyran derivatives. The synthesis of target compounds was accomplished by one pot multicomponent reaction of aldehydes, malononitrile and dimedone or 4-hydroxycoumarin, aldehyde in under reflux temperature. The corresponding 4H-benzo[b]pyrane derivatives were obtained in good excellent yield under optimized reaction conditions. The methodology prescribed here was found to be adventitious over reported protocols in terms of generality, environment friendliness and economic viability.

Keywords: Magnesium sulphate, 4H-Benzo[b]pyran, Dimedone, Aldehyde, Malononitrile, Water medium.

I. INTRODUCTION

The multicomponent reactions for the synthesis of heterocyclic compounds has gain much attention due to their potential utility in the construction of several bonds in a single step.[1-4] In the medicinal chemistry, these type of transformations attract researchers because of their remarkable molecular diversity, good atom economy, release of minimum waste and easier purification processes.[5-7] Therefore, researchers are attempting multicomponent protocols for the construction of C–C, C–N and C–O bonds in a single operation whenever there is requirement of more than one synthetic step to achieve the goal.[8]

The benzopyran and its derivative have gain substantial attention due to their promising biological and pharmacological properties such as spasmolytic, anticoagulant, diuretic, anticancer and antianaphyletic.[9-10] They have been also used in the treatment of neurogenerative diseases, AIDS associated dementia, Down's syndrome, schzophrenia and myoclonus.[11] The polysubstituted 4*H*-benzo[*b*]pyrans constitute structural unit of the several natural products.[12,13] Moreover, they have been used as a precurssor for the preparation of numerous biologically active compounds such as pyranopyridine derivatives,[14] polyazanaphthalenes,[15] pyrano[2]pyrimidines,[16] pyridin-2-one derivatives[17] and photoactive material.[18-20]

By realizing the importance of 4*H*-benzo[*b*]pyran derivatives, many methods have been reported for their synthesis. For instance, the conventional method involved the condensation of aldehyde, dimedone and malanonitrile in acetic acid under reflux conditions.[14] The various catalysts reported so far includes 1,1,3,3-*N*,*N*,*N*,*N*-teramethylguanadium tetrafluoroacetate (TMGT),[15] [bmIm]OH,[16] dihydrogen phosphate(DAHP),[17] molecular I_2,[21] hexadecyldimethylbenzylammoniumbromide(HDMBAB),[22] NaBr,[23] piperidine,[24,25] KF-alumina[26] and ammonium hydrogen phosphate.[27] Recently, nanosize $Ce_1Mg_xZr_{1-x}O_2$,[28] electrochemical method[29] and microwave heating in solid state[17] has been reported as an alternative methods for the synthesis of 4*H*-benzo[*b*]pyaran derivatives. Consequently, each of the above reported method has its own merits but some of these methods are limited in terms of laborious work-up procedures, long reaction time, effluent pollution and use of luxurious catalysts. Therefore, there is scope for further development of alternative methods for the synthesis 4*H*-benzo[*b*]pyran derivatives under environmentally benign and economically viable procedures. In the view of the conservation of environment and current emphasis of green chemistry, the application of transition metal free, environmentally safe catalytic procedure for multicomponent reactions has always great demand. Magnesium sulphate is cheap, non-toxic and biodegradable reagent. It has been used as an efficient catalyst for various organic transformations

such as bis-(indolyl)methanes,[30] phenazine and quinoxaline derivatives[31] and intermolecular Wittig reaction of dialkyl-2-(1-acetyl-2-oxopropyl)-3-(triphenylphosphoranylidene)succinates with ninhydrin.[32]

Herein, the synthesis of highly functionalized 4*H*-beno[*b*]pyran derivatives was accomplished by one pot multicomponent reaction of aldehydes, malononitrile and dimedone or 4-hydroxycoumarin, aldehyde in water under reflux conditions (Scheme 1 and 2). One of the requirements of the graduate Science, Engineering and Technology courses is that you conduct research and write a research paper on some aspects of software engineering. The paper may present original work, discuss a new technique, provide a survey and evaluation of recent work in a given area, or give comprehensive and taxonomic tutorial information. The paper must emphasize concepts and the underlying principles and should provide authentic contribution to knowledge. If your paper does not represent original work, it should have educational value by presenting a fresh perspective or a synthesis of existing knowledge. The purpose of this document is to provide you with some guidelines. You are, however, encouraged to consult additional resources that assist you in writing a professional technical paper.

II. METHODS AND MATERIAL

All chemicals were of analytical grade. The melting points were determined on the open capillary tube and were uncorrected. The IR spectra were recorded on Bomen FT-IR MB-104 Spectrophotometer with KBr disc in cm^{-1}. ^{1}NMR were recorded on Brucker AC-300 MHz in DMSO-d^6.Products were all known compounds and were identified by comparison of their physical and spectral data with those of reported in literature.

General procedure for the synthesis of 4*H*-benzo[*b*]pyran derivatives

To a mixture of aldehyde (5mmol), dimedone (5mmol) or 4-hydroxy coumarin (5mmol) and malononitrile (5mmol) in water (5 mL), magnesium sulphate (20 mole %) was added. The reaction mixture was heated under reflux for specified time (Table 3 and 4). After completion of reaction (as indicated by TLC), the reaction mixture was cooled. The crystalline product was separated which was collected by filtration and recrystallized from ethanol afforded pure crystalline 4*H*-benzo[*b*]pyran derivatives.

Spectral data of representative compounds

2-Amino-3-cyno-7,7-dimethyl-4-(phenyl)-5-oxo-4H-5,6,7,8-tetrahydrobenzopyran (**4a**):
IR(KBr): ν_{max}=3392, 3250, 2966, 2192, 1674, 1607, 1594 cm^{-1} H^1 NMR(DMSO-d^6)- δ ppm= 1.02(s,3H), 1.18 (s, 3H), 2.20-2.34(q,2H), 2.42-2.53 (m, 2H), 4.40 (s, 1H), 4.65(s, 2H), 7.20-7.40 (m, 5H) Mass (m/e): $C_{18}H_{18}N_2O_2$ (M.W = 294) = 293.78(M^+)

2-Amino-3-cyno-7,7-dimethyl-4-(4-chlorophenyl)-5-oxo-4H-5,6,7,8-tetrahydrobenzopyran (**4b**):
IR(KBr): ν_{max}=3412, 3315, 3012, 2236, 1696, 1582 cm^{-1} H^1 NMR(DMSO-d^6)- δ ppm= 1.08(s,3H), 1.06 (5, 3H), 2.12 (d,1H) , 2.20 (d,1H,J=16Hz), 2.26 (d,1H), 2.46-2.51 (m, 2H), 4.50 (s, 1H), 6.97 (d, 2H), 7.35 (s, 2H), 7.40 (m, 2H) Mass (m/e): $C_{18}H_{17}ClN_2O_2$ (M.W = 328.5) = 309.4(M^+).

2-Amino-3-cyno-7,7-dimethyl-4-(4-methoxyphenyl)-5-oxo-4H-5,6,7,8-tetrahydrobenzopyran (**4d**):
IR(KBr): ν_{max}= 3382, 3215, 3187, 2964, 2203, 1678, 1612, 1596 cm^{-1} H^1 NMR(DMSO-d^6)- δ ppm= 0.96(s,3H), 1.02 (s, 3H), 2.12 (d,1H) , 2.25 (d,1H), 2.43-2.58(m,2H),3.82 (s,3H), 4.46 (s, 1H), 6.82 (d, 2H), 6.88 (s, 2H), 7.08 (d. 2H) Mass (m/e): $C_{19}H_{20}N_2O_3$ (M.W = 324) = 325.28(M^+).

2-Amino-3-cyno-7,7-dimethyl-4-(3,4-methylenedioxyphenyl)-5-oxo-4H-5,6,7,8-tetrahydrobenzopyran (**4j**):
IR(KBr): ν_{max}= 3409, 3320, 3210, 2940, 1672, 1652, 1610, 1556 cm^{-1} H^1 NMR(DMSO-d^6)- δ ppm= 0.94(s, 3H), 1.02 (s, 3H), 2.12 (d,1H) 2.24 (d,1H), 2.29 (d,1H) 2.41-2.50 (m,2H), 4.47 (s, 1H), 5.89 (s, 2H), 6.91 (s, 2H), 7.0-7.17 (m, 3H) Mass (m/e): $C_{20}H_{18}N_2O_4$ (M.W = 350) = 351.07(M^+).

7-Amino-5-(phenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (**6a**):
IR(KBr): ν_{max}=3350, 3288, 3180, 2194, 1716, 1606, 1578 cm^{-1} H^1 NMR(DMSO-d^6)- δ ppm= 4.6(s,1H), 4.80 (s, 2H), 7.36 (s, 2H), 7.35-7.50(m, 6H), 7.60-7.65 (m,

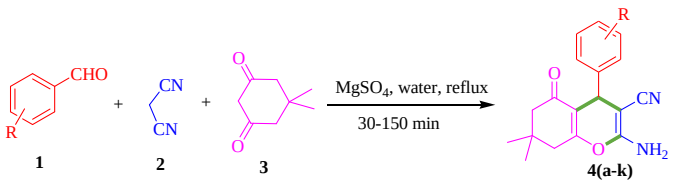
6H), 7.81-7.87 (d, 1H,), 7.72 (t, 1H), 7.94 (t, 1H); Mass (m/e): $C_{19}H_{12}N_2O_3$ (M.W = 316) = 315.98(M^+)

7-Amino-5-(4-chlorophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (**6b**):

IR(KBr): ν_{max}=3470, 3430, 3315, 3190, 2192, 1717, 1680, 1610, 1595 cm^{-1} H^1 NMR(DMSO-d^6)- δ ppm= 4.60(s,1H), 7.34 (d, 2H), 7.36 (s, 2H), 7.38(s, 2H), 7.45 (d, 2H), 7.51 (s, 1H,), 7.72 (t, 1H), 7.94 (t, 1H); Mass (m/e): $C_{19}H_{11}ClN_2O_3$ (M.W = 320) = 309.9(M^+).

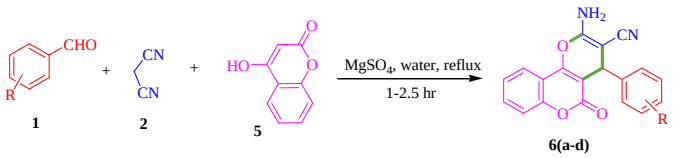
III. RESULTS AND DISCUSSION

In continuation to our ongoing research on the development of novel methods using green techniques,[33] herein we have developed an efficient method for the synthesis of 4*H*-benzo[*b*]pyran. For optimization of reaction conditions, the synthesis of 2-amino-4-phenyl-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydro-2*H*-chromene-3-carbonitrile (**4a**) was tried from the reaction of dimidone(2mmol), benzaldehyde(2 mmol) and malononitrile(2mmol) The reaction progress was studied under catalyst free conditions at room temperature, 40, 50 °C reflux temperatures, the formation of **4a** was not observed even after prolonged time in water and ethanol. When the reaction was conducted using $MgSO_4$(10-30 mol%) in water at reflux temperature, the product **4a** was formed in 71, 86 and >99% yield. Encouraged by the above results, the catalytic efficacy of the other metal sulphates such as Na_2SO_4, K_2SO_4, $NiSO_4$, $Fe_2(SO_4)_3$ and $Al(SO_4)_3$, was checked for the formation of **4a**. It has been found that the magnesium sulphate is the superior for the formation of desired product over other metal sulphates (TABLE I). With the optimized reaction conditions, we have conducted the present multicomponent reaction of by employing various aromatic aldehydes with diverse functionality. Apparently, aromatic aldehydes possessing electron-withdrawing groups (TABLE II, Entries **4a, 4d-f**) undergo reaction in faster rates compared to aldehydes possessing electron releasing groups (TABLE II, Entries **4c, 4i, 4k**).The formation of good to excellent product yields for all the entries indicated the efficiency of the present method (Table 2).



Scheme 1. Synthesis of 4*H*-benzo[*b*]pyrans catalyzed by magnesium sulphate in water.

Besides, the present method was successfully employed for the multicomponent condensation of 4-hydroxycoumarin, aldehydes and malononitrile (Scheme 2). All the reactions progressed competently and the corresponding 2-amino-4-aryl-5-oxo-*4H,5H*-pyrano-[*3,2-c*]chromene-3-carbonitrile derivatives were obtained in good to excellent yield(Table 3, Entries **6a-d**).



Scheme 2. Magnesium sulphate catalyzed synthesis of 2-amino-4-aryl-5-oxo-*4H,5H*-pyrano-[*3,2-c*]chromene-3-carbonitrile in water.

Table 1. comparison of catalytic efficiency of various metal sulphates for the formation of '4A'

Entry	Metal sulphate	Solvent	Cat. Conc. (mol%)	Time (hr)	Yield (%) 4A
1.	Na_2SO_4	Solvent free	20	4.5	-[a]
		EtOH	20	4.5	-[b]
		Water	20	4.5	72
2.	K_2SO_4	Solvent free	20	4.5	-[a]
		EtOH	20	4.5	65
		Water	20	4.5	81
3.	$NiSO_4$	Solvent free	20	4.5	-[a]
		EtOH	20	4.5	Sluggish[b]
		Water	20	4.5	-[b]
4.	$Fe_2(SO_4)_3$	Solvent free	20	3.5	-[a]
		EtOH	20	3.5	78
		Water	20	3.5	-[b]
5.	$Al(SO_4)_3$	Solvent free	20	4.0	Sluggish[a]

		EtOH	20	4.0	-[b]
		Water	20	4.0	-[b]
6.	$MgSO_4$	Solvent free	20	2.5	-[a]
		EtOH	20	2.5	77
		Water	10	1.5	86
			20	1.5	91
			30	1.5	>99
			40	1.5	>99

[a] Reaction was conducted at 100°C temperature.
[b] Reaction was conducted at 60°C temperature.

Table 2. synthesis of 4h-benzo[b]pyran catalyzed magnesium sulphate in water (4).

Entry	Ar	Product	Time (min)	Yield (%)[a]	M.P.(°C)
1.	C_6H_5	**4a**	90	>99	226-228
2.	4-ClC_6H_4	**4b**	45	98	240-241
3.	2-ClC_6H_4	**4c**	30	83	220-222
4.	4-NO_2 C_6H_4	**4d**	30	>99	177-179
5.	3-$NO_2C_6H_4$	**4e**	30	>99	213-215
6.	2-NO_2 C_6H_4	**4f**	40	>99	183-185
7.	4-$MeOC_6H_4$	**4g**	40	91	197-198
8.	4-OHC_6H_4	**4h**	135	90	199-200
9.	4-MeC_6H_4	**4i**	150	78	220-222
10.	2-Furyl	**4j**	50	90	194-195
11.	3,4-OCH_2O C_6H_3	**4k**	120	79	218-220

[a] Yield of the isolated products and spectroscopic data was confirmed with reported data.

Table 3. Synthesis of 4*H*-benzo[*b*]pyran catalyzed Magnesium sulphate in water.

Entry	Ar	Product	Time (hr)	Yield (%)[a]	M.P. (°C)
1.	C_6H_5	**6a**	2.5	89	257-259
2.	4-ClC_6H_4	**6b**	1.5	94	261-264
3.	4-$NO_2C_6H_4$	**6c**	1.0	>99	257-258
4.	4-$MeOC_6H_4$	**6d**	2.5	92	142-143

[a] Isolated yields of the products.

The proposed mechanism of $MgSO_4$ catalyzed multicomponent reaction of diemidone, aldehyde and malanonitrile is represented in Figure 2. The reaction of aldehyde with malanonitrile to formed α-cynocinnamonitrlie (**A**). The Knoevenogel reaction of Mg(II) stabilized enol form of diemidone(**B**) with α-cynocinnamonitrlile(**A**) to form intermediate 'C' which on further protonation gives 4*H*-benzo[*b*]-pyran(**4**)(Figure 1).

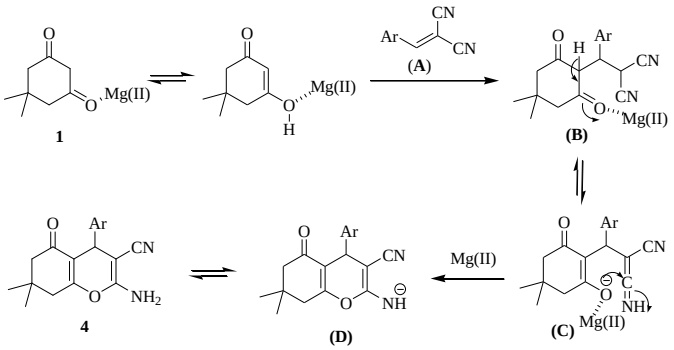


Figure 1. Proposed mechanism of $MgSO_4$ catalyzed synthesis of 4*H*-benzo[*b*]pyrans.

IV.CONCLUSION

In conclusion, we have described a clean and green method for the synthesis of highly functionalized *4H*-benzo[*b*]pyran derivatives.The method presented here in valuable addition for development of green chemistry and field of catalysis. The corresponding 4*H*-benzo[*b*]pyrane derivatives were obtained in good excellent yield under optimized reaction conditions. The methodology prescribed here was found to be adventitious over reported protocols in terms of generality, environment friendliness and economic viability.

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Biological Evolution of Metal Amide Complexes

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ABSTRACT

The Present research work describes biological activity of amide group containing ligands and their Mn(II), Ni(II), Co(II) and Cu(II) complexes against E.coli and S.aureus. The standard disc diffusion method has been employed for investigations. The data obtained during study has been correlated for structure activity relationship and a trend has been pointed for a series of complexes.

Keywords : Antibacterial, Transition Metal

I. INTRODUCTION

Amide ligand possesses a wide range of bioactivities and their chemical, pharmacological applications have been extensively investigated. These emerged as important class of nitrogen and oxygen or sulfur ligands particularly for transition metal ions in the last twenty years. These transition metal complexes have a large variety of biological activities i.e. antifungal, antibacterial, antitumoral or antiviral. Many of these compounds possessed wide spectrum of medicinal properties, including activity against influenza, protozoa, smallpox, certain kinds of tumor, leprosy, bacterial and viral infections, psoriasis, rheumatism, tripanosomiasis, coccidiosis, malaria and as a pesticides and fungicides. These activities due to their ability to chelate trace metals and in few cases, it has been proved that metal ions enhance the biological activity of amide group containing ligands [1-8]. Bacterial infections often produce pain and inflammation. Chemotherapeutic, analgesic and anti- inflammatory drugs are prescribed simultaneously in normal practice. These complexes possessing all three activities i.e. anti- inflammatory, analgesic and antipyretic activities are not common. Anti- inflammatory, analgesic and antipyretic activities are known for some Pyridine and phenol derivatives [8-10]. These transition metal complexes of amide ligands are able to block cartilage destruction during the inflammatory process and thus are a promising class of anti-inflammatory compounds [11]. Manganese complexes have been screened against a number of pathogenic fungi and bacteria with most of them showing better sensitivity than the ligands [12-14]. Complexes of Iron (III) have been synthesised by quinoline derivative and use in malaria treatment [15].

II. Scope of the Present research work

The investigations on antimicrobial activity of different types of compounds are not only useful for the development of new drugs but it is also essential to ascertain the toxic nature of the compound. In this research paper the biological activity in terms of their growth inhibition property on specific known bacterial of the four synthesized amide ligands and of their metal complexes with Mn (II), Ni (II), Co (II) and Cu (II) have evaluated by standard "disc diffusion" method. The bacterial subcultures of *E. coli* and *S. aureus* have been used as test organisms and all the samples are tested against these stains at different concentration.

III. Experimental

The evaluation of antimicrobial activities involved following general steps:

1. Treatment of glass apparatus and its sterilization

All the glass apparatus, including petridishes were cleaned with chromic acid followed by washing with distilled water. These were then sterilized by heating at 120°C in an oven fully wrapped in inert foil for 6-8 hours.

2. Preparation of the media and its sterilization.

Nutrient agar and Czapek Dox agar slants were used as culture media for bacterial cells and fungal spores respectively.

Composition of Nutrient agar medium is as;

Peptone	= 5g
Sodium chloride	= 5g
Beef extract	= 1.5g
Yeast extract	= 1.5g
Agar	= 15g
Distilled water	= 1000ml (pH=7.4±0.2)

Czapek Dox Agar medium was composed of;

Sodium nitrate	= 2g
Dipotassium hydrogen Phosphate	= 1g
Magnesium sulphate	= 0.05g
Potassium chloride	= 0.05g
Ferrous sulphate	= 0.0lg
Sucrose	= 30.0g
Agar	= 15g
Distilled Water	= 1000ml

(pH=7.3±0.2)

For the preparation of media, all the ingredients except agar were dissolved in half of the water with gentle warming wherever required. In the other half of distilled water, agar was dissolved by heating with constant stirring. The two solutions were mixed and heated to make a homogenous solution. The one liter solution of each media was filtered through cotton and a clear solution was obtained. This was then sterilized properly plugged in a conical flask by autoclaving at 120°C for 30 min.

3. Pouting of the media into sterilized petridishes and its solidification

The 15-20 ml of sterilized media was poured homogenously into sterilized petridishes and used for the inoculation.

4. Inoculation of the media with the test organisms.

Bacterial cells (0.5 ml) was added on the petridishes, prepared by the method as described above and spreaded with the help of a sterile spreade. These petridishes were kept in laminar for 10 minutes for inoculation.

5. Preparation of the solutions and control

Solutions of concentration range in between 25 to 100 ppm have been prepared by diluting stock solution appropriately and used for study of antimicrobial activity.

6. Preparation of test plates

Filter paper discs were soaked into above solution of test compound and these paper discs were placed on the petridish and incubated at 37°C temperature for 24 hours.

7. Measurement of the zone of inhibition

Zone of inhibition was measured for each compound separately with respect to control and also compared to a standard drug.

Recommended procedure for the determination of Antimicrobial activity

A saturated solution of Nutrient agar (75 g) was prepared in double distilled water and it was autoclaved for 15 min, than poured in petriplates in the laminar. After its solidification loan of bacteria (i.e. Escherichia coli and Staphylococcus aureus) against which antimicrobiological activity is to be investigated has been applied. Solutions were prepared of all the eight ligand and their complexes with Mn (II), Ni (II), Co (II) and Cu (II). A separate paper disc was soaked in each solution for 10 minutes. Thus prepared paper disc was placed into petriplate and finally prepared petriplates were kept in incubator at 37°C for 24 hour. After 24 hour, petriplates were removed and checked for measuring zone of inhibition in mm.

IV. Result and Discussion

Antibacterial activity of all amide group containing ligand and their complexes with Mn(II), Co(II), Ni(II) and Cu(II) have been reported on two microbias i.e., *E.coli* and *S.aureus*.

The results of antibacterial activity have been given in table 1 and have also been represented in Fig. and Photographs of Ligand and complexes.

Following few results which have been observed during investigation are as:

1. All the amide group containing ligands and their complexes possess at least one type of biological activity up to substantial level.

2. On the basis of results of antimicrobial activity a trend of structure activity relationship have reported for different amide ligand systems.

(a) (Against *E.coli*)

N46DM2PB>N2PA>N46DM2PA>N2PB

(b) (Against *S.aureus*)

N46DM2PB>N26DH4PB>N2PA>N6H2MC4PB=N6H2MC4PA=

N26DH4PA>N2PB=N46DM2PA

4. Results of structure activity relationship of different Mn(II), Co(II), Ni(II) and Cu(II) complexes of amide group containing ligands against *E.coli* and *S.aureus* are as:

(a) (Against *E.coli*)

(i) $[Co\text{-}(N2PB)_3]Cl_2$>$[Mn\text{-}(N2PB)_2]Cl_2$>$[Cu\text{-}(N2PB)_3]Cl_2$>$[Ni\text{-}(N2PB)_3]Cl_2$

(ii) $[Co\text{-}(N2PA)_3]Cl_2$>$[Cu\text{-}(N2PA)_3]Cl_2$>$[Mn\text{-}(N2PA)_2]Cl_2$>$[Ni\text{-}(N2PA)_3]Cl_2$

(iii) $[Cu\text{-}(N46DM2PB)_3]Cl_2$>$[Mn\text{-}(N46DM2PB)_2]Cl_2$>

$[Co\text{-}(N46DM2PB)_3]Cl_2$>$[Ni(N46DM2PB)_3]Cl_2$

(iv) $[Mn\text{-}(N46DM2PA)_2]Cl_2$>$[Co\text{-}(N46DM2PA)_3]Cl_2$ =

$[Cu\text{-}(N46DM2PA)_3]Cl_2$ = $[Ni\text{-}(N46DM2PA)_3]Cl_2$

(v) $[Cu\text{-}(N6H2MC4PB)_3]Cl_2$>$[Mn\text{-}(N6H2MC4PB)_2]Cl_2$ >

$[Co\text{-}(N6H2MC4PB)_3]Cl_2$ > $[Ni\text{-}(N6H2MC4PB)_3]Cl_2$

(vi) $[Cu\text{-}(N6H2MC4PA)_3]Cl_2$ > $[Co\text{-}(N6H2MC4PA)_3]Cl_2$ >

$[Mn\text{-}(N6H2MC4PA)_2]Cl_2$ > $[Ni\text{-}(N6H2MC4PA)_3]Cl_2$

(vii) $[Cu\text{-}(N26DH4PB)_3]Cl_2$ > $[Mn\text{-}(N26DH4PB)_2]Cl_2$ >

$[Co\text{-}(N26DH4PB)_3]Cl_2$ > $[Ni\text{-}(N26DH4PB)_3]Cl_2$

(viii) $[Cu\text{-}(N26DH4PA)_3]Cl_2$ = $[Co\text{-}(N26DH4PA)_3]Cl_2$ >

$[Mn\text{-}(N26DH4PA)_2]Cl_2$ = $[Ni\text{-}(N26DH4PA)_2]Cl_2$

(b) (Against *S.aureus*)

(i) $[Cu\text{-}(N2PB)_3]Cl_2$ > $[Co\text{-}(N2PB)_3]Cl_2$ > $[Mn\text{-}(N2PB)_2]Cl_2$ > $[Ni\text{-}(N2PB)_3]Cl_2$

(ii) $[Cu\text{-}(N2PA)_3]Cl_2$ = $[Mn\text{-}(N2PA)_2]Cl_2$ > $[Co\text{-}(N2PA)_3]Cl_2$ = $[Ni\text{-}(N2PA)_3]Cl_2$

(iii) $[Co\text{-}(N46DM2PB)_3]Cl_2$ > $[Cu\text{-}(N46DM2PB)_3]Cl_2$ >

$[Ni\text{-}(N46DM2PB)_3]Cl_2$ > $[Mn\text{-}(N46DM2PB)_2]Cl_2$

(iv) $[Cu\text{-}(N46DM2PA)_3]Cl_2$ > $[Co\text{-}(N46DM2PA)_3]Cl_2$ >

$[Mn\text{-}(N46DM2PA)_2]Cl_2$ > $[Ni\text{-}(N46DM2PA)_3]Cl_2$

(v) $[Co\text{-}(N6H2MC4PB)_3]Cl_2$ > $[Mn\text{-}(N6H2MC4PB)_2]Cl_2$ >

$[Cu\text{-}(N6H2MC4PB)_3]Cl_2$ > $[Ni\text{-}(N6H2MC4PB)_3]Cl_2$

(vi) $[Cu\text{-}(N6H2MC4PA)_3]Cl_2$ = $[Co\text{-}(N6H2MC4PA)_3]Cl_2$ =

$[Ni\text{-}(N6H2MC4PA)_3]Cl_2$ > $[Mn\text{-}(N6H2MC4PA)_2]Cl_2$

(vii) $[Co\text{-}(N26DH4PB)_3]Cl_2$ > $[Cu\text{-}(N26DH4PB)_3]Cl_2$ =

$[Mn\text{-}(N26DH4PB)_2]Cl_2$ > $[Ni\text{-}(N26DH4PB)_3]Cl_2$

(viii) $[Co\text{-}(N26DH4PA)_3]Cl_2$ > $[Cu\text{-}(N26DH4PA)_3]Cl_2$ =

$[Ni\text{-}(N26DH4PA)_3]Cl_2$ > $[Mn\text{-}(N26DH4PA)_3]Cl_2$

5. Antibacterial activity of Mn(II), Co(II), Ni(II) and Cu(II) complexes of amide group containing ligand is in general, greater against *E.coli* than *S.aureus.* with few exceptions

V. Conclusion

Biological activity of amide group containing ligands and their Mn(II), Ni(II), Co(II) and Cu(II) complexes has been investgated. The standard disc diffusion method has been employed for study. *E.coli* and *S.aureus* as bacterial subcultures have been used for study of antibacterial activity of the compounds. The study indicates that most of ligands having better antibacterial activity than complexes (except of few complexes).

VI. Acknowledgements

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Table 1. Biological activity of amide group containing, ligands and complexes (medium-Nutrient Agar)

S.No.	**Ligands/Complexes**	**Zone of inhibition (in mm)**	
		E.coli	*S. aureus*
1.	N2PB	0.0	0.0
	$[Co\text{-}(N2PB)_3]Cl_2$	9.0	5.5
	$[Mn\text{-}(N2PB)_2]Cl_2$	6.0	5.0
	$[Cu\text{-}(N2PB)_3]Cl_2$	5.0	6.0
	$[Ni\text{-}(N2PB)_3]Cl_2$	0.0	0.0
2.	N2PA	5.5	5.5
	$[Co\text{-}(N2PA)_3]Cl_2$	7.5	5.5

	$[Mn\text{-}(N2PA)_2]Cl_2$	6.6	6.0
	$[Cu\text{-}(N2PA)_3]Cl_2$	7.0	6.0
	$[Ni\text{-}(N2PA)_3]Cl_2$	5.0	5.5
3.	N46DM2PB	6.0	7.0
	$[Co\text{-}(N46DM2PB)_3]Cl_2$	4.5	7.5
	$[Mn\text{-}(N46DM2PB)_2]Cl_2$	5.0	0.0
	$[Cu\text{-}(N46DM2PB)_3]Cl_2$	5.5	6.5
	$[Ni\text{-}(N46DM2PB)_3]Cl_2$	0.0	4.5
4.	N46DM2PA	4.5	0.0
	$[Co\text{-}(N46DM2PA)_3]Cl_2$	5.5	6.0
	$[Mn\text{-}(N46DM2PA)_2]Cl_2$	6	4.5
	$[Cu\text{-}(N46DM2PA)_3]Cl_2$	5.5	6.5
	$[Ni\text{-}(N46DM2PA_3]Cl_2$	5.5	0.0

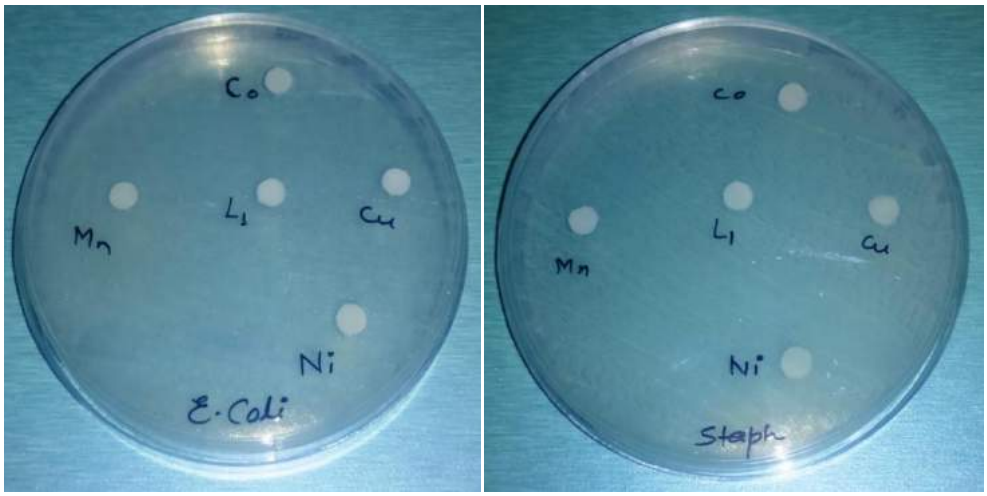

Figure 1. Biological activity of amide group containing, ligands and complexes (medium-Nutrient Agar)

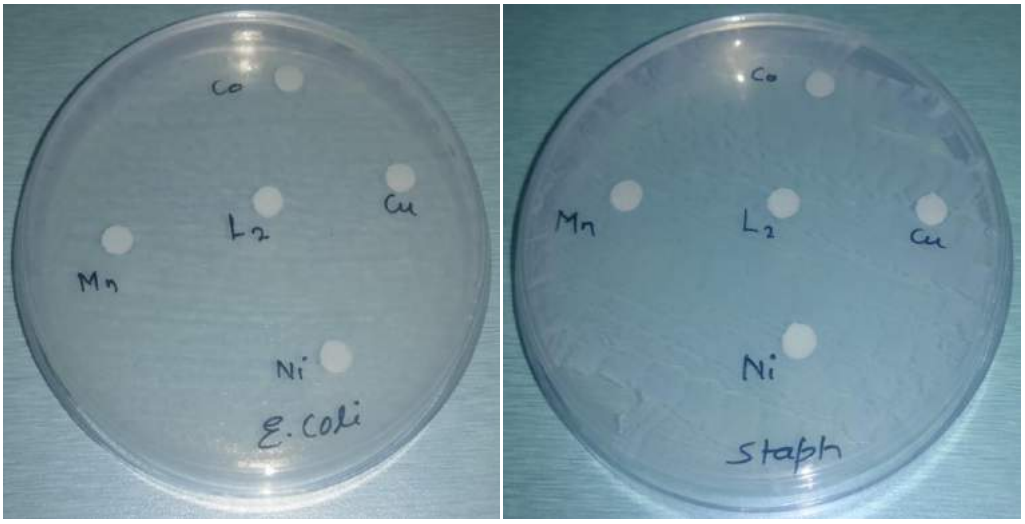

Figure 2. Biological activity of amide group containing ligands and complexes

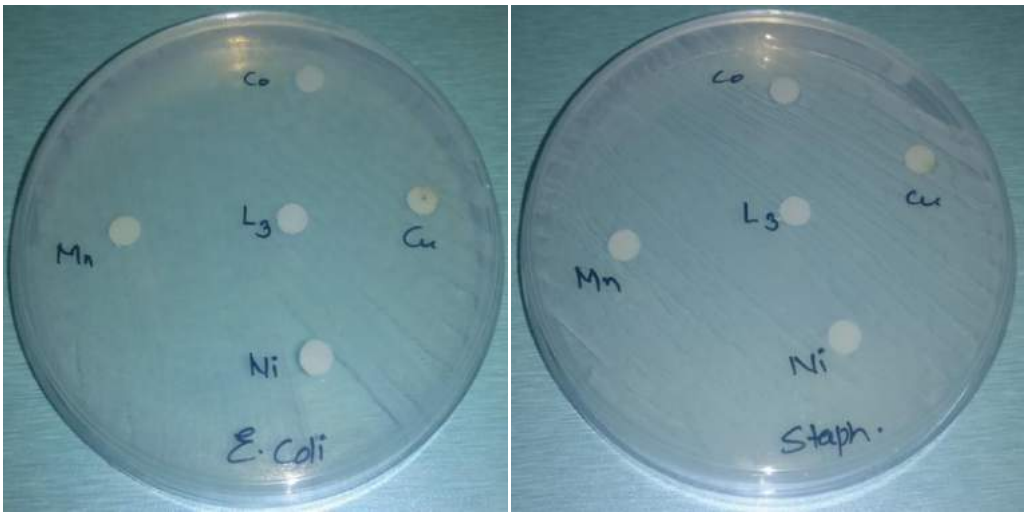

Figure 3. Biological activity of amide group containing ligands and complexes

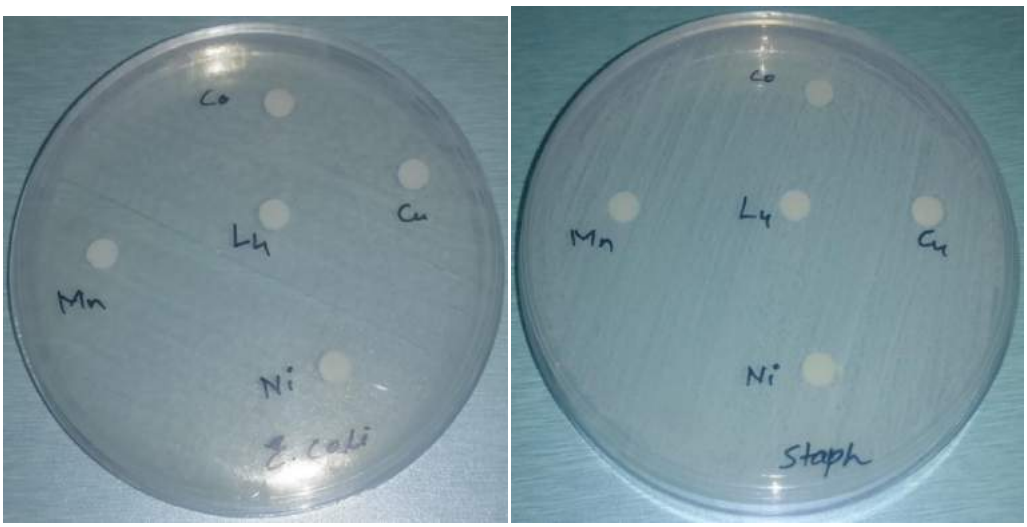

Figure 4. Biological activities of amide group containing, ligands and complexes

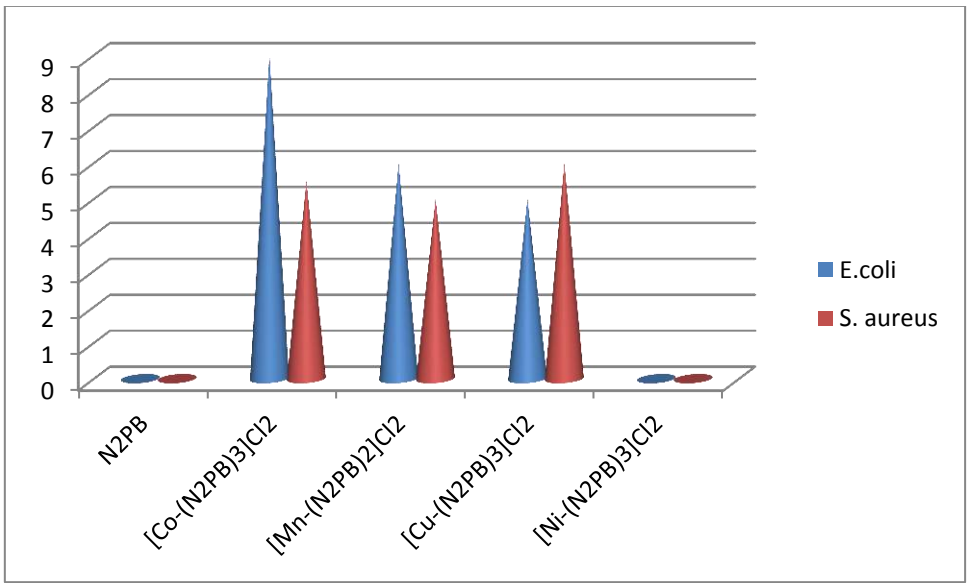

Figure 5. Biological activities of amide Ligands and their metal complexes.

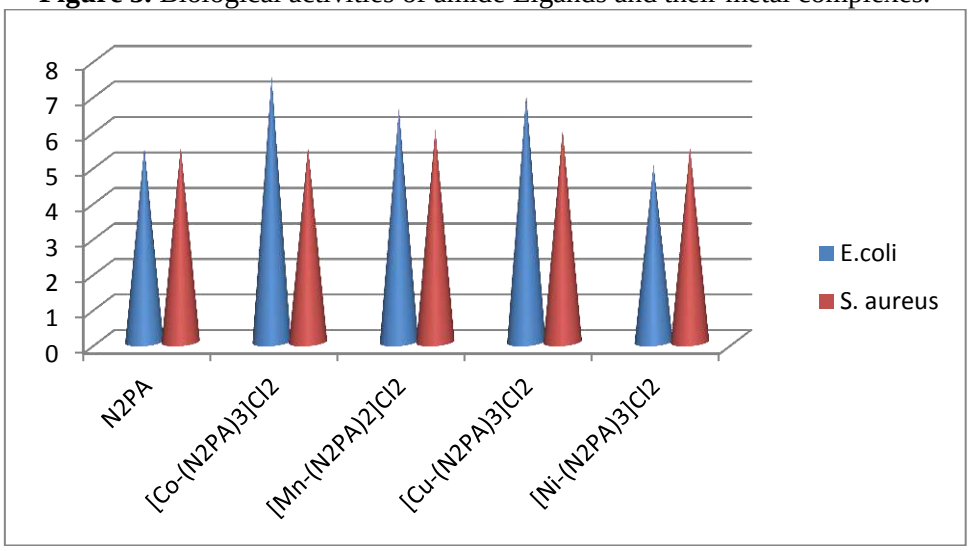

Figure 6. Biological activities of amide Ligands and their metal complexes.

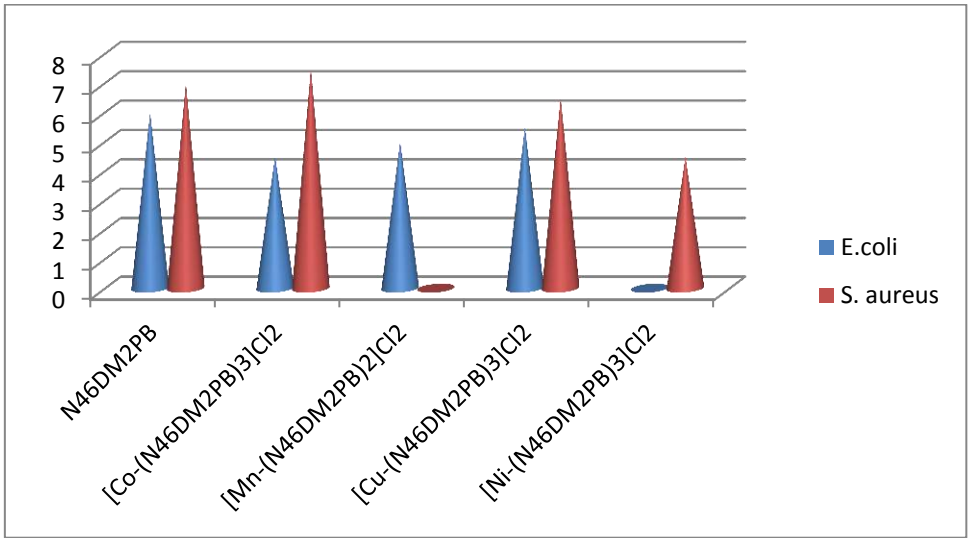

Figure 7. Biological activities of amide Ligands and their metal complexes.

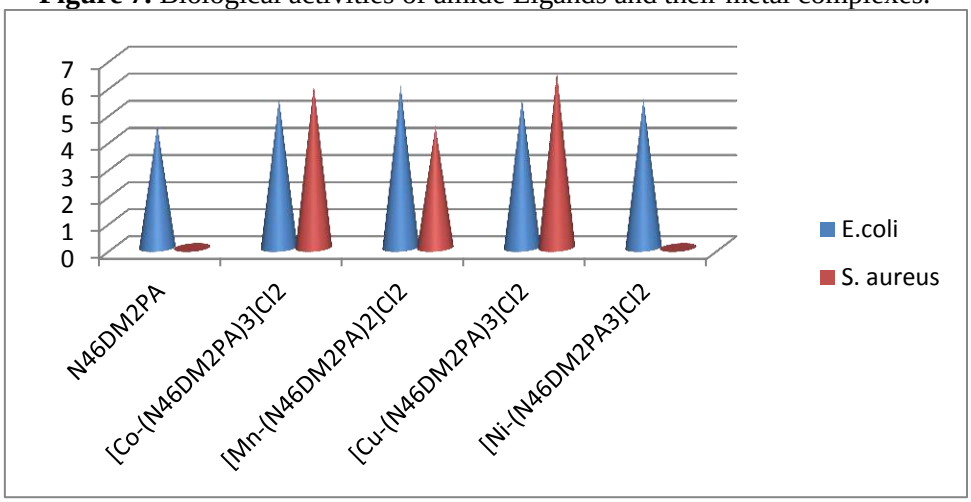

Figure 8. Biological activities of amide Ligands and their metal complexes.

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Variation of β-radiation counts with water content in Ocimum Tenuiflorumand AzadirachtaIndica Plant Leaves

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ABSTRACT

Our aim is to study the changes in β-radiation counts with water content in OcimumTenuiflorum (Tulasi) and AzadirachtaIndica(Kadunimb) plant leavesusing beta source Tl204. Counts were measured for one minute (60 seconds) using Geiger Muller counter. The same leaf was observed for ten days. Counts vary as the amount/percentage of water content in the leaf gets changed. It was observed that leaf absorbs more radiation when it is fresh than dry. This study will useful for quantitative evaluation of interaction of radiations with leaves of plants.Keyword: Counter, leaf, radioactive sources, water, etc.
Keywords: GM Counter, leaf, radioactive sources, water, etc.

I. INTRODUCTION

In India, Tulasi and Kadunimb plants both have medicinal as well as religious importance. Tulasi is called as 'Queen of Herbs of India'. Various parts of tulasi are used in ayurvedic medicines. Its extracts is used for common cold & cough, headache, soreness, stomach disorder, heart sickness, in some poisoning cases and is also in malaria disease. It is also useful to reduce ill effects of radiotherapy of cancer. Extracts of tulasi is helpful in reducing swelling and pain. It can cure skin rashes, itching and is also effective in insects bite. Its leaves act as nerving tonic. Extracts of tulasi leaves is used to reduce pimples, acne and scars. It is valuable in constipation, indigestion and intestinal parasites. It acts as cardiac tonic and purifies blood. Seeds of it are valuable in impulsive ejaculation and mild aphrodisiac. Dried leaves of it are mixed with stored grains to repel insects. And most importance, these days, it is effective in reducing the effects of stress on the body as tulasi is abundant in essential oils and antioxidants[1].

The Kadunimb tree is called as 'Wonder Tree of India' as it's every part is useful in almost all fields such as medicinal, industrial, agricultural areas and has veterinary uses and plays an important role in environment protection. Its oiland leaves are act as anticlotting, antiulcer, antituberculosis, antitumor, anti-inflammatory, antiviral agent, etc. and in making soaps, shampoos, toothpastes, cosmetics, etc. Twigs are used as tooth cleaner. It is natural source of pesticides, insecticides and agrochemicals. It increases soil fertility and water holding capacity of soil. It has high rate of photosynthesis and liberates significant amount of oxygen. Its product can be used in water purifying activity[2].

The measurement of leaf water content has very much importance in field of farming as well as to horticulturists, plant physiologists or biochemists. This information is useful in irrigation management and helps to avoid plant drought stress.Leaves are heterogeneous matter containing water and other solid organic matter. Water content of the leaves of the plants varies with their type and the environmental conditions. When leaves dried up, they mainly loss their water content.Geiger Muller counter is a fundamental device and very simple to operate in radiation detection technique. We studied the changes in beta radiation counts of fresh and dry leavesof*OcimumTenuiflorum*and*AzadirachtaIndica*plants using beta source Tl^{204}.

Chaudhari L.M.[3] studied the attenuation coefficient of leaves of Ashoka plant by using Cs and Tl sources. The results show that the water content in the leaves was used to determine their attenuating characteristics. The

linear and mass attenuation coefficients were obtained.Pattanashetti I.I. and GalagaliM.N.[4] studied the attenuation coefficient and water content of Almond leaves using beta radiation. The water content was determined based on their attenuating characteristics to beta particles. The mass attenuation coefficient was obtained.Kirandeep K., Bala P. and Sharma A.[5,6]studied water content in vegetable leaves and Broccoli leaves using beta attenuation technique. The mass attenuation coefficient was obtained from the slope of graph between leaf thickness and logarithm of relative transmission intensity. The interaction of beta radiation with material occurs at fundamental level of atoms or their elementary constituent like electron and the nucleus. The attenuation studies are very much useful in the field of physical sciences, bio-sciences, agricultural sciences and medicinal sciences for solving various problems. Beta particle attenuation gives basic information on material composition such as thickness, water content, etc.Havaraddi B.N.[7] determined radiation absorption of beta rays by different plant leaves of Banana, Mango, Custard Apple, Hibiscus and Teak wood. The radiation absorption coefficient was calculated.The work of C. Jördens,M. Scheller, B. Breitenstein, D. Selmar&M. Koch[8] demonstrated that the dielectric material parameters can be used to determine the leafwater status in plant leaves. They have developed an electromagnetic model for the permittivity of plant leaves in thefrequency range between 0.3 to 1.8 THz.Mahajan C.S.[9]measuredmass attenuation coefficients of beta particles in some of the elements and found to be in good agreement with empirical relation.Rocca P. and Riggi F.[10]measuredbeta radiation absorption for different materials used as absorbers (brass, Al and cardboard).Baldacci L., Pagano M., Masini L., Toncelli A., Carelli G., Storchi P. and Tredicucci A.[11]usedterahertzspectroscopic techniques for measuring leaf water content.Nakayana F. and Erhler W.[12] used beta ray gauging technique to measure water content in cotton leaf. Ram N., Rao I.S.S. and Mehta M.K.[13] studied the mass absorption coefficient of some elements Be, Al, Cu, Ag &Pb. Practical range of beta spectrum from mass absorption coefficient values was obtained. However, in present work the variation of beta radiation counts with water content of same leaf is observed for 10 days by using Geiger Muller counter.

II. Experimental Method

Geiger Muller Counter, a radiation detector based on ionization effect of radiation to count beta and gamma rays with radioactive sources $Tl^{204}$and Cs^{137}Nucleonix Hyderabad made is available in our college.We made standard connections and arrangement between G.M. Counting System, detector, absorber and source. Placed a beta source in the source tray at about 4 cm from the end window of the GM tube. Starting voltage and Upper threshold of plateau, Plateau length, Operating voltage and Slope (%) of plateau was determined (study of the characteristics of a GM Tube) as per the procedure given in the manual provided with the instrument. Set the GM voltage at the operating voltage (465V) of the GM tube. Leaves to be investigated were washed with water and then socked for a few minutes in layers of blotting paper. Then we took fresh leaf (absorber) of Tulasi and were cut for same dimension and were placed in the sample holder between end window detector and source holder. We measuredthe counts for a present time of 1 minute (60 sec) without any absorber (background counts) and then measured counts with absorber (fresh leaf) for the same period of time. The same leaf was studiedfor 10 days. The mass of leaf was determined by weighing with a single pan digital balance which has accuracy of 0.001.

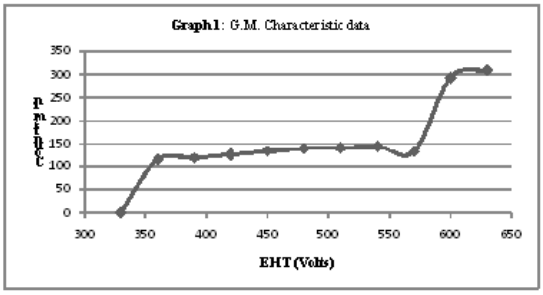
III. Result & Discussion

The variation of count rate with applied voltage (EHT) was studied and thereby plateau, operating voltage and slope of the plateau were determined using Table 1. Graph 1 shows the characteristics of G.M. tube.

Table 1. G.M. Characteristic data

Sr.No.	EHT (Volts)	Counts per minute (N)	Background counts (N_0)	Corrected counts ($N-N_0$)
1.	330	0	0	0
2.	360 (V_1)	119	05	114 (N_1)
3.	390	123	05	118
4.	420	131	06	125
5.	450	139	06	133
6.	480	147	08	139
7.	510	149	09	140
8.	540	155	11	144
9.	570 (V_2)	145	13	132 (N_2)

10.	600	308	15	293
11.	630	325	15	310



1. Starting voltage of plateau V_1 = 360 V

2. Upper threshold of the plateau V_2 = 570 V

3. Plateau length = $(V_2 - V_1)$ = 570 – 360 = 210 V

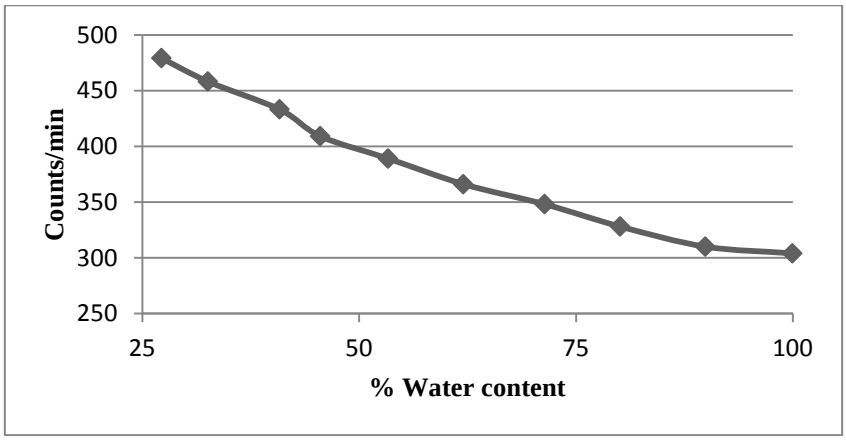
4. Operating voltage $V_0 = (V_2 + V_1)/2$ = 465 V

5. Slope (%) = $[(N_2-N_1)/N_1] \times [100/(V_2 - V_1)] \times 100$ = 7.58%

Table 2 and Table 3 shows the variation of counts of fresh and dry OcimumTenuiflorum (Tulasi) Leaf and AzadirachtaIndica (Kadunimb) Leaf respectively.Graph-2 and Graph-3 shows decrease in counts as amount of water in plant leaf increases. It is observed that leaf absorbs more radiation when it is fresh than dry hence number of counts for fresh leaf are less. Percentage of water in the leaf is calculated by using the formula:

Table 2. Ocimum Tenuiflorum (Tulasi) Leaf

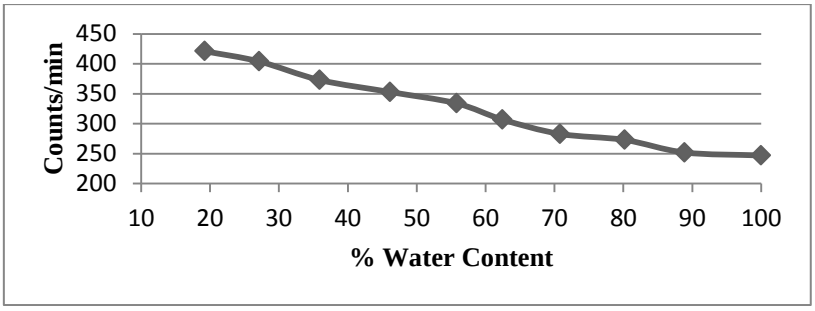
Days	Counts per minute				Corrected Counts/min	% Water content
	I	II	III	Mean		
1 (Fresh Leaf)	308	313	312	311	304	100.00
2	316	317	318	317	310	89.95
3	334	334	336	335	328	80.13
4	353	356	354	355	348	71.43
5	374	372	372	373	366	62.05
6	398	391	400	396	389	53.35
7	418	420	411	416	409	45.53
8	443	436	441	440	433	40.85
9	461	467	466	465	458	32.59
10	487	482	490	486	479	27.23



Graph 2. Ocimum Tenuiflorum Leaf Data

Table 3. AzadirachtaIndica (Kadunimb) Leaf

Days	Counts per minute				Corrected Counts/min	% Water content
	I	II	III	Mean		
1 (Fresh Leaf)	253	255	253	254	247	100.00
2	256	262	260	259	252	88.89
3	281	276	282	280	273	80.17
4	289	292	290	290	283	70.79
5	319	310	312	314	307	62.44
6	337	341	343	340	334	55.78
7	360	359	362	360	353	46.11
8	382	379	378	380	373	35.91
9	409	413	410	411	404	27.10
10	423	432	429	428	421	19.23



Graph 3. Azadirachta Indica Leaf

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Urea + DAP Briquette Increases Yield and Reduce Fertilizer Cost of Paddy Crop

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ABSTRACT

In initial years of KVK assess the problems are faced by the tribal farmers during the production of Paddy crop in western sides of KVK. In case of Paddy crop due to heavy rainfall there is a leaching losses of fertilizers added by farmers or fertilizers washout in running water. So that in consideration to this KVK assess the performance of Use of Urea + DAP Briquette in Khamgaon Village which is near by Junnar Tahsil with the help of Line dept. (ATMA). Finally KVK comes up with the recommendations of complete package of Four Fold Rice Cultivation technology which covers recycling of crop residues (Paddy), Use of green manures (Glyricidia), Plantation of seedling in proper spaces (15 x 25 cm or 20 x 25 cm) and application of Urea + DAP Briquette (170 kg/ ha.). Using urea briquette fertilizer the farmers getting more no. of tillers and obtaining more yield than that of his traditional method. i.e. Broadcasting of fertilizers. Before demonstrations yield of farmers is 28 Q/ha. and after the assessment yield increases up to 39 Q/ha. And recovery percentage is 55 to 60.

Keywords: Briquette.NPK Ferilizers ,Rice crop.

I. INTRODUCTION

Assessment area comes under western part of Maharashtra which include Tahasils like Junnar, Ambegaon, Khed, Maval and Mulshi with average annual precipitation of 2500 to 4000 mm (80% of rainfall received during June to September) and maximum temperature ranges from 29 to 39 ^{0} C. Minimum temp. ranges from 13-20 ^{0} C. Soils of these parts are Warkas i.e. light lateritic and reddish brown, distinctly acidic, poor fertility low in organic matter, Phosphorus and Potash content. The measure cropping pattern is Paddy followed by Wheat or Gram in case of heavy rainfall. Fertilizers applied by farmers are loss with running water and mainly micronutrients Zn, Fe are not getting by crops so there is reduction of yield day by day.

In operational villages the Paddy is a main crop for farmers. In year 2012-13 we have approach three villages for the use of Urea + DAP briquette with four fold rice cultivation technique and also conducted some demonstration in these villages. KVK select farmers for use Urea+ DAP briquette technique in Paddy crop and taken detailed methodological information on spacing of plantation, fertilizer management with and without briquette, problems in paddy, yield etc. Before the implementation of programme KVK getting support from Agriculture Department.

Application of Urea + DAP Briquette

Proper spacing for use of Urea Briquette

Increase in No. of Tillers

II. Methods And Material

Rice is being grown in Northern part Pune district on large scale. Major area under rice cultivation is in Junnar, Ambegaon, Khed, Maval & Mulshi Tahasils in the

jurisdiction of KVK. Rice is being grown traditionally .The yield obtained are at low levels due to use of traditional varieties, lack of recommended management practices. In this situation KVK has taken the lead to enhance the productivity of rice crop and also uplifting the farmers economic status.

KVK has under taken survey of rice growing villages in Junnar Tahsil. Group discussions with rice growing farmers were arranged to understand the problems in rice cultivation. Khamgaon village was selected for conducting assessment of Use of Urea + DAP Briquette in rice cultivation which is 8 km away from Junnar Tahshil. In Khamgaon village major crop is rice and annual rainfall is near about 3500 mm. In this village farmer were growing rice by traditional method in low land area. KVK conducted the OFT by using recommended technology of four fold rice cultivation, which covers recycling of crop residues (Paddy), Use of green manures (Glyricidia), Plantation of seedling in proper spaces (15 x 25 cm or 20 x 25 cm) and application of Urea + DAP Briquette (170 kg/ ha.).

III. Observations

The observation tare taken for this assessment are Seed rate, No. of seedling planted per hill, No. of tillers per plant, fertilizer use, yield B : C ratio etc are taken on both conventional Method and assessment trial by KVK. Yield and return are found higher in assessment trial as compared to conventional method. This rice cultivation technique is helpful for healthy growth of seedlings at initial stage due to application of silicon through use of rice plant residues. Also use of *Glyricidia* leaves is helpful in enriching the soil with organic carbon. It is again helpful for reduction in application of nitrogenous fertilizers. . After transplanting of seedling urea briquettes 67 kg per acre were applied in rice field one briquette at the center of each square. Urea briquette application resulted into better availability of nitrogen & phosphorus to the plants and also minimizes the losses due to volatilization and leaching.

Particulars	**Traditional Method/acre**	**Four fold rice cultivation/acre**
Seed	30 kg	16 kg
No. of seedling planted per hill	10 -12	2-3
Fertilizer used kg	Urea 1oo kg .50 kg DAP	Urea +DAP Briquette 67 kg
No. of tillers per plant	10-12	20-25
Yield per acre	11.2 q/acre	15.6 q/acre
Cost of cultivation (Rs.)	24700/-	23100/-
Gross Income (Rs.)	49200/-	66000/-
Net Income (Rs.)	24500/-	42900/-
B:C Ratio	1.98	2.85

IV. Conclusion

By adopting this technique yield obtained per unit area is increased. The intercultural operation becomes easier their by saving labor cost & time. The incidence of pest and diseases was minimized. The losses of fertilizers are minimized. This method of rice cultivation is much easy for weed management. The produce quality obtained is superior their by fetching better prices in market. The economic returns per unit area is more in Four Fold Rice Cultivation technique. soil health is maintained and minimizes the use of nitrogenous fertilizers .

The analysis of this assessment indicates the use of Briquettes will improve the no. of tillering and grain filling capacity of crop which will be resulted in increase in yield of Paddy as compared to traditional method. Since last year KVK have make briquettes of NPK and micronutrient mixtures which will be benefitted to farmers of Aster, Sugarcane, Marigold, Tomato and Cabbage, Cauliflower. With the help of these briquettes farmer getting better results and save their costing of fertilizer management.

V. Acknowledgment

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Direct One Pot Synthesis of Iodoarenes from Aromatic Amine Using TCT-Wet.Sio2 as an Effective Heterogeneous Catalyst

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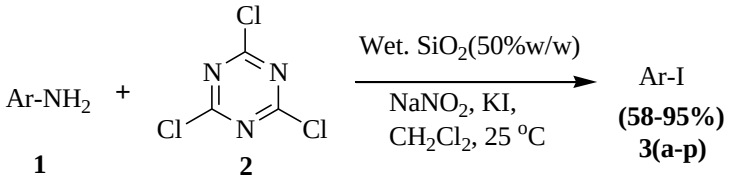
ABSTRACT

The present article described the one pot direct synthesis of structurally diverse aryl iodides from primary aromatic amines in aprotic media. 1,3,5-Trichlorotriazene (TCT)-Wet. SiO_2 (50 % W/W) was found to be an effective heterogeneous catalyst for in situ generation of diazonium salt followed by iodination with potassium iodide. The methodology presented here was worked well for the variety of aromatic amines possessing electron donating as well as electron withdrawing substituents on aromatic ring at room temperature. The corresponding aryl iodides are obtained in good to excellent yield.

Keywords: Trichlorotriazene, diazonium salt, HCl



Keywords: Aromatic amine, diazotisation, 1,3,5-Trichlorotriazene, iodoarenes, heterogeneous catalyst.

I. INTRODUCTION

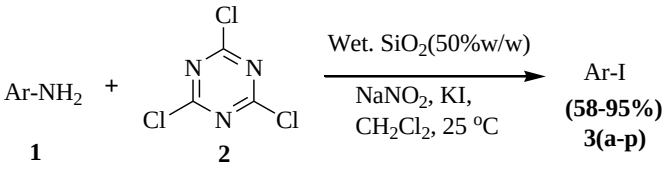
Aryl iodides are well known for their versatile synthetic utility as precursor for the synthesis of diverse biologically active compounds.[1] Moreover, iodo compounds are valuable as diagnostic aids and versatile synthetic intermediate for the synthesis of antimicrobial agents as well as in immunoassay studies along with in magnetic imaging study.[2] They have been radically fictionalized through C-N and C-C bond formation of diarenes, ethylenic or acetylenic condensation using transition metal catalyst bonds.[3] The direct iodination of aromatic compounds with molecular iodine was found to be difficult due to its low reactivity. Hence, more powerful iodinating species is required for direct iodination.[4]

In recent years, direct iodination is extensively developed using various catalytic systems.[5] However, the direct iodination method involves use of hazardous or toxic reagents, high reaction temperature for long reaction time with low product yields. In these methods large amount of aromatic compounds were needed and reactions had conducted under strongly acidic conditions It has been observed that in order to carry out the direct iodination reaction under milder condition, catalytic activation of an iodinating agents with Lewis acids[6] or adding various oxidizing agents such as iodic acid, periodic acid, peracetic acid or silver (I) salts and recently reported periodinanes.[7] In addition, P. R. Singh et al in 1972 have described the efficient method for the synthesis of para substituted iodobenzenes by nucleophilic aromatic substitution with KI in various reaction atmosphere such as nitrogen and oxygen. The iodoproucts obtained shows lower yield as 28-45% at 0 ^oC.[8]

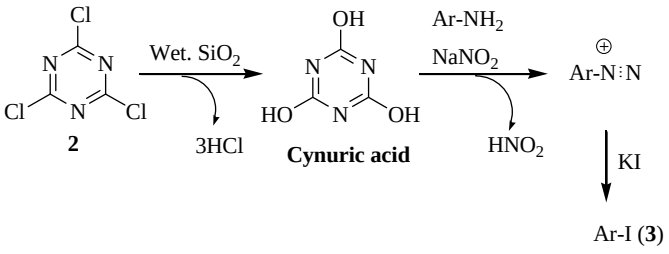
One of the commonly used methods for preparation of aryl iodides from primary amine is the Sandmeyer's reaction.[9] The method discovered by Sandmeyer has advantages over direct iodination. In addition, this method was superior for the selective introduction of iodine at specified position on aromatic ring.[10] However, the method discovered by Sandmeyer involved two step

process of diazotization-iodination by in situ generated nitrous acid from sodium nitrite and strong acid such as HCl or H_2SO_4 at 0 ^oC temperature followed by the reaction of KI in presence of transition metal catalyst such as Cu(I) iodide.[11]

Apart from these traditional methods, there are some recent reports for the synthesis of title compound by modified Sandmeyer's reaction using HI/KNO_2 in DMSO,[12] Wet.CSA/$NaNO_2$/KI,[13] Resin NO_2^-, p-TsOH, H_2O,[14] KI/$NaNO_2$/PTSA in MeCN,[15] $NaNO_2$/sulfonated-resin/KI in H_2O,[16] PTSA/$NaNO_2$/KI in water-paste form.[17] Some of these reported methods were associates with different disadvantages such as long reaction time, low product yield, tedious reaction work-up and multistep reaction strategy. To overcome these problems we have developed new and efficient silica catalytic system. Herein, we have reported TCT-wet. SiO_2/$NaNO_2$/KI in CH_2Cl_2 catalyzed synthesis of aryl iodides from primary aromatic amines at 25 ^oC. **(Scheme 1)**. The method presented here involves reduction in release of waste during workup procedures. It has been found that the said catalyst works well during the course of reaction.



Scheme 1. Synthesis of aryl iodides underheterogeneous conditions.



Scheme 2. Plausible mechanism for the synthesis of aryl iodides(**3**).

II. METHODS AND MATERIAL

All chemicals are of analytical grade. The melting points were determined on the open capillary tube and are uncorrected. The IR spectra were recorded on Bomen FT-IR MB-104 Spectrophotometer. 1H NMR were recorded on Brucker AC-300 MHz in $CDCl_3$ using TMS as an internal standard. Products were all known compounds and were identified by comparison of their physical and spectral data with those of reported in literature.

A General procedure for the synthesis of aryl iodides. To a mixture of primary amine (5 mmol) and wet.SiO_2 (0.25 g, 50% w/w) in CH_2Cl_2 10ml), KI (7 mmol) was added. The reaction mixture was stirred magnetically for specified time at room temperature. After reaction (as indicated by TLC), the reaction mixture was filtered. The solvent was removed under reduced pressure to afford the desired aryl iodide products with good to excellent yield. All the synthesized compounds are known compounds and confirmed by their spectroscopic data along with their physical constants.

III. RESULTS AND DISCUSSION

In continuation to our ongoing research on the development of novel methods using green techniques,[18] herein we have reported the direct method for the synthesis of aryl iodides from primary aromatic amines.

During the course of our study, we have conducted the optimization of reaction by employing aniline (5 mmol), cynuric chloride (5 mmol), $NaNO_2$ and KI in water(10 mL) at room temperature. It has been observed that when reaction directly in water medium showed the formation of iodobenzene (**3a**) in low yield (37%). However, when same reaction was conducted in presence of wet silica (50%w/w) and aprotic medium such as dichloromethane (5 mL), the corresponding iodobenzene (**3a**) product is obtained in 95% yield (**Table 1**). Hence, further reactions for the formation of aryl iodides were conducted in heterogeneous medium. Various aromatic amines possessing electron donating as well as electron withdrawing groups are subjected to the formation of aryl iodides. The results obtained were summarized in Table 1. Moreover, aliphatic amines such as n-octyl amine reacts slowly to afford noctyliodide in 58% yield (**entry 3n**). All the synthesized compounds are known compounds and confirmed by their spectroscopic data along with their physical constants.

A plausible mechanism for the formation of aryl iodide via diazotization of primary amine (**1**) was depicted in Scheme 2. From the literature survey it was clear that cynuric chloride (**2**) reacts with water to form cynuric acid and HCl.[19, 20] In situ generated HCl and cynuric acid may assist the diazotization by the formation of nitrous acid from sodium nitrite (Scheme 2).

IV. CONCLUSION

In conclusion, we have developed a new direct method for the synthesis of aryl iodides from aromatic amines using heterogeneous catalytic system in aprotic medium. 1,3,5-Trichlorotriazene (TCT)-Wet. SiO_2 (50 % W/W) was found to be an effective heterogeneous catalyst for in situ generation of diazonium salt followed by iodination with potassium iodide. The methodology presented here was worked well for the variety of aromatic amines possessing electron donating as well as electron withdrawing substituents on aromatic ring at room temperature. The corresponding aryl iodides are obtained in good to excellent yield.

Table 1. synthesis of aryl iodides from aromaticamines (3) in heterogeneous medium

Entry	Ar-NH2	Aryl iodide	Compound No	Time(min.)	Yield (%)
1.	$C_6H_5NH_2$	C_6H_5I	**3a**	30	95
2.	2-$NO_2C_6H_4NH_2$	2-$NO_2C_6H_4I$	**3b**	45	89
3.	3-$NO_2C_6H_4NH_2$	3-$NO_2C_6H_4I$	**3c**	40	95
4.	4-$NO_2C_6H_4NH_2$	4-$NO_2C_6H_4I$	**3d**	40	92
5.	4-$MeOC_6H_4NH_2$	4-$MeOC_6H_4I$	**3e**	30	73
6.	4-$MeC_6H_4NH_2$	4-MeC_6H_4I	**3f**	30	70
7.	4-$IC_6H_4NH_2$	4-IC_6H_4I	**3g**	30	79
8.	4-$NH_2C_6H_4NH_2$	4-$NH_2C_6H_4I$	**3h**	30	74
9.	4-$COOHC_6H_4NH_2$	4-$COOHC_6H_4I$	**3i**	30	86
10.	2-$COOHC_6H_4NH_2$	2-$COOHC_6H_4I$	**3j**	40	90
11.	2,6-Di,$MeC_6H_3NH_2$	2,6-Di,MeC_6H_3I	**3k**	50	84
12.	2,4,6-Tri-$NO_2C_6H_2NH_2$	2,4,6-Tri-$NO_2C_6H_2I$	**3l**	30	92
13.	2,4-Di-$NO_2C_6H_3NH_2$	2,4-Di-$NO_2C_6H_3I$	**3m**	30	87
14.	$CH_3(CH_2)_7NH_2$	$CH_3(CH_2)_7I$	**3n**	30	58
15.	2-$MeC_6H_4NH_2$	2-MeC_6H_4I	**3p**	30	61

[a] The yields refer to the pure isolated products. [b] All products were characterized by IR and ^{1}HNMR and compared with authentic samples

V. ACKNOWLEDGEMENTS

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