Vidya Bharati Shaikshanik Mandal, Amravati's

# VIDYA BHARATI MAHAVIDYALAYA, AMRAVATI

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# 3.3.2 Number of research papers per teachers in the Journals notified on UGC website during the Academc Year 2015-16

| SN | Title of paper | Name of the author/s | Department of the teacher | Name of journal | Year of publication | ISSN number | Link to the recognition in UGC enlistment of the Journal |
|---|---|---|---|---|---|---|---|
| 73 | Extraction of Natural Dye from *Ixora coccinea* (Linn.) Flowers for Cotton Fabric Colouration | Monali U. Ghurde, M.M.Padwad, V.R.Deshmukh, | Botany | International Journal of Science and Research (IJSR) PP.1272-1276 | 2015-16 | 23197064 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| 74 | Causes of Poverty in India | Dr. Arunsingh D. Chauhan | Sociology | International Quarterly Research Bulltin | 2015-16 | 22311025 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| 75 | Major Trends of Rural Social Change in India | Dr. Arunsingh D. Chauhan | Sociology | International Quarterly Research Bulltin | 2015-16 | 22311025 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| 76 | A Floristic survey of flowering plants from vidyabharati mahavidyalaya campus, Amravati (maharashtra)India. | Wagay Nasir Aziz,Deshmukh VR and Rothe SP | Botany | International journal of life sciences. | 2015-16 | 23207817 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| 77 | Phytochemical, ethno medicinal and anatomical study of *Canthium parviflorum* | Pulate P.V. Wagay Nasir Aziz and Deshmukh V. R. | Botany | World Journal of Pharmacy and Pharmaceutical Sciences. | 2015-16 | 22784357 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| 78 | "The Trials of Brother Jero " of Wole Soyinka" | S.S. Dete & Dr. P.S. Yenkar | English | Vidyabharati International Interdisciplinary Research Journal | 2015-16 | 23194979 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| 79 | Portrait of Billy as Distressed Self in Arun Joshi's The Strange Case of Billy Biswas | Dr. P.S. Yenkar | English | Vidyabharati International Interdisciplinary Research Journal | 2015-16 | 23194979 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| 80 | Breaking the Silence: A New Feministic Approch Revealed in Shashi Deshpande's Novel, That Long Silence | Dr. P.S. Yenkar | English | Vidyabharati International Interdisciplinary Research Journal | 2015-16 | 23194979 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| 81 | Ketan Pimpalapure yanchya kavitetil Samajikta Ani Saundarya | Prof. Dr. Gajanan Bansod | Marathi | Sarvadhara | 2015-16 | 22493034 | Not listed in present UGC approved list as well as in deleted approved UGC List |
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| 83 | Balshram: Manvidhikar Hanan ka krur Yatharth | Dr. D. S. Wankhade | Physical Education and Sports | Human Rights | 2015-16 | 23950315 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| 84 | Low Temperature H2S Gas Sensor Based on Fe2O3 Modified ZnO-TiO2 Thick Film | R. B. Pedhekar, F. C. Raghuwanshi, V. D. Kapse | Physics | International Journal of Materials Science and Engineering | 2015-16 | 23154527 | Not listed in present UGC approved list as well as in deleted approved UGC List |

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| **85** | SYNTHESIS, STRUCTURAL AND GAS SENSING PROPERTIES OF PURE ZINC OXIDE NANO THICK FILM | S.D.Charpe, F.C. Raghuwanshi | Physics | Journal of Electron Devices | 2015-16 | 16823427 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| **86** | NANOCRYSTALLINE MIXED METAL OXIDE SEMICONDUCTOR SYNTHESIZED BY HYDROTHERMAL METHOD | R. B. Pedhekar, F. C. Raghuwanshi, | Physics | INTERNATIONAL JOURNAL OF PURE AND APPLIED RESEARCH IN ENGINEERING AND | 2015-16 | 2319507X | Not listed in present UGC approved list as well as in deleted approved UGC List |
| **87** | Usefulness of PCR in Survillance of Malaria infection in Melghat Region (M.S.),India | Tantarpale SA<br>PS Joshi<br>VT Tantarpale | Zoology | Review of Research | 2015-16 | 2249894X | Not listed in present UGC approved list as well as in deleted approved UGC List |
| **88** | Seasonal diversity and population Dyanamics of Ohpidian Fauna in Buldhana Dist. Maharashtra, India. | P.S.Joshi V.T.Tantarpale & K.M. Kulkarni | Zoology | Indian Journal of Sci. Res. | 2015-16 | 9762876 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| **89** | Diversity of Saurian Fauna from Jalgaon (Jamod) Territory , Buldhana Dist.( M.S) India. | Pandharikar S.D, Joshi P.S and V.T. Tantarpale | Zoology | Journal of Asia-Pacific Biodiversity | 2015-16 | 23213485 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| **90** | Diversity of Anuran Fauna from Jalgaon (Jamod) Territory , Buldhana Dist. (M.S) India. | Pandharikar S.D, Joshi P.S and V.T. Tantarpale | Zoology | Weekly Sci. Research Journal | 2015-16 | 23217871 | Not listed in present UGC approved list as well as in deleted approved UGC List |
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| **93** | Ichthyological Fauna of Amravati District (M.S | V.R.Wankhade (Tantarpale) | Zoology | Golden research Thoughts | 2015-16 | 22315063 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| **94** | Record of Leucism in Green Keel Back Macropisthodon Plumbicolor (Cantor, 1839) in Amravati Dist. Maharashtra, India. | Amjad Hussain , P.S. Joshi and V.T. Tantarpale | Zoology | Int. Weekly Sci. Research Journal, | 2015-16 | 23217871 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| **95** | Synthesis, characterization and antimicrobial study of some novel chloro substituted Isoxazoles. | V.D.Mane,D.T.Mahajan and P.R.Rajput | Chemistry | Am. J. Pharm. Tech Res. 2015. 5(4), 517-522. | 2015-16 | 22493387 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| **96** | Synthesis characterization of some Nitro–substituted 1,3-thiazines and their antimicrobial activities. | M. M. Rathore, Vandana V. Parhate, P. R. Rajput | Chemistry | IJSEAS, 1(8), 2015. 423. | 2015-16 | 23953470 | Not listed in present UGC approved list as well as in deleted approved UGC List |

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| **97** | Study of Acoustical parameters of chalcone in DMSO solvent with different concentration using ultrasonic inter refractometer. | P.S.Nandurkar,M. M. Rathore, P. R. Rajput | Chemistry | Int. Journal of advance scientific and technical research 5 (7) 2015. 60. | 2015-16 | 22499954 | Not listed in present UGC approved list as well as in deleted approved UGC List |
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| **99** | 3D-QSAR and docking studies on adenosine $A_{2A}$ receptor antagonists by the CoMFA method | E. Pourbasheer, S. Shokouhi Tabar, V. H. Masand, R. Aalizadeh and M. R. Ganjali | Chemistry | SAR and QSAR in Environmental Research, 2015, Volume 26, Issue 6, pages 461-477 | 2015-16 | 1062936X | Not listed in present UGC approved list as well as in deleted approved UGC List |
| **100** | Optimization of Antiproliferative Activity of substituted Phenyl 4-(2-Oxoimidazolidin-1-yl) benzenesulfonates: QSAR and CoMFA analyses | V. H. Masand, D. T. Mahajan, A. M. Alafeefy, S. N. A. Bukhari and N. N. Elsayed | Chemistry | European Journal of Pharmaceutical Sciences, 2015, | 2015-16 | 9280987 | Not listed in present UGC approved list as well as in deleted approved UGC List |
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| **103** | Synthesis of (e)-1-(5-chloro-2-hydroxy-4-methylphenyl)-3-(4-bromophenyl)prop-2-en-1-one and 4-chloro-5-methyl-2-(5-(4-bromophenyl)-4,5-dihydro-1H-pyrazol-3-yl)phenol and its derivatives | Charita B. Patil, Vijay H. Masand | Chemistry | International Journal on Recent and Innovation Trends in Computing and Communication, 2015, 3(10), 5745-5747 | 2015-16 | 23218169 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| **104** | Synthesis, Characterization and Antimicrobial screening of some Azo compounds derived from Ethyl vanillin | Dr Pravin S. Bodkhe | Chemistry | Research Journal of Chemical Science (Res. J. Chem. Sci.) Vol. 5(7), 20- | 2015-16 | 2231606X | Not listed in present UGC approved list as well as in deleted approved UGC List |
| **105** | Effect of systemic fungicide benlate (benomyl) on seedling germination and growth in *Allium cepa* L | Pulate P.V. | Botany | International Journal of Pharma and Bio Sciences | 2015-16 | 9756299 | Not listed in present UGC approved list as well as in deleted approved UGC List |
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| **107** | Investigation of aloe vera tooth gel containing active salt and alum by time kill test | DR. MADHURI D. PARDESHI | Cosmetic Technology | International journal of research in economics & social sciences | 2015-16 | 22497382 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| **108** | Formulation & evaluation of aloe vera gel with active salt & alum – as a new dentifrice | DR. MADHURI D. PARDESHI | Cosmetic Technology | International journal of research in economics & social sciences | 2015-16 | 22497382 | Not listed in present UGC approved list as well as in deleted approved UGC List |
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| **111** | Ramesh Patil yanchya katetil Dalit ashayavishva | Prof. Dr. Gajanan Bansod | Marathi | Aksharvaidarbhi | 2015-16 | 9760296 | Not listed in present UGC approved list as well as in deleted approved UGC List |
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| **113** | Synthesis and Structural Properties of Nanocomposite of PANI/ZnO by in – Situ polymerization | S.D. Charpe, F.C. Raghuwanshi, P.P. Raut and G.T. Lamdhade | Physics | Research Journal of Chemical Sciences | 2015-16 | 2231606X | Not listed in present UGC approved list as well as in deleted approved UGC List |
| **114** | Diversity of Saurian Fauna in the Buldhana Dist. (M.S) India | P.S. Joshi, V.T.Tantarpale | Zoology | Journal of Asia Pacific Biodiversity | 2015-16 | 2287884X | Not listed in present UGC approved list as well as in deleted approved UGC List |
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| **117** | The pH metric study of synthesized heterocyclic compound isoxazoline with Cu (II) and Fe (III) metal ions. | V.D.Mane,D.T.Mahajan and P.R.Rajput | Chemistry | World journal of pharmacy and pharmaceutical sciences, 5(2), 2016, 1147- | 2015-16 | 22784357 | Not listed in present UGC approved list as well as in deleted approved UGC List |
| **118** | A Study On The Ultrasonic Behaviour Of Some Chalcones And Their Mixtures | T. S. Bante, M. M. Rathore and P. R. Rajput | Chemistry | Imperial Journal of Interdisciplinary Research (IJIR) Vol.2, Issue-1 , 2016 | 2015-16 | 24541362 | Not listed in present UGC approved list as well as in deleted approved UGC List |

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| **119** | Molecular structure investigation and biological evaluation of Michael adducts derived from dimedone | A. Barakat, A. M. Al-Majid, M. S. Islam, I. Warad, V. H. Masand, S. Yousuf and M. I. | Chemistry | Res Chem Intermed, 2016, 42, 4041-4053 | 2015-16 | 9226168 | Not listed in present UGC approved list as well as in deleted approved UGC List |
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# Extraction of Natural Dye from *Ixora coccinea* (Linn.) Flowers for Cotton Fabric Colouration

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**Abstract:** *In the present study, experiments were carried out to use an extract isolated from floral petals of Ixora coccinea (Linn.) with aqueous and methanol as a natural dye. The dye potential of the extract was evaluated by dyeing on cotton fabrics under the normal dyeing conditions and tested for their colour fastness to washing properties. The pigments were isolated from fresh flowers of Ixora coccinea (Linn.) and studied in order to understand the process of dying during cotton cloth coloration using different mordants such as Alum, Copper sulphate, ferrous sulphate and Stannous chloride. The various shades were obtained by Ixora coccinea (Linn.)Flower on cotton fabrics. Aqueous extract without mordant (Control) exhibits Windsor cream 6860 shade that is matched with Walnut cream 8778, Riverbed Sand 8462, Dark ash 8776 and Pampered Pink 8696 shades obtained in Alum (5%), Copper sulphate (2%), Ferrous sulphate (2%) and Stannous chloride (2%) respectively. Shades generated in mordants were all unique and different than control. The results revealed that the Methanolic extract of Ixora coccinea (Linn.) flower extracted more pigments and exhibits dark shades on cotton fabric as compared to aqueous. Methanol Control exhibits bright Rose petal 0208 shade that is matched with shades obtained in respective mordants i.e. Sparrow feather 8659, Quarry stone 8658, Digital grey 8312 and Dash of purple respectively. The shade obtained is matched with Asian-paint color shades card which makes it easier for the user to communicate about the shade without actually sending sample. The changes in shades of some of the colors have been noticed after washing with soap. The Spectroscopic analysis of dye color have also been made for identification of certain bonding /functional groups present in the dye extract, the technique can used to identify the interaction of the dye with mordents. Secondly, mordanting with the different metal salts exhibited variation in color hue because of their ability to form coordination complexes with the dye molecules, which resulted in different shades to cotton fabrics. These findings revealed that the extract of floral petals of Ixora coccinea (Linn). can be used for cotton fabric coloration.*

**Keywords:** *Ixora coccinea*, Natural dye, Mordents, Asian paint charts, Cotton fabric.

## 1. Introduction

Nature expresses itself in a wide spectrum of colours all around us. Dyeing is an ancient art and it was practicised during the Bronze Age in Europe. Primitive dyeing techniques were included sticking plants to fabric or rubbing crush pigments into cloth. The method became more sophisticated over time but presently there s an excessive use of synthetic dyes. The production and application of which release vast amount of waste and unfixed colourants, causing serious health hazards and disturbing the eco-balance of nature. Currently ecological considerations are becoming an important factor in the selection of consumer goods all over the world. Natural dyes are known for their use in the selection of food substrata, leather as well as natural protein fibres like wool, silk and cotton as the major areas of application since prehistoric time. Dyeing is an antiquated art as well as modern science complex. Presently there is an excessive use of synthetic dyes estimated at around 10,000,000 tonns per annum [3], the production and application of which release vast amount of waste and unfixed colorants causing serious health hazard and disturbing eco-balance of nature [4]. Natural dyes are the colours derived from plants and animals or insect matter without any chemical processing [10],[9]. They can offer not only a rich and varied source of dye stuff, but also the possibility of an income through sustainable sale of these dye plants. But the certain problems with the use of natural dyes in the textile dyeing are colour yield, complexity of dyeing process, reproducible results, limited shades and inadequate fastness properties[11[,[13] but these problems can be overcome by using chemicals called mordants. Mordants are the metal salts which produce an affinity between dye and fabri [15[,[12]. In general, it has been observed from the literature that the identification of natural dyes in textiles involves selective extraction of dyes and comparison of each dye by various characterization techniques, viz. UV-Visible and IR spectroscopy, TLC, HPLC, ecotoxicity (LD-50) and bio-assay, including methods of identification of vegetable dyes on cellulose fibres, animal fibres and man-made fibres. UV visible spectra of any colourant/dye show its peaks at predominating wavelength, indicating main hue. For natural dyes, the spectra specially indicate different peaks for mixed colourants available in their extract in both UV and visible region. UV/ Visible spectroscopic studies of different natural dyes were carried out [1] using different solvents for extraction.

*Ixora coccinea* Linn. (Rubiaceae) is also known as Jungle Geranium or Flame of the Woods or Vetchi in Ayurveda. It is a common flowering shrub native to Asia. The plant is a dense, much branched evergreen shrub, commonly 4-6 ft (1.2-2m) in height, but capable of reaching up to 12ft (3.6 m). Leaves are sessile to short-petiolate, glossy, leathery, oblong and are about 10 cm long, with entire margins and are arranged in opposite pairs or whorled on the stem, stipules basally sheathing, Flowers small, sessile, tubular and are

arranged in dense rounded clusters, calyx lobes short, triangular, persistent,corolla tube usually 1-1.5 inches long, lobes lanceolate to ovate, acute or sometimes obtuse, Fruit fleshy and reddish black. The plant is traditionally used as hepatoprotective, Chemoprotective, antimicrobial, anti-oxidant, anti–mitotic and anti-inflammatory activities [14].

The present work has tried to document the methodology of dye extraction from *Ixora coccinea* (Linn.) flowers, also to study the interaction of dye with different mordants for variation in shades on cotton fabric. The shade obtained is matched to the Asian paint colour shade which makes it easier for the user to communicate about the shade without actually sending sample. Second part of study is spectroscopic analysis of dye colour, for identification of certain bonding elements/functional groups present in the dye extract; the technique can used to quantitatively indentify the presence of these groups.

## 2. Materials and Methods

### 2.1 Materials

1) **Source:** A dark red healthy variety of *Ixora coccinea* (Linn.) flowers were collected from the campus of VidyaBharati Mahavidyalaya, Amravati.
2) **Substrate:** Cotton fabric were obtained from Khadi-Gramodhogh Amravati and used for dyeing.
3) **Chemicals:** 5% Alum, 2% copper sulphate, 2% ferrous sulphate, 2% stannous chloride

### 2.2 Methods

**a) Extraction of Dye**
Fresh floral petals of *Ixora coccinea* (Linn.) were crushed dissolved and boiled in water and methanol at 80°C for 2hrs and were found floral petals to discharge color in methanol very easily than water. Increasing the quantity of floral petals accompanied with the increase in color strength and depth in color [9]. It was observed that, color of the dye extract was dark red. The solution was filtered for immediate use.

**b) Pre- treatment (Scouring of cotton):**
Cotton fabric were washed in a solution containing 0.025 g/ L sodium carbonate ($Na_2CO_2$) and 0.06 g / L non- ionic detergent solution at 50°C for 25 min. keeping the material to liquor ratio 1 : 40. The scoured material was thoroughly washed with tap water and dried at room temp. The scoured material was soaked in clean water for 30 minutes prior to dyeing or mordanting [4],[6].

**c) Mordanting**
Accurately weighed scoured cotton fabric cotton samples were treated with different metal salt before dying. The mordant 2% (owf) was dissolved in water to make liquor ratio 1: 40. The wetted samples were dipped into the mordant solution and then brought to heating. Temperature of the dye bath was raised to 80°C over a period of half an hour and left at that temperature for another 30 minutes. The mordant material was then rinsed with water thoroughly squeezed and dried. The cotton fabrics soaked in various mordants are used immediately for dyeing because some mordants are very sensitive to light.

**d) Dying**
The mordant cotton fiber was dyed with dye extract. Keeping M: L ratio as 1: 40; however, for cotton dyeing it was used directly. Dying was done by the conventional dyeing method. After dyeing, the dyed material was washed with cold water and dried at room temperature. It was then dipped in brine for dye fixing. After this it was washed with non- ionic detergent and dried under shade.

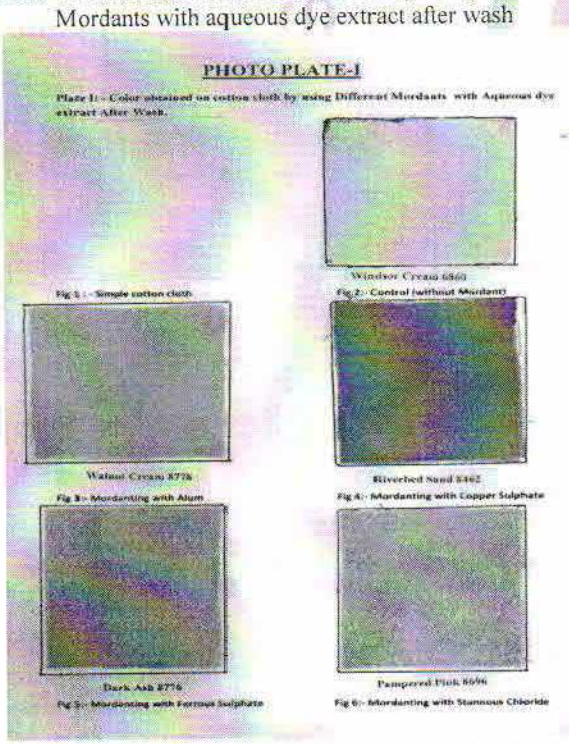
**e) UV- Visible Spectroscopic study**
UV visible spectra of any colorant/dye show its peaks at predominating wavelength, indicating main hue. For the natural dyes, the spectra specially indicate different peaks for mixed colorants available in their extract in both UV and visible region. 190nm to 1100nm UV-VIS spectroscopic analysis was carried out on UV-VIS Elico-spectrophotometer.

## 3. Results and Discussion

The objectives of this study were to evaluate the light fastness of natural dyes extracted from *Ixora coccinea* flowers and the effect of some commonly use mordants to fix colour and to obtain different shades on the cotton fabric. The natural dyes present in plants and animals are pigmentary molecules, which impart colour to the materials. These molecules containing aromatic ring structure coupled with a side chain are usually required for resonance and thus to impart colour. There is a correlation of chemical structure with colour, chromogen-chromophore with auxochrome [8]. Mordants play very important role in imparting color to the fabric. The mordants used in combination in different ratios gave varying shades. Better color strength results are dependent on the metal salt used [5]. The resistance of a dye or pigment to chemical or photochemical attack is an inherent property of the dye chromophore, but at the same time the auxochrome may also substantially alter the fastness. Wash fastness of dye is influenced by the rate of diffusion

of dye and state of dye inside the fiber. The dye extracted from *Ixora* flowers exhibits good to excellent wash fastness. Secondly, they have a tendency to aggregate inside the fiber and hence exhibit good wash fastness. Mordants used in the present study also have the effect of insolubilizing the dye, making it color fast. Present study indicated that a changes of some colours in the dyed samples of cotton fabric with different mordents (Plate No. I and II). Natural dyes mostly require a mordant to be fixed onto the fiber. The cotton fabrics were dyed with chemical mordants. It was observed that, the dye uptake was good in pre-mordanting method as shown in photoplate I/II. Various hues of color were obtained from pre-mordanted cotton with alum, copper sulphate, ferrous sulphate and stannous chloride. They have an affinity for the dye and the fiber that forms an insoluble precipitate with the dye in the fiber [4]. Different type of mordants and method of mordanting significantly affect the rate and extent of photo fading.The various shades were obtained by *Ixora coccinea* (Linn.) flower on cotton fabric. Methanolic extract of *Ixora coccinea* (Linn.) extracted more pigments as compared to aqueous. Among all the shades, the shades obtained in aqueous and methanolic extract on cotton fabric in control (without mordants) exhibits light shades i.e. Windsor cream 6860 and Rose petal 0208 respectively. Aqueous extract without mordant (Control) exhibits light shades i.e.Windsor cream 6860 that is matched with Walnut cream 8778, Riverbed sand 8462 Dark ash 8776 and Pampered pink 8696 shades were obtained in Alum (5%), Copper sulphate (2%), Ferrous sulphate (2%) and Stannous chloride (2%) respectively (Photo Plate – I). Shades generated in mordants were all unique and different than control.

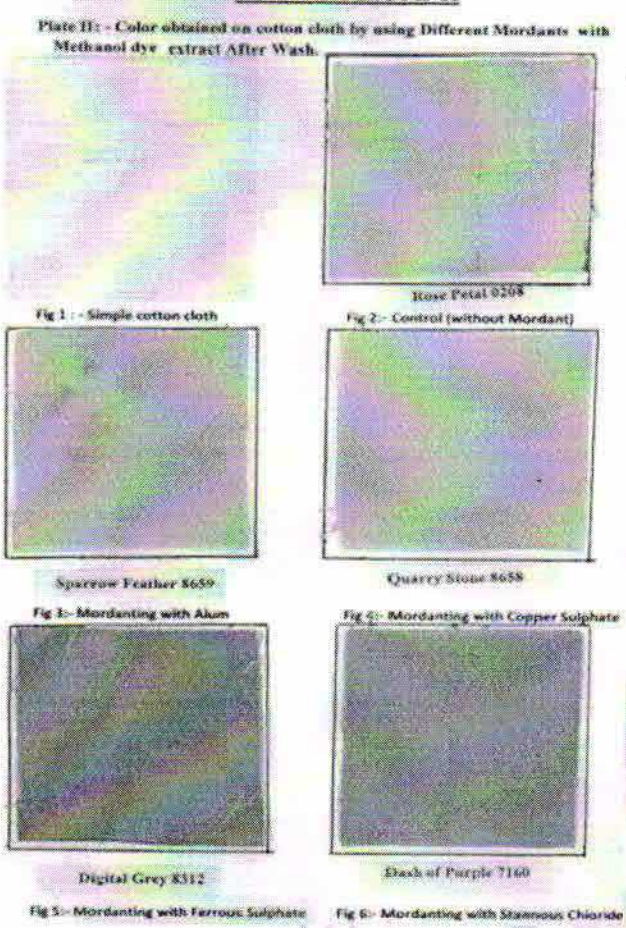
**Plate 1:** Color obtained on cotton cloth by using Different Mordants with aqueous dye extract after wash




Methanolic extract of *Ixora coccinea* (Linn.) extracted more pigments as compared to aqueous. Methanol control exhibits bright and light shadeRose petal 0208 that is matched with Sparrow feather 8659, Quarry stone 8658, Digital grey 8312 and Dash of purple 7160 were obtained in Alum (5%), Copper sulphate (2%) Ferrous sulphate (2%) and Stannous chloride (2%) respectively (Photo Plate –II). Significant variations were obtained in this group; Alum (2%) and Copper sulphate (2%) generated light shades i.e.Sparrow feather 8659 and Quarry stone 8658 respectively whereas, 2% Ferrous sulphate and Stannous Chloride generated unique and dark shades to cotton fabric exhibitsDigital grey 8312 in Ferrous sulphate and Dash of purple 7160 in Stannous chloride. Comparatively Ferrous sulphate (Digital grey 8312) and Stannous Chloride (Dash of purple 7160) of methanolic extracts and copper sulphate (Riverbed sand 8462) of aqueous extracts fixes color to the fabric more deeply as compared to the rest of the mordants in both aqueous as well as methanolic extracts.Sample dyed with *Ixora* dye exract by using the mordants exhibits good light wash fastness (Photoplate I and II).Wash fastness of the dye is influenced by the rate of diffusion of dye and state of dye as well as tendency to aggregate inside the fibre. Methanolic extracts generated unique shades in all mordants. Thus various light and brighter shades were obtained by using different mordants on cotton fabric. Ferrous sulphate and Copper Sulphate have the ability of forming co-ordination complexes [6]. Good light fastness by using copper sulphate and ferrous sulphate as a mordants due to strong co-ordination tendency of Fe enhances the interactions between the fiber and the dye, resulting in high dye uptake as well as protects the chromophore from photolytic degradation [4]. The use of copper or ferrous sulphate gives high resistance to fading, whereas stannous chloride or alum does not. Both aqueous and methanol extracts generated unique shades in all mordants. Natural dyes have better biodegradability and generally have higher compatibility with the environment. They are non-toxic, non-allergic to skin, non-carcinogenic, easily available and renewable [6].

**Plate 1:** Color obtained on cotton cloth by using Different Mordants with Methanol dye extract after wash

**PHOTO PLATE-II**




**The Analysis of UV- VIS Spectroscopy:**

The Pigments obtained from UV-VIS spectrum of *Ixoracoccinea*(Linn.) flowers extracted in distilled water and methanol is shown in Table I with absorption at 190 nm to 1100 nm. Absorption spectrum shown in Table I indicated that after an addition of different mordants in aqueous extracted dye, the organic pigments showed polarity towards the cotton fabric.UV analysis of the dye extract gives, Absorption at maximum wavelength for aqueous dye extract at 525 nm for anthocyanins, 535nm for cyanidin, 538 nm for betalains, 430 nm for chl a, chl b at 450 nm, 500nm for carotenoids, 475nm for xanthophyll, 618nm for phycocyanin and 576 nm for phycoerythrin . The red/pink color was obtained with interaction of anthocyanins, betalains and carotenoids at 520nm, 538nm and 500 nm.With addition of mordent alum 2% the polarity of bonds increases and attachment organic compound firmly to the chromophore loosely or tightly according to formation of bonding is complex structure (Table 1). After addition of alum to extracted aqueous flower extracted dyes anthocyanin peak at 520nm, cyanidin at 535nm, betalins at 538nm, Chloa at 430nm, Chlo b at 642nm,carotenoids at 500nm, xanthophylls at 475nm, phycocyanin at 623nm while phycoerythrin peak at 490nm.

**Table 1**: UV-Vis absorption spectrum of Aqueous and Methanol extracted dye pigments and its interaction with Different Mordents from *Ixora coccinea*(Linn.) flowers (Red).

| Pigments | Aqueous extracted dyes without mordant (nm) | Aqueous extracted dye + 5% Alum (nm) | Aqueous extracted dyes+ 2% Copper sulphate (nm) | Aqueous extracted dye + 2% Ferrous sulphate (nm) | Aqueous extracted dye + 2% Stannous Chloride (nm) | Methanol extracted dye without mordant (nm) | Methanol extracted dye + 5% Alum (nm) | Methanol extracted dye + % Copper sulphate (nm) | Methanol extracted dye + % Ferrous sulphate (nm) | Methanol extracted dye + % Stannous Chloride (nm) |
|---|---|---|---|---|---|---|---|---|---|---|
| Anthocyanins | 525 | 520 | 526 | 520 | 527 | 518 | 520 | 520 | 521 | 524 |
| Cyanidin | 535 | 535 | 535 | 535 | 535 | 535 | 535 | 535 | 535 | 535 |
| Betalains | 538 | 538 | 538 | 538 | 538 | 476 | 538 | 538 | 538 | 538 |
| Chl a | 430 | 430 | 430 | 430 | 430 | 430 | 430 | 430 | 436 | 436 |
| Chl b | 450 | 642 | 640 | 640 | 458 | 640 | 454 | 450 | 640 | 458 |
| Carotenoids | 500 | 500 | 500 | 400 | 400 | 500 | 400 | 500 | 500 | 400 |
| Xanthophyll | 475 | 475 | 450 | 475 | 475 | 475 | 445 | 445 | 475 | 425 |
| Phycocyanin | 618 | 623 | 618 | 620 | 623 | 618 | 626 | 618 | 618 | 618 |
| Phycoerythrin | 576 | 490 | 576 | 576 | 576 | 576 | 490 | 576 | 490 | 490 |

Each mordent produced unique and dark shades to the cotton fabric, might be due to the interaction of chl a and chl b with the other red colored pigment which helps to fix the color more to the fabric (Photo plate- I) With the addition of alum and other different mordents in methanolic extracted dye, the organic pigments mainly carotenoids, xanthophylls, anthocyanin, betalains and phycoerythrin showed polarity which owes unique shades to the cotton fabric while the mordants like ferrous sulphate and stannous chloride generated dark and bright shades to the cotton fabric as compared to other mordents that might be due to the interaction of chl a and chl b with the other red colored pigment which increases polarity of bonds that helps to fix the color more deep to the fabric (Photo plate- II) . The dye absorption for the dyes extracted from *Mimusop selengi* and *Terminalia arjuna* showed that depending on the concentrations of dyes in the dye bath, the dye absorbed on the fiber varies from 21.94 % to 27.46 % and from 5.18 % to 10.78% respectively [2]. The color components isolated from most of the barks contain flavonoid moiety.

## 4. Conclusion

The present study revealed the dyeing potential of *Ixora coccinea* (Linn.) flowers as a source for cotton dyeing. The whole process of extraction and dyeing is ecologically safe.Different shades of color were obtained by using different chemical mordants in both the solvent systems.Good light and washing fastness exhibited by the dyed cloth is because of the mordants used. Both the solvent extracts exhibits unique shades and affix it deeply to the cotton fabric.Spectral analysis showed different binding affinity with different chromophore groups within the pigments which can acts as chelating agents affix to the fabric and gives different shades to the fabric. *Ixora* dye has good scope in the commercial dyeing of textiles.

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(5) Users must have a computer and access to the internet to use the library thus certain populations will have limited or no access to the library. This is especially so for remote or rural populations, or for populations living in poverty.

(6) Digital libraries must keep up with rapid changes in technology ( including **Software, Hardware and the Internet**) otherwise, the resources it provides will quickly become out dated or inaccessible.

**CONCLUSION :**

Today, Information Technology plays great role in higher education, Librarians are knowledge centers with full of information & for proper utilization of information technology that in computer technology provide fast & easy access to information. It provide fast information in any form, any time & any where. Hence now terms come. Digital library, virtual library etc. So for the development of library Information technology is very useful, because in today's time fast growing world Development in library without technology is not possible. So use Internet with information technology and do better development in this **E- WORLD** of Library.

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## CAUSES OF POVERTY IN INDIA

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**INTRODUCTION**

A large proportion of India's poor are living in poverty. Lack of resources or asset-lessens - lack of access to land, water, forests, housing, credit, literacy, capital – are all characteristics of poverty and that the poor are often hungry, lacking in shelter and clothing, sick and not cared for, illiterate and not schooled, and more vulnerable to events outside their control, as

well as lacking in voice and power in the institutions of the state and society. Poverty in India is widespread, and a variety of methods have been proposed to measure it. The official measure of Indian government, before 2005, was based on food security and it was defined from per capita expenditure for a person to consume enough calories and be able to pay for associated essentials to survive. Since 2005, Indian government adopted the Tendulkar methodology which moved away from calorie anchor to a basket of goods and used rural, urban and regional minimum expenditure per capita necessary to survive. The World Bank has similarly revised its definition and benchmarks to measure poverty since 1990, with $1.25 per day income on purchasing power parity basis as the definition in use from 2005 to 2013. Some semi-economic and non-economic indices have also been proposed to measure poverty in India; for example, the Multi-dimensional Poverty Index placed 33% weight on number of years spent in school and education and 6.25% weight on financial condition of a person, in order to determine if that person is poor. The different definitions and different underlying small sample surveys used to determine poverty in India, have resulted in widely different estimates of poverty from 1950s to 2010s. In 2013, the Indian government stated 21.9% of its population is below its official poverty limit. The World Bank, in 2010 based on 2005's PPPs International Comparison Program, estimated 32.7% of Indian population, or about 400 million people, lived below $1.25 per day on purchasing power parity basis.[I] According to United Nations Development Programme an estimated 29.8% of Indians lived below poverty line in 2009-2010. From the above analysis of secondary data the main objectives of this paper is To find out main causes of poverty in India.

**Causes of Poverty in India –** According to Puja Mondal Four main causes of poverty in India are as follows –

**1. Climatic factors :-** Climatic conditions constitute an important cause of poverty. The hot climate of India reduces the capacity of people especially the ruralites to work for which production severely suffers. Frequent flood, famine, earthquake and cyclone cause heavy damage to agriculture. Moreover, absence of timely rain, excessive or deficient rain affect severely country's agricultural production.

**2. Demographic factors :-** The following demographic factors are accountable for poverty in India.

**(i) Rapid growth of population :-** Rapid growth of population aggravates the poverty of the people. The growth of population exceeds the rate of growth in national income. Population

growth not only creates difficulties in the removal of poverty but also lowers the per capita income which tends to increase poverty. The burden of this reduction in per capita income is borne heavily by the poor people. Population growth at a faster rate increases labour supply which tends to lower the wage rate.

**(ii) Size of family :-** Size of the family has significant bearing on rural poverty. The larger the size of family, the lower is the per capita income, and the lower is the standard of living. The persistence of the joint family system has contributed to the health and earning capacity of the ruralites.

**3. Personal causes :-** The following personal causes are accountable for poverty in India.

**(i) Lack of motivation:-** Lack of motivation is an important cause of rural poverty. Some ruralites do not have a motive to work hard or even to earn something. This accounts for the poverty of the ruralites.

**(ii) Idleness:-** Most of the rural people are lazy, dull and reluctant to work. Hence they rot in poverty.

**4. Economic causes:-** The following economic causes are accountable for poverty in India.

**(i) Low agricultural productivity:-** Poverty and real income are very much interrelated. Increase in real income leads to reduction of the magnitude of poverty. So far as agricultural sector is concerned, the farmers even today are following the traditional method of cultivation. Hence there is low agricultural productivity resulting in rural poverty.

**(ii) Unequal distribution of land and other assets:-** Land and other forms of assets constitute sources of income for the ruralites. But, unfortunately, there has been unequal distribution of land and other assets in our economy. The size-wise distribution of operational holdings indicates a very high degree of concentration in the hands of a few farmers leading to poverty of many in the rural sector.

**(iii) Decline of village industries:-** At present consequent upon industrialization new factories and industries are being set up in rural areas. Village industries fail to compete with them in terms of quality and price. As a result they are closed down. The workers are thrown out of employment and lead a life of poverty.

**(iv) Immobility of labour:-** Immobility of labour also accounts, for rural poverty. Even if higher wages are offered, labourers are not willing to leave their homes. The joint family system makes people lethargic and stay-at-home. The ruralites are mostly illiterate, ignorant, conservative, superstitious and fatalistic. Poverty is considered as god-given, something pre-ordained. All these factors lead to abysmal poverty in rural India.

**(v) Lack of employment opportunities:-** Unemployment is the reflection of poverty. Because of lack of employment opportunities, people remain either unemployed or underemployed. Most of these unemployed and underemployed workers are the small and marginal farmers and the landless agricultural labourers.

**5. Social causes:-** The following social causes are accountable for poverty in India.

**(i) Education:-** Education is an agent of social change and egalitarianism. Poverty is also said to be closely related to the levels of schooling and these two have a circular relationship. The earning power is endowed in the individual by investment in education and training. But this investment in people takes away money and lack of human investment contributes to the low earning capacity of individuals. In this way people are poor because they have little investment in themselves and poor people do not have the funds for human capital investment.

**(ii) Caste system:-** Caste system in India has always been responsible for rural poverty. The subordination of the low caste people by the high caste people caused the poverty of the former. Due to rigid caste system, the low caste people could not participate in the game of economic progress.

**(iii) Joint family system:-** The joint family system provides social security to its members. Some people take undue advantage of it. They live upon the income of others. They become idlers. Their normal routine of life consists in eating, sleeping and begetting children In this way poverty gets aggravated through joint family system.

**(iv) Social customs:-**The ruralites spend a large percentage of annual earnings on social ceremonies like marriage, death feast etc. As a result, they remain in debt and poverty.

**(v) Growing indebtedness:-** In the rural sector most of the ruralites depend on borrowings from the money-lenders and land-lords to meet even their consumption expenses.

Moneylenders, however, exploit the poor by charging exorbitant rates of interest and by acquiring the mortgaged land in the event of non-payment of loans. Indebted poor farmers cannot make themselves free from the clutches of moneylenders. Their poverty is further accentuated because of indebtedness. Such indebted families continue to remain under the poverty line for generations because of this debt-trap.

## CONCLUSION:

From the analysis of data collected by secondary source it is found that there are many causes are accountable for poverty in India such as Climatic factors, Rapid growth of population, Size of family, Lack of motivation, Idleness, Low agricultural productivity, Unequal distribution of land and other assets, Decline of village industries, Immobility of labor, Lack of employment opportunities, Education, Caste system, Joint family system, Social customs and Growing indebtedness.

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# HUMAN RESOURCE MANAGEMENT (HRM) IN THE NEW MILLENNIUM

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## INTRODUCTION:

Human beings are social beings and hardly ever live and work in isolation. We always plan, develop and manage our relations both consciously and unconsciously. The relations are the outcome of our actions and depend to a great extent upon our ability to manage our actions. From childhood each and every individual acquire knowledge and experience on understanding others and how to behave in each and every situations in life. Later we carry forward this learning and understanding in carrying and managing relations at our workplace. The whole context of Human Resource Management revolves around this core matter of

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# MAJOR TRENDS OF RURAL SOCIAL CHANGE IN INDIA

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## INTRODUCTION :

Social change may refer to the notion of social progress or socio cultural revolution, th philosophical idea that society moves forward by dialectical or evolutionary means. It may ref to a paradigmatic change in the socio-economic structure, for instance a shift awa from feudalism and towards capitalism. Accordingly, it may also refer to social revolution, suc as the Socialist revolution presented in Marxism, or to other social movements, suc as Women's suffrage or the Civil rights movement. Social change may be driven by cultura religious, economic, scientific or technological forces. Developmental psychology can play role in social change. The scenario of transition in rural society, specially in post-independenc era suggests that the process of planned development has transformations in rural society. Th changes in rural India have brought about a process of rapid social restructuration. It is leadin to a breakdown in the seminary mode of social change. It has resulted in rise of new middl class to power. There has been massive use of science and technology in agriculture. Substanti changes in values and beliefs are also taking place in rural India. The green revolution signifie not merely growth in agricultural production but also the use of new technology and soci relationship in production process. These developments make the new phase of changes in rur economy and society a distinct process. A new interaction among technology, social relationshi and culture is now taking place in the rural society. This has resulted in social mobilit emergence of new power structure and mode of exploitation of the deprived classes.Hence th main aim of this paper to focus on Major Trends of Rural Social Change in India.

**Major Trends of Rural Social Change in India** – According to Sam Hillyard,that Newb offers a different approach, which introduces no new empirical results but draws together hi own research to offer a commentary on rural society. The text was more popularists in tone an adopted a more historical approach. Newby argued that social changes were all rooted in chang in agricultural industry – and its decline – as 'English rural society is no longer entirely, nc even predominantly, an agrarian society' (Newby 1985: 183), the result of which was tha significant changes had occurred in the social and occupational composition of rural population who were no longer dependent upon farming for their living. Newby distinguished thos dependent upon agriculture for employment as the 'truly rural' and contrasted these with the ex

urbanite newcomers. The impact of this latter group also marked 'changes in the economic and social organization of agriculture. Thomas G. Johnson and James K. Scott stated that technological change is so ubiquitous that it heads most lists of change. From the perspective of rural communities, technological change effects more than just the way in which products and services are produced. Technological change has and will change the very economic bases of rural areas, their relationship with the rest of the national and global economies and their internal social structure. In production, the most significant economic forces are the rising importance of information, communication, robotics, artificial intelligence, genetic engineering, and other embodiments of technology. In addition to the direct effects of these changes on employment, they have led to increased use of services (particularly, information-related services), and reduced use of goods (particularly, raw materials) in the production processes of other manufacturers. Among the earliest human groups, gathering was the main source of food. Gradually man acquired the skill and knowledge in agriculture. With the development of agriculture, people began to lead a settled life and human communities became more stationary. The emergence of village signified that man has passed from nomadic mode of collective life to the settled one. India is a land of villages. A great majority of villages are small with only around five hundred populations each. Mahatma Gandhi's view that India lives in villages still holds good, at least from the demographic point of view. The village social life has its own peculiar characteristics. The village social life norms strengthen the authoritarian and hierarchical norms in administration. The village social life, which is based on the hierarchical exchange relations greatly influence the behavior of civil servants in public organizations. Sociologists think that for defining an Indian village, its population, physical structure, and modes of production are definitely important. Usually, a village has less than five thousand individuals. It is rightly said 'India is a country of villages'. Agriculture is the main occupation of the Indians and majority of people in India live in the villages. Our villages help in strengthening our social bonds and bringing stability to our society in many ways. Our villages also help our society in another way namely that of preserving our culture. The Indian rural society has undergone considerable change in the recent past, particularly since the Independence as a result of a series of the land reform legislations that have accelerated the pace of this change. India has a rich cultural heritage and is a land of diversities. The diversity in social life is reflected in multi-social, multi-lingual, multi- religious and multi-caste nature of the society. The important features of the Indian social structure are- predominant rural habitation in small villages; multi-religious and multi-caste social identities and important role of family in

the social life.According to above analysis it is noticed that there are following Major Trends o Rural Social Change in India –

- Rapid transformation of agrarian society from subsistence economy to market economy.
- Rapid transformation followed by the introduction of modern technology.
- Emergence of various associations and institutions having linkages with urban an national organizations.
- The transition of agrarian society from subsistence base to market based agrarian sector.
- The introduction of modern technology and devices to transform the underdevelope colonial agrarian economy into a, well knit compact one and its organic integration int the total national economy.
- State interventions in adopting different measures to strengthen certain communitie groups or classes on the one hand and weaken others, on the other.
- Emergence of dominant group like neo-rich peasants, intermediary castes etc. and thei tightened hold over avenues of political power.

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## BIOCHEMICAL CHANGES IN BLOOD DURING OESTROUS CYCLE IN *FUNAMBULUS PENNANTI*


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**ABSTRACT :**

*The present study is an attempt to find out some biochemical changes in blood during oestrous cycl (sex cycle ) in squirrel , Funambulus pennanti .*



***KEY WORDS**:-squirrel , F.pennanti, biochemical parameter, glucose, plasma cholesterol and plasm protein*

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RESEARCH ARTICLE

# A floristic survey of flowering plants from Vidyabharati Mahavidyalya Campus, Amravati (Maharashtra) India

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## ABSTRACT

One of the grand tasks of current taxonomy is to prepare a checklist of plants of the globe. This work is largely based on collecting information from regional floras and databases. Till this date, the progress is relatively slow, as the number of common names, synonyms, poorly resolved aggregates is high. For this purpose regional flora, checklists and databases with reliable taxonomy and complete coverage of critically examined data are required. The majority of novelties come from the tropics; but certain areas remain poorly explored as well, and numerous species in these areas still await recognition. In the present work, the studied area is Vidyabharati Mahavidyalaya campus which is situated in the prime location of the Amravati city. Amravati is a district in the state of Maharashtra with its district headquarters situated at 20°55′33″ N and 77° 45′53″ E. The district is situated at 343m (1,125ft.) asl. The present study deals with the floristic diversity of campus in the former sense, i.e., the number of individual species in the area. The present paper attempts to highlight the diversity of vast plant resources of the campus in a conservation perspective. A total of 91 species of flowering plants are documented in which 43 were herbs, 25 shrubs, and 24 angiospermic trees distributed in 22, 13, and 12 families respectively.

**Key words:** taxonomy, explored, survey, diversity, conservation

## INTRODUCTION

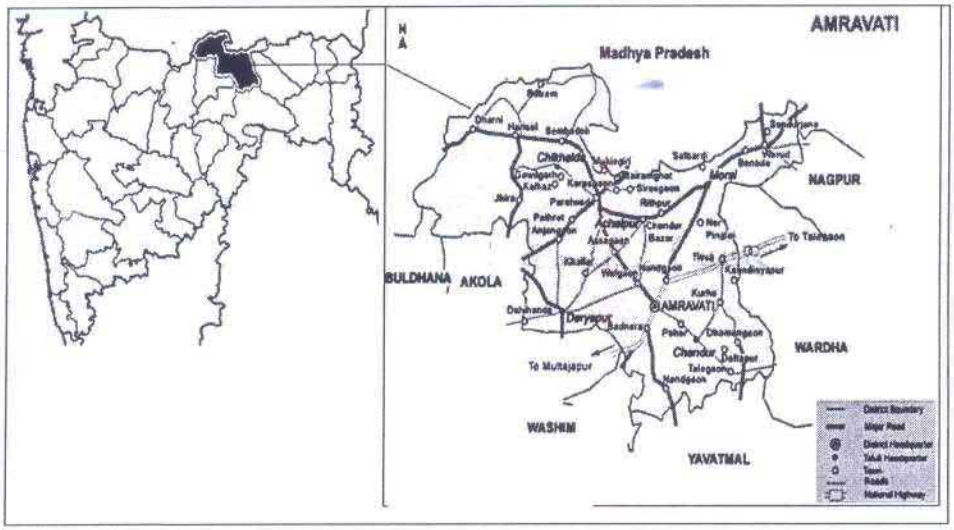
From the very beginning of inception of human beings on the earth man has relied on plants to fulfill his basic needs for his survival. Plants provide food, shelter and health. It is estimated

that about ten million species of plants inhabit the planet earth of which, however only 1.7 million species are known to science. It is therefore the need of the hour to explore the floristic wealth of the earth so as to know what we have. The plant diversity however is under serious threat due to various anthropogenic factors and many plant species are disappearing. Many species are becoming extinct even before their discovery. This scenario necessitates the urgent need of conservation of this diversity. To formulate various strategies for this purpose, the first important step is to explore and inventories the flora. Keeping this perspective in view the present studies were conducted to explore and inventorize the plant species. Therefore an attempt has been made to study the plant species present in the campus. Different Morphological characters are being studied like habit, height, leaf, inflorescence, flowers, and fruits etc representing diversity of plants in the campus of Vidyabharati Mahavidyalaya college.

Floristic diversity can be defined as the variety and variability of plants in a given region. It refers to the number of types or taxa in a given region or group. Floristic diversity can be measured at any level from overall global diversity to ecosystem, community, species, populations, individuals and even to genes within a single individual. The present survey deals with the floristic diversity of college campus in the former sense, i.e., the number of individual species in the area. The present paper attempts to highlight the diversity of vast plant resources of the college campus in a conservation perspective. In this survey we have focused only on the flowering plants of the campus Although the lower groups of plants (Pteridophytes, Lichens, Bryophytes) form a important part of vegetation and contribute significantly to the floristic diversity, they have been excluded in the present discussion.

**Area of study:**

Amravati is a district in the state of Maharashtra with its district headquarters situated at 20°55′33″ N and 77° 45′53″ E. The district is situated at 343m (1,125ft.) asl. The Amravati district has an area of 270 km². Vidyabharati College is situated in the prime location of the Amravati city. It has a set of beautiful buildings along with a play ground & Gardens situated over the 7.77 acres of a piece of a land. The total area under the gardens is about 30,000 sq.feet. The study area has well demarcated four seasons as a hot summer, heavily raining monsoon, a brief autumn and a mild winter. The area has sub tropical climatic conditions with ample rainfall in the monsoon resulting in a rich diversity of vascular plants.




**Map: Amravati a district in the state of Maharashtra**

## MATERIAL AND METHODS

Plants were observed during all seasons of the year 2012-13. During observation field notes were recorded in field notebooks and voucher specimens of these species were collected. The collected specimens were processed using usual taxonomic methods of drying and mounting. The specimens were identified with the help of existing literature (Bentham & Hooker, 1862-83 ; Cooke, 1901-1908; Dhore, 1986; Naik, 1966,1977,1998; Singh *et al.*,2000; Singh *et al*; 2001) and have been preserved in the herbarium of Department of Botany, Vidya Bharati Mahavidyalya, Amravati.

## RESULTS AND DISCUSSION

The Present study deals with the documentation of the total number of herbs, shrubs and angiospermic trees, which are the native of different countries. Some of these plants have been brought here from different areas of the country & cultivated over here in the garden, and some grow wildly in this area. A list of plant species in the catchment area starting by herbs, then shrubs, and at last angiospermic trees. A total of **91** species of flowering plants are documented in which **43** were herbs, **25** shrubs, and **24** angiospermic trees distributed in **22**, **13**, and **12** families respectively.

**Table 1 : list of herbs**

| Sr. No. | Botanical Name | Family |
|---|---|---|
| 1 | *Vernonia cineria* (L.)Less. | Asteraceae |
| 2 | *Calendula officinalis* L. | Asteraceae |
| 3 | *Zinnia peruviana* (L) | Asteraceae |
| 4 | *Zinnia angustifolia* kunth. | Asteraceae |
| 5 | *Blainvillea acmella* L. | Amaranthaceae |
| 6 | *Aerva Lanata* ( L.) Juss. | Amaranthaceae |
| 7 | *Achyranthus aspera* L. | Amaranthaceae |
| 8 | *Amaranthus poligonides* L. | Amaranthaceae |
| 9 | *Andrographis paniculata* (Burm.f.)Wall ex Ness | Acanthaceae |
| 10 | *Diplocyclous palmatus* L. | Cucurbitaceae |
| 11 | *Cocculus hirsutus* ( L. ) Deils | Menisparnaceae |
| 12 | *Oxalis corniculata* L. | Oxalideaceae |
| 13 | *Colocasia esculanta* (L.) Schott | Araceae |
| 14 | *Ocimum sanctum* L. | Lamiaceae |
| 15 | *Catharanthus roseus* (L.) | Apocynaceae |
| 16 | *Datura metal* L. | Solanaceae |
| 17 | *Withania somnifera* (L) Dunal. | Solanaceae |
| 18 | *Acalypha indica* L. | Euphorbiaceae |
| 19 | *Curcuma longa* L. | Zingiberaceae |
| 20 | *Zingiber officinale* Rosc. | Zingiberaceae |
| 21 | *Ipomoea cairica* (L.) Sweet. | Convolvulaceae |
| 22 | *Passioflora edulis* Sims. | Passifloraceae |
| 23 | *Aloe vera* L. | Liliaceae |
| 24 | *Asparagus racemosus* (L.) Willd. | Liliaceae |
| 25 | *Cissus qudrangularis* L. | Vitaceae |
| 26 | *Agave americana* (L.)A.L.Juss. ex Schutt | Agavaceae |
| 27 | *Hymenocallis littoralis* (Jacq.) | Amaryllidaceae |

**Table No.1 : Continued...**

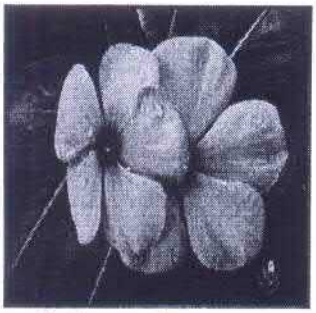
| Sr. No. | Botanical Name | Family |
|---|---|---|
| 28 | *Jasminum auriculatum* Roxb. | Oleaceae |
| 29 | *Dianthus chinensis* L. | Caryophyllaceae |
| 30 | *Trigonella foenumgraecum* L. | Fabaceae |
| 31 | *Cynodon dactylon* (L.)Pers | Poaceae |
| 32 | *Dicanthium annulatum* (Hook.f.) Blatt. & Mc C. | Poaceae |
| 33 | *Lophopogon tridentatus* Hack. | Poaceae |
| 34 | *Andropogon pumilus* Roxb. | Poaceae |
| 35 | *Aristida hystrix* L.F. | Poaceae |
| 36 | *Chloris virgata* Swartz. | Poaceae |
| 37 | *Dactylotenium aegyptium* ( L) P.Beauv. | Poaceae |
| 38 | *Eleusine indica*(L.)Gaertn. | Poaceae |
| 39 | *Setaria pumilla* (poir)R. | Poaceae |
| 40 | *Melanocenchris jacquemontii* Jaub.and Spach. | Poaceae |
| 41 | *Alpuda mutica* | Poaceae |
| 42 | *Eragrostis namaquensis* Schard var.*diplachnoides* (Steud) | Poaceae |
| 43 | *Eragrostis tanella* | Poaceae |

**Table No. 2: List of Shurbs**

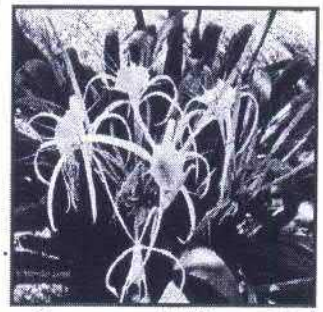
| Sr. No | Botanical name | Family |
|---|---|---|
| 1 | *Hibiscus rosa-sinensis* L. | Malvaceae |
| 2 | *Abelmoschus moschatus* L. | Malvaceae |
| 3 | *Lawsonia inermis* L. | Lithraceae |
| 4 | *Murraya koenigii* (L.) Spr. | Rutaceae |
| 5 | *Citrus aurantiifolia* (Christm.) Sw. | Rutaceae |
| 6 | *Hamelia patens* Jacq. | Rubiaceae |
| 7 | *Ixora coccinea* L. | Rubiaceae |
| 8 | *Coffee arabica* Ritter Ron. | Rubiaceae |
| 9 | *Nyctanthes arbortristis* L. | Oleaceae |
| 10 | *Nerium oleander* L. | Apocynaceae |
| 11 | *Tabernaemontana divaricata* (L.) R. Br. | Apocynaceae |
| 12 | *Calotropis procera* (Ait) R. Br. | Asclepiadaceae |
| 13 | *Solanum nigrum* L. | Solanaceae |
| 14 | *Barleria cristata* L. var. *cristata* | Acanthaceae |
| 15 | *Adhatoda beddomei* Hong Gao | Acanthaceae |
| 16 | *Vitex trifolia* L. | Verbenaceae |
| 17 | *Lantana camara* L. var. *aculeatea*(L.) Mold | Verbenaceae |
| 18 | *Jatropha curcas* L. | Euphorbiaceae |
| 19 | *Ricinus communis* L. | Euphorbiaceae |
| 20 | *Acalypha wilkesiana* Muell. Arg. | Euphorbiaceae |
| 21 | *Euphorbia tithymaloides* L. | Euphorbiaceae |
| 22 | *Cajanus cajan*(L.)Millsp DC.nom. cons. | Fabaceae |
| 23 | *Calliandra calothyrsus* (Meisn.) | Fabaceae: Mimosoideae |
| 24 | *Indigofera tinctoria* L. | Fabaceae: Papilionaceae |
| 25 | *Punica granatum* L. | Punicaceae |

**Table No. 3: List of Angiospermic Trees**

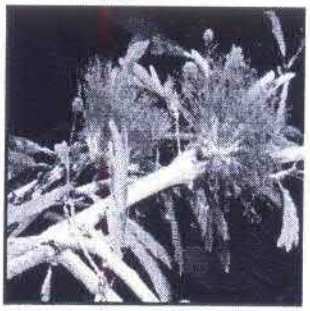
| Sr. No | Botanical name | Family |
|---|---|---|
| 1 | *Azardirecta indica* A. Juss. | Meliaceae |
| 2 | *Ficus benghalensis* L. | Moraceae |
| 3 | *Ficus religiosa* L. | Moraceae |
| 4 | *Ficus glomerata* Roxb. | Moraceae |
| 5 | *Aegle marmelos* (L.) Corr. | Rutaceae |
| 6 | *Feronia limonia* L. | Rutaceae |
| 7 | *Mangifera indica* L. | Anacardiaceae |
| 8 | *Emblica officinalis* Gaertn. | Euphorbiaceae |
| 9 | *Psidium guajava* L. | Myrtaceae |
| 10 | *Santalum album* L. | Santalaceae |
| 11 | *Tectona grandis* L. f. | Verbenaceae |
| 12 | *Cocos nucifera* Linn. | Arecaceae |
| 13 | *Ziziphus mauritiana* L. | Rhamnaceae |
| 14 | *Butea monosperma* (Lam.) Taub. | Fabaceae |
| 15 | *Gliricidia sepium* (Jacq.)Walp. | Fabaceae |
| 16 | *Pongamia pinnata* (L.) pierre | Fabaceae |



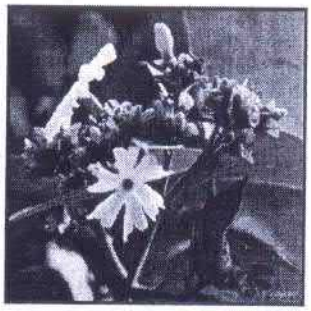
*Catharanthus roseus*



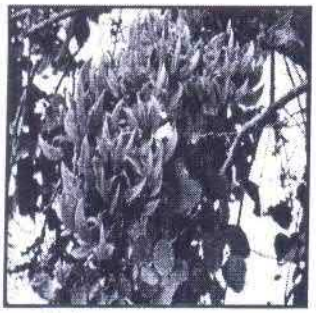
*Hymenocallis littoralis*



Calliandra calothyrsus

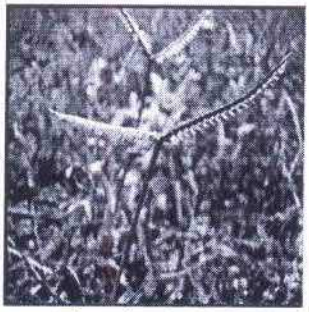


*Nyctanthes arbortristis*

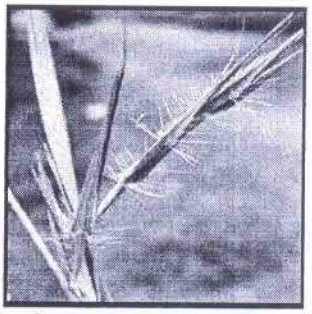


*Butea monosperma*

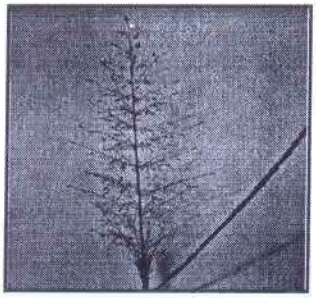
*Delonix regia*



*Eleusine indica*



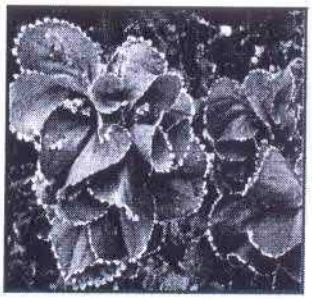
*Themada quadrivalvis*



*Eragrostis namaquensis*

*Dianthus chinesis*

*Barleria cristata*



*Acalypha wilkesiana*

**Fig. 1:**

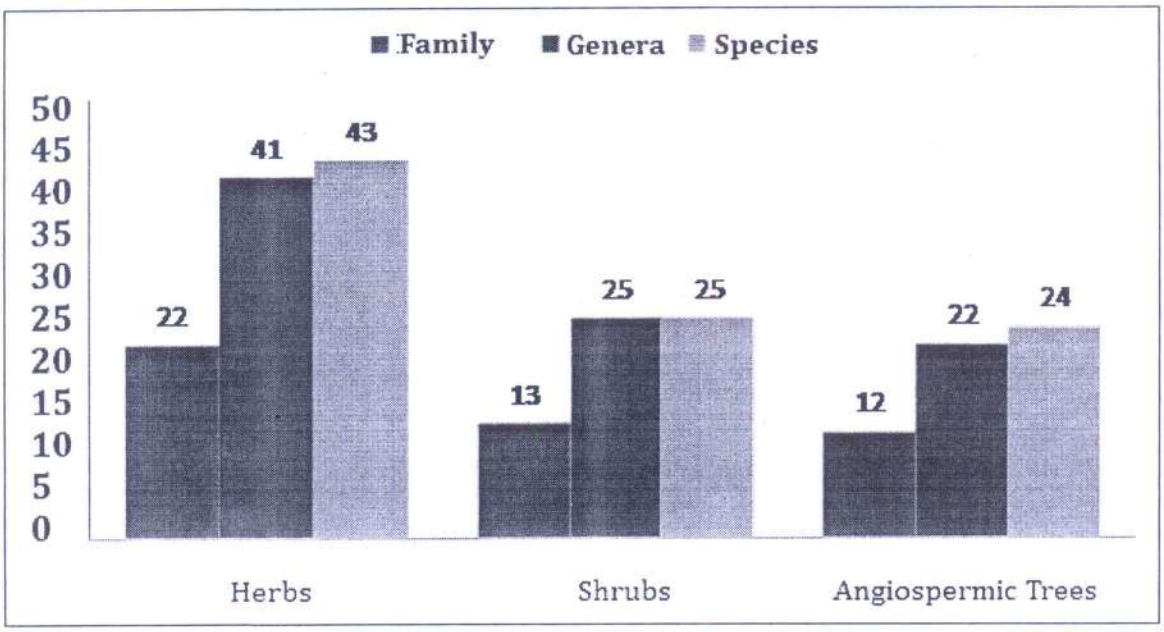



**Fig. 2: showing number of Herbs, Shrubs, and Angiosperms with respect to their families, genera and species in the studied area**

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# PHYTOCHEMICAL, ETHNOMEDICINAL AND ANATOMICAL STUDY OF *CANTHIUM PARVIFLORUM*

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## INTRODUCTION

Nature is the best source of medicinal constituents. From the vast natural resources, the plants are being used for therapeutic purposes from the beginning of the civilization (Kirtikar and Basu; 1980). Medicinal plants are bioactive constituents which form one of the major resources of raw material for drugs in preventive and curative constituents from one of the major sources of raw material for drugs in preventive and curative applications (Baliga *et. al;* 2003). Plant derived medicine has made largest contribution to human health and well-being all over the world. The basic medicinal property of these plants lies in some chemical substances. These chemical substances produce a definite physiological action on human body which is generally known as phytochemical. These chemicals are non nutritive and act like shield against diseased. The most important of these phytochemical are alkaloids, flavonoids, tannins and phenolic compounds (Hill A. F.; 1952). Around 1900, 80% of the drug was derived from plants (Adetunji *et al*; 2011). A knowledge of the chemical constituents of plants is desirable not only for the discovery of therapeutic agents, but also because such information may be of great value in disclosing new sources of economic phyto-compounds for the synthesis of complex chemical substances and for discovering the actual significance of folkloric remedies (Fouche *et al;* 2001). The traditional medicine all over the world is now a day's revalued by an extensive activity of research on different plant species and their therapeutic principles.

After decades of serious obsession with the modern medicinal system, people have started looking at the ancient healing systems like Ayurveda, Siddha and Unnani. This is because of the adverse effects associated with synthetic drugs and also the increasing cost, non

availability of modern drugs, and limited access to adequate health; these reasons have compelled about 80% world population to use traditional pharmacopeia for primary health care especially in the tropical and sub tropical regions. The last few years have seen a revival of interest in the use of herbal medicine in the developed world. Herbal medicines are in great demand in both developed and developing countries as a source of primary health care owing to their attributes having wide biological and medicinal activities, high safety margins and lesser costs. Among the developed countries, Germany holds the lead and has published individual monographs on therapeutic benefits of more than 300 herbs. In developing countries, China has compiled / generated data on over 800 medicinal plants and exports large amounts of herbal drugs. India has prepared only a few monographs and its exports are dismal.

The World Health Organization (WHO) has defined traditional medicine (including herbal drugs) as comprising therapeutic practices that have been in existence, often over hundreds of years, before the development and spread of modern medicine and are still in use today (WHO, 1991). About 25% of all modern medicines prescribed worldwide are directly or indirectly derived from higher plants (WHO, 2005).

India is one of the world's twelve leading biodiversity centers with the presence of over 45,000 different plant species. Out of these about 1,500- 2,000 plants have good medicinal properties of which only about 750-800 are being used by traditional practitioners. The Siddha system of medicine uses around 600, Ayurveda 700, Unani 700 and modern medicine about 30 plant species (Mukharjee, 2002). Though our ancient literatures provide a good account of description on plants along with different formulations of drugs, symptoms and diagnosis of diseases, methodology followed in preparation of medicines as well as mode of application. Ancient Indian literature incorporates a remarkably broad definition of medicinal plants and considers all plant parts to be potential sources of medicinal substances (Khare, 2007). However a key obstacle, which has hindered the acceptance of the alternative medicines in the developed countries, is the lack of documentation and stringent quality control. The system of classification, adopted in these literatures creates some confusion in nomenclature of medicinal plants. Sometimes, the description of a plant, given in these ancient medical literatures shows affinity with altogether unrelated two or three plant species belonging to different families. This has led to a great difficulty in identification of appropriate samples of medicinal plants, prescribed for treatment of specific disease. Correct

identification and quality assurance of the starting materials is an essential prerequisite to ensure reproducible quality of herbal medicine which will contribute to its safety and efficacy. Hence, there is a need for documentation of research work carried out on traditional medicines (Dahanukar, 2000).

With this backdrop, it becomes extremely important to make an effort towards standardization of the plant material to be used as medicine. The process of standardization can be achieved by stepwise pharmacognostic studies (Trease and Evans, 2002). Pharmacognosy and phytochemistry are important tools for the study of crude drug obtained from natural sources treated scientifically. These tools used in standardization of plant material include its morphological, anatomical and biochemical characteristics (Anonymous, 1989). These studies help in identification and authentication of the plant material.

A knowledge of the chemical constituents of plants is desirable not only for the discovery of therapeutic agents, but also because such information may be of great value in disclosing new sources of economic phytocompounds for the synthesis of complex chemical substances and for discovering the actual significance of folkloric remedies.

*Canthium* is a genus of about 230 species of shrubs or small trees. The *Canthium parviflorum* Lam. (syn: *Plectoria parviflora*) of Rubiaceae. *Canthium parviflorum* Lamk is a shrubby and woody plant found throughout the Western Ghats. It also occurs in peninsular India, coramandel coast, dry plains. Plant pacifies vitiated kapha, diarrhea, fever, leucorrhea, worm infestation and general debility. In siddha system of medicine the plant was used in respiratory disorder, diuretic, diabetic, obesity. In Ayurvedha system of medicine the plant was used in cough, diuretic, tumor and as anthelmintic ( Anonymous, 1991).

## MATERIALS AND METHODS

The present study deals with Pharmacognostic studies on *Canthium parviflorum* and was conducted along with the standardized methods for quality control and assurance to provide a base line to commercialize its constituents for herbal products.

### 3.1 Collection and identification of plant material

The selected plant for the study i.e., *C. parviflorum* was collected during the period of flowering and fruiting from Amravati region during September 2013. The herbarium specimens of selected plant was prepared, identified with the help of standard floras (Cooke,

1967; Kamble and Pradhan, 1988; Naik, 1998; Almeida, 2001; Singh and Karthikeyan, 2001) and authenticated by Dr. S.P. Rothe, Professor and Head, Department of Botany, Shri Shivaji college of Arts , Science and Commerce, Akola, Maharashtra. The voucher specimens were deposited in the herbarium of Department of Botany, Vidya Bharti Mahavidyalaya, Amravati (Maharashtra) India.

**3.2 Ethno-medicinal uses**

Meanwhile the medicine men, vaidoo's and people from tribal communities of Melghat forest region were interviewed to investigate the ethnomedicinal importance of plant under study.

**3.3 Organoleptic evaluation**

Selected plant was collected washed 2-3 times with distilled water and separated the plant part i.e. leaves, stem and root and dried under shade. These dried plant parts materials were grinding into a powdered and packed in polythene bags until further experimentation. Organoleptic evaluation of the drug refers to the evaluation of drug by colour, order, taste, and special features including texture. It is helpful for collecting the basic information on the identity, purity and quality of material can be drown form these observations. They are of primary importance before any further testing can be carried out. Organoleptic evaluations can be done by mean of organ of sense which include the above parameter and there by define some specific characteristics of the material which can be consider as a first step towards the establishment of identity of degree of purity (Kokate *et al*.,, 2005).

**Colour**

The colour is of use in indicating the general origin of the drug i.e. material derive from aerial plant part is usually green and underground part material is devoid of green colour for proper examination the untreated sample are examined under diffused sun light.

**Odour and Taste**

To an expert odour and test of crude material are extremely sensitive criteria based on individual perception the strength of odour like weak, distinct, strong, aromatic, and fruity.

**Surface characteristics**

Texture is best examined by taking a small quantity of material and rubbing it between thumb and fore finger. It is usually rough, smooth, and granular. All this characteristics are valuable in indicating the general type of material and presence of more than one component.

### 3.4 Anatomical study

The collected fresh material of selected plants were washed 2-3 times with sterile distilled water and preserved in 3% formalin solution then used for the anatomical investigation. The transverse sections of leaves, petiole and stem were taken with the help of fine laboratory razor and observed under microscope to note details. The section proceed for double staining successively through the various solvent grade system by using 1% safranine for 5 min, 30%, 50%, and 70% alcohol grades respectively for 5 min. to remove excessive stain and proper hydrolyze the section then section were put into 0.5 % light green for 2 min. the again put into 70%, 90% and absolute alcohol for 5 min. to remove excessive stain and later passing through Xylene:Alcohol (1:3), Xylene: alcohol (1:1) and pure Xylene to hardening and clearing of section also remove air bubble. Then the sections were mountain in DPX and cover slip was put over the section and later photographed were obtained by processing the image captured using Carl Zeiss standard Universal microscope (Oberko-Chen/Wartenberg, Germany).

### 3.5 Powder microscopy

Powder microscopy shows the characters which play a major role in drug identification. The plant drug contain some basic cell type i.e. Parenchyma, collenchyma, sclerenchyama, epidermis and vascular component like xylem and phloem etc. along with special characteristics i.e. presence of starch, calcium oxalate, calcium carbonate, silica and different other cell contains. Analysis of the plant drug based on the distribution of these various cell types within different organ is important to ensure the identity and quality of herbal drugs. Powder study enables to give a picture of all tissue distribution in many plants. A little quantity of powder was taken onto a microscopic slide. 1-2 drops of 0.1% fluoroglucinol solution and a drop of conc. HCl were added, mounted it in glycerol, covered with a cover slip and observed under the microscope with 10x10 magnification and characteristic features of plant powder were recorded. Powder microscopy was carried out by using the method mentioned in Ayurvedic Pharmacopeia of India (1966).

### 3.6. Extractive Values

The procedures recommended in Ayurvedic Pharmacopeia of India (1966) were followed for calculating extractive values. Extractive values of crude drug are useful for their evaluation especially when the constituents of a crude drug cannot be readily estimated by any other mean, further these value indicate the nature of constituent present in crude drug. The

percentage of extractive values were calculated using different solvent i.e. petroleum ether, benzene, chloroform, acetone, ethanol and water. Each parts of the plant, of 5 g air dried drug coarsely powdered were macerated with 100 ml of respective solvent in a closed flask for 24 hours; it shacked frequently during 6 hours and allowed to stand for 18 hours. Then it was filter rapidly with taking precautions against loss of solvent, evaporated 25 ml of the filtrate to dryness in a tarred flat bottomed shallow dish, and dried and was weighed. The percentage of extractive values was calculated.

**3.7 Chemical behavioral analysis:** This analysis was carried out by using the standard method mentioned in Ayurvedic Pharmacopeia of India (1966). Behavior of powdered plant materials with different chemical reagents i.e. conc. $H_2SO_4$, $HNO_3$, HCl,, 10% NaOH, Iodine Solution, Ferric chloride, Potassium iodide, 1N $H_2SO_4$, $HNO_3$, HCl was observed under day light.

**3.8 Phytochemical analysis**

**3.8.1 Qualitative phytochemical analysis**

It involves testing of different classes of compounds. The methods used for detection of various phytochemicals were followed by qualitative chemical test to give general idea regarding the nature of constituents present in crude drug (Kokate, 2005; Harborne, 1998; Sadashivan and Manickam, 2005). The leaf, stem extracts of *Canthium parviflorum* were analyzed for the presence of phytoconstituents like carbohydrates, cardiac glycosides, alkaloids, flavonoids, tannin, phenolics, steroids and saponin.

**Tests for carbohydrates**

**i) Fehling's Test:** 1 ml Fehling's A solution and 1 ml of Fehling's B solution were mixed and boiled for one minute. Now the equal volume of test solution was added to the above mixture. The solution was heated in boiling water bath for 5-10 minutes. First a yellow, then brick red precipitate was observed.

**ii) Benedict's test:** Equal volumes of Benedict's reagent and test solution were mixed in a test tube. The mixture was heated in boiling water bath for 5 minutes. Solution appeared green showing the presence of reducing sugar.

**iii) Molisch's test:** Equal volumes of Molisch's reagent and test solution were mixed in a test tube. The mixture was heated in boiling water bath for 5 minutes. Appearance of violet or purple colour ring showing the presence of reducing sugar.

**Tests for proteins**

i) **Biurret Test:** To the small quantity of extract 1-2 drops of Biurret reagent was added. Formation of violet colour precipitate showed presence of proteins.

ii) **Million's Test:** To the small quantity of extract 1-2 drops of Million's reagent was added. Formation of white colour precipitate showed presence of proteins.

**Tests for Anthraquinone glycosides**

**Borntrager's Test:** To the 3ml of extract, dil. $H_2SO_4$ was added. The solution was then boiled and filtered. The filtrate was cooled and to it equal volume of benzene was added. The solution was shaken well and the organic layer was separated. Equal volume of dilute ammonia solution was added to the organic layer. The ammonia layer turned pink showing the presence of glycosides.

**Tests for Cardiac glycosides**

**Keller- Killiani Test:** To the 5ml of extract, 1ml of conc. $H_2SO_4$, 2ml of Glacial acetic acid and 1 drop of $FeCl_3$ solution was added. Appearance of Brown ring shows the presence of cardiac glycosides.

**Test for steroids**

**Salkowski Test:** To 2 ml of extract, 2 ml of chloroform and 2 ml of conc. $H_2SO_4$ was added. The solution was shaken well. As a result chloroform layer turned red and acid layer showed greenish yellow fluorescence.

**Tests for alkaloids**

i) **Hager's Test:** To the 2-3 ml of filtrate, few drops of dil. HCl and Hager's reagent was added and shake well. Yellow precipitate was formed showing the presence of alkaloids.

ii) **Mayer's Test:** To the 2-3 ml of filtrate, few drops of dil. HCl and Mayer's reagent was added and shake well. Formation of yellow precipitate showed the presence of alkaloids.

iii) **Dragendroff's Test:** To the 2-3 ml of filtrate, few drops of dil. HCl and Dragendroff's reagent was added and shake well. Formation of orange-brown precipitate showed the presence of alkaloids.

**Tests for flavonoids**

**Lead Acetate Test:** To the small quantity of extract lead acetate solution was added. Formation of yellow precipitate showed the presence of flavonoids.

**Tests for Tannins and Phenolics compound**

i) **$FeCl_3$ Solution Test:** On addition of 5% $FeCl_3$ solution to the extract, deep blue black colour appeared.

ii) **Lead Acetate Test:** On addition of lead acetate solution to the extract white precipitate appeared.

**Test for Saponin**

**Foam Test:** To 1ml extract 20ml distilled water was added and shakes well in measuring cylinder for 15 min. Then 1cm layer of foam was formed.

**3.8.2 Crude quantification of the major phytoconstituent**

The crude quantifications of major phytochemicals were done using precipitation method. Each sample was analyzed in triplicates. Only alkaloids, flavonoids and saponin from the different parts of the plant under study were quantified.

**1) Alkaloid**

5 gm of sample was weighed in 250 ml beaker and 200 ml 20% acetic acid in ethanol was added and covered to stand for about 4 hrs. This was filtered and extract was concentrated using water bath to $1/4^{th}$ of original volume. Concentrated Ammonium hydroxide was added drop wise to the extract till its complete precipitation. The whole solution was allowed to settle and precipitate was collected and weighed.

**2) Flavonoids**

10 gm of sample was extracted repeatedly in 100 ml of 80% aqueous methanol at room temperature. The whole solution was filtered through Whatman paper no. 42. The filtrate then transferred to a crucible and evaporated to dryness over a water bath and weighed.

**3) Saponin**

10 gm of plant powder was taken in 200 ml 20% ethanol to make a suspension. This was heated for about 4 hrs over hot water bath ($55^oC$) continuous stirring. The mixture was filtered and the residue was re-extracted with 200 ml 20% ethanol. The combined extract was reduced to $1/10^{th}$ of the original volume. The concentrate was taken into 250 ml separating funnel, to this added 20 ml diethyl ether and shaken vigorously. The aqueous layer was recovered while the ether layer was discarded. This purification process was repeated for 2-3 times. Then 60 ml n-butanol was added to it. The combined solution was then washed twice with 10 ml 5% aqueous sodium hydroxide. The remnant was heated in a water bath for

complete evaporation and dried. This dried content was calculated as Saponin percentage in a sample.

### 3.9 Chromatographic analysis

The chromatographical study was carried out by using the standard procedure described by Harborne, (1998); Mukharjee, (2002); Sadashivan & Manickam, (2005).

### Thin Layer Chromatography (TLC)

Thin layer chromatography (TLC) is an important analytical tool in the separation, identification and estimation of different class of natural product. Thin layer chromatography is performed on an aluminum foil, 60 F254 which is coated with a thin layer of adsorbent material, usually silica gel. After the sample has been applied on the plate, a solvent or solvent mixture is drawn up the plate via capillary action. Because different analyses ascend the TLC plate at different rates, separation is achieved.

The leaf, stem and root methanol extracts of the *Canthium parviflorum* were subjected to thin layer chromatographic analysis to find out the presence of number of chemical constituents. Only alkaloid and flavonoids TLC fingerprints were carried out. The details of procedure are as following**.**

The Methanolic extracts were applied as a single spot in a row centre of chromo plate, about 2 cm from the edge, by using capillary tubes. The TLC plate containing the sample spot was placed at $45^0$ angles in the development chamber covering the bottom of the plate by the solvent up to nearly 1 cm. The solvent front was marked and the plate was finally allowed to dry. The colored substances were visual on the chromatogram. Colourless components were detected by using visualizing agent, iodine vapors. The qualitative evaluation of the plate was done by determining the migrating behavior of the separated substances given in the form of $R_f$ value.

$$\text{Resolution factor } (\mathbf{R_f}) = \frac{\text{Distance traveled by the solute from the origin}}{\text{Distance traveled by the solvent from the origin}}$$

## OBSERVATION AND RESULTS

The present study deals with the pharmacognostic studies on *Canthium parviflorum* . Standardization and quality control of plant, is of growing concern over ensuring purity of raw material before processing. Yet alternative medicines based on plant substances are

extremely popular, even though their safety and efficacy have not been scientifically proven. Now-a-day's routine pharmacognosy has changed demanding interdisciplinary research. Various pharmacognostic standards like botanical description, microscopy, extractive values, microscopic characteristics of powder, preliminary and quantitative phytochemical study, TLC analysis of bioactive compounds of the plant could be useful for the compilation of a suitable monograph for its proper identification.

**Classification**

| | | |
|---|---|---|
| Division | : | Phenerogams |
| Class | : | Gamopetalae |
| Order | : | Gentianales |
| Family | : | Rubiaceae |
| Genus | : | *Canthium* |
| Species | : | *parviflorum* |

**4.1 Morphology**

The Rubiaceae are trees, shrubs or infrequently herbs compirsing about 450 genera and 6500 species, including some lianous forms. The leaves are simple and usually entire, and are opposite or sometimes whorled; stipules are present and interpetiolate. The flowers are nearly always bisexual and actinomormphic, often heterostylous, and usually are in cymose inflorescences. The calyx is somewhat reduced and 4-5 lobes or sometimes the lobes are absolute or rarely one of them greatly expanded and brightly colour. The sympetalous corolla is mostly 4-5 lobed, occasionally with 3 or upto 10 lobes. The androecium consists of as many stamens as corolla lobes and is adnate to the corolla tube or epigynous zone, alternate with the lobes. The gynoecium consists of a single compound pistil of 2 or seldom more carpels, a single style, and a nearly always inferior ovary with the number of locules.

**4.2 Ethno-medicinal uses**

*Canthium parviflorum* (Rubiaceae), a medicinal plant, has been widely used in Ayurvedha in conditions of *kapha*, diarrhea, strangury, fever, leucorrhoea, intestinal worms, and general debility. This plant has been traditionally known to treat snakebite in some villages of Shimoga district in Karnataka, India and to possess wound-healing property. The present study focused on determining the antioxidant ability of solvent extracts of *C. parviflorum.*

The roots of this plant are traditionally used by the tribes of Orissa in treatment of swelling of neck and fruits in headache. This plant is reported for its pharmacological uses as an

astringent, anthelmintic, antidysentric, antispasmodic and as a diuretic. From the ethno medical survey we came to know that many people from Vellore district are using the plant and its various parts traditionally practicing widely throughout those areas for various infections. Hence the whole plant was utilized for our present evaluation to study about the presence of various phytoconstituent and its concomitant activity.

Plant pacifies vitiated kapha, diarrhea, fever, leucorrhea, worm infestation and general debility. In siddha system of medicine the plant was used in respiratory disorder, diuretic, diabetic, obesity. In Ayurvedha system of medicine the plant was used in cough, diuretic, tumor and as anthelmintic. An antioxidant, wound healing activity and antitumor acitivity were reported. D-mannitol, phenolic acid, phenolic compounds, carbohydrates, proteins were found from *Canthium parviflorum. (*Sathish kumar et al 2008).

Pharmacological activities such as antimicrobial, antioxidant, antidiabetic, wound healing, diuretic, anti-inflammatory, antinociceptive, antitumor and antipyretic from various species of *Canthium* has been reported. (Elayaraja et al 2007).

**4.3: Table: Organoleptic evaluation of powder of *Canthium parviflorum***

| S.N. | Particulars | Plant parts | |
|---|---|---|---|
| | | Leaves | Stem |
| 1 | Colour of Powder | Green | Creamish |
| 2 | Odour | Mild | Mild |
| 3 | Taste | Bitter | Tasteless |
| 4 | Texture | Smooth | Rough |

**4.4 Anatomical study of *Canthium parviflorum***

**4.4.1 T.S of leaf**

The T.S. of leaf passing through the mid rib projects strongly at lower side and elevated at upper side and lamina is dorsiventral. The leaf has mid rib and lateral veins. The epidermis is thin epidermis is lies a layer of palisade cells. There is presence of parenchymatous cell with vascular bundles. Canals are present within it and oil droplets are also detected within it.

**4.4.2 T.S of Stem**

The T.S. of stem shows cuticle followed by the epidermis. There is presence of vascular bundles after that there is a parenchymatous cells showed. In the cortical bundles absent, medullary bundles are absent. The anomalous secondary thickening when present, via concentric cambia. Primary medullary rays narrow.

The vessels are small, typically numerous, solitary or radially paired. The vessels end walls exclusively simple in mature wood. The fibres w ithout spiral thickening. The secondary phloem not stratified. The wood not storied.

### 4.5 Powder microscopy

**Table: Powder study of *C. parviflorum***

| S. No. | Plant part | Observe in powder study |
|---|---|---|
| 1 | Leaf | Starch grain, epidermal cell, calcium oxalate crystals, cortical cells, parenchymatous cells. |
| 2 | Stem | Starch grain, Cork cell, collenchymatous cells, sclerenchymatous cells, pitted vessels, tracheid, and fibres. |

### 4.6 Analytical study of *C. parviflorum*.

#### 4.6.1 Extractive values

**Table: Extractive values of *C. parviflorum*.**

| S.N. | Parameter studied | Leaf (% w/w) | Stem (% w/w) |
|---|---|---|---|
| 1 | Petroleum ether | 2.6 % | 2.9 % |
| 2 | Benzene | 7.1 % | 8.0 % |
| 3 | Chloroform | 6.9 % | 4.9 % |
| 4 | Acetone | 8.12 % | 13.15 % |
| 5 | Ethanol | 16.23 % | 15.88 % |
| 6 | Water | 13.22 % | 17.40 |

### 4.7 Chemical behavioral analysis

**Table: Behavioral characteristics of powder of *C. parviflorum* with different chemical reagent under visible light.**

| S. No | Powder + Reagent used | Stem | Leaf |
|---|---|---|---|
| 1 | Powder as such | Creamish | Green |
| 2 | Powder + Conc. $H_2SO_4$ | Dark Green | Pale Green |
| 3 | Powder + Conc. $HNO_3$ | Orange | Light Brown |
| 4 | Powder + Conc. HCl | Green | Light Green |
| 5 | Powder + 10% NaOH | Light Brown | Light Green |
| 6 | Powder + Iodine solution | Brown | Light Green |
| 7 | Powder + 5% Ferric Chloride | Brown | Light Green |
| 8 | Powder + KI | Brown | Dark Green |
| 9 | Powder+ Ethyl acetate | Pale Yellow | Light Green |

### 4.8 Phytochemical analysis

### 4.8.1 Qualitative phytochemical screening

**Table : Qualitative Phytochemical screening of Leaf of *Canthium parviflorum***

| S. N. | Constituents | Chemical Tests | Extracts | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | P. E. | B | C | A | E | W |
| 1 | Alkaloids | Mayer's Test | -- | -- | -- | -- | -- | -- |
| | | Dragendroff's | -- | -- | -- | -- | -- | -- |
| 2 | Carbohydrates & Glycosides | Fehling's Test | -- | -- | -- | -- | -- | -- |
| | | Benedict's test | + | + | + | + | + | + |
| | | Molisch's Test | + | + | + | + | + | + |
| 3 | Steroids | Salkowski Test | -- | -- | -- | + | -- | -- |
| 4 | Saponin | Foam Test | + | + | + | + | + | + |
| 5 | Phenolics & Tannin | $FeCl_3$ Sol. Test | -- | -- | -- | -- | -- | -- |
| | | Lead Acetate Test | + | + | + | -- | -- | -- |
| 6 | Proteins | Biuret Test | -- | -- | -- | -- | -- | -- |
| | | Million's Test | + | + | + | -- | -- | -- |
| 7 | Anthraquinone glycosides | Borntrager's Test | -- | -- | -- | -- | -- | -- |
| 8 | Cardiac glycosides | Keller-Killiani Test | + | -- | -- | -- | -- | -- |
| 9 | Flavonoids | Lead Acetate Test | + | -- | + | -- | + | + |

{Where, P.E.= Petroleum ether, B= Benzene, C= Chloroform, A= Acetone, E= Ethanol and W= Water.}

**Table: Qualitative Phytochemical screening of stem of *Canthium parviflorum*.**

| S. N. | Constituents | Chemical Tests | Extracts | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | P. E. | B | C | A | E | W |
| 1 | Alkaloids | Mayer's Test | -- | -- | -- | + | + | -- |
| | | Dragendroff's Test | -- | -- | -- | -- | + | -- |
| 2 | Carbohydrates & Glycosides | Fehling's Test | -- | -- | + | -- | -- | -- |
| | | Benedict's test | + | + | + | + | + | + |
| | | Molisch's Test | -- | -- | -- | -- | -- | -- |
| 3 | Steroids | Salkowski Test | + | -- | + | -- | + | -- |
| 4 | Saponin | Foam Test | + | + | + | + | + | + |
| 5 | Phenolics & Tannin | $FeCl_3$ Sol. Test | -- | -- | -- | -- | -- | -- |
| | | Lead Acetate Test | -- | -- | -- | + | + | + |
| 6 | Proteins | Biuret Test | -- | -- | -- | -- | -- | -- |
| | | Million's Test | -- | -- | -- | -- | -- | -- |
| 7 | Anthraquinone glycosides | Borntrager's Test | -- | -- | -- | -- | -- | -- |
| 8 | Cardiac glycosides | Keller-Killiani Test | + | -- | + | + | + | -- |
| 9 | Flavonoids | Lead Acetate Test | -- | -- | -- | + | + | -- |

{Where, P.E.= Petroleum ether, B= Benzene, C= Chloroform, A= Acetone, E= Ethanol and W= Water.}

### 4.8.2 Quantitative phytochemical analysis

**Table : Quantitative phytochemical screening of *Canthium parviflorum***

| S. no | Phytochemical | Leaf (g/100g) | Stem (g/100g) |
|---|---|---|---|
| 1 | Alkaloids | 85.7± 0.10 | 75.7 ± 0.24 |
| 2 | Flavonoids | 80.45 ± 0.12 | 88.05 ± 0.02 |
| 3 | Saponin | 41.35 ± 0.04 | 15.98± 0.06 |

Whereas, results are depicted as mean ± SD of three determinants.

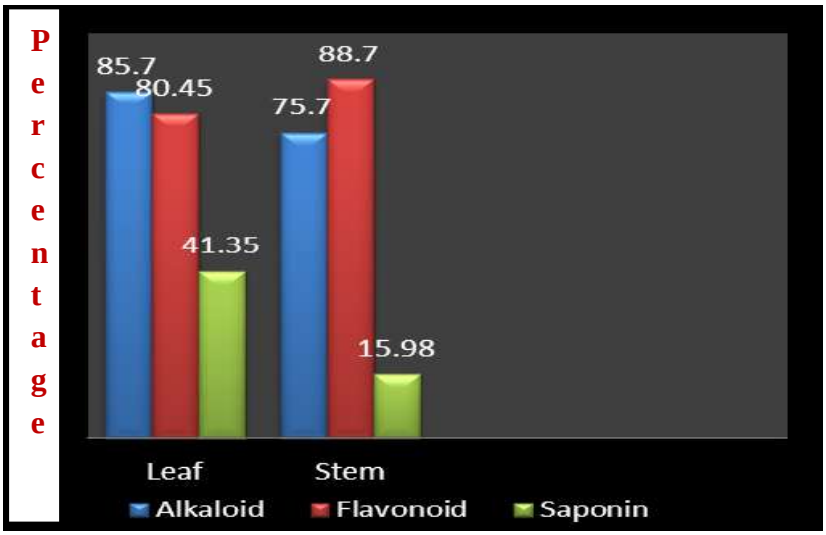



**Figure 1: Quantitative phytochemical Screening of *Canthium parviflorum***

### 4.9 Chromatographic analysis

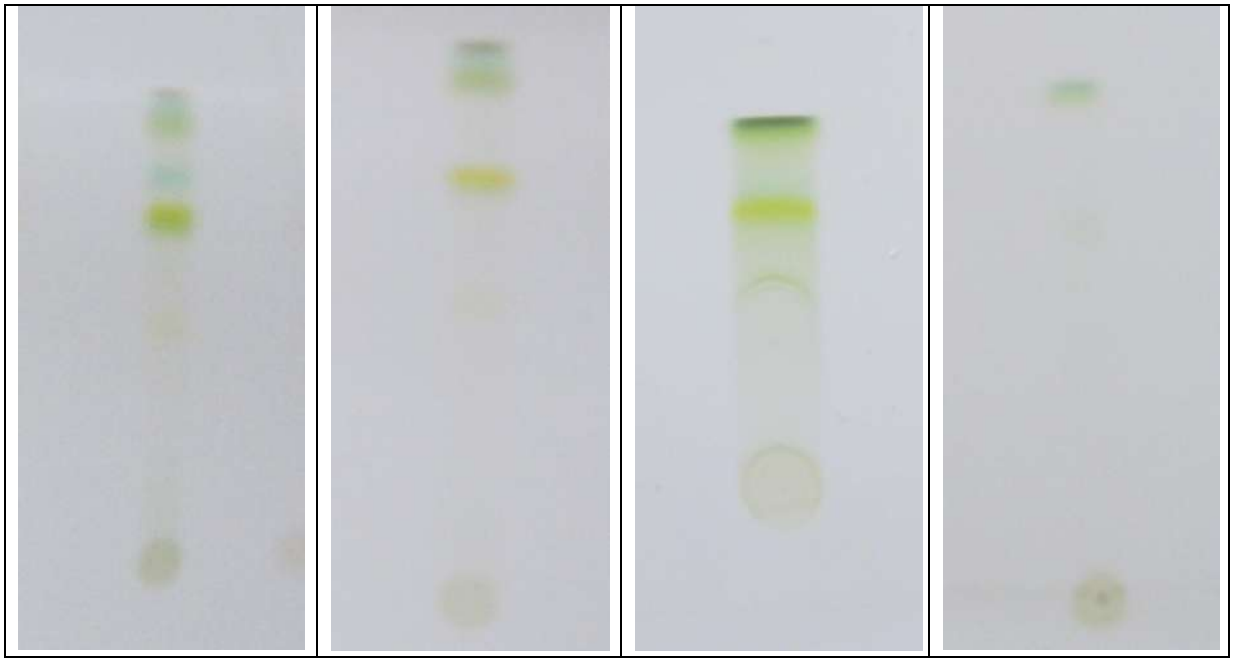
### TLC Profile

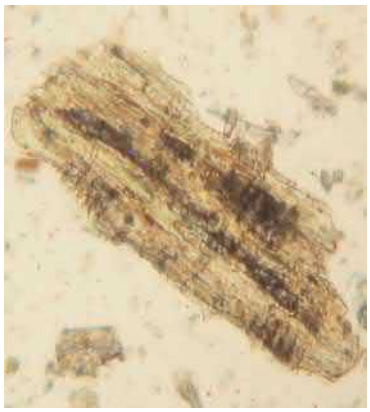
The TLC of methanolic extract of samples were carried out on silica gel 60F254 plate.

**Table : TLC profile of methanolic extract of *C. parviflorum*.**

| S.no | Plant parts | Chemical constituents | Solvent system | Rf Values | Total Bands | Spray reagents |
|---|---|---|---|---|---|---|
| 1 | Leaf | Alkaloids | Toluene : Acetone : Ethanol : Ammonia Solution (40:40:6:2) | 0.30,0.28,0.26 | 3 | Dragendroff's |
| | | Flavonoids | Chloroform : Ethyl acetate (60:40) | 0.35,0.3,0.29 | 3 | 5% $FeCl_3$ |
| 2 | Stem | Alkaloids | Toluene : Acetone : Ethanol : Ammonia Solution (40:40:6:2) | 0.3,0.29 | 2 | Dragendroff's |
| | | Flavonoids | Chloroform : Ethyl acetate (60:40) | 0.37 | 1 | 5% $FeCl_3$ |

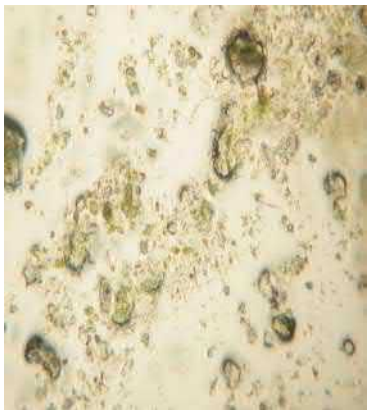
**PHOTO PLATES**



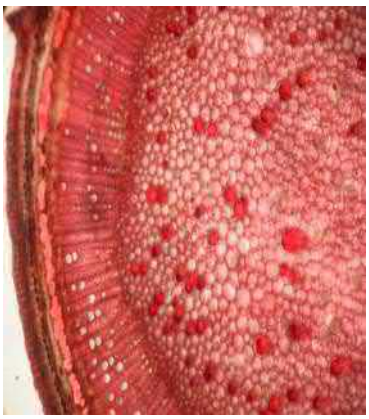
**Cork Cells (Stem)**

**Fibres (Stem)**

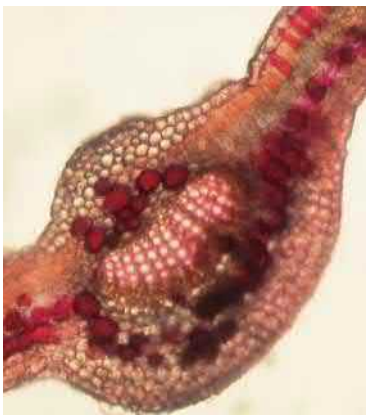


**Starch Grains (Leaf)**

**Starch Grains (Stem)**



**T.S. of Stem**



**T.S. of Leaf**

**DISCUSSION**

The commonly found phytochemicals in plants are alkaloids, flavonoids, tannins and phenols, steroids and terpenoids, saponins, carbohydrates, glycosides, proteins and amino acids. Therefore the present study involves a preliminary screening of the phytochemicals in leaf and stem extracts of *Canthium parviflorum*. Although in traditional medicine, water is used as solvent for plant extraction but present studies have shown that organic solvent extracts show greater biological activity than the aqueous extract. Hence, five solvents were used, i.e., petroleum ether, benzene, chloroform, acetone, ethanol and also water as the sixth solvent. The extracts of both the plant parts were used for the analysis to identify the best solvent for phytochemical extraction. The phytochemical analysis was done in three phases, viz; qualitative, quantitative, chromatographic techniques.

The phytochemical screening of leaves and stem of *Canthium parviflorum* showed, primary and secondary metabolites like Carbohydrates, Proteins, Anthraquinone glycosides, cardiac glycosides, Coumarins, Quinone, Steriods, Alkaloids, Flavonoids, Saponin, Tannins and Phenolic compounds.

Alkaloid is present in leaf /stem of *Canthium parviflorum*. Steroids present in stem but absent in leaf. Saponin is present in both part of this plant. Phenolic compound are absent in both part of the plant but tannins are present in leaf as well as stem. The plant parts yield alkaloids, saponin and flavonoids, which are used in various antibiotics for treating common pathogenic strains. Anthraquinone glycosides are absent in both the parts, but Cardiac glycosides are present. Flavonoids, Quinone and Coumarins are also present in leaf and stem of the *Canthium parviflorum*. The results obtained in this study thus suggest the identified phytochemical compounds may be the bioactive constituents and these plants are proving to be an increasingly valuable reservoir of bioactive compounds of substantial medicinal merit.

TLC fingerprints of methanolic extract of *C. parviflorum* were developed by using solvent system Toluene: Acetone: Ethanol: Ammonia Solution (40:40:6:2) by using Dragendroff's as a spraying reagent for the alkaloid. Whereas, TLC profiles were recorded for flavonoids in Methanolic extract by using solvent system Chloroform: Ethyl acetate (60:40) using FeCl3 as a spraying reagent. This chromatographic investigation revealed that *Canthium parviflorum* leaf and stem contain different types of alkaloids and flavonoids which correspond with results of phytochemical screening. So, the present study have clearly revealed that, the plant under study will be beneficial to the researchers who are in this field for further pharmaceutical studies and therapeutic uses of *C. parviflorum* for total drug evaluation.

## CONCLUSION

The evidence presented in this study has showed that *Canthium parviflorum* has great potential to be integrated into conventional medical practice for the treatment of various disease complications. Development and research on *Canthium parviflorum* through modern pharmaceutical technologies and analytical protocols is essential to assure its quality, safety and efficacy.

The present study has clearly revealed that, it will be beneficial to establish or to start pharmaceutical industry for the production of herbal drugs of purity, safety and high therapeutic values with more commercial profits. The present study also provides an opportunity to investigate and establish the status of *Canthium parviflorum* will find their use for the utilization in different ailments. It is anticipated that this work will provide some valuable information for ongoing explorations of this fascinating species and its phytochemicals. This pharmacognostic screening will be very useful in future product development also, particularly for the life style diseases and disorders.

Future research on *Canthium parviflorum* would not only provide much needed knowledge on this popular herbal medicine, but would also offer a noticeable socio-economic impact in turning a common weed into beneficial nutraceutical and pharmaceutical products.

## AKNOWLEDGEMENTS

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There are many other landmarks created by the diasporic literature. It has helped to understand and form potentials and core competencies. Access made available to educational, social, professional opportunities and political empowerment. It has made possible the removal of all kinds of limitations and barriers- traditional, cultural, linguistic etc. It ignites and synergies common and shared values in addition to coalition building among the social and political Diaspora. In addition to strengthening, it also enhances ties and bonds with others countries. To mention a few are the neighbouring countries including Pakistan, China, Bangladesh and other Asian Countries. Diaspora literature also helps countries to bring about a strategic partnership based on prosperity, security and commitment to freedom and peace. These are actually a very few features to name. If planned and monitored positively, Diaspora literature can also aid to fight larger evils such as terrorism, drug trafficking, environment degradation, combating the spread of contagious disease and actually fighting many other common political and social hurdles. Looking at it optimistically, Diaspora literature also helps in creating good will, a cordial relationship and in spreading values, virtues and universal peace.

Shri A. B. Vajpayee speaking on his expectations from the Pravasi Bharatis i.e. N.R.I's said

"What we seek is a broader relationship, in fact a partnership among all children of Mother India, so that our country can emerge as a major global player. We value the role of people of Indian origin as unofficial ambassadors providing a link between India and the rest of the world". No doubt, many of the Indians have left their motherland to seek anchor in various other countries. The reason for this movement ranges from indentured labour to seeking better prospects. No matter where we all are scattered across the globe, we are brought closer through the medium of films, songs, concerts and of course the Diaspora literature. This literature has helped in providing a link between India and the rest of the world. And this coming together and closer has helped creating tremendous self confidence with a combative spirit. The awareness that they are articulate, artistic, talented, creative, practical and adaptable has also dawned upon them. In the past, the Indians were intellectually fed on the thoughts of Dickens, Scott and the likes. Today, people all over the world are being nourished by the writers of the Indian Diaspora namely V.S. Naipaul, Rushdie, Mistry, Vikram Seth, Mukherjee, Vassanji etc. The European voyagers, travelers, traders and the orientalists rediscovered the cosmopolitan culture of India. The writers of the Indian Diaspora, through their literary contributions have greatly enriched the English literature. They have been aiming at re-inventing India through the rhythms of ancient legends, the cadences of mythology, the complexities of another civilization, cultural assimilation and nostalgia. They dive deep into the realms of imaginations and the ocean of memory to paint something quite different and distinct from that portrayed by fellow novelists. The writers of the Indian Diaspora write about India painting the vastness and the complexities of the home country which contains everything in multitudes – multiple truths, multiple crisis, multiple realities and this diversity is portrayed for the world wide reading public.

**Conclusion**

Diaspora is therefore, a scattering of the seed in the wind, the fruits of which are a new creation and a fight to survive. Every Diaspora movement holds a historical significance, as it carries within itself the kernel of the nations' history. Diaspora is a journey towards self-realization, self-recognition, self-knowledge and self-definition. There is an element of creativity present in the Diaspora writings and this creation stands as a compensation for the many losses suffered.

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## THE TRIALS OF BROTHER JERO OF WOLE SOYINKA

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**Abstract**

This research paper focuses on the social ills prevalent in the African societies with the view of correcting them in order to make the contemporary society a better place to live. Drama is called as a mirror of a society. By using drama as an effective tool, the renowned Nigerian writer Wole Soyinka depicts the socio-economic evils prevailing

in the society. These evils are being satirized to bring about a social reformation. Through this drama a sociological approach is employed by the play Wright in order to bring out the religious hypocrisy, moral decadence, and marital imbalance in the society. This research paper brings out the evils inherent in African social system and how the dramatist makes an effective use of **Satire** as a corrective measure social change especially in the prevailing society.

Soyinka captures worldwide issues by using a West African setting .The satirical message in the text is conveyed through redialing of the vices and follies of the contemporary Nigerian society via religious institution. His fictive output belongs to the Horatian mode of satire which ridicules the follies with the intention of reformation in the society.

Through satire and humor, the aberrant and corrupt nature of our religious leaders are exposed. Moral decadence, prevalent in the society is also dealt with. The text centers around a bar beach prophet Jero who pretends to be a true prophet but in the actual sense, he is cheat , a rogue, and in fact the devil's incarnate. As the play unfolds Soyinka presents prophet Jero as a representative of hypocritical religious person. He presents him in a humorous and comical way that we see through the front of the holy hermit which he puts on for the benefit of his deluded worshippers.

The wrong mentality or orientation of some so called prophets is brought to the core. Prophet hood ought to be a call to selfless and sacrificial living towards God and mankind. However prophets like Jero don't have this mental set-up. For Jero it's a business, a profit making venture, the easiest way to meet one's material needs. In one word its a trade, just as he calls it. To present it in his own words, Jero says, "I am glad here before any customers- I mean worshippers well, customers if you like. I always get that feeling every morning that I am a shopkeeper waiting for customers," (p.20)

There is a clear picture about how Brother Jero views the divine call, his prophethood. This is not far- fetched from what is obtainable in the contemporary Nigerian society. A lot of pastors or men of God have this mentality just like Jero. Since their orientation is wrong, there is bound to be the abuse of the religion. This is exposed and justified by Soyinka.

Furthermore, the character or attitude of some religious leaders negates what they preach. The exploitative nature of prophet Jero is exposed: how he chats on other to achieve his selfish interest. One of the victims of this bad attitude of his is the old prophet, prophet Jero grew up under his tutelage. He pretends to be working together with his master to acquire a piece of land. Again, Brother Jero's exploitative and pretentious attitude is seen in his relationship with his worshippers whom he calls customers. Brother Jero likes keeping his members unhappy. He believes that as long as men are unhappy and dissatisfied, they will seek the prophet.

Prophet Jero keeps his worshipers in bondage which is contradictory to the message of freedom that Christianity as a religion spells. The whole idea of keeping people dissatisfied and helpless is baseless in Christian ethics. It is simply exploitation in its highest order.

Chime is another victim of Brother Jero's exploitative character. Soyinka satirizes religious leaders and how they work on the ignorance or gullibility of their worshippers to achieve self – convenience and accumulate wealth.

Amope who is the wife of Chime, doubles as Brother Jero's creditor. Unknowing to prophet Jero, he discourages Chime from beating his wife in a bid to keep him dissatisfied.

Jero's weakness is not a hidden thing. It is obvious that he has passion for women. We begin to wonder what is divine in lustfully looking at a woman who has just had her bath. Prophet Jero's divine transformation is not achieved from studying the world of God but from lusting after a woman. After all a woman is his weakness. In another instance, we see prophet Jero being carried away with a woman's naked wombs instead of blessing the water for his worshippers. Many religious leaders who profess to be holy are the false victims of one type of weakness or the other. We hear of great men of God having extra marital affairs. This is highly wrong not only morally but also religiously. A man of God is supposed to be a virtuous, morally upgraded as he is works as a Torch – Bearer for others in Justifying the Ways of God to Men.

There is a deliberate commercialization of religion by the so called custodians of sacred institution. In this case it is not only Christianity; Brother Jero represents, religious practices observed all over the world.

Soyinka very boldly satirizes such ill practices existing on a large scale in Nigerian society."The Trials of Brother Jero" is a satiric comedy which aims of correcting the evil in leading social institutions from society.

**Conclusion**

An attempt has been made to examine the social issues existing in the contemporary Nigerian society by Wole Soyinka. The playwright has made use of the popular technique of satire in order to bring about an re-orientation of the Nigeria citizens.

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# R.K. NARAYAN'S 'THE FINANCIAL EXPERT' A PORTRAIT OF SOCIAL AND FAMILIAL INDIAN MIDDLE CLASS

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**Abstract**

Primarily, R.K. Narayan is a writer of social and familial novels. His novels revolve round the family and the society, the society in which he inhabites. His remarkable grasp of the social structure and his concern towards middle class life enables him to delineate Indian middle class social life with perfection. "His dispassionate social detachment suggests a personal endeavour to attain an equation with life to overcome and rationalize the profound and unmitigated loneliness of life. He does not keep only to surface reality. His vision is truly comprehensive." Narayan's social vision is marked by a greater degree of affirmation and optimism. "It has been cliche to regard Narayan as a delineator of middleclass people. Since the typical middle-class milieu constitutes the matrix of all the Malgudi novels. Its significance may hardly be exaggerated."

The middle class provides him desiered material to dramatize his conception of humanity and the notion of man's existence. What in fact the middle class milieu brings into light is that although Narayan is "fully immersed in his material", and his confined to his South India middle class, he seems to have acquired the representative in his regional world and thus, in the final analysis, seems to touch the chord of universality, dealing with the tale of the common man." It is through the human spectacle of the middle class that Narayan seems to the dramatize theatre of the absurd. The typology also notes the reflection of the novelist autobiographical elements, the clear indication of his sacrosanct tradition and his faith in the internal spirit of India, through the middle class portrayal.

Right from *Swami and Friends* Narayan has peopled his fiction with the Indian middle class- a class close to him as palm skin. "His strict confinement to the portrayal of the middle class milieu often finds Narayan bracketed with Jane Austen (in the context of her 'two inch ivory tower')". Significantly, all typological frames underline the average and the ordinary middle class protagonist as he plays the central consciousness and dramatizes the theme of illusion versus reality. In fact, the middle class portrayal seems to have become Narayan's strategy to project several issues.

Fundamentally, Narayan's fiction is Indian in the sense that they explicitly exhibit the social pattern of life existing in India. *The Financial Expert*, is an excellent example of his keen ears and observation of Indian middle class social life. Its protagonist Morgayya, rises before us from a very humble position to be a very big banking magnet. We are not only witness of his rise but also beholder of his down fall. Accumulation of money and more money, by hook and by crook is his only obsession. Lakshmi the Goddess of

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# PORTRAYAL OF BILLY AS DISTRESSED SELF IN ARUN JOSHI'S 'THE STRANGE CASE OF BILLY BISWAS'

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**Abstract**

*In the modern era a man is always under the pressure of social taboo to maintain dignity and social prestige. As a result his inner urge is suppressed and self distressed is created in his mind. Arun Joshi is one of the distinguished Indian novelists who explore the innermost depths of human psyche and the chaotic underworld of human mind through their novels. All his protagonists are mostly men for whom self distressed is the sole natural condition.In all his novels Arun Joshi is more concerned with thought, emotion, sensation than with action. His protagonists emotional traumas sometimes lead to violent death in the end of the novel. A certain awareness of man's restlessness and the consequential estrangement from the society and self is the keynote of Arun Joshi's unique vision of predicament of modern man in contemporary Indian English fiction. According to G.S. Amur ''his novels take us to the heart of darkness- one of the most favourite metaphores is the Labyrinth - but he is not a prophet of despair. All his novels hold out promise of regeneration and redemption''.[1] In research paper an attempt has been made to explore distressed of the modern man in Arun Joshi's novel '' The Strange Case Of Billy Biswas'' on the basis of the portrayal of characters and situations. The strange Case of Billy Biswas is a story of inner psyche of the protagonist Billy who is unable to survive in civilized façade of modern life. The story is unfolded from the witness narrator point of view. The first part of the novel gives us the glimpses of the restlessness of Billy's soul in the midst of the upper class Indian society, which is lost in superficialities of life.*

The narrator Romesh Sahai is a friend of Billy. Despite being a concerned friend in Billy's life, Rimi finds Billy's character to be enigma. Billy has an impressive though a strange personality. What one strikes about him not only his aristocratic background but also his elegant demeanor: '' he was one of these rare men who have poise without that pose''.[2] One would never fail to notice'' the strong, rather British accent of his speech'' [3]with ''words had a cadence, a compulsive quality engaged you in spite of yourself. ''[4]

He has a strong fascination for the tribal life. Its beginning when he is fourteen years old at Bhubaneswar. His visit to the sculpture at Konark sun temple urged him on to think of his own identity. He is fascinated by the imagery of the sculpture. For the first time he feels that the true beauty of imagination is appreciated only by the Adivasis. Also that spirit may be very old, older than human existence itself, yet the knowledge of truth is embedded with the tribal behind dark in securable faces. His visits to the tribal village with the chauffer proves to be a turning point in the life of Billy Biswas as he is for the first time ,overwhelmed by erotic energy in the tone and tune of the folk music while dancing and celebrating life. The young Billy feels: Something has gone wrong with my life. This is where I belong. This is what I always dreamt of.

His interest in primitive is continues even when he goes to America for further study. Despite his father's unwillingness he studies anthropology. During his stay in America he prefers to live in Harlem, the black ghetto of America. He thinks it '' the most human place.''[5]White America is too much civilised for him. It is his urge for the primitive that he plays the pair of banjo drums creating a strange hush on the scene in a music party in George's apartment. Billy's friend Tuula, the Swedish researcher and Romi, the narrator '' who had any clue to what went on it dark, inscrutable, unsmiling eyes of Bimal Biswas.''[6] Tula informs Romi that ''a great force urkraft a----------a primitive force'' [7]lying suppressed in the personality of Bimal Biswas.Billy stays in America for a long but does not suffer much except some passing spell of loneliness. He is not bothered about cultural alienation, what teases him is the superficialities of a grossly materialistic civilization. The elite foreign society is not congenial to the quest of identity for Billy and he returns to India .During his stay in India he finds Delhi is not different from American society. Further he feels that all the rich societies all over the world are superficial. His inherent

protest against mechanized dehumanized civilized world i reflected in his letters to Tuula.

He writes: 'I see a roomful of finely dressed men and women seated on the downy sofas and while I am looking at them under my very nose , they turn into a kennelof dogs yawning ( their large teeth showing) or snuggling against each other or holding whisky glasses in their furred paws''[8]

The imagery of dogs with large teeth and furred paws reveals the hatred of Billy and the character he thinks they bear. He has no love for the modern civilization. Billy feels that civilization is a monster. It is not civilization ,but degradation'' . He says :'' I some times wonder whether civilization is anything more than the making and spending money.''[9]

Due to his search for the viable alternatives he gets a job as a lecture at Delhi University. In order to study the life of primitive communities in hills and forests he undertakes numerous expeditions. But he remains very upset by his hallucinations. They reduce him to such panic condition. As a result he feels marriage is only remedy to stop them. He marries Meena Chatterjee , a sensuous ,gorgeous and good looking woman.

With passing of days in conjugal life , Billy realizes his blunder that hurried marriage is not a solution for his perennial problems. His wife fails to satisfy his inner urge and their conjugal life turns to be the most precarious of battlefield . For Meena ''Billy is getting stranger and stranger with every passing day ''.[10]She is unable to give him peace and satisfaction that he badly requires. Billy hates the worldly pleasures, but Meena is fond of money, market and the materialism, supposedly true identity of the elite society.As a result Billy starts getting estranged from his wife and family.

Whatever may be the psychological reason for the separation between Meena and Billy, it can be aptly concluded that the step Billy taken to start his new identity is a complete failure. Arun Joshi reveals the fact here that his protagonists is not an abnormal person. Rather he also takes efforts to integrate with the society and find out the meaning to life by establishing a family. But Billy is destined by his very nature for some other person and places .It can be concluded that Billy`s character is the character of destiny.

Marriage fiasco has the negative impact upon psyche and personality of Billy. He feels in civilised society like pinned down there like a dead butterfly. He starts to take wine and to lie and sham. Even in his family, he feels alone and alienated like Camus`s outsider.

His trauma is reflected in a letter written to Tuula : '' It seems , my dear Tuula that we are softly losing what is known as one's grip on life .Why else this constant blurring of reality ? Who am I? Who are my parents? My wife? my child ? At times I look at them, sitting at the dinner table, and for a passing moment I cannot decide who they are or what acident of creation has brought us together''.[11]

The aforementioned statements make it amply clear that he is in conflict with his identity. His exploration of the real inner being makes him an existentialist being, estranged and alienated. He never feels himself at home because one thing is clear to him that he is not the man of civilized society and his real destination is some other places. His health fails and his intellectual understanding starts declining. It is during his degradation he seduces Rima Kaul, an innocent girl in Bombay . The seduction of Rima Kaul is the evidence of his estrangement not only from his family and society but also from his true self. He comes extremely irritable with his behavior. Seduction of Rima Kaul is the last warning signal to Billy which gives him a preview of the corrupting force which awaits him if he continues to defy what his soul longed for.

In reality, Billy is a misfit in both the societies : of the twilight city of charm in America and elite like socializing society of Delhi, both of which have gone barren and spiritually bankrupt, madly comforts pursuing physical. They are appropriately materialistic and money doubles the centric worlds of technology. His hatred for the civilised world is so intense that he blindly supports the superstitions and the blind rituals of the primitive society in the case of child sacrifice by a clerk. His study of anthropology becomes the tool to justify the same by giving examples world around from Africa, Indonesia, Japan and many reports about the same happening in the rural parts of India when his father against him.

Despite being a member of the aristocratic heritage he longs for unlimited freedom of choice that awaits him in the primitive life.The very epigraph of the novel is from Arnold`s ''Thyrisis'' :It irked him to be here .he could not rest.'' make thematic direction of the novel clear. Like Arnold`s scholar Gipsy, Billy too flees from the so-called civilized society and seeks shelter in the idyllic Maikala hills.

## Conclusion

Billy has a family, a tradition, a set of values. Even though he ''considers himself a misfit, misplaced and does not enjoy the role he has earned for himself by

virtue of his qualification. He finds contentment neither in family nor in teaching. He seems to be misfitten in a world which he does not seem to fit in."[12] Thus Arun Joshi's the second novel 'The Strange Case Of Billy Biswas' is a study of the total estrangement of the protagonist from upper-upper crust of society and his resultant quest for meaningful life. Billy realizes that the meaning of life "lies not in glossy surfaces of our pretensions, but in those dark mossy labyrinths of the soul that languish forever, hidden from the dazzling light of the sun".[13] Through this novel Arun Joshi seems to give message that parents should not suppress inner urge of children otherwise they will have to pay heavy price for that. At last Billy realizes that all his efforts to integrate with the society are futile. He is so much mentally tortured that he dislikes the civilized and wants to get away from the greedy, avaricious and hypocritical world of the civilized. Therefore, he decides to listen his inner self and joins the tribal world.

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# PROBLEMS OF IMMIGRANTS IN DIVAKARUNI'S *THE MISTRESS OF SPICES*


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## Abstract

*Chitra Banerjee Divakaruni is an Indo-American immigrant author. She investigates through her novels the issues of immigrants who have been getting by in the clash of conventional Indian identity, inalienable as a part of their identity and their fascination for westernization. She fits in with post-modern group of Indian authors who have been writing in English. Her written work fundamentally has managed the encounters of the immigrant women. In her novel, Mistress of Spices Divakaruni depicts that women break the hindrances of exhausted customary values and live free lives. Tilotamma (past name Nayantara) is the hero of the novel, Mistress of Spices. Her guardians consider her as the load however she has the ability to anticipate what's in come. Her magical powers and acclaim spread all around. The old lady told Tilotamma that she ought to stay secluded and ought not get in to excessively included in anybody's life. It implies that she ought not utilize the spices for her own particular purposes. Tilotamma opens a little spice store in Oakland, California. The clients of Tilotamma speak to the concealment and difficulty of women in an alien land. Tilotamma cures the mental anguish of the woman clients with the assistance of her spice. This [illegible] the issues of immigrants in her novel Mistress of Spices.*

(Christian 1985:176).Despite its limitation, it contributes in shaping the image of African-American woman.

With PauleMarshell new period of female characters in African-American letters emerged.It shows her desire for self-understanding.In her first novel BrowngirlBrownstones (1959), Marshell portrays a woman caught between her own desire and life imposed upon her.InThe Chosen Place Timeless People (1969) Marshellrepresents the shared life and communal responsibility.In The Praisesong for the Widow (1970), she represents complex women characters.

Alice Walkers works changed the scenario OF African-American women's literature.She represents woman as a creator.Her first novel Third Life of a Grage Copeland represents struggle for wish to change.Social dimensions are mentioned in The Merridian(1976).The Color Purple(1982) is written in the series of letters.

Toni Morrison is one of the eminent African-American women writers. She has won the Nobel Prize for literature.With her works, she fills the literary corpus with varied colours.Her first novel The Bluest Eye (1970) is a story of African-American girl striving for blue eyes and measuring herself with the white beauty standards.Her Second novel Sula (1973) marked her as a significant voice in America.Her Song of Solomon (1977) is a folkloric novel, where she celebrates African culture.Her Tar Baby (1981) reflects cultural conflict.Beloved (1987) is a story of live experience of former slave Sethe, who kills her daughter in fear of slavery.Then her novels Jazz and Paradiseappeared. She wrote Love (2000) with a religious theme.

There are many other African-American women writers who are coming forward and blossomming their literary tradition. To sum up the African-American women writers are standing at the top of the literary world with their talent, skill, and capacity of resistance. Their work is a celebration of African-American culture, folklore, community, sisterhood and the strength to live and teach the human values.

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# BREAKING THE SILENCE: A NEW FEMINISTIC APPROACH REVEALED IN SHASHI DESHPANDE'S "THAT LONG SILENCE"

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**Abstract**

Shashi Deshpande's novel "That Long Silence" reveals the plight of women, their quest for self, an exploration into the female psyche and an awareness of the mysteries of life and the place of protagonist in it. A woman has to go beyond the society's ordained roles of mother, sister, wife , daughter etc., she has to find out who she is ? This paper presents the feministic approach of Shashi Deshpande's "That Long Silence." The word "silence" is the key metaphor in this novel. At last the patience of silence and endurance of Jaya, the protagonist, is broken and its outcome is a New Woman with Self affirmations and emotional explosions.

Shashi Deshpande's 'That Long Silence', a Sahitya Akadami Award winner novel published in 1988 looks at social history from the perspective of the family. It explores man-woman relationship in Indian society. Deshpande, in this novel offers readers an intimate and domestic chronicle of the subtle tyrannies suffered by women and the pain of coming to self-knowledge. The title of the novel, 'That Long Silence' suggests a belated reaction, a postponement of offensive behaviour for long till the postponement cannot be made anymore. In this novel Shashi Deshpande deals mainly with the silence of an Indian house-wife. She shows her

protagonist 'Jaya' to be in a great inner conflict and a quest for her identity.

The entire novel is written in the mode of retrospective narration. Jaya, the narrator and the protagonist of the novel speaks about her childhood as well as her marital life. The first person narration makes the novel 'an intense one'. Jaya's consciousness becomes the central pivot of the novel.

Jaya's silence is similar to the fate suffered by a majority of women the world over. Silence is a suppressive device, it signifies death. It also means long, untold suffering, mostly mental, which ultimately overcomes the need to express one's thoughts as an individual. It negates the self. The metaphor suggests withdrawal. That Long Silence reverberates with many silences some imposed on the characters and others embarked upon willingly.

The title also suggests the female psyche during the quest of the protagonist for 'self'. 'That Long Silence' is the period of self introspection of the woman to explore her true identity. The protagonist Jaya is caught in the midst of a domestic storm. Her husband, Mohan is accused of corrupt practices at office and the couple leaves their posh flat at Bombay's Churchgate to an old Dadar flat of theirs. The children go out for a holiday. That gives space to Jaya for self-interrogation. Traditionally, a woman has an identity only as 'husband's wife or father's daughter or son's mother'. She can never have her own identity. Ten different mirrors show ten different faces. Thus the individuality of Jaya cannot be defined. She can be defined only in relation to others.

Jaya is a conservative, educated middle class "Smiling, placid motherly woman" who learns to suppress her own wishes and acts according to her husband's. She cannot dare to protest. Mohan is an engineer who cares for money, status and material comforts. Working in the purchase section of his office, he prospers well, looks arrogant and brash. Unfortunately, he is caught taking commission and an enquiry is on. He has to take refuge in their Dadar flat. He takes Jaya for so much granted that she is not consulted about shifting. Yet she quietly accepts his decision and follows him. However, Jaya seems to have gained confidence as he begins to lose it, being in trouble, When Mohan demands the key, Jaya refuses to hand it over to him. She opens the door herself symbolizing her refusal to be servile.

Her Dadar flat is in no way comparable to her elegant, well furnished Churchgate home. Yet, she is perfectly at ease here, relating herself easily to her neighbours and servants. Away from the routine, she is now prepared to look at herself with utmost objectively and examines her relationship with her husband. Emulating Mohan's mother and sister, she tries to adjust and compromise with her lot though every compromise shatters her individuality. She surrenders herself so totally that she is afraid of expressing her likes and dislikes. Now she is a stereotyped housewife who is "nervous, incompetent, needing male help and support."

Outwardly, she is a satisfied housewife married to an apparently caring man with a comfortable home, with no dearth of material comfort, But on scrutiny, it is revealed that to achieve this stage of fulfillment as a wife, Jaya has systematically suppressed even-aspect of her personality that refuses to fit in with her image as a wife and mother besides a failed writer.

Ruminating on the past, Jaya sees how her marriage has reduced her to a mere automation. She realizes how she wasted away the most valuable time of her life in arranging and re-arranging things, dusting, polishing, washing, ironing, cleaning the fridge and changing the sheet She is bewildered to find in her dairies that she had spent her life engrossed in such trivialities as what she bought, how much she paid for it, the dates the children's schools had begun, the servant's absence, the advance they had taken etc.

Jaya, as a girl, was taught by her father to have confidence in herself. He named her Jaya which stands for **victory** and has encouraged her to be resilient and courageous. He has made her feel that she is someone special, and someone different from the other girls who would normally end up becoming house wives. He would dream that Jaya either bags an international award or goes to Oxford. However, his untimely death shatters her dreams and makes her to face the reality that she is after all like any other middle class girl destined to be a wife and a mother. As a child she was chided by her grandmother for asking too many questions and was told that no husband could be comfortable with a woman who asked questions and retorts. Her early training at home has made her obedient and submissive towards her husband. Her relatives taught her the importance of being with a husband, "a husband is like a sheltering tree." After so many years, the words came back to her. A sheltering tree, without the tree, you are dangerously

unprotected and vulnerable." And Jaya proceeds to "Keep the tree alive and flourishing, even if you have to water it with desert and lies" And since a husband is the protector, a woman should never complain or protest. Mohan's mother does not, though his father piles humiliations upon her. Mohan had given the description of his mother's endurance. All the children would have their food, except their mother, who would always wait for her husband to return, though he never gave the intimation of when he would come back. She would finish off the children's dinner and again cook rice for him as he had made it clear to her, that he would not eat what he called "Your children's disgusting leavings". He always wanted fresh and hot rice from the untouched vessel. She had just finished her cooking and was waiting for her husband, hoping that he would not be late, because lighting the fire again, "that was unthinkable." When he returned back and sat for the dinner, he questioned, 'why is there no fresh chutney today?', when she mumbled something, the next moment he picked up his heavy brass plate and threw it, not at her but deliberately at the wall and jerking his shirt off the peg walked out of the house. Mohan' s mother then silently cleared the mess and asked Mohan to get some chilies from next door." She lit the fire again and put rice to cook. She began grinding the chutney and also nursed and breast fed the baby. When the baby was asleep, "she was still sitting there in front of the fire, silent, motionless." Mohan saw strength in the woman sitting silently in front of the fire, but Jaya saw 'despair'. She saw despair so great that it would not voice itself. She writes. "I saw a struggle so bitter that silence was the only weapon. Silence and surrender" The pathetic end of Awa, Mohan's mother, about which Vimala had told secretly to Jaya, also speaks of the trauma and suffering of a housewife. "Strange isn't it? Vimala had said to Jaya, 'how different I am from my mother? Five years married now - I have no children, while Awa almost all my childhood I remember her as being pregnant. She didn't want that last child. She'd lost four or five babies by then, and she was desperate."

Vimala clearly remembers the day when the mother began hitting herself on the face. Her hands were all floury. Soon there were red patches as she went on and on hurting herself. Vimala recalls: "I tried to stop her, I tried to stop her screams, I tried to hold her hands, but I could do nothing. Her hands were like steel."

She just went on saying that, she couldn't bear it all now. She lay still near the fire moaning. A week later she died as she had gone to a midwife and tried to get herself aborted. Thus there was the end of her silence, her long endurance and struggle.

Though Vimala is quite different from her mother 'Awa', Jaya finds something common in them. 'some thing that links the destinies of the two the "silence" in which they died'.

The sufferings of women are put forward again through the character of Vimala. When she was taken to the doctor by Mohan and Jaya, the doctor had asked: "You mean to say, she didn't tell anyone about her illness? When she was suffering so much?"

When Vimala had been in bed over for a month her mother-in-law had complained, that she had never seen women taken to doctors for such a thing. As if other women don't have heavy periods, she had grumbled. The doctors had pronounced that it was too late for a surgery. Vimala sank into coma and died a week later, 'her silence intact'. Here, ends the silent fate of another woman who struggled to death, keeping intact the silence, tradition bound and imbibed in them since childhood. Jaya, since, her childhood, has designed her life in according to her family members' desires. She marries Mohan not out of choice but out of convenience. As he is from the same caste, decent, good looking and had a good job, Jaya had no reason to reject him. After marriage, Jaya also seeks to conform to the pattern the other women in Mohan's house do. She learns to suppress her own wishes and act according to her husband's. She, for example, likes to see advertisements that precede a movie show, for they give her "the illusion of happiness" within the wall of the home. Over the years, she shapes herself "so resolutely to his desires" that in the end she is left with no identity of her own. "Just emptiness and silence "Deshpande brings the picture of enduring women who bear all tortures silently.

Jaya remembers how Jeeja came to work bruised and hurt, but she never complained. Jeeja silently faced all the problems, and there seemed to be no anger behind her silence. Jeeja represents those suffering lot of the lower class women, who bear all the traumas inflicted upon them by their husbands silently and worn themselves out to earn their livelihood. The fate of Jeeja is the fate of many women, who have a drunkard husband but they still endure all the pains and sufferings just because a

husband holds a superior position and after all he is the Kumkum for a woman. The same is the fate of her daughter - in - law Tara. as Rajaram. Jeeja's Stepson is also a drunkard and beats up his wife Tara.

Tara had none of Jeeja's reticence or stoicism. She cursed and reviled her husband and sobbing loudly, moaned her fate. When once Tara cursed Rajaram and wished death for him. Jeeja sternly shuts her up saying that a woman is nothing without a husband.

Thus through Jaya, the protagonist and other female characters like, Vanitamami, Kusum, Jeeja, Tara, Vimala, the novelist presents the plight of women. Deshpande gives minute details from the protagonist's personal life. Like other women novelists, Shashi Deshpande also has chosen a woman narrator. The novel gives the details of a predicament, anguish, sufferings of women, some of them belonging to the middleclass, some are illiterate and rural and some are servants. Deshpande gives their different life pattern.

Through the character of Jaya, Shashi Deshpande has thus expressed the ambivalence attitude of contemporary educated women in India who can neither reconcile themselves to a new situation, when their husbands ignore them and crush their ambition in life nor cast off their husbands simply because a husband is like a sheltering tree, they cannot afford to live without. In a way, Jaya is a representative figure of the modern woman who resents her husband's callousness. By implications attitude, the character of Jaya represents modern women's ambivalent and becomes the victim of circumstances. By implicating the attitude, the character of Jaya represents modern women's ambivalence to married life.

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# CONTEXTUALIZING LITERATURE: TEACHING AND LEARNING

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## Abstract

*In order to make the study of literature effective and to make it as a special form of knowledge with imaginative sensibility, it is necessary that the classroom teaching should reach to the effect of literary comprehension. The text as another name for literature must be analysed in terms of its relative areas and theme. There are three worlds in the understanding of the text- the world of the writer, the world of the text itself and the world of the reader. The intentions and the perceptions of the writer need to be taken into consideration while studying any work of art. It is the responsibility of a teacher to bridge the writer with his reader to bring the text towards his students.*

From centuries the study of literature has been shifting in the manner of its definitions and approaches. The term 'literature' is constantly modifying and evolving. The definition of Aristotle about what is literature is no more static. It undergoes such tremendous changes that litterateure and thinkers don't look at it as merely imitation of life. According to some writers literature is the work of excellence, beauty and art. Literature should illuminate some particular predicament of a man. This definition denotes that literature should reflect the gaiety and the grief of life. On the other hand, it should give pleasure to its reader. Scholars have talked about different aspect and functions of literature. 'Literature is the language well used.' According to Ezra Pound, 'Great literature is simply language charged with meaning to the utmost degree.' While Channing relates literature to the socio-political content while he says, 'literature is the expression of the

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प्रेषक
डॉ. सुखदेव ढाणके, 'सर्वमंगल', ४२ - सहजानंद नगर,
मोर्शी रोड, अमरावती. ४४४ ६०३

हा अंक संपादक, मुद्रक, प्रकाशक,मालक डॉ. सुखदेव ढाणके यांनी बोके प्रिंटर्स, गांधी नगर, अमरावती येथे छापून 'सर्वमंगल',४२, सहजानंद नगर, मोर्शी रोड, अमरावती. ४४४ ६०३, येथे प्रसिद्ध केला.

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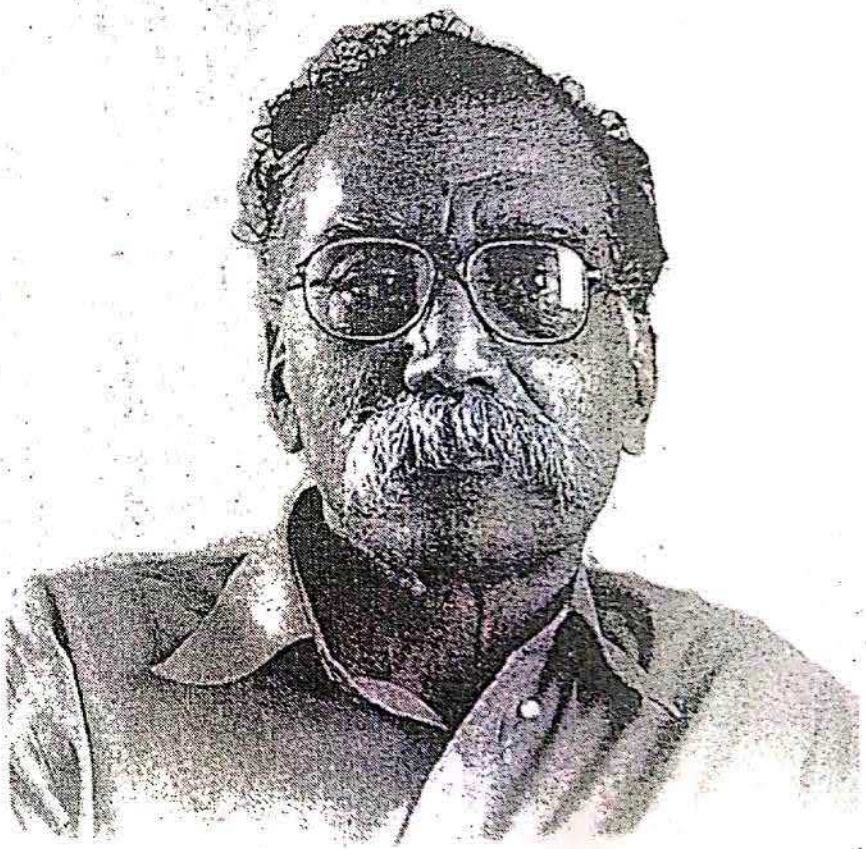

ज्ञानपीठ या सर्वोच्च पुरस्काराने सन्मानित
डॉ. भालचंद्र नेमाडे

# केतन पिंपळापुरे यांच्या कवितेतील सामाजिकता आणि सौंदर्य

डॉ. गजानन बनसोड

आधुनिक मराठी काव्यविश्वातील प्रतिभावंत कवी म्हणून केतन पिंपळापूरे यांचा उल्लेख होतो. 'सूर्यकंकण', 'मार्शलरेस', 'डेमोफून', 'मकाबी' आणि 'हेमलॉक' या कवितासंग्रहातील कवितातून त्याच्या संवेदनशीलतेची व सर्जनशीलतेची साक्ष पटते. जीवनविषयक मूल्यसंघर्षाची जाण असणाऱ्या या कवीला समकालीन सामाजिक वास्तवाचे तर्कशुद्ध भान आहे. केतन आपल्या कवितेतून समताधिष्ठित कल्याणकारी राज्याची स्वप्ने लोकांच्या पुढ्यात ठेवतो. शब्दाला वाकविण्याची जबरदस्त ताकद या कवीजवळ असून तितकीच विवेकशील ऋजुता त्याच्या कवितेत जाणवते.

समाजजीवनात वावरतांना आलेल्या अनुभवाचं, पाहिलेल्या वास्तवातून आलेल्या अस्वस्थेतेचं प्रतिबिंब त्याच्या कवितेत उमटते. धकाधकीच्या काळातील बदलत्या सामाजिक प्रश्नांची उकल तो आपल्या कवितेत करतो आणि म्हणूनच कवी केतन पिंपळापुरे म्हणतो,

> ''मावळेल जिथे अंधार आणि प्रकाशेल आयुष्य नव्याने
> असे आपलेही एक क्षितिज असेल.'' (मार्शलरेस पृ. २२)

अशी समष्टीची संवेदना व्यक्त करतांना कवी कमालीचा आशावादी झालेला आहे. अस्पृश्य म्हणून ज्यांना हजारो वर्षापासून छळले, त्यांचे जगणे असह्य केले. अशा वेदनांकित जीवनातील काळोख नाहिसा व्हावा असे कविला वाटते. महात्मा फुले, शाहू महाराज व डॉ. आंबेडकरांच्या प्रेरणेने प्रेरित झालेला हा कवी म्हणतो,

> ''मी चैत्यभूमीच्या निद्रिस्त ज्वालामुखीच्या काळजावर
> हात ठेवून घेतली आहे टेनिस कोर्टाची शपथ
> आणि बाबासाहेबांच्या डोळ्यातील स्वप्नांच्या दिशेने
> मी दौडवित नेईन माझ्या युगाचा क्रांतिरथ'' (मार्शलरेस पृ. २१)

मानवी स्वातंत्र्याची बीजं ज्या फ्रान्सच्या भूमित रूजली. त्या मातीशी कवी आपली नाळ जोडतो. तिथल्या 'टेनिसकोर्टच्या शपथेची' आठवण करून देतो. युगपुरूष सिद्धार्थ गौतम बुद्धांपासून तर डॉ. बाबासाहेब आंबेडकरांपर्यंत मानवी स्वातंत्र्यांचा



पुरस्कार अनेक युगनायकांनी केला. तरीही विसाव्या शतकापर्यंत वर्णव्यवस्थेची पकड मजबूत राहिली. या व्यवस्थेने अस्पृश्यांचे अपरिमित नुकसान केले. परंतु डॉ. बाबासाहेब आंबेडकरांनी मानवमुक्तीचे लढे उभारले. संविधानातून समता, स्वातंत्र्य, न्याय, बंधुत्वतेचे मूल्य रूजविले, म्हणूनच कवीला डॉ. आंबेडकरांनी दाखविलेल्या स्वप्नांच्या दिशेने या युगाचा रथ पुढे न्यायचा आहे. कवी समस्त मानवाच्या दु:खमुक्तीच्या लढ्यांचा गौरव करतो.

समाज परिवर्तनाचा आग्रह धरणारी केतन पिंपळापुरेंची कविता आहे. तिच्यामध्ये वैश्विक सामाजिक भान आहे. हिटलर, मुसोलिन, स्टॅलिन, ग्लासनोस्त, पेरेस्त्रोईका, लेनिन ह्या पाश्चात्यांचा समाचार तो कवितेत घेतो. तो फक्त भारतातील वंचितांचे प्रश्न कवितेतून मांडत नाही. तर जागतिक मानवी जीवनातील शोषणाचे पडसादही त्यांच्या कवितेत उमटतात. आंबेडकरी समुदायांच्या सामाजिक जाणिवेच्या संदर्भात प्रा.रा.ग. जाधव म्हणतात की, ''सामाजिक जाणिवांची ही जन्मसिद्ध अंतसृष्टी नाना कळांची, नाना रूपांची आहे. तिच्यात इतिहास पुराणांचे जग जसे सामावते, तसेच सद्य:कालीन वास्तवही वावरते. तिच्याच दलित व्यक्तीची व्यक्ती म्हणून असणारी चित्रविचित्र अनुभव सृष्टी जशी आढळते. तशीच दलित दलितेतर संबंधातील सामाजिक ताणाबाणांची रहदारीही दिसते.''(१) मूळात माणूस ऐतिहासिक घटनांचा मागोवा घेत भविष्याचा वेध घेण्याचा प्रयत्न करतो. सद्याच्या वास्तववादी साहित्यात एकोणिसाव्या शतकातील प्रबोधन व विसाव्या शतकातील राजकीय, सामाजिक चळवळी याचे पडसाद उमटले दिसतात. कवी हा कार्यकर्त्यांची भूमिका बठवतो त्यामुळेच त्याच्या काव्यात सामाजिक जाणिवेचा आविष्कार होतो.

रिडल्स आणि नामांतर आंदोलनाच्या वेळी आंबेडकरी जनतेची झालेली गळचेपी कवी व्यक्त करतो. नामांतराच्या लढ्यात पोचिराम कांबळे, चंदरचा झालेला खून अशा घटना अजूनही घडतांना कविला दिसतात. खैरलांजीची धग शांत होत नाही तर खर्ड्याला शाळकरी विद्यार्थ्यांची हत्या घडते. जातियवादी मानसिकेतून, श्रमजीवी माणसांचा, वंचिताचा आवाज नेहमीच दडपल्या जातो. सत्ता आणि संपत्तीच्या बळावर माणूसकीचा मुडदा पाडल्या जातो. सद्य:स्थितीतील हे जळजळीत वास्तव कवी अधोरेखित करतो.

सिद्धार्थ गौतम बुद्धांनी अडीच हजार वर्षापूर्वी जी धर्मचिकित्सा केली. मानवाचे मूल्य अंकित केले. तरीही धर्मग्रंथाच्या नावावर पुराणकर्त्यांनी विषमता टिकवून ठेवली. माणसांमाणसांत भेदाभेद केले. विषमतेमुळे शुद्र अतिशूद्रांचे हजारो वर्ष शोषण झाले.

त्यांना मानवी अधिकार नाकारले गेले. जो ईश्वर शोषणाची व्यवस्था निर्माण करतो. त्या ईश्वराविषयी कवी केतन पिंपळापूरे प्रश्नचिन्ह उभे करतो. ईश्वर नावाची संकल्पना रूजविलेल्याच्या सडक्या, कुजलेल्या मेंदूची शवचिकित्सा करण्यासाठी कवी सज्ज झाला आहे. एका सजग कार्यकर्त्याची भूमिका निभावण्याचा प्रयत्न कवी करतो आहे. आंबेडकरी काव्यातील सामाजिकतेविषयी आपले मत नोंदवतांना, प्रा.रा.ग. जाधव म्हणतात की, ''मराठी साहित्यात सामाजिक जाणिवांचे सौंदर्य निर्माण करण्याची ताकद आज तरी फक्त दलित साहित्यिकांतच आहे, असे मला वाटते. कारण सामाजिक जाणिवांचा अस्सलपणा व सखोलता अनुभवण्याचा भोगवटा दलितांच्या वाट्याला आलेला आहे. तो मूलगामी व म्हणूनच विलक्षण सौंदर्यक्षम व सर्जनक्षम आहे.''(२)

कविला मानवी संवेदना बोथट होतांना दिसतात. सत्ता संपली आणि प्रतिष्ठेसाठी नीती, अनीतीचा व्यवहार होतांना दिसतो. तेव्हा उद्विग्न होऊन कवी म्हणतो,

''जात, धर्म, पंथ, संप्रदाय आणि वंशवादाच्या सूडचक्रात
भोळ्याभाबड्या अज्ञ पामरांना ओरबाडणाऱ्या
या रथयात्रा कुणाच्या?
महागाई, भूक, बेरोजगारी, लूट, दंगली आणि
छिनाल राजकारणासाठी चाललेल्या या मतयात्रा कुणाच्या?''
(मकाबी पृ. १५)

धर्मांध राजकारणामुळे वंचितांच्या आयुष्याचा वाळवंट होतांना कवी पाहतो, तेव्हा त्याचे मन गलबलून जाते. त्याला धर्मसंस्कृतीचे संदर्भ गडद होतांना दिसतात. गुलामगिरीतून मुक्ती मिळविण्यासाठी माणसांची चाललेली धडपड कवी पाहतो. ग्रंथपंथाच्या तार्किक घोटाळ्यात अडकलेल्या माणसाची सहीसलामत सुटका करण्याचा तो प्रयत्न करतो. ज्या महामानवांनी अमानुषतेच्या अरण्यातून सर्व शोषितांना मुक्त केले. त्यांना वंदन करतांना कवी म्हणतो,

''मी तथागतांच्या डोळ्यातील स्वप्नांचा राजहंस आहे
मी शील आहे, मी विवेक आहे, मी आहे अमर्याद करूणा
द्वेष, मत्सर, विकार, विकृती व हिंसेची तीव्र घृणा...
माझ्या स्पर्शाने पाषाणाचे होत असतात सुवर्णशिल्प
माझ्या अस्तित्वाने काळोखाचे साम्राज्य ठरते 'अल्प'
(मार्शलरेस पृ.१५)



केतन पिंपळापुरेंच्या कवितेतूनच त्याची भूमिका अधिकाधीक स्पष्ट होते. स्वत:ला कवी विश्वशांतीचा पहाटपक्षी म्हणतो व या शतकातल्या बांधावर करूणेचे झाड लावण्याची प्रतिज्ञा करतो डॉ. बाबासाहेब आंबेडकरांच्या समग्र समाजक्रांतीचे धम्मध्येय पूर्ण होऊ शकले नाही ही खंत कवी, 'मी तथागताच्या डोळ्यातील विश्वशांतीचा राजहंस आहे' या कवितेत मांडतो.

''आपण आपल्या खोपटात सूर्य बंदिस्त करू नये
दारं, खिडक्या उघडून प्रकाश बाहेर जाऊ द्यावा
प्रज्ञेचा झरा आपण आपल्यापूरता अडवू नये
कुण्या अंधारयात्रिकांना उजेड पिऊ द्यावा
आणि त्यांच्या तृप्त आयुष्याचा दुवा घ्यावा'' (सूर्यकंकण पृ. १०)

विचारसंपृक्त अशी वाक्यरचना केतन पिंपळापुरेंच्या कवितेची आहे. काही कवितेत पल्लेदार वाक्य असूनही त्या कवितेतील सौंदर्यात्मकता अबाधित राहते. कवी 'स्व' पेक्षा 'आम्ही' ची भाषा वापरतो. बाबासाहेबांनी दिलेला प्रज्ञेचा वारसा घराघरात पोहचविण्याचा इरादा कवी करतो. सर्वच अंधार यात्रिकांचे जीवन बदलावे असे कविला वाटत असून शोषितांच्या मुक्तीचे गाणे गाणारा हा कवी आहे.

ज्यांच्या स्वप्नांची भ्रृणहत्या होते त्या आदिम, कष्टकरी माणसांच्या व्यथा-वेदनेला कवी मुखर करतो. ऊनवारा, पाऊस सोसत घाम गाळणाऱ्या श्रमीकांची वेदना कवी व्यक्त करतो. जात धर्म, पंथ, वर्ण, वर्ग व लिंग ही सर्व शोषणाची अस्त्रे आहेत. राजकीय, सामाजिक शैक्षणिक, सामाजिक घटकांच्या माध्यमातून मारसाची लूट होते. याची जाणीव कवीला आहे. केतन पिंपळापुरेंच्या कवितेतील सौंदर्य जाणिवेविषयी आपले मत नोंदवतांना डॉ.मा.प. थोरात म्हणतात, 'सुंदरमानव समाज उत्पन्न करणारी जाणीव 'सौंदर्य' जाणीव होय'(३) पुढील ओळीतून केतनच्या काव्यातील सौंदर्य प्रतित होते,

''जीवनाची सुंदरता म्हणजे मैत्री
काळजातील असीम उदारता म्हणजे मैत्री
मैत्री : मानवतेचं लोभस रूप
मैत्री : निर्मल स्मृतीचा स्तूप
मैत्री : त्यागाचा सुगंधी धूप'' (डेमोफून-२३)

अर्थगर्भ अशी केतनची कविता असून तिच्यामध्ये असणारी समाजनिष्ठा पदोपदी

जाणवते. कवितेतील सौंदर्यात्मकतेविषयी आपले विचार व्यक्त करतांना प्रा.रा.ग. जाधव म्हणतात, ''अपूर्वता, उत्कटता व काव्यात्मता ही साहित्यातील सौंदर्याची लक्षणे ठरतात''(४)

'माय डिअर जिंदगी' या कवितेत कवी केतन पिंपळापुरे म्हणतात,

''इथे तर भाकरच ठरली आहे
आम्हा गरिबांसाठी उंबराचे फूल
आणि उदास प्राण्यांच्या कबरीवर
कुणी पांघरत नाही मायेची झूल'' (हेमलॉक पृ. ६५)

जाणिवेच्या कक्षा रूंदवणारे काव्यशिल्प केतन पिंपळापुरे यांच्यामुळे आंबेडकरी काव्य सृष्टीला लाभले आहे. केतन कवितेत पारंपारिक मिथ्थकांचा वापर करीत नाही तर जाणिवपूर्वक आंबेडकरी, बौद्ध, प्रतिके, प्रतिमा वापरतो. 'मार्शलरेस' मध्ये भीमा कोरेगावच्या शौर्यस्तंभाला सलामी देतांना 'अमृतनाम' 'सोमनाक' या अस्पृश्यांतील लढवय्यांची आठवण कवी करून देतो. लेखनातून तो आपल्या आंबेडकरी निष्ठेला तडा जाऊ देत नाही. तथागत बुद्ध, सम्राट अशोक, डॉ. बाबासाहेबांच्या भूमित कविला मानवतेच्या विचाराचा प्रसार करावयाचा आहे.

बुद्ध तत्वज्ञानावर आधारित जीवनाच नवं पंचशील मांडतांना, जीवन असावं गतिशील नवनिर्मिती करणाऱ्या हातासारखं, तर 'मैत्री' ही मानवतेचं लोभस रूप आहे असे केतन म्हणतो. कवितेतील आशयसधन वाक्यरचनेतून, नवं शब्दातून कवी त्या कवितेला सौंदर्य बहाल करतो. जसे 'दगडी पहाडावर हिरवळ फुलवणे', 'बेबंद दुनियेच बेहरम अरण्य', 'उदात्त जीवनमूल्यांचा शाश्वत दीप', 'ढगांच्या पाठीवर विजेचे प्रतोद', 'अग्नीच्या प्रपाताची विद्रोही कविता', 'मानवतेच्या तृषार्त ओठांवर करूणेचे तत्त्वथेंब', 'काळ सुतारपक्षासारखा माणसाचे काळीज पोखरतो'. अशा सौंदर्यपूर्ण विधानात्मक वाक्यातून तर 'साथी', 'शोषणशाहीचं ब्लडबँक', 'अग्निकमल', 'भावचिंब आसमंत' या शब्दातून कविता संवादी बनते. सौंदर्यपूर्ण शब्दकळेमुळे कवितेतील काव्यात्मक बाजही सांभाळला जातो.

केतन पिंपळापूरे हे अग्निफुलाची वाटपांघरून क्रांतीची पाहाट पाहणारे कवी आहेत. त्याच्या कवितेत वैचारिक एकसंघता जाणवते. कवितेमध्ये अभिव्यक्तीचा वेगळेपणा आहे. परिवर्तनवादी विचारकांचे व संघटनेचे सामर्थ्य वाढविणारी केतनची कविता आहे. या देशातील उपेक्षित वंचितांच्या सार्थ अपेक्षा प्रकट करणारी त्यांची कविता आहे. आंबेडकरी चळवळीला उर्जा बहाल करणारी केतन पिंपळापुरे यांची



कविता आहे. त्याच्या कवितेत समाजाभिमुख चिंतन आहे. त्याची कविता समष्टीची संवेदना व्यक्त करते. वंचितांचे दुःख दैन्य पाहून तो कवितेतून अस्वस्थता प्रकट करतो. बदलत्या वास्तवाचे प्रतिबिंब केतनच्या कवितेतून उमटते. सैरभैर शब्दाची मांडणी तो करत नसून प्रत्येक शब्दात, वाक्यात आशय ठासून भरलेला आहे. कवी आपल्या विचारांशी, आपल्या मातीशी, आपल्या माणसांशी प्रमाणिक असल्याची अनुभूती त्यांच्या कवितेतून होते.

**संदर्भ :**


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**। साभार पोच ।**

आकाशवाणी चिंतने/डॉ. शे.मा. हराळे/मेघा प्रकाशन/अमरावती
आगाजा/विनोद कुमरे/लोकवाङ्मयगृह/मुंबई
ठसे बदललेल्या मुक्कामावरुन/विनायक येवले/काव्याग्रह प्रकाशन/वाशिम
दिशांतराच्या गोष्टी/उर्मिला राघवेंद्र चाकूरकर/पैठणी प्रकाशन, औरंगाबाद

# Kantowski- Sachs Dark Energy Model in a Scalar Tensor Theory of Gravitation

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## Abstract

Kantowski- Sachs cosmological model with anisotropic dark energy is presented in a scalar tensor theory of gravitation proposed by Saez and Ballester (1986). Equation of state (EoS) for a dark energy $\omega$ is found to be time dependent and its existing range for derived models is in good agreement with the recent observations. To obtain exact solution of the field equation using special law of variation for the Hubble parameter, which yields a constant value of the deceleration parameter. The physical aspect of the models have also been studied.

**Keywords**: Scalar tensor theory , Dark Energy

## Introduction

In recent years there has been an immense interest in scalar –tensor theories of gravitation. Brans and Dicke (1961) formulated a scalar- tensor theory of gravitation which introduces an additional scalar field $\phi$ besides the metric tensor $g_{ij}$ and a dimensionless coupling constant. This theory goes to general relativity for large values of the coupling constant greater than 500 . Saez and Ballester (1986) proposed a scalar-tensor theory of gravitation in which the metric is coupled with a dimensionless scalar –field in a simple manner. This coupling gives a satisfactory description of the weak fields. Inspite of the dimensionless character of the scalar field an antigravity regime appears in this theory. Also, this theory, suggests a possible way to solve missing matter problems in non-flat FRW cosmologies.

Supernova 1a data [Perlmutter et al. (1998), Riess et al.(1998)] and the observations of anisotropies in the cosmic microwave background(MCB) radiation and the large scale structure have confirmed the accelerated expansion of the universe

[Bennett et al. (2003),Verde et al. (2002), Hawkins et al. (2003), Abazajian et al. (2004)]. Astrophysical observations indicate that this expansion of the universe is driven by an exotic energy with large negative pressure which is known as dark energy (DE). Inspite of all the observational evidence dark energy is still a challenging problem in theoretical physics. The data indicates that the universe is spatially flat and is dominated by 76% dark energy 24% by other matter (20% dark matter and 4% other cosmic matter). Several models have been proposed such as quintessence [Sahni (2003), Padmanabhan (2008)] phantom field [Sen (2002), Padmanabhan (2002)], interacting dark energy models, Chaplygin gas [Kamenshchik (2001),Bento (2002)] , holographic models [Wang (2005), Setare (2006) etc. However, none of these models can be regarded as being entirely convincing so far.

Recently, Rodrigues (2008) and Koivisto & Mota (2008a,b) have investigated cosmological models with anisotropic equation of state (EoS). Rodrigues has constructed a Bianchi type-I _CDM cosmological model with a DE component which is nondynamical but wields anisotropic vacuum pressure in two ways: (i) by implementing of anisotropic vacuum pressure consistent with energy-momentum tensor conservation;(ii) by implementing a Poisson structure deformation between canonical momenta such that rescaling of the scale factor is not violated [17]. He suggests to fine tune the DE so as to not wipe out the anisotropic imprints in the inflationary epoch. On the other hand, Koivisto & Mota have proposed a different approach to resolve CMB anisotropy problem; even if the CMB formed isotropically at early time, it could be distorted by the direction dependent acceleration of the later universe in such a way that it appears to us anomalous at the largest scales. They have investigated a cosmological model containing a DE component which has a non-dynamical anisotropic EoS and interacts with the perfect fluid component. They have also suggested that cosmological models with anisotropic EoS can explain the quadrupole problem and can be tested by SNIa data [Koivisto & Mota (2008a,b)].

Spatially homogeneous and anisotropic cosmological models play a significant role in the description of large scale behaviour of universe and such models have been widely studied in framework of General Relativity in search of a realistic picture of the universe in its early stages. Dark Energy has been conventionally characterized by the equation of state (EoS) parameter mentioned which is not necessarily constant. Recently, the parameter $\omega(t)$ is calculated with some reasoning which reduced to

some simple parameterizations of the dependences by some authors Huterer and Turner (2001) .The simplest dark energy candidate is the vacuum energy $\omega = -1$ , which is mathematically equivalent to the cosmological constant$(\wedge)$. The other conventional alternatives, which can be described by minimally coupled scalar fields, are quintessence $(\omega > -1)$, phantom energy $(\omega < -1)$,and quintom and have time dependent EoS parameter. Recently dark energy models with variable EoS parameter have been studied by Ray et al. (2010) , Akarsu and Kilinc(2010a,b), Yadav et al.(2010) Yadav and Yadav (2010) , Pradhan et al. (2011a,b), Amirhashchi et al. (2011)

It is well known that spatially homogeneous and a anisotropic cosmological models in the presence of scalar fields play a vital role in the discussion of large scale structure of the universe. With this motivation we investigate, in this paper, we have discussed

Kantowski-Sachs dark energy universe with variable EoS parameter in Saez- Ballester scalar- tensor theory of gravitation

**[2] Metric and Field Equations**

We consider the Kantowski-Sachs space-time in the form

$$ds^2 = -dt^2 + a^2 dr^2 + b^2(d\theta^2 + \sin^2 d\phi^2) \ , \tag{2.1}$$

where the scale factors a and b are functions of cosmic time only. By preserving the diagonal form of the energy momentum tensor in a consistent way with the above metric, the simplest generalization of EoS parameter of perfect fluid may be to determine it separately on each spatial axis. Therefore the energy momentum tensor of perfect fluid is taken as

$$T_i^{\ j} = diag[T_0^0, T_1^1, T_2^2, T_3^3] \ . \tag{2.2}$$

Thus, one may parameterize it as follows

$$\begin{aligned} T_i^{\ j} &= dia[\rho, -p_x, -p_y - p_z] \\ &= dia[1, -\omega_x, -\omega_y, -\omega_z]\rho \\ &= dia[1, -\omega, -(\omega+\delta), -(\omega+\delta)]\rho \end{aligned} \tag{2.3}$$

where $\rho$ is the energy density of the fluid $p_x, p_y, p_z$ are the pressures and $\omega_x, \omega_y, \omega_z$ are the directional EoS parameters along the $x, y, z$ respectively, $\omega(t) = p/\rho$ is the deviation free EoS parameter of the fluid. We have parameterized the deviation from

isotropy by setting $\omega_x = \omega$ and then introducing skewness parameter $\delta$ which is the deviation from $\omega$ along both $y$ and $z$-axes.

The field equations given by Saez and Ballester [1] for the combined scalar and tensor fields are

$$R_{ij} - \frac{1}{2} R g_{ij} - \varpi \phi^n (\phi_{,i}\, \phi_{,j} - \frac{1}{2} g_{ij} \phi_{,k}\, \phi^{,k}) = -T_{ij} \tag{2.4}$$

And the scalar field $\phi$ satisfies the equation

$$2\phi^n \phi^i_{,i} + n\phi^{n-1} \phi_{,k} \phi^{,k} = 0 \ , \tag{2.5}$$

where $\varpi$ and n are constants, $T_{ij}$ is the energy momentum tensor of the matter and comma and semicolon denote partial and covariant differentiation respectively.

By adopting commoving coordinates the field equations (2.4), for the Kontowski-Sachs space-time, the field equations take the form

$$\frac{2a_4 b_4}{a\,b} + \frac{1}{b^2} + \frac{b_4^{\,2}}{b^2} + \varpi \phi^n \frac{\phi_4^{\,2}}{2} = \rho \quad , \tag{2.6}$$

$$\frac{a_{44}}{a} + \frac{b_{44}}{b} + \frac{a_4 b_4}{ab} + \varpi \phi^n \frac{\phi_4^{\,2}}{2} = -(\omega + \delta)\rho \ , \tag{2.7}$$

$$\frac{2b_{44}}{b} + \frac{1}{b^2} + \frac{b_4^{\,2}}{b^2} - \varpi \phi^n \frac{\phi_4^{\,2}}{2} = -\omega\rho \, . \tag{2.8}$$

Using equation (2.5), we get

$$\frac{\phi_{44}}{\phi} + \frac{a_4}{a} + 2\frac{b_4}{b} + \frac{n}{2}\frac{\phi_4}{\phi} = 0 \ , \tag{2.9}$$

where a subscript 4 indicates differentiation with respect to t.

**[3] Solutions of the field equations**

According to the proposed law, the variation of the mean Hubble parameter for the Kantowski-Sach metric may be given by

$$H = k(ab^2)^{-\frac{n}{3}} \ , \tag{3.1}$$

where $k > 0$ *and* $n \geq 0$ are constants. The spatial volume is given by

$$V = R^3 = ab^2 \ , \tag{3.2}$$

where $R$ is the mean scale factor. The mean Hubble parameter $H$ is given as

$$H = \frac{R_4}{R} = \frac{1}{3}\frac{V_4}{V} = \frac{1}{3}\left(\frac{a_4}{a} + 2\frac{b_4}{b}\right) . \tag{3.3}$$

The directional Hubble parameters in the directions of *x,y and z* respectively may be defined as

$$H_x = \frac{a_4}{a} \qquad and \quad H_y = H_z = \frac{b_4}{b} \quad . \tag{3.4}$$

The volumetric deceleration parameter is

$$q = -RR_{44} \Big/ R_4^{\,2} \quad . \tag{3.5}$$

On integrating, after equating (3.1) and (3.3), we obtain

$$ab^2 = c_1 e^{3kt} \qquad for \quad n = 0 \quad . \tag{3.6}$$

$$ab^2 = (nkt + c_2)^{\frac{3}{n}} \qquad for \quad n \neq 0 \quad . \tag{3.7}$$

here $c_1$ *and* $c_2$ are positive constants of integration. Using (3.1) with (3.6) for $n = 0$, and with (3.7) for $n \neq 0$ mean Hubble parameters are

$$H = k \quad for \quad n = 0 \quad . \tag{3.8}$$

and

$$H = k(nkt + c_2)^{-1} \quad for \quad n \neq 0 \quad . \tag{3.9}$$

Using (3.6), (3.7) and (3.2) in (3.5), we get constant values for the deceleration parameter for the mean scale factor as:

$$q = n - 1 \quad for \quad n \neq 0 \quad . \tag{3.10}$$

and

$$q = -1 \quad for \quad n = 0 \quad . \tag{3.11}$$

The sign of $q$ indicates whether the model accelerate or not. The positive sign of $q$ $(i.e. n > 1)$ corresponds to decelerating models whereas the negative sign $-1 \le q < 0$ *for* $0 \le n < 1$ indicates acceleration .

Integration , after subtracting equation (2.8) from (2.7) , we get

$$\left(\frac{a_4}{a} - \frac{b_4}{b}\right)\left(\frac{V}{\lambda}\right) = \exp\left\{\int\left(-\delta\rho + \frac{1}{b^2}\right)\left(\frac{a_4}{a} - \frac{b_4}{b}\right)^{-1} dt\right\} , \tag{3.12}$$

where $\lambda$ is an integration constant. The integral term in above equation vanishes for

$$\delta = \frac{1}{\rho b^2} . \tag{3.13}$$

Using equation (3.13) in equation (3.12) it follows that

$$\frac{a_4}{a}-\frac{b_4}{b}=\frac{\lambda}{V}\ , \tag{3.14}$$

by considering (3.8) and (3.9) we obtain

$$\frac{a_4}{a}-\frac{b_4}{b}=\frac{\lambda}{c_1\exp(3kt)} \qquad for\ \ n=0\ , \tag{3.15}$$

$$\frac{a_4}{a}-\frac{b_4}{b}=\frac{\lambda}{(nkt+c_2)^{3/n}} \qquad for\ \ n\neq 0\ , \tag{3.16}$$

**Model for** $n=0 \quad (q=-1)$

On integration of (3.15) and using (3.6) we get the following exact expression for the scale factors:

$$a=\left(\frac{c_1}{k_1{}^2}\right)^{\frac{1}{3}}\exp\left\{kt-\frac{2\lambda}{9c_1k}e^{-3kt}\right\}\ , \tag{3.17}$$

$$b=\left(\frac{c_1}{k_1}\right)^{\frac{1}{3}}\exp\left\{kt+\frac{\lambda}{9c_1k}e^{-3kt}\right\}, \tag{3.18}$$

where $k_1$ is positive constant of integration.. The spatial volume of the universe is found as

$$V=c_1e^{3kt}\ . \tag{3.19}$$

The directional Hubble parameters are

$$H_x=k+\frac{2\lambda}{3c_1}e^{-3kt}\ , \tag{3.20}$$

$$H_y=H_z=k-\frac{\lambda}{3c_1}e^{-3kt}\ , \tag{3.21}$$

The anisotropy parameter of the $(\Delta)$ is defined as

$$\Delta=\frac{1}{3}\sum_{i=1}^{3}\left(\frac{H_i-H}{H}\right)^2\ , \tag{3.22}$$

where $H_i\,(i=1,2,3)$ represents the directional Hubble parameters in the direction $x, y, and\ z$ respectively.

By using (3.8) ,(3.20) , (3.21) in (3.22) , we get

$$\Delta = \frac{2}{9}\left[\frac{\lambda^2}{{c_1}^2 k^2} e^{-6kt}\right] \quad . \tag{3.23}$$

The expansion scalar $\theta$ is found as

$$\theta = 3k = 3H \quad . \tag{3.24))}$$

The shear scalar $\sigma^2$ is found as

$$\sigma^2 = \frac{3}{2}\Delta H^2 = \frac{\lambda^2}{3{c_1}^2} e^{-6kt} \quad . \tag{3.25}$$

Using equation (2.9), the scalar field is found as

$$\phi = \left[\frac{n+2}{2}\left(\frac{-\alpha}{3k} e^{-3kt} + \beta\right)\right]^{\frac{2}{n+2}} \quad . \tag{3.26}$$

Using equations (3.26) ,(3.4), (3.20), (3.21) in (2.6), we obtain the energy density for the model as

$$\rho = 3k^2 - \frac{\lambda^2}{3{c_1}^2} e^{-6kt} + \left(\frac{k_1}{c_1}\right)^{\frac{2}{3}} \exp\left\{-2kt - \frac{2\lambda}{9c_1 k} e^{-3kt}\right\} + \frac{1}{2}\varpi\alpha^2 e^{-6kt} \tag{3.27}$$

Using equations (3.27) in (3.13), we obtain the deviation parameter as

$$\delta = \frac{\left(\frac{k_1}{c_1}\right)^{2/3} \exp\left\{-2kt - \frac{2\lambda}{9c_1 k} e^{-3kt}\right\}}{3k^2 - \frac{\lambda^2}{3{c_1}^2} e^{-6kt} + \left(\frac{k_1}{c_1}\right)^{\frac{2}{3}} \exp\left\{-2kt - \frac{2\lambda}{9c_1 k} e^{-3kt}\right\} + \frac{1}{2}\varpi\alpha^2 e^{-6kt}} \tag{3.28}$$

Using equation (3.20) (3.21),(3.27) and (3.28) in equation (2.7), we obtain the deviation –free parameter as

$$\omega = -\frac{3k^2 + \frac{\lambda^2}{3{c_1}^2} e^{-6kt} + \left(\frac{k_1}{c_1}\right)^{\frac{2}{3}} \exp\left\{-2kt - \frac{2\lambda}{9c_1 k} e^{-3kt}\right\} - \frac{1}{2}\varpi\alpha^2 e^{-6kt}}{3k^2 - \frac{\lambda^2}{3{c_1}^2} e^{-3kt} + \left(\frac{k_1}{c_1}\right)^{\frac{2}{3}} \exp\left\{-2kt - \frac{2\lambda}{9c_1 k} e^{-3kt}\right\} + \frac{1}{2}\varpi\alpha^2 e^{-6kt}} \tag{3.29}$$

**Physical behaviour of the model for $n = 0$ $(q = -1)$:**

For this model $q=-1$ *and* $\frac{dH}{dt}=0$, which implies the greatest value of the Hubble parameter and the fastest rate expansion of the universe. Thus, this model may represent the inflationary era in the early universe and the very late times of the universe.

The spatial volume $V$ is finite at $t=0$, expands exponentially as $t$ increases and becomes infinitely large at $t=\infty$. The directional Hubble parameters $H_x$ *and* $H_{y,z}$ are finite at $t=0$.

The expansion scalar is constant throughout the evolution of the universe. The scalar is also finite at $t=0$ .The anisotropy of the expansion decreases monotonically as *t* increases .

The ratio $\frac{\sigma^2}{\theta^2}\to 0$ *as* $t\to\infty$ . Hence the model isotropizes for large value of the *t.*

The EoS parameter of the DE $\omega$ may begin in phantom $(\omega<-1)$ or quintessence $(\omega>-1)$ region and tends to -1 (cosmological constant $\omega=-1$) by exhibiting various patter as t increases.

**Model for** $n\neq 0$ *and* $q\neq -1$**:**

On integration (3.15) and using (3.7) we obtain the following exact expressions for the scale factors:

$$a=c_3^{2/3}(nkt+c_2)^{\frac{1}{n}}\left\{\exp\left(\frac{2\lambda}{3k(n-3)}\right)(nkt+c_2)^{\frac{n-3}{n}}\right\}, \tag{3.30}$$

$$b=c_3^{-1/3}(nkt+c_2)^{\frac{1}{n}}\left\{\exp\left(\frac{-\lambda}{3k(n-3)}\right)(nkt+c_2)^{\frac{n-3}{n}}\right\}, \tag{3.31}$$

where $c_3$ is the positive constant of integration. The spatial volume of the universe is found as

$$V=(nkt+c_2)^{\frac{3}{n}} \quad . \tag{3.32}$$

The directional Hubble parameters are found as

$$H_x=(nkt+c_2)^{-1}k+\frac{2\lambda}{3}(nkt+c_2)^{-3/n} \quad , \tag{3.33}$$

$$H_y=H_z=(nkt+c_2)^{-1}k-\frac{\lambda}{3}(nkt+c_2)^{-3/n} \quad . \tag{3.34}$$

Using (3.33), (3.34)in (3.22) we get

$$\Delta = \frac{2}{9}\frac{\lambda^2}{k^2}(nkt + c_2)^{2\left(1-\frac{3}{n}\right)} \quad , \tag{3.35}$$

for the anisotropy parameter of the expansion. The expansion and shear scalars are, respectively, found as

$$\theta = 3H = 3k(nkt + c_2)^{-1} \ , \tag{3.36}$$

$$\sigma^2 = \frac{\lambda^2}{3}(nkt + c_2)^{-\frac{6}{n}} \ . \tag{3.37}$$

Using equation (2.9), the scalar field is found as

$$\phi = \left[\left(\frac{n+2}{2}\right)\left(\frac{P}{n-3}\right)(nkt + c_2)^{n-3/n}\right]^{\frac{2}{n+2}} \ . \tag{3.38}$$

Using (3.33), (3.34), (3.38) in (2.6) we get the energy density for the model as

$$\rho = 3k^2(nkt + c_2)^{-2} - \frac{1}{3}\lambda^2(nkt + c_2)^{-\frac{6}{n}} + c_3^{2/3}(nkt + c_2)^{-2/n} \exp\left\{\frac{2\lambda}{3(n-3)k}(nkt + c_2)^{\frac{n-3}{n}}\right\} + \frac{1}{2}\varpi P^2 k^2 (nkt + c_2)^{-\frac{6}{n}} \tag{3.39}$$

Using (3.39) in (3.13) , we get the deviation parameter as

$$\delta = \frac{c_3^{2/3}(nkt + c_2)^{\frac{-2}{n}}\left\{\exp\left(\frac{2\lambda}{3k(n-3)}\right)(nkt + c_2)^{\frac{n-3}{n}}\right\}}{3k^2(nkt + c_2)^{-2} - \frac{1}{3}\lambda^2(nkt + c_2)^{-\frac{6}{n}} + c_3^{2/3}(nkt + c_2)^{-2/n} \exp\left\{\frac{2\lambda}{3(n-3)k}(nkt + c_2)^{\frac{n-3}{n}}\right\} + \frac{1}{2}\varpi P^2 k^2 (nkt + c_2)^{-\frac{6}{n}}} \tag{3.40}$$

Using (3.33),(3.34),(3.38) and (3.40) in (2.8) we get the deviation- free parameter as

$$\omega = -\frac{(3-2n)k^2(nkt + c_2)^{-2} + \frac{\lambda^2}{3}(nkt + c_2)^{-6/n} + c_3^{2/3}\left[(nkt + c_2)^{-2/3}\exp\left\{\frac{2\lambda}{3(n-3)k}(nkt + c_2)^{\frac{n-3}{n}}\right\}\right] - \frac{1}{2}\varpi P^2 k^2 (nkt + c_2)^{-\frac{6}{n}}}{3k^2(nkt + c_2)^{-2} - \frac{1}{3}\lambda^2(nkt + c_2)^{-\frac{6}{n}} + c_3^{2/3}(nkt + c_2)^{-2/n} \exp\left\{\frac{2\lambda}{3(n-3)k}(nkt + c_2)^{\frac{n-3}{n}}\right\} + \frac{1}{2}\varpi P^2 k^2 (nkt + c_2)^{-\frac{6}{n}}} \tag{3.41}$$

**Physical behaviour of the model for** $n \neq 0 \ \ (q \neq -1)$

The universe accelerates for $0 < n < 1$, decelerates for $n > 1$ and expands with constant velocity for $n = 1$. The spatial volume $V$ is finite at $t = 0$ and becomes infinitely large as $t \to \infty$. In this model , the average scale factor $R = (nkt + c_2)^{\frac{1}{n}}$ . It has point singularity at $t = -\frac{c_2}{nk}$. The Hubble parameters $H_x, H_y, H_z$ *and* $H$ are infinite at this point but here the spatial volume vanishes.

The anisotropy of the expansion $\Delta \to null$ as $t \to \infty$ for $m > 3$ while $\Delta \to \infty$ as $t \to \infty$.

The EoS parameter of the DE $\omega$ may begin in phantom $(\omega < -1)$ or quintessence $(\omega > -1)$ region and tends to -1 (cosmological constant $\omega = -1$) by exhibiting various patter according to the choice of the parameter.

The ratio $\frac{\sigma^2}{\theta^2} \to 0$ *as* $t \to \infty$ . Hence the model isotropizes for large value of the *t* ( *for* $0 < n < 3$).

**Conclusion**

Exact solutions of Einstein's field equations have been obtained by assuming a special law of variation for the mean Hubble parameter, which yields a constant value of the deceleration parameter and is not inconsistent with observations. Some basic geometrical and kinematical features of the models and the dynamics of the anisotropic DE in these models have been examined.

The space approaches to isotropy in the models for large value of the $t$.

The energy density of the fluid and the deviation free EoS parameter $\omega$ and the deviation parameter $\delta$ are dynamical.

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# बालश्रम : मानवाधिकार हनन का क्रुर यथार्थ

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**प्रस्तावना :-**

बालश्रम एक सामाजीक बुराई है। बालश्रम को एक राष्ट्रीय कलंक भी कहा गया है। लेकिन इसे समाप्त करने के कारणोंपर कितना ध्यान गया है। यह हमारे लिए आत्म आलोचना का विषय है। बालश्रम समस्या अत्यंत व्यापक और समाज मे एक प्रथा की तरह गहराई तक फैली हुई है। बालश्रम की समस्या विश्व के सभी देशो में कमअधिक स्तर मे विद्यमान है लेकिन विकासशील देशों मे इसका प्रमाण अत्याधिक है। भारत मे १९८० तक बालश्रम को सुरक्षा प्रदान करने तथा उसका उन्मूलन करने के कोई व्यवस्था नही कि गई। इसके पश्चात देश में बालश्रमिको की दिन प्रति दिन बढती समस्या पर भारत सरकार का ध्यान गया।

बालश्रम प्रथा की जडे औद्योगिक क्रांन्ति में खोजी जा सकती है, ज्योंकी इस क्रांन्ति के दौरन मुनाफाखोर द्वारा बालको को श्रमबाजार मे घसीट लिया गया था। जैसे जैसे पूंजीवाद विकास की विभिन्न अवस्थाओ से गुजरात गया, वैसे वैसे विकासशील अर्थव्यवस्था ओ अथवा उन श्रमो मे बलश्रम का जमान बढता चला गया। निर्धनता, निरक्षरता या अन्य सामाजिक समस्या ओ की तरह बालश्रम भी समाज की गहरी समस्या के रुप मे उभरा है। बालश्रम समस्या पूरे विश्व की समस्या है। यह विकसित तथा विकासशील दोनोही तरह देशों के लिऐ चुनौती है। सर्वाधिक बाल श्रमिक एशिया मे है, जहा कुछ देशो मे २० प्रतिशत से अधिक बालक काम करते है।

**बालश्रम की परिभाषा :-**

'बालश्रम' शब्द का प्रयोग सामान्यतथ 'रोजगार में नियोजित बालक' या 'का कर रहे बालक' के पर्याय रुप से किया जाता है। इस दृष्टी से 'बालश्रम' पद बालक द्वारा किये जानेवाले उस प्रत्येक कार्य के समान है, जिसे बालक लाभ प्राप्त करने के लिए करता है, किन्तु बालकों द्वारा किए जाने वाले कार्य को सामान्यत ऐसा कार्य समझा जाता है जो घृणित है और जिसमें शोषण का पुर मौजुद है।

अन्तराष्ट्रीय श्रम संगढने के अनुसार बाल श्रमिक वे बालक है जो स्थायी तौर पर वयस्को की तरह जीवन जी रहे है, कम मजदूरी पर कई-कई घन्टे ऐसी कार्य – दशाओ में काम करते है, जिनसे उनका स्वास्थ खराब होता है तथा शारीरिक एंव मानसिक विकास रुक जाता है, इन छार्य के कारण कभी अपने परिजनों से दुर भी रहना पडता है इस कारण वश उनका शिक्षा एवं प्रशिक्षण संबंधी अवसरो से वंचित रहना पडता है. जिनके कारण उनके बेहतर भविष्य के रास्ते खुलते है ''बालश्रम'' की अवधारणा के साथ बालक ऐसी आर्थिक मजबूरिया जुडी होती है जिनके कारण उसका समय निकल जाता है. एवं शारीरिक उर्जा खर्च हो जाती है। वह मनोरंजन, खेलकूद एवं शैक्षिक कार्य कलापों में हिस्सा लेने से वंचित हो जाता है। एस प्रकार बालश्रम वह कार्य है जो बच्चे के स्वस्थ बने रहने एंव उसके विकास मे बाधा पहुचती है।

अन्तराष्ट्रिय श्रम संगठन के अनुसार विकासशिल देशोमें ५ से १४ वर्ष की आयुवर्ग मे काम करने वाले बालको की सख्या अनुमानित २५ करोड है। १२ करोड बालक पूर्ण कालिक कार्यो में लगे है जिसका विवरण निचे दिया है – एशिया – ६१% आफ्रिका, ३२% एवं अमेरिका, ०७%

भारत मे ५ से १४ वर्ष के बालको की कुल संख्या २९.७ करोड है। इन बालको का बडा हिस्सा बालश्रमि कों का है। कुल २९.७ करोड बालको में से ५ से १४ वर्ष के बालको की संख्या २०.३३ करोड है, इन में से ११.६२ करोड बालक पूर्ण कालिक विद्यार्थी है। ११ करोड २७ लाख पूर्ण कालिक श्रमिक है, १ करोड ५ लाख बालक सीमान्त कर्मकार है तथा ७ करोड ४४ लाख बालक नातो विद्यार्थी है ओर नही श्रमिक है। वे केवल स्कुल नही जाते। बाल श्रमिको की संख्या भारत मे कुल श्रमबाल का ५.२ प्रतिशत है जबकि तुर्की में २७.३% यादुलण्ड में २०.७% बांगल देशो मे १९.५% पाकिस्तान मे १६.६% मे क्स्की को मे ११.५% श्रीलंका में ४.४ % तथा ब्रामिल में १८.८ प्रतिशत है। भारत मे काम करने वाले बाजकों का १० प्रतिात ग्रामिण श्रेत्रो में है।

**बालश्रमिकोकी समस्या के प्रति हमारा भावी दृष्टीकोण क्या होना चाहिए**

बालश्रम समस्या के सामाजिक – आर्थिक आकलन से यह समझा और देखा जा सकाता है कि बालश्रम की समस्या अत्यन्त व्यापक और समाज मे एक प्रथा की तरह गहराई तक फैली हई है। इसमें श्रमिक के माता पिता के रुप मे भागीदार है इस समस्या के निदान हेतु एक सावधानी भरे योजना बध्द संघर्ष की आवश्यकता है। बालश्रमिक समस्या स्वय मे उपयुक्त वर्णित समस्योसे जनित एक समस्या है। और यह कितनी समयस्याओं को जन्म देती है, जिससे बचो के शरीरिक मानसिक विकास में अवरोध पैदा होता है जिस के चलते शिक्षा में व्यवधान पैदा न होने से उसकी दक्षता का स्तर भी उँचा नही उठपाता। इसलिए हमें स्पष्ट समझ लेना होगा कि बालश्रम समस्या के विरुध्द संघर्ष वास्तव में गरीबी और गरीबी के कारणो के विरुध्द संघर्ष होगा।

कोई भी देश अपने बचपन के लिए बुनियादी शिक्षा को अनिवार्य किये बिना बालश्रम को खत्म नही कर सकता। प्राथमिक शिक्षा पर खर्च करना भारत के भावी विकास के लिए बहुत ही महत्व पूर्ण है। इससे बालक बालिकाओं को कक्षा ओं मे सीखने का खुशगवार अनुभव हासिल होता है और ऐसे सामाजिक नियम स्थापित होते हैं. जो माँ-बाप और समुदाय को तमाम बालक-बालिकाओं को स्कुल भेजने के लिए तैयार करते है, यही भारत में बाल मजदुरी खत्म करने का सबसे कारगर तरीका है। साथ ही, बालश्रम के उन्मूलन हेतू सामाजिक मानसिकता के बदलाव के लिए निम्नालिखीत कमगार कदम उठाए जाने की नितान्त आवश्यकता है।

१) राज्य मे असंगठित एवं अनौपचारिक क्षेत्रोसहित विभिन्न उद्योगो व प्रक्रिया ओं मे लगे बाल श्रमिकां की समस्या के विभिन्न पहलुओं की जाँच कर उन क्षेत्रो को चिन्हित करना जाहें बालश्रम बहुतायत में लगा है।

२) बालिका श्रमिकोंकी समस्या पर विशेष ध्यान देना।

३) श्रमिको एवं माता-पिता सहित परिजनों में विशेष शिक्षाप्रद अभियान चलाना ताकि भारतीय समाज में एक प्रथा की तरह फैली हुई इस महामारी को समाप्त करने हेतू सामूहिक प्रयास किएजा सके।

४) बालकों के लिए निःशुल्क एवं अनिवार्य प्राथमिक शिक्षा, निःशुल्क दोपहर का भोजन, कापी, किताबें अच्छे की मॉग उढाना

५) बुनियादी स्वच्छता प्रबन्ध, स्वास्य, सामाजिक सुरक्षा एवं कल्याण कारी उपायों को सुनिश्चित करना चाहिए

६) भूमि सुधार सहित गरीनी उन्मूलन के मौसिक कार्यक्रम चलाने की मॉग करना चाहिए

७) रोजगार बढाने की मॉग करना चाहिए रोजगार के अधिकार को मौलिक अधिकार का संविधानिक स्तर प्रदान करना चाहिए।

८) राष्ट्रीय मजदूरी नीति, समान काम के लिए समान मजदूरी तथा आवश्यकता आधारित मजदूरी की मॉग करना चाहिए.

९) बालश्रम कानुन में आवश्यक सुधार, उन्हे प्रभावपुर्ण तरी के से लागू करता तथा कानू का उल्लंघन करने वालो को कडे दण्ड देना चाहिए।

१०) बालश्रम समस्या के समाधान हेतु संगठित क्षेत्र के मजदुरो, किसानो, खेतिहर मजदुरों, नौजवानों छाबो, महिलाओ के तमाम जन संगठनो सहित दुसरे विचारो वाले समू हो व संस्था ओ से सहयोग प्राप्त करना आवश्यक है।

**निष्कर्ष :-**

बालश्रम के समस्त सामाजिक, आर्थिक राजनितीक, हष्टीकोणो पर विचार करने के पश्चात इस गहन समस्या क मानवीय पक्ष पर ध्यान आकर्षित करना आवश्यक है। बालश्रम समस्या के प्रति हमारा राष्ट्र जडता की स्थिती मे है। यहा न्यायाधिपति वि. आर. कृष्णा अय्यर द्वारा बालश्रम कानुन एक अवलोकन के प्रस्तावनामें पूछते है मै विदीर्ण हृदय से आंतकित होकर यह पूछता हूँ, हमरा राष्ट्र जडता की स्थिती में है ? इसलिए नही की प्रशासन कई रुपो में बहुत से अन्यायपूर्ण गम्भीर उपराध और भ्रष्टाचार करता है बल्कि इसालिए कि प्रत्येक बालक अश्रपूरित होकर प्रतिदिन बन्धुआ श्रम के मानसिक आघात को चुपचाप सहन करता है। कानुन द्वारा इस अमानवीय कार्य पर रोक लगाई गई है। कानून के माध्यम से इस प्रथा पर प्रतिबन्ध लगाया गया है। यह अपराधिक बुराई भारत के लगया गया है। यह अपराधिक बुराई भारत के कई भागो मे व्याप्त है। उद्योग, कालीन उद्योग, माचिस उद्योग आतिषबाजी और बीडी उद्योग तो केवल उदाहरण मात्र है। स्वतंत्र्य भारत के बालकोपर होने वाले अत्याचार कानुन को चुनैती देरही है।

बालश्रम की समस्या के समाधान हेतू न्याय प्रशासन के पुनीत कार्य में लगे न्यायाधीशों की अपरिहार्य भूमिका अन्य विचारधारा ओं के साथ नही मिलाया जा सकता एक जागरुक एवं विवेकशील व्यक्ती अथवा न्यायिक अधिकारी बालको के प्रति होने वाली इस बर्नरता का मूकदृष्टनही बन सकाता। इसी सन्दर्भ में राष्ट्रीय मानवाधिकार आयोग तथा महिला आयोग को भी यह अधिकारता प्रदान की जानी जाहिए जहॉ से भी उन्हे बन्धुआ मजदुर, बलश्रम या मानविय शोषण के बारे मे सूचना प्राप्त होती है, वे उस श्रेत्र में अधिकारपूर्वक कार्यवाही करने के लिऐ किसी एक व्यक्ती या संघटन को भेज सके। जहॉ बालश्रम कानुनों की खुले रुप मे अवहेलना होती हो वहा कार्य करने का अधिकार मिलना चाहिए न की किसी अधिकारी की कृपा अथवा नियोजन की अनुमति। बालश्रम से मुक्त कराये गये बालको की शिक्षा और पुनर्वास सम्बंधी योजना ओ के लिए इस बात की माहिती आवश्यक है।

संविधान के अनुच्छेद ३९ (क) की स्वीकृति देश मे निःशुल्क विधिक सहाय्यता आन्दोलन को बालश्रम के क्षेत्र में प्रवेश करने की जोखिम उठाने की आवश्यकता है। समस्त महाविद्यालयीन छात्रो को सम्मिलित कर इस आन्दोलन को सक्रिय बनाया जाना चाहिए। राष्ट्रपिता महात्मा गांधी तथा स्वतंत्र भारत के प्रथम प्रधानमंत्री पंजाबराव जवाहरलाल नेहरु मानविय मुल्यों के गहरे पक्षधर थे। उनकी एवं अन्य राष्ट्रीय चिन्तकों की पवित्र आस्थाओ. को सुस्पष्ट रुप से संविधन मे अन्तर्निहीत किया गया है। इन सबके बावजुद यादि हम देश के भविष्य को मानवाधिकार उपलब्ध नही करा पाते है. तो आने वाली पीठीयाँ हमें कभी माफ नही करेंगी।

**संदर्भ:-**

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# Low Temperature H2S Gas Sensor Based on Fe2O3 Modified ZnO-TiO2 Thick Film

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**Abstract:** Nanocrystalline ZnO-TiO2 (~ 49-56 nm) was synthesized by hydrothermal method. Thick films were prepared by using synthesized nanocrystalline ZnO-TiO2 (with molar ratio 9:1, 7:3 and 1:1) and their gas sensing characteristics were investigated at different operating temperature. ZnO-TiO2 thick film (with molar ratio 7:3) exhibited good response to H2S as compared to other investigated compositions. Further, ZnO-TiO2 thick films (with molar ratio 7:3) were modified by different concentrations of Fe2O3 and their H2S sensing characteristics were investigated. The 0.2M Fe2O3 modified ZnO-TiO2 thick film (with molar ratio 7:3) exhibited excellent H2S sensing characteristics such as, high response (~ 314.67 at 40 oC), quick response time (~ 8 s), less recovery time (~ 30 s), excellent repeatability and stability, good selectivity towards H2S as compared to the other test gases like CO2, LPG and NH3 at 40 oC. The experimental results demonstrated that the Fe2O3 modified ZnO-TiO2 thick film is a very promising material to fulfills the practical requirement for the fabrication of H2S sensors with good sensing characteristics.

**Key words:** Nanocrystalline, ZnO-TiO2; Fe2O3, gas sensor, H2S.

## 1. Introduction

Hydrogen sulfide ($H_2S$) is a toxic and inflammable gas. It is released from coal mines, oil and natural gas industries [1]. Also, $H_2S$ gas is used in different chemical industries, research laboratories, as a process gas in the production of heavy water, etc. Human exposure to higher concentration of $H_2S$ gas results in neurobehavioral toxicity [2]. Therefore it is essential to monitor and control the concentration level of $H_2S$ gas. Consequently, it is today's need to have $H_2S$ sensors with high sensitivity, excellent selectivity, reproducibility, stability, quick response and fast recovery. There are many parameters of materials for gas sensor applications such as adsorption ability, catalytic activity, sensor reponse, stability, etc. Semiconductor metal oxide like ZnO, $SnO_2$, $In_2O_3$, $WO_3$, $ZrO_2$, $CeO_2$, $Fe_2O_3$, have been reported as gas sensors [3]-[13]. But very few of them are suitable to fulfilled all the requirements. To overcome these limitations recently researchers focus on composite materials, like $SnO_2$-ZnO [14], $Fe_2O_3$-ZnO [15], ZnO-CuO [16] etc. In addition to binary metal oxide there are number of ternary and complex metal oxides which are emerged as promising candidates for gas detection [17]-[20]. It has been recognized that sensor based on the two components mixed together are more sensitive than individual component alone due to synergistic effect

between two metal oxides [15]. Preparation of mixed oxides leads to the alteration of the electronic structure of the system, which causes changes in the bulk as well as in the surface properties. Surface properties are expected to be affected by new boundaries between grains of different chemical composition. It is anticipated that all these phenomena will contribute favorably to the gas sensing mechanism [21], [22].

A careful control of the sensor operating temperature and adequate selection of specific impurities is concerned with an optimum response for a specific gas. Materials like CuO, Cr2O3, CeO2 etc. when dispersed onto the semiconductor oxide films, enhance the sensor response to the reducing gas [23]-[25].

It is important to mention here that physical and chemical properties of materials depend on synthesis routes, governed by the synthesizing conditions. In literature, several routes are described for synthesis of nanomaterials, such as chemical, mechanical, gas phase and molten salt synthesis. Hydrothermal technique is one of the chemical synthesis routes that allow in fabrication of shaped and size oriented materials without melting steps. There are a number of advantages of this technique such as: the short duration of the experiments as compared to classical synthesis methods, crystal size and the level of agglomeration can be controlled, costs of the instrument and energy requirement is low as compared to other synthesis routes and it is an eco-friendly method [26], [27].

The objective of this work is to synthesize nanocrystalline ZnO-TiO2 by hydrothermal method and to study the effect of Fe2O3 modification on H2S gas sensing properties of ZnO-TiO2 based thick films.

## 2. Materials and Method

### 2.1. Synthesis of Nanocrystalline ZnO-TiO2

For obtaining nanocrystalline ZnO-TiO2 with molar ratio 9:1 (sample A), accurately weighted analytical grade ZnO (3.607 g) and TiO2 (0.393 g) were dispersed in aqueous NaOH solution followed by hydrothermal treatment at 180 oC for 24 h in Teflon-lined autoclave. Then it was allowed to cool naturally and the obtained precipitate was isolated from solution by centrifugation at 5,000 rpm for 30 min. and subsequently washed with distilled water and then ethanol and dried at 120 oC for 12 h. The same procedure was followed for synthesis of ZnO-TiO2 with molar ratio 7:3 (sample B) and ZnO-TiO2 with molar ratio 1:1 (sample C). The synthesized materials were examined by X-ray diffraction (XRD, XPERT-PRO) and transmission electron microscopy (TEM, Techai G2 20).

### 2.2. Fabrication of Sensor Element and Gas-sensing Measurements

Thixotropic paste was formulated by mixing synthesized ZnO-TiO2 powder with ethyl cellulose and mixture of organic solvent such as butyl cellulose, butyl carbitolacetate and terpineol. Then the prepared paste was screen printed on glass substrate. Furthermore, the thick film of ZnO-TiO2 (with molar ratio 7:3) was modified by dipping it into 0.1M, 0.2M and 0.3M aqueous solutions of Iron (III) chloride for 30 min. These films were dried in air and then fired in muffle furnace at 450 oC for 24 h. These films are termed as Fe2O3 modified ZnO-TiO2 thick films.

For the measurements of gas sensing properties of all these films, silver electrodes was used for electrical contacts. Gas-sensing measurements were carried out on a computer-controlled static gas-sensing system. A small Ni-Cr alloy coil was used for heating and a chromel-alumel thermocouple was used to monitor temperature. Keithley 6487 picometer cum voltage source was used to measure the sensor current. Test gas was injected into the chamber through an inlet port. The concentration of gas was kept 286 ppm and the % relative humidity was kept 20. The sensor response (S) was defined as the ratio of resistance in air (Ra) to that in target gas (Rg) [28].

$$S = R_a / R_g \quad (1)$$

## 3. Results and Discussion

### 3.1. Material Characterization

Fig. 1 shows X- ray diffraction (XRD) patterns of synthesized ZnO-TiO2 powder samples (A to C). From XRD, it is revealed that materials are polycrystalline in nature with mixed hexagonal and tetragonal phases. The characteristic peak in the XRD pattern matches with hexagonal ZnO (JCPDS card no. 00-036-1451) and tetragonal TiO2 (JCPDS card no 01-071-1166). Also the peaks which appeared at 2θ = 29.95°, 36.83°, 56.74°, 62.18° and 70.41° corresponds to Zn2TiO4 (JCPDS card no. 01-073-0578). The extra peak appeared at 2θ = 44.8° is related to surface hydroxyl groups on the ZnO-TiO2 surface [29]. The average crystallite size (D) was determined by using Debye-Scherrer formula [30]:

$$D = 0.9\,\lambda / \beta \cos\theta \qquad (2)$$

where λ is the wavelength of incident beam (1.5406 A°), β is the full width at half maxima (FWHM) of the peak in radians and θ is the diffraction angle.

The average crystallite size of samples (A to C) was calculated from bordering of the diffraction line and found to be in the range of 49-56 nm.

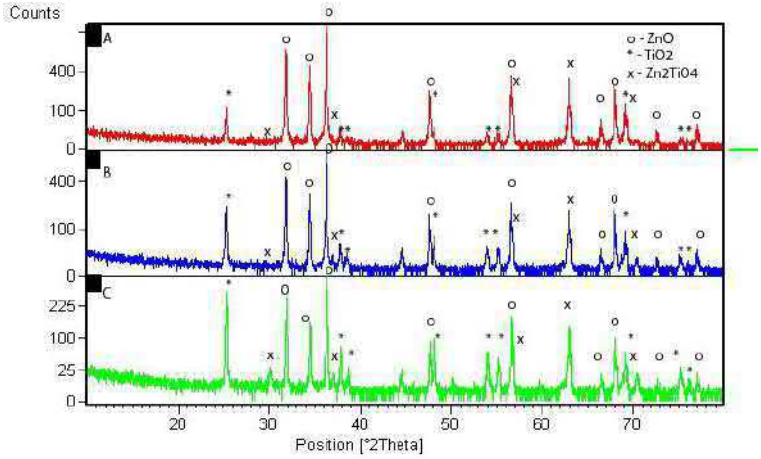
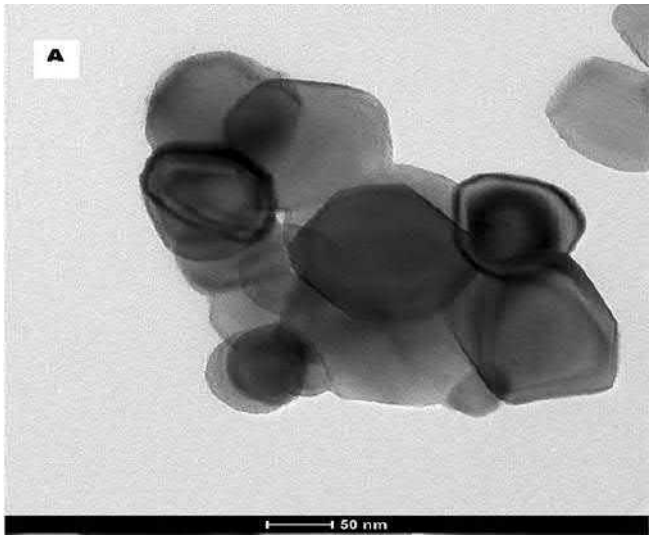



Fig. 1. XRD patterns of synthesized ZnO-TiO2 with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1.



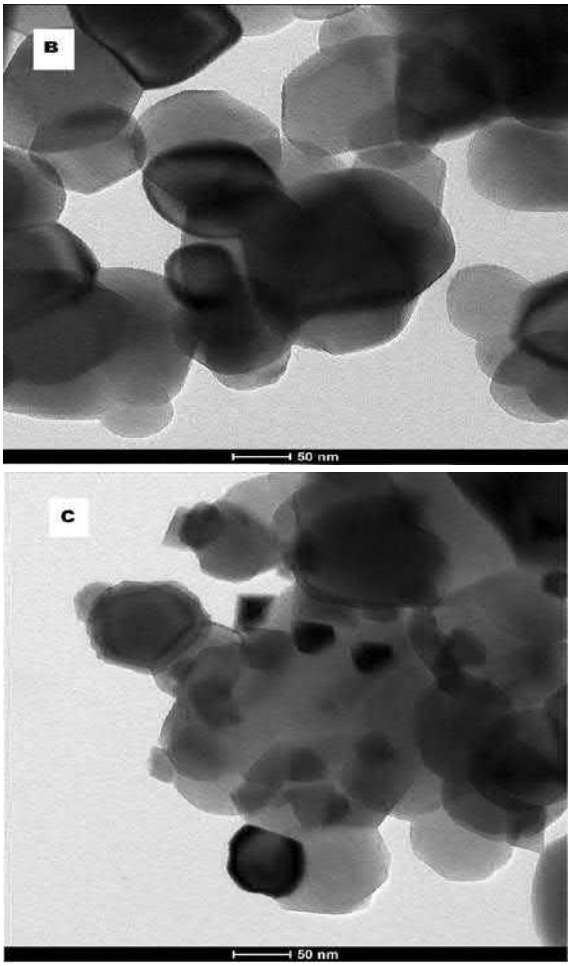
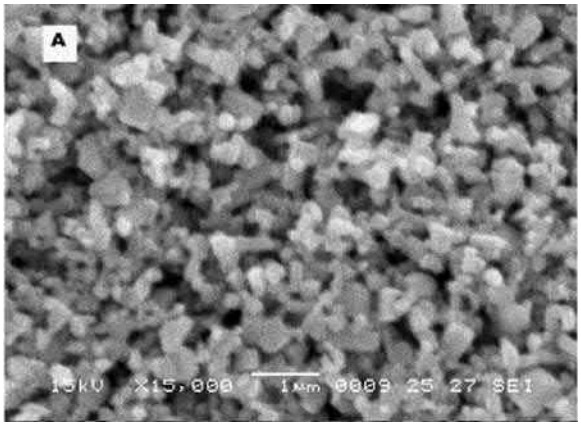



Fig. 2. TEM images of synthesized ZnO-TiO2 with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1.

The morphology of synthesized material samples was investigated by transmission electron microscopy (TEM). Fig. 2 illustrates TEM images of synthesized ZnO-TiO2 powder samples with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1. The small amount of agglomerations can be seen in the micrographs. TEM images indicate that the average crystallite size of synthesized material is in nanometer range.

The surface morphology and nature of ZnO-TiO2 thick films with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1 was analyzed by using scanning electron microscope (SEM, JEOL JSM 6380A). SEM micrographs of ZnO-TiO2 thick films with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1 is shown in Fig. 3. It can be seen that the films particles are evenly distributed.



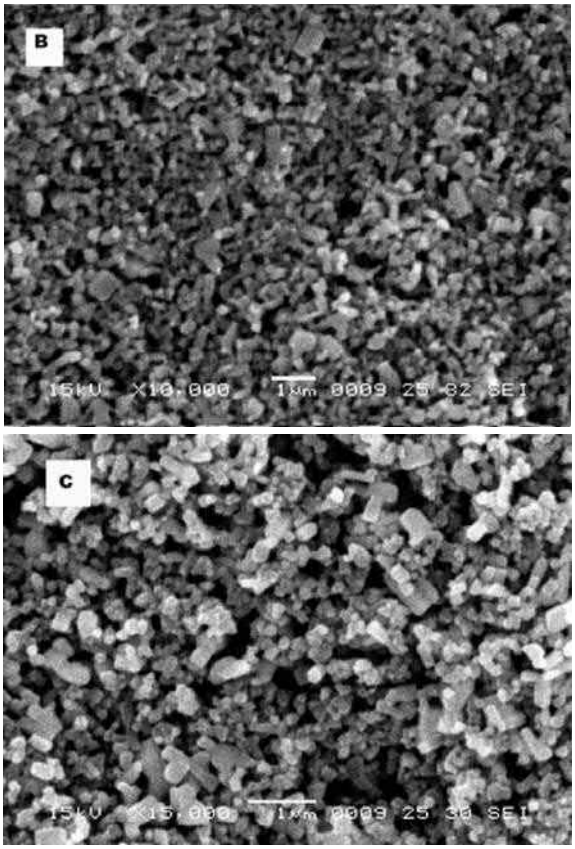



Fig. 3. SEM images of ZnO-TiO2 thick films with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1.

The elemental composition of Fe2O3 modified ZnO-TiO2 thick films (with molar ratio 7:3) were analyzed by using energy-dispersive spectrometer (EDS). Fig. 4 shows EDS spectrum of 0.2M Fe2O3 modified ZnO-TiO2 thick film (with molar ratio 7:3). From the spectrum, it can be seen that there are no other elements than O, Ti, Zn and Fe in the film.

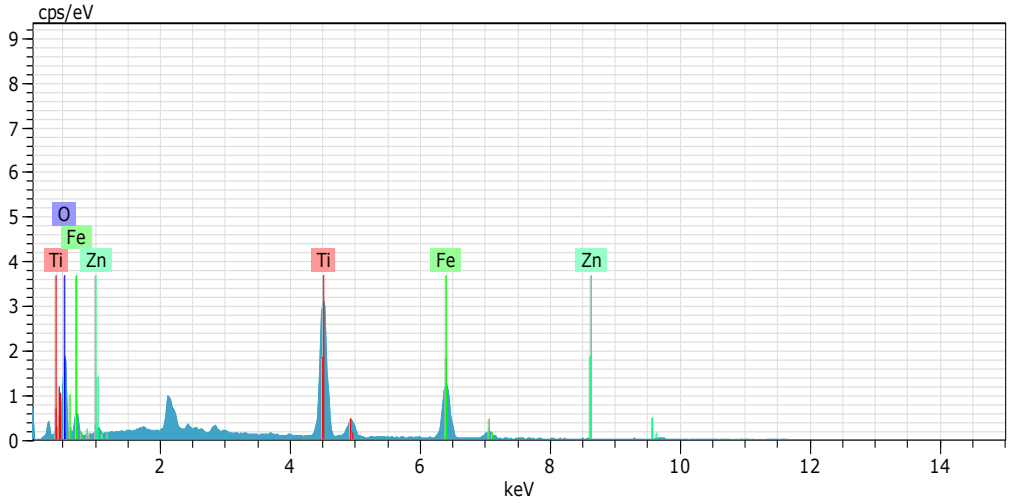



Fig. 4. EDS spectrum of 0.2M Fe2O3 modified ZnO-TiO2 thick film (with molar ratio 7:3).

Fig. 5 indicates SEM image of 0.2M Fe2O3 modified ZnO-TiO2 thick film (with molar ratio 7:3). It indicates that microstructure of 0.2M Fe2O3 modified film is uniform with adequate dispersion of Fe2O3.

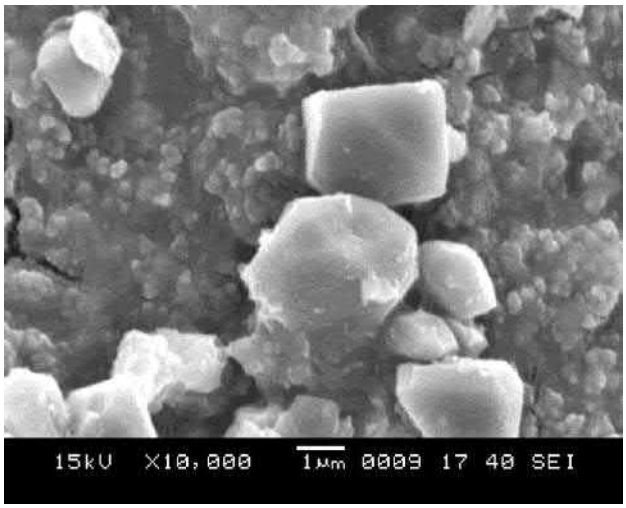



Fig. 5. SEM image of 0.2M Fe2O3 modified ZnO-TiO2 thick film (with molar ratio 7:3).

## 3.2. Gas Sensing Characteristics

Fig. 6 illustrates the response of ZnO-TiO2 thick films with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1 towards 286 ppm H2S. From the figure it can be seen that in the studied temperature range, among the tested compositions, ZnO-TiO2 thick film (with molar ratio 7:3) shows good response.

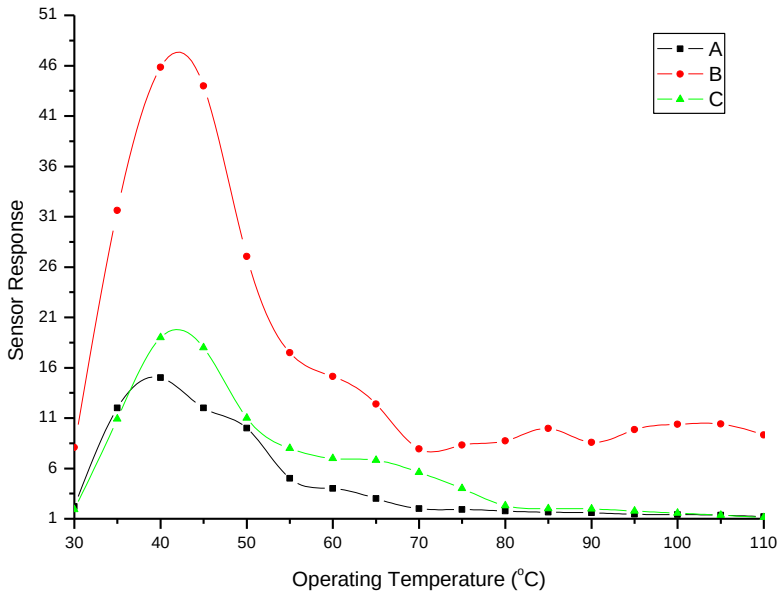



Fig. 6. Response of ZnO-TiO2 thick films with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1 towards 286 ppm H2S.

Regarding the sensing mechanism of semiconductor oxide based materials, the sensing mechanism and change in electrical transport properties are generally depends on the oxygen molecules adsorption and desorption on the surface of materials and/or direct action of lattice oxygen or interstitial oxygen with test gases [31]-[37]. When ZnO-TiO2 thick films are exposed to air, oxygen molecules interact with it to form adsorbed oxygen ions like O2- or O- or O2- by capturing electrons from the conduction band, which decreases the concentration of electrons in the conduction band. The reactions are as follows [38]:

$$O_2\,(gas) \leftrightarrow O_2\,(ads) \quad \text{(i)}$$

$$O_2\,(ads) + e^- \leftrightarrow O_2^-\,(ads) \quad \text{(ii)}$$

$$O_2^-\,(ads) + e^- \leftrightarrow 2O^-\,(ads) \quad \text{(iii)}$$

$$O^-\,(ads) + e^- \leftrightarrow O^{2-}\,(ads) \quad \text{(iv)}$$

When we expose the H2S to the sensor element, H2S interact with the adsorbed oxygen and hydroxyl species present on the sensor. Fig. 6 indicates that the ZnO-TiO2 thick film (with molar ratio 7:3) respond well to H2S and exhibited the highest response at 40 °C among all investigated compositions. The response of ZnO-TiO2 thick film towards H2S can be explained by the interaction of H2S with surface. In this interaction the adsorption of H2S accounts for the consumption of oxygen and this reaction leads to decrease in sensor resistance. The sensor response was improved with increasing amount of TiO2 content in the film; this indicated that there was increase in amount of chemisorbed oxygen ions. This is because electrons induced by Ti4+, enter into ZnO lattice and this conformed to more chemisorbed oxygen on the surface [28]. When the optimum amount of TiO2 in ZnO-TiO2 thick film, TiO2 species would be distributed uniformly throughout the surface of film. As a result the initial resistance of the film is high and this amount would be sufficient to promote the catalytic reaction effectively and overall change in the resistance on the exposure of H2S leading to an increase in sensor response. At an operating temperature of 40 oC, the adsorption of H2S molecules was maximum. The sensor response to H2S can be explained with the overall reaction of H2S molecules with adsorbed oxygen as [39]:

$$H_2S + 3/2\ O_{2\,(ad)}^- \rightarrow H_2O + SO_2 + 3/2\ e^- \quad \text{(v)}$$

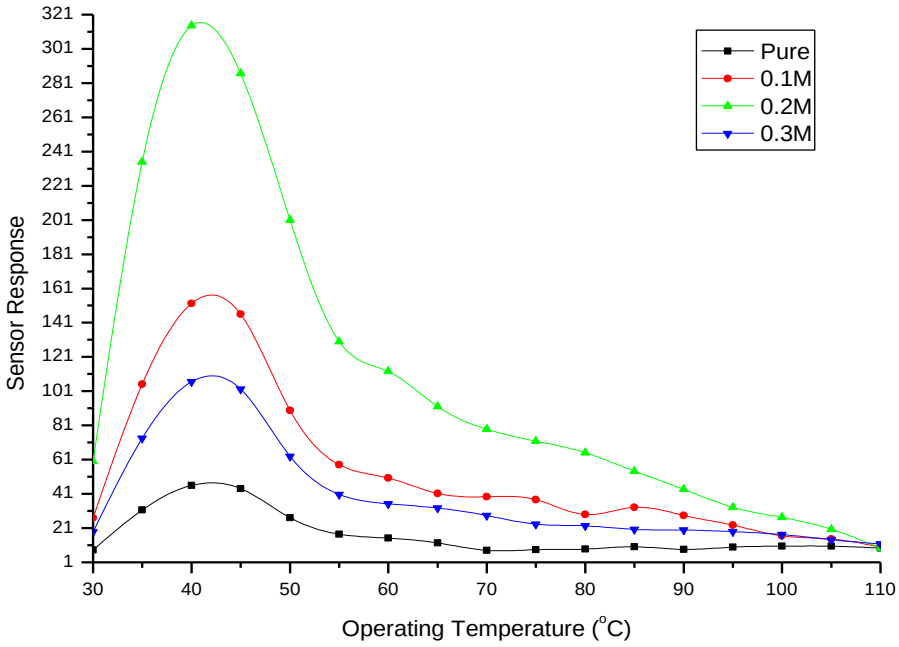



Fig. 7. Response of 0.1M, 0.2M and 0.3M Fe2O3 modified and unmodified ZnO-TiO2 thick film (with molar ratio 7:3) towards 286 ppm H2S.

Fig. 7 illustrates the sensing response of 0.1M, 0.2M and 0.3M Fe2O3 modified ZnO-TiO2 thick films (with molar ratio 7:3) towards 286 ppm of H2S with different operating temperatures. The figure illustrates that the sensing response of the film is a function of Fe2O3 content. It is clearly seen that the response is significantly higher for Fe2O3 modified ZnO-TiO2 thick films especially at lower temperature. 0.2M Fe2O3 modified ZnO-TiO2 thick film respond at room temperature and exhibits remarkable response 314.67 at 40 °C. This can be attributed to the optimum and systematic Fe2O3 distribution in ZnO-TiO2 matrix. The amount and distribution of Fe2O3 in ZnO-TiO2 matrix play an important role in governing the H2S sensing response. The maximum response may be due to Fe2O3 selectively catalyze the reaction rate of H2S on the surface of film.

The H2S sensing mechanism for Fe2O3 modified ZnO-TiO2 thick film can be explain as; upon exposure of H2S to the sensor, a surface reaction reduces the coverage of oxygen, causing returning of electron, here Fe-O sites may be acting as active centers. The adsorption of H2S may be initiating from absorbed oxygen species on Fe, resulting H2S dissociation with the formation of SO2 and H2O with the release of electrons. Due to this process electrons are made free for conduction and causing increase in sensing response.

Fig. 8 illustrates the response of 0.2M Fe2O3 modified ZnO-TiO2 thick film (with molar ratio 7:3) toward different gases (286 ppm each) like NH3, CO2, H2S & LPG at 40 oC. The sensor exhibited maximum response of 314.67 towards 286 ppm H2S as compared to other gases like CO2, LPG and NH3. It is negligible for CO2 and LPG. The high selectivity at low operating temperature may relate to the distribution of Fe2O3 which favors the adsorption of H2S as compared with other gases. The adsorption configuration of H2S molecules and surface reaction on the Fe-O sites are responsible for the low temperature sensing response towards H2S selectively.

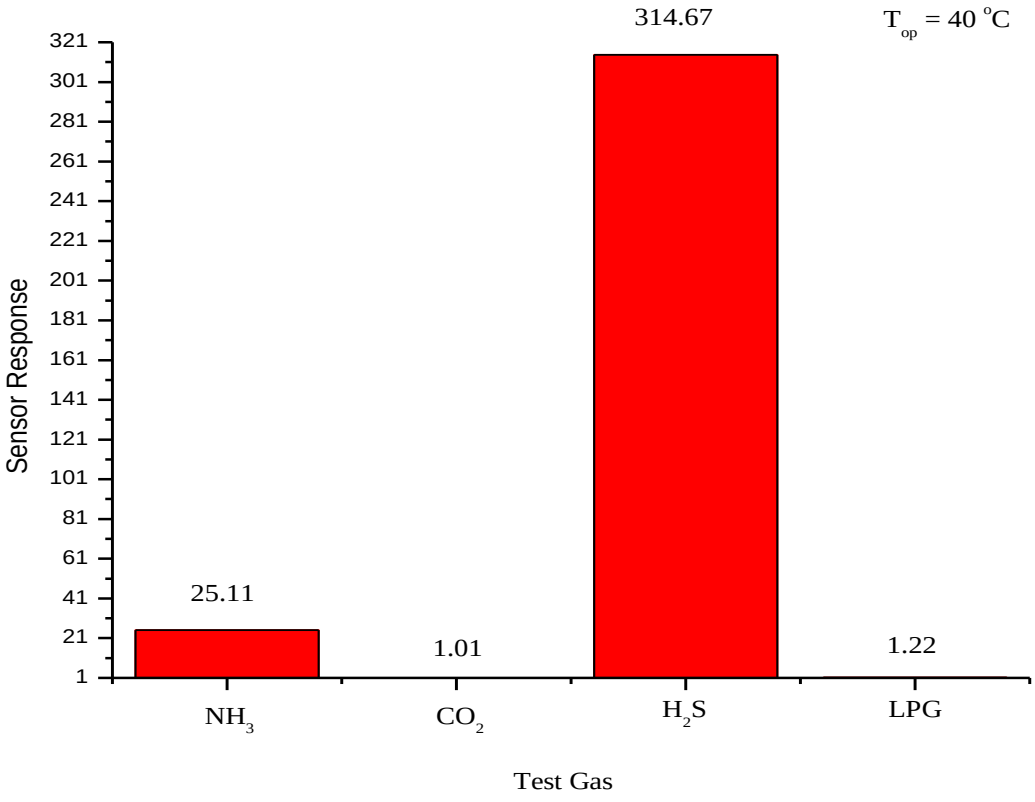



Fig. 8. Response of 0.2M Fe2O3 modified ZnO-TiO2 thick film (with molar ratio 7:3) toward NH3, CO2, H2S & LPG at 40 oC.

In practical application, response and recovery times of sensor for the particular gas are the important factors. Response and recovery times are defined as the time reaching 90% of the final stable values. Fig. 9 illustrates response and recovery time of 0.2M Fe2O3 modified ZnO-TiO2 thick film (with molar ratio 7:3) towards 286 ppm H2S at 40 oC. It indicates that response time and recovery time of sensor is 8 s and 30 s respectively. This result may be recommended for practical applicability of the sensor to detect H2S.

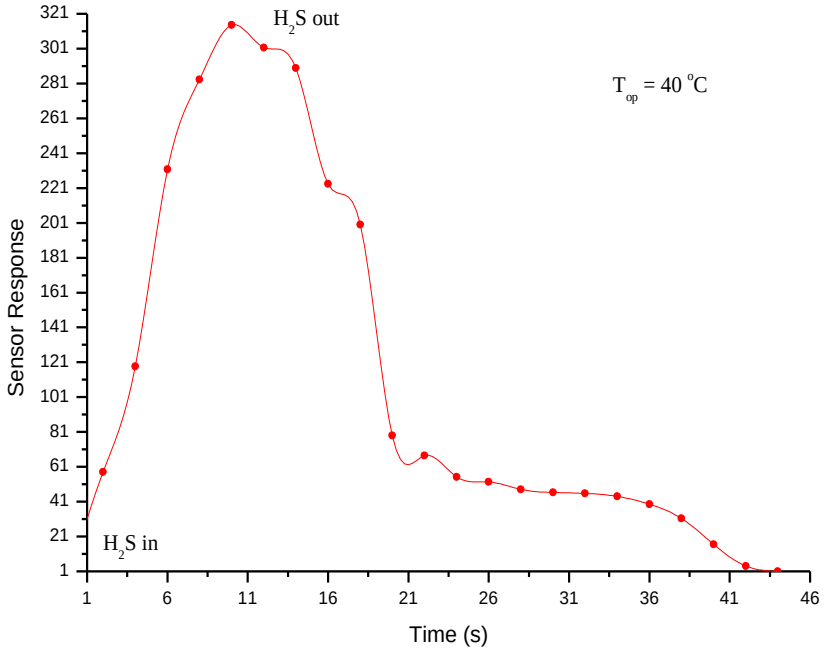



Fig. 9. Response and recovery time of 0.2M Fe2O3 modified ZnO-TiO2 thick film (with molar ratio 7:3) towards H2S at 40 oC.

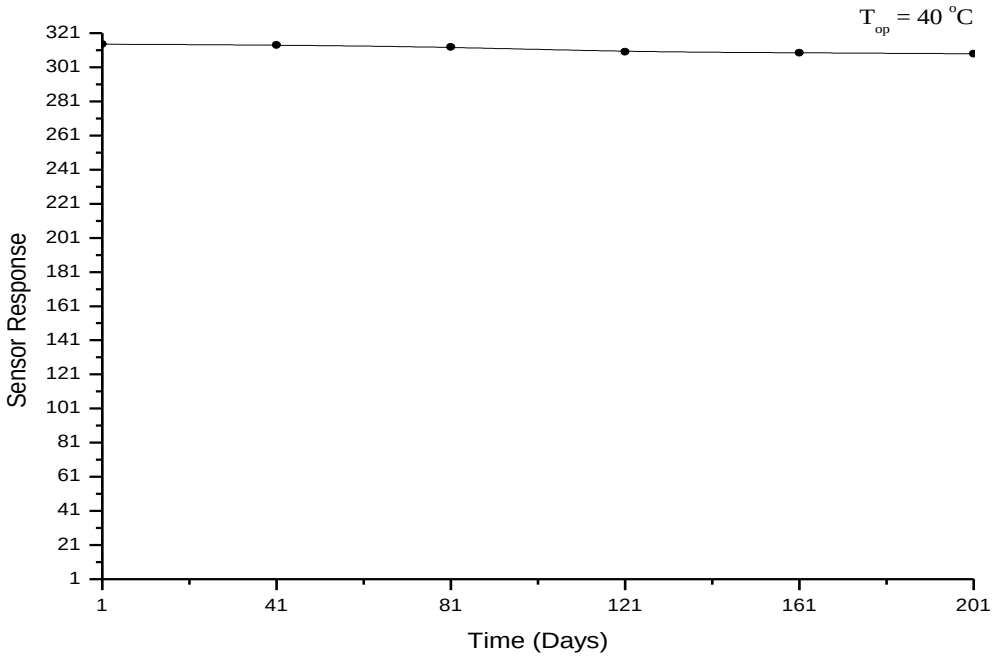



Fig. 10. Stability of 0.2M Fe2O3 modified ZnO-TiO2 thick film (with molar ratio 7:3) towards 286 ppm H2S at 40 oC.

Fig. 10 demonstrated response of 0.2M Fe2O3 modified ZnO-TiO2 thick film (with molar ratio 7:3) towards 286 ppm H2S at 40 oC for the period of 201 days in the interval of 40 days. It is observed that there is no noticeable deviation in the sensor response. This is due to presence of TiO2 [40].

## 4. Conclusions

On the basis of experimental results and its discussions, the following conclusions can be made:

(i) Nanocrystalline ZnO-TiO2 materials were successfully synthesized by hydrothermal method. The crystallite size of synthesized materials is of the order of 49-56 nm.

(ii) The sensor element based on 0.2M Fe2O3 modified ZnO-TiO2 thick film (with molar ratio 7:3) exhibited good response to 286 ppm H2S at room temperature and highest response of 314.67 at 40 oC.

(iii) The sensor element based on 0.2M Fe2O3 modified ZnO-TiO2 thick film (with molar ratio 7:3) is more selective toward H2S as compared to CO2, LPG and NH3. Also it exhibited quick response (8 s), rapid recovery (30 s) and long time stability.

Hence sensor based on 0.2M Fe2O3 modified ZnO-TiO2 thick film (with molar ratio 7:3) fulfills the practical requirement to detecting H2S at low operating temperature.

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# SYNTHESIS, STRUCTURAL AND GAS SENSING PROPERTIES OF PURE ZINC OXIDE NANO THICK FILM.

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## ABSTRACT

The ZnO nanostructures have been synthesized and studied as the sensing element for the detection of$H_2S$ gas. The ZnO nanostructures were synthesized by Sol-gel method followed by sonication. By using screen printing method, thick films of synthesized ZnO nanostructure were deposited on glass substrate. Gas sensing properties of ZnO nanostructure thick films were studied for low concentration $H_2S$gas at different temperature. ZnO nanostructure synthesized by this method can be used as a promising material for semiconductor gas sensor to detect gas like $H_2S$ at above room temperature with high sensitivity and selectivity.

**Keywords:** Nanostructure, ZnO, UV, FTIR, XRD, TEM, SEM, $H_2S$ Sensor.

## 1. INTRODUCTION

Today, when the world is prevailing on the roof of technology and electronics, mostly dominated by compatible electronic equipments and thereby creating the need for materials possessing useful properties. The world now demands a material that should possess inherent properties like larger band gap, higher electron mobility as well as higher breakdown field strength. So on making investigation about such a material the name of compound comes out is “Zinc Oxide” which is a wide gap semiconductor material very well satisfying the above required properties. Zinc oxide possessed many versatile properties for UV electronics, spintronic devices and sensor applications. This ignites many research minds all over the world and creates interest to develop proper growth and processing techniques for the synthesis of Zinc oxide.

The electrical, optical, magnetic, and chemical properties can be very well tuned by making permutation and combination of the two basic structural characteristics that is cations with mixed valence states, and anions with deficiencies (vacancies). Thus, making them suitable for several application fields such as semiconductor, superconductor, ferroelectrics, magnetic and gas sensing.

Nanostructured materials such as ZnO, $SnO_2$, and $WO_3$ have shown good electrical properties [1-13]. Among these nanostructure-semiconducting materials, ZnO has been studied extensively for electrical application and gas sensing. Due to its versatility and multifunctionality creates attention in the research field related to its electrical applicationsand gas sensing. A wide number of synthesis techniques also been developed by which ZnO can be grown in different nanoscale forms. Efforts were made to synthesize ZnO nanostructure with innovative morphology by Sol-gel method. The synthesized ZnO shows good electrical conductivity. In the present work, the efforts are made to study Characterizationand gas sensing of low cost (ZnO).

$H_2S$ is a toxic gas produced from the coal, oil and natural gas industries. In order to enhance the sensitivity and selectivity of $H_2S$, many attempts were made to synthesized nanostructure ZnO with different morphologies [14-18].

## II. EXPERIMENTS

### II.1. Synthesis of ZnO Nanostructure

All the chemicals used in this study were of GR grade purchase from Sd-Fine, India (purity 99%). The chemicals are used without any further purification. Zinc acetate dehydrate $Zn(O_2CCH_3)_2(H_2O)_2$, sodium hydroxide, Methanol and deionized water was used during reaction.

In preparation Zinc Oxide (ZnO) 0.2M Zinc Acetate dehydrates was dissolved in 100 ml deionized water was ground for 15 min and then mixed with 0.02 M solution of NaOH with the help of glass rod. After the mixing the solution was kept under constant magnetic stirring for 15 min. and then again it was ground for 30 min. The white precipitate product was formed at the bottom. Then abundant liquid was discarded and the product was washed many times with the deionized water and methanol to remove by products. The final products was then filtered by using Wattman filter paper and obtain precipitate in the form of white paste, now this paste was kept in a vacuum oven at $80^oC$ for 4hrs so the moisture will removed from the final product and we will get dry product. Then this dry product was crushed into a find powder by using grinding machine and finally this fine nano-powder of ZnO was calcinated at temperature $800^oC$ for 6 hrs in the auto controlled muffle furnace *(*Gayatri Scientific, Mumbai, India.*)* so that the impurities from product will be completely removed and get a final product of ZnO nanoparticles.

### II.2 Preparation of Thick Films

Thick films of synthesized nanostructure ZnO were prepared by using screen printing technique. In present process, thixotropic paste was formulated by mixing the synthesized ZnO

powder with ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butylcellulose, butyl carbitol acetate and turpineol. The ratio of ZnO to ethyl cellulose was kept at 95:05. The ratio of inorganic to organic part was kept as 75:25 in formulating the pastes. The thixotropic pastes were screen printed on a glass substrate in desired patterns. The films pre-pared were fired at 500°C for 12 hr. Prepared thick films were called as pure ZnO thick films.

## III. MATERIALS CHARACTERIZATION

### III.1. Thickness Measurement

Thickness of all ZnO thick films were measured by using technique "Marutek film Thickness Measurement System" with the help of provided equipment. The thicknesses of all films were observed in the range from 35 μm. Thick films of approximately uniform thick-nesses were used for further characterization.

### III.2. UV-visible absorption spectrum

UV-visible absorption spectroscopyis widely used toolfor checking the opticalproperties of nanosized particles.Figure 1 shows the UV-visible absorption spectrum of ZnO nanoparticlescalcined at temperature 800$^{o}$C for 6 Hrs. From the spectrum four peaks are observed at 362nm, 318nm, 344nm and 296nm, out of this at 318 nm wavelength has been found maximum absorption, if we calculate band gap for this wavelength it is 3.30eV, which is very close tothe band gap of ZnO 1s–1s electron transition (3.37eV) [19].

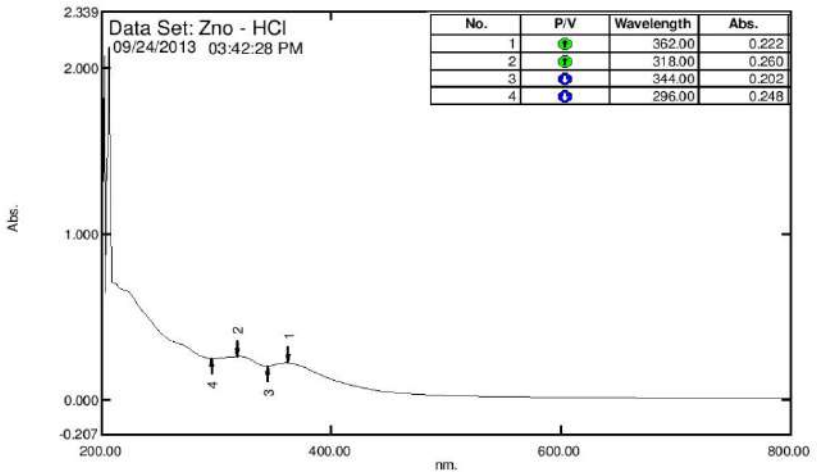


**Figure 1:** UV-visible absorption spectrumof Pure ZnO

### III.3. FTIR analysis

FTIR analysis spectrum shown in figure 2, indicating significant absorption peaks at wave numbers 4350, 4200, 3900, 3850, 1700, 1550 and 600, 510 cm$^{-1}$. The absorption band at 600 and 510 cm$^{-1}$ is obtained due existence of Zn-O bond stretching vibration [20]. The peaks at 1700 and

1550 $cm^{-1}$ shows H-O-H bending vibration due to the adsorption of moisture, when FTIR sample disks were prepared in an open air atmosphere. The remaining peaks between 4350 to 3850 $cm^{-1}$ are corresponding to O-H stretching vibrations [21].

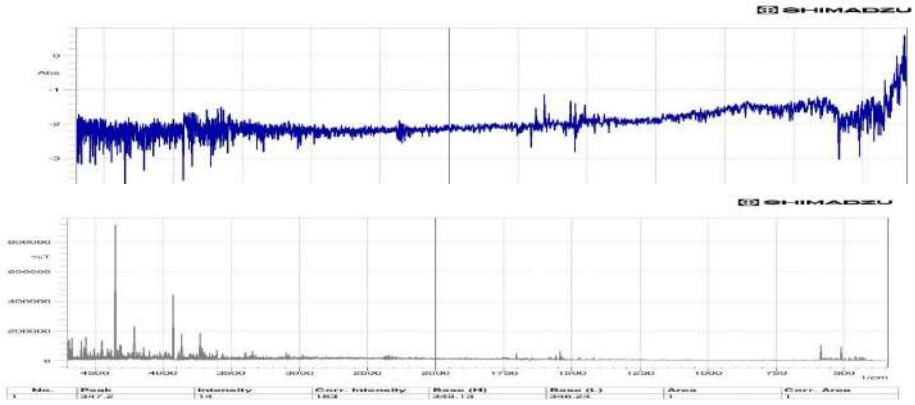


**Figure 2:** FTIR absorption/transmission spectrum of Pure ZnO

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### III.4. X-Ray Diffraction Studies

The crystallographic structure of the synthesized ZnO nanostructure was characterized by powder X-ray diffraction (Philips X-ray diffractometer) with Cu-α source and 2$\theta$ range of 10° - 70°. Fig 3shows the XRD pattern of the ZnO nanostructure. The recorded XRD pattern confirmed that synthesized ZnO are highly crystalline in nature. The corresponding X-ray diffraction peak for (100), (002), (101), (102) (110), (103) and (112) planes confirm the formation of hexagonal wurtzite structure of ZnO (JCPDS card no.-01-080-0075). The domain size of the crystal can be estimated from the full width at half maximum (FWHM) of the peaks by means of the Scherrer formula $D = k\lambda/\beta\sin\theta$ , where $\lambda$ is the wavelength of incident beam (1.5406 Å), $\beta$ is the FWHM of the peak in radians, $\theta$ is the diffraction angle and $K$ is Scherrer constant. The average particle size was calculated from (101) peak ZnO is found to be 78 nm.

Using X'pert High Score Plus software it is confirm that synthesized zinc oxide powder contains Zn and O elements only, not any impurity and another element.

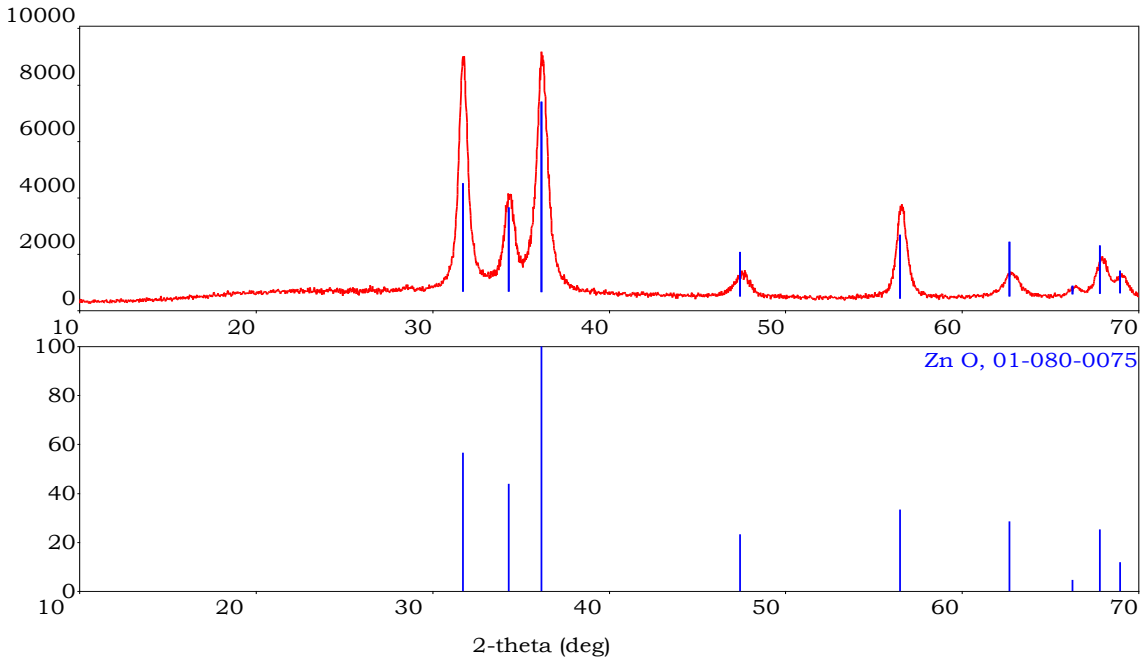


**Figure 3:** X- Ray diffraction Pattern of Pure Zinc Oxide (ZnO)

### III.5. Transmission electron microscope

Figure 4(a, b):shows transmission electron microscope image of ZnO nanostructure synthesized by liquid-phase co-precipitation method. It is clearly seen from the TEM image that the ZnO powders consist of large number of nanosphere which were cumulated to form superior size crystal.

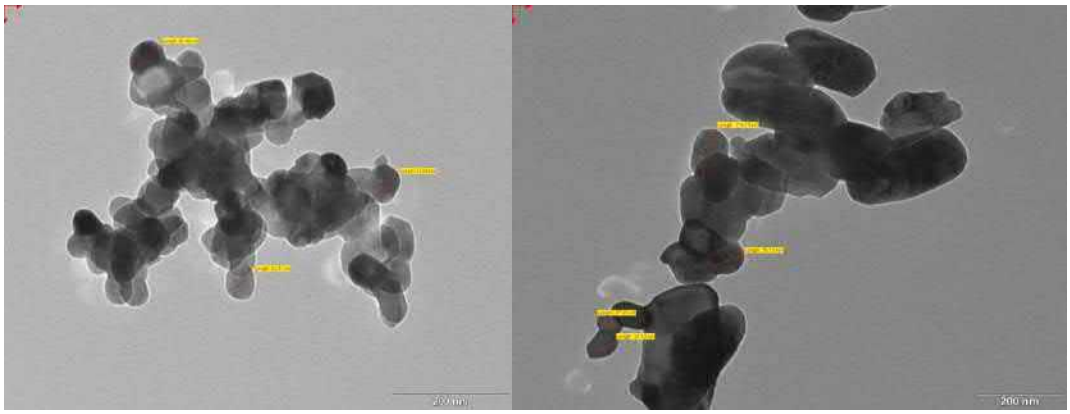

**Fig 4 (a)** **Fig 4 (b)**

**Figure 4:** Transmission Electron Microscope Pattern

### III.6. Scanning Electron Microscopic Study

Figure 5 shows typical SEM images of the pure ZnO thick film prepared by screen printing technique. The ZnO synthesized by liquid-phase co-precipitation method consist of randomly distributed nanosphere as shown in Figure 5a and Figure 5b. Due to such a deposition of nanosphere, surface to volume ratio of the ZnO may be increased.

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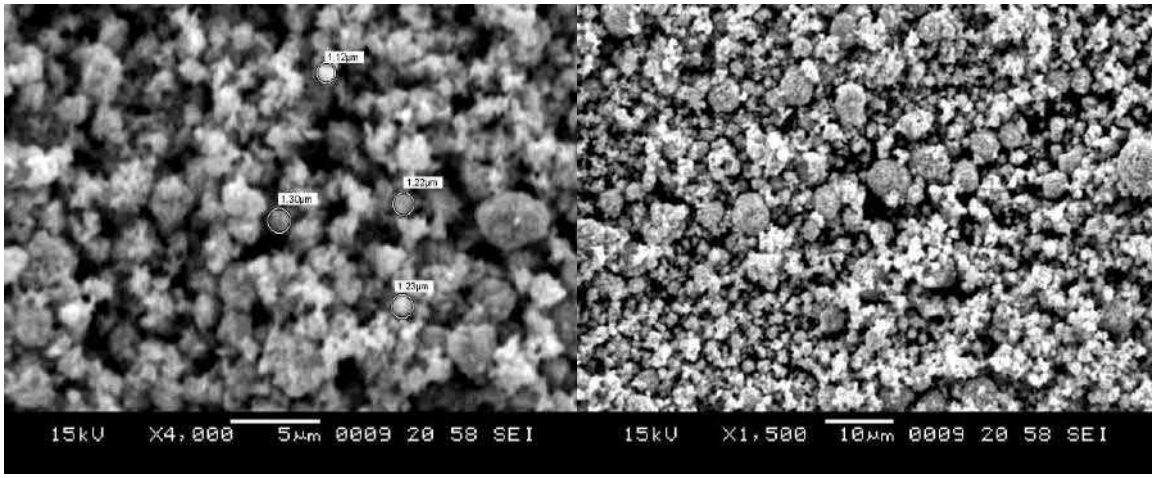


**Fig 5 (a)** **Fig 5 (b)**

**Figure 5:** Scanning Electron Microscope Pattern

## IV. GAS SENSING PROPERTIES

The gas response of the sensor was defied as the ratio of the change in conductance of a sample upon exposure to the target gas to the original conductance in air. Figure 6shows the gas responses of ZnO thick films to $H_2S$ at operating temperature. This high response of ZnO thick film to $H_2S$ may be due to the interaction of ZnO with $H_2S$, forming ZnS [22-23]. ZnS exhibits higher electronic conductivity as compared to pure ZnO.

Figure 6 also indicates the pure ZnO have maximum gas response to low concentration $H_2S$. The higher response ZnO nanostructure upon exposure to $H_2S$ may be attributed to the decrease in concentration of oxygen adsorbents ($O^{2-}$) and a resulting increase in concentration of electron.

The gas response was mainly dependent upon two factors. The first was the amount of active sites for oxygen and the reducing gases on the surface of the sensor materials. It is seen form TEM images Figure 4 (a), (b) .The surfaces pure ZnO contain more active sites .This could explain why the response of pure ZnO thick films was higher than other thick films.

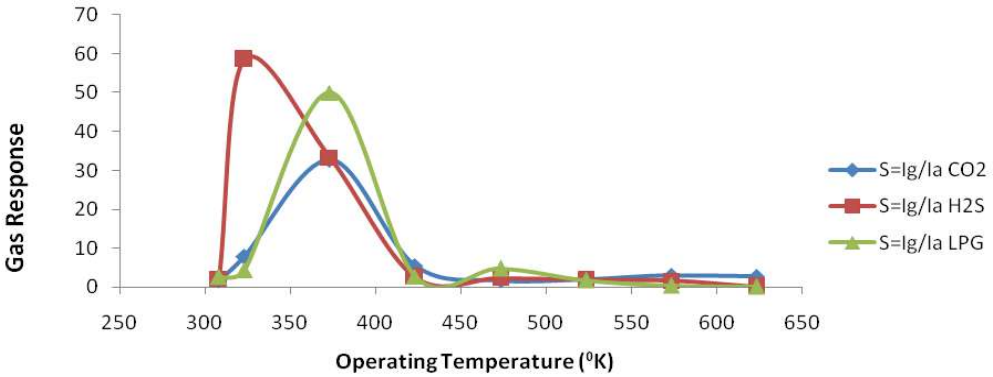


**Figure 6: Sensitivity of gas from mixture of gases**

## V. CONCLUSION

In summary, sensors were fabricated with ZnO nanostructures, which were synthesized by a liquid-phase co-precipitation method followed by sonication, and their gas sensing properties were measured. The results demonstrated that pure ZnO is very sensitive to low concentration $H_2S$. Such nanomaterials with innovative structure can be used for gas sensors to monitor hazards gas like $H_2S$.

## Acknowledgement

The present work was supported by UGC –MRP and also Dr.F.C. Raghuwanshi, my guide and supervisor for his excellent guidance, competent advice, admirable support and persistent encouragement through the course of my research work, without which the successful completion of this work would not have been possible.

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A PATH FOR HORIZING YOUR INNOVATIVE WORK

# NANOCRYSTALLINE MIXED METAL OXIDE SEMICONDUCTOR SYNTHESIZED BY HYDROTHERMAL METHOD

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**Abstract:** This paper covers the synthesis of nanocrystalline mixed metal oxide by using hydrothermal method. Common themes related to the synthesis are outlined and their advantages over conventional reactions are described. Nanostructure ZnO-$TiO_2$ mixed metal oxide was synthesized by hydrothermal technique. Structural characteristics of synthesized material were studied by using X-ray powder diffraction (XRD), Fourier transform Infrared spectrometer (FTIR), scanning electron microscope (SEM), energy dispersive spectrometer (EDS) and transmission electron microscope (TEM). The average particle size of synthesized mixed metal oxide (ZnO-$TiO_2$) was found to be in the range of 56 nm. The transition from microparticles to nanoparticles can lead to a number of changes in physical properties. Nanoparticles are currently made out from wide variety of materials. The most common name prominently used in the generation of nanocystalline ceramics, is transition metal oxide such as ZnO-$TiO_2$. Because it can provides solutions to variety of engineering and scientific problems.

**Keywords:** ZnO: TiO2; Nano-material; Ceramic; Hydrothermal Techniques

**Corresponding Author: MR. R. B. PEDHEKAR**

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## INTRODUCTION

Nano-meter sized particles of metal oxide semiconductors are important because of their novel electrical, optical, magnetic and chemical properties. It is important to mention here that physical and chemical properties of materials depend on synthesis routes, governed by the synthesizing conditions. The effect of particle size on the electronic and optical properties of the nanosized particles during the growth of crystallite from molecular level to the bulk material is important. In literature, several routes are described for synthesis of nanomaterials. These are chemical, mechanical, gas phase and molten salt synthesis [1]. Hydrothermal technique is the chemical synthesis method that allows fabrication of shape and size oriented materials without involving any melting steps [2]. The advantages of the hydrothermal technique are [3]: the duration of the experiments is reduced by two orders of magnitude compared to classical synthesis procedures, crystal size, morphology and controls the level of agglomeration for different ceramic oxides. It requires low cost instruments and less consumption of energy as compared to other synthesis routes. It is also an eco-friendly method [2]. Hence the hydrothermal technique is treated as the green technology which is useful for synthesis of nanocrystallile metal oxide semiconductors.

Because of significant optical and electrical properties of ZnO, this material has been studied extensively. Low cost of precursors, simplicity and high efficiency of its chemical synthesis method encourage scientists to investigate on nano-ZnO. Note to this facts, ZnO has different nano-morphologies at various synthesis conditions where by different properties can be obtained [4, 5].

Titanium dioxide has promising applications in covering materials, air purification, self-cleanliness, functional ceramics, cosmetics, catalysts, and waste water treatment [6, 7]. That is due to its numerous particular physicochemical properties, such as large specific area, high surface activity, good thermal diffusivity etc.

Nanocrystalline mixed metal oxides could be extended to the potential applications such as chemical sensors, optoelectronic devices, photocatalysis, antibacterial activity etc. [4, 5]. Beside this , the mixed metal oxide getting from transition metal oxides are started to use as humidity and gas sensor. Use of these nanocrystalline materials can provide solution to difficult engineering problems. ZnO-$TiO_2$ nano-composites have strong physical and chemical interaction with adsorbed species and thereby these nano-composites have a variety of applications as gas sensing materials, antistatic films, surface acoustic wave devices, catalysts and antireflection coatings in solar cells [8-10]. Although a large volume of literature is available on the synthesis of oxide nano-composite powders, very little attention has been given to the

hydrothermal synthesis of ZnO-$TiO_2$ mixed metal oxide semiconductor. It is interesting to know how the morphology and size distribution of obtained particles change by using this technique.

The objective of this work is to synthesize the nanocrystalline mixed transition metal oxide by hydrothermal technique for different engineering and scientific applications.

## 2. EXPERIMENTAL DETAILS

For obtaining nanocrystalline ZnO-$TiO_2$ with molar ratio 1:1, analytical grade ZnO and $TiO_2$ were dispersed in aqueous NaOH solution followed by hydrothermal treatment at 180 $^oC$ for 24 h in Teflon-lined autoclave. Then it was allowed to cool naturally and the obtained precipitate was isolated from the solution by centrifugation at 5,000 rpm for 30 min. and subsequently washed with distilled water and ethanol and then dried at 120$^oC$ for 12 h. The synthesized material was examined by X-ray diffraction (XRD, XPERT-PRO), Fourier transform infrared spectrometer (FTIR, IR Affinity, SHIMADZU), scanning electron microscope (SEM, JSM6380, JEOL), energy dispersive spectrometer (EDS, Bruker) and transmission electron microscope (TEM, Techai G2 20). All the chemicals used in the present work were of AR grade without further purification.

## 3. RESULTS AND DISCCUSTION

### 3.1 X-ray diffraction pattern

Fig.1 shows XRD patterns of synthesized ZnO-$TiO_2$ powder sample. From XRD, it is seen that the material is polycrystalline in nature with mixed hexagonal and tetragonal phases. The characteristic peak in the XRD pattern matches the hexagonal ZnO (JCPDS card no. 00-036-1451) and tetragonal $TiO_2$ (JCPDS card no 01-071-1166). Also the peaks which appeared at 2θ = 29.95°, 36.83°, 56.74°, 62.18° and 70.41° correspond to $Zn_2TiO_4$ (JCPDS card no 01-073-0578). The extra peak appeared at 2θ = 44.8° is related to surface hydroxyl groups on the ZnO-$TiO_2$ surface [11].

The average crystallite size (D) was determined by using Debye-Scherrer formula [12]:

$D = 0.9 \lambda / \beta \cos \theta$ .....(2)

Where λ is the wavelength of incident beam (1.5406 Å), β is the full width at half maxima (FWHM) of the peak in radian and θ is the diffraction angle. The average crystallite size of sample was calculated from bordering of the diffraction line and found to be in the range of 56 nm.

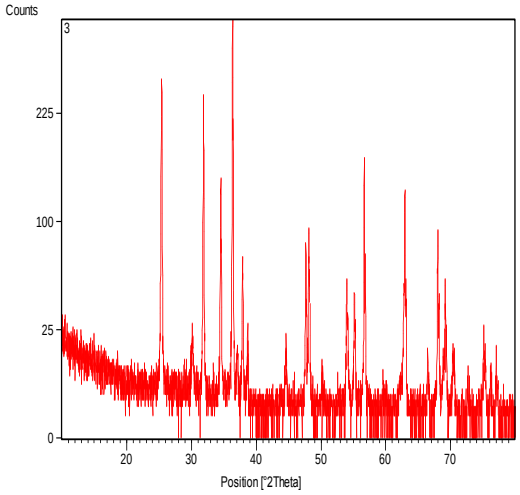


**Fig.1. X-ray diffraction pattern of synthesized ZnO-$TiO_2$.**

### 3.2 Scanning electron microscope (SEM)

The SEM image of Synthesized ZnO-$TiO_2$ nanoparticles is shown in fig.2. Surface morphology and structure were observed by SEM. From the image it is observed that the ZnO-$TiO_2$ particles are of aggregate star like structure.

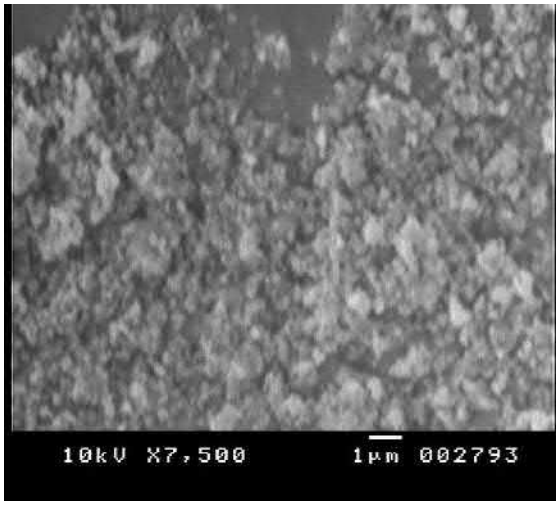


Fig.2. SEM image of synthesized ZnO-$TiO_2$.

### 3.3 Transmission electron microscopy (TEM)

Fig.3 illustrates TEM image of synthesized ZnO-$TiO_2$ powder sample. The small amount of agglomerations can be seen in the micrographs. TEM image indicates that the average crystallite size of synthesized material is in the range of nanometer.

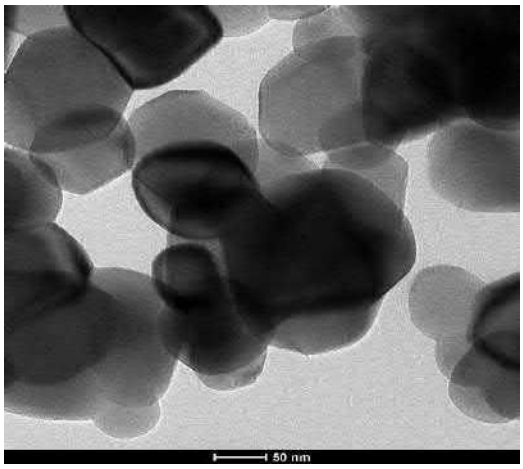


**Fig.3. TEM image of synthesized ZnO-$TiO_2$.**

### 3.4 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectrum of synthesized ZnO-$TiO_2$ material is recorded between 4000 – 400 $cm^{-1}$ and presented in fig. 4. It is seen that the spectrum manifests several bands in the range of 1000 – 400 $cm^{-1}$ related to the oxygen-metal linkage [13].

The band which had appeared at 406 $cm^{-1}$ is due to the stretching vibrations of Zn-O [14]; 419 $cm^{-1}$ corresponds to wurtzite zinc oxide [15] and band at 439 $cm^{-1}$ appeared due to anatase $TiO_2$ [16]. The absorption bands in 3600 – 3200 $cm^{-1}$ are connected to stretching vibration of hydroxyl group. This is assigned to the physical absorption of water [17]. The FTIR results are in good accordance with XRD data.

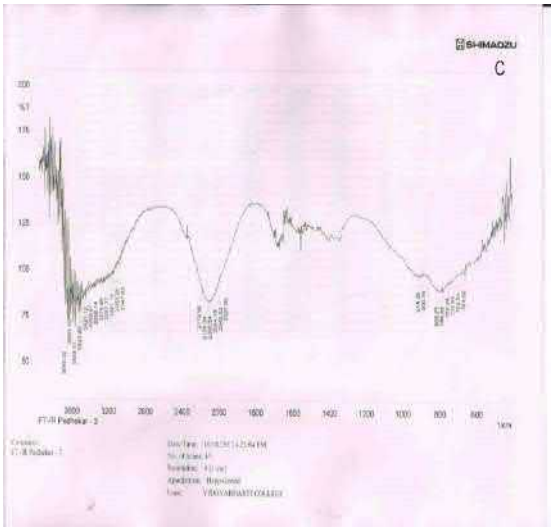


**Fig. 4 FTIR spectrum of synthesized ZnO-$TiO_2$.**

### 3.5 Energy dispersive spectrometery (EDS)

The elemental composition of synthesized nanocrystalline ZnO-$TiO_2$ (with molar ratio 1:1) was analyzed by using energy-dispersive spectrometer (EDS). Fig.5 shows EDS spectrum synthesized ZnO-$TiO_2$ (with molar ratio 1:1). From the spectrum, it can be seen that there are no elements other than O, Ti and Zn. The elemental composition of synthesized ZnO-$TiO_2$ (with molar ratio 1:1) is shown in table 1.

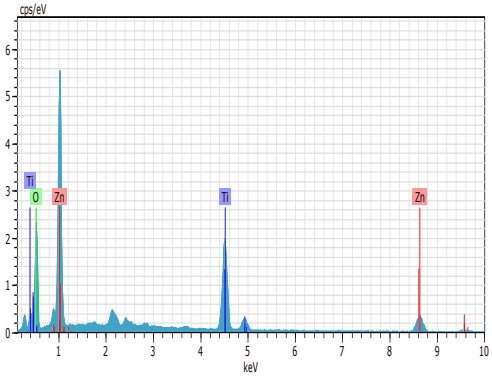


**Fig.5: EDS spectrum of synthesized ZnO-$TiO_2$.**

### 4. CONCLUSION

The nanocrystalline ZnO-$TiO_2$ mixed metal oxide semiconductor have been synthesized successfully by hydrothermal technique. The average size of synthesized material was

calculated by using XRD Scherrer formulae and it comes out to be in the range of 56 nm. The XRD, FTIR, SEM, EDS and TEM characterization of synthesized material confirm the formation of nanocrystalline ZnO-$TiO_2$.

**Table 1. Composition of nanocrystalline ZnO-$TiO_2$.**

| Element | ZnO-$TiO_2$ (molar ratio 1:1) | |
|---|---|---|
| | Norm. wt.% | Atom. at.% |
| O | 32.58 | 63.30 |
| Zn | 40.66 | 19.33 |
| Ti | 26.76 | 17.37 |

**ACKNOWLEDGEMENTS**

The authors express gratitude to Dr. S. S. Bhoga, Department of Physics, RTM Nagpur University, Nagpur for providing XRD facility. Department of Material Technology, VNIT, Nagpur for SEM and EDS characterization. Department of Physics, Pune University, Pune for TEM characterization.

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# USEFULNESS OF PCR IN SURVEILLANCE OF MALARIA INFECTION IN MELGHAT REGION (M.S.) INDIA

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## ABSTRACT

The present study was an attempt to diagnose the usefulness of PCR in surveillance of malaria infection in Melghat (M.S.) India. The 23 complicated cases where the morphologic characteristics of malaria parasites fail were selected for the present study. The diagnostic band for *P. vivax* infection was represented with size of 120 bp while for *P. falciparum* with size of 205 bp. From study, PCR was observed to be more sensitive and specific than all other techniques for confirmation of malaria in complicated cases where morphological characteristics of malaria parasites fails due to blood film parasitaemia below the detectable level.

KEYWORDS :*PCR, Malaria and Melghat Region.*

## INTRODUCTION :

Melghat is a mostly remote area of Amravati district of Maharashtra (India) located between $20^0$ 51'- $21^0$ 46' N and $76^0$ 38'- $77^0$ 33' E in Northern part. Due to heavy rain and existence of conditions which help breeding of mosquitoes, area is badly infested with malaria. According t WHO (1986), Malaria continues to remain a major public health problem in many countries even after more than four and half decades of organized anti-malaria control measures, initiated after the declaration of World Health Assembly in 1955 (Kondrashin and Rashid, 1987). Molecular methods have shown a promise in this aspect. Analysis of DNA by the polymerase chain reaction (PCR) can be a useful tool for diagnosis of malaria when the results of conventional techniques are negative, especially since PCR allows accurate species identification and can detect low level parasitaemia. PCR, a more sophisticated technique, requires infrastructural support, is expensive and time taking than the conventional thin smear examination and immuno-chromatography (Morassin *et al.*, 2010).

The present study was attempted to diagnose the usefulness of PCR in surveillance of malaria infection in Melghat (M.S.) India.

## METHODOLOGY

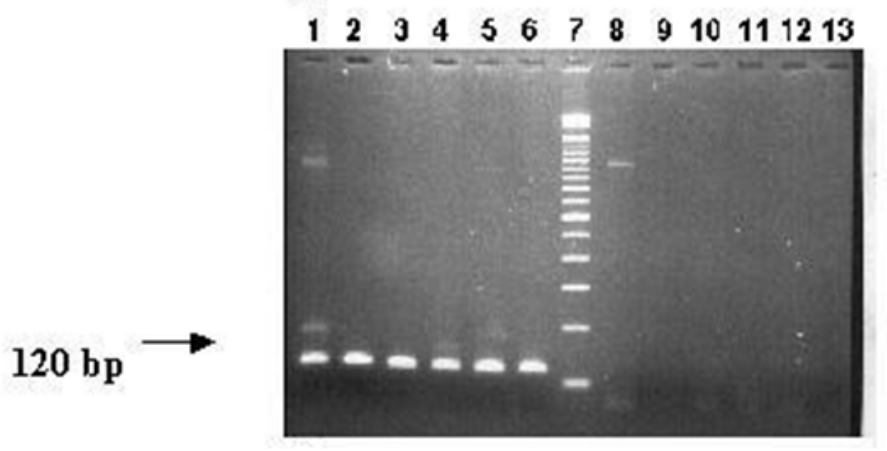
The present study was conducted during February 2012-January 2014. The 23 complicated

malarial cases were selected for confirmatory molecular diagnostic tests. The molecular tests such as PCR can detect parasites in specimens where the parasitaemia is below the detectable level of blood film examination. The Agarose gel (2%) analysis of a PCR diagnostic test for species-specific detection of *Plasmodium* DNA was performed using nested primers of Snounou et al., (1993). Plasmodium genomic DNA is extracted from 200 µl whole blood using the QIAamp Blood Kit. Detection and identification of Plasmodium to the species level is done with a two step nested PCR using the primers of Snounou *et al.*, (1993). In the first step (PCR 1), 1 µl of extracted DNA is amplified using genus specific primers; in the second step (PCR 2), 1 µl of PCR1 amplification product is further amplified using species specific primers. Ten µl of each PCR2 amplified DNA product is separated by 2% agarose gel electrophoresis stained for 15 min with Ethidium bromide and visualized by UV illumination (Zakeri *et al.*, 2002).

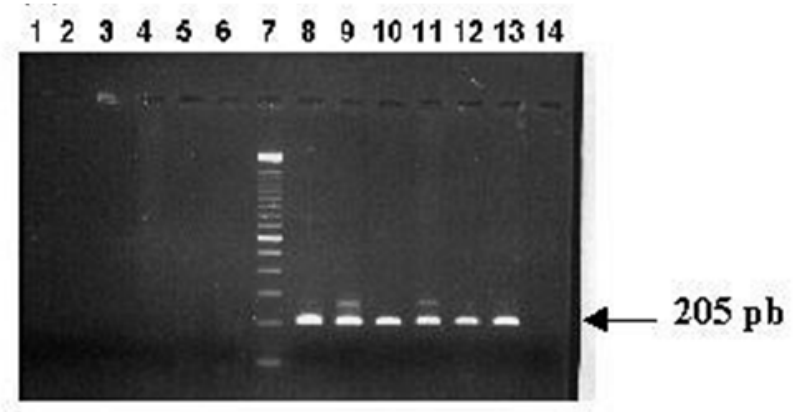
## RESULTS AND DISCUSSION

The diagnostic band for P. vivax was represented with size of 120 bp while for *P. falciparum* with size of 205 bp (Figure.1 and 2). The findings were in well agreements with Snounou *et al*. (1993), Machado et al., (1998) and (Zakeri et al., 2010). It is well accepted that molecular methods are developed and became more applicable in routine diagnosis. These methods also provide the information about drug-resistance and genetic diversity of malaria parasites that led scientists to apply these methods more commonly. Snounou et al. (1993) have reported that PCR has proven to be more sensitive and accurate than routine diagnostic microscopy in detection and identification of the parasites. WHO (2000) reported that PCR is more sensitive and specific than all other techniques. It is, however, a lengthy procedure that requires specialized and costly equipment and reagents, as well as laboratory conditions that are often not available in the field. Humar *et al.* (1997) have reported that it is difficult to evaluate the specificity of PCR for the identification of *P. falciparum* or *P. vivax* in a single sample with very low Plasmodium concentration; however, the evaluation of PCR method together with the thin smears can be accepted as the gold standard (Tantarpale and Tantarpale 2014).

Figure.1: Schematic representation of agarose gel electrophoresis of nested PCR products is from clinical specimens using species-specific Oligonucleotide pairs for A (*P. vivax*), B (*P. falciparum*)



(A) The representative microscopically *P. vivax* diagnosed samples, which were positive by using *P. vivax*-specific primers (left panel), and negative by *P. falciparum*-specific primers (right panel).




(B) The representative microscopically *P. falciparum* diagnosed samples, which were positive by using *P. falciparum*-specific primers (right panel), and negative by *P. vivax*-specific primers (left panel)

## CONCLUSION

In concluding the above results, it is cleared that the PCR is observed to be more sensitive and specific than all other techniques for confirmation of malaria in complicated cases where Morphologic characteristics of malaria parasites fails due to blood film parasitaemia was below the detectable level . It is, however, a lengthy procedure that requires specialized and costly equipment and reagents, as well as laboratory conditions that are often not available in the field.

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# SEASONAL DIVERSITY AND POPULATION DYNAMICS OF OPHIDIAN FAUNA IN BULDHANA DISTRICT MAHARASTRA INDIA

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Former Vice- Chancellor, S. R. T. M University, Nanded, Maharashtra, India

## ABSTRACT

**The present paper provides the information about the seasonal diversity and population dynamics of ophidian fauna from Buldhana District Maharashtra, India. The study conducted during February 2012 to January 2014. During study the effective protocol was adopted. Study reveals the presence of thirty three varieties of snakes belonging to six families of which ten species were Abundant, four species were Common, eight species were Occasional, and six species Frequent while five were Rare. A general trend of increased population was reported in monsoon while decreased reported during winter to early monsoon.**

**KEYWORDS :** Diversity, Population, Ophidian Fauna, Buldhana.

Snakes! the very word evoke feelings of horror and disgust in most of us. Snakes are also perceived as messenger of death. They fascinate us more than any other animals of the world. Snakes occupied deserts, forests, marshy, swampy places, lakes, streams and rivers of difficult terrains (Dhamankar 2006). The different anthropogenic activities and modifying environment are the biggest threats to the fauna and our current knowledge about behaviour, natural history and status of ophidian species is far from complete. So, one of the prime objectives of study was to build a reliable data-base about the seasonal diversity and population dynamics of these fascinating snakes from Buldhana District (M.S.) India.

Buldhana district is situated in Amravati division of Maharashtra state in Western India. It is situated at the westernmost border of Vidarbha region of Maharashtra and is 500 km from the state capital, Mumbai. It lies between 19°51' and 21°17' N. latitude and 75°57' and 76°59' E. longitude. It has a total area of 9745 square kilometers (3761 square miles). The climate of this district is characterized by a hot summer, well-distributed rainfall during the south-west monsoon season and generally dry weather during the rest of the year. The cold season is from December to February (Joshi, 2011, Joshi et al., 2014).

## METHODOLOGY

The study conducted during February 2012 to January 2014 aims to examine monthly and seasonal diversity and population dynamics of ophidian fauna from Buldhana district, (M.S.) India. After detection, specimen was photographed and identified with the help of visible structural features. For identification and comparative studies of observed specimens, keys and methods suggested by Daniel (2002) Whitaker and Captain (2004), and Khaire (2010) were adopted. The Diversity data was quantified with the help of PAST Version 1.60 software (Hammer et al. 2001). The differences between the diversity and evenness indices of snakes among different seasons were statistically analyzed using Analysis of Variance.

## RESULTS AND DISCUSSION

Buldhana district of Maharashtra (India) has healthy environment and climatic condition, with classical demography setup as mountainous terrain, rugged configuration and sudden fall in elevation is phenomenal. The thirty three varieties of snakes belonging to six families have been identified within two years of search in the Buldhana district. In these, the maximum species were non venomous representing the Colubridae family. Such community composition was also observed by Nande and Deshmukh (2007) in Amaravati and Melghat (M.S.) India. In the observations, characters were found almost same as per existing records (Whitaker and Captain, 2008., Khaire, 2010).

A fauna was observed to be most diversified during monsoons. A general trend of increased population was also reported in monsoon while decreased reported during winter to early monsoon. Such trends were shown by

[1]**Corresponding author**

**Table 1: Representing the Status of Ophidian Species in Buldhana District Maharastra India**

| Sr. No. | Scientific Name* | Common Name* | Type | Length Max. (inch) | Relative Domin -ance | Occurr -ence Status |
|---|---|---|---|---|---|---|
| **Family: Typhlopidae** | | | | | | |
| 1. | *Grypotyphlops acutus* | Beaked worm snake | NV | 014 | 1.175 | F |
| 2. | *Ramphotyphlops braminus* | Common worm snake | NV | 006 | 4.837 | C |
| **Family: Pythonidae** | | | | | | |
| 3. | *Python molurus molurus* | Indian rock python | NV | 124 | 0.361 | O |
| **Family: Boidae** | | | | | | |
| 4. | *Gongylophis conicus* | Common sand boa | NV | 038 | 3.165 | F |
| 5. | *Eryx johnii* | Red sand boa | NV | 036 | 0.814 | R |
| **Family: Colubridae (NV)** | | | | | | |
| 6. | *Amphiesma stolatum* | Striped keelback | NV | 018 | 1.537 | F |
| 7. | *Argyrogena fasciolata* | Banded racer | NV | 040 | 5.244 | A |
| 8. | *Coronella branchyura* | Indian smooth snake | NV | 012 | 0.271 | O |
| 9. | *Coelognathus h. helena* | Common trinket snake | NV | 048 | 5.289 | A |
| 10. | *Coelognathus h. monticollaris* | Montane trinket snake | NV | 030 | 0.407 | O |
| 11. | *Dendrelaphis tristis* | Bronzback tree snake | NV | 046 | 1.627 | F |
| 12. | *Lycodon aulicus* | Common wolf snake | NV | 018 | 8.002 | A |
| 13. | *Lycodon flavomaculatus* | Yellow spotted wolf snake | NV | 014 | 3.526 | C |
| 14. | *Lycodon striatus* | Barred wolf snake | NV | 016 | 5.154 | A |
| 15. | *Macropisthodon plumbicolour* | Green keelback | NV | 024 | 3.526 | C |
| 16. | *Oligodon arnesis* | Common kukri snake | NV | 018 | 6.419 | A |
| 17. | *Oligodon taeniolatus* | Russell's kukri snake | NV | 014 | 0.723 | O |
| 18. | *Ptyas mucosa* | Indian rat snake | NV | 090 | 10.17 | A |
| 19. | *Sibynophis subpunctatus* | Black headed snake | NV | 018 | 0.949 | O |
| 20. | *Xenochrophis piscator* | Checkered keelback | NV | 048 | 10.26 | A |
| **Family: Colubridae (SV)** | | | | | | |
| 21. | *Ahaetulla nasuta* | Common vine snake | SV | 036 | 0.769 | O |
| 22. | *Boiga trigonata* | Indian cat snake | SV | 030 | 6.103 | A |
| 23. | *Elachistodon westermanni* | Indian egg eater | SV | 030 | 0.045 | R |
| 24. | *Psammophis condanarus* | Condanarus sand snake | SV | 042 | 1.763 | F |
| 25. | *Psammophis leithii* | Leith's sand snake | SV | 036 | 0.587 | O |
| 26. | *Psammophis longifrons* | Stout sand snake | SV | 048 | 0.587 | O |
| **Family: Elapidae** | | | | | | |
| 27. | *Bungarus fasciatus* | Banded krait | V | 036 | 0.045 | R |
| 28. | *Bungarus caeruleus* | Common krait | V | 060 | 4.611 | C |
| 29. | *Calliophis melanurus* | Slender coral snake | V | 015 | 0.135 | R |
| 30. | *Naja naja* | India spectacled cobra | V | 075 | 6.645 | A |
| **Family: Viperidae** | | | | | | |
| 31. | *Daboia russelii* | Russell's viper | V | 048 | 6.238 | A |
| 32. | *Echis carinatus* | Saw-scaled viper | V | 024 | 1.356 | F |
| 33. | *Trimeresurus gramineus* | Green pit viper | V | 016 | 0.090 | R |
| **Type:** NV- Non Venomous; SV - Semi Venomous; V - Venomous | | | | | | |
| **Occurrence Status:** A- Abundant; C- Common; F-Frequent; O- Occasional; R- Rare | | | | | | |

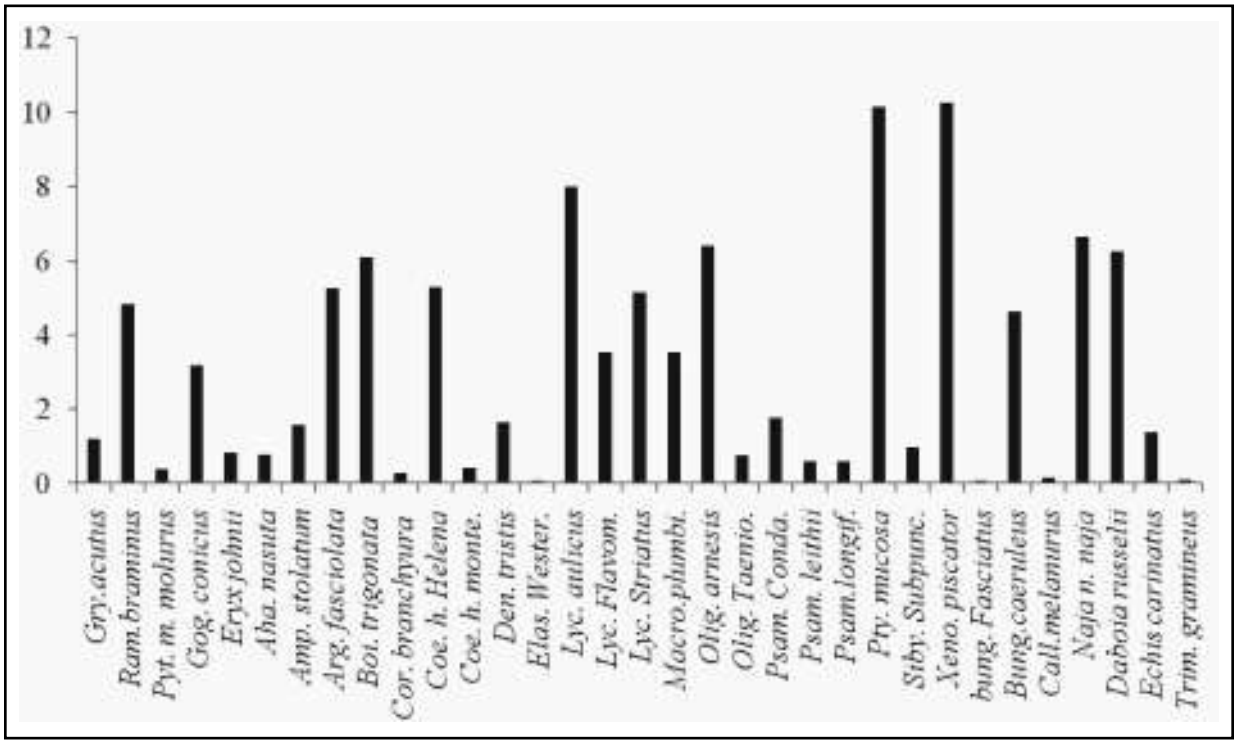



**Figure 1: Representing Status of Ophidian Species in Buldhana District Maharastra, India**

**Table 2: Representing Status of Ophidian Families in Buldhana District Maharastra India**

| Sr. No. | Family | Percent occurrence | Relative occurrence | Occurrence Status |
|---|---|---|---|---|
| **1.** | **Typhlopidae** | 6.060 | 6.009 | F |
| **2.** | **Pythonidae** | 3.030 | 0.366 | R |
| **3.** | **Boidae** | 6.060 | 3.977 | O |
| **4.** | **Colubridae** | 63.64 | 70.55 | A |
| **5.** | **Elapidae** | 12.12 | 11.42 | C |
| **6.** | **Viperidae** | 9.090 | 7.678 | F |
| **Occurrence Status:** A- Abundant; C - Common; F -Frequent; O - Occasional; R- Rare | | | | |

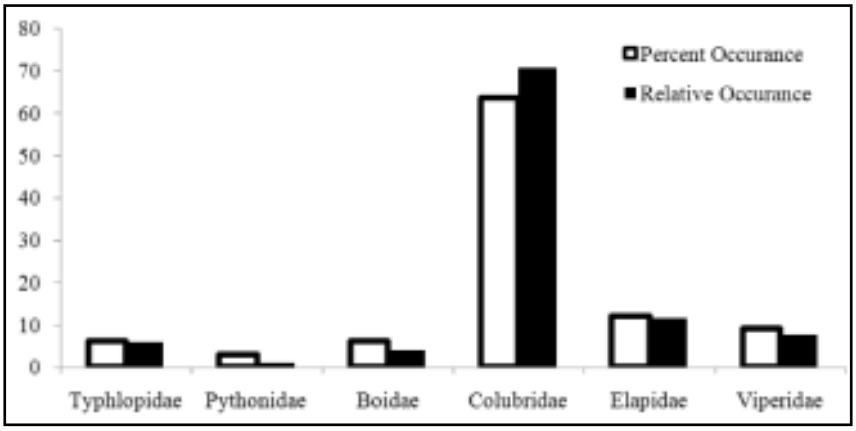



**Figure 2 : Representing Status of Ophidian Families in Buldhana District Maharastra India**

**Table 3: Diversity of Ophidian Fauna During February 2012 to January 2014 in Buldhana District Maharastra India**

| Year / Month | No. of species | Mean % abundance[a] | Shannon diversity[b] | Equitability[c] | Species richness[d] |
|---|---|---|---|---|---|
| **2012-13** | | | | | |
| **Summer** | 22 | 09.684 | 2.851 | 0.9224 | 4.667 |
| **Monsoon** | 28 | 27.994 | 2.981 | 0.8947 | 5.403 |
| **Winter** | 21 | 11.472 | 2.664 | 0.8750 | 4.289 |
| **2013-14** | | | | | |
| **Summer** | 19 | 09.324 | 2.671 | 0.9071 | 4.041 |
| **Monsoon** | 27 | 28.357 | 3.056 | 0.9274 | 5.117 |
| **Winter** | 25 | 13.169 | 2.964 | 0.9208 | 4.706 |

a = Mean percent abundance of snake populations was significantly different ($F=31.413$, $df=05$, $p<0.05$). b = Diversity values of snake populations was significantly different ($F=8.191$, $df=05$, $p<0.05$). c = Species equitability among different seasons was significantly different ($F=17.274$, $df=05$, $p<0.05$). d = Species richness among different seasons was significantly not different ($F=1.412$, $df=05$, $p>0.05$).

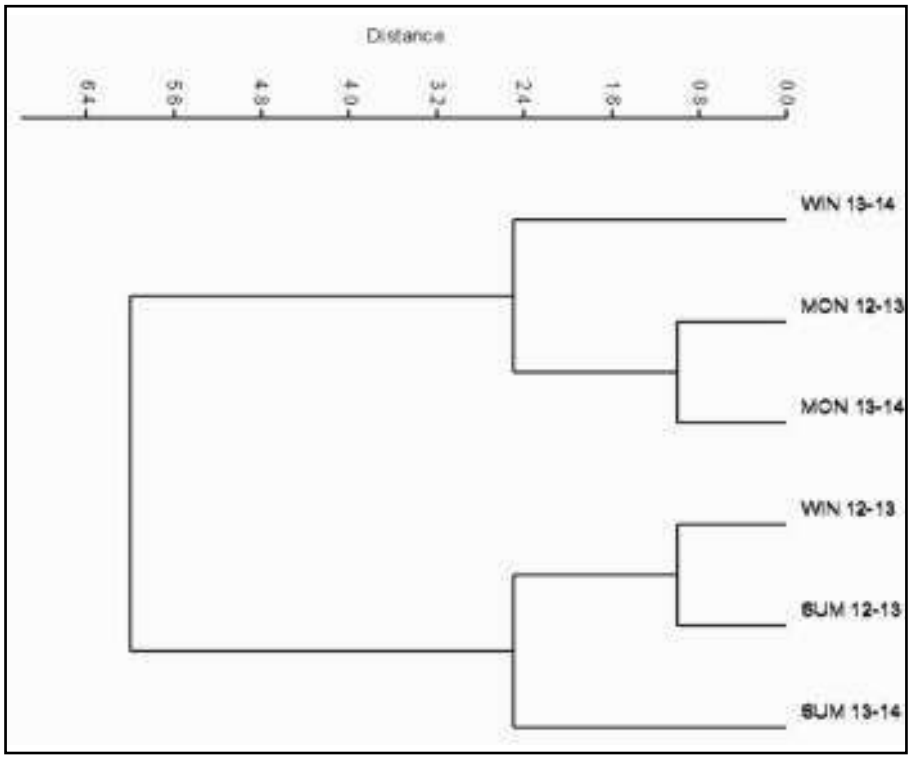



**Figure 3.1 : Dendrogram Showing the Similarity of Ophidian Fauna in Different Seasons During February 2012 to January 2014 in Buldhana District Maharastra India**

every species from all families of snakes. As the Snakes are cold-blooded animals accordingly during winter to early summer they hibernate in their burrows or resting places, which was the cause behind their minimum diversity in the winter to early summer season. Due to favourable environmental condition, monsoon is the breeding season for most of the snakes' which leads to their maximum population in rainy season (Joshi 2009, Pal et al. 2012).

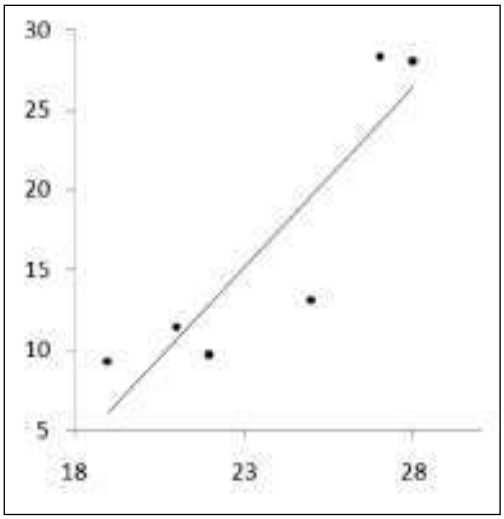
The following tables provide complete information about all the observed species.

The *Ptyas mucosa* and *Xenochrophis piscator* were showed the maximum while *Calliophis melanurus*, *Elachistodon westermanni* and *Trimeresurus gramineus* were observed with least relative dominance. (Figure 1)

The Colubridae family contributes maximum percent as well relative occurrence while least was showed by Pythonidae and Viperidae. (Figure 2)

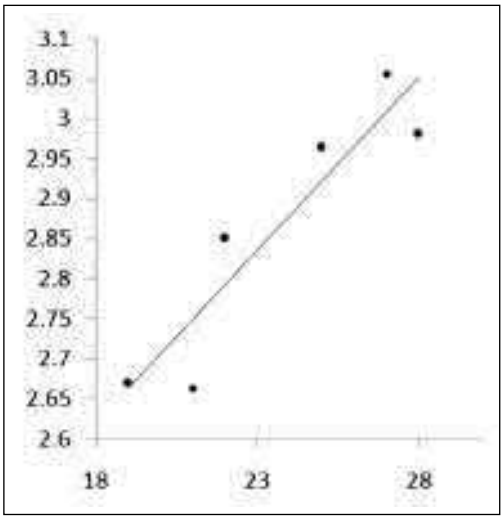
The similarity in species composition with number of species was observed maximum in Monsoon followed by winter and summer (Figure 3.1). The number of species in different seasons showed the significant relationship with different diversity indices (Figure 3.2).

$R^2$= 0.261 / P< 0.0001



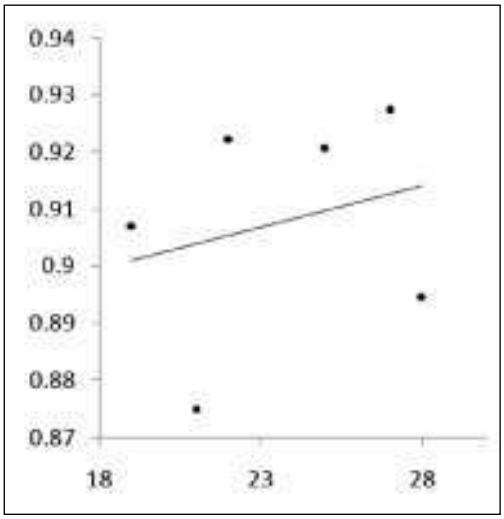

**a. No. of Species Vs. Mean % Abundance**

$R^2$= 0.356 / P< 0.0001



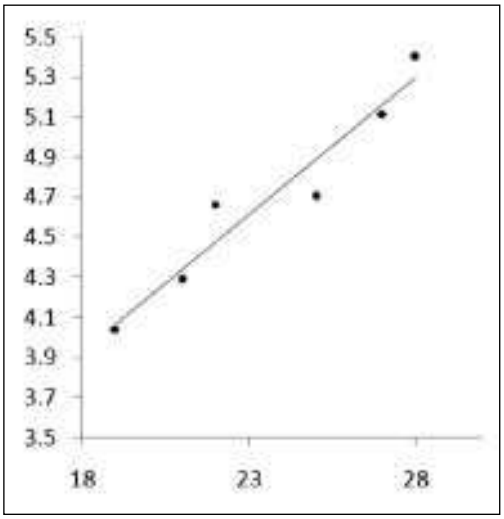

**b. No. of Species Vs. Shannon Diversity**

$R^2$= 0.195 / P< 0.0001




**c. No. of Species Vs. Equitability**

$R^2$= 0.205 / P< 0.0001




**d. No. of species Vs. Species Richness**

**Figure 3.2. Relation Between No. of Ophidian Species And Different Diversity Indices**

## CONCLUSION

According to the observations, it has been concluded that the Buldhana district Maharastra India, has healthy environmental and demographic setup which accommodates rich ophidian diversity. The snakes are the Keystone species which plays an important role in ecosystem functioning but are threatened by anthropogenic activities as well as environmental alternation. The laws and legislation are not just sufficient for protection of these animals but it is necessary to raise the awareness levels by providing important information about snakes to different sections of people for conservation of ophidian biodiversity in Buldhana district Maharastra, as well as neighborhood. Because it is clear that disappearance of snakes will have tremendous social and ecological implications.

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Original article

# Diversity of Saurian fauna in the Buldhana district, Maharashtra, India

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ABSTRACT

The present report provides knowledge about the diversity of Saurian fauna in the Buldhana district of the Indian state of Maharashtra as a model geographic area to promote conservation management. The presented study is based on the field work carried out in the study sites during February 2014 to January 2015. The study revealed the presence of 14 Saurian species belonging to 5 families dominated by Gekkonidae (43.05%), Scincidae (29.15%), Agamidae (21.35%), Varanidae (6.1%), and Chamaeleonidae (0.35%). The relative dominance of species varied with different months, apparently indicating that the Buldhana district has a healthy environmental and demographic setup that accommodates rich Saurian diversity.



## Introduction

The biological diversity of the earth and its origins has long been a source of amazement and curiosity (Tantarpale 2015). The study of biological diversity encompasses both the intrinsic and anthropocentric values associated with it. The values of the biological elements are recognized in correspondence to the perceived importance by the human being, which is realized in terms of the ecosystem services (Daily 1997; Baumgartner 2007). Biological diversity is the base for upholding the ecosystems and the functional aspects of the species that provide goods and services for human well-being. Monitoring of species diversity of a region enables estimation of the prospective functional roles of the species. In any ecosystems, monitoring species diversity can be used as a tool to reduce human mismanagement and pollution in urbanized, industrial, rural, and other managed areas (Wilson 1997). Extending this view, studies on species diversity in any ecosystems are necessary to understand the effect of anthropocentric development on the integrity and sustenance of an ecosystem.

The diversity of reptiles has been emphasized in many studies owing to their dominance in the terrestrial and aquatic ecosystems and provision of ecosystem services such as pest control and ecological maintenance (Joshi 2014). Among reptiles, saurian fauna is a diverse group that changes from the primitive to the specialized, phylogenetically, and their structural modifications exhibit greater variations than any other group of reptiles (Smith 1935). Lizards are members of the suborder Sauria which is one of the two suborders of the order Squamata (Class: Reptilia). They are poikilothermous, insectivorous, and oviparous to ovoviviparous (Matthew 2007). Presently, lizards are one of the most diversified groups of vertebrates that have ever lived on earth over the past 250 million years. Over 5,000 species of lizards have lived on earth, inhabiting a variety of habitats ranging from the highest mountainous peak to the low-lying terrestrial and aquatic habitats (Lalrinchhana et al 2015). South Asia, including the Indian subcontinent, is the home for herpetological diversities in the tropical region with India harboring 228 Saurian species in different biophysical zones (Venugopal 2010).

In this context, the conservation of lizards is necessary to sustain varied kinds of ecosystem services for human well-being. In view of the essential ecosystem services rendered by lizards and to promote conservation management, the present study was aimed at the estimation of the saurian diversity in the Buldhana District, Maharashtra, India. The results of the study are expected to supplement the necessary information on the conservation management and enhance the ecological roles of the saurian species in the Buldhana District and similar geographical regions.

## Materials and methods

### *Study area*

The Buldhana district (Figure 1) is one of the most diversified regions in Maharashtra State of India, with respect to biodiversity.

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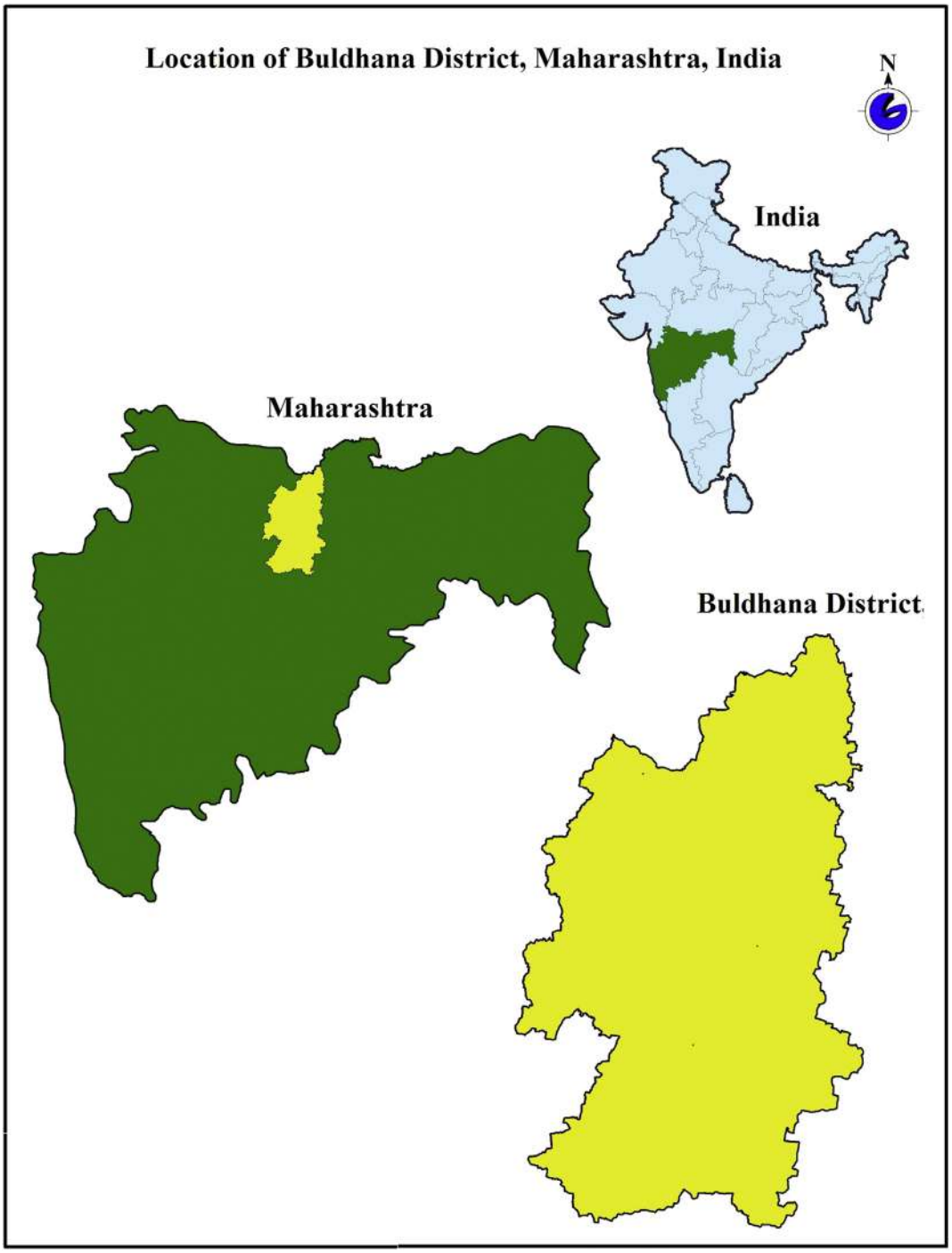


**Figure 1.** Buldhana District, Maharashtra, India.

**Table 1.** Diversity of Saurian fauna during February 2014 to January 2015 in the Buldhana district, Maharashtra, India.

| Family | Scientific name | Common name | No. of individuals | IUCN national | Local status |
|---|---|---|---|---|---|
| Agamidae | *Calotes versicolor* (Daudin, 1803) | Indian garden lizard | 42 | NE | Abundant |
| | *Calotes rouxii* (Dumeril and Bibron, 1844) | Indian forest lizards | 16 | NT | Occasional |
| | *Psammophilus blanfordanus* (Stoliczka, 1871) | Blanford's rock agama | 5 | NE | Rare |
| Chamaeleonidae | *Chamaeleo zeylanicus* (Stoliczka, 1872) | Indian Chamaeleon | 01 | NE | Rare |
| Gekkonidae | *Hemidactylus brookii* (Gray, 1930) | Brook's house gecko | 12 | LC | Rare |
| | *Hemidactylus flaviviridis* (Murray, 1886) | Yellow-green House Gecko | 35 | LC | Common |
| | *Hemidactylus frenatus* (Dumeril and Bibron, 1844) | Asian house gecko | 25 | LC | Frequent |
| | *Hemidactylus giganteus* (Stoliczka, 1871) | Giant Indian gecko | 03 | NE | Occasional |
| | *Hemidactylus leschenaultii* (Dumeril and Bibron, 1844) | Common bark gecko | 42 | LC | Abundant |
| | *Hemidactylus triedrus* (Daudin, 1802) | Termite hill gecko | 10 | NT | Rare |
| Scincidae | *Eutropis carinata* (Schneider, 1799) | Keeled grass skink | 34 | NT | Common |
| | *Eutropis macularia* (Blyth, 1853) | Bronze grass skink | 40 | LC | Abundant |
| | *Lygosoma punctatus* (Gmelin, 1799) | Spotted supple skink | 12 | NT | Rare |
| Varanidae | *Varanus bengalensis* (Daudin, 1803) | Bengal monitor lizard | 18 | VU | Frequent |

LC = least concern; NE = not evaluated; NT = nearly threatened; VU = vulnerable.

Its healthy climate, mountainous terrain, rugged configuration, and sudden fall in elevation are phenomenal (Joshi et al 2015). It is in the Amravati division of Maharashtra state in Western India. It is situated at the westernmost border of the Vidarbha region of Maharashtra, and is 500 km from the state capital, Mumbai. It lies between 19°51′ N and 21°17′ N latitude and 75°57′ E and 76°59′ E longitude. It has a total area of 9,745 km$^2$ (3,761 square miles). The climatic condition of this district is characterized by a hot summer, well-distributed rainfall during the south-west monsoon season, and generally dry weather during the rest of the year. The cold season is from December to February. The average annual rainfall in the district is 796.6 mm (31.37 inches). During summer, the mean daily maximum temperature was 42.3°C and the minimum was 27.4°C, and it decreased toward winter with a mean daily maximum temperature of 27.6°C and a minimum of 15.1°C (Buldhana Gazetteer 2015).

### *Survey methods*

The present study is based on the field work carried out in the study sites during February 2014 to January 2015. During the survey, an efficient protocol was adopted. The survey was made using a "visual encounter survey" method (Doan 2003) as well as by employing randomized walking (Whitaker 2006). The selected area

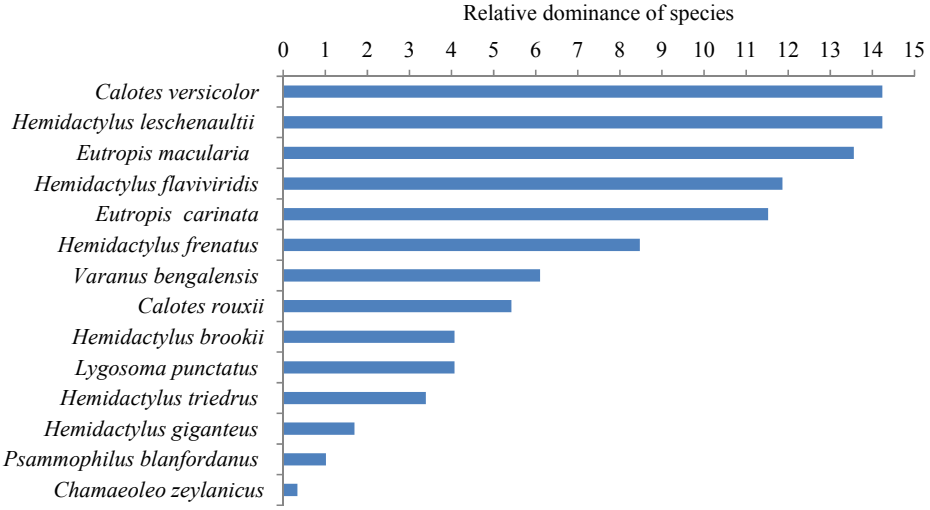


**Figure 2.** Relative abundance of saurian species in the Buldhana district, Maharashtra, India.

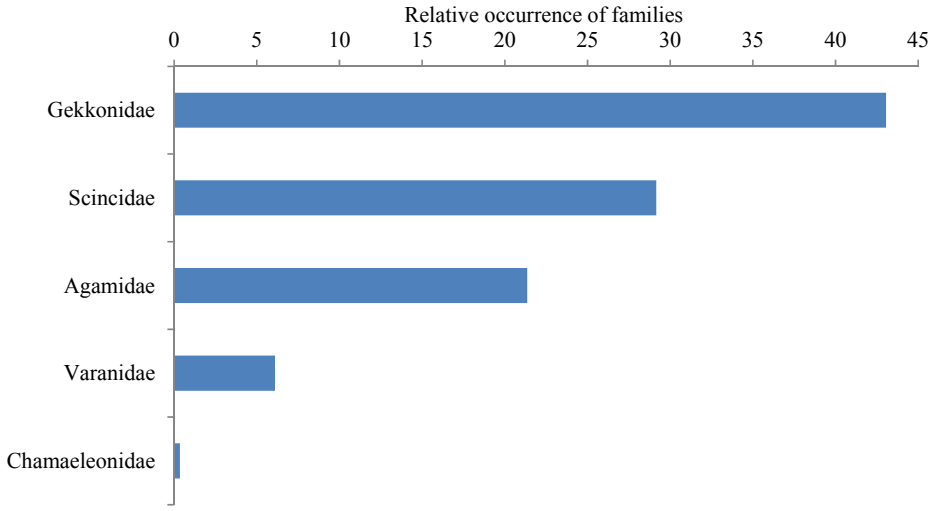


**Figure 3.** Relative dominance of saurian families in the Buldhana district, Maharashtra, India.

was randomly explored on the basis of habitat structure and the possibility of availability of species.

*Species identification*

After detection, a specimen was identified with the help of visible structural features. For identification and comparative studies of observed specimens, keys and methods suggested by Daniel (2002), Das (2002), and Ahmed et al (2009) were adopted. The International Union for Conservation of Nature (IUCN) status of each encountered species was categorized on the basis of Molur et al (1998), Kumbhar et al (2013), and Alexandar and Jayakumar (2014).

*Data analysis*

Species occurrence analysis was carried out by using the following formulas. Relative dominance (RD) of species was calculated as [RD = Ni × 100/Nt], where Ni is the number of individuals of species and Nt is the total number of individuals of all

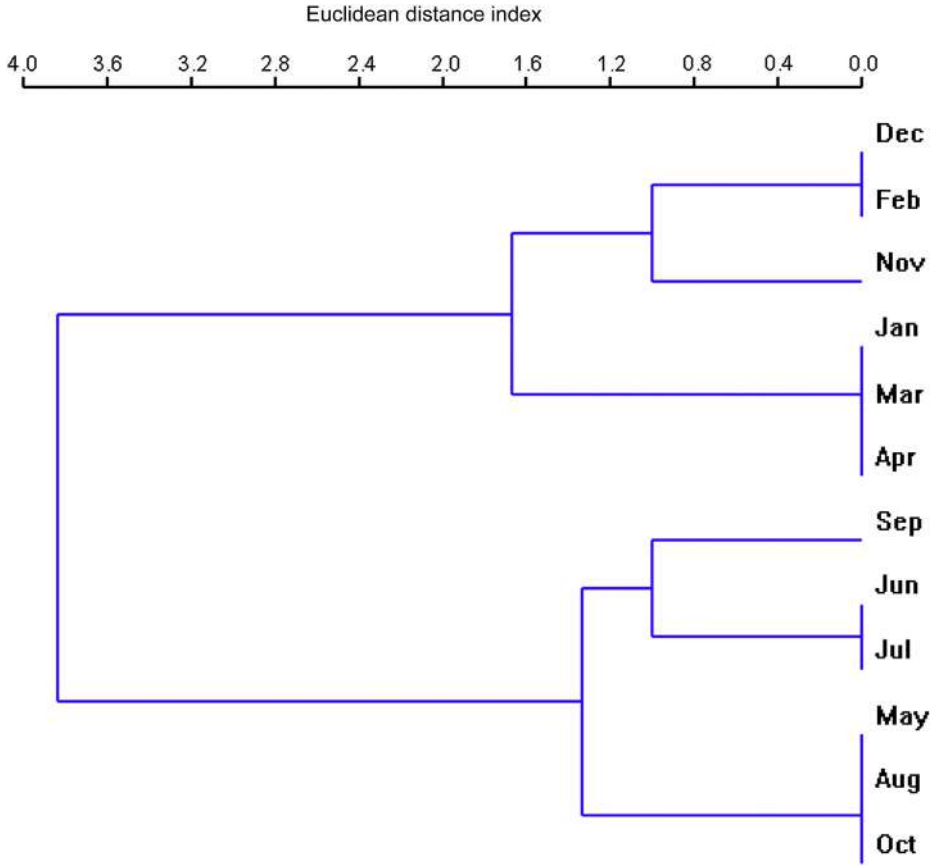


**Figure 4.** Dendrogram showing similarity in number of saurian species composition among the studied month during February 2014 to January 2015.

species (Basavarajappa 2006; Joshi 2014). Relative occurrence (RO) of the family was calculated as [RO = Ns × 100/Nt] where Ns is the number of species of each family and Nt is the total number of all species (Basavarajappa 2006; Joshi 2014). Mean percent occurrence (M%) for a month was calculated as [M% = Nm × 100/Nt] where Nm is the number of individuals in each month and Nt is the total number of individuals during the complete study tenure (Basavarajappa 2006; Joshi 2014). The mean values of the pooled species occurrence data were used to calculate the monthly diversity of and to categorize the local status of species.

The diversity assessment enabled highlighting the observed species richness pattern of the saurian species. The diversity indices were quantified with the help of PAST Version 1.60 software (Palaeontological Asso., Norway; Hammer et al 2001). The species diversity was calculated using the Shannon diversity index that calculated [$H' = -\sum_{i=1}^{R} Pi \log Pi$], where *Pi* is the proportion of the first species which is given by *Pi* = ni/N, where ni is number of individual in particular month and N is total number of species; species richness was obtained by using the Margalef equation [R = (S-1)/log N], where R is the index of species richness, S is total number of species and N is the total number of individuals (Magurran 1988); while species equitability was determined by the equation of Pielou [$J = N_1/N_0$] where $N_1$ is the number of abundant species in the sample and $N_0$ is the number of species in the sample (Hammer et al 2001). The similarity association matrix upon which the cluster was based was computed using the nearest neighbor pair linkage algorithm of Euclidean distance index for the presence and absence data (Hammer et al 2001).

The differences between the diversity and evenness indices among different study months were statistically analyzed using analysis of variance. The statistical analyses were performed following Zar (1999) using the SPSS version 10 (SPSS Inc., Chicago, IL, USA; Kinnear and Gray 2000).

## Results

During the study, a total of 295 individuals of 14 saurian species belonging to 5 families were identified (Table 1). From the observed species, 3 were abundant, 2 were common, 2 were frequent, 2 were occasional, and 5 were rare. The maximum abundance was shown by *Calotes versicolor* followed by *Hemidactylus leschenaultii* and *Eutropis macularia*, while *Chamaeleo zeylanicus* was the most rarely observed with least abundance (Figure 2). During the study, the Gekkonidae family was observed to be more dominant over the Scincidae, Agamidae, Varanidae, and Chamaeleonidae families (Figure 3).

A monthly comparison of saurian species occurrence showed the highest number of species during June to September and the lowest during February to May. A dendrogram developed by Euclidean distance cluster analysis was observed to be multifaceted and showed variation in the level of similarity in the number of saurian species in 12 months. The months with the minimum to moderate number of species belong to one cluster, whereas the rest of the months with moderate to maximum number of species formed another cluster (Figure 4).

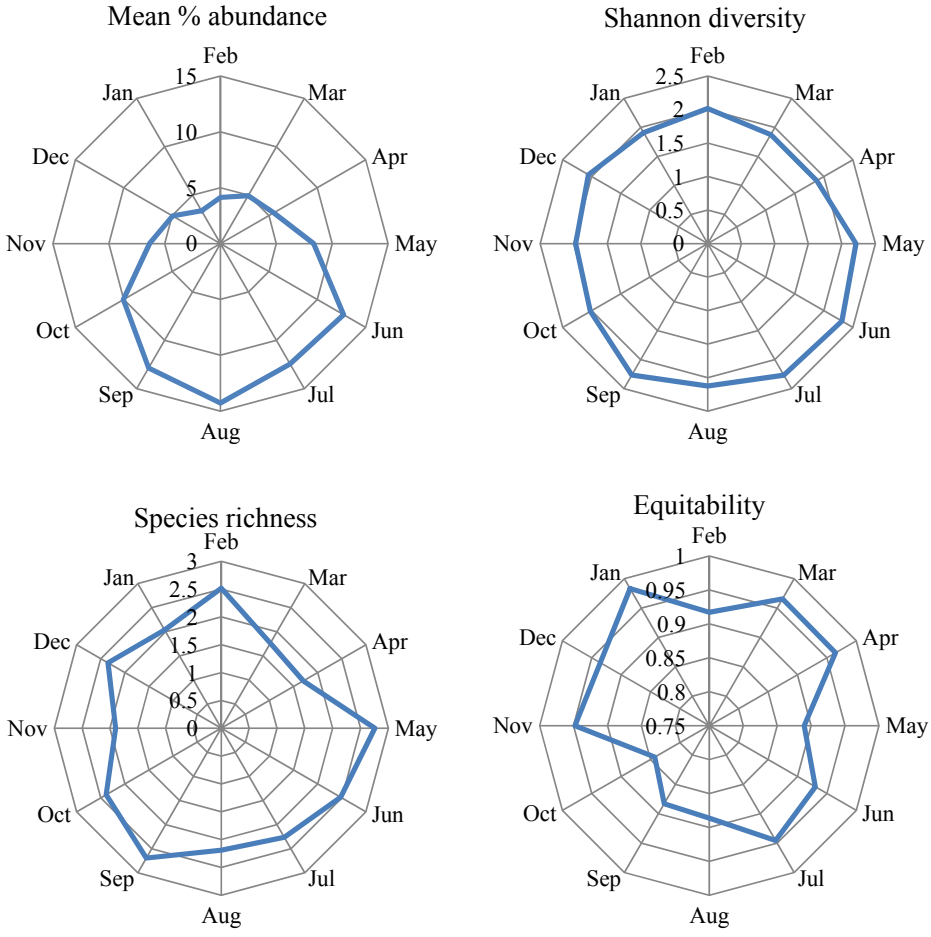


**Figure 5.** The values of the diversity indices in different months observed through the random sampling of the Saurian fauna in the Buldhana District, Maharashtra, India.

A monthly comparison of species diversity attributed to saurian fauna in the studied area revealed that faunal diversity was highest during June to September while lowest during February to May. Mean percent abundance of saurian fauna was significantly different ($F = 30.314$, $df = 11$, $p < 0.05$); Shannon diversity values of saurian fauna were significantly different ($F = 9.813$, $df = 11$, $p < 0.05$); species evenness among different months was significantly different ($F = 16.824$, $df = 11$, $p < 0.05$) while species richness among the study months was not significantly different ($F = 1.526$, $df = 11$, $p > 0.05$) showing a contradictory pattern. A trend in mean % abundance was noted to be nearly similar to that of Shannon diversity although species richness and species equitability showed contradictory patterns (Figure 5).

## Discussion

The utility of saurian species as indicators of environmental conditions is a basis for studying seasonal saurian diversity. Observations on the saurian diversity provided information about the variations in the species richness and the abundance shaped by the seasons. The differences in the diversity can be attributed to the monthly changes in the climatic conditions. In the present context, a monthly comparison of saurian species occurrence showed the highest number of species during June to September and the lowest during February to May.

The possible cause behind their minimum diversity in the winter months to early summer months is the cold-blooded nature of reptiles. Lizards preferred to hibernate in their burrows or resting places during winter to early summer. Species were generally observed more during monsoon months. According to Pal et al (2012) and Joshi (2014), due to favorable environmental conditions, the monsoon season is the breeding season for most of the reptiles, which leads to their maximum abundance in rainy months. Earlier studies on the saurian diversity in various parts of Maharashtra show consistency with the present observations (Wadatkar 2003; Deshpande et al 2012; Kumbhar et al 2013; Pandharikar et al 2015).

As revealed through the present study, at least 14 saurian species belonging to 5 families were recorded during all the studied months. In the observations, characters of the studied species were found to be almost the same as per existing records of Daniel (2002) and Ahmed et al (2009). The maximum abundance was shown by *Calotes versicolor* followed by *Hemidactylus leschenaultia* and *Eutropis macularius*, while *Chamaeleo zeylanicus* was the most rarely observed with the least abundance. During the study, the Gekkonidae family was observed to be more dominant over Scincidae, Agamidae, Varanidae, and Chamaeleonidae.

In parity with the species diversity observed in the Buldhana district, it may be assumed that the saurian species carry out diverse functional roles for the sustenance of the ecosystems. The availability of the green space and the heterogeneity of the habitats in terms of the available vegetation and allied factors that render stability to the population and species assemblages in the landscapes are possibly important contributors to the observed variations in the saurian species observed in the present study. The present diversity study is confined to a limited area and selected habitats. There is, in the future, a chance of more species being reported because of few pockets and habitats in the studied area requiring more extensive exploration.

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**Topic:-DIVERSITY OF ANURAN FAUNA FROM JALGAON (JAMOD) TERRITORY, BULDHANA DISTRICT (M.S.), INDIA.**

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# BASKING ACTIVITY OF INDIAN MONITOR LIZARD (VARANUS BENGALENSIS)IN BULDHANA DISTRICT OF MAHARASHTRA (INDIA)

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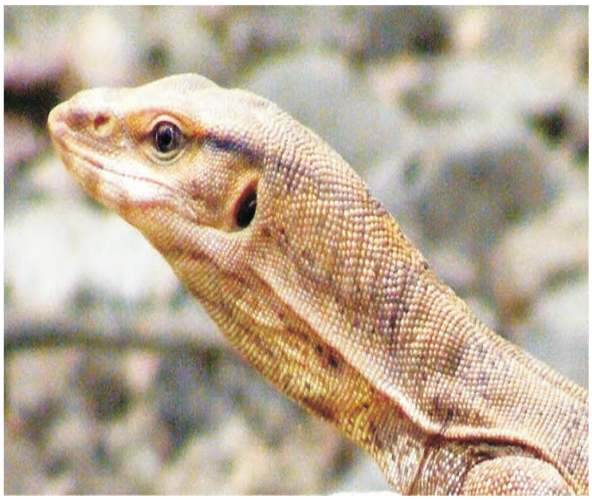


## ABSTRACT

The current report is on the basking activity of Indian monitor lizard that was noted during 18 to 24 October of 2014 from an agriculture field of Jalgaon (Jamod), District Buldhana of Maharashtra (India) (Table1). Indian Monitor Lizard Varanus bengalensis (Daudin, 1802) is diurnal and ectothermic animal that rely largely on external heat sources such as sunlight for thermoregulation. The species exhibited basking at morning to afternoon and some time showed twice a day that is in morning and afternoon both. After basking, species became more active, showed fast movement and quick capture of their prey.

**Keywords:** Varanus bengalensis, Basking activity, Buldhana, Maharashtra.

## Introduction

The Indian monitor lizard Varanus bengalensis (Daudin, 1802) found widely distributed over the Indian Subcontinent (Daniel, 2002; Böhme, 2003; Venugopal, 2010). It has 'Least Concern' status in IUCN Red List of Threatened Species (Papenfuss et al., 2013). Indian monitors are usually solitary and mostly found on the ground, although the young are often seen on trees. It is ectothermic animal that rely largely on external heat sources such as sunlight to achieve their optimal body temperature for various bodily activities and thermoregulation. As species is diurnal, becoming active around 6 A.M. and bask in the morning sun (Auffenberg, 1994). Here this report provides the knowledge about basking activity of Varanus bengalensis from Buldhana District of Maharashtra (India).

## Methodology

The basking activity of Varanus bengalensis were observed over 07 consecutive days during 18 to 24 October 2014 from Agriculture field of Jalgaon (Jamod), District Buldhana of Maharashtra (India). The habitat located between N 210 02' 31.2" and E 760 31' 56.64" at elevation of 291 m.

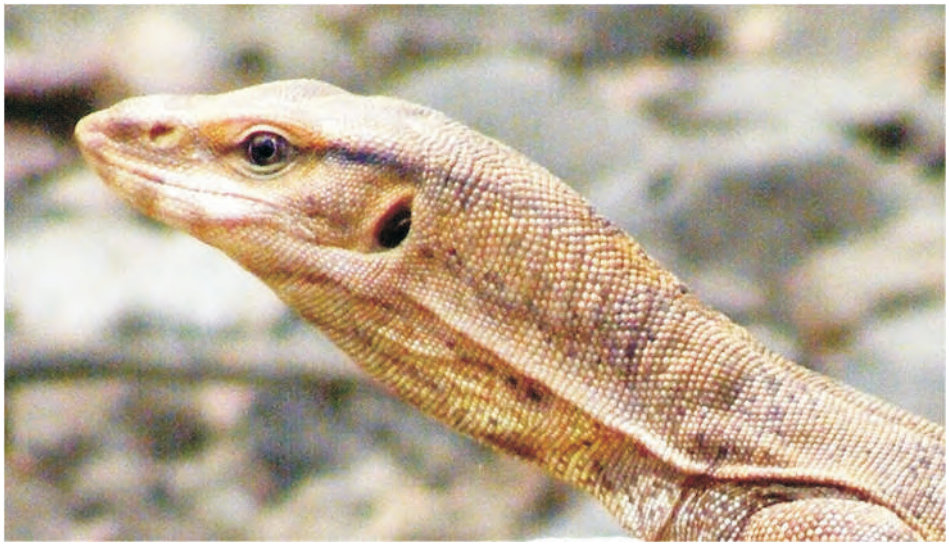
During study period, climate was generally dry as no rain occurred. The observations were made by 'Visual encounter method' suggested by Campbell and Christman (1982) for reptiles. The continuous observations were made with the help of using binoculars as well with necked eyes from early morning to late evening. During studied hours, temperature was also noted to establish their correlation with basking tenure.

**Figure 1.Google Earth Map of Study area from Agriculture field of Jalgaon (Jamod), District Buldhana (M.S.) India with location of habitat occupied by Varanus bengalensis**


## Observations and Results

The current report is on the basking activity of Indian monitor lizard Varanus bengalensis. The Habitat of species was structurally a long hollow crevice with an opening width of size near about 50-60 cm. The species exhibited basking at morning to afternoon and some time show twice a day that is in morning and afternoon both. Morning basking observed begins around 07.30 A.M. to 09.30 A.M. while afternoon basking begins near about 01.00 P.M. to 02.00 P.M., and continues until 03.00 P.M. Species showed out its head from crevice opening at early morning suggesting that animal is waiting for the maximum sun light. As the light radiate to the opening of habitat, species move very slowly, comes straight out from crevice to gain maximum sun light. During basking activity, species remain steady for about an hour. After then species moved slowly up its head in direction of stimulus, captured prey or turn back to its crevice. Nearly same observations were also noted at afternoon period but the duration of exposures was less than morning hours. These observations were clears that the duration of basking increases with decrease in temperature (Figure 3). After basking, species was observed to be more active.

**Figure 2: The Indian monitor lizard Varanus bengalensis (Daudin, 1802)**

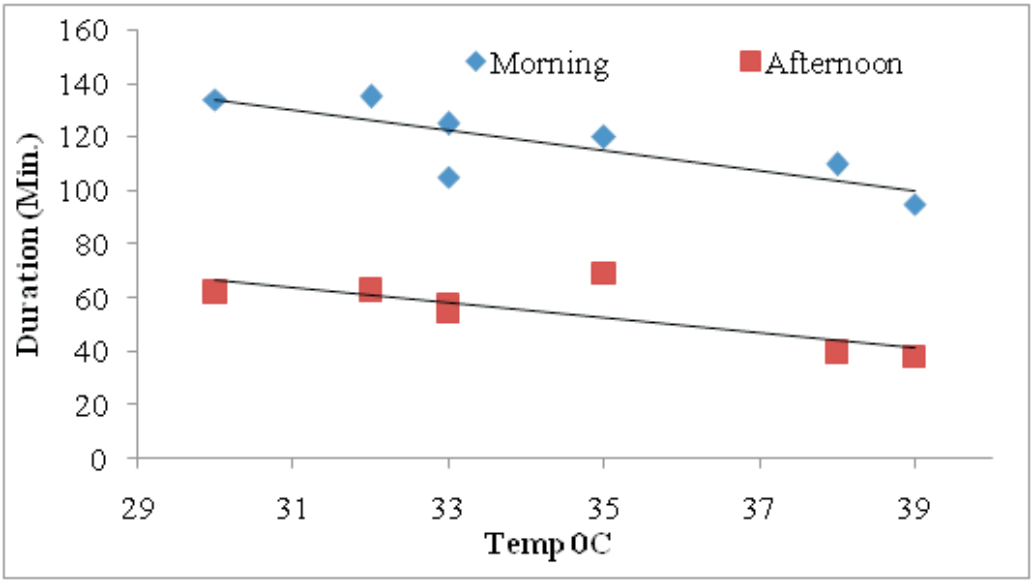


The observations on basking behaviour of Indian monitor lizard were as tabulated below.

Table 1. Observation on basking activity of Indian monitor lizard

| Sr. | Date | Basking Duration (Min.) | | Temperature ($^0$C) |
|---|---|---|---|---|
| | | Morning | Afternoon | |
| 01 | 18-10-2014 | 110 | 040 | 38 |
| 02 | 19-10-2014 | 095 | 038 | 39 |
| 03 | 20-10-2014 | 125 | 057 | 33 |
| 04 | 21-10-2014 | 135 | 063 | 32 |
| 05 | 22-10-2014 | 120 | 069 | 35 |
| 06 | 23-10-2014 | 134 | 062 | 30 |
| 07 | 24-10-2014 | 105 | 055 | 33 |

**Figure 3: Relation between Temperature and Basking duration**



## Discussion

Study area has healthy environment and climatic condition, with classical demographic setup (Joshi et al., 2015). The available environment supports the life history of Varanus bengalensis. The monitor lizards basks by taking advantage of sun exposure (Pianka and King, 2004; Murthy, 2010; Islam and Saikia, 2013) that is evidence of their ectothermic nature which supports the thermoregulation mechanism of their body (Auffenberg 1994). With basking activity, monitor lizard increase its body temperature to the optimum level that physiological functions viz. heart rate and cardiovascular control can be well operated (Christian and Bedford, 1996; Seebacher and Grigg, 2001).

After basking, the Varanus bengalensis was observed to be more active, showed fast movement and quick capture of their prey. The present observations are in accordance with Traeholt (1997), in which the monitor followed sunlight to receive solar radiation and to increase its body temperature before commencing its daily activities (Rathnayake et al., 2003). This observation is also in agreement with the compiled knowledge that many reptiles regulate their body temperatures by basking in the sun until the temperature rises to the level requisite for their normal activity. Basking before returning to its refuge should be required in order to maintain physiological activity (Duengkae, 2008; Deungkae and Chuaynkern, 2009; Vitt and Caldwell, 2009).

The monitor lizard does not make its refuge. As found in previous research (Pattanavibool, 1993; Poonswad, 1997); it prefers to inhabit the refuge like long hollows crevice rather than burrows. Hence, the available refuge like long hollows crevice are an essential factor that supports the occurrence of Varanus bengalensis in the studied area from Buldhana District of Maharashtra (India) and should be considered as an important factor for the management and conservation of this incredible species or its congener.

## Conclusion

In conclusion, the Varanus bengalensis is usually solitary and mostly found on the ground. It is diurnal ectothermic animal that rely largely on external heat sources such as sunlight to achieve their optimal body temperature for various bodily activities and thermoregulation. The species exhibits basking at morning to afternoon and some time show twice a day that is in morning and afternoon. After basking, species became more active, showed fast movement and quick capture of their prey.

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Authors are thankful to Dr. K. M. Kulkarni, Former Vice Chancellor (S. R. T. M. University, Nanded) and Former Director (Higher Education, Government of Maharashtra, Pune) for their guidance during conduct of this study.

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# EFFECTS OF DIETARY GARLIC ON GROWTH PERFORMANCE IN THE FRESH WATER FISH *CLARIAS BATRACHUS* (LINN.)

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**Abstract**:
The aim of this study was to assess the effect of garlic (*Allium sativum*) on growth performance in the fresh water fish *Clarias batrachus* (Linn.) A total number of 80 fish (average weight 20.86±0.27 g) was used. Fish were divided into four groups fed on diets containing garlic in different levels and the control group diet was without garlic. The experiment extended for two months. The results showed that, significant weight gain and growth performance increased in all groups fed on garlic. The results of this study show that addition of garlic *Allium sativum* to fish diet can promote growth of fish.
**Keywords**: garlic (*Allium sativum*), growth factors, fresh water fish (*Clarias batrachus*).

## Introduction

Feed and feeding are among the most important factors influencing growth, feed utilization and tissue composition of the fish in intensive culture (Okumus and Mazlum, 2002). Garlic is an important vegetable extensively cultivated in many countries. It is used as food for humans as well as some animals and as remedy for several diseases, as reported in folk medicine (Shalaby *et al.,* 2006). It is probably one of the earliest known medicinal plants. In recent years, the concern about bacterial resistance to antibiotics in livestock industry has led to legislation minimizing/eliminating the use of such compounds. Garlic contains sulfur containing compounds. Alliin, is converted to the antimicrobial active allicin, when the bulb is cut or bruised. The fresh bulb contains Alliin, Allicin and volatile oils. Allicin gives garlic its characteristic pungent smell. Also, it contains vitamins and minerals and trace elements (selenium and germanium) (Skidmore-Roth, 2003). Allicin (diallythiosulfinate) is the most abundant compound representing about 70% of all thiosulfinates present, or formed in crushed garlic (Block, 1992; Han *et al.,* 1995). Using of garlic in fish farming has become popular for as a growth promoter (Diab *et al.,* 2002; Metwally, 2009) also it increased body gain, feed intake and feed efficiency ratio (Abd-El Allatif and Ebraheem, 1996; Metwally, 2009).

This work was carried out to study the effect of different values of garlic on growth factors in *Clarias batrachus.*

## Material and Methods

1. **Experimental fish**: The *Clarias batrachus* (20.88±0.25 g) were obtained from a commercial farm and were transferred to the place of experiment and acclimated for 2 weeks. During the acclimation, fish were fed the experimental diet to satiation twice a day at 09:00 and 15:00 hours. After acclimation, fish were fasted for one day; batch weighted and randomly distributed among density of 20 fish per tank.
2. **Experimental diet and feeding regime:** The basal experimental diets were formulated with the commonly available ingredients. The formula and analyzed proximate composition of the basal diet are shown in Table 1. The ingredients were grinded, milled, weighed, mixed and pelleted with meat mincer through a 2 mm die. After pelleting, the feeds were air dried and put in an air-tight container. During the experiment, fish were fed the experimental diet to satiation third a day at 08:00, 12:00 and 16:00 hours.
3. **Measurements and sample analysis:** It was carried out each 20 days. Water temperature was 15°C, O2 7-8 mgl-1, pH 7-8 and light: dark cycle of 12:12 h was maintained during the feeding trial. Proximate composition of diets and tissues were carried out using the Association of Analytical Chemists (AOAC, 2000) methods.
4. **Calculations and statistical analysis:** The following variables were calculated:

a) Body weight increase (BWI) = Wt – W0 (Tacon, 1990)

b) Specific growth rate (SGR) = (ln Wt – ln W0) × 100 $t^{-1}$ (Hevroy *et al.,* 2005)

Where, Wt and W0 = Final and initial fish weights (g), respectively,

(t) = the experimental period in da

c) Feed conversion ratio (FCR)=$\frac{\text{Total dry feed consumed (g)}}{\text{total weight gained (g)}}$ (Shalaby *et al.,* 2006)

d) The data obtained from the trial is expressed as mean (±SD).

## Results and Discussion:

Growth performances of the fishes after 60 days of feeding are summarized in Table 2. Third fish group had higher final weight, weight gain, and SGR than fish fed on other levels of garlic and control. The highest amounts of dry feed intake (g/fish/day) were seen in the same third fish groups. Results also show that FCR decreased significantly to 1.39±0.01 in the third group.

It is clear that garlic is a main vegetable extensively cultivated in many countries. It is used as food for humans as well as some animals and as remedy for several diseases, as reported in folk medicine (Shalaby *et al.,* 2006). In this study the highest growth performance was observed in fish fed diets containing garlic, especially on 30 g garlic. It agrees with studies results of Diab *et al.,* (2002), Abou-Zeid, (2002), Shalaby *et al.,* (2006). Feed intake increased with increasing *Allium sativum* levels. Feed conversion ratio decreased with increasing *Allium sativum* levels. These results are also in agreement with those obtained by Gomes *et al.,* (1993), Degani *et al.,* (1997), Khattab *et al.,* (2004) and Farahi *et al.,* (2010).

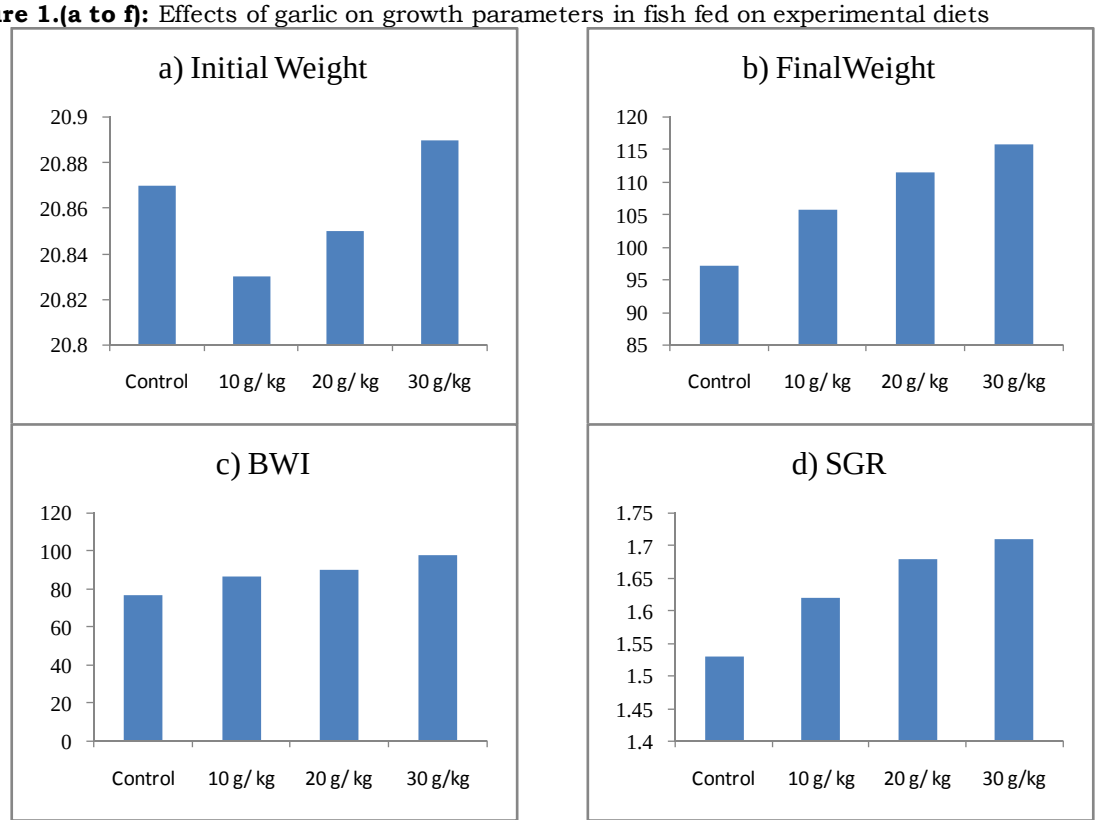
Table 1. Formulation and proximate composition of the basal fish diets

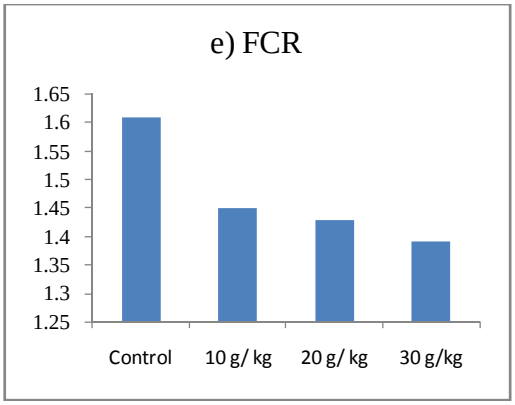
| Ingredients | **Control** | ***Allium sativum* diets Ingredients (g /100g diet)** | | |
|---|---|---|---|---|
| Meat | 25 | 25 | 25 | 25 |
| Wheat | 50 | 47 | 44 | 41 |
| Soybean | 20 | 20 | 20 | 20 |
| Soybean oil | 05 | 05 | 05 | 05 |
| Garlic | 00 | 03 | 06 | 09 |

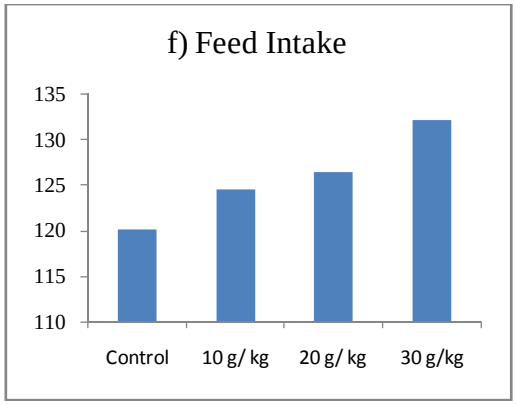
Table 2: Effects of garlic on growth parameters in fish fed on experimental diets(g/100g)

| Parameters | **Control** | **I** | **II** | **III** |
|---|---|---|---|---|
| Initial weight(g) | 20.87±0.30 | 20.83±0.09 | 20.85±0.34 | 20.89±0.33 |
| Final weight (g) | 97.05±3.10 | 105.76±4.12 | 111.51±4.23 | 115.88±2.51 |
| BWI (g) | 76.81±3.39 | 86.81±4.13 | 90.03±4.56 | 98.02±3.42 |
| SGR | 1.53±0.06 | 1.62±0.05 | 1.68±0.04 | 1.71±0.03 |
| FCR | 1.61±0.05 | 1.45±0.04 | 1.43±0.05 | 1.39±0.01 |
| Feed intake (g) | 119.12±1.29 | 123.35±2.31 | 127.24±1.33 | 133.02±2.12 |

**Figure 1.(a to f):** Effects of garlic on growth parameters in fish fed on experimental diets






## Conclusions

From obtained results, it could be recommended that garlic (*Allium sativum*) can be used as a growth promoter in *Clarias batrachus* so garlic should be added to the diets of fish.

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# ICHTHYOLOGICAL FAUNA OF AMRAVATI DISTRICT (M.S.) INDIA

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ABSTRACT

Amravati district is a district of Maharashtra state in central India. It is transverse by many rivers like Tapi river, Purna river, Wardha river, Chandrabhaga river, Shahanoor river and river River with their numerous tributaries. The study was conducted during June 2013 to September 2014. These river hosts many of fish species; total of 36 species belonging to 11 families were recorded. These families were; Cyprinidae (20), Channidae (03), Mastocembelidae (03), Ambassidae (02), Bagridae (02), Siluridae (02), Gobiidae (01), Notopteridae (01), Saccobranchidae (01), Clariidae (01), and Belonidae (01). The river and tanks of studied area have faced major alterations in the recent years due to several anthropogenic activities like increasing urbanization, industrialization and various recreational activities. Since the fish fauna in Amravati District also supports the livelihood of several economic classes. So there is an urgent need to understand the conservation priorities and to design and implement conservation action plans.

KEYWORDS :*Amravati, Freshwater fish fauna, River ecosystem, Threats.*

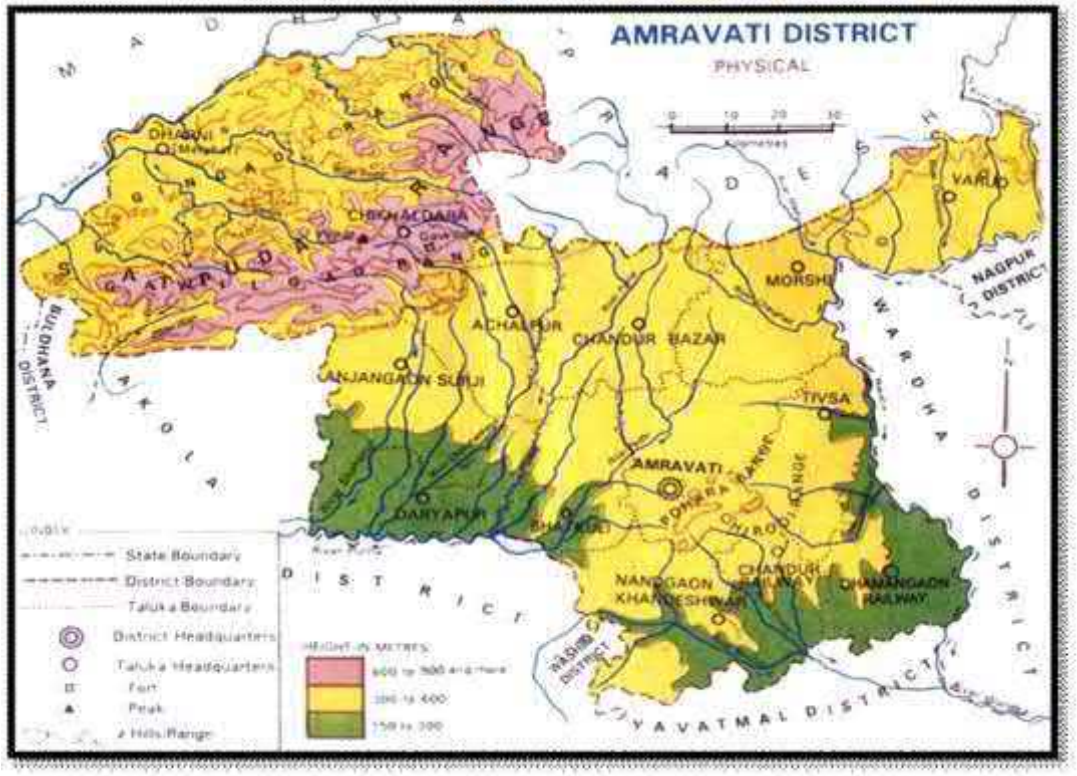
## INTRODUCTION :

The biological diversity of the earth and its origins has long been a source of amazement and curiosity (Joshi et al., 2013). The diversity of fish has long been a source of amazement and curiosity. Around the world approximately 22,000 species of fishes have been recorded out of which 11 % are found in India that is about 2500 species of fishes of which, 930 live in freshwater and 1,570 are marine (Kar, 2003; Ubharane et al., 2011). From 18 century till to date various pioneers have been studied about Taxonomy and Ichthyofaunal diversity (Hamilton, 1822; Day, 1878; Menon, 1992) from different rivers. However scanty information is available on fishes hence an attempt has been made here to present piscine inventory from the Amravati District (M.S.).

Amravati district is district of Maharashtra state in central India. The district is situated between 200 32' and 210 46' north latitudes and 760 37' and 780 27' east longitudes with tropical climate.. The district occupies an area of 12,235 sq.km. The district is bounded by Baitul District of Madhya Pradesh state to north, and Nagpur district to northeast, Wardha to the east, Yavatmal to the

south, Washim to the southwest, and Akola and Buldhana district to the west. The district comprises of several rivers and impounded water sources. The Wardha river forms the eastern boundary of district and the eastern portion of the district lies within its water shade. The Purna drains the southwestern portion of district while the northwest is drained by the Tapti river. The other important rivers are Chandrabhaga, Shahanoor, Waan river etc. with their numerous tributaries (Amravati Gazetteer 2015).

Figure 1. Amaravati District (M.S.) India




These rivers and Tanks have faced major alterations in the recent years due to increasing urbanization, industrialization and various recreational activities. Reassessment of the fish fauna and identifying the threats, so as to build baseline information for possible conservation action plans are thus a priority. For the current study, stretches of the rivers were sampled to identify the current status and threats to the freshwater fish fauna of Amravati District (M.S.) India.

## METHODOLOGY:

Fish were collected from local fisherman and local markets located on the rivers from June 2013 to September 2014. Fish were preserved in 4% formaldehyde and identified using available literature (Day, 1996; Menon, 1987, 1992; Talwar and Jhingran, 1991; Jayaram, 2010; Eschmeyer and Fricke, 2011). Assuming that the fishing effort for a given type of net (gill net or drag net) was constant, the relative abundance of the fish was grossly categorized (for each type of net separately) into four categories, namely: abundant (76–100 % of the total catch), common (51–75 % of the total catch), moderate (26–50 % of the total catch) and rare (1–25 % of the total catch). The Diversity data was quantified with the help of PAST Version 1.60 software (Hammer et al. 2001). The differences between the diversity and evenness indices of fishes among different rivers were statistically analyzed using Analysis of Variance.

## RESULTS AND DISCUSSION:

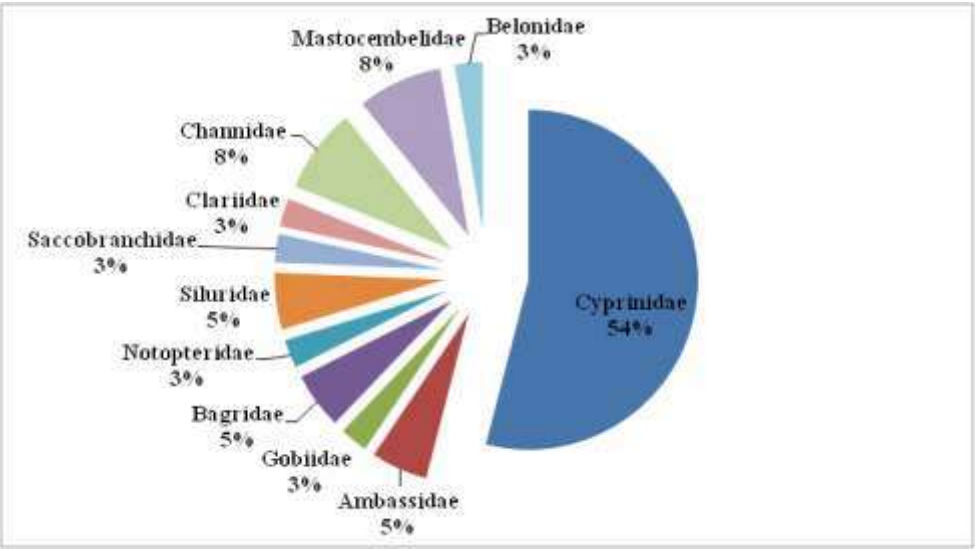
During study, total of 36 species belonging to 11 families were recorded (Table 1). These families were; Cyprinidae (20), Channidae (03), Mastocembelidae (03), Ambassidae (02), Bagridae (02), Siluridae (02), Gobiidae (01), Notopteridae (01), Saccobranchidae (01), Clariidae (01), and Belonidae (01) were recorded(Figure 1). Of these species; 08 were Abundant, 09 were Common, 14 were Moderate while 05 were Rare. From the observed species, Catla catla, Labeo rohita and Clarias batrachus are most commercially important fishes. Previously Lohar and Borse (2003) was reported 24 fish species belonging to 7 families in Tapi river. As well Joshi et al., (2012) were reported 20 species of 7 families from Purna river. In these reported fishes, Cyprinidae family was more dominant. Many researchers reported the strong dominance of Cyprinidae family in their investigations.

**Table 1: Ichthyological Fauna of Amravati District of Maharashtra (India).**

| Sr. | Family | Species | Author | Abundance |
|---|---|---|---|---|
| 1. | **Cyprinidae** | *Acanthocobities murreh* | Sykes, 1839 | Abundant |
| 2. | | *Amblypharyngodon mola* | Hamilton, 1822 | Moderate |
| 3. | | *Catla catla* | Hamilton, 1822 | Abundant |
| 4. | | *Cirrhina mrigala* | Hamilton, 1822 | Abundant |
| 5. | | *Crossocheilus latius* | Hamilton, 1822 | Moderate |
| 6. | | *Ctenopharyngodon idella* | Steindachner, 1866 | Moderate |
| 7. | | *Cyprinus carpio* | Linnaeus, 1758 | Rare |
| 8. | | *Garra Mullya* | Sykes, 1839 | Common |
| 9. | | *Labeo baggut* | Sykes, 1839 | Rare |
| 10. | | *Labeo bata* | Hamilton, 1822 | Rare |
| 11. | | *Labeo calbasu* | Hamilton, 1822 | Moderate |
| 12. | | *Labeo rohita* | Hamilton, 1822 | Common |
| 13. | | *Osteobrama cotio* | Hamilton, 1822 | Moderate |
| 14. | | *Pethia ticto* | Hamilton, 1822 | Common |
| 15. | | *Puntius saphore* | Hamilton, 1822 | Common |
| 16. | | *Puntius sarana* | Hamilton, 1822 | Rare |
| 17. | | *Puntius ticto* | Hamilton, 1822 | Moderate |
| 18. | | *Rasbora daniconious* | Hamilton, 1822 | Common |
| 19. | | *Salmophasia bacaila* | Hamilton, 1822 | Common |
| 20. | | *Salmophasia balooki* | Sykes, 1839 | Common |
| 21. | **Ambassidae** | *Chanda nama* | Hamilton, 1822 | Moderate |
| 22. | | *Parambassis ranga* | Hamilton, 1822 | Common |
| 23. | **Gobiidae** | *Glossogobius giuris* | Hamilton, 1822 | Moderate |
| 24. | **Bagridae** | *Mystus cavasius* | Hamilton, 1822 | Abundant |
| 25. | | *Sperata seenghala* | Sykes, 1839 | Moderate |
| 26. | **Notopteridae** | *Notopterus notopterus* | Gunther, 1839 | Rare |
| 27. | **Siluridae** | *Ompok bimaculatus* | Bloch, 1793 | Moderate |
| 28. | | *Wallago attu* | Schlegel, 1839 | Moderate |
| 29. | **Saccobranchidae** | *Heteropneustes fossilis* | Bloch, 1793 | Moderate |
| 30. | **Clariidae** | *Clarias batrachus* | Linnaeus, 1758 | Abundant |
| 31. | **Channidae** | *Channa punctatus* | Bloch, 1793 | Abundant |
| 32. | | *Channa striatus* | Bloch, 1793 | Abundant |
| 33. | | *Channa orientalis* | Bloch, 1793 | Common |
| 34. | **Mastocembelidae** | *Mastocembelus armatus* | Lecepede, 1800 | Moderate |
| 35. | | *Mastocembelus pancalus* | Hamilton, 1822 | Moderate |
| 36. | **Belonidae** | *Xenentodon cancila* | Hamilton, 1822 | Abundant |

* Taxonomic status as per Jayaram (2010)

Figure 1. Percent Occurrence of different Ichthyological families from Amravati District (M.S.) India




The differences between the diversity and evenness indices of fishes among different rivers were statistically analyzed (Table 2).

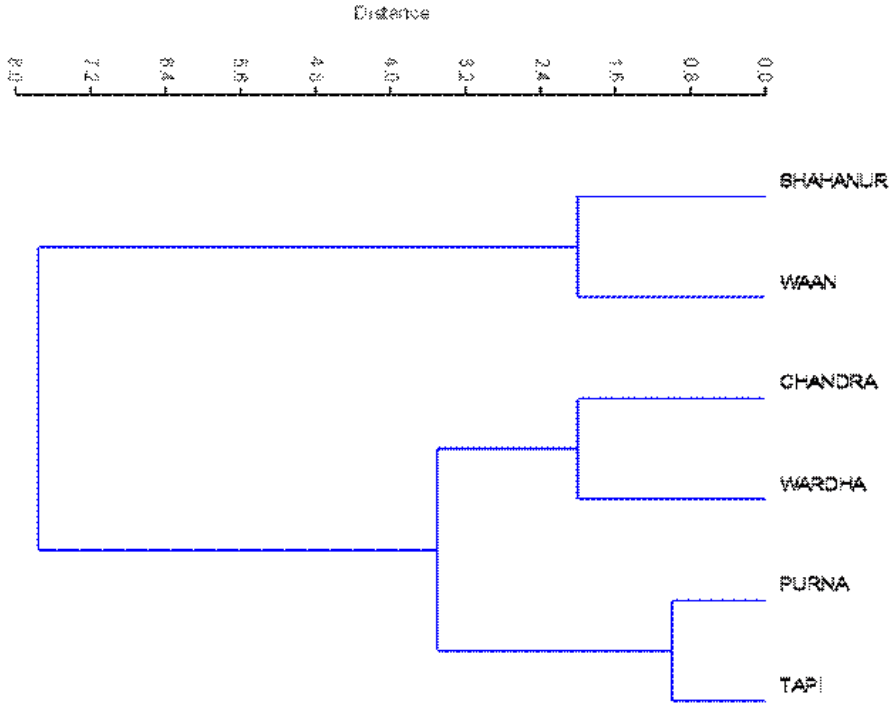
**Table 2: Diversity measures Ichthyological fauna in different seasons during June 2012 to May 2014 from Amravati District, Maharashtra (India)**

| Year / Month | No. of species | Relative abundance[a] | Shannon diversity[b] | Equitability[c] | Species richness[d] |
|---|---|---|---|---|---|
| **Tapi** | 36 | 19.25 | 3.045 | 0.8941 | 5.413 |
| **Purna** | 35 | 18.71 | 2.870 | 0.9267 | 5.124 |
| **Wardha** | 33 | 17.64 | 2.853 | 0.8761 | 4.278 |
| **Chandrabhaga** | 31 | 16.58 | 2.740 | 0.9219 | 4.713 |
| **Shahanoor** | 27 | 14.43 | 2.569 | 0.9279 | 4.659 |
| **Waan** | 25 | 13.36 | 2.553 | 0.9068 | 4.038 |

a = Mean percent abundance among different rivers were significantly different ($F=28.138$, $df=05$, $p<0.05$). b = Diversity values among different rivers were significantly different ($F=8.206$, $df=05$, $p<0.05$). c = Species equitability among different rivers were significantly different ($F=15.176$, $df=05$, $p<0.05$). d = Species richness among different rivers were significantly not different ($F=1.536$, $df=05$, $p>0.05$).

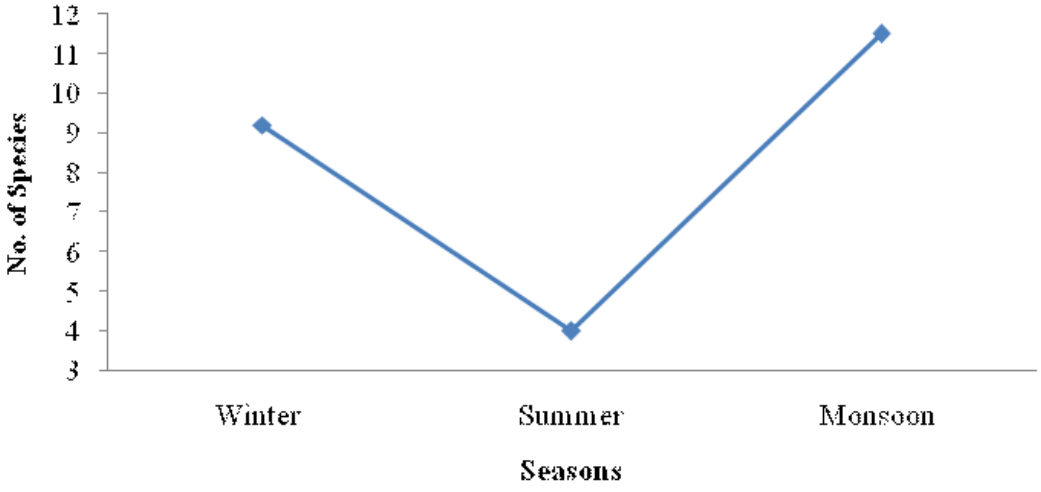
Cluster analysis was carried out to assess the similarity in number of fish's species composition among the studied rivers. The similarity association matrix upon which the cluster based was computed using the nearest neighbour pair linkage algorithm of Euclidean distance index for presence and absence data. Cluster shows the maximum number of species were reported from Tapi followed by Purna, Wardha , Chandrabhaga, Shahanoor and lowest from Waan (Figure 2).

Figure 2. Dendrogram showing similarity in number of fish species composition among the different seasons



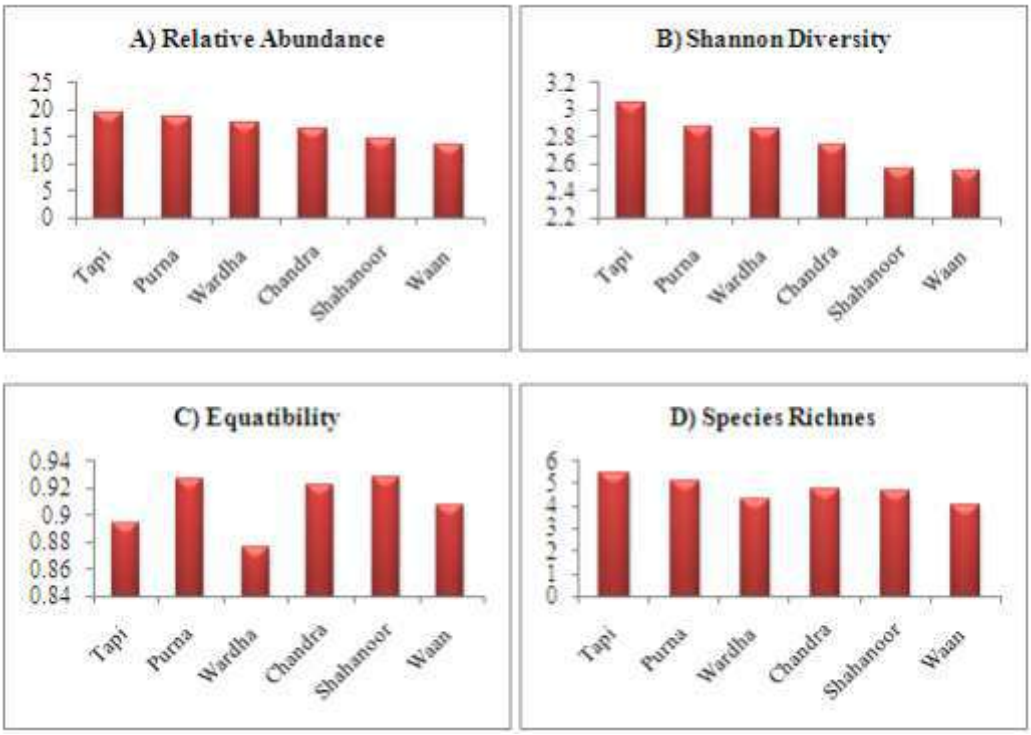

During study, the average number of specimens collected in different seasons. For comparing the catch success in different season, the average values of catch success were used as a simple mean of total species collected per attempt. Catch success was highest in Monsoon months followed by winter while it was comparatively low in Summer (Figure 3).

Figure 3. An average catch Success in different Seasons



A comparison of species diversity attributed to fish fauna among different rivers of Amravati District revealed that faunal diversity was highest at Tapi followed by Purna, Wardha, Chandrabhaga, Shahanoor then lowest observed from Waan river. A trend in Mean % Abundance was noted to be nearly similar to that of Shannon Diversity though Species Richness and Species Equitability shows contradictory pattern (Figure 4. A to D).

Figure 4: (A to D): Diversity measures of Ichthyological fauna in major rivers from Amravati district (M.S.) India




Previously, Sakhare (2001) was reported 23 species belonging to 07 order where Cyprinidae family is dominant with 11 species from Jawalgaon reservoir Solapur district Maharashtra. Battul et al. (2007) reported 18 species from Ekruckh lake Solapur district where Cyprinidae family is dominant with 8 species, Khedkar and Gynanath. (2005) reported 37 species from Issapur dam district Yavatmal where Cyprinidae family is dominant with 20 species. Sharma (2008) reported 87 species under 36 genera under the Cyprinidae family from freshwater of Nepal. Shinde (2009) observed 11 species under 10 genera under the Cyprinidae family from Harsul Savangi dam district Aurangabad (M.S). Ubharane et al (2011) observed that the27 species belongs to 11 families where Cyprinidae family was dominant with 13 species from Ambadi dam of Aurangabad (M.S.) India.

The fishing operation goes on by the local fisherman throughout the study period with low catches in monsoon compare to high harvest in post monsoon season. river ecosystem of Amravati district hosts a number of fish species. But the ichthyological fauna of rivers is under threat as a result of several anthropogenic interferences. Other anthropogenic activities such as deforestation leading to siltation, recreational activities and sand mining are common in most of the stretches of the river. The fish fauna of rivers is also subjected to over fishing for consumption. Inorganic pollution of the river due to industrial and agricultural activities is another important threat to the fish fauna.

In conclusion, the rivers of Amravati District hosts a number of freshwater fish species.

However, the fish fauna in the study area is threatened due to several anthropogenic activities like deforestation, over fishing, sand mining, recreational activities, brick kiln, and organic and inorganic pollution. Since the fish fauna in Amravati District also supports the livelihood of several economic classes. So there is an urgent need to understand the conservation priorities. Fishery department should adopt Legislative measure for conservation of commercially significant fishes which may disappear from rivers of Amravati District (M.S.) India.

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Amjad Hussain

# RECORD OF LEUCISM IN GREEN KEELBACK *MACROPISTHODON PLUMBICOLOR* (CANTOR, 1839) IN AMRAVATI DISTRICT, MAHARASHTRA, INDIA

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**ABSTRACT**

The present paper provides the information about a record of leucism in *Macropisthodon plumbicolor* (Cantor, 1839).Leucistic wild individuals are less common in nature. A specimen with a length of approximately 21 inch was observed on 23 July 2015 from a field near MIDC old bye pass road of Amravati district (M.S.) India. It was observed, photographed and identified with the help of visible morphological characters.

**KEY WORDS:** *Macropisthodon plumbicolor*, Leukism, Amravati, India.

**INTRODUCTION :**

Unusual coloration in vertebrates does not occur frequently in nature, yet it is recorded in a large variety of species (Bried *et al.*, 2005, Franz and Fleck, 2009). In general, colour and pattern in reptiles is produced by a combination of pigments and structural compounds (Bechtel, 1995). There are multiple varieties of chromatophores, the failure to produce a normal amount of pigment in one cell type does not generally alter the ability of the other chromatophores. Thus, various aberrant colours and patterns in reptiles are expressed and the most striking colour pigment anomaly is albinism and leucism (Gamble *et al.*, 2006).

Albinism and Leucism have already been recorded in fish (Veena *et al.*, 2011), amphibians (Mitchell and Church, 2002), reptiles (Krecsak, 2008), birds (Nogueira and Alves, 2011) and mammals (Reisinger *et al.*, 2009). Albinism, derived from a Latin word 'albus' which means 'White', is a form of

hypopigmentary congenital disorder, characterized by lack of melanin pigment and an animal with such a condition could have either pure or partial albinism (Cyril, 2009). Albinism is caused by the absence of the tyrosinase enzyme, which is necessary for the synthesis of melanin, resulting in the absence of pigment in the skin, the iris and the choroid. Further, it is due to a genetically inherited condition in which a recessive gene affects enzymes involved in the metabolism of various chromatophore pigments (Spadola and Toro 2007). Leucistic snakes have a diminished number of iridophores and probably very low number or no melanophores and xanthophores (Bechtel, 1991). Leucism is a form of partial albinism characterized by the normal pigmentation of eyes, legs and beak, while skin or feathers present lowered or absent coloration (Sage, 1962; Forrest and Naveen, 2000).

Many researchers consider leucism as partial albinism (McCardle, 2012; Costa de Noronha *et al.*, 2013). Albinism is caused by several different genes (Summers, 2009), while leucism is controlled by a single recessive allele (Owen and Shimmings, 1992). Inherited color defects, such as albinism and leucism, are well known in several animal species including snakes (Bechtel, 1991). Wild albino and leucistic animals are rare (Walter, 1938), mainly due to their low survival rates. Albinotic and leucistic individuals are less common in nature, but are popular and intentionally selected by herpetoculturists, who breed color variants of several species of Pythononiae and Colubridae (Bechtel, 1995).

**Methodology**

Healthy climatic and ecological condition of Amravati district (M.S.) India is well known for its rich biodiversity. On 23 July 2015, a white color snake was observed in a field near MIDC old bye pass road Amravati district (M.S.) India. Area lies between 20°55'33"N and 77°45'53" E. Specimen was observed, photographed and identified by observing morphological characters. For identification of the observed snake, keys and methods suggested by Daniel (2002), Whitaker and Captain (2008), and Khaire (2010) were used.

**Observation and Discussion**

Observed snake specimen was identified as adult *Macropisthodon plumbicolor* (Cantor, 1839) with leucism. Body of specimen was stout with approximate length of 21 inch. Dorsally, the snake was white in colour with light brown small bands from anterior to posterior part of body. An inverted V shaped light brownish coloured mark was present on the head. The dorsal scales were strongly keeled. Ventrally the belly was whitish to light cream in colour without any spots or markings. Eyes were large and green with round pupil as found in normal specimen. Tongue was pinkish in color. Tail was short (fig. 1 and 2).

Generally, the normal specimens have bright or dull green body, sometimes with faint irregular black bands. Body structure is rounded. Eye fairly large and the rostral scale are just visible from above. The dorsal scales are strongly keeled, in 23 to 27 rows. Young snakes have a bright yellow or orange inverted V shaped mark on neck, bordered on both sides by a dark blue-black area and also have a black stripe from eye to angle of mouth (Whitaker and Captain, 2004). Naturally feeds on toads, lizards and frogs.

A perusal of literature revealed that there are a number of instances of complete, incomplete and partial albinism in Indian reptiles in general and snakes in particular (Lahiri, 1955; Whitaker, 1971; Basu and Srivastava, 2003; Cyril, 2009; Vyas 2012, 2013; Vyas et al., 2012; Sayyed, 2012; Hoshing et al., 2013). Cases of albinism and leucism among viperinae have been also reported from Europe (Krecsák, 2008). Few cases of total albinos have been reported in *Macropisthodon plumbicolor* with yellowish

body (Sayyed 2012) and whitish-pinkish body (Hoshing et al., 2013). A case of leucism has also reported in Pseudoboa nigra in southern Amazon, Brazil (Costa de Noronha et al., 2013).

Albinism can be defined in several different ways, but there are a few distinctive types of albinism depending on certain defining characteristics. True or complete albinism is the total absence of integumentary and retinal pigmentation (Sandoval et al., 2006). Partial albinism occurs when pigment is reduced or absent from the skin, feathers, or eyes (Berdeen and Otis, 2011). Leucism or leukism is a form of partial albinism characterized by retention of color in the eyes, bill, and legs but the skin or plumage contains no color pigment (Forrest and Naveen, 2000).

Vyas (2013) has pointed out that the further research is needed on histopathology and biopsies of skin tissue and 'dopa test' to enrich the knowledge on colour anomaly in reptilian species. Further, a substantial quantitative data is required to analyze the pattern of occurrence of leucism in snakes.

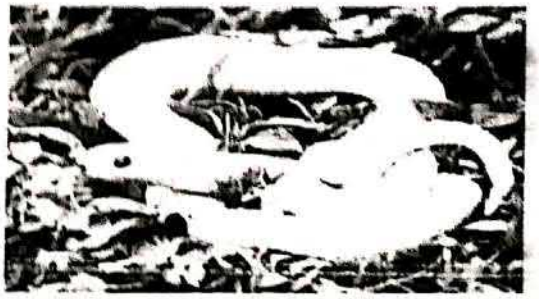

**Image.1 Leucistic *Macropisthodon plumbicolor***

**Image .2 Leucistic *Macropisthodon plumbicolor***

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# Synthesis, Characterization and Antimicrobial Study of Some Novel Chloro Substituted Isoxazoles

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## ABSTRACT

In the present study a series of 3-(2-Hydroxy-3, 5-dichlorophenyl)-5-(4-chloro phenyl) isoxazole (8a) and 3-(2-Hydroxy-3, 5-dichlorophenyl)-5-(2, 4-chloro phenyl) isoxazole (8b) have been synthesized by refluxing the chalconedibromide (6a) and (6b) with hydroxyl amine hydrochloride in ethanol containing catalytic amount of piperidine. The formation of the above synthesized compounds was confirmed on the basis of their chemical tests and spectral analysis. The synthesized heterocycles then screen for their antimicrobial activity against some kahrip plant pathogens viz. *AlternariaMacrospor, XanthomonasCampestris, Pseudomonas syringae and Fusarium Spp.* From the above study the result revealed that isoxazole derivatives shows good to moderate antimicrobial activity against plantpathoges.

**Keywords**: Chalcones, chalconedibromide, plant pathogens, antimicrobial activity, isoxazole.

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## INTRODUCTION

Isoxazole is a five membered heterocyclic compound containing oxygen and nitrogen atoms in the 1,3 positions placed in the heterocyclic ring. From the literature survey it is revealed that many workers have synthesized different isoxazole[1-5]. Heterocyclic compounds are veryuseful moiety in the fields of medicinal and pharmaceutical chemistry and have been reported to exhibit a variety of biological activities[6,7] such as antimicrobial[8], antiarthetic[9], anticoagulant[10]

## MATERIALS AND METHOD

The all the heterocyclic compounds have been synthesized by using conventional method in laboratory

**Preparation of 2-hydroxy 3, 5-dichloroacetophenone (2a)**

2-hydroxy 3, 5-dichloroacetate (50 ml) was mixed with anhydrous $AlCl_3$ (120 gm) and heated at 120$^oC$ for 45 minutes on the paraffin oil bath. The reaction mixture were decomposed by taking ice cold water containing a few amount of HCl acid and allowing the solution to fall drop by drop into cold water with constant stirring . A greenish white solid of compound (2a) was obtained.

**Preparation of 2-hydroxy-3, 5-dichlorophenyl-4-p-chlorochalcone (3a, 3b)**

2-Hydroxy-3, 5-dichloroacetophenone (2a) (0.01mol) and p-chlorobenzaldehyde and p, m-dichlorobenzaldehyde (0.01mol), was dissolved in ethanol (25ml). after that in this solution the 40% 30 ml NaOH solution is added drop wise with constant stirring getting the saffron color solid kept it overnight after that acidify this solid by 50% HCL solution, affords a yellow solid was filtered, washed with sodium bicarbonate (10%) followed by water. The crude product was crystallized from ethanol acetic acid.

**Synthesis of 2-hydroxy 3, 5-dichlorophenylchalconedibromide (6a, 6b)**

2-hydroxy 3, 5-dichlorophenyl chalcone (3a) and(3b) (0.01 mol 3.26, 3.65gm respectively) was dissolved in bromine -acetic acid reagent (25%, w/v) (6.4 ml). The reagent was added drop wise with constant stirring. After complete addition of reagent, the reaction mixture was kept at room temperature for about 30 minutes. The solid product thus separated was filtered and washed with a little petroleum ether to get the compound (6a) and (6b).

**Synthesis of 2-hydroxy-3, 5-dichlorophenyl isoxazole (8a, 8b)**

A mixture of chalconedibromides (6a) and (6b) (0.01 mol, 4.84 and 5.18 g, respectively) and hydroxyl amine hydrochloride (0.02 mol, 2.78gm) was refluxed in ethanol (20 ml) and piperidine (1ml) for about 3.5 hours. After cooling the reaction mixture was acidified with dil. HCl (1:1). The solid product separated was filtered, washed with sodium bicarbonate solution (5 %) and water.

The product was finally crystallized from ethanol-acetic acid mixture to get the compound (8a) and (8b).

**Characterization of the compounds**

Melting points of all synthesized compounds were determined in open capillaries and are uncorrected. IR spectra were recorded on Perkin-Elmer 1000 Spectrophotometer in KBr. NMR spectra were recorded on Bruker advance 400 NMR spectrometer using TMS as internal standard and chemical shift were expressed in δ ppm.

**1. Compound: Chalcone (3a)**

I.R. (KBr): cm – 3500 (-OH phenolic), 3074 (=CH str. in alkene), 1643 (>C=O str. in ketone), PMR: δ 7.44 -7.91 (m, 2H, -CH=CH); 7.44 -8.37 (m, 6H, Ar H); 13.26 (s, 1H, Ar-OH). U. V.:- λ max 344 nm. Corresponding to n →π*

**2. Compound: Chalcone (3b)**

I.R. (KBr): cm-3368-3500 (-OH phenolic), 3068 (aromatic –CH stretching). 1641 (>C=O str.in ketone), PMR: δ 8.27-8.31(m, 5H, Aromatic) 7.2-7.78 (2H, CH-CH); 13.19 (s, 1H, Ar-OH) U. V:- λ max 344 nm. Corresponding to n →π* shows conjugation in aromatic molecule

**3. Compound: Dibromide (6a)**

I.R. (KBr): cm – 3700 (-OH phenolic), 2981 (aromatic str.), 2882 (aliphatic CH str.), 1654(-C=O str.), 1319 (O-H bending).1093(C-Cl str.), PMR: δ 2.5 (d, 1H, -CO-CH-Br); 3.5 (d, 1H,-CHBr-CHBr); 7.4-8.4 (m, 6H, Ar-H).12.04(s, 1H, Ar-OH), U. V.:- λ max 314 nm. Corresponding to n →π*

**4. Compound: Dibromide (6b)**

I.R. (KBr): cm – 3700 (-OH phenolic), 3074 (aromatic str.), 3007 (aliphatic CH str.), 1654(-C=O str.), 1313 (O-H bending),1103(C-Cl str.) , PMR: δ 3.9 (d, 1H, -CO-CH-Br); 7.5-7.7 (d,1H,-CHBr-CHBr); 7.1-8.4 (m, 5H, Ar-H).11.90(s, 1H, Ar-OH), U. V.:- λ max 300 400 nm. Corresponding to n →π*

**5. Compound: Isoxazole (8a)**

I.R. (KBr): cm – 3600 (w, -OH phenolic), 3082 (s, aromatic str.), 1462 (-C-N str.), 1282 (s,- N=N-str.),1107 (Cl-C) PMR: δ 6.7 (isoxazole proton), 7.3-7.5 (d, 2H, C-H),7.5-8.5 (d, 2H, C-H), 7.87 (s, 1H, C-H), 7.6 (d, 2H, C-H), U. V.:- λ max 400 nm. Corresponding to n →π*

**6. Compound: Isoxazole (8b)**

I.R. (KBr): cm – 3600 (w, -OH phenolic), 3070 (s, aromatic str.), 1462(-C-N str.), 1282(s,- N=N-str.), 1091 (Cl-C)PMR: δ 8.0 (d HAr-H).10.53(s, 1H, Ar-OH), 7.75, 7.5, 7.9, 7.6 (d H Ar-H), 8.1 (s H isoxazole proton ) U. V.:- λ max 400 nm. Corresponding to n →π*

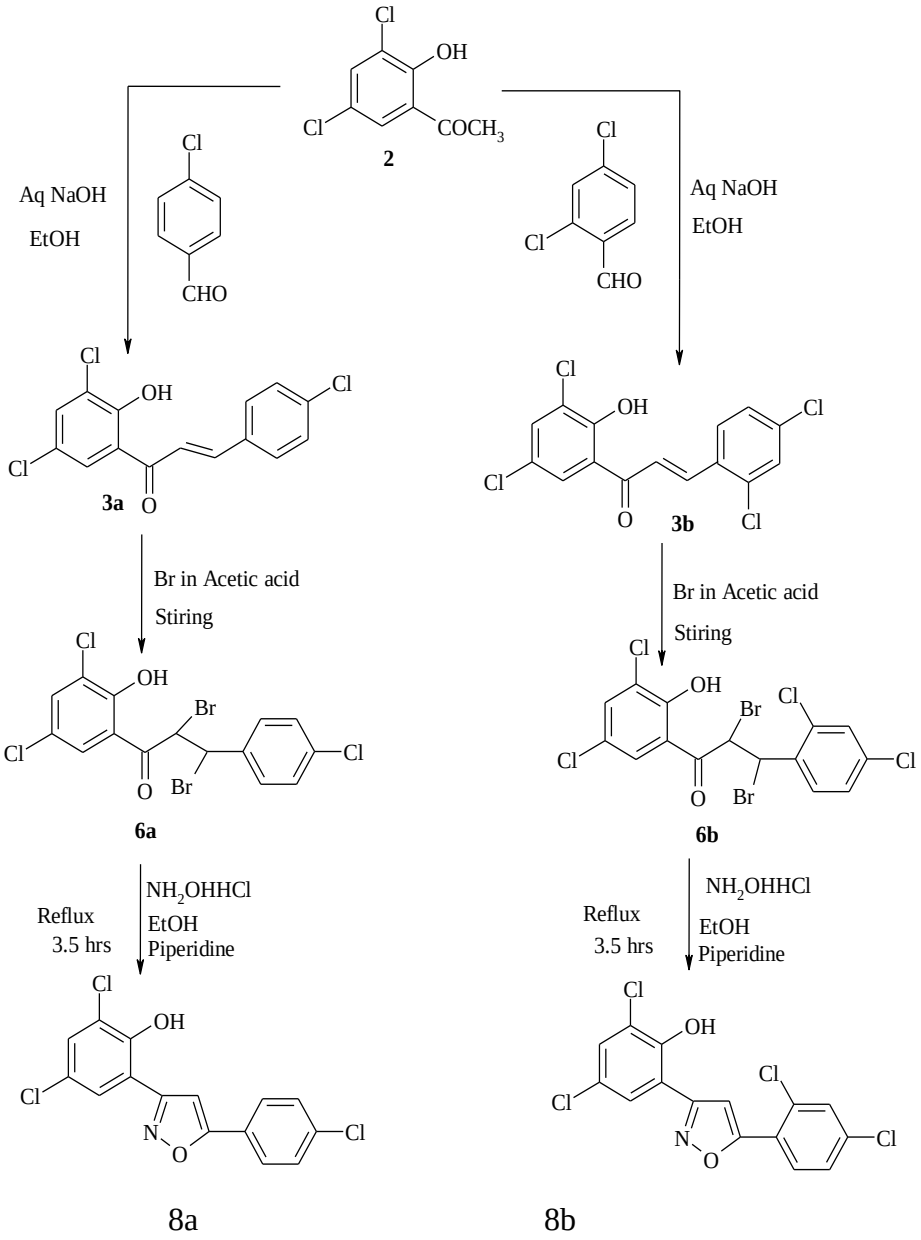


**Figure 1: The flow diagram of the isoxazole synthesis.**

## RESULTS AND DISCUSSION

**Table 1: Physical data of the synthesized compounds**

| Sr. No. | Name of the compounds | M.P. $^{o}$C | R f value |
|---|---|---|---|
| 1 | 2 | 93 | 0.84 |
| 2 | 3a | 215 | 0.62 |
| 3 | 3b | 176 | 0.66 |
| 4 | 6a | 190 | 0.71 |
| 5 | 6b | 170 | 0.78 |
| 6 | 8a | 120 | 0.58 |
| 7 | 8b | 95 | 0.62 |

**Antimicrobial activity**

Antimicrobial activities of all synthesized compounds were determined by cup plate method. All plant pathogens were purchased from NCIM Pune, Institute of Microbial Technology, Chandigarh and Plant pathology department ICAR New Delhi. The agar medium and PDA were purchased from Hi- media lab. Mumbai. The stock solution of test 1000µg/ml were prepared by dissolving appropriate quantities of test compounds in DMSO, The stock inoculums of the microbes was prepared by the inoculation the 5o ml nutrient broth with test organisms and incubating it at $37\pm2^0$C for 24 hrs the zone of inhibition was measured by Himedia scale[11,12].

**Table 2: Antimicrobial screening of the synthesized compounds**

| Sr. No. | Name of the compounds | Zone of Inhibition (mm) | | | |
|---|---|---|---|---|---|
| | | ***Xanthomonas Campestris*** | ***Alternaria Macrospora*** | ***Fusarium Spp.*** | ***Pseudomonas syringae*** |
| 1 | 2 | 17 | 12 | 22 | 23 |
| 2 | 3a | --- | 12 | 15 | 15 |
| 3 | 3b | 12 | 15 | 15 | 19 |
| 4 | 6a | 33 | 26 | 25 | 13 |
| 5 | 6b | 30 | 30 | 18 | 16 |
| 6 | 8a | --- | 25 | 17 | 14 |
| 7 | 8b | 16 | 18 | 11 | 11 |
| 8 | Control | 18 | 16 | 14 | 14 |

## CONCLUSION

The above result revealed that the synthesized compounds have showed good to moderate antimicrobial activity against all plant pathoges.

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# Synthesis characterization of some nitro-substituted-1, 3-thiazines and their antimicrobial activities.

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*ABSTRACT*

Some new nitro-substituted 1,3 thiazines have been synthesized by the condensation of 2-hydroxy-3-nitro-5-chlorochalcones with thiourea, phenylthiourea & diphenylthiourea in ethanol containing aqueous KOH solution. The structures of newly synthesized nitro-substituted have been analyzed on the basis of their analytical data, molecular weight determination study and UV, IR & NMR spectral results. The newly synthesized titled compounds were screened for their antibacterial activity against some common pathogens *viz* . . *S. aureus* ,*B. subtilus* . *E. Coli* and *P. aerugiuosa*.

**Keywords:** Thiazines, antibacterial activities, thiourea, phenyl thiourea, diphenyl thiourea.

## INTRODUCTION

In organic chemistry a series of heterocyclic compounds containing an unsaturated six membered ring which contain two carbon one nitrogen and one sulphur atom are termed as thiazines. Various methods have been worked out for their synthesis[1] .Their derivatives have wide variety of biological properties such as Antiparkinsonian[2] Anti-Inflammatory[4] antibacterial .[7-9] Taking this into consideration the nitro -substituted thiazines were synthesized and assayed for their anti-microbial activity against some common pathogens viz: *S. aureus* ,*B. subtilus* . *E. Coli* and *P. aerugiuosa*. The reaction of various formes of thiourea with chalcone gives 1-3 thiazines. It is found that the presence of 4-phenyl nitro -substitute and 2-substituted imino group in thiazine enhanced the biological activities.

## Material and method

**Preparation of 2-hydroxy-3-nitro-5-chloroacetophenone (2a)**

2-Hydroxy-5-chloroacetophenone (3g) was dissolved in glacial acetic acid (3ml). bromine in acetic acid was added drop wise with constant stirring to this reaction mixture . The temperature of the reaction mixture was maintained below 0°C. The mixture was allowed to stand for 1hour. It was poured into ice cold water with stirring. A yellow solid then obtained was filtered, dried and crystallized from ethanol.

**Preparation of 2-hydroxy-3-nitro- 5-chlorochalcones (3a-c)**

2-Hydroxy-3-nitro-5-chloroacetophenone (3a), (0.1M) was dissolved in ethanol (50 ml) and aldehyde (Benzaldehyde,Propanaldehyde & Valeraldehyde separately ) (0.1M) was added to the above solution and the mixture was heated to boiling. Aq. sodium hydroxide solution (40%, 40 ml) was added drop wise with constant stirring. The mixture was stirred mechanically at room temperature for about half an hour and kept overnight. It was then acidified by hydrochloric acid solution (50%). The solid separated was filtered and washed with sodium bicarbonate (10%) followed by water. The crude product was crystallized from ethanol acetic acid mixture (3a-c).

**Preparation of 4-(2-hydroxy-3-nitro-5-chlorophenyl)-6-(alkyl or aryl)-2-imino- 3,6 dihydro-1, 3-thiazines (4a-c)**

2-Hydroxy-3-nitro-5-chlorochalcone (3a-c), (0.01M) and thiourea (0.01M) were dissolved in ethanol (25 ml).To this aq. KOH solution (0.02M) was added (prepared from KOH in small amount of distilled water). The reaction mixture was refluxed for 2.5 hours, cooled, diluted with water and acidified with 1 :1 HCl. The product was filtered, dried and crystallized from ethanol (4a-c).

**Preparation of 4-(2-hydroxy-3-nitro-5-chlorophenyl)-6-(alkyl or aryl)-2-iminophenyl- 3,6 dihydro-1, 3-thiazine (5a-c)**

2-hydroxy-3-nitro-5-chlorochalcone (4a-c), (0.01M) dissolved in ethanol (25 ml) were added to phenylthiourea (0.01M).To this aq. KOH solution (0.02M) was added . The reaction mixture was refluxed for 2.5 hours, cooled, diluted with water and acidified with conc. HCl. The product was filtered, dried and crystallized from ethanol (5a-c).

**Preparation of 4-(2-hydroxy-3-nitro-5-chlorophenyl)-6-(alkyl or aryl)-2-iminophenyl-6H-3-phenyl-1, 3-thiazine (6a-c)**

Compounds (6a-c) were synthesized similarly as (5a-c), except that phenylthiourea, diphenylthiourea was used.

The compounds (3a,3b,3c,4a,4b,4c,5a,5b,5c,6a,6b & 6c) thus synthesized were assigned on the basis of elemental analysis molecular weight determination results and spectral data are as follows. Physical characterization data of all the compounds are given in Table 1.

**Characterization of the compounds:**

Melting points of all synthesized compounds were determined in open capillaries and are uncorrected. IR spectra were recorded on Perkin-Elmer 1000 Spectrophotometer in KBr. NMR spectra were recorded on Bruker advance 400 NMR spectrometer using TMS as internal cal shistandard and chemical shift were expressed in δ ppm.

**1. Compound 2a:**

I.R. (KBr): $cm^{-1}$ 3400 (-OH phenolic), 1720 (>C=O in ketone),701 (Ar-Br), 1324 (-OH bending in phenol), 650 (C-Cl stretching).
PMR: δ 2.75; (s, 3H, $-COCH_3$); 7.35 -7.73 (m, 2H, ArH); 12.61 (s, 1H, Ar-OH).
U. V.: λ max 344 nm.

**2. Compound 3a:**

I.R. (KBr): $cm^{-1}$ 3455 (-OH phenolic), 2990 (aliphatic –CH stretching).
1705 (>C=O in ketone), 789( Ar-Br stretching),1314 (-OH bending in phenol) 1641.42 (-C-CH=CH asymmetric stretching), 759(C-Cl stretching).
PMR: δ 3.75(d, 1H, -CH=CH); 4.23(d, 1H, -CH=CH) 7.0-8.0 (s, 2H, ArH); 12.7(s, 1H, Ar-OH);
U.V.: λ max 343.5 nm

**3. Compound 4a:**

I.R (KBr): $cm^{-1}$ 3403 (-OH phenolic), 3236 (N-H stretching); 2950 (Aliphatic C-H stretching); 1304 (OH bending in phenol); . 700.16( Ar-Br stretching), 700 (C-Cl stretching).
PMR: δ 2.70 (s, 1H, $-CH_3$); 4.4 (s, 1H, -NH ); 3.6(t,1H,CH-C=C); 5.47(m,1H,CH=CH); 5.70 (m,1H,CH=CH); 6.7 to 8 (s, Ar-H); 4.7 (s, 1H, -NH stretching); 12 (s, 1H, ArOH).

**4. Compound 5a:**

I.R (KBr):$cm^{-1}$ 3440 (-OH phenolic), 3266 (N-H stretching); 2950 (Aliphatic C-H stretching);1660(-C=N stretching)1444(Ar-NO2 stretching); 1312 (-CN stretching) 1304 (OH bending in phenol); 699 (C-Cl stretching).
PMR: δ 2.40 (s, 3H, $-CH_3$); 3.7 (s, 1H, -NH stretching); 3.4(t,1H,CH-C=C); 5.57(m,1H,C=CH-CH3); 5.74(m,1H,CH=CH-CH3); 6.6(d,1H,NH-C=CH); 7.1 to7.8 (m,7H, Ar-H); 10.9 (s, 1H, ArOH).
UV: λ max 330 nm.

**5. Compound 6a:**

IR (KBr): $cm^{-1}$ 3435 (-OH phenolic stretching); 1650 (-C=N stretching); 1313 (-CN stretching); 692 (C-Cl stretching).

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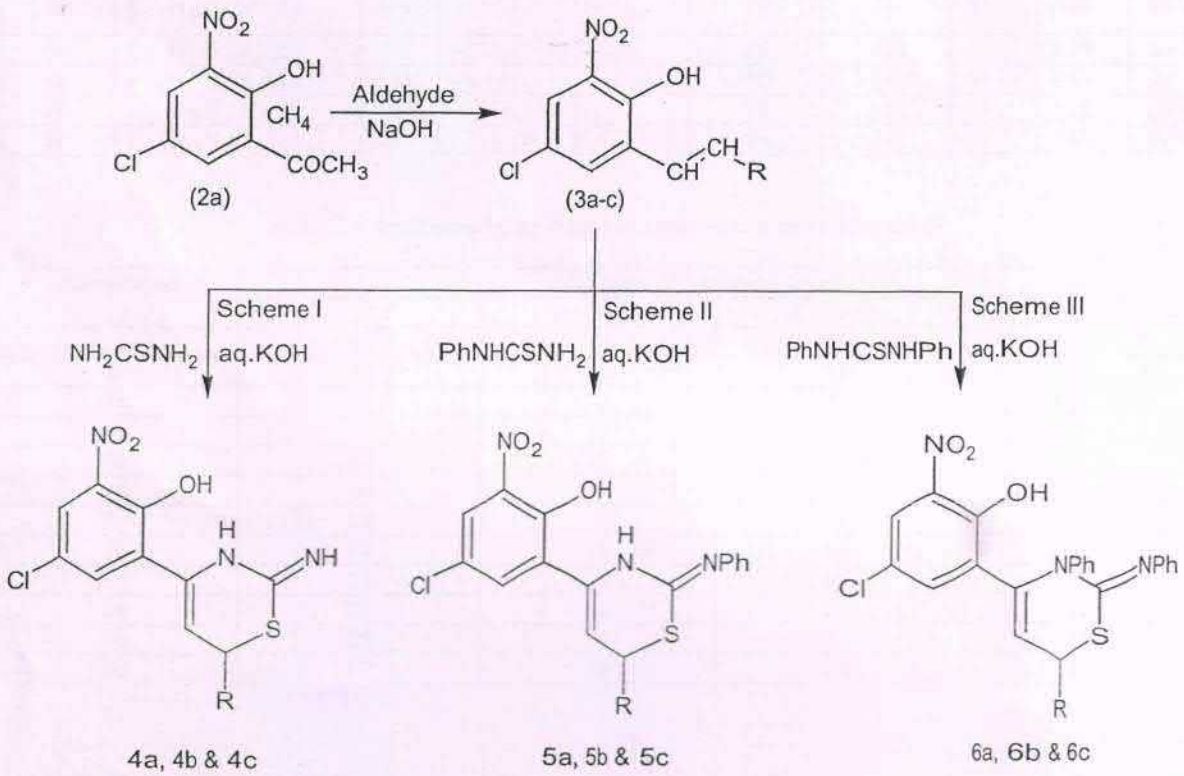
PMR: δ 2.5 (s, 3H, -$CH_3$ ); 4.8 (s, 1H, NH stretching); 4.17(d,1H,C=C-H); 5.5(d,1H,CH=C); 6.5(d1,H,C=CH) 6.9 to 7.8 (s,12H, Ar-H); 11.99 (s, 1H, ArOH).
UV: λ max 340 nm

**Scheme: Synthesis of nitro-substituted 1,3 thiazines**




Where R = -$C_6H_5$, -CH=CH-$CH_3$, -$(CH_2)_3CH_3$

Aldehyde a = Benzaldehyde; b = Crotonaldehyde; c = Valeraldehyde

**RESULTS AND DISCUSSION:**

The compounds (3a,3b,3c,4a,4b,4c,5a,5b,5c,6a,6b and 6c were screened for their antibacterial activity against some gram positive bacteria viz. *S. aureus* and *B. subtilus* and gram negative bacteria viz. *E. Coli* and *P. aeruginosa* species at conc. of 1000 μm gentamycine as a standard. DMF was used as a solvent control using agar plate techniques. The zones of inhibition formed were measured in mm and shown in Table- 2.

**Table- 1- Physical and analytical characterization of data of newly synthesized compound**

| Compd. | Mol.Formula | Mol. Wt. | R | Yield(%) | m.p.(°C) | Found Cal.% | | $R_f$ |
|---|---|---|---|---|---|---|---|---|
| | | | | | | C | N | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 1a | $C_8H_7O_2Cl$ | 171 | --- | 75 | --- | 56 | | 0.62 |
| 2b | $C_8H_6O_4NCl$ | 215 | --- | 80 | --- | 44 | 6.5 | 0.59 |
| 3a | $C_{15}H_{10}O_4NCl$ | 303 | $-C_6H_5$ | 78 | 85 | 59 | 6.0 | 0.72 |
| 3b | $C_{12}H_{10}O_4NCl$ | 267 | $-CH=CH-CH_3$ | 70 | 85 | 53 | 6.01 | 0.90 |
| 3c | $C_{13}H_{14}O_6NCl$ | 283 | $-CH_2CH_2CH_2CH_3$ | 60 | 102 | 55 | 4.55 | 0.70 |
| 4a | $C_{16}H_{12}O_5N_3SCl$ | 361 | $-C_6H_5$ | 74 | 170 | 53 | 6.55 | 0.79 |
| 4b | $C_{13}H_{12}N_3SO_5Cl$ | 325 | -CH=CH-CH3 | 70 | 138 | 55 | 7.15 | 0.52 |
| 4c | $C_{14}H_{16}O_5N_2SCl$ | 317 | $-CH_2CH_2CH_2CH_3$ | 76 | 145 | 49 | 3.56 | 0.66 |
| 5a | $C_{22}H_{16}O_5N_3SCl$ | 437 | $-C_6H_5$ | 72 | 140 | 60 | 5.56 | 0.51 |
| 5b | $C_{19}H_{16}N_3SO_3Cl$ | 401 | $-CH=CH-CH_3$ | 70 | 142 | 58 | 4.46 | 0.35 |
| 5c | $C_{20}H_{20}O_5N_3SCl$ | 417 | $-CH_2CH_2CH_2CH_3$ | 76 | 120 | 57 | 5.79 | 0.69 |
| 6a | $C_{28}H_{20}O_5N_3SCl$ | 515 | $-C_6H_5$ | 70 | 132 | 65 | 4.83 | 0.49 |
| 6b | $C_{25}H_{20}N_3SO_5Cl$ | 509 | $-CH=CH-CH_3$ | 71 | 138 | 62 | 5.15 | 0.34 |
| 6c | $C_{26}H_{24}N_3O_5SCl$ | 469 | $-CH_2CH_2CH_2CH_3$ | 73 | 157 | 63 | 5.00 | 0.55 |

**Table-2 - Antibacterial activities of synthesized new compound**

| Compound | Zone of inhibition (mm) | | | |
|---|---|---|---|---|
| | *E .Coli* | *S. aureus* | *S. subtilus* | *P. aeruginosa* |
| 3a | 15 | 14 | 14 | 13 |
| 3b | 16 | 13 | 19 | 12 |
| 3c | 22 | 12 | 14 | 15 |
| 4a | 12 | 13 | 15 | 14 |
| 4b | 17 | 16 | 15 | 17 |
| 4c | 20 | 16 | 12 | 15 |
| 5a | 12 | 13 | 16 | 20 |
| 5b | 14 | 16 | 15 | 15 |
| 5c | 23 | 15 | 13 | 15 |
| 6a | 21 | 26 | 27 | 22 |
| 6b | 25 | 26 | 25 | 24 |
| 6c | 17 | 18 | 15 | 16 |

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# "Study of Acoustical parameters of chalcone in DMSO solvent with different concentrations using Ultrasonic interefractometer."

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**Abstract:-**

Ultrasonic is the branch of acoustic, which consists of waves of high frequencies. The measurements of ultrasonic velocities have been employed to understand the nature of molecular interactions in liquid and liquid mixtures. Present study includes a discussion on acoustical properties of chalcones in DMSO solvent to understand the intermolecular interactions at different molar concentrations. The study of acoustical parameters such as velocity (U), adiabatic compressibility ($\beta_{ad}$), apparent molar volume ($\Phi_{v)}$, relative association ($R_A$), intermolecular free length (L*f*), acoustic impedance (z), apparent molar adiabatic compressibility ($\Phi_k$).

**Keywords:-**

Chalcone, DMSO solvent, Velocity, Adiabatic compressibility, Apparent molar volume and other acoustical parameters.

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## Introduction:-

Ultrasounds are sound waves with frequency higher than the upper audible limit of human beings. Ultra sound devices operate frequencies from 20 kHz up to several gigahertzes. It used detect objects and measure distances. Animals such as bats and porpoises use ultrasound for locating their prey and obstacles. Scientists are also studying ultrasound using grapheme diaphragms as a method of communication. Ultrasonic imaging applications include industrial non-destructive testing, quality control and medicinal use.

Ultrasonic is the branch of acoustic, which consists of waves of high frequencies. The measurements of ultrasonic velocities have been employed to understand the nature of molecular interactions in liquid and liquid mixtures. Recently some co-workers have investigated acoustic parameters of some bromo substituted chalcone at 303K [1].A. Dash *et*

*al* studied ultrasonic studies on ternary liquid mixture at different frequencies [2]. A. Kulshrestha *et al* have studied acoustical study of some chalcones of furfuraldehyde in different solvents [3]. Baskaran *et al* studied ultrasonic velocities and thermo acoustical parameters of anisaldehyde and benzene [4]. V. Hariharakrishnam *et al* have studied intermolecular interaction of maltose through ultrasonic studies [5]. S. Khangar *et al* studied ultrasonic characterization of aqueous polyvinyl pyrrolidone. Present study includes a discussion on acoustical properties of chalcones in DMSO solvent to understand the intermolecular interactions at different molar concentrations. The study of acoustical parameters such as velocity (U), adiabatic compressibility ($\beta_{ad}$), apparent molar volume ($\Phi_{v}$), relative association ($R_A$), intermolecular free length (L*f*), acoustic impedance (z), apparent molar adiabatic compressibility ($\Phi_k$).

## Experimental section:-

### (*) Ultrasonic Interefractometer:-

An ultrasonic interefractometer for liquid F-80D model (Mittal Enterprises Delhi) having frequencies 2 MHz and accuracy $\pm$0.03% was used for the measurement of ultrasonic velocity in solutions.

### (*) Balance: -

Weighing was made on Electronic Balance with High Accuracy class-II model AB-300 made in Maharashtra. ($\pm$0.01gm).

Density bottle is used in the present investigation for the measuring densities. Densities of different molar solution calculate on density bottle.

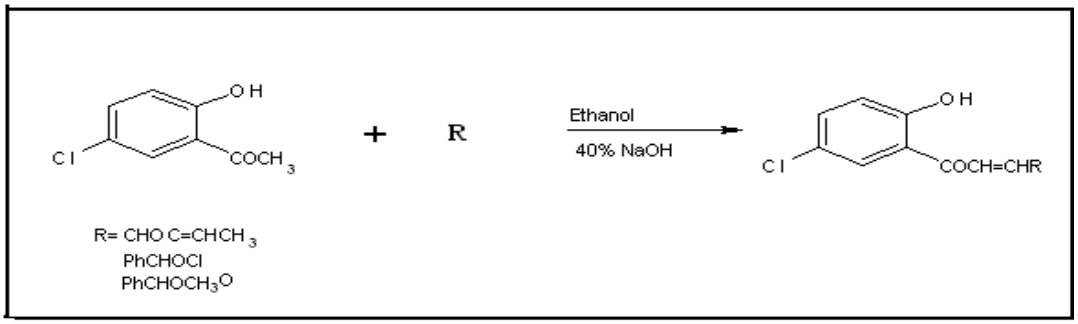
## Material and Method:-

(P1) 1. Chalcone of Crotonaldehyde.
IUPAC Name: - (2z)-1-(5-chloro-2-hydroxyphenyl)3-hex-2, 4ene-1-one

(P2) 2. Chalcone of anisaldehyde.
IUPAC Name: - 1-(2- hydroxyl-5-clorophenyl)-3-(4-methoxyphenyl)-prop-2-en-1-one.

(P3) 3. Chalcone of p-chlorobenzaldehyde.
IUPAC Name: - (E)-1-(5-Chloro-2-hydroxyphenyl)-3-(4-chlophenyl)-prop-2-en-1-one.

## Reaction Scheme: -




These chalcones were synthesized by known method in this context the chalcones that is P1, P2, and P3 with different molar concentrations were dissolved in DMSO.

The samples thus prepared were taken in appropriate quantity and placed in ultrasonic interefractometer to measure sound waves at 1 MHz. The inner diameter of the tube of ultrasonic interefractometer was 1.1 cm while the diameter of reflector rod was 1 Cm. The

solution was actually poured in cylinder and then fitted it with movable reflected rod. The needle of ammeter was adjusted in the 5 with the help of "ADj" knob. Standing wave pattern was resulted due to reflected rod. As we move the rod the instrument showed deflection of the needle. To movement of rod was continued to get 5 deflections. After retuning back to its original position, micrometer reading was noted. The difference between these two reading gave the distance travelled by screw for getting five maxima. The distance between two maxima was actually equal to $\lambda/2$.

The apparent molar volume ($\Phi_v$), Adiabatic compressibility ($\beta_{ad}$), Velocity (U), Density ($\rho$), Acoustic impedance (z), Intermolecular free length ($Lf$), Relative association ($R_A$) can be calculated by the following formulae.

## Formulae:-

1. Adiabatic compressibility $\beta_{ad} = 1/U^2 \rho$
2. Apperant molar volume $\Phi_v = 1000(\rho_0 - \rho_s)/C.\ \rho_s.\ \rho_0 + M/\rho_s$
3. Acoustical impedance $z = \rho * U$
4. Intermolecular free length $Lf = Kj\ (\beta_{ad})^{1/2}$
5. Relative association $R_A = \rho_s/\rho_0 \text{ x } (U_o / U_s)^{1/3}$
6. Apparent molar adiabatic comp. $\Phi_k = 1000(\beta_s.\rho_0 - \beta_0.\ \rho_s)/C.\ \rho_s.\ \rho_0 + \beta_s\ M/\rho_s$

Where,

U = Velocity.
$\rho_0$ = Density of solvent.
$\rho_s$ = Dnsity of solution.
M = Molecular weight.
C = Concentration.
$\beta_s$ = Compressibility of solution.
$\beta_0$ = Compressibility of solvent.
Kj = Jacobson's constant.

**Table 1. Acoustical Parameters f=1MHz**

| Chalcone | Conc. | √c | U | ρ | βad | Φv | RA | Lf | z | Φκ |
|---|---|---|---|---|---|---|---|---|---|---|
| P1 | 0.01 | 0.1 | 1431 | 1.009 | 4.8 | 3048 | 6747 | 7.224 | 1443 | 1.45 |
| | 0.03 | 0.17 | 1451 | 1.019 | 4.7 | 2643 | 6674 | 7.07 | 1478 | 1.05 |
| | 0.05 | 0.22 | 1471 | 1.029 | 4.5 | 1466 | 6645 | 6.77 | 1513 | 0.965 |
| | 0.07 | 0.26 | 1491 | 1.039 | 4.3 | 974 | 6615 | 6.47 | 1549 | 0.97 |
| | | | | | | | | | | |
| P2 | 0.2 | 0.44 | 1588 | 1.2 | 3.3 | 148 | 7200 | 4.96 | 1905 | 0.801 |
| | 0.4 | 0.63 | 1493 | 1.21 | 3.8 | 29 | 7777 | 5.71 | 1806 | 0.91 |
| | 0.6 | 0.77 | 1400 | 1.23 | 4.1 | 73 | 8426 | 6.17 | 1722 | 0.964 |
| | 0.8 | 0.89 | 1288 | 1.25 | 4.8 | 93 | 11258 | 7.22 | 1610 | 1.109 |
| | | | | | | | | | | |
| P3 | 0.006 | 0.06 | 1510 | 1.01 | 4.37 | 14833 | 6278 | 6.32 | 1525 | 1.85 |
| | 0.007 | 0.07 | 1600 | 1.02 | 3.84 | 11285 | 6072 | 5.98 | 1632 | 1.57 |
| | 0.008 | 0.08 | 1740 | 1.05 | 3.22 | 5444 | 5757 | 4.84 | 1827 | 0.286 |
| | 0.009 | 0.09 | 1787 | 1.06 | 3.03 | 3900 | 5664 | 4.54 | 1894 | 1.073 |

Where,

**Conc**. = Concentration.

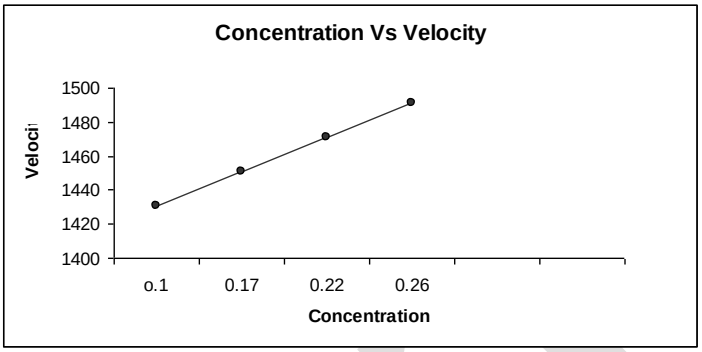
$\sqrt{c}$ = Root of concentration

## Result and Discussion:-

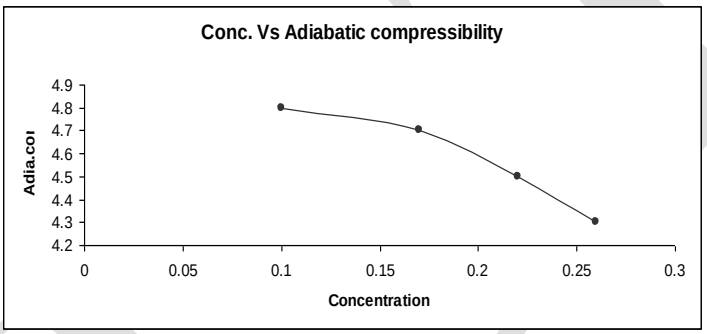
The P1, P2, P3 chalcones were prepared in Different molar concentrations. In case of P1 chalcone with increase in concentration velocity and acoustic impedance also increased. The apparent molar volume and adiabatic compressibility continuously decreased with increased in concentration.

## 1. Graph of Crotonaldehyde: - $P_1$

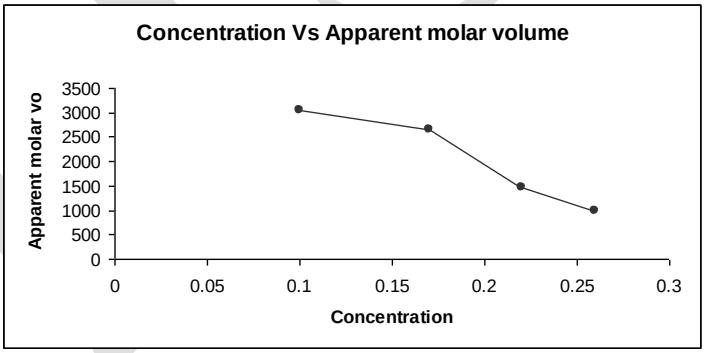
**1.1-Graph**

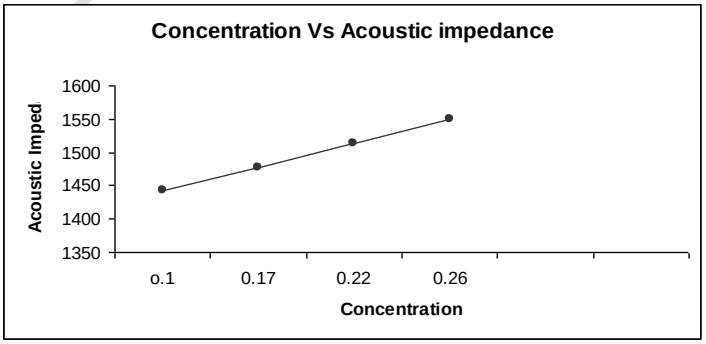



**1.2- Graph**




**1.3- Graph**



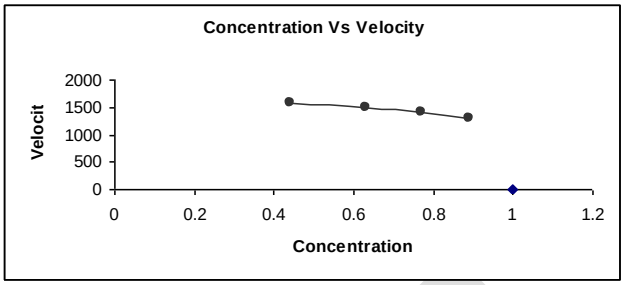




**1.4- Graph**

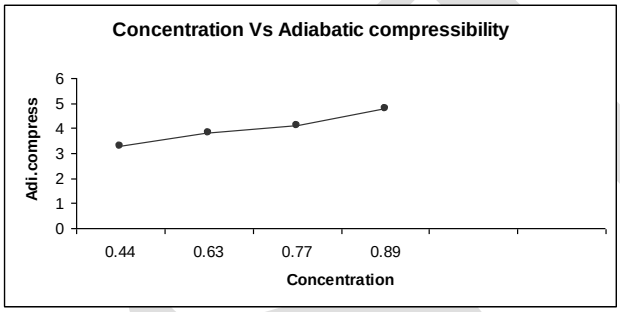
In case of P2 chalcone the concentration increased when velocity and acoustic impedance decreases. Adiabatic compressibility increases with concentration. Apparent molar volume shows variations in graph.

## 2. Graph of Anisaldehyde: - $P_2$

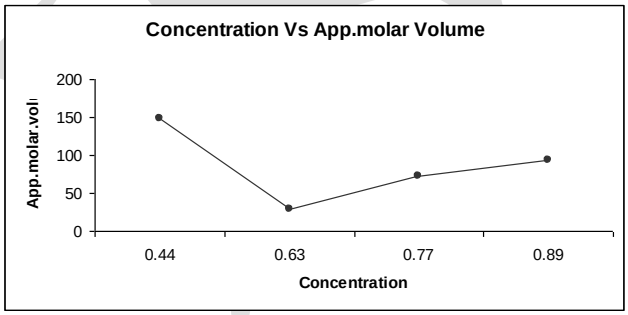
**2.1- Graph**

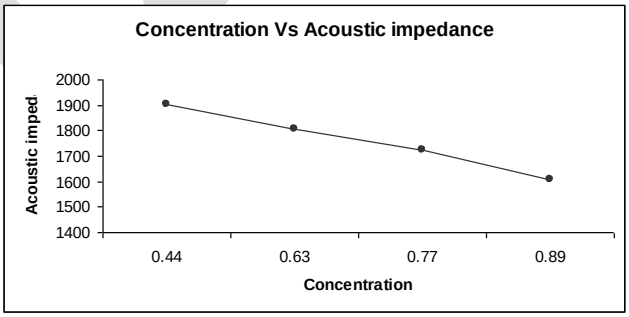



**2.2- Graph**




**2.3- Graph**



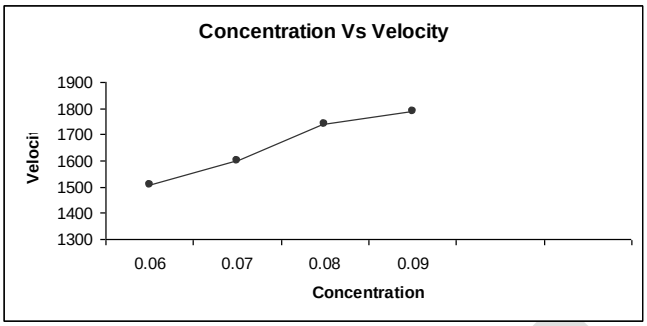




**2.4 - Graph**

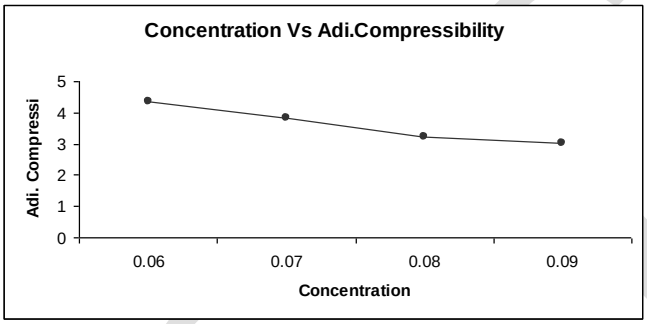
In P3 Chalcones increase in concentration is observed when velocity and acoustic impedance increases. The apparent molar volume and adiabatic compressibility decreases with increase in concentration.

## 3. Graph of p-chloro benzaldehyde: - $P_3$

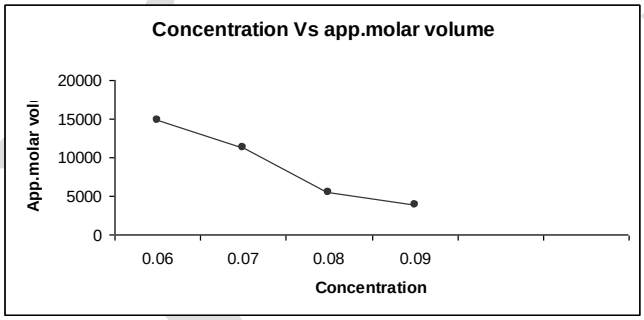
**3.1 -Graph**

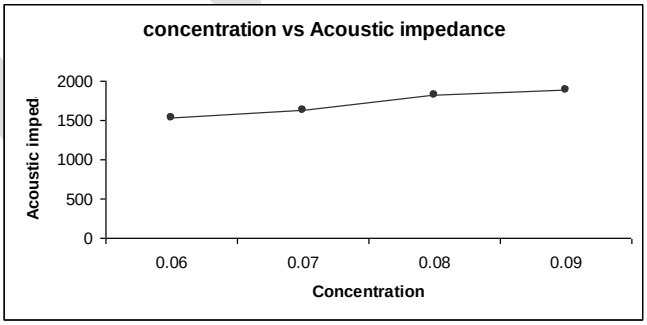



**3.2 -Graph**




**3.3 -Graph**




**3.4 -Graph**

## Conclusion:-

The graphical data reveals that the molecular interaction in chalcones varies with change in molar concentrations. The change in velocity is always assisted by the functional groups present in the structural constitution of the chalcones. It has also been observed that halogens help to increase velocity as compared to other groups.

**Acknowledgement:-**

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# MICROWAVE ASSISTED SOLVENT FREE SYNTHESIS OF FEW THIAZOLE DERIVATIVES AS POTENT ANTIFUNGAL AGENT

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**ABSTRACT:-** In this research work one pot synthesis of 1,3-substituted thiazolidin-4-ones,(IVa-IVh) have been carried out from carbonyl compound, amine and thiocarboxylic acid in molar proportion under microwave irradiation for 1-2 minutes, in solvent free condition. In vitro assay of newly synthesized compound were carried out to test antifungal activity by disc diffusion method against Fusarium oxysporum and Rhizoctonia solani.

**Keywords:-** 1,3-thiazolidin-4-ones, microwave irradiation, antifungal Activity

## INTRODUCTION

Thiazoles are a familiar group of heterocyclic compounds possessing wide variety of biological activities, and their usefulness as medicines are well established. Thiazole nucleus is also an integral part of all the available penicillin's, which have revolutionized the therapy of bacterial diseases [1]. Thiazoles have attracted continuing interest because of their varied biological activities [2], which have found applications in the treatment of allergies [3], hypertension [4], inflammation [5], schizophrenia[6], microbial infections [7,8], HIV infections [9], hypnotics [10] and for the treatment of pain [11]. They have been also used as fibrinogen receptor antagonists with antithrombotic activity [12] and as new inhibitors of bacterial DNA gyrase B [13]. Recently reported studies on the microwave irradiation for the synthesis of heterocyclic compound revealed that it is safe, rapid, economic and convenient, eco-friendly method for chemical synthesis. Pollution free synthesis, lesser reaction time, easy workup and minimum use of solvent are the major advantages of this technique A serious constrain of this method is selection of

appropriate solvent, which can be avoided by synthesis under solid phase solvent free condition. These facts have promoted us to synthesize some new thiazolidiones using microwave irradiation under solvent free condition.

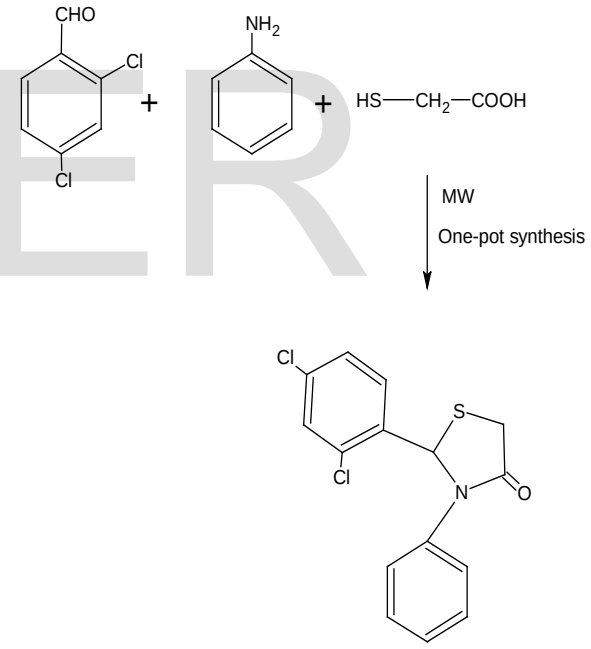
**EXPERIMENTAL –**

All the synthesized compounds have been characterized on the basis of chemical properties, elemental and spectral analysis. The melting points were measured in a open glass capillary and are uncorrected**.**IR spectra in KBr were recorded on instrument Perkin Elmer - Spectrum RX-IFTIR. $^{1}$H-NMR spectra were recorded on FT NMR Spectrometer model Advance-II (Bruker) Its $^{1}$H frequency is 400 MHz, while for $^{13}$C the frequency is 100 MHz. ($CDCl_3$ and DMSO-$d_6$) using TMS as an internal standard. All reactions were monitored by TLC using silica gel 60-f-254plates. All reactions were carried out in scientific microwave oven (Scientific microwave system model RG31lL1,700w, 2450MHz).satisfactory C,H,N analysis were carried out for most of the compounds on Thermo Scientific (FLASH 2000) CHN Elemental Analyzer at RSIC, Punjab university, Chandigarh.

**Table I: Physical data of synthesized 1,3-thiazolidin-4-ones**

| Compound | R | R' | M.P.($^0$C) | MOLECULAR FORMULA | YEILD(%) |
|---|---|---|---|---|---|
| 4a | -$C_6H_5$ | -$C_6H_5$ | 155 | $C_{15}H_{13}NOS$ | 85 |
| 4b | -$C_6H_5$ | -$C_6H_4Cl$ | 163 | $C_{15}H_{12}ClNOS$ | 80 |
| 4c | -$C_6H_5$ | -$C_6H_4Br$ | 145 | $C_{15}H_{12}BrNOS$ | 84 |
| 4d | -$C_6H_5$ | -$C_6H_3Cl_2$ | 169 | $C_{15}H_{11}Cl_2NOS$ | 82 |
| 4e | -$C_6H_5$ | -$C_4H_3O$ | 131 | $C_{13}H_{11}NO_2S$ | 83 |
| 4f | -$C_6H_5$ | -$C_2H_5$ | 123 | $C_{11}H_{13}NOS$ | 78 |
| 4g | -$C_6H_5$ | -$C_6H_4OH$ | 137 | $C_{15}H_{13}NO_2S$ | 76 |
| 4h | -$C_6H_5$ | -$C_6H_4OCH_3$ | 136 | $C_{16}H_{15}NO_2S$ | 84 |

**Synthesis of 2-(substituted phenyl)-3-phenylthiazolidin-4-one(**IVa-IVh**)** - A neat rection technology for one pot synthesis of the starting material 2-(substituted phenyl)-3-phenylthiazolidin)-4-one by condensation of aromatic aldehyde(0.01M), aniline(0.01M), and thioglycolic acid(0.01M). Reaction carried out under scientific microwave oven for 1-1.5 min. The reaction mixture was cooled at room temperature and poured in ice-cold water. The product thus separated out was filtered and crystallized from ethanol to get fine crystals of 2-(substituted phenyl)-3-phenylthiazolidin-4-one . (IVa-IVh)






## RESULT AND DISCUSSION -

Literature survey revealed that thiazolidiones belong to an important group

of heterocyclic compounds with diverse biological activity and synthesized by using multistep protocol. The present work describe solvent less one pot synthetic methodology towards the construction of series of thiazolidione derivative under microwave irradiation. This is a three Component reaction involving amino compound ,aldehyde and thioglycolic acid under M.W. irradiation .PMR spectra shows doublet at 3.23 and 3.30 due to germinal coupling of cyclic CH grp , a singlet for CH at 2.7 and aromatic protons with 7.0 to 7.5δ. singlet at 10.1 and a singlet at 3.7 also confirms the possibility of keto enol tautomerism in the molecule .IR frequency also agrees with the fact by showing frequencies at 1649 C=O(keto form), 3296(C-OH stretch (enol form) and other frequencies . $^{13}$CNMR spectra also showing two signals in aliphatic region 43.27(CH) and 28.34($CH_2$) WHERE AS 168.4 (C=O) ,slight lower values due to nitrogen and aromatic rings and 166.6 C-OH (enol form) furthermore confirms the keto enol tautomerism in the compounds,remaining signals are in the aromatic region 119 -138δ

The reaction has been suggested to proceed via imine formation followed by attack of sulphur nucleophile on the imine carbon. The reaction involves intramolecular cyclisation with the elimination of water to give thiazolidione derivative. Microwave irradiation facilitate the easy removal of water within few minute.

**1) 2-(2,4-dichlorophenyl)-3-phenylthiazolidin-4-one(IVd)-**

brown crystalline solid, M. P..169$^0$C,IR in $cm^{-1}$ - 3296 [C-OH stretch (enol form)], 3089,3146 (C-H aromatic stretch), 2944,2876 (C-Stretch aliphatic), 1804-1949 (Combination band), 1649 C=N, 1649 C=O(keto form), 1598,1551,1482 (C=C), 1333 (C-N), 903(1,2,4trisubstituted oop),692(monosubstitued oop)

$^1$HNMR400 MHz (CDCl3): -Chemical Shift (δ)-2.7 ( s,1H, CH) , 3.30(dd,1H,CH) ,3.23(d,1H,CH) ,3.7(s,1H, =CH) ,7.0 - 7.5(m,8H, Ar-H) , 10.1[s,1H, C-OH(enol)]

$^{13}$CNMR-100 MHz.($CDCl_3$andDMSO$d_6$) - Chemical Shift(δ)-43.27, 28.34, 168.4, 138.9, 128.3, 119.27, 123.43, 128.54, 138.6, 119.07, 128.55, 123.24, 128.55, 119.07

Observed %C= 55.54, %N=4.12, %S=9.85, %Cl =21.84, %H=3.41, %O=4.81

Calculated %C= 55.57, %N=4.32, %S=9.89, %Cl =21.87, %H=3.42, %O=4.93

**ANTIFUNGAL ACTIVITY**-: All the synthesized compounds were screened for their antifungal activity viz. *fusarium oxysporum, Rhizoctonia solani* by using disc diffusion method for their antifungal activity.The punch discs of 6.25 mm diameter of Whatman filter paper no. 1 were prepared and dispensed in the batches of 100 each in screw capped bottles. These were sterilized by dry heat at $140^0$C for 60 minutes. The solutions of 1000 ppm and 100 ppm concentrations of test compounds were prepared in dimethyl formamide (DMF) solvent separately. The discs were soaked, assuming that each disc will contain approximately 0.01 ml of test solution

**Table 2 - In vitro antifungal screening of above tested compounds**

| Sr.No. | Tested Compounds | Fungus (zone of inhibition in mm) | | | |
|---|---|---|---|---|---|
| | | *Fusarium oxysporum* | | *Rhizoctonia solani* | |
| | | 100 ppm | 1000 ppm | 100ppm | 1000ppm |
| 1 | IVa | 8 | 12 | 10 | 13 |
| 2 | IVb | 20 | 22 | 22 | 23 |
| 3 | **IVc** | 18 | 19 | 20 | 21 |
| 4 | IVd | - | 3 | 6 | 10 |
| 5 | IVe | **21** | **28** | **20** | **28** |
| 6 | IVf | 18 | 18 | 19 | 21 |
| 7 | IVg | **19** | **27** | **22** | **29** |
| 8 | IVh | 11 | 15 | 12 | 18 |

The observations show that activity of compound IVe and IVg are maximum against both the fungi . Almost all the compounds were active against all the test pathogens. The compound IVe and IVg is the most dominant among all the test compounds. Their inhibitory impact on the bacterial growth is remarkable.

**CONCLUSION**-: This was an attempt to synthesize biologically potential heterocyclic moiety in solvent free reaction condition that leads to considerable saving in the reaction time and energetically

profitable. The solvent free condition contributes to saving in cost, time and diminishes the waste disposal problem and environmental pollution this work may bring research fraternity towards sustainable development.

**ACKNOWLEDGEMENT** -: The authors are thankful to the Principal, Vidyabharati Mahavidyalaya, Amravati, Dr. F.C.Raghuwanshi and Director, SAIF, Punjab University, India, for providing spectral data of the compounds

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# 3D-QSAR and docking studies on adenosine $A_{2A}$ receptor antagonists by the CoMFA method

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http://dx.doi.org/10.1080/1062936X.2015.1049666

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# 3D-QSAR and docking studies on adenosine $A_{2A}$ receptor antagonists by the CoMFA method

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Parkinson's disease affects millions of people around the world. Recently, adenosine $A_{2A}$ receptor antagonists have been identified as a drug target for the treatment of Parkinson's disease. Consequently, there is an immediate need to develop new classes of $A_{2A}$ receptor antagonists. In the present analysis, three-dimensional quantitative structure–activity relationship (3D-QSAR) studies were performed on a series of pyrimidines, using comparative molecular field analysis (CoMFA). The best prediction was obtained with a CoMFA standard model ($q^2$ = 0.475, $r^2$ = 0.977) and a CoMFA region focusing model ($q^2$ = 0.637, $r^2$ = 0.976) combined with steric and electrostatic fields. The structural insights derived from the contour maps helped to better interpret the structure–activity relationships. Also, to understand the structure–activity correlation of $A_{2A}$ receptor antagonists, we have carried out molecular docking analysis. Based on the results obtained from the present 3D-QSAR and docking studies, we have identified some key features for increasing the activity of compounds, which have been used to design new $A_{2A}$ receptor antagonists. The newly designed molecules showed high activity with the obtained models.

**Keywords:** 3D-QSAR; docking; CoMFA; $A_{2A}$ receptor antagonists; drug design

## 1. Introduction

Parkinson's disease (PD) is the second most prevalent neurodegenerative disorder, affecting up to 10 million people worldwide [1]. A disease that typically affects individuals of an advanced age, PD is often difficult to diagnose before the appearance of the typical signs and symptoms of advancing disease; the lack of an early diagnosis contributes to increased overall morbidity and decreased quality of life [2]. It is characterized by a motor impairment caused by the degeneration of dopaminergic neurons located in the substantia nigra pars compacta and by the reduction of dopamine levels in the striatum [3]. This reduction is responsible for the major symptoms of the disease, such as bradykinesia, muscular rigidity and tremor [4]. Adenosine is a neuro-modulator that coordinates responses to dopamine and other neurotransmitters that play important roles for motor function, mood, and memory [5–8]. Adenosine is known to act via four major receptor subtypes, $A_1$, $A_{2A}$, $A_{2B}$ and $A_3$, which have been

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characterized according to their primary sequences [9]. At present, it is believed that $A_{2A}$ receptor antagonists can be used in combination with the dopamine precursor L-DOPA to minimize the motor symptoms of patients with PD [10]. Selective $A_{2A}$ antagonists have been a much sought-after target for the symptomatic relief of dopamine [11–13], with some reports suggesting that they may also slow disease progression because of their neuroprotective potential [14]. The potential of these antagonists has been deduced from considerable investigation of the functional interactions between dopamine and adenosine receptors in the basal ganglia [10]. These interactions can activate the dopamine receptor, or alternatively block the adenosine $A_2$ receptor as a means to improving the symptoms of PD. Recently, a novel series of benzyl substituted thieno[2,3-d] pyrimidines was identified as potent $A_{2A}$ receptor antagonists by Shook et al. [15].

Computational chemistry has recently developed extensively and provided the rational drug design approach. Quantitative structure–activity relationship (QSAR) modelling results in a quantitative correlation between chemical structure and biological activity [16–21]. Typically, a 3D-QSAR analysis allows the identification of some key features around special substituents in a molecular graph for increasing the activity of compounds, and provides guidelines for the design of next-generation compounds with enhanced bioactivity or selectivity. A successful 3D-QSAR model not only helps in better understanding of the structure–activity relationships of any class of compounds, but also provides researchers an insight at the molecular level about lead compounds for further development [22]. The first applicable 3D-QSAR method was proposed by Cramer et al. in 1988 [23]. Among the current 3D-QSAR methods, comparative molecular field analysis (CoMFA) is widely used in drug design, because it allows rapid prediction of the biological activities of newly designed molecules [24–30]. In CoMFA, the biological activity of molecules is correlated with their steric and electrostatic interaction fields. However, the combination effects of fields around a molecule should be studied carefully for successful interpretation and designing of novel compounds, which is sometimes difficult due to insufficient experimental information. Another major problem with CoMFA modelling is its reduced sensitivity regarding the conformation of compounds but higher dependency on the alignment process. Therefore, to compensate for these deficiencies molecular docking analysis can be run to detect all interaction information, leading to better drugs. Coupling this information with that obtained by 3D-QSAR could result in a better understanding of regional effects with regard to biological activities.

In the present work, CoMFA and CoMFA region focusing studies were carried out on some pyrimidines such as adenosine $A_{2A}$ receptor antagonists to understand the influence of different physico-chemical and structural parameters on these compounds. Molecular docking studies were also performed to detect the interactions leading to potent inhibitors, and based on the derived results some novel potent $A_{2A}$ receptor antagonists have been designed.

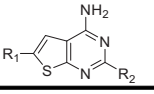
## 2. Material and methods

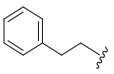
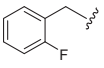
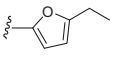
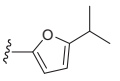
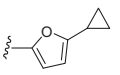
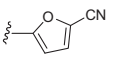
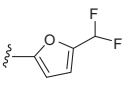
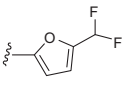
### 2.1 *Data set*

All pyrimidines and their biological activities ($K_i$) were taken from the literature [15]. A set of 46 compounds was divided into the training set (80% of compounds), and test set (20% of compounds) comprising 37 and nine molecules, respectively, by using the hierarchical clustering technique (Figure S1, available via the Supplementary Material section online). For smoother partial least-squares (PLS) analysis for the CoMFA model, all the reported affinity values of the pyrimidines were converted to $pK_i = -\log K_i$ (M). These molecules have wide

range of affinity values ($K_i$). The test set compounds represent both the distribution of biological data and structural diversity. Molecular structures and their $pK_i$ values are presented in Table 1. It can be seen that except for the highest and lowest activity, compounds were

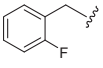
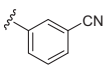
Table 1. $A_{2A}$ receptor antagonists and their observed and predicted activities.




| | | | | Pred. | | | |
|---|---|---|---|---|---|---|---|
| *No.* | *$R_1$* | *$R_2$* | *Exp.($pIC_{50}$)* | *CoMFA-1* | *Res.* | *CoMFA-2* | *Res.* |
| 1 | H |  | 6.96 | 7.03 | –0.07 | 7.07 | –0.11 |
| 2 | Ph |  | 7.17 | 7.17 | 0.00 | 7.23 | –0.06 |
| 3 | Bn |  | 7.95 | 7.82 | 0.13 | 7.73 | 0.22 |
| 4 |  |  | 6.69 | 6.82 | –0.13 | 6.86 | –0.17 |
| 5[a] |  |  | 7.96 | 8.34 | –0.38 | 8.37 | –0.41 |
| 6 |  |  | 8.54 | 8.38 | 0.16 | 8.36 | 0.18 |
| 7 |  |  | 8.43 | 8.33 | 0.10 | 8.29 | 0.15 |
| 8 |  |  | 7.40 | 7.54 | –0.14 | 7.48 | –0.07 |
| 9[a] | Bn |  | 7.31 | 7.43 | –0.12 | 7.60 | –0.29 |
| 10 | Bn |  | 6.77 | 6.72 | 0.05 | 6.82 | –0.05 |
| 11 | Bn |  | 6.58 | 6.59 | –0.01 | 6.56 | 0.02 |
| 12 | Bn |  | 6.52 | 6.60 | –0.08 | 6.50 | 0.02 |
| 13 | Bn |  | 7.60 | 7.70 | –0.10 | 7.58 | 0.02 |
| 14 |  |  | 7.88 | 7.87 | 0.01 | 7.77 | 0.11 |

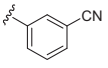
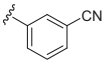
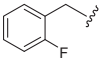
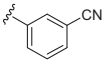
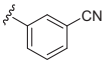
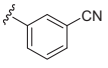
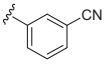
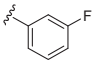
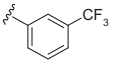
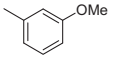
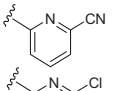
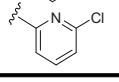
(*Continued*)

Table 1. (*Continued*).

| | | | | Pred. | | | |
|---|---|---|---|---|---|---|---|
| *No.* | $R_1$ | $R_2$ | *Exp.*($pIC_{50}$) | *CoMFA-1* | *Res.* | *CoMFA-2* | *Res.* |
| 15 | Bn |  | 6.17 | 6.14 | 0.03 | 6.10 | 0.07 |
| 16[a] | Bn |  | 8.33 | 8.53 | –0.20 | 8.51 | –0.18 |
| 17 | Bn |  | 8.05 | 8.34 | –0.29 | 8.32 | –0.27 |
| 18 | Bn |  | 7.79 | 7.59 | 0.20 | 7.54 | 0.25 |
| 19 |  |  | 7.88 | 7.95 | –0.07 | 8.03 | –0.15 |
| 20 |  |  | 8.16 | 8.32 | –0.16 | 8.28 | –0.12 |
| 21 |  |  | 8.01 | 8.06 | –0.05 | 8.09 | –0.08 |
| 22 |  |  | 7.00 | 6.99 | 0.01 | 7.11 | –0.11 |
| 23 |  |  | 7.51 | 7.49 | 0.02 | 7.51 | 0.00 |
| 24 |  |  | 6.97 | 6.91 | 0.06 | 6.92 | 0.05 |
| 25 | Bn |  | 7.24 | 7.30 | –0.06 | 7.20 | 0.04 |
| 26 | Bn |  | 6.27 | 6.20 | 0.07 | 6.23 | 0.04 |
| 27 | Bn |  | 6.30 | 6.43 | –0.13 | 6.39 | –0.09 |
| 28 | Bn |  | 6.68 | 6.60 | 0.08 | 6.58 | 0.10 |
| 29 | Bn |  | 7.53 | 7.38 | 0.15 | 7.40 | 0.13 |
| 30 | Bn |  | 7.94 | 7.92 | 0.02 | 7.94 | 0.00 |

(*Continued*)

Table 1. (*Continued*).

| | | | | Pred. | | | |
|---|---|---|---|---|---|---|---|
| *No.* | $R_1$ | $R_2$ | *Exp.*($pIC_{50}$) | *CoMFA-1* | *Res.* | *CoMFA-2* | *Res.* |
| 31 |  |  | 8.21 | 8.44 | –0.23 | 8.42 | –0.20 |
| 32 |  |  | 8.85 | 8.67 | 0.18 | 8.72 | 0.13 |
| 33[a] |  |  | 8.14 | 8.35 | –0.21 | 8.50 | –0.35 |
| 34[a] |  |  | 6.47 | 7.71 | –1.24 | 7.77 | –1.30 |
| 35[a] |  |  | 7.20 | 7.85 | –0.65 | 7.98 | –0.78 |
| 36 |  |  | 6.65 | 6.61 | 0.04 | 6.66 | –0.01 |
| 37 | Bn |  | 7.38 | 7.30 | 0.08 | 7.36 | 0.02 |
| 38 | Bn |  | 5.99 | 6.01 | –0.02 | 5.94 | 0.05 |
| 39 | Bn |  | 6.93 | 6.83 | 0.10 | 6.99 | –0.06 |
| 40[a] | Bn |  | 6.23 | 7.15 | –0.92 | 7.20 | –0.97 |
| 41[a] | Bn |  | 6.67 | 6.16 | 0.51 | 6.30 | 0.38 |
| 42 | Bn |  | 7.17 | 7.19 | –0.02 | 7.23 | –0.06 |
| 43 | Bn |  | 8.62 | 8.46 | 0.16 | 8.51 | 0.11 |
| 44 | Bn |  | 7.77 | 7.77 | 0.00 | 7.83 | –0.06 |
| 45[a] | Bn |  | 7.59 | 7.67 | –0.08 | 7.83 | –0.24 |
| 46 | Bn |  | 6.76 | 6.83 | –0.07 | 6.79 | –0.03 |

[a]Compounds used as test set.

included in the training set, and the test set compounds have a range of biological activity values similar to that of the training set.

### 2.2 *Molecular modelling and alignment*

All molecular modelling and calculation studies were performed using the SYBYL X.1.1.1 [31] software package. The position of each atom is important to CoMFA because the descriptors are calculated based on the 3D space grid [32]. Energy minimization was performed using the Tripos force field with a distance-dependent dielectric and the Powell conjugate gradient algorithm with a convergence criterion of 0.01 kcal/mol Å. Partial atomic charges were calculated using the Gasteiger–Hückel method [33]. A good alignment of the complete data set is another essential element for successful CoMFA analysis. The quality and the predictive ability of the models are directly dependent on the alignment rules [34]. The lowest energy conformation of compound **32** was used as a template because it had the highest activity, and all other compounds were aligned on the basis of the common substructure. The structure of compound **32** with bold common substructure and aligned compounds are displayed in Figures 1 and 2.



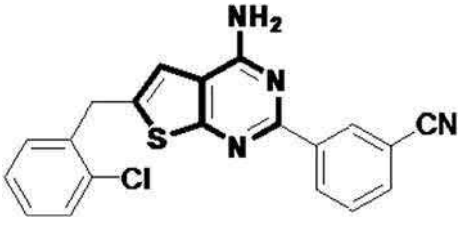



Figure 1. Structure of template compound (molecule **32**), common substructure is in bold.

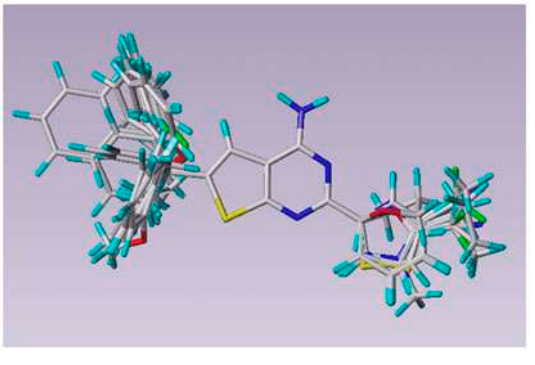


Figure 2. Alignment of training and test compounds on compound **32**.

### 2.3 *CoMFA setup*

CoMFA is a powerful and well-established tool for building 3D-QSAR models that can be applied to drug design [35,36]. The steric and electrostatic field energies for CoMFA were calculated at each lattice intersection of a regularly spaced grid of 2 Å. The lattice was defined automatically and is extended at least 4 Å beyond the van der Waals volume of all aligned molecules in X, Y and Z directions. The steric field represented by Lennard-Jones potential and the electrostatic field represented by coulombic potential were calculated using the Tripos force field and distance-dependent dielectric solvation treatment. A $sp^3$ carbon atom with a van der Waals radius of 1.52 Å and 1.0+ charge served as the probe atom to calculate these fields. The steric and electrostatic contributions were confined to the default 30 kcal/mol [27]. CoMFA region focusing is a method of application of weights to the lattice points in a CoMFA region to enhance or attenuate the contribution of these points to subsequent analysis. Here, 'StDev*-Coefficients' values and different weighing factors were applied in addition to grid spacing to achieve a better model [37].



### 2.4 *Partial least-squares analysis*

Finding the best predictive model is the major objective of CoMFA analysis. PLS methodology was performed to quantify the relationships between the CoMFA descriptors and the biological activity. Column filtering was set to 1.0 kcal/mol to speed up the analysis and reduce the noise. The CoMFA descriptors were used as independent variables, and $pK_i$ values as dependent variables in PLS regression analysis to derive 3D-QSAR models using the standard implementation in the SYBYL package [31]. The predictive ability of the models was evaluated by leave-one-out (LOO) cross-validation. This results in the cross-validation correlation coefficient ($q^2$) and the optimum number of components $N$. The final model was developed with an optimum number of components yielding the highest $q^2$ [16]. Then, the PLS analysis was performed without cross-validation, applying no column filtering. After this, the coefficient of determination ($r^2$) values, standard error of predictions and $F$ values are calculated. The bootstrapping [38] and the leave-group-out cross-validation (10 groups out) techniques were carried out and confirmed by the average value for 10 runs from each cross-validation.

### 2.5 *Molecular docking*

The most active compound in the data set was docked into the active site of the $A_{2A}$ receptor to provide the interactions between the ligand and receptor. The docking study was carried out using AutoDock 4.2 [39]. This program starts with a ligand molecule in an arbitrary conformation, orientation and position, and finds favourable dockings in a protein-binding site using both simulated annealing and genetic algorithms. Among crystallized complexes, PDB ID: 4EIY [40] was selected based on the resolution and the size of the co-crystal ligand which is similar to the experiment set. Initially, the protein was prepared by removing all water molecules, and polar hydrogen atoms and Kollman charges were introduced into the protein [41]. The grid box size and the grid spacing were set as 70, 70, 70 A˚ and 0.375 A˚, respectively. The number of docking runs was set to 50. The best docking result can be considered to be the conformation with the lowest energy. Pharmacophore studies were performed using the LigandScout 3.03 program [42].

## 3. Results and discussion

### 3.1 *CoMFA analysis*

The 3D-QSAR model was established by CoMFA analysis, and its statistical parameters are listed in Table 2. The best results were obtained at a column filtering of 1.0 kcal/mol for both steric and electrostatic fields. The cross-validation [23,43] analysis was performed using the LOO method in which one compound is removed from the data set, and its activity is predicted using the model derived from the rest of the data set. This resulted in the cross-validation correlation coefficient ($q^2$) of 0.475 with an optimum number of components of six. Next, non-cross-validated PLS regression was performed using the six previously obtained factors, which resulted in the regression coefficients $r^2$ of 0.977, $F$ = 210.564 and a standard error of estimate (S) of 0.155. The steric field descriptors explained 48.7% of the variance, while the electrostatic descriptors explained 51.3%.

The predicted activities for both training and test sets and also their residuals are listed in Table 1. Figure 3(a) depicts the correlation between the predicted activities and the experimental activities of the CoMFA model. From Figure 3(a), it can be seen that almost all points are rather uniformly distributed around the regression line, indicating no existence of systematic errors in the model, which further proves the satisfactory predictive ability of the derived model. The outlier status is due to the higher residual between the observed and predicted biological activity [44]. As can be seen, by inclusion of compound **34**, the model shows poor predictive ability with an $r^2$ of 0.578 for the test set. Omission of compound number **34** results in an increased $r^2_{test}$ value to 0.715. Therefore, compound number **34** in the optimum CoMFA model is treated as an outlier. After excluding the outlier, the activities predicted by the constructed CoMFA model are in good agreement with the experimental data, suggesting that a reliable CoMFA model was successfully constructed.

Region focusing was considered as an additional strategy to improve $q^2$. As an iterative procedure, it involves giving additional weight to the lattice points in a given CoMFA region to enhance or attenuate the contribution of those points in a further analysis [34]. A new model (CoMFA-2) was generated with increased predictive power ($q^2$), enhanced resolution, tighter grid spacing and greater stability at the same number of components [37]. It can be seen from the CoMFA-2 model in Table 2 that the application of region focusing resulted in

Table 2. Statistical results of CoMFA models.

| | *CoMFA-1* | *CoMFA-2(after region focusing)* |
|---|---|---|
| PLS statistics | | |
| LOO cross $q^2$ /SEP[a] | 0.475/0.592 | 0.637/0.492 |
| Group cross $q^2$ /SEP | 0.481/0.589 | 0.612/0.509 |
| Non-validated $r^2$ /SEE[b] | 0.977/0.155 | 0.976/0.128 |
| $CCC_{tr}/CCC_{ext}$ | 0.988/0.669 | 0.988/0.632 |
| F | 210.564 | 199.982 |
| $r^2_{bootstrap}$ | 0.984 ± 0.005 | 0.973 ± 0.011 |
| $S_{bootstrap}$ | 0.105 ± 0.062 | 0.168 ± 0.081 |
| Optimal compounds | 6 | 6 |
| $r^2_{test}$ | 0.715 | 0.728 |
| Field distribution % | | |
| Steric | 48.7 | 46.8 |
| Electrostatic | 51.3 | 53.2 |

[a]SEP: standard error of prediction.
[b]SEE: standard errors of estimate.

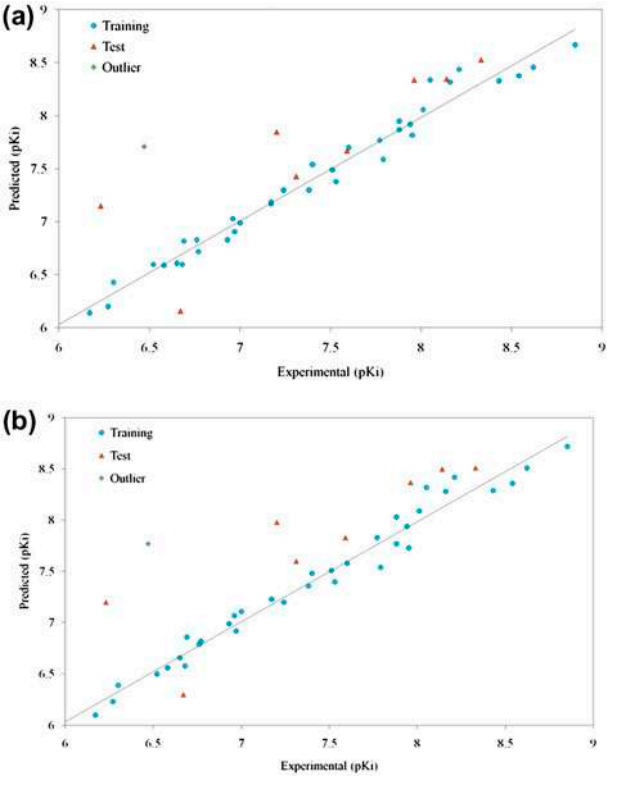



Figure 3. Plot of the calculated vs. observed $pK_i$ values using CoMFA (a) and CoMFA region focusing (b) analysis.

a significant increase for the internal validity ($q^2$) from 0.475 to 0.637. The steric and electrostatic field contributions to the final CoMFA-2 model were 46.8% and 53.2%, respectively. A graph of observed versus predicted activities of the CoMFA region focusing model was plotted, as shown in Figure 3(b). For the CoMFA region focusing model, molecule **34** is also regarded as an outlier since its residual between the experimental value and the predicted value is high. By inclusion of this compound, the model shows poor predictive ability with $r^2_{test}$ of 0.602, and omission of compound **34** results in an increased $r^2_{test}$ value to 0.728. This analysis revealed that the proposed CoMFA model could also adequately predict all the compounds in the test set. This suggests that the CoMFA model is reliable for predicting structural requirements to improve potency of the target chemicals. Y-randomization analysis was also performed over CoMFA results (Figure S2, available on the article's online page), and after 15 randomly iterations of Y-response, the results indicated that the derived CoMFA model could be accepted and the difference between $q^2$ and $r^2$ values will not generate a significant problem.

### 3.2 *Contour maps*

To visualize the information content of the derived 3D-QSAR models, CoMFA contour maps were generated. Such contour maps provide some information (such as steric and electrostatic) on factors affecting the activity of the studied compounds. This is particularly

important when increasing or reducing the activity of a compound by changing its molecular structure [45]. The CoMFA contour maps of steric and electrostatic fields for CoMFA and CoMFA region focusing are shown in Figures 4 and 5, respectively. As can be seen, the contour maps of CoMFA are well correlated with the CoMFA region focusing contour maps.

The contour maps using region focusing are of better quality because the region focusing resulted in a sort of image enhancement. The CoMFA green contours (contribution level of 80%) indicate the area in which steric bulk might have a positive effect on activity, while the yellow regions (contribution level of 20%) are favourable for small groups. Similarly, the blue contours indicate regions where the addition of electropositive substituent increases activity (contribution level of 80%); red indicates regions where the addition of an electronegative substituent increases activity (contribution level of 20%).

The steric contour map of CoMFA-2 region focusing (Figure 5(a)) shows the large green contours around the $R_1$ substituent. This indicates that bulky groups around the $R_1$ substituent are beneficial to activity. This conclusion is in agreement with the experimental results by Shook et al. [15]. According to molecules1 and 2 in the data set (see Table 1), the two molecules have the same structure except in the $R_1$ position, while the $R_1$ substituent is H and Ph for compounds 1 and 2, respectively. As can be seen, by increasing the size of $R_1$ from H to Ph, the $pK_i$ values will increase from 6.96 to 7.17. Several small yellow regions near the $R_2$

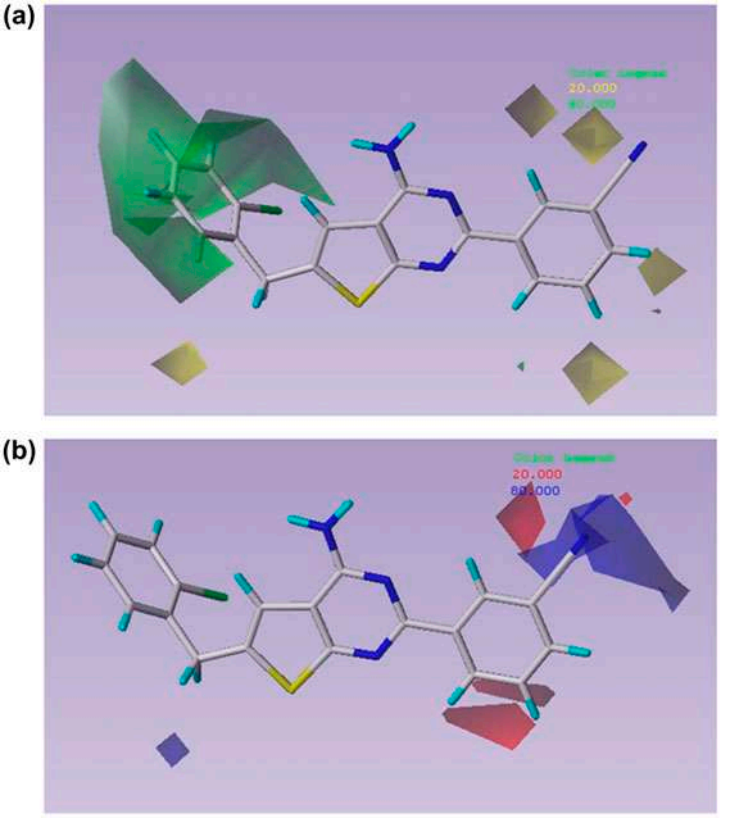



Figure 4. Contour maps of CoMFA: steric (a) and electrostatic (b) based on compound **32**.

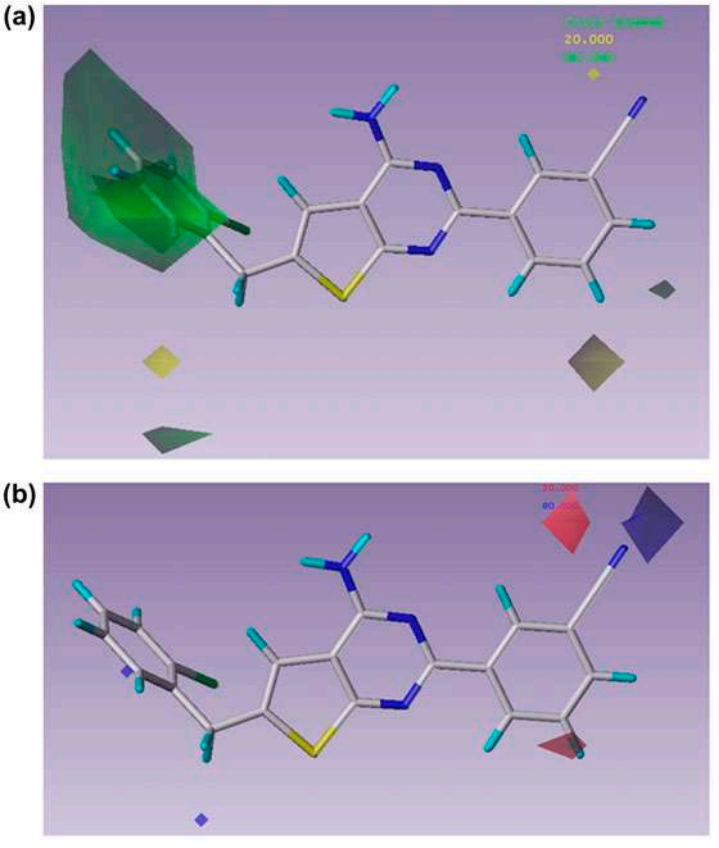



Figure 5. Contour maps of CoMFA region focusing: steric (a) and electrostatic (b) based on compound **32**.

position indicate that the less bulky substituents are preferred for higher activity. This may be the reason why compounds with small substituents in this area, for example compounds 3 and 9, have higher biological activity than molecules with bulky substituents, such as compounds 11 and 10.

The electrostatic contour map is displayed in Figure 5(b) for the CoMFA-2 model. Two regions of red beside the $R_2$ substituent (between positions 1 and 2 and also at position 4 of the benzene ring) show that presence of the electronegative substituents such as CN and F is very important for increasing biological activity ($pK_i$), in such a way that compounds 13 and 30 are more potent than compounds 10 and 29. A blue region near $R_2$ (at position 2 of the benzene ring) means that electropositive substituents at this region would increase the biological activity ($pK_i$). This information will be used for the design of new $A_{2A}$ receptor antagonists.

### 3.3 *Docking result of the most potent molecule*

We selected the most potent inhibitor **32** in the experiment to perform the docking study. Figure 6 represents the interaction model of that with $A_{2A}$ receptor, in which the inhibitor is

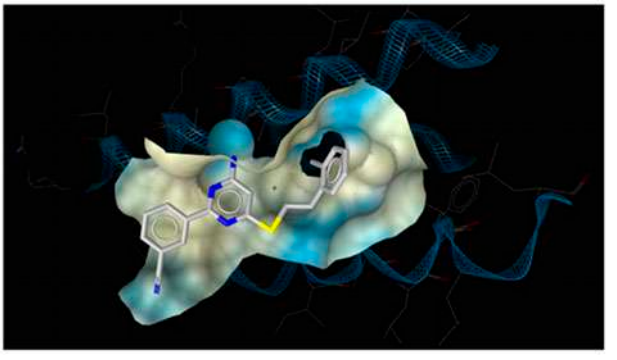


Figure 6. Docking conformation of the most potent inhibitor 32 with corresponding binding pocket of $A_{2A}$ receptor.



suitably situated at the binding site. As can be seen, there are various interactions between the inhibitor and the binding region of the enzyme. The two-dimensional representation for the interaction mode between compound **32** and the $A_{2A}$ receptor generated by the LigandScout 3.03 program is shown in Figure 7. The phenyl and methyl groups showed hydrophobic interactions with Leu 194, Leu 190, Alu 243, Val 239 and Leu 194, Alu 236, Tyr 197 and Val 239 residues, respectively. Also, one hydrophobic interaction is formed between the benzonitrile ring of compound **32** and the Phe 201 residue. Therefore, according to structural analyses and study of existing interactions, we can conclude that these residues play an important role in compound affinity potency with the $A_{2A}$ receptor. As a result, the docking mode of compound **32** provided some important information for the development of novel $A_{2A}$ receptor antagonists. For more details about molecular docking results, the Discovery studio program

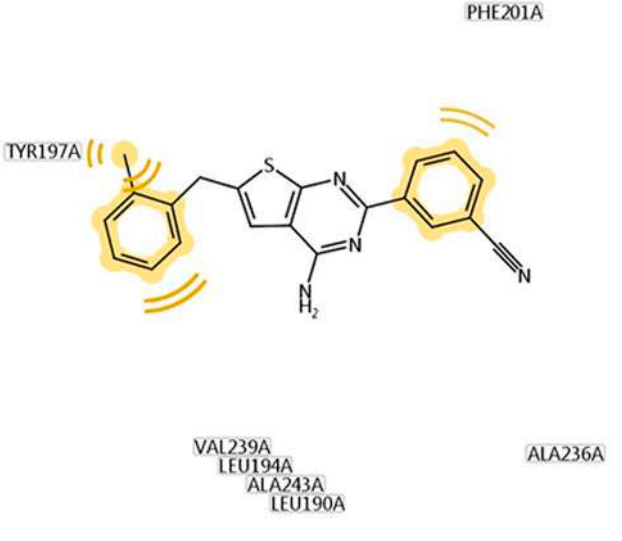
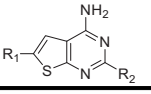
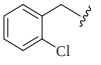
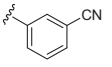
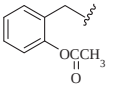
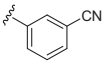
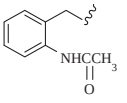
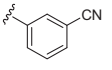
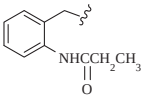
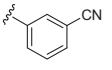
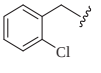
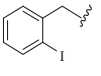
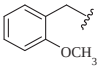
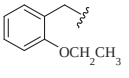
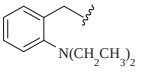
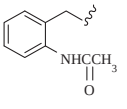
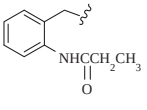
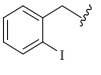



Figure 7. 2D structure of interaction sketched by LigandScout program.

Table 3. Structure and predicted $pIC_{50}$ values of newly designed compounds.




| | *Substituents* | | *Predicted $pIC_{50}$* | |
|---|---|---|---|---|
| *No.* | *$R_1$* | *$R_2$* | *CoMFA-1* | *CoMFA-2* |
| **32** |  |  | **8.67** | **8.72** |
| N1 |  |  | 8.65 | 8.61 |
| N2 |  |  | 8.50 | 8.38 |
| N3 |  |  | 8.61 | 8.54 |
| N4 |  |  | 8.95 | 9.08 |
| N5 |  |  | 8.92 | 9.06 |
| N6 |  |  | 8.81 | 8.98 |
| N7 |  |  | 8.61 | 8.80 |
| N8 |  |  | 8.62 | 8.76 |
| N9 |  |  | 8.96 | 8.93 |
| N10 |  |  | 9.00 | 8.99 |
| N11 |  |  | 8.61 | 8.91 |

was also used, and the results can be found in the supplementary information (available online). Meanwhile, docking analysis was also employed for the main ligand (4-{2-[(7-amino-2-furan-2-yl [1,2,4] triazolo [1,5-a] [1,3,5] triazin-5-yl) amino] ethyl} phenol) of receptor (4EIY) to compare with residuals derived for compounds **32** and N4. The results were amended in SIF and showed some similar residuals responsible for increasing the biological activities of these inhibitors.

### 3.4 *Design of new $A_{2A}$ receptor antagonists*

Based on the structure–activity relationship obtained these 3D-QSAR models, a series of new $A_{2A}$ receptor antagonists was designed and predicted by the obtained models (Table 3). The most potent molecule (compound **32**) was used as a reference structure to design new molecules. These new proposed compounds were generated by combining some bulky and electron-donating groups, such as a substituents containing -NHCOR, -$N(CH_2CH_3)_2$, -$OCOCH_3$, -OR, $NH_2$, Cl and I groups at the $R_1$ position, and some electron-withdrawing groups such as CN and electron-donating group such as  at $R_2$ position, and some new compounds were designed. Most of them greatly enhanced $A_{2A}$ receptor activity in comparison with the reference molecule; in particular, compound N4 showed the strongest activity with its predicted $pK_i$ = 9.08. Other compounds as well as compound **32** also exhibited predicted activity well. Such results further suggest that these CoMFA models have strong predictive ability and can be prospectively used in molecular design or structural modification. Docking analyses were also performed for the most potent designed compound (N4) and amended to SIF. The results of docking showed that the designed compound has a large number of interactions with its receptor and indicated higher biological activity.

## 4. Conclusion

The 3D-QSAR models of 46 pyrimidines as adenosine $A_{2A}$ receptor antagonists were developed using the CoMFA technique. The CoMFA region focusing model provided the most significant correlation of steric and electrostatic fields with biological activity. The developed model had high internal validity ($q^2$ above 0.5) and high predictive ability (test set $r^2$ above 0.5). The CoMFA region focusing contour maps emphasized important regions in 3D space where modifications of steric and electrostatic properties would be strongly associated with concomitant changes in observed activity. The docking results showed that hydrophobic interactions were highly correlated with the activities of $A_{2A}$ receptor antagonists. Some potent compounds were designed based on analysis of contour maps. The proposed models are being used to predict the $A_{2A}$ receptor antagonist activity of newly designed compounds. These models could provide useful information for the design of new potent $A_{2A}$ receptor antagonists.

## Supplementary material

The supplementary material for this paper is available online at http://dx.doi.org/10.1080/1062936X.2015.1049666.

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# Optimization of antiproliferative activity of substituted phenyl 4-(2-oxoimidazolidin-1-yl) benzenesulfonates: QSAR and CoMFA analyses

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ABSTRACT

Multiple separate quantitative structure–activity relationships (QSARs) models were built for the antiproliferative activity of substituted Phenyl 4-(2-Oxoimidazolidin-1-yl)-benzenesulfonates (PIB-SOs). A variety of descriptors were considered for PIB-SOs through QSAR model building. Genetic algorithm (GA), available in QSARINS, was employed to select optimum number and set of descriptors to build the multi-linear regression equations for a dataset of PIB-SOs. The best three parametric models were subjected to thorough internal and external validation along with *Y*-randomization using QSARINS, according to the OECD principles for QSAR model validation. The models were found to be statistically robust with high external predictivity. The best three parametric model, based on steric, 3D- and finger print descriptors, was found to have $R^2 = 0.91$, $R^2_{ex} = 0.89$, and $CCC_{ex} = 0.94$. The CoMFA model, which is based on a combination of steric and electrostatic effects and graphically inferred using contour plots, gave $F = 229.34$, $R^2_{CV} = 0.71$ and $R^2 = 0.94$. Steric repulsion, frequency of occurrence of carbon and nitrogen at topological distance of seven, and internal electronic environment of the molecule were found to have correlation with the anti-tumor activity of PIB-SOs.



## 1. Introduction

Recent reports from WHO and other organizations clearly highlights cancer as a leading cause of mortality, and economic problems for millions of peoples (WHO, 2012, 2013). Chemotherapy is a preferred method of treatment, although, various therapies like radiation, different types of surgeries etc. are available Chemotherapy for cancer treatment usually involves three or four anti-cancer drugs in combination (Aziz et al., 2013; Natarajan and Senapati, 2012; Temirak et al., 2012). Few examples of anticancer drugs are presented in Fig. 1. Despite high treatment success in many cases, severe side effects and emergence of resistance for marketed anti-cancer drugs are serious concerns for modern chemotherapy (Fortin et al., 2011; Krishnegowda et al., 2011; Temirak et al., 2012). Therefore, extensive search for a drug with high activity against cancer and good ADMET (Absorption, Distribution, Metabolism, Excretion and Toxicity) profile is a challenge for modern medicinal chemistry.

Modern medicinal chemists employ different strategies to optimize the pharmacological activity, the ADMET profile and a viable synthesis route for an available lead candidate (i.e. lead optimization). In modern drug designing process, computer-aided drug design (CADD) is helpful in identifying new potent compounds and saves drug development time, and money. It provides a useful alternative to animal testing, as well. CADD is a method of choice in drug designing process due to its faster, economical, and result oriented high success rate (Mahajan et al., 2012, 2013; Masand et al., 2012a,b, 2013a,b). QSAR, molecular docking, pharmacophore modeling, etc. are some of the successful brushwood of CADD that have led to the introduction of many drugs in the market (Jawarkar

*Abbreviations:* CoMFA, comparative molecular field analysis; PIB-SOs, Phenyl 4-(2-Oxoimidazolidin-1-yl)-benzenesulfonates; GA, genetic algorithm; MLR, multiple linear regression; QSAR, quantitative structure–activity relationship; ADMET, Absorption, Distribution, Metabolism, Excretion and Toxicity; CADD, computer aided drug designing; OLS, ordinary least square; QSARINS, QSAR insubria.

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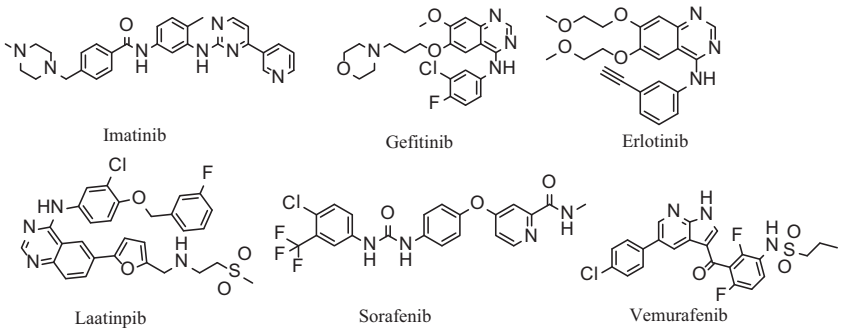



**Fig. 1.** Few examples of approved anti-cancer drugs.

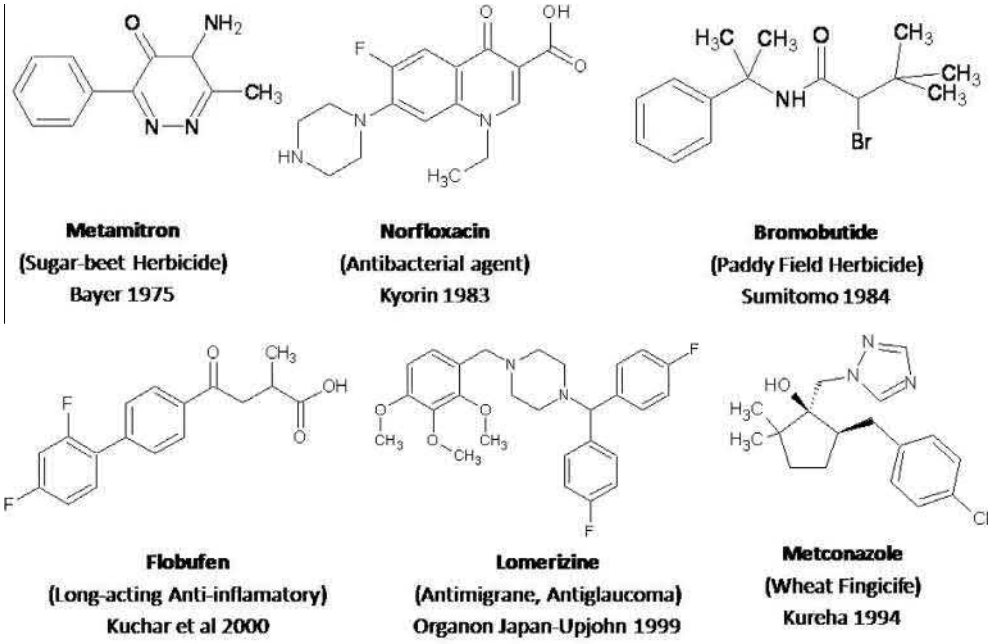



**Fig. 2.** Some of the commercial drugs developed using QSAR.

et al., 2010; Mahajan et al., 2010, 2012, 2013; Masand et al., 2011, 2012a,b, 2010a,b, 201s3a,b) (see Fig. 2).

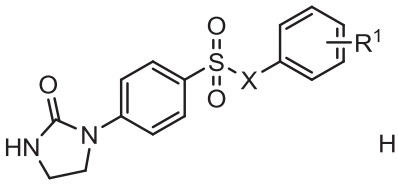
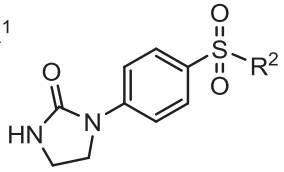
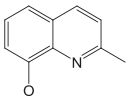
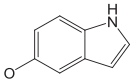
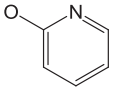
Molecular docking can be effectively used for optimization of drug when the 3D structure of the protein/enzyme with which the drug interacts is known (Mahajan et al., 2012). According to one school of thought, in absence of information about the target protein/receptor, QSAR and pharmacophore modeling are preferable techniques for lead optimization (Mahajan et al., 2012). Since the exact mechanism of action and the receptors with which PIB-SOs interact are unknown (Fortin et al., 2011; Turcotte et al., 2012), we have performed extensive QSAR, and CoMFA (ligand based drug design) analyses on PIB-SOs to determine the structural features that control their anti-proliferative activity. This will provide understanding of drug mechanism for PIB-SOs class and will help in developing potentially active and better drug candidates against cancer.

The selected dataset (Fortin et al., 2011; Turcotte et al., 2012) consists of ninety seven PIB-SOs having diverse substituents like $-NH_2$, $-OH$, $-OCH_3$ and $-Cl$. The compounds were assayed against skin melanoma M-21 cell lines according to the NCI/NIH Developmental Therapeutics Program (Fortin et al., 2011; Turcotte et al., 2012). The activity expressed as the concentration of drug inhibiting cell growth by 50% ($IC_{50}$) was converted to $pIC_{50}$ ($-\log_{10}$ $IC_{50}$) for QSAR analysis (Jawarkar et al., 2010; Mahajan et al., 2010, 2012; Masand et al., 2013a). The substituents, experimental $IC_{50}$ and $pIC_{50}$ have been listed in Table 1.

The standard procedure as specified in SYBYL was followed to build a database of ninety-seven PIB-SOs. For thriving CoMFA analysis, proper alignment of 3D structures of the molecules is very important (Mahajan et al., 2012; Masand et al., 2012a, 2010a). To enhance the fruitfulness of CoMFA analysis, Gasteiger–Marsili partial charges were assigned to all the molecules before carrying out descriptor calculation and alignment. The lowest energy conformer of most active compound **92** was used as a template structure for aligning the compete set of molecules. The molecules in their respective lowest conformations were superimposed on the template using the atom based alignment option in SYBYL. It was followed by partial least square (PLS) analysis and 3D contour generation with optimum number of components set to 5. Default settings and procedure as implemented in SYBYL were used throughout the work.

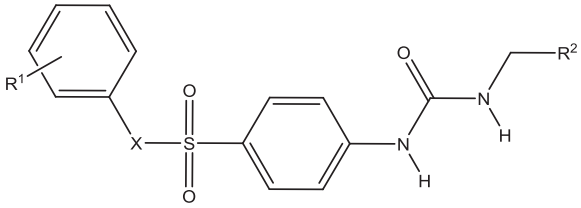
The central idea of the present work is to use conventional QSAR to obtain extensive information about the structural features that govern the activity. Therefore, a new strategy was employed, in which, multiple models were built using 50% training set and validating them on remaining set (50% prediction set) using random splitting. In next step, the training and the prediction sets were interchanged for model building and validation. Thus, new

**Table 1**
Experimental data showing $IC_{50}$ and $pIC_{50}$ for substituted *N*-phenyl ureidobenzenesulfonate derivatives.

| S. no. | X | $R^1$ or $R^2$ | $IC_{50}$ (μM) (M-21) | $pIC_{50}$ (M) (M-21) |
|---|---|---|---|---|
| |  |  | | |
| 1. | O | 2-Me | 26 | 7.585 |
| 2. | O | 3-Me | 54 | 7.268 |
| 3. | O | 4-Me | 93 | 7.032 |
| 4. | O | 4-OMe | 98 | 7.009 |
| 5. | O | 4-$NMe_2$ | 350 | 6.456 |
| 6. | O | 2-Et | 52 | 7.284 |
| 7. | O | 2-Prop | 61 | 7.215 |
| 8. | O | 2-OMe | 130 | 6.886 |
| 9. | O | 2-OEt | 24 | 7.62 |
| 10. | O | 2-Cl | 45 | 7.347 |
| 11. | O | 2-F | 34 | 7.469 |
| 12. | O | 2-I | 40 | 7.398 |
| 13. | O | 2-$NO_2$ | 150 | 6.824 |
| 14. | O | 2-Me,3-Me | 17 | 7.77 |
| 15. | O | 2-Me,4-Me | 39 | 7.409 |
| 16. | O | 2-Me,5-Me | 8.5 | 8.071 |
| 17. | O | 2-Me,4-Me, 5-Me | 41 | 7.387 |
| 18. | O | 2-Cl,4-Cl, 5-Cl | 31 | 7.509 |
| 19. | O | 2-Cl,4-Cl, 6-Cl | 120 | 6.921 |
| 20. | O | 2-F,4-F | 35 | 7.456 |
| 21. | O | 2-F,6-F | 15 | 7.824 |
| 22. | O | 2-F,3-F,4-F,5-F, 6-F | 220 | 6.658 |
| 23. | O | 3-Prop | 27 | 7.569 |
| 24. | O | 3-OMe | 24 | 7.62 |
| 25. | O | 3-OEt | 12 | 7.921 |
| 26. | O | 3-Cl | 9.2 | 8.036 |
| 27. | O | 3-F | 31 | 7.509 |
| 28. | O | 3-I | 10 | 8 |
| 29. | O | 3-$NO_2$ | 48 | 7.319 |
| 30. | O | 3-$NH_2$ | 170 | 6.77 |
| 31. | O | 3-Me,5-Me | 16 | 7.796 |
| 32. | O | 3-Me,4-Me,5-Me | 15 | 7.824 |
| 33. | O | 3-OMe,4-OMe | 45 | 7.347 |
| 34. | O | 3-OMe,5-OMe | 4.3 | 8.367 |
| 35. | O | 3-OMe,4-OMe,5-OMe | 4 | 8.398 |
| 36. | O | 2-Cl,5-Cl | 8.2 | 8.086 |
| 37. | O | 3-F,4-F | 47 | 7.328 |
| 38. | O | 3-F,5-F | 15 | 7.824 |
| 39. | O | 3-F,4-F,5-F | 43 | 7.367 |
| 40. | O | 3-Me,4-$NO_2$ | 100 | 7 |
| 41. | O | 3-Me,4-$NH_2$ | 360 | 6.444 |
| 42. | O | 4-Et | 120 | 6.921 |
| 43. | O | 4-Prop | 59 | 7.229 |
| 44. | O | 4-secBut | 830 | 6.081 |
| 45. | O | 4-OEt | 39 | 7.409 |
| 46. | O | 4-OProp | 96 | 7.018 |
| 47. | O | 4-OBut | 530 | 6.276 |
| 48. | O | 4-Cl | 58 | 7.237 |
| 49. | O | 4-F | 89 | 7.051 |
| 50. | O | 4-I | 110 | 6.959 |
| 51. | O | 4-$NO_2$ | 570 | 6.244 |
| 52. | O | 4-$NH_2$ | 920 | 6.036 |
| 53. | O |  | 130 | 6.886 |
| 54. | O |  | 65 | 7.187 |
| 55. | O |  | 290 | 6.538 |
| 56. | O | 3-OMe,4-OMe,5-OMe | 240 | 6.62 |

(*continued on next page*)

Table 1 (*continued*)

| S. no. | X | $R^1$ | $R^2$ | $IC_{50}$ (μM) (M-21) | $pIC_{50}$ (M) (M-21) |
|---|---|---|---|---|---|
|  | | | | | |
| 57. | O | 4-OH | 4-CEU | 2.8 | 5.553 |
| 58. | O | 2-Me | 3-CEU | 7.2 | 5.143 |
| 59. | O | 2-$CH_2$-$CH_3$ | 3-CEU | 21 | 4.678 |
| 60. | O | 2-$(CH_2)_2$-$CH_3$ | 3-CEU | 18 | 4.745 |
| 61. | O | 4-OH | 3-CEU | 43 | 4.367 |
| 62. | O | 2-$CH_2$-$CH_3$ | 4-CEU | 1.2 | 5.921 |
| 63. | O | 2-$(CH_2)_2$-$CH_3$ | 4-CEU | 40 | 4.398 |
| 64. | NH | 2-Me | 3-CEU | 4.8 | 5.319 |
| 65. | NH | 2-$CH_2$-$CH_3$ | 3-CEU | 17 | 4.77 |
| 66. | NH | 2-$(CH_2)_2$-$CH_3$ | 3-CEU | 73 | 4.137 |
| 67. | NH | 2-Me | 4-CEU | 13 | 4.886 |
| 68. | NH | 2-$CH_2$-$CH_3$ | 4-CEU | 2.1 | 5.678 |
| 69. | NH | 2-$(CH_2)_2$-$CH_3$ | 4-CEU | 91 | 4.041 |
| 70. | O | 2-Me | 3-CPU | 65 | 4.187 |
| 71. | O | 2-$CH_2$-$CH_3$ | 3-CPU | 17 | 4.77 |
| 72. | O | 2-$(CH_2)_2$-$CH_3$ | 3-CPU | 63 | 4.201 |
| 73. | O | 4-OH | 3-CPU | 68 | 4.167 |
| 74. | O | 2-Me | 4-CPU | 29 | 4.538 |
| 75. | O | 2-$CH_2$-$CH_3$ | 4-CPU | 29 | 4.538 |
| 76. | O | 2-$(CH_2)_2$-$CH_3$ | 4-CPU | 24 | 4.62 |
| 77. | O | 4-OH | 4-CPU | 15 | 4.824 |
| 78. | NH | 2-Me | 3-CPU | 49 | 4.31 |
| 79. | NH | 2-$CH_2$-$CH_3$ | 3-CPU | 25 | 4.602 |
| 80. | NH | 2-$(CH_2)_2$-$CH_3$ | 3-CPU | 15 | 4.824 |
| 81. | NH | 2-Me | 4-CPU | 13 | 4.886 |
| 82. | NH | 2-$(CH_2)_2$-$CH_3$ | 4-CPU | 47 | 4.328 |
| 83. | O | 2-Me | 4-CEU | 60 | 4.222 |
| 84. | O | 2-$CH_2$-$CH_3$ | 3-EU | 23 | 4.638 |
| 85. | O | 4-OH | 3-EU | 38 | 4.42 |
| 86. | O | 2-Me | 4-EU | 51 | 4.292 |
| 87. | O | 2-$CH_2$-$CH_3$ | 4-EU | 30 | 4.523 |
| 88. | O | 2-$(CH_2)_2$-$CH_3$ | 4-EU | 25 | 4.602 |
| 89. | O | 4-OH | 4-EU | 42 | 4.377 |
| 90. | O | 3-Me | 4-CEU | 3.1 | 5.509 |
| 91. | NH | 2-Me | 3-EU | 2.5 | 5.602 |
| 92. | NH | 2-$CH_2$-$CH_3$ | 3-EU | 0.8 | 6.097 |
| 93. | NH | 2-$(CH_2)_2$-$CH_3$ | 3-EU | 4.3 | 5.367 |
| 94. | NH | 2-$CH_2$-$CH_3$ | 4-EU | 131 | 3.883 |
| 95. | O | 4-Me | 4-CEU | 60 | 4.222 |
| 96. | O | 4-OMe | 4-CEU | 90 | 4.046 |
| 97. | O | 4-$N(Me)_2$ | 4-CEU | 41 | 4.387 |

CEU: 2-chloroethylurea; PIB-SO: Phenyl 4-(2-oxoimidazolidin-1-yl)benzenesulfonate; PUB-SO: *N*-phenyl ureidobenzenesulfonate; PUB-SA: *N*-phenyl ureidobenzenesulfonamide; CPU: 3-chloropropylurea; EU: ethylurea;

multiple models were built and validated on prediction set (which was initially the training set). This ensures that all the relevant information about the structural features that governs the anti-tumor activity of these molecules is expressed in the developed QSAR models. Additionally, multiple QSAR models were built using whole dataset (no splitting) to verify the capturing of all the relevant structural and activity information (see Fig. 3).

Modeling subjective feature selection using genetic algorithm (GA) in QSARINS was employed for selecting optimum number and set of descriptors for ordinary least square (OLS) model development. The heuristic search was limited to three variables per model in order to develop easy and informative GA-MLR QSAR models. The selected descriptors were used to build the statistically robust OLS QSAR models followed by thorough statistical validation according to the OECD principles for QSAR model validation. QSARINS was used to build tri-parametric OLS models with default settings, except for Lack of Fit (LOF) which was set to a value of 0.5. The selected fitness function used to maximize in GA was $Q^2$, this avoids naive $Q^2$ also. All the models having low internal and external predictivity were rejected. The descriptors that were selected in model-1 to 12 are provided in supplementary information.

All the models were subjected to thorough internal as well as external validation along with *Y*-scrambling using QSARINS to eliminate over-fitting and spurious models. Various parameters for internal validation include: determination coefficient $R^2$, leave-one-out (LOO) cross-validation $Q^2$, leave-many-out (LMO) cross validation $Q^2_{LMO}$, coefficient of determination for *Y*-scrambling $R^2_{Yscr}$, and root mean squared error (*RMSE*). The LMO were repeated 500 times with 30% of the objects left out randomly from the training set each time; the mean value of $Q^2_{LMO}$ has been reported. The external validation parameters are $RMSE_{ex}$, $MAE_{ex}$, $R^2_{ex}$, $Q^2_{F1}$, $Q^2_{F2}$, $Q^2_{F3}$, and $CCC_{ex}$.

Model validation was carried out also by checking the model applicability domain (AD), which was verified by the Williams plots. AD is a theoretical region defined by the physico-chemical,

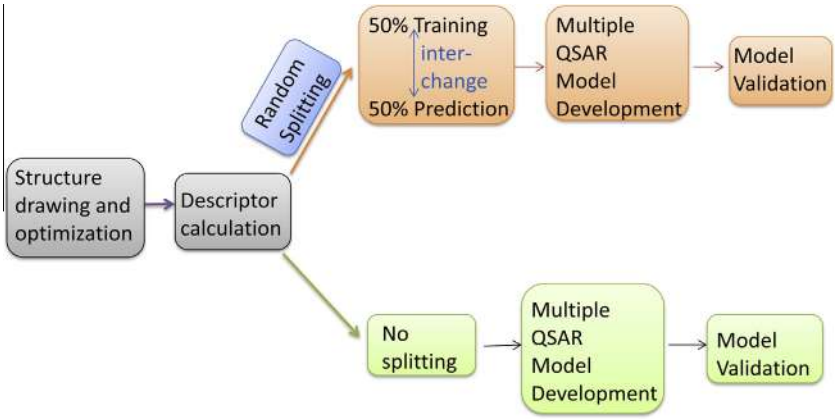



**Fig. 3.** Flowchart diagram for the methodology used in the present study.

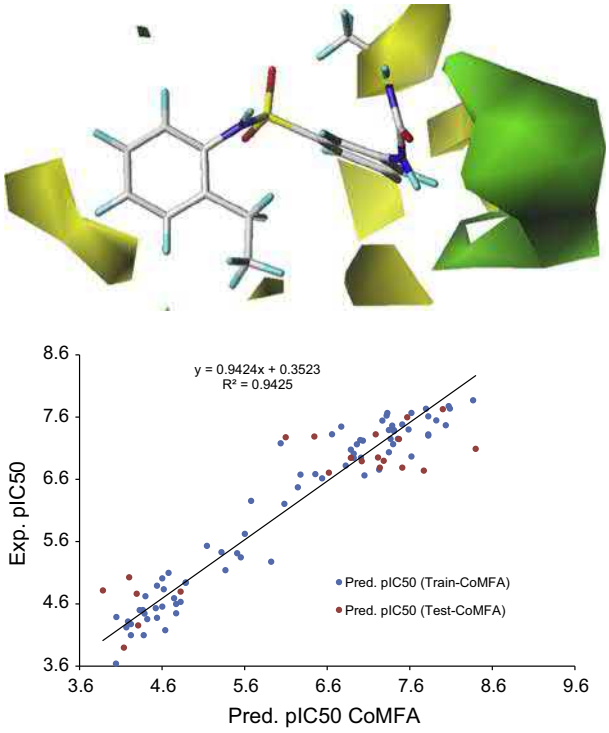



**Fig. 4.** CoMFA contour maps for PIB-Sos with compound **92** as representative along graph correlation between experimental and predicted $pIC_{50}$ (CoMFA model).

structural or biological space on which the model has been developed using the training set, it's applicable to make predictions for new compounds. Thus, AD is related to interpolation rather than extrapolation. A widely accepted method for AD determination is based on leverage calculation from the diagonal values of the hat matrix using modeling modelecular descriptors. It is evaluated by leverage (or hat) analysis using the formula: $h_i = x_i\ (X^T\ X)^{-1}\ x_i^T$ where ($i = 1, \ldots, m$), $x_i$ is the descriptor row-vector of the query compound $i$, $m$ is the number of query compounds and $X$ is the $n \times p$ matrix of the training set ($p$ is the number of descriptors in the model and $n$ is the number of compounds in the training set). The limit of the model domain is quantitatively defined by the leverage cut-off $h^*$ and is set as $3(p + 1)/n$. A leverage bigger than $h^*$ for the training set means that the compound is very dominant in determining the model. For the prediction set ($X$ outlier), it means that the prediction is the substantial extrapolation of the model and could be unreliable. Also, a compound with a

**Table 2**
Multiple separate GA-MLR QSAR models for antiproliferative activity of PIB-SOs.

| S. no. | Variable | Coefficient | Std. Coeff. | C. I. 95% |
|---|---|---|---|---|
| Model-1 | *Intercept* | 49.77 | | 4.17 |
| | *X3A* | −177.39 | −0.71 | 24.74 |
| | *BEHp6* | −3.35 | −0.28 | 1.26 |
| | *F07[C-N]* | −0.67 | −0.29 | 0.22 |
| Model-2 | *Intercept* | 58.21 | | 6.58 |
| | *MAXDP* | −1.95 | −0.22 | 0.87 |
| | *X3A* | −215.22 | −0.86 | 22.85 |
| | *F07[C-N]* | −0.73 | −0.31 | 0.22 |
| Model-3 | *Intercept* | 44.15 | | 4.51 |
| | *X3A* | −188.50 | −0.75 | 24.92 |
| | *RDF020u* | −0.22 | −0.22 | 0.10 |
| | *F07[C-N]* | −0.84 | −0.36 | 0.21 |
| Model-4 | *Intercept* | 42.53 | | 4.78 |
| | *X3A* | −197.012 | −0.79 | 23.69 |
| | *R4e+* | 35.29 | 0.21 | 16.08 |
| | *F07[C-N]* | −0.79 | −0.34 | 0.22 |
| Model-5 | *Intercept* | 42.94 | | 4.73 |
| | *X3A* | −181.94 | −0.73 | 26.48 |
| | *R7u* | −1.98 | −0.23 | 0.91 |
| | *F07[C-N]* | −0.85 | −0.37 | 0.21 |
| Model-6 | *Intercept* | 41.51 | | 5.08 |
| | *X3A* | −170.69 | −0.68 | 29.75 |
| | *R8e* | −3.42 | −0.27 | 1.61 |
| | *F07[C-N]* | −0.71 | −0.31 | 0.23 |
| Model-7 | *Intercept* | 16.53 | | 4.88 |
| | *Xt* | −120.44 | −0.52 | 21.12 |
| | *VEA2* | 113.18 | 0.80 | 13.35 |
| | *F07[C-N]* | −0.54 | −0.21 | 0.23 |
| Model-8 | *Intercept* | 13.95 | | 5.45 |
| | *Xt* | −115.31 | −0.50 | 23.73 |
| | *VEA2* | 113.71 | 0.80 | 14.31 |
| | *RDF110v* | 0.16 | 0.20 | 0.08 |
| Model-9 | *Intercept* | 15.90 | | 5.37 |
| | *Xt* | −121.54 | −0.53 | 23.40 |
| | *VEA2* | 116.92 | 0.83 | 14.26 |
| | *F06[C-N]* | −0.39 | −0.17 | 0.23 |
| Model-10 | *Intercept* | 13.90 | | 5.73 |
| | *Xt* | −96.15 | −0.42 | 32.64 |
| | *VEA2* | 94.73 | 0.67 | 22.92 |
| | *nHDon* | −0.49 | −0.28 | 0.30 |
| Model-11 | *Intercept* | 17.18 | | 5.40 |
| | *Xt* | −127.03 | −0.55 | 22.97 |
| | *VEA2* | 114.81 | 0.81 | 15.23 |
| | *B01[N-S]* | −0.64 | −0.16 | 0.43 |
| Model-12 | *Intercept* | 19.43 | | 5.63 |
| | *Xt* | −133.04 | −0.58 | 22.56 |
| | *VEA2* | 122.21 | 0.87 | 13.95 |
| | *R4v* | −4.63 | −0.13 | 3.27 |

C. I. – Confidence interval and Std. coeff. – Standardized Coefficient.

**Table 3**
Statistical parameters for multiple separate GA-MLR QSAR models 1–12 for antiproliferative activity of PIB-SOs.

| S. no. | Statistical parameter | Model-1 | Model-2 | Model-3 | Model-4 | Model-5 | Model-6 |
|---|---|---|---|---|---|---|---|
| 1. | $N_{tr}$ | 49 | 49 | 49 | 49 | 49 | 49 |
| 2. | $N_{ex}$ | 48 | 48 | 48 | 48 | 48 | 48 |
| *Fitting parameters* | | | | | | | |
| 3. | $R^2_{tr}$ | 0.92 | 0.91 | 0.91 | 0.91 | 0.90 | 0.90 |
| 4. | $R^2_{adj.}$ | 0.91 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 |
| 5. | *LOF* | 0.17 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| 6. | $RMSE_{tr}$ | 0.38 | 0.40 | 0.40 | 0.40 | 0.41 | 0.41 |
| 7. | $MAE_{tr}$ | 0.30 | 0.31 | 0.32 | 0.31 | 0.28 | 0.30 |
| 8. | $CCC_{tr}$ | 0.96 | 0.95 | 0.95 | 0.95 | 0.95 | 0.95 |
| 9. | *s* | 0.40 | 0.42 | 0.42 | 0.42 | 0.43 | 0.43 |
| 10. | *F* | 167.87 | 147.15 | 145.54 | 145.05 | 143.65 | 141.82 |
| *Internal validation parameters* | | | | | | | |
| 11. | $R^2_{cv}$ ($Q^2$) | 0.89 | 0.88 | 0.88 | 0.88 | 0.88 | 0.88 |
| 12. | $RMSE_{cv}$ | 0.43 | 0.46 | 0.45 | 0.46 | 0.46 | 0.46 |
| 13. | $MAE_{cv}$ | 0.33 | 0.35 | 0.35 | 0.34 | 0.31 | 0.33 |
| 14. | $CCC_{cv}$ | 0.94 | 0.94 | 0.94 | 0.94 | 0.94 | 0.93 |
| 15. | $Q^2_{LMO}$ | 0.90 | 0.89 | 0.89 | 0.89 | 0.89 | 0.89 |
| 16. | $R^2_{Yscr}$ | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 |
| *External validation parameters* | | | | | | | |
| 17. | $RMSE_{ex}$ | 0.55 | 0.48 | 0.55 | 0.59 | 0.49 | 0.54 |
| 18. | $MAE_{ex}$ | 0.43 | 0.38 | 0.40 | 0.45 | 0.39 | 0.42 |
| 19. | $R^2_{ex}$ | 0.85 | 0.89 | 0.85 | 0.83 | 0.88 | 0.86 |
| 20. | $Q^2_{F1}$ | 0.85 | 0.89 | 0.85 | 0.83 | 0.88 | 0.86 |
| 21. | $Q^2_{F2}$ | 0.85 | 0.89 | 0.85 | 0.83 | 0.88 | 0.86 |
| 22. | $Q^2_{F3}$ | 0.83 | 0.87 | 0.83 | 0.80 | 0.86 | 0.83 |
| 23. | $CCC_{ex}$ | 0.92 | 0.94 | 0.92 | 0.91 | 0.94 | 0.92 |

| S. no. | Statistical parameter | Model-7 | Model-8 | Model-9 | Model-10 | Model-11 | Model-12 |
|---|---|---|---|---|---|---|---|
| 1. | $N_{tr}$ | 48 | 48 | 48 | 48 | 48 | 48 |
| 2. | $N_{ex}$ | 49 | 49 | 49 | 49 | 49 | 49 |
| *Fitting parameters* | | | | | | | |
| 3. | $R^2_{tr}$ | 0.92 | 0.91 | 0.91 | 0.91 | 0.90 | 0.90 |
| 4. | $R^2_{adj.}$ | 0.92 | 0.91 | 0.90 | 0.90 | 0.90 | 0.89 |
| 5. | *LOF* | 0.19 | 0.22 | 0.23 | 0.23 | 0.24 | 0.24 |
| 6. | $RMSE_{tr}$ | 0.40 | 0.42 | 0.44 | 0.44 | 0.44 | 0.45 |
| 7. | $MAE_{tr}$ | 0.31 | 0.34 | 0.34 | 0.34 | 0.35 | 0.35 |
| 8. | $CCC_{tr}$ | 0.96 | 0.95 | 0.95 | 0.95 | 0.95 | 0.95 |
| 9. | *s* | 0.42 | 0.44 | 0.45 | 0.46 | 0.46 | 0.47 |
| 10. | *F* | 171.77 | 152.31 | 142.73 | 141.37 | 136.90 | 134.20 |
| *Internal validation parameters* | | | | | | | |
| 11. | $R^2_{cv}$ ($Q^2$) | 0.91 | 0.90 | 0.89 | 0.89 | 0.89 | 0.89 |
| 12. | $RMSE_{cv}$ | 0.44 | 0.46 | 0.47 | 0.48 | 0.48 | 0.48 |
| 13. | $MAE_{cv}$ | 0.34 | 0.37 | 0.37 | 0.37 | 0.38 | 0.38 |
| 14. | $CCC_{cv}$ | 0.95 | 0.95 | 0.94 | 0.94 | 0.94 | 0.94 |
| 15. | $Q^2_{LMO}$ | 0.91 | 0.90 | 0.89 | 0.89 | 0.89 | 0.89 |
| 16. | $R^2_{Yscr}$ | 0.07 | 0.07 | 0.07 | 0.06 | 0.06 | 0.06 |
| *External validation parameters* | | | | | | | |
| 17. | $RMSE_{ex}$ | 0.53 | 0.73 | 0.63 | 0.58 | 0.67 | 0.70 |
| 18. | $MAE_{ex}$ | 0.40 | 0.52 | 0.45 | 0.42 | 0.46 | 0.49 |
| 19. | $R^2_{ex}$ | 0.86 | 0.76 | 0.81 | 0.83 | 0.80 | 0.78 |
| 20. | $Q^2_{F1}$ | 0.84 | 0.70 | 0.77 | 0.81 | 0.75 | 0.72 |
| 21. | $Q^2_{F2}$ | 0.84 | 0.70 | 0.77 | 0.80 | 0.74 | 0.72 |
| 22. | $Q^2_{F3}$ | 0.86 | 0.74 | 0.80 | 0.83 | 0.78 | 0.76 |
| 23. | $CCC_{ex}$ | 0.92 | 0.86 | 0.90 | 0.91 | 0.88 | 0.87 |

$R^2$ – correlation coefficient, $Q^2$ – leave-one-out 'cross validated $R^{2'}$, $R^2_{adj}$ – adjusted $R^2$, SEE – standard error of estimates, *RMSE* – root mean squared error, *MAE* – mean absolute error, *CCC* – concordance correlation coefficient, for the training (tr), and test (ex) sets; *LOF* – lack of fit, *F* – Fischer's value; $R^2_{LMO}$ and $Q^2_{LMO}$ – leave many-out correlation coefficient and cross-validation coefficients; $R^2_{Ycr}$ and $Q^2_{Ycr}$ – *Y*-scramble correlation and cross-validation coefficients;

standardized residual greater than $3\sigma$ ($3 \times$ standard deviation units) is recognized as a *Y* outlier.

Though Fortin et al. performed CoMFA analysis for a dataset of PIB-SOs, the developed CoMFA model was based on a relatively small dataset of thirty seven molecules with moderate statistical performance ($R^2_{CV} = 0.552$). The present CoMFA model, based on a larger dataset of ninety-seven PIB-SOs, is statistically robust with $CCC_{ex} = 0.892$, $R^2_{ex} = 0.91$ for $N_{ex} = 21$. For $N_{train} = 76$, $CCC_{tr} = 0.970$. A higher value of $CCC_{ex}$ along with $R^2_{ex}$ confirms the good external predictivity of the CoMFA model. The leave-one-out (LOO) correlation coefficient ($R^2$cv) and $R^2$ were found to be 0.712 and 0.942, respectively. Further, standard error of estimate was found to be 0.338 with an optimized component of **5**. This implies that the model is not only trustworthy in capturing the essence of structural features that govern the anti-cancer activity but it is very good at predicting the anti-cancer activity of PIB-SOs also. The $pIC_{50}$values predicted by CoMFA model have been depicted in Fig. 4.

From Fig. 4, it is evident that the biological activity is predominantly governed by steric factors.

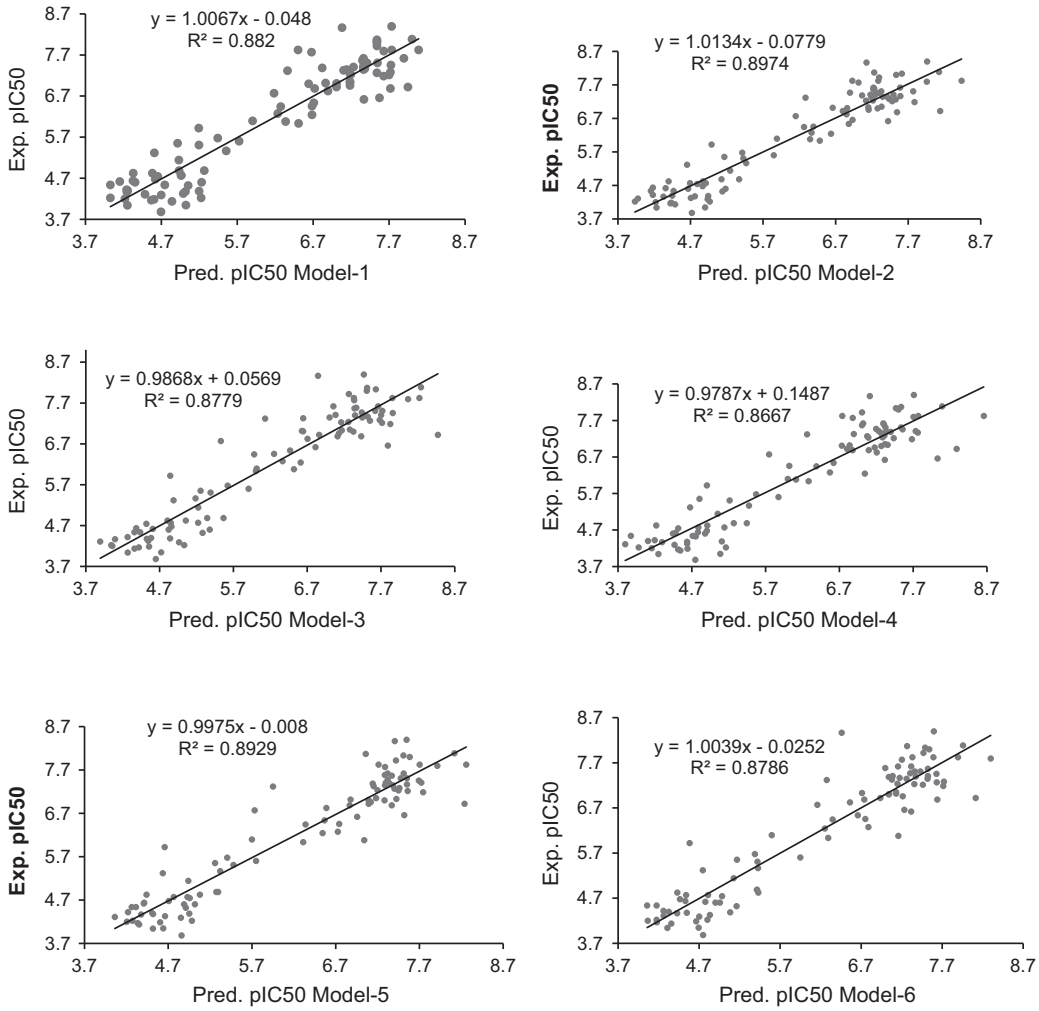



**Fig. 5.** Graph between experimental and predicted $pIC_{50}$ (on *Y*-axis) vs. molecule number (on x-axis).

The presence of a green colored contour near the ring A indicates that bulky groups are favoured in this region. This could be a possible reason for the differences in the activity of compounds: **84** with **59** and **71**, **86** with **74**, **89** with **57** and **77**. A yellow contour near to ring A suggests that presence of bulkier groups in this region is unfavourable for the anti-cancer activity. Another yellow contour present in the close vicinity of nitrogen at substituted urea moiety indicates that bulkier groups need to be avoided as substituent on this nitrogen. In a nut shell, steric factors play crucial role in deciding the anti-cancer activity of PIB-SOs.

The GA-MLR analysis resulted in many statistically acceptable QSAR models, listed in Table 2. The analysis was able to shed light on the structural features that steer the anti-cancer activity.

The different parameters for model 1–12, depicted in Table 3, indicate that all the models satisfy many statistical parameters like $R^2_{tr}$, $Q^2_{Fn}$, $R^2_{ex}$ and $CCC_{ex}$. These parameters are necessary to establish the internal and external predictive ability of a model. The predicted $pIC_{50}$ values by different models have been depicted in Fig. 5 (predicted $pIC_{50}$ values are available in Tables S3 and S4 provided as supplementary information).

From Table 3, it is clear that *X3A* (Average connectivity Index that a represents of the steric character of the molecule) and *F07[C-N]* (frequency of occurrence of carbon and nitrogen at topological distance of seven) are continually present in model 1–6. Similarly *Xt* (Total structure connectivity index, a representative of the steric character of the molecule) and *VEA2* (average eigenvector coefficient sum from adjacency matrix) are present in model 7–12. For *X3A*, a connectivity index, the coefficient (−194.319 in model-1) and standard coefficient (std. coeff. = −0.743 in model-1) are negative, which indicate its negative correlation with the activity. Same is applicable to *F07[C-N]*, a 2D frequency fingerprint descriptor, and *BEHp6* (highest eigenvalue *n*. 6 of Burden matrix/weighted by atomic polarizabilities), both have negative std. coeff. and coefficients in model 1. This observation is more clarified and vindicated by the CoMFA analysis. That is, CoMFA and QSAR analyses are complementary and supporting to each other. For better activity, the values of *X3A*, *BEHp6* and *F07[C-N]* should be as low as possible. *X3A* accounts for the multiplicity of the bond and for the presence of hetero atoms in the molecule, especially the hydrogen bond donor/acceptor atoms. For better anticancer activity of PIB-SOs, heteroatoms capable of forming H-bonding must be placed as far as possible.

From model 2–6, it is clear that *MAXDP* (maximal electrotopological positive variation), *RDF020u* (Radial Distribution Function – 2.0/unweighted), *R7u* (R autocorrelation of lag 7/unweighted) and *R8e* (R autocorrelation of lag 8/weighted by atomic Sanderson electronegativities) have negative correlation with the activity. The only descriptor that was found to have positive correlation (see model 4) with activity is *R4e+*(R maximal autocorrelation of lag 4/weighted by atomic Sanderson electronegativities).

Further a model based on undivided dataset was developed using the same parameters as for model 1–12 to understand the inclusion of new molecules in dataset for descriptor selection i.e. effect of augmentation of dataset size.

**Model-13:** $p\mathrm{IC}_{50} = 8.559\ (\pm 4.043) - 55.8097\ (\pm 23.1356)\ Xt + 71.0572\ (\pm 18.4287)\ VEA2 - 0.7420\ (\pm 0.2572)\ nHDon.$

$N_{tr} = 97,\ Q^2 = 0.85,\ R^2_{tr} = 0.87,\ R^2_{adj} = 0.86,\ LOF = 0.27,\ K_{xx} = 0.44,\ \Delta K = 0.15,\ RMSE_{tr} = 0.50,\ RMSE_{cv} = 0.52,\ S = 0.51,\ F = 205.12,\ CCC_{tr} = 0.93,\ CCC_{cv} = 0.92,\ MAE_{tr} = 0.38,\ MAE_{cv} = 0.40,\ R^2_{LMO} = 0.87,\ Q^2_{LMO} = 0.86,\ R^2_{Yscr} = 0.03.$

The model 13 is found to be similar to model 10 (see above table) apropos of selected descriptors only. The statistical parameters for model 13 clarifies that inclusion of more molecules in the dataset has acceptable influence on the statistical performance. Thus, the developed models are able to capture all the essential features that influence the anti-cancer profile of PIB-SOs. The training set of the models 7–12 has a distribution of data more similar to the full set, this could be a plausible reason for similarity between model 10 and 13.

In conclusion, various QSAR models and CoMFA model are developed and they are found to be statistically acceptable with good internal and external predictive ability. Both analyses reveal that steric repulsion has important correlation with the activity. The anti-cancer activity (against M 21 cell lines) of PIB-SOs is found to be largely influenced by the steric factors. The developed QSAR and CoMFA model insinuate constructive hints for optimization of PIB-SOs with improved activity profile. The models could be used to design new ligands with better activity, prior to their actual synthesis.

## Acknowledgements

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## Appendix A. Supplementary material

The experimental methodology for QSAR and CoMFA analyses, correlation matrix for descriptors, values of descriptors, etc. are available in supplementary file. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ejps.2015.06.001.

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## Research Article

### DESIGN, SYNTHESIS AND ANTI-MICROBIAL EVALUATION OF XANTHONE NUCLEUS UNIFIED WITH THIADIAZOLES AND SCHIFF'S BASE SCAFFOLDS

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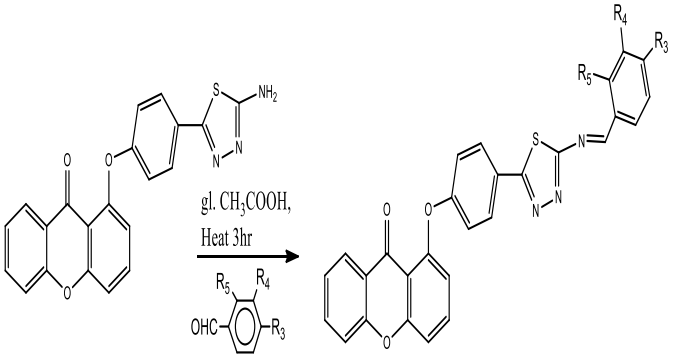
## Abstract

In the present work, a simple convenient and high yielding synthetic route has been employed for the synthesis of targeted molecules 1-(4-(5-(substitutedbenzylideneamino)-1,3,4-thiadiazol-2-yl)phenoxy)-9H-xanthen-9-one **2a-d**. The structures were confirmed by elemental analyses, UV-Vis, FT-IR, $H^1$NMR, Mass and physical properties. The synthesized compounds were screened for anti-microbial analysis against *E. coli, P. aerogenosa and S. aureus*. The compounds are found to be highly active, henceforth, could be attractive lead molecules for developing new therapeutics against tested microorganisms.

**Keywords:**Xanthone, thiadiazoles, Schiff's bases, synthesis, antimicrobial

**Graphical abstract:**




## Introduction

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Xanthone (dibenzo-γ-pyrone), a tricyclic oxygen based heterocycle (see figure 1), has widespread existence in a good number of natural compounds exhibitingattractive agricultural and medicinal applications like inhibitor of growth of variety of tumor cell lines,anti-asthmatic, anti-allergic, anti-parasitic, cardiovascular, neuropharmacological, analgesic, cytostatic activities, analeptic, anti-epileptic, anti-arrhythmic, anti-oxidant, herbicidal [1]. Substituted 1,3,4-thidiazoles (see figure 1) are associated with diverse biological activities probably by virtue of the toxophoric –N=C-S- grouping[2-4].

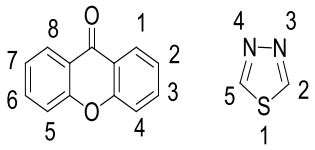


**Figure 1**: Xanthoneand 1,3,4-thiadiazole scaffolds

It has been widely observed that the desired profiles viz. biological and physico-chemical of a molecule alters significantly on integration of the parent nucleus with different scaffolds. At present, limited xanthones are commercially available and relatively limited type and position of the substituents on xanthone have been explored[1-2]. It has been observed that Schiff's base derivatives of 1,3,4-thiadiazole possess wide spectrum of biological application[5]. All these observations encouragedus to associate the titled scaffolds with the presumption that the integration of xanthones with substituted Schiff bases of thiadiazolecould be a new prospect of compounds with anticipated biological properties and fascinating chemistry.

**Experimental Section**

All melting points were carried out in open capillary and are uncorrected. UV spectra were recorded on Systronics 119. $H^1$-NMR spectra were recorded on BruckerAvance 400 MHz spectrometer and recorded as chemical shift values (PPM) with reference to TMS as internal standard and DMSO/$CDCl_3$ as a solvent. FT-IR spectra were recorded on on Shimadzu 8110 S series. All compounds gave correct elemental analyses.

**Synthetic route**

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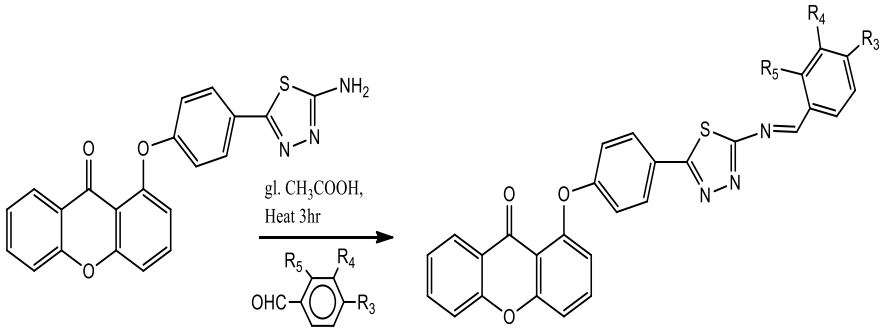
The synthetic route of targeted molecules 1-(4-(5-(substitutedbenzylideneamino)-1,3,4-thiadiazol-2-yl)phenoxy)-9H-xanthen-9-one **2a-d**has been depicted in figure 2.




**1** **2a-d**

**Figure 2.**Synthetic route of targeted molecules 1-(4-(5-(substitutedbenzylideneamino)-1,3,4-thiadiazol-2-yl)phenoxy)-9H-xanthen-9-one **2a-d**

**General procedure**

An equimolar mixture of 1-(4-(5-amino-1,3,4-thiadiazol-2-yl)phenoxy)-9H-xanthen-9-one **1** (0.01 mol), appropriately substituted benzaldehyde (0.01 mol) with glacial $CH_3COOH$ (10ml) in a 50 ml round bottom flask fitted with a water condenser was refluxed for 3hr. The reaction content was kept overnight and then poured in ice cold water. The solid separated out was filtered, washed several time with cold water and recrystallized from suitable solvent.

**1-(4-(5-(benzylideneamino)-1,3,4-thiadiazol-2-yl)phenoxy)-9H-xanthen-9-one 2a:**

Yield: 80%, Molecular Formula = $C_{28}H_{17}N_3O_3S$, Molecular weight = 475.51, m.p.112$^oC$. Elemental analysis: Found: C = 70.65, H = 3.58, N = 8.83, S = 6.76, Calc. C = 70.72, H = 3.60, N = 8.84, S = 6.74. UV-Vis (acetone-ethanol): 261nm (absorbance = 0.73) and 308 nm (absorbance = 0.81). FT-IR ($cm^{-1}$): 3071.79 and 3017.16 (Aromatic C-H stretch), 1660.81 (-C=O of xanthonic nucleus), 1611.25 (-C=N- stretch), 1557.12 and 1442.35 (C=C stretch of aromatic ring), 1249. 51 and 1032.41 (C-O-C of ether linkage), 800.64 and 751.27 (p-disubstituted aromatic ring), 694.55 (C-S stretch). $H^1$-NMR (δ): 7.15-8.07 (multiplet, Aromatic H), Mass: 475.1 ($M^+$).

**(E)-1-(4-(5-((2-hydroxybenzylidene)amino)-1,3,4-thiadiazol-2-yl)phenoxy)-9H-xanthen-9-one2b:** Yield: 75%, Molecular Formula = $C_{28}H_{17}N_3O_4S$, Molecular weight = 491.51, m.p.98$^oC$

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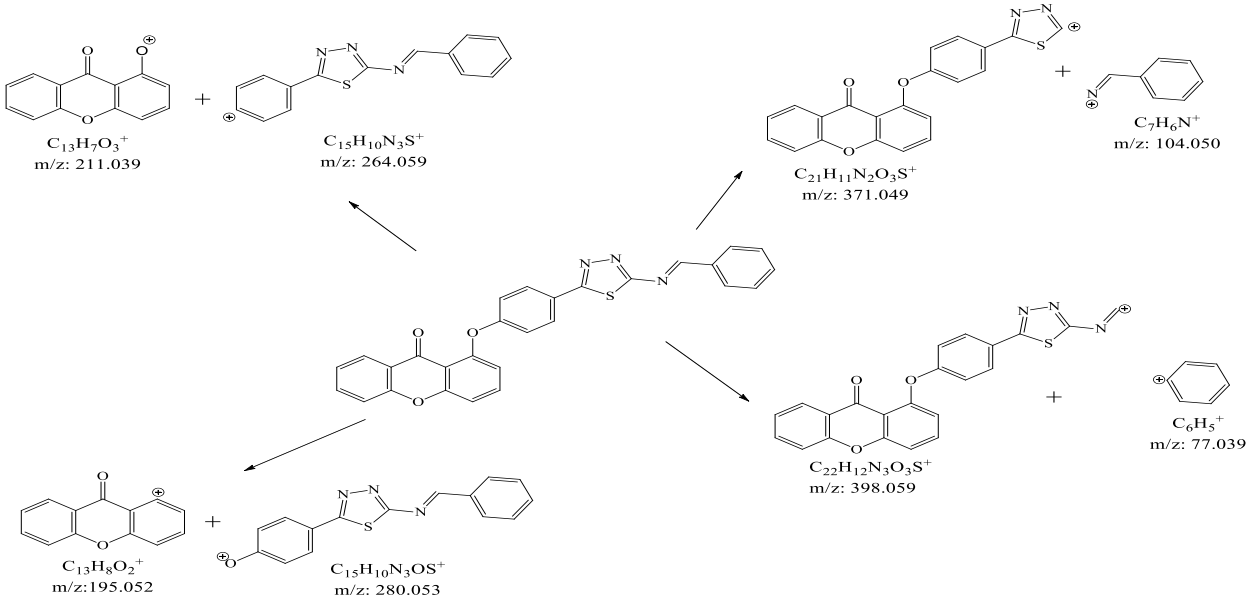
**(E)-1-(4-(5-((4-methoxybenzylidene)amino)-1,3,4-thiadiazol-2-yl)phenoxy)-9H-xanthen-9-one 2c:** Yield: 78%, Molecular Formula = $C_{29}H_{19}N_3O_4S$, Molecular weight = 505.54, m.p.142$^oC$

**(E)-1-(4-(5-((3-nitrobenzylidene)amino)-1,3,4-thiadiazol-2-yl)phenoxy)-9H-xanthen-9-one 2d:** Yield: 65%, Molecular Formula = $C_{28}H_{16}N_4O_5S$, Molecular weight = 520.51, m.p.176$^oC$

## Results and Discussion

The synthetic protocol (see figure 2) employed for the synthesis of the target molecules is highly eco-benign, easy and efficient ensuing in high yields. The compounds were characterized by spectral and elemental analyses. The Mass spectrum for **2a** exhibited peaks at 475.1 (Base peak 100% abundance), 398.06, 371.05, 280.05, 264.06, 211.04, 195, 188, 131, 104.05, 77.04, and 47. The fragmentation pattern can be depicted as following:




**Fragmentation pattern for 2a**

The PMR spectrum of the compound **2a** exhibited following chemical shifts, which have been correlated as following (see figure 3):

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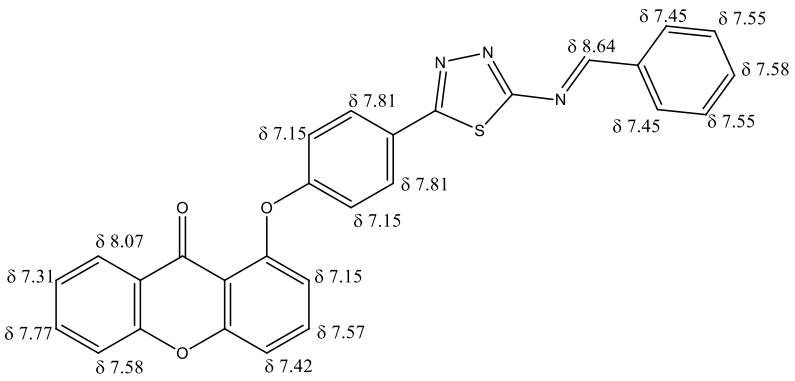


**Figure 3.**$H^1$-NMR chemical shift assignment to different protons

**Biological Evaluation:**

The newly synthesized compounds were screened against *E. coli, P. aerogenosa and S. aureus*. The standard protocol mentioned in the literature was followed to determine the anti-microbial efficacy of the compounds **2a-d** using Chloroamphenicol as a reference. The results have been summarized in Table 1.

**Table 1.**Antibacterial activity of synthesized compounds**2a-d**with zone of inhibition in mm

| **Sr. No.** | **Compound** | **Zone of inhibition(mm)** | | |
|---|---|---|---|---|
| | | ***E. coli*** | ***S. aureus*** | ***P. aerogenosa*** |
| | **Chloramphenicol** | 14 | 12 | 12 |
| 1 | **2a** | 13 | 13 | 10 |
| 2 | **2b** | 13 | 12 | 10 |
| 3 | **2c** | 13 | 10 | 10 |
| 4 | **2d** | 13 | 16 | 09 |

From table 1, it is evident that the test compounds **2a-d**possess good activity against *E. coli, P. aerogenosa*and *S. aureus*.

**Conclusion:**

In conclusion, an efficient, simple and economical protocol has been followed to synthesize new molecules bearing xanthone nucleus in combination with thiadiazole and Schiff's bases scaffolds. The route provides moderate to high yields of targeted compounds. The compounds exhibit good anti-bacterial activity against *E. coli*, *P. aerogenosa*and *S. aureus*.

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# Analytical studies on lubrication properties of different vegetable oils blends at different temperatures

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**ABSTRACT**

*Different vegetable oils viz. soybean oil, olive oil, almond oil, amla oil, castor oil, groundnut oil, cottonseed oil, coconut oil, sesame oil, sunflower oil, mustard oil were purchased from the local standard market. Different blends of vegetable oils were prepared in different proportions and lubrication properties like cloud point, pour point, flash point, fire point and % carbon residues were determined. From this study, it's found that given lubrication properties changes with changing vegetable oil blends. This study will help the lubricant producing industry to check out most ecofriendly, economical vegetable oil blends as industrial lubricant at lower as well as at higher temperatures.*

**Keywords:** Vegetable oils, lubricant, blends, ecofriendly, temperature

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## INTRODUCTION

Lubricants are most important products obtained from crude mineral oils. Lubricating oils have wide range of application including proper functioning of every machine, equipment and instrument. Lubricating oils aremainly known for their five essential functions like lubrication, coolant, carrier, protecting and sealant. Lubricating oil keeps parts of machine which touching each other and reduces friction of moving parts like bearings, etc. Zhang G. et al. [1]. As a coolant lubricating oil carries away the heat of friction and gas compression to keep machine at moderate temperature. Lubricating oil as a carrier removes wear particle and other particle in suspension results minimizing damage. These particle eventually removed by oil changes or filtration. As protectant, oil protects the machine from corrosion. Lubricating oil improve efficiency by creating deep ultimate vacuum in device like vacuum pumps. In lubricating market, most of the lubricants are made up from mineral oil. Lubricants made from mineral oil have many disadvantages after use. Itcauses environmental pollution like soil pollution, air pollution, water pollution etc. K.M. Talkit et al. [2]. Due to increasing use of mineral oil base lubricant leads to increasing concentration of greenhouse gases in atmosphere resulting in global warming effect. To minimize all given problems related to environment, worldwide lubricating industry has developing interest for the use of biolubricant. S. Kango et al. [3]. Vegetable oil base lubricant shows excellent biodegrability, low temperature stability, high viscosity index etc. due to all lubricating properties vegetable oils act as intimate substitute for mineral oil base lubricant. Many researchers have studied vegetable oil as industrial lubricants. L. A. Quinchia et al. [4]. An overview on cloud point extraction as sample preparation technique for trace element analysis was investigated by Nabil Ramdan Badera et al [5]. In this work, cloud point extraction, mechanism advantage, disadvantage and other some application have been discussed. Nadia Salih et al [6]. Carried study on biolubricant from chemically modified plant oil including

ricinoleic acid base tetraester. From the above research, it's found that these derivatives have good antiwear and friction reducing properties at relatively low concentration and simply used as biolubricant base stocks.]. A. Gohari, Ardabili, R. Farhoosh and M. H. Haddad Khodaparast [7]. Investigate Chemical Composition and Physicochemical Properties of Pumpkin Seeds (*Cucurbitapepo*Subsp. pepo Var. Styriaka) Grown in Iran. From this study it revealed that pumpkin seed oil could be used as biodiesel. Studies on flash point of lubricating oil including engine oil and recycle lubricating oil by acid/clay treatment, distillation/clay acid treatment and activated charcoal/clay treatment have been done by J.D. Uddon [8] and Ihsan Hamawand [9]. M.I. Oseni et al [10] was determined extraction and analysis of physical and chemical properties of yellow oleander oil as lubricant from the result obtained its proved that given oil can be used as lubricant in environmental sensitive areas including marine ecosystem and total loss of lubrication with associated positive environmental and economic impact. Recycling of used engine oil as industrial lubricant by composite solvent method, acid treatment method and single solvent method was investigated by Rashid Abro et al [11]. From result obtained shows that by using this methods flash point, viscosity, pour point, specific gravity and ash percentage was improved and best result was shown by composite solvent method. O. G. Lgbum et al [12]. Studied variables in characteristics of methyl ester obtained from four virgin tropical seed oil in Nigeria. Performance of C.I. engine by using biodiesel prepared from mahuna seed oil investigated by sudhirnandi [13]. From the given study, it's proved that mohuna seed oil biodiesel could be used as economical biodiesel. From the above literature review, it's confirmed that lubrication properties of vegetable oils can beenhanced by using various methods. In the present research work, one such attempt has been made to evaluate lubrication properties of vegetable oil blends to find out such blends which show better lubrication properties at lower as well as higher temperatures.

## MATERIALS AND METHODS

### 2.1 Test oils

In the measurement of lubrication properties, test vegetable oils used in this work were soybean oil, olive oil, almond oil, amla oil, castor oil, groundnut oil, cottonseed oil, coconut oil, sesame oil, sunflower oil and mustard oil and their blends in different proportion. During blending process soybean oil blends with other oils stirred continuously to ensure uniform mixing.

### 2.2Flash point and fire point measurements

**Flash point of soybean oil and their blends with other vegetable oils was determined by clevends open cup flash point apparatus**

The experimental procedure involves following steps:

1. Thoroughly clear and dry the oils
2. Fill the cup with sample so that the top of miniscus is exactly at the filling marks. If too much is added removed by pipetting.
3. Place the cup on heating stove and insert the thermometer in a vertical position with the bottom of bulb 0.4 mm from bottom of cup.
4. Light the test flame by adjusting the gas flow. Adjust it 3.2 to 4.8mm diameter.
5. Switch on heater and adjust regulator for heating such that temperature rise of sample is $15^0$c per minute.
6. Record the flash point as the temperature when first flash appears at any point on the surface of oil.
7. In order to find out the fire point continue heating at the rate of $5^0$c to $6^0$c per minute.
8. Continue application of test flame as before until the oil emits and continues to burn for at least 5 second.
9. Record this temperature as fire point of oil.

### 2.2Cloud point measurements

**Cloud point of soybean oil and their blends with other vegetable oils was determined by Cloud Point apparatus**

The experimental procedure involves following steps

1. Bring the test oil to a temperature at least $14^0$c above the expected cloud point.
2. In order to remove any moisture present in the sample, add preheated anhydrous sodium sulphate 1gm/50ml of sample. Keep like that at least for 10minutes and then filter through ordinary filter paper.
3. Pour this clean oil sample in to test jar to the level mark (5157 mm).
4. Tightly close the test jar by cork carrying test thermometer in vertical position in center jar with thermometer bulb resting on bottom of jar.
5. Place the disc in the bottom of jar and insert the test jar with ring gasket 25mm from bottom in jacket.

6. Maintained the temperature of cooling bath at $-1^0$c to $+2^0$c by wing crushed ice and water as cooling mixture.
7. After every $1^0$c fall in temperature remove the test jar from jacket.
8. When oil does not show a cloud when cooled to $-7^0$c, place jar in third bath maintained at $-26^0$c with crystal ice and $cacl_2$ crystal for maintaining very low temperature both solid $CO_2$ and acetone or petroleum naphtha may use up to $-57^0$c.
9. When such inspection shows distinct cloudiness or haze at bottom of test jar record the reading of thermometer as cloud point.

**2.3 Pour point measurements**

**Pour point of soybean oil and their blends with other vegetable oils was determined by Pour Point apparatus**

The experimental procedure followed by following steps

1. Pour the oil in to test jar to height between 5-5.7 cm.
2. Close the jar with cork carrying test thermometer in vertical position with the bulb immersed about 3mm below surface of the oil.
3. Heat the oil sample to $46^0$c without stirring and cool in air to $35^0$c if expected pour point between $+32^0$c and $-34^0$c.
4. If expected pour point is above $32^0$c heat the oil sample to $46^0$c or to a temperature approximately $8^0$c above expected pour point.
5. If expected pour point is below $-34^0$c heat the oil without stirring to $46^0$c and cool to $16^0$c.
6. Place the disc in the bottom of jacket and insert the test jar with ring gasket 25mm from bottom in jacket bath at -1 to $2^0$c by using crushed ice and water only as cooling mixture.
7. Beginning at the temperature $12^0$c above the expected pour point remove the test jar from jacket carefully, after ever $3^0$c fall in temperature.
8. If the oil has not ceased to flow when temperature reached to $9^0$c. Place the jar in second cooling bath maintained at $-18^0$c to $-15^0$c with crushed ice and sodium chloride crystals and if necessary to third bath maintained at $-26^0$c with crushed ice and sodium chloride crystal.
9. Continue the test in this manner till a point is reached when oil shows no movement when test jar is held in horizontal position for this is freezing point of oil.
10. Pour point is $3^0$c more than freezing point.

**2.4 % Carbon residue measurements**

**% Carbon residue of soybean oil and their blends with other vegetable oils was determined by Condrason carbon residue apparatus**

The experimental procedure followed by following steps

1. Weigh the clean and dry crucible with two glass head
2. Weight about 10gm of the sample to the nearest 5gm.
3. Place this crucible in the center of skidmore crucible.
4. Level the sand in the largest sheet iron crucible and set the skidmore crucible in the center of the iron crucible.
5. Place the cover to the both skidmore and iron crucible.
6. Keep the crucible resting on the wire triangle which is supported on the tripod stand.
7. Cover the whole thing with iron hood.
8. Heat the burner adjusts the flame so that the preignition period is 10 ± 1.5 minute.
9. When smoke appear above the chimney move the burner to ignite vapour.
10. The period of burning the vapour is ± 13 minutes.
11. After the vapour ceases to burn heat the crucible to red heat for 7 minutes.
12. Remove the burner for cool the apparatus

$$\% \text{ Carbon residue} = \frac{A \times 100}{W}$$

Where, A= Weight of carbon residue in grams

W= Weight of sample in gram

**Table 1 Shows cloud point, pour point, flash point, fire point and %carbon residue of different vegetable oils blends**

| Sr. No. | Test Sample | Mixture Ratio | Cloud Point | Pour Point | Flash point | Fire Point | % Carbon Residue |
|---|---|---|---|---|---|---|---|
| 1 | Soybean oil + Olive Oil | 10+90 | $-6^0$c | $-15^0$c | $327^0$c | $358^0$c | 0.3723% |
| 2 | Soybean oil + Almond Oil | 90+10 | $-10^0$c | $-22^0$c | $286^0$c | $330^0$c | 0.6309% |
| 3 | Soybean oil + Amla Oil | 10+90 | $-5^0$c | $-7^0$c | $324^0$c | $352^0$c | 0.5271% |
| 4 | Soybean oil + Castor Oil | 10+90 | $-11^0$c | $-15^0$c | $318^0$c | $332^0$c | 3.3764% |
| 5 | Soybean oil + Groundnut Oil | 10+90 | $-5^0$c | $-10^0$c | $342^0$c | $355^0$c | 0.7942% |
| 6 | Soybean oil + Cottonseed Oil | 30+70 | $-6^0$c | $-14^0$c | $322^0$c | $344^0$c | 1.3683% |
| 7 | Soybean oil + Coconut Oil | 90+10 | $-5^0$c | $-19^0$c | $326^0$c | $342^0$c | 0.7653% |
| 8 | Soybean oil + Sesame Oil | 10+90 | $-4^0$c | $-13^0$c | $332^0$c | $348^0$c | 0.7372% |
| 9 | Soybean oil + Sunflower Oil | 70+30 | $-7^0$c | $-16^0$c | $334^0$c | $358^0$c | 1.2219% |
| 10 | Soybean oil + Mustard Oil | 20+80 | $-5^0$c | $-18^0$c | $328^0$c | $345^0$c | 0.6626% |

## RESULTS AND DISCUSSION

### 3.1 Cloud point

Cloud point denotes as temperature at which crystallization of solid occur in the form of cloud when oil is cooled at specified rate in standard apparatus. Cloud point expresses low temperature stability of lubricating oil. From the above table shows that soybean castor oil blend possesses lower cloud point due to presence of large number of saturated fatty acid while soybean sesame oil blend possesses higher cloud point due to presence of more polyunsaturated fatty acid.

### 3.2 Pour point

Pour point is denoted as temperature at which oil is just ceases to flow when cooled at specified rate in standard apparatus. From above table and figure it's found that soybean almond oil blend possesses low pour point increasing cis unsaturation or low molecular weight fatty acid while soybean amla oil blend possesses high pour point due to increasing high molecular weight fatty acid.

### 3.3 Flash point

Flash point of oil expressed as minimum temperature at which oil gives sufficient vapours to ignite momentarily when a flame of standard dimension brought near the surface of oil for a prescribed rate in apparatus of specified dimension. From above table it's found that soybean groundnut oil blend shows high flash point due to presence of more unsaturation in fatty acid while soybean castor oil blend possesses low flash point due to presence of volatile matter andmore free fatty acid molecule.

### 3.4 Fire point

Fire point of oil expressed as minimum temperature at which oil give sufficient vapours to ignite momentarily at least 5 seconds when a flame of standard dimension brought near the surface of oil for a prescribed rate in apparatus of specified dimension. From the above table and figure it's found that soybean olive oil blend possesses high fire point while soybean almond oil blend possesses low fire point than remaining vegetable oil blends. High fire point of given blend due to more stability of triglyceride at high temperature and low amount of free fatty acid form after heating. Low fire point of given blend due to more amount of free acid form after heating occur due to large degradation of triglyceride in to free fatty acid.

### 3.5 % Carbon residue

Carbon residue expressed in terms of percentage carbon that is left on evaporating known quantity of fuel under specified condition in specified apparatus. Carbon residue occurs mainly due to byproducts of fuel and lubricants. It's mainly related to percentage of free fatty acid, glyceride, and polyunsaturated fatty acid. From the above table and figure it's found that % carbon residue of soybean amla oil blend is lower while soybean castor oil blend is higher than other vegetable oil blends. Lower carbon residue due to decreasing amount of free fatty acid, glyceride and polyunsaturated fatty acid in given oil blends while % carbon residue increases due to increasing same.

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# Synthesis of (e)-1-(5-chloro-2-hydroxy-4-methylphenyl)-3-(4-bromophenyl)prop-2-en-1-one and 4-chloro-5-methyl-2-(5-(4-bromophenyl)-4,5-dihydro-1H-pyrazol-3-yl)phenol and its derivatives

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***Abstract*—** In continuation of earlier work, the simple and efficient protocol was adopted to synthesize bromo-pyrazoline derivatives. The synthetic protocol instigates with acetylation of properly substituted phenol **1a**, subsequently, Fries migration was performed to afford substituted acetophenone **2a**. The product **2a** was then treated with appropriately substituted aromatic aldehyde to afford the corresponding chalcone **3a**. The chalcone **3a** was then reacted with hydrazine hydrate to provide 1H-pyrazoline **4a** and its derivatives **4b-d** using acetylation, benzoylation and nitrosoation in moderate to high yields. The structures of the intermediate **1a**, **2a**, **3a, and** pyrazolines **4a-d** were established using chemical reactivity, elemental and spectral analyses.

***Keywords-*** *Bromo substituted Chalcone, Pyrazoline, synthesis, IR, PMR*

*****

## I. INTRODUCTION *(HEADING 1)*

The chemistry of heterocyclic molecules is integral part of modern organic chemistry. The knowledge and applications of heterocyclic molecules have been widely accepted and continued in the field of catalysis, reagents, medicines, dyes, polymers, etc. [1-4]. Heterocyclic molecules encompassing multiple heteroatoms are important compounds in pharmaceutical, agronomy and other fields for synthesis of a range of compounds with various applications and preferred activity. Nirogen heterocycles viz. pyrazoles, imidazoles, etc. have expanded the horizons of heterocyclic chemistry and are at prime consideration and high regard of researchers due to their therapeutic properties like anti-cancer, anti-HIV, anti-inflammatory, etc., a few to mention [5-12, 14]. Recently, Bandgar *etal* highlighted the various methods of synthesis and applications of pyrazoline derivatives as anti-inflammatory and anti-oxidants [13].

From the literature survey [1-7], it has been found that bromo substituted chalcones have never been employed for the synthesis of respective pyrazolines using simple reported method. Therefore, in the present work, the synthesis of pyrazolines has been accomplished following a simple yet very efficient route, reported earlier. The emphasis in the present work is on expanding the utility of earlier synthetic protocol for easily scalable and competent route for bromo derivatives of pyrazolines.

**Experimental section:** All the chemicals were of analytical grade and used as supplied. The m.p. were recorded in an open capillary and are uncorrected. The FT-IR spectra were recorded on Agilent Spectrophotometer and reported in $cm^{-1}$. The PMR were recorded in DMSO-d6 using TMS as an internal standard and reported in ppm.

**Synthesis of chalcone 3a** [1-8]**:** Appropriately substituted acetophenone 2a (0.01 mol) and bromobenzaldehyde (0.012 mol) were dissolved in ethanol (20 ml), then the mixture was brought to boiling. To this hot solution, NaOH (0.03 mol) was added with constant stirring and solution was kept overnight. The sodium salt obtained was decomposed by aq. HCl (1:1) in cold condition. The yellow solid obtained was filtered, washed with $NaHCO_3$ (2%) and then with water. The product was crystallized from ethanol to get yellow crystal of (E)-1-(5-chloro-2-hydroxy-4-methylphenyl)-3-(4-bromophenyl)prop-2-en-1-one **3a**. Yield: 80%, m.p.: 142°C. FT-IR ($cm^{-1}$): 3432 (presence of free –OH group), 1644 (-CO- in conjugation with -C=C-), 1584 (-C=C- moiety), 1051 and 1071 (aromatic C-Cl and C-Br stretch), 815, 795 and 737 (presence of substituted benzene ring). PMR (δ): 12.46 (phenolic -O**H**), 2.35 and 2.54 (-C**H** = C**H**-), 6.91-8.28 (multiplet, aromatic C**H**)

**Synthesis of pyrazoline 4a** [1-8]**:** The chalcone **3a** (0.01 mol) and hydrazine hydrate (0.012 mol) in 20 ml ethanol was refluxed for 2 hr, and the mixture was then concentrated. On cooling, the resulting solid was filtered, and crystallized from ethanol. Yield: 80%, m.p.: 200°C. FT-IR ($cm^{-1}$): 3300 (broad –OH and -NH ($2^o$ amine)), 3062 (aromatic C-H stretch), 1609 (-C=N- of pyrazoline), 1589 (aromatic C=C), 1437 (-$CH_2$- of pyrazoline ring), 1063 and 1071 (aromatic C-Cl and C-Br stretch), 820, 791, and 735 (substituted benzene ring). PMR (δ): 11.80 (phenolic –O**H**), 1.08 (-C**H**$_3$), 2.31 (-C**H**$_2$), 4.80 (-N**H**) and 6.86-8.31 (multiplet, aromatic C**H**).

**Synthesis of 4b-d pyrazoline derivatives** [4-9]**:**

**Synthesis of 4b:** A mixture of **4a** (0.01 mol) and acetic acid (10 ml) was refluxed for 2 hr. On cooling, the resulting solid was filtered, and crystallized from ethanol. Pale yellow solid. Yield: 75%, m.p.: 280°C.

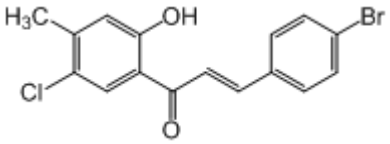
**Synthesis of 4c:** An equimolar mixture of **4a** (0.01 mol) and benzoyl chloride was dissolved in dry pyridine (10 ml) and stirred at room temperature for 1 hr. The reaction mixture was treated with cold dil HCl (2N). The resulting solid was filtered, washed with water, cold NaOH (2N) and again with water. The crude solid was crystallized from ethanol to give brownish-yellow solid. Yield: 75%, m.p.: 180°C.

**Synthesis of 4d:** A mixture of **4a** (0.01 mol) was dissolved in ice cold 2 ml HCl (1:1) and cooled to 0°C and 10% $NaNO_2$(6

ml) was added dropwise with constant stirring. The mixture was stirred for 30 minutes at room temperature. The resulting solid was crystallized from ethanol to afford the yellowish solid. Yield: 75%, m.p.: 268°C.

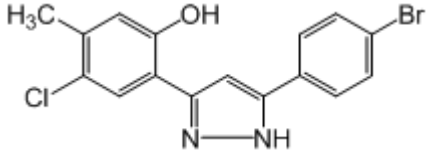
**Results and discussion:** The synthesis of targeted pyrazolines **4a-d** commenced with the acetylation of appropriately substituted phenol **1a**, followed by Fries migration employing the literature method to afford substituted acetophenone **2a**. The next step comprises reaction of **2a** with substituted benzaldehyde in the presence of NaOH in ethanol as solvent to provide corresponding substituted chalcone **3a**. In the further step, the chalcone **3a** was condensed with hydrazine hydrate to give 1H-pyrazoline **4a**, which was then converted to **4b-d**. The synthesis scheme adopted in the present work has been depicted in figure 1.

The FT-IR of **3a** showed an absorption signal at 3432 indicating the presence of free –OH group. The signal at 1644 could be assigned to -CO- in conjugation with -C=C-. The presence of -C=C- moiety is indicated by the signal at 1584. The signal at 1071 indicates the presence of aromatic C-Br stretch. The peaks at 815, 795 and 737 point the presence of substituted benzene ring. The PMR spectrum of **3a** is with a peak at 12.46 indicating the presence of phenolic –O**H**. The peaks at 2.35 and 2.54 were correlated with -C**H** = C**H**-. The multiplet at 6.91-8.28 indicates the presence of aromatic C**H**. In addition, **3a** decolorized the bromine water and gave red colour with $FeCl_3$, thus it contains unsaturation and phenolic –OH group. On the basis of elemental analysis, chemical reactivity and spectral data (FT-IR and PMR), the compound **3a** was assigned the following structure:



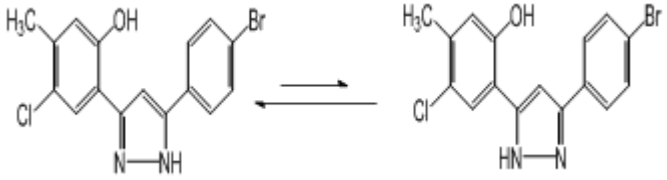

**3a**

The FT-IR of **4a** showed a broad absorption signal at 3300 specifying the presence of –OH and -NH (2° amine) groups. The peak at 3062 is due to the aromatic C-H stretch. The presence of -C=N- moiety of pyrazoline is indicated by the signal at 1609. The 1437 peak indicates the presence of $-CH_2-$ moiety present in the pyrazoline ring. The signals at 1071 and 1009 arose due to the aromatic C-Br and C-Cl stretch, respectively. The peaks at 820, 791, and 735 point the presence of substituted benzene ring. The PMR spectrum of **4a** is with a peak at 11.80 indicating the presence of phenolic –O**H**. The peak at 1.08 is indicative of $-CH_3$. The peaks at 2.31 can be assigned to $-CH_2$. The -N**H** proton gave peak at 4.80. The multiplet at 6.86-8.31 indicates the presence of aromatic C**H**. In addition, **4a** gave red colour with $FeCl_3$, thus it contains phenolic –OH group. On the basis of elemental analyses, chemical reactivity and spectral data (FT-IR and PMR), the compound **4a** was assigned the following structure:




**4a**

Interestingly, the PMR of **4a** revealed additional peaks, which might have arose due to the plausible tautomerism as depicted below:




| *Sr.No.* | *Compound* | *Percent yield (%)* | *Melting point(°C)* |
|---|---|---|---|
| *1* | 3a | 80 | 142°C |
| *2* | 4a | 80 | 200°C |
| *3* | 4b | 75 | 280°C |
| *4* | 4c | 75 | 180°C |
| *5* | 4d | 75 | 268°C |

**Table 1.** List of synthesized compounds, their melting points and percent yield

## II. CONCLUSION

In conclusion, the earlier reported procedure is very efficient synthetic protocol for the synthesis of bromo-chalcone and bromo-pyrazoline involving use of effortlessly available starting materials and reaction conditions. The reaction provides good yields and scalable, also.

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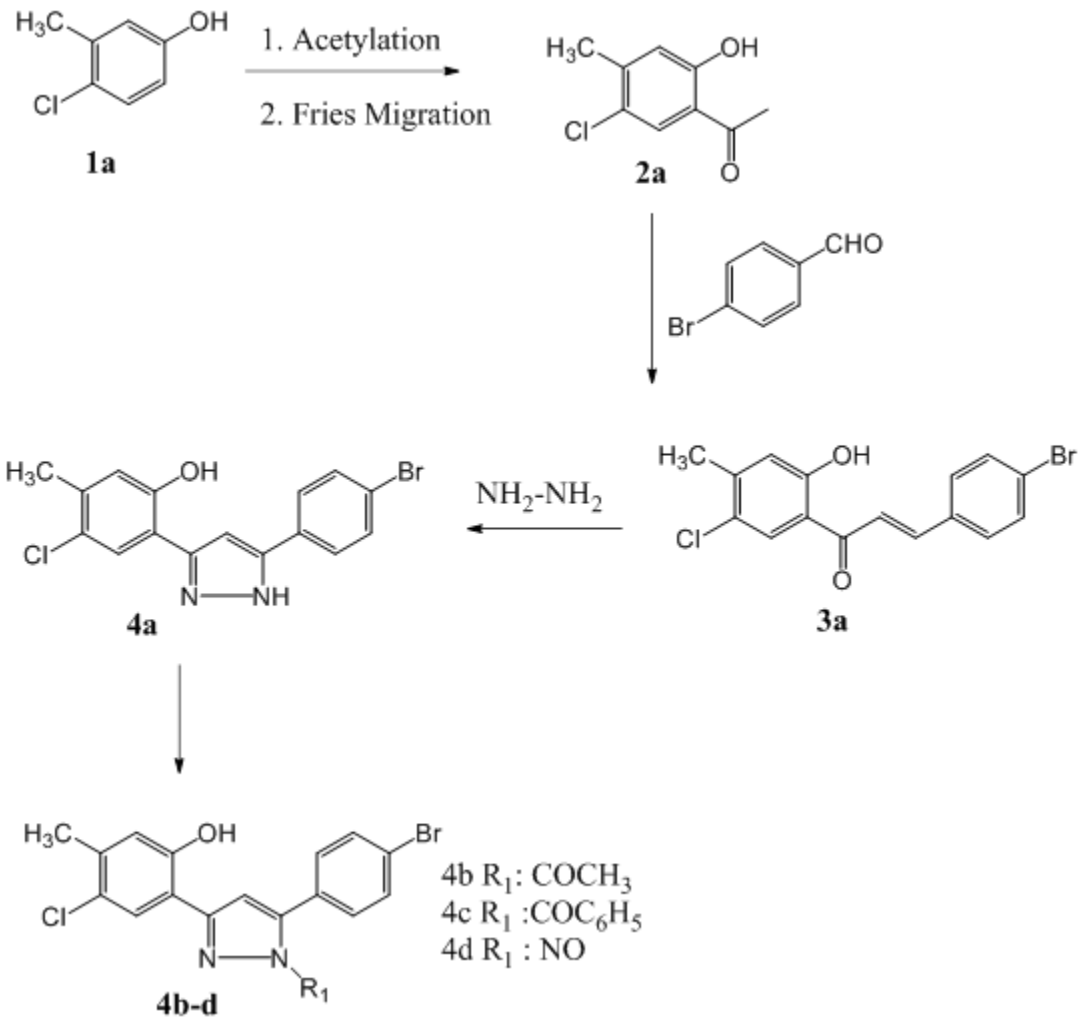


**Figure 1.** Synthetic scheme used in the present work for the synthesis of bromo substituted pyrazolines

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# Synthesis, Characterization and Antimicrobial screening of some Azo compounds derived from Ethyl vanillin

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## Abstract

***Azo compounds were synthesized in excellent yield by diazotization of some substituted aromatic amines using $NaNO_2$ and concentrated HCl followed by coupling with ethyl vanillin in alkaline medium. These azo compounds were characterized by FTIR and $H^1$ NMR spectroscopic technique and have been tested against the growth of five gram positive and negative microorganisms in order to assess their antimicrobial activity.***

**Keywords:** Azo compounds, ethyl vanillin, diazotization, antimicrobial activity.

## Introduction

Azo compounds are mostly used as dyes due to its various applications in the fields such as textile fibres, colouring of different materials, biomedical studies and organic synthesis[1-2]. The azo dyes containing azo linkages have advanced applications in high technology areas like lasers[3], LCD color filters[4]. In addition to this, azo dyes were reported to have variety of biological applications like antineoplastics, antidiabetics, antiseptics, anti-inflammatory and other useful chemotherapeutic agents[5-8]. Scarlet red and diamazon are the most commonly used azo dyes which are antiseptics. Several azo compounds derived from thymol[9], aspirin[10], paracetamol[11], m-cresol[12], resorcinol[13] and vanillin[14] moieties have been frequently reported and exhibit excellent biological properties. In the present work, we have synthesized four azo compounds derived from ethyl vanillin and characterized by FTIR and $H^1$ NMR spectral technique. The antimicrobial potential of synthesized azo compounds of ethyl vanillin has been tested against the growth of five gram positive and negative microorganisms using agar well diffusion method.

## Material and Methods

In the present synthesis, chemicals and reagents used were of analytical grade, Merck and Alfa Aesar Company Ltd. The azo compounds were characterized by FTIR and $H^1$ NMR spectroscopic techniques. The Perkin-Elmer spectrum One FTIR instrument was used for characterization of IR spectra in the form of KBr pallet. Bruker Avance II 400 MHz NMR spectrometer was used for characterization of $H^1$ NMR spectra of azo compounds using $CDCl_3$ as a solvent and TMS as an internal standard. The purity of all the compounds was checked by thin layer chromatography and were recrystalised from hot ethanol. The melting points were measured by open capillary method and they are uncorrected.

**Procedure for the synthesis of azo compounds[9-10]:** Aromatic amines (0.01 mole) were mixed with 2.5 ml of concentrated HCl. To this resultant solution, 25 gm of crushed ice and 2.5 ml of $NaNO_2$ (4N) was added with constant stirring. The temperature of the reaction mixture was kept constant up to 0-$5^0$C. The diazonium salt solution prepared was added to the alkaline solution of ethyl vanillin drop by drop with constant stirring for 10-25 minutes at constant temperature of 5-$10^0$C. The colored precipitate given out was filtered and washed with water number of times. The colored product was recrystallised from hot ethanol. The general reaction scheme for synthesis of azo compounds of ethyl vanillin is shown in figure-1.

**Antimicrobial Activity:** The azo compounds 1a-d were analysed for their antibacterial activity against five gram positive and negative pathogens viz. ***Escherichia coli, Pseudomonas aeroginosa, Salmonella typhi, Bacillus subtilis and Staphylococcus aureus*** by using agar well diffusion method[15-16]. These compounds were mixed in DMSO to form solutions of concentration 1mg/ml. Sterile discs were dipped in this solutions, dried it and placed on nutrient agar plates spreaded with the bacteria. The plates were further incubated for 24 to 48 hours at $37^0$C and the diameters of zones of inhibition were measured in millimeter.

## Results and Discussion

The data of synthesized azo compounds of ethyl vanillin (i.e. symbols, compounds name, molecular formulae, molecular weights, melting points and percentage yield) are given in table-1. The FTIR and $H^1$ NMR spectroscopic data of synthesized azo compounds are illustrated in table-2 and are shown in figure-6 to 13. A total four azo compounds of ethyl vanillin have been synthesized, recrystalised and used separately to study its antimicrobial activity against five gram positive and negative microorganism's viz. ***Escherichia coli, Pseudomonas aeroginosa, Salmonella typhi, Bacillus subtilis and***

***Staphylococcus aureus***. The data on antimicrobial activity of azo compounds of ethyl vanillin 1a-d against five pathogens are presented in table-3. From the results it was observed that the azo compounds of ethyl vanillin have showed miraculous antibacterial potential against all five pathogens. The compound 1a showed 10.4 and 9.6 mm zones of inhibition against the test pathogens ***Escherichia coli*** and ***Staphylococcus aureus*** respectively as shown in figure-2 and do not showed any inhibitory action against ***Salmonella typhi***, ***Pseudomonas aeroginosa and Bacillus subtilis.*** The azo compound 1b showed 10.6, 12.7, 11.8 and 9.8 mm zones of inhibition against the test pathogens ***Escherichia coli, Salmonella typhi, Bacillus subtilis*** and ***Staphylococcus aureus*** respectively shown in figure-3 but do not showed any inhibitory action against ***Pseudomonas aeroginosa.*** The azo compound 1c showed 10.3, 13.1, 13.5 and 12.8 mm zones of inhibition against the pathogens ***Escherichia coli, Salmonella typhi, Bacillus subtilis*** and ***Staphylococcus aureus*** respectively as shown in figure-4 but do not showed any inhibitory action against ***Pseudomonas aeroginosa.*** The azo compound 1d showed 13.6, 12.8, 15.6 and 14.4 mm zones of inhibition against the test pathogens ***Escherichia coli, Salmonella typhi, Pseudomonas aeroginosa*** and ***Staphylococcus aureus*** as shown in figure-5. Compound 1d showed 11.3 mm zone of inhibition against the pathogen ***Bacillus subtilis.***

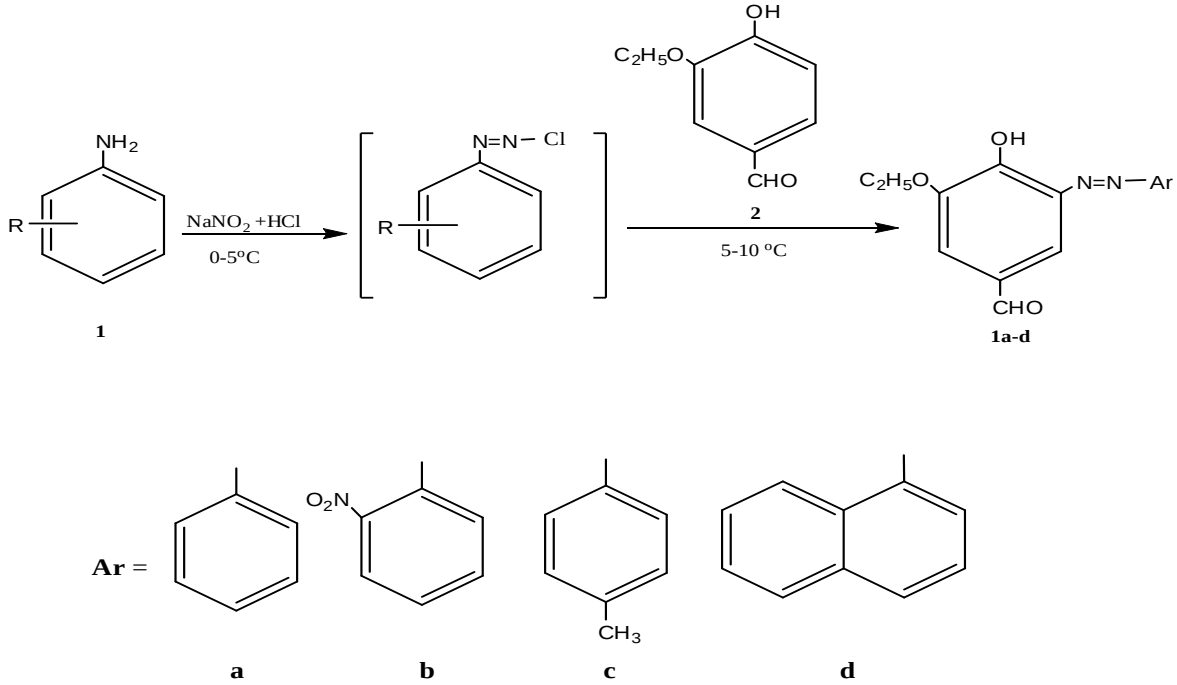



**Figure-1**
**The general reaction scheme for synthesis of azo compounds of ethyl vanillin**

**Table-1**
**The symbols, compounds name, molecular formulae, molecular weights, melting points and percentage yield of synthesized azo compounds of ethyl vanillin**

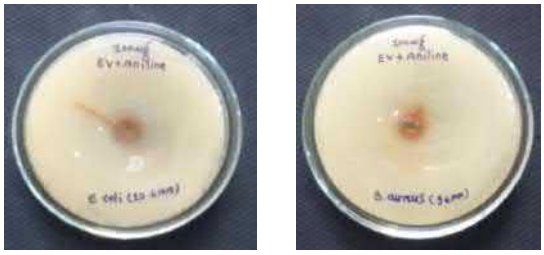
| Symbols for antimicrobial activity | Symbols for FTIR and $H^1$ NMR | Compounds Name | Molecular Formulae | Molecular Weights | Melting points ($^0$C) | Yield (%) |
|---|---|---|---|---|---|---|
| 1a | 4P | 3-ethoxy-4-hydroxy-5-(phenyldiazenyl)benzaldehyde | $C_{15}H_{14}N_2O_3$ | 270.28 | 67 | 67 |
| 1b | 4Q | 3-ethoxy-4-hydroxy-5-((2-nitrophenyl)diazenyl)benzaldehyde | $C_{15}H_{13}N_3O_5$ | 315.28 | 128-130 | 65 |
| 1c | 4R | 3-ethoxy-4-hydroxy-5-(p-tolyldiazenyl)benzaldehyde | $C_{16}H_{16}N_2O_3$ | 284.31 | 64 | 72 |
| 1d | 4S | 3-ethoxy-4-hydroxy-5-(napthalen-1-yldiazenyl)benzaldehyde | $C_{19}H_{16}N_2O_3$ | 320.34 | 127-129 | 80 |

**Table-2**
**FTIR and $H^1$ NMR data of synthesized azo compounds of ethyl vanillin**

| Symbols for compounds | Types of spectra | FTIR and $H^1$ NMR spectral data |
|---|---|---|
| 4P | FTIR (KBr,$cm^{-1}$) | 3362 (OH of Phenol), 2829 (C-H of H-C=O), 1686 (C=O), 1516 (C=C), 1255 (C-O), 1280 (C-N), 1579 (N=N). |
| | $H^1$ NMR (δ ppm) | 1.4 (t, 3H of -$CH_3$), 4.2 (q, 2H of -$OCH_2$), 6.2 (s, 1H of Phenolic -OH), 9.8 (s, 1H of -CHO), 7.0 to 7.5 (m, 7H of Aromatic-H). |
| 4Q | FTIR (KBr,$cm^{-1}$) | 3398 (OH of Phenol), 2882 (C-H of H-C=O), 1673 (C=O), 1519 (C=C), 1262 (C-O), 1232 (C-N), 1590 (N=N). |
| | $H^1$ NMR (δ ppm) | 1.5 (t, 3H of -$CH_3$), 4.4 (q, 2H of -$OCH_2$), 4.2 (s, 1H of Phenolic -OH), 9.8 (s, 1H of -CHO), 7.0 to 8.5 (m, 6H of Aromatic-H), 9.9 due to moisture. |
| 4R | FTIR (KBr,$cm^{-1}$) | 3363 (OH of Phenol), 2828 (C-H of H-C=O), 1681 (C=O), 1514 (C=C), 1281 (C-O), 1168 (C-N), 1580 (N=N). |
| | $H^1$ NMR (δ ppm) | 1.5 (t, 3H of -$CH_3$), 4.3 (q, 2H of -$OCH_2$), 6.3 (s, 1H of Phenolic -OH), 9.8 (s, 1H of -CHO), 7.0 to 7.4 (m, 6H of Aromatic-H). |
| 4S | FTIR (KBr,$cm^{-1}$) | 3333 (OH of Phenol), 2842 (C-H of H-C=O), 1682 (C=O), 1515 (C=C), 1261 (C-O), 1231 (C-N), 1592 (N=N). |
| | $H^1$ NMR (δ ppm) | 1.5 (t, 3H of -$CH_3$), 4.1 (q, 2H of -$OCH_2$), 4.3 (s, 1H of Phenolic -OH), 9.8 (s, 1H of -CHO), 7.0 to 8.5 (m, 9H of Aromatic-H). |

**Table-3**
**Antimicrobial activities of the synthesized azo compounds of ethyl vanillin**

| Symbols for compounds | Microbial species and diameter of zone of inhibition in mm | | | | |
|---|---|---|---|---|---|
| | ***Escherichia coli*** | ***Salmonella typhi*** | ***Pseudomonas aeroginosa*** | ***Bacillus subtilis*** | ***Staphylococcus aureus*** |
| 1a | 10.4 | No inhibition | No inhibition | No inhibition | 9.6 |
| 1b | 10.6 | 12.7 | No inhibition | 11.8 | 9.8 |
| 1c | 10.3 | 13.1 | No inhibition | 13.5 | 12.8 |
| 1d | 13.6 | 12.8 | 15.6 | 11.3 | 14.4 |



***E. coli*** ***S. aureus***

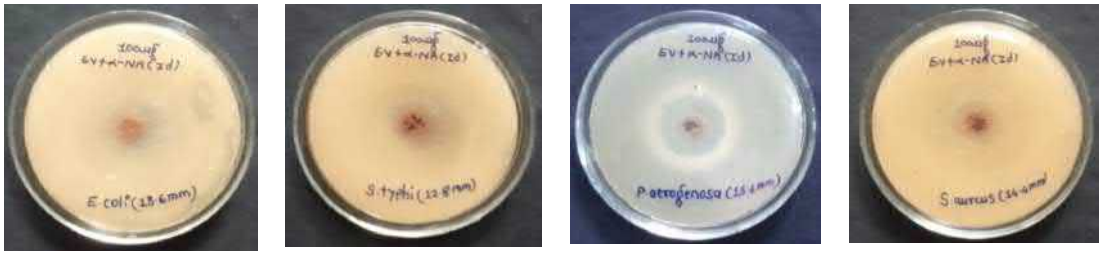
**Figure-2**
**Zone of inhibition of azo compound 1a**

***E. coli*** ***S. typhi*** ***B. subtilis*** ***S. aureus***

**Figure-3**
**Zone of inhibition of azo compound 1b**

***E. coli*** ***S. typhi*** ***B. subtilis*** ***S.aureus***

**Figure-4**
**Zone of inhibition of azo compound 1c**



***E. coli*** ***S. typhi*** ***P. aeroginosa*** ***S.aureus***

**Figure-5**
**Zone of inhibition of azo compound 1d**

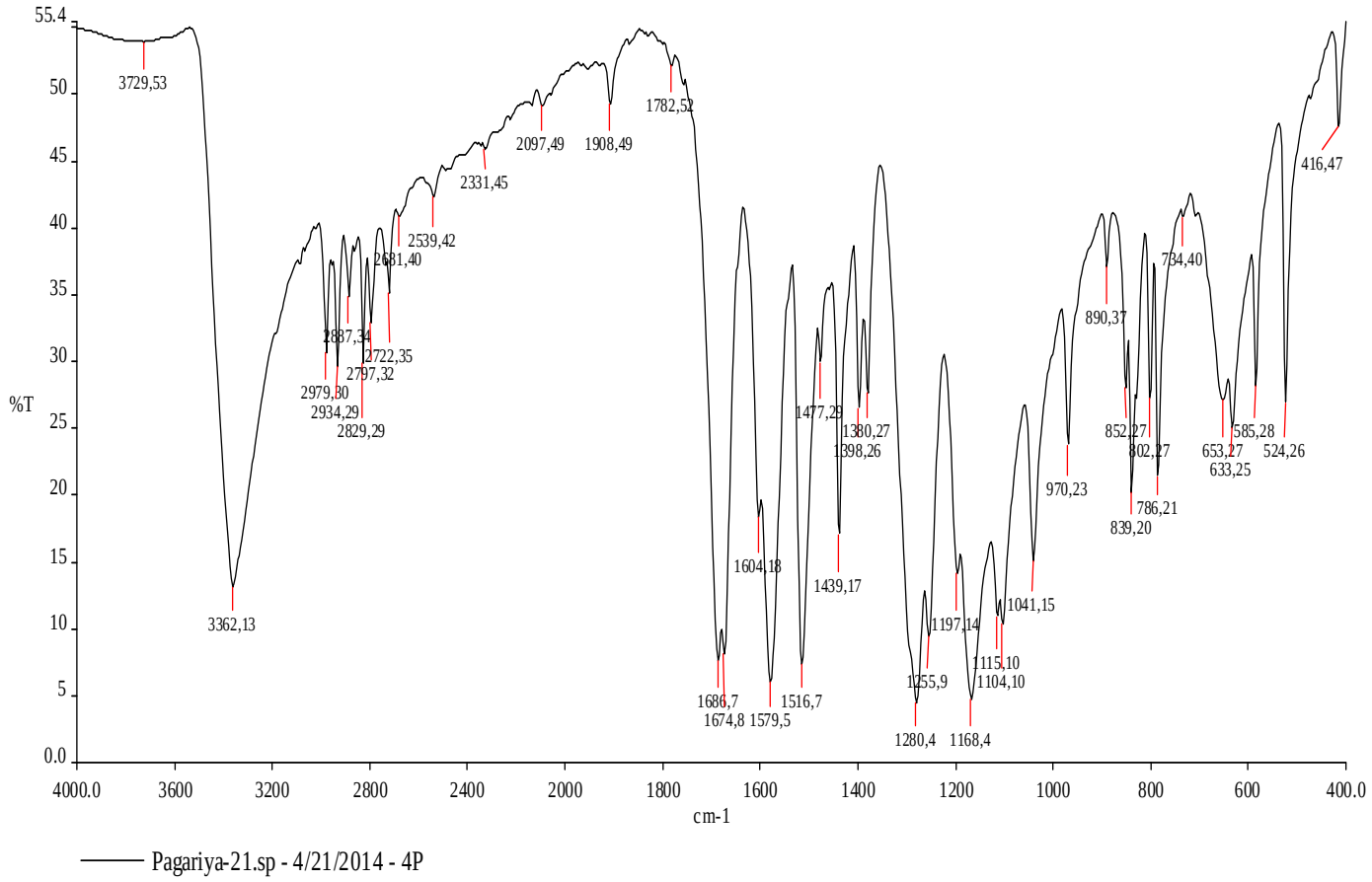



**Figure-6**
**FTIR spectrum of azo compound 1a**

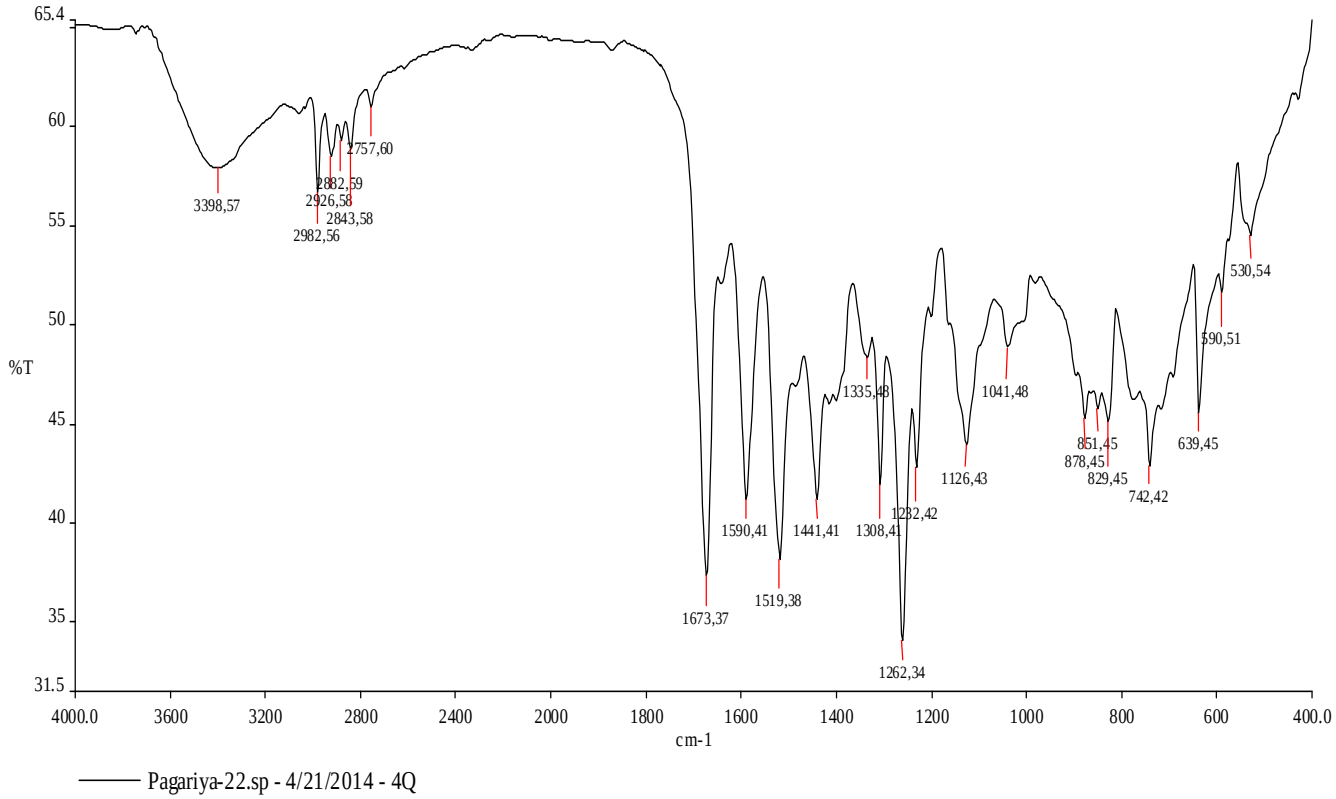



**Figure-7**
**FTIR spectrum of azo compound 1b**

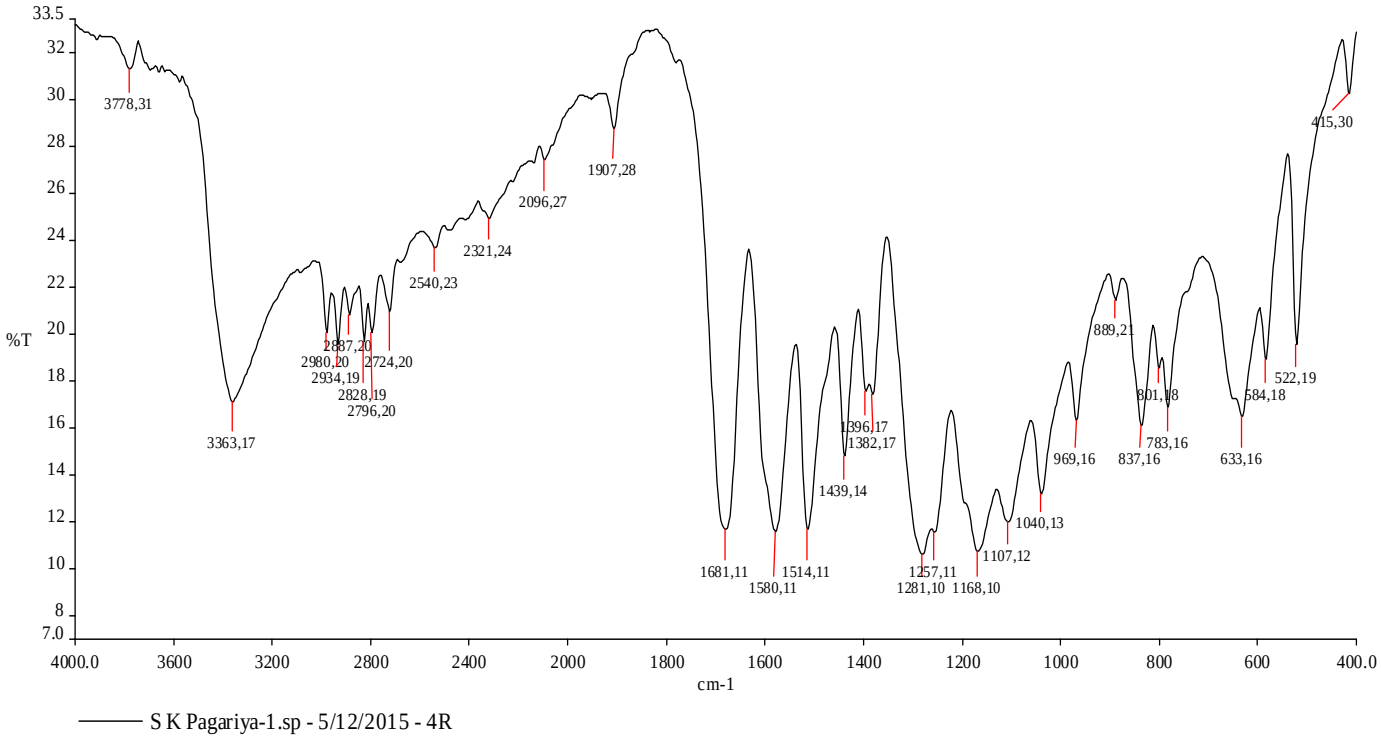



**Figure-8**
**FTIR spectrum of azo compound 1c**

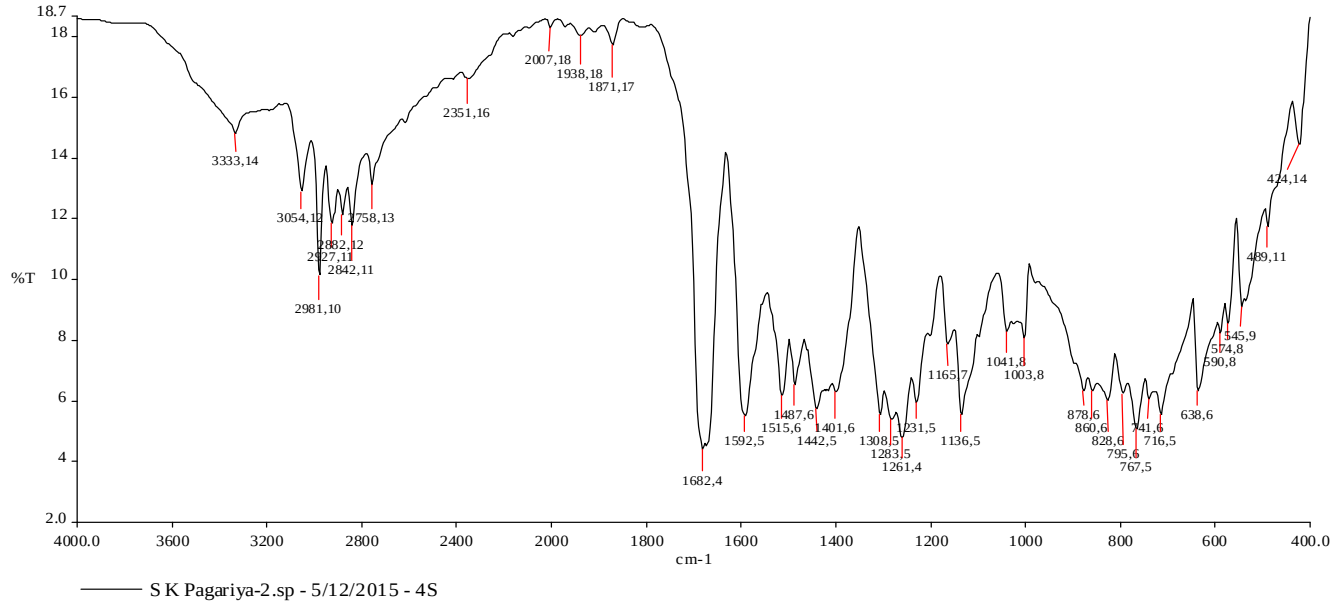



**Figure-9**
**FTIR spectrum of azo compound 1d**

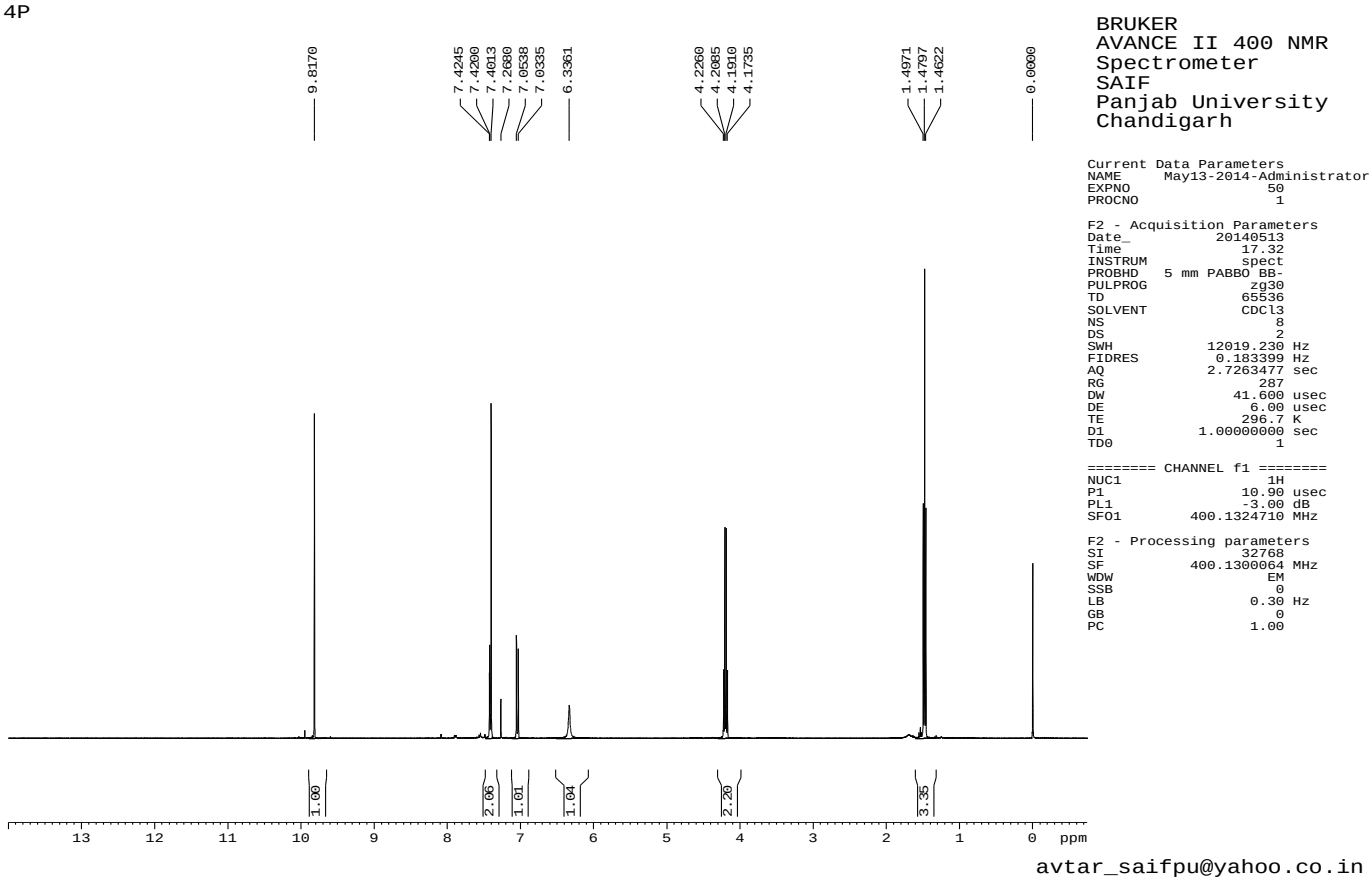



**Figure-10**
**$H^1$ NMR spectrum of azo compound 1a**

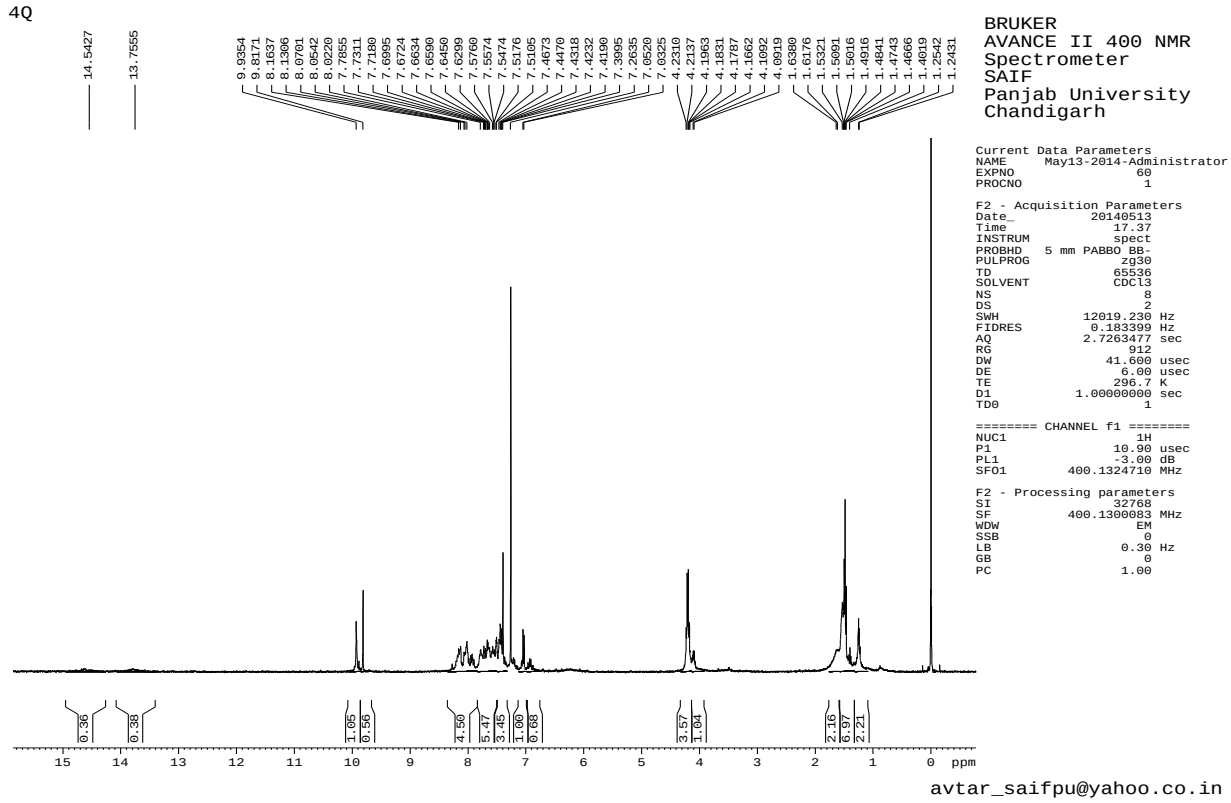



**Figure-11**
**H[1] NMR spectrum of azo compound 1b**

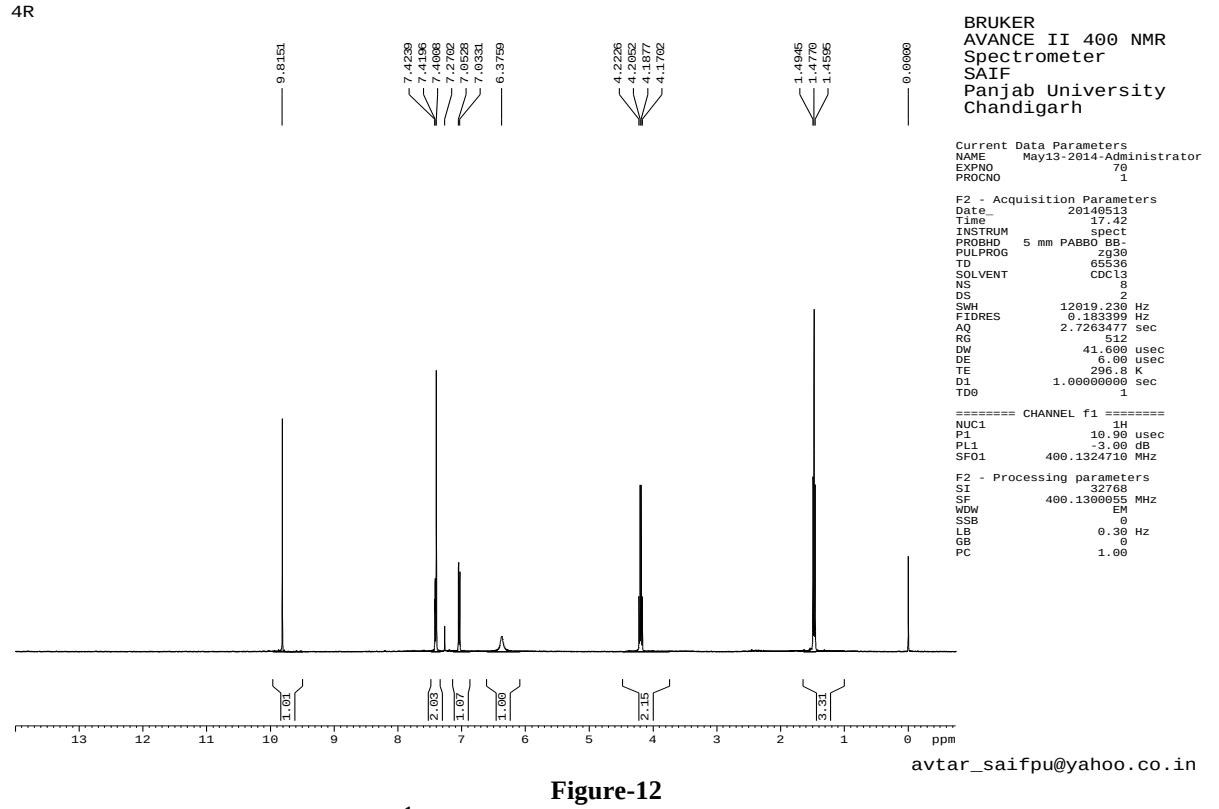



**Figure-12**
**H[1] NMR spectrum of azo compound 1c**

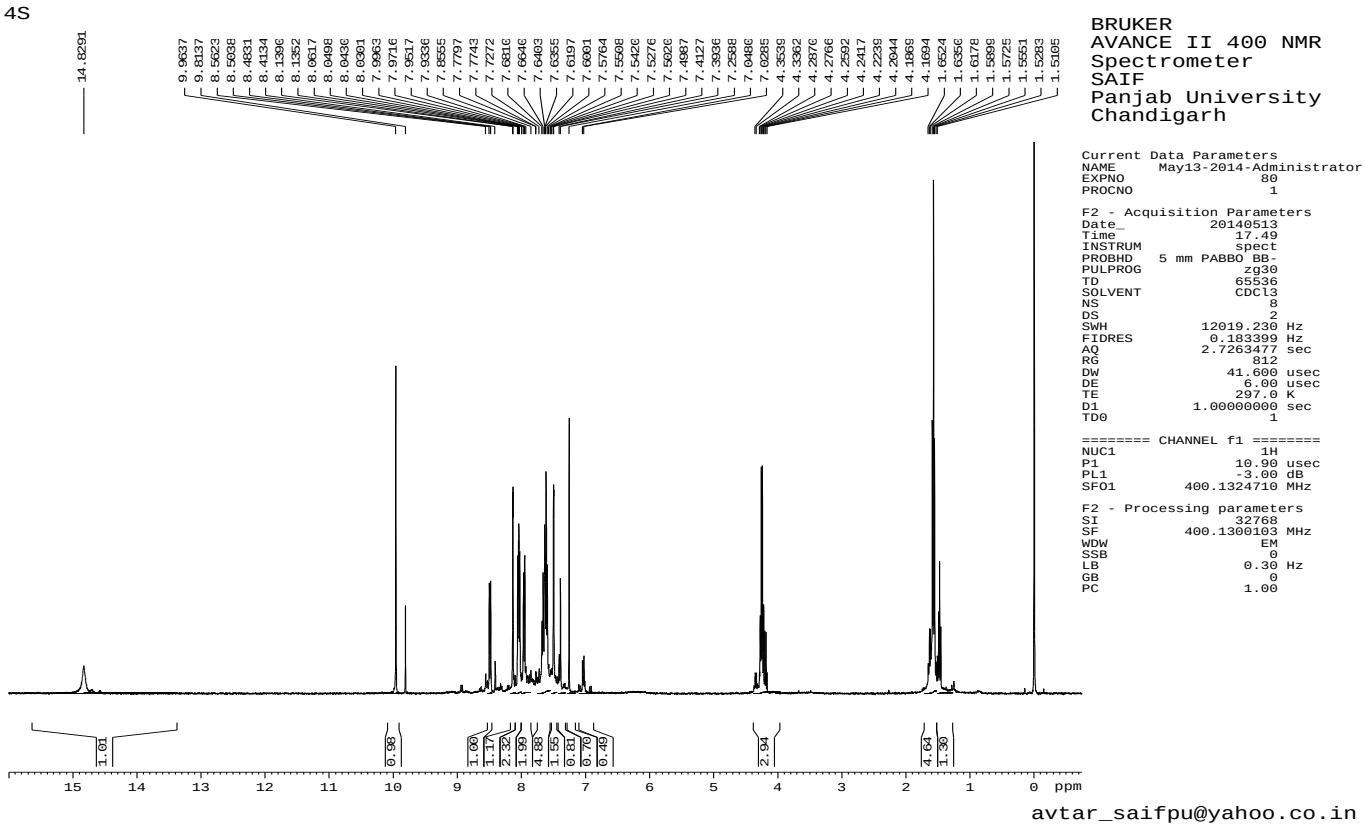



**Figure-13**
**H[1] NMR spectrum of azo compound 1d**

## Conclusion

The current investigation reveals that, there was a miraculous inhibition of compound 1d shows antibacterial activity against all the tested organisms while the compound 1a was found to be most resistant by the pathogens. The highest zone of inhibition was obtained for 1d against ***Pseudomonas aeroginosa*** (15.6 mm) while lowest zone was recorded for 1a against ***Staphylococcus aureus*** (9.6 mm). The compounds 1b and 1c shows moderate inhibition of growth against tested pathogens.

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# EFFECT OF SYSTEMIC FUNGICIDE BENLATE (BENOMYL) ON SEEDLING GERMINATION AND GROWTH IN *ALLIUM CEPA* L.

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## ABSTRACT

The seeds of *Allium cepa* L.Var.N-53 were selected and used for following research. The healthy, untreated and uniform seeds were treated with different concentration of benlate (0.02%, 0.04%, 0.06% and 0.08%) for 3, 6, 9, 12 hours treatment periods. Germination parameters like seed germination percentage, seedling height and root length were studied. All three parameter revealed gradual decrease from lower doses to higher doses in given treatments of fungicides benlate.

**KEYWORDS:** **Fungicide, *Allium cepa*, Seed Germination, Seedling Height, Root Length.**

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## INTRODUCTION

The use of systemic chemicals against harmful organisms of crop plants is an accepted application at the present time. Nowadays many modern pesticides are in use all over the world; among them, systemic fungicides are extensively used in agriculture. Benlate are systemic fungicides used for the control of diseases such as smut, grey mold, leaf spot, brown patch, downy mildew, powdery mildew, and rust in wheat[1]. In benomyl the active ingredient is benlate WP and benlate DF (Du Pont) is especially effective because it penetrates plants better than carbendazim (MBC: methyl 2-benzimidazolecarbamate), its fungitoxic breakdown product[2]. Despite its enormous application, priority should be given to the possible side effects of these chemicals on non-targeted host (plant). There are many reports where the application of benlate produced chlorosis and irregular depression at the central and the marginal portion of saffron leaves[3]. Triarimol inhibits the seedling growth of pea[4] now there are many reports about side effect of benomyl on different plants system. Carbendazim delays senescence in wheat (*Triticum aestivum* L.)[5]. Benomyl show cytokinin-like activity in soyabean (*Glycine max* L.) callus, radish (*Raphanus sativus* L.) cotyledons[6]. Benomyl was also phytotoxic. Benomyl reduced the growth of cucumber (*Cucumis sativus* L.)[7]. American elm (*Ulmus americana* L.)[8]. Due to its cytokinin like structure benomyl was found sometimes to promote the growth of the treated plants[9].Which could be attributed to some positive alterations in plant metabolism[10]. Due to these two beneficial characteristiscs, benomyl deserves to be intensively studied. Thus the aim of the present work was to obtain additional information concerning its effects on some seedling germination and growth of *Allium cepa* L.

## MATERIALS AND METHODS

Healthy and dry seeds of untreated *Allium cepa* L var. N-53 were obtained from National Horticultural Research and Development Foundation (NHRDF) Chittagong, Nasik. Seeds (1,500) were pre-soaked in tap water for 6 hours and then treated with four different concentrations (0.02%, 0.04%, 0.06%, 0.08% ) of benlate fungicide for 3, 6, 9 and 12 hours. The pretreatment soaking, treatment and post-treatment germination was carried out at REMI growth chamber conditions of temperature 28$\pm$ $2^{O}$ C, photoperiod of 16 hours having 45 *m*mole $m^{-2}$ $S^{-1}$ illumination provided by cool white fluorescent tubes. The temperatures of the chamber were maintained according to International Seed Testing Association (ISTA 2008)[11] standard, throughout the germination period. Three replicates of each concentration were performed twice. The germination percentage, seedling height and root length (longest root) in cms was recorded on the $7^{th}$ day. Germination percentage calculates by Rehman[12]. Root and shoot length of seedlings were recorded using the standard centimeter scale Kabir[13]. The percentage of inhibition was calculated using formula described by Sundra and Pote[14].

## RESULTS

In seed germination concentration of 0.02%, when used for 3 and 6 hours durations, appeared to be less effective dose and hence showing higher percentage of germination (75% each). As against this, 9 and 12 hours durations of treatments with the same dose it was more inhibitory (68 and 52%). Similar situation appeared in connection with 0.04% concentration where treatment at 3 and 6 hours duration was less effective (84 and 76% germination). In the case of 0.06% concentration, with the increase in duration it was from 68 to 51%. This reduction was from 57-48% in the case of 0.08% concentration. Thus, 0.08% concentration dose was seen to be more effective than 0.06% dose. Benlate had moderate action at 0.02% concentration. At 0.04% concentration it was the least effective for 3 and 6 hours duration and moderate at 9 and 12 hours duration. With the exception of 9 hours at 0.06% and of 12 hours at 0.08% concentration, it was a moderately effective fungicide. It was only the pesticide which showed inducing effect on root length; at 3 hours treatment at 0.02% concentration having 7.67 cms root length in relation to the control, 7.51 cms. The root length 7.43 cms on 6 hours treatment was almost equal to that of control, indicating negligible inhibition i, e 1.07%. From 9 hours onwards, the activity of benlate seemed to produce some good effects. It was for the first time, that at 9 hours treatments, 19.31% inhibition was noted with 6.06 cms root length. The root length was further reduced to 5.70 cms (24.11% inhibition) at 12 hours (Table I). At 0.04% concentration there was duration dependent reduction from 3 to 12 hours. Increase in duration from 9 to 12 hours did not show any significant retarding effect on root length. This was evident from a meager difference of 0.17 cms between the two values. The same trend was maintained at 0.06% treatment i.e; the decrease from 4.43 to 2.72 cms root lengths with the increase in duration from 3 to 12 hours. The treatment at 0.06% concentration revealed two noteworthy points, - 1) the shortest root length 2.72 cms recorded a 12 hours treatment 2) The values of root length at 3 hours (4.43 cms) and 12 hours (2.72 cms) indicated exactly 62.79% inhibition with an increase from 3 to 12 hours durations (Table I). The values of root lengths for 3 to 12 hours treatment were 3.09, 2.86 cms 3.27 and 2.75 cms respectively, and indicated that 12 hours was the most effective duration at 0.08% concentration. Benlate revealed the least effective for 3 and 12 hours duration and moderate at 6 and 9 hours treatment at 0.02% concentration. From 0.04 to 0.08% concentrations, it was the least effective fungicide for all the durations of treatment. At 0.06% with 3 hours treatment, 4.43 cms root length revealed 48.40% inhibition than that of control, 7.51 cms. The root length recorded at 0.02%, with 6 hours treatment was 7.43 cms in comparison with 4.02 at 0.06% , 6 hours duration revealing 46.48%

inhibition (Table-I). It exhibited dose dependant inhibition of length over 0.02 to 0.08% concentrations at all four duration i.e. at 3 hours, 7.67-3.09 cms, 6 hours, 7.43-2.86 cms 9 hours, 6.06-3.27 cms and 12 hours, 5.70-2.75 cms. This revealed the significance of all 4 concentrations in benlate treatment in above respect. A duration dependant decrease in root length i.e. from 7.67 to 5.70 cms at 0.02% from 5.13 to 3.43 cms at 0.04% and from 4.43 to 2.72 cms at 0.06% was noticed with increasing duration from 3 to 12 hours. At 0.02% concentration with 3 hours duration there was a stimulating effect of 1.23 cms over that of the average seedling height in control (17.56 cms). At the same time there was 7.43% inducing effect seen in the growth of the treated seedlings. The statement is based on the assumption that the control seedlings growth was 100 %. At 6 hours there was also an inducing effect but it was marginal (0.14 cms) i,e; it showed an inducing effect of only 0.84% growth in the treated seedlings as compared to that of control (Table I). It was noted that instead of having an inducing effect as recorded earlier, 9 and 12 hours treatments were inhibitory to the seedlings. The height which was reduced to 15.66 cms with 10.83% growth inhibition at 9 hours had gone down to 13.77 cms with 21.59% inhibition at 12 hours duration. At 0.04%, the trend in the reduction in the seedling height was 12.42 > 8.10> 7.12> 7.08 cms with the increasing duration from 3 hours to 12 hours. Identical values of height at 9 and 12 hours showed that there was no impact of rise in duration by three hours. At 0.06% concentration also, there was a dose related reduction in the seedling height from 8.96 to 4.62 cms with the increase in duration from 3 to 12 hours. One important feature of 0.06% concentration for 12 hours treatment was that it exhibited the most retarding effect on the seedling height among all the benlate treatments. Very small differences in the values of the seedling heights (0.11, 0.54, 0.15 cms) showed that there was very little impact of 3 and 6 hours, 6 and 9 hours and 9 and 12 hours respectively ,on the inhibiting power of 0.08 % treatment. Benlate exhibited the least effectiveness for 9 and 12 hours treatment at 0.02% concentration. At 0.04%, it was a moderate fungicide except for the duration of 3 hours. At 0.06 and 0.08% concentration, it was a moderate fungicide in total. It was thrice the least effective at 0.04% to 0.08% concentration. At 0.06% 3 hours the seedling height was 8.96 cms with 48.98% inhibition in relation to 17.56 cms at control. The height at 0.02/9 hours treatment i.e. 15.66 cms was reduced to 7.89 cms with 55.07 % inhibition at 0.06% concentration with 6 hours treatment. At all four concentration there was a duration dependant decrease in height from 3 to 12 hours at 0.02% (from 18.79 to 13.77 cms); 0.04% (from 12.42 to 7.08 cms) 0.06% (from 8.96 to 4.62 cms); and 0.08% (from 6.39 to 5.59 cms). This indicated importance of all four durations from 3 to12 hours in Benlate treatment in this regard (Table I).

## DISCUSSION

Seed germination is an important parameter used to measure the response of plant to mutagenic treatments[15].The percentage of germination may reflect the reaction rate of plant seeds to their living environment[16]. In the present work, after 6 hour treatment with 0.08% concentration of fungicide benlate, the germination was lowered down to 52% from 87% in control. According to Gordon[17], the inhibition in seed germination might be due to inhibition of auxin synthesis in mutagen treated seeds. Reduction in germination due to mutagenic treatment has been explained due to delay or inhibition in physiological and biological processes necessary for seed germination which include enzyme activity, hormonal imbalance and inhibition of mitotic activity[18,19]. Seedling height is widely used as an index for determining the biological effects of various mutagens[20]. After 6 hour treatment, 7.09 cms and 5.27 cms height were recorded at 0.04% and 0.08% in comparison to control, 17.56 cms. The study by Heisy[21] proposed that exposure of plants to fungicide create chemical stress facilitating the production of compounds that are potential inhibitor of germination and seedling growth. Baig[22] investigated the effect of glyphosate applications on seedling growth of *Pisum sativum*. Root length is another important parameter used to test mutagen sensitivity. Ratsch[23] concluded that inhibition of root elongation was a valid and sensitive indicator of environmental toxicity. Benlate inhibit of root growth due to the breakdown product n-butylamine, which can reduce root growth of *Hyoscyamus alba* and *Datura stramonium*[24].

**Figure 1**
***Effect of fungicide benlate on seed germination (%) in Allium cepa L. in $M_1$ generation***

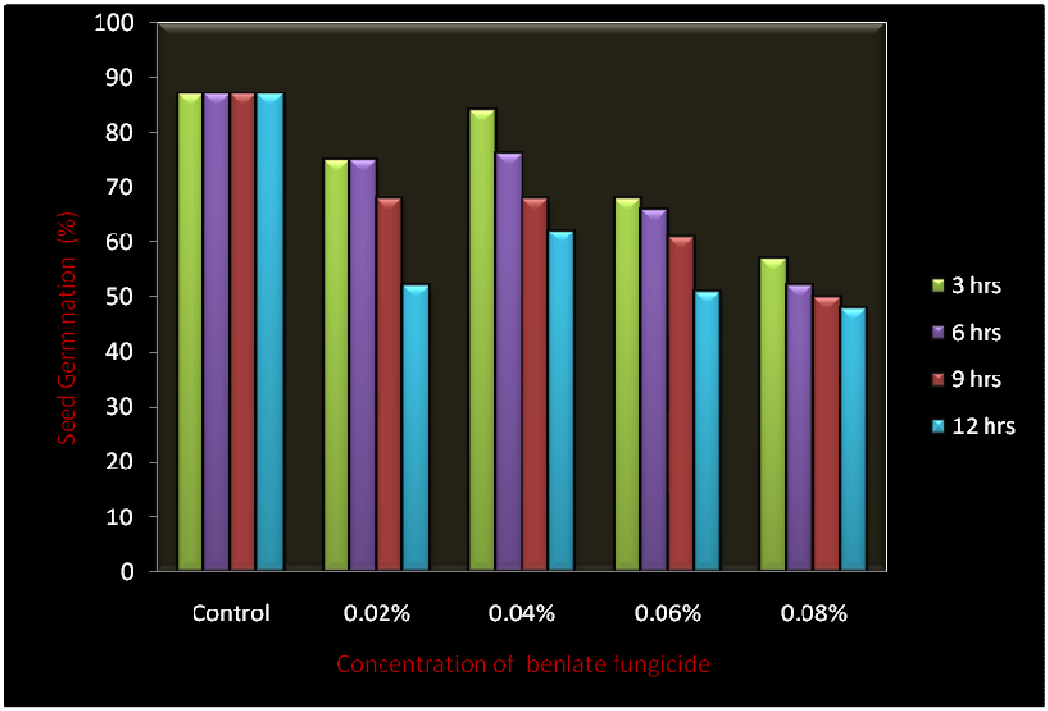


**Figure 2**
***Effect of fungicide benlate on percentage seedling height in Allium cepa L. $M_1$ generation***

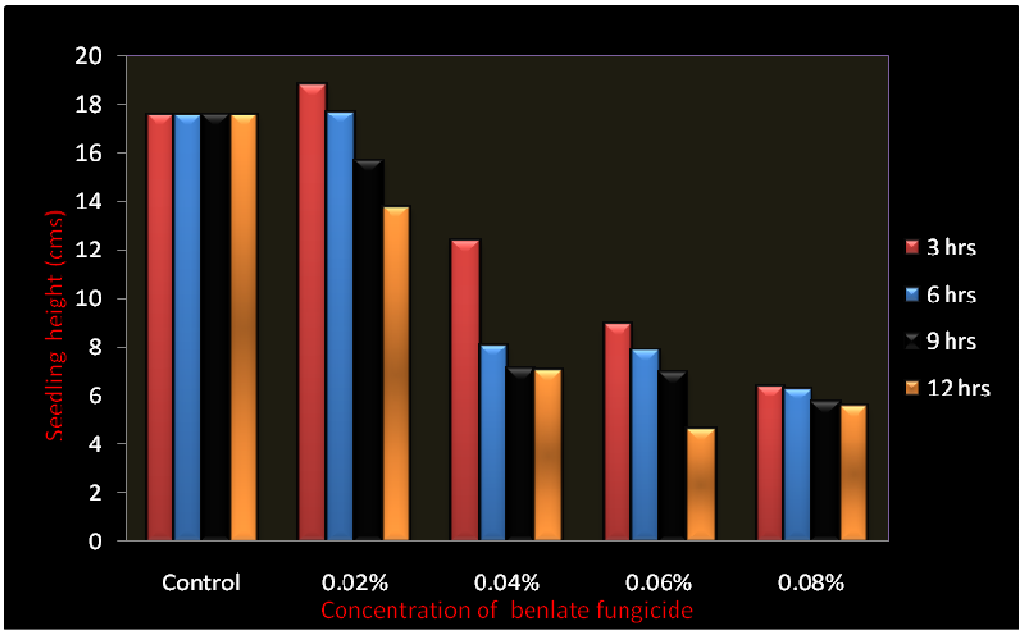

**Figure 3**
***Effect of fungicide benlate on percentage root length in Allium cepa L. in $M_1$ generation***

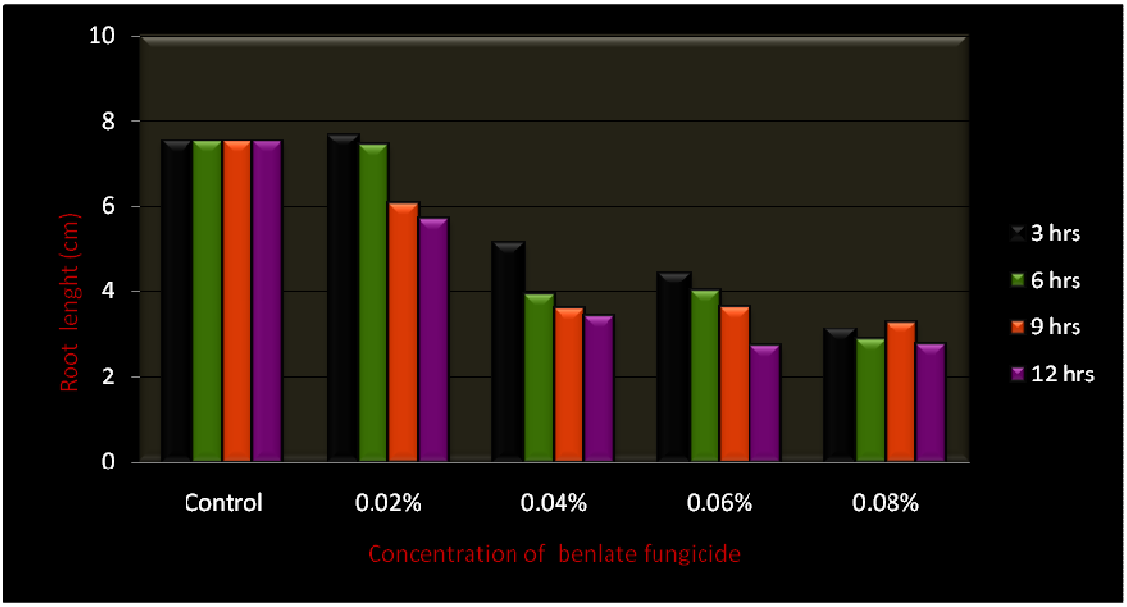


**Table 1**
***Effect of benlate fungicide on percent of seed germination, Root Growth Inhibition (R.G.I.) Seedling Growth Inhibition (S.G.I.) in Allium cepa L.***

| Concentration of fungicide | Duration of treatment (hrs) | (%) of S.G.(cms) | R.L. (cms) | R.G. | R.G.I | S.H. | S.G. | S.G.I |
|---|---|---|---|---|---|---|---|---|
| 0.02% | 0 | 87.00 | 7.51 | 100.0 | N.D | 17.56 | 100.0 | N.D |
| | 3 | 75.00 | 7.67* | 102.13* | N.D | 18.79* | 107.00 | N.D |
| | 6 | 75.00 | 7.43 | 98.93 | 1.07 | 17.70 | 100.79 | N.D |
| | 9 | 68.00 | 6.06 | 80.69 | 19.31 | 15.66 | 89.17 | 10.83 |
| | 12 | 52.00 | 5.70 | 75.89 | 24.11 | 13.77 | 78.41 | 21.59 |
| 0.04% | 0 | 87.00 | 7.51 | 100.0 | N.D | 17.56 | 100.0 | N.D |
| | 3 | 84.00 | 5.13 | 68.30 | 31.70 | 12.43 | 70.72 | 29.28 |
| | 6 | 76.00 | 3.97 | 52.86 | 47.14 | 8.10 | 46.12 | 53.88 |
| | 9 | 68.00 | 3.60 | 47.93 | 52.07 | 7.12 | 40.54 | 59.46 |
| | 12 | 62.00 | 3.43 | 45.67 | 54.33 | 7.08 | 40.31 | 59.69 |
| 0.06% | 0 | 87.00 | 7.51 | 100.0 | N.D | 17.56 | 100.0 | N.D |
| | 3 | 68.00 | 5.43 | 58.98 | 41.02 | 8.96 | 51.02 | 48.98 |
| | 6 | 66.00 | 4.02 | 53.52 | 46.48 | 7.89 | 44.93 | 55.07 |
| | 9 | 61.00 | 3.64 | 48.46 | 51.54 | 6.97 | 36.69 | 60.31 |
| | 12 | 51.00 | 2.72 | 36.21 | 63.79 | 4.62 | 26.30 | 73.07 |
| 0.08% | 0 | 87.00 | 7.51 | 100.0 | N.D | 17.56 | 100.0 | N.D |
| | 3 | 57.00 | 3.09 | 41.45 | 58.86 | 6.39 | 36.38 | 66.49 |
| | 6 | 52.00 | 2.85 | 38.08 | 61.92 | 6.28 | 35.76 | 67.15 |
| | 9 | 50.00 | 3.27 | 43.54 | 56.46 | 5.74 | 32.68 | 70.41 |
| | 12 | 48.00 | 2.75 | 36.61 | 63.39 | 5.59 | 31.83 | 71.32 |

***O-Control, * -Stimulating effect, R.L-Root Length, R.G-Root Growth, R.G.I. -Root Growth Inhibition, S.H-Seedling Height, S.G-Seedling Growth, S.G.I.-Seedling Growth Inhibition, N.D- Not Detected.***

## CONCLUSION

The present results concluded that these concentrations of Benlate fungicides suitable for germination of seedlings, but concentration higher than these recommended can be unsuitable for germination of seedlings.

## ACKNOWLEDGMENT

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of Vidya Bharti Mahavidyalaya, camp, Amravati

has participated and presented the paper entitled Teaching Employee Involvement in corporate Governance at multinational Level

at the **International Conference On Developments in Commerce, Economics, Engineering, Management, Science & Healthcare** held on 22nd & 23rd January, 2016 at Smt. Kesharbai Lahoti Mahavidyalaya - Amravati

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# TEACHING EMPLOYEE INVOLVEMENT IN CORPORATE GOVERNANCE AT THE MULTINATIONAL LEVEL

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## A. Different Forms of Employee Involvement in Corporate Governance:

As the transactions of companies overrun the borders of countries, the roles of corporate Constituencies increasingly gain cross-border nature. Employees as one of the corporate Constituencies have been playing an increasingly important role at the transnational level. Nevertheless, employees' roles in the corporate governance differ among states since regulations of companies are quite different from one country to another even though the increasing number of companies now has activities beyond the national borders. For example, in cross-border mergers and acquisitions, as the form of growth and internationalization, the relations between the management and workers in the companies involved, may be subject to laws and regulations of more than one country, where there is great diversity. At one extreme, employee participation which provides participation for employees in corporate decision making, together with the two-tier board structure, is regulated. At other extreme, employees are only provided with information and consultation in major corporate decisions. The diversity between the employees' role in the governance of companies is one of impediments to major corporate transactions in the globalized world, which adversely affects the economic relations between countries and creates an obstacle to the development of the world economy.

There are efforts to approximate differences of employees' role in companies. For example, in the European Union (EU) it seems that major steps have been taken to harmonize different systems of employee involvement in the corporate governance. In 1994 the EU adopted European Works Council Directive[1] which requires member states to set up a general framework for employees' information and consultation rights in multinational companies. Under the Directive, consultation is defined as a two-way communication process; the exchange of views and establishment of dialogue between employees and management.[2] The Directive imposes on member states the establishment of a Works Council in Community scale undertakings or groups of undertakings which have at least 1,000 or in companies which have at least 150 employees in each of two or more member states and where employees or their representatives request this.[3] Put simply, the Directive provides a collective voice through a central information and consultation forum.

The National Works Council Directive[4] also imposes on national companies of member states to set up minimum requirements for employees' information and consultation rights to complement the European Works Council Directive. Under the Directive employees are to be informed and consulted on a regular basis on major corporate decisions concerning employees' interests. Information and consultation are achieved through works councils, or in rare cases, through direct contact between management and employees or their representatives. Further, employee involvement in Societies European (SE) is regulated by the Directive[5] supplementing the Regulation for a European company (European Company Statute)[6] which introduced a new legal entity under EU law. The purpose of the Regulation for a European company is to offer a company with a European dimension free from the obstacles arising from the disparity and the limited territorial application of national company law.[7] The European company, which is primarily governed by the same rules, can therefore move freely from one country to another without legal restrictions imposed on national entities. The European company will permit cross-border mergers and the cross-border transfer of a company's registered office without the need for liquidation and for the formation of a new company.

The Directive supplementing the Regulation for a European company then provides employee involvement in companies moving from one country to another to be subject same provisions. The Directive[8] supplementing the Regulation for a European company, drawing on experiences and laws

of member states, governs three forms of employee involvement in the corporate decision making: participation, consultation and information[9]. Employee participation should be clearly distinguished from other forms of employee involvement. This is because; of the three forms of employee involvement under the Directive only participation affects the structure of the company.

Nevertheless, there are still major divergences between the laws of member states concerning employee involvement in corporate governance. This stems from the fact that the employees' role in corporate governance is related to not only laws and regulations of corporate governance of countries, but also the underlying philosophy of corporate governance. The shareholder primacy prevails in the Anglo-American countries where the company is considered a profit making organization. This philosophy encourages corporate directors to maximize corporate profit. The directors are elected by the shareholder, which ensures the responsibility of the directors only to shareholders.[10] The directors act, as agents of shareholders, in the best interests of shareholders. The shareholders are the owners of the company carry the risk of investment. They, in turn, should be the one who decides in the company.[11] The Anglo-American corporate governance system has therefore mainly drawn on contractual theory. This leads to the relationship between corporate constituencies and the companies to be treated as contract.12 Therefore, employees as one of corporate constituencies are regarded as outsiders. Their contractual rights are supplemented by certain statutory protections for the individual worker, and by collective rights of bargaining and consultation.[13]

The stake holding approach, on the other hand, prevails on the Continent. The company is regarded as the institution in which the interests of different corporate constituencies, such as employees, suppliers, certain long-term customers, environment and society are reconciled. Employees, as one of corporate constituencies, or of stakeholders are protected within the company through mainly two tier board structure. The members of supervisory board are elected by shareholders and employees, and those of the management board are elected by the supervisory board. This structure of the company makes it possible for employees to participate in the decision making of companies[14]. Therefore, employee voice is related to corporate culture, historical, political and sociological development of countries that shape legal rules of employee involvement in the decision-making of companies.

**B. Teaching Employee Involvement in Corporate Governance from a Comparative Perspective:**

The laws and regulations relating to employee involvement in corporate governance which have evolved in different cultural, sociological, historical and economic development of countries can be thought from a comparative perspective. Different roles of employees can be illustrated by explaining laws of UK, Germany and the Netherlands concerning employee involvement in corporate governance. Examining law of the UK about shareholder primacy together with employee involvement will show that employees can only have information and consultation rights in major corporate decisions. On the other hand, an explanation of laws of Germany and the Netherlands relating to employee participation can make a fuller understanding how the corporate structure enables the interest of company to include the interests of shareholders, creditors, employees and society.

Information and consultation rights in UK law stem from the implementation of Directives[15] which impose on member states to regulate, at least, the lowest level of employee involvement. Employees' information and consultation rights are not likely to provide influence upon decisions on corporate policies whereas participation must at least have the capacity to influence decisions and policies. Information and consultation, on the other hand, can be deemed as the essential step in the process of participation[16] Two-tier board system, as the corporate structure, comprising the supervisory board and the management board is the major characteristics of laws of Germany and Netherlands providing for employee participation. However, while employee involvement in these two countries can be referred to as employee participation, there are differences in these two countries' laws concerning employee involvement. Explanation of the laws of Germany and the Netherlands about employees' role, in a comparative way, will help the students to understand

different types of employee participation, which is also reflected in the Directive[17] supplementing the Regulation for a European Company.

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- See Council Directive 2001/86/EC of 8 October 2001 supplementing the Statute for a European company with regard to the involvement of employees, annex standard rules part 3. See also Council Regulation (EC) No. 2157/2001 of 8 October 2001 on the Statute for a European Company (SE), article 40.
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# INVESTIGATION OF ALOE-VERA TOOTH GEL CONTAINING ACTIVE SALT AND ALUM BY TIME KILL TEST

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## ABSTRACT

The aim of the present study was to investigate efficacy and performance of Aloevera tooth gel against selected bacteria and fungi This test method measures the changes of a population of Aerobic microorganism with in a specified time period, when tested against Staphyllacoccus aureus, Streptococcus mutans, Candida albicans, Escherichia coli and Pseudomonas aeruginos a which were selected as a test micro-organism against which Aloe-vera tooth gel was tested. It included the evaluation of dentifrices by antimicrobial testing.

This investigation showed that newly formulated tooth gel has shown 99.99% reduction of test bacteria viz Staphyllacoccus aureus, Streptococcus mutans, Escherichia coli, Pseudomonas aeruginosa and Candida albicans in 30 sec, 60 cec and 2 minutes, Bright Tooth Paste has shown >99.99% reduction of test bacteria Staphylococcus aureus, Streptococcus mutans, Escherichia coli in 30 sec, 60 sec and 2 minutes, Bright Tooth Paste has shown no reduction of Pseudomonas aeruginosa in 30 sec, 60 sec and 2 minutes, when analysed as per ASTM E 2315 – 03 (Re. 2008) Method.

**Key words :** Aloe gel dentifrice, Staphylococcus aureus, Streptococcus mutans, Candida albicans, Escherichia Coli, Pseudomonas aeruginosa.

## Introduction :-

Dental Caries, Cavities and other oral diseases are the most common diseases world-wide including both developed and developing countries affecting peoples of all ages and sex. These diseases are Caused by a mixture of micro-organism and food debris. Specific types of acid producing bacterias like Streptococcus mutans colonize the dental surface structure in the prcsence of fermentable Carbohydrates, for example sucrose, fructose and glucose. Also other microflora are also associated with it. Teeth provides a unique environment for bacterial colonization, Since unlike other parts of the mouth they are non-shedding inorganic structure retentative areas.

Aloe-vera is a stemless or very short succulent, Cacturs like plant that actually is part of lily family, growing to 60-100 cm (24-39 inches) tall, spreading by off sets. There are more than 300 varieties of the Aloe plant but the Aloe-barbadensis variety exhibits the best medicinal properties. It has been suggested for a wide variety of ailments but its use in dentistry is limited.

Literature survey showed that though Aloe-vera gel were studies and can be used for minor burns, skin abrasions and moisturizing properties but comparatively less works has been reported on its use in dentistry. In the view of this, the present study the Aloe tooth

gel was prepared by incorporating Aloe-vera along with active salt and Alum in it and then the formulation was screened for time kill test.

Time Kill Test is a basic microbiology method of assessment of Antimicrobial activity of an Anti-Microbial test material or Disinfectant. The kill time test is carried out to evaluate the microbial reduction by a disinfectant against selected bacteria or fungi. Various organism are studied depending upon the type of analysis and test materials. However most common organism tested include : Staphylococcus aureus, Pseudomonas aeruginosa, E-coli etc.

The test product or a dilution of the test product is brought into contact with a known population on of micro-organisms approximately $10^6$ CFU/ml specified period of time at a specified temperature. At selected time points including zero time aliquots are removed and placed into a neutralizer blank. Dilutions of the neutralizer are made and selected dilutions plated onto agar. Colonies are enumerated.

The percentage or log reduction or both form either on initial microbial population, or test blank is calculated. The amount of sample required is 100 ml per lot per organism.

## Materials and Methods :

For this purpose following materials were requested to different companies for samples are ;

1. Aloe-vera extract – kingvish Company, Mumbai
2. Precipitated silica (ABSIL – Madhu silica Pvt. Ltd.Gujrat)
3. Hydrated Silica (M-Fil – Madhu Silica Pvt. Ltd Gujrat)
4. Carraeingn gum (VTP-Sarin industries FMC Biopolymer Navi-Mumbai. )
5. Clolours – Neelikon food Dyes and chemicals Ltd. Mumbai.

All the reagents used were of analytical grade. After collecting all the Samples, Aloe-vera tooth gel were formulated by incorporating Aloe-vera, active salt and alum as are active ingredients, to checkout the effectiveness against different micro-organisms with in a specified period of time.

## EXPERIMENTAL WORK :

Finalized base formulation for gel tooth paste with aloe – vera extract , salt and alum as an active ingredients with other common ingredients of gel dentifrice.

**Table 1: Formulation of Aloe-Vera Gel containing dentifrice**

| S. N. | Ingredients | % (w/w) |
|---|---|---|
| 1 | Sorbitol | 65.00 |
| 2 | VTP Gum ( Carrageenan gum) | 0.55 |
| 3 | F - Sil 100 ( Abbrasive Silica ) | 13.5 |
| 4 | M - Fil 100 ( Hydrated Silica ) | 6.5 |
| 5 | Poly ethylene glycol 400 | 0.5 |
| 6 | Sodium Saccharin | 0.3 |
| 7 | Sodium fluoride | 0.22 |
| 8 | Sodium lauryl sulphate | 2.5 |
| 9 | Methyl Paraben | 0.1 |
| 10 | Propyl Paraben | 0.01 |
| 11 | Colour | 0.1 |
| 12 | Flavour | 0.5 |
| 13 | Water | 0.92 |
| 14 | Aloe – vera gel | 9.0 |
| 15 | Sodium salt | 0.2 |
| 16 | Alum | 0.1 |

## Preparation of Aloe Tooth gel :

In order to optimize the concentration of gelling agent to achieve proper consistency of the gel formulations were prepared with different gel formers, Carboxy methylcellulose sodium, Carbomer 934, HPMC and different concentration of viscosity enhancer vis. 1.0, 2.0, 3.0 and 4.0 % were tried and finally gel that showed good spreadability and consistency was selected.

Weigh all the ingredients. Take sufficient quantity of water . Add sodium saccharin, Sodium fluoride , preservatives , colour, Sodium salt, alum in it . Mix it properly. Then warm the water up to 45 – 50$^{0}$c . Then at this temperature add VTP gum. Then add sorbitol, Poly-ethylene glycol. Then add both silica powder i.e. abrasive silica & hydrated silica to it. Mix it 15 minutes. The add Aloe – vera gel & flavour to it and mix it 10 -15 minutes properly. Lastly add sodium lauryl sulphate to the formulation by making a slurry. Slight amount of foam will generate. Remove air by vacuum.

Finalized base formulation for gel tooth paste with aloe – vera extract , salt and alum as an active ingredients with other common ingredients of gel dentifrice.

**Antimicrobial Analysis of Aloe Tooth Gel by Time Kill Test :**

**Name of Test :** Time Kill Test

**Test Standard ;** ASTM E 2315 – 03 (Re 2008)

**Test Inoculum :**

1. Staphylococcus aureus ATCC 6538
2. Streptococcus mutans ATCC 25175
3. Escherichia coli ATCC 10535
4. Psedomonas aeruginosa ATCC 9027
5. Candida albicans ATCC 10231

**Test Conditions :**

| | | |
|---|---|---|
| Test Product | : | 1:2 dilution |
| Diluent / Neutraliser | : | DE broth |
| Contact Time | : | 30 seconds, 60 seconds and 2 minutes |
| Contact Temperature | : | Room Temperature |
| Media and Reagent | : | Soyabean-casein digest agar, plates incubated at 37°C; Sabourauds Dextrose agar, incubated at 28°C |

**Procedure :**

1:2 dilution product was inoculated with test organisms bacteria / fungi indivudually (approximately 106 CFU /ml). After the specified exposure time of 30 seconds, 60 seconds and 2 minutes, surviging microorganisms were recovered by drawing an alliquot, neutralizing it and performing Standard Pour Plate Technique, Culture count was ascertained by dilution Blank. Adequate Validation of Neutralizing agent was also carried. Test was carried out in duplicate and average count was taken as CFU/ml.

Sample Measurement Tube Vortex Shaker

Remove Sample with Micropipette

Mixing Sample in

Preparation of Plates

Inoculation of Microbial Plate

Spiral Plater

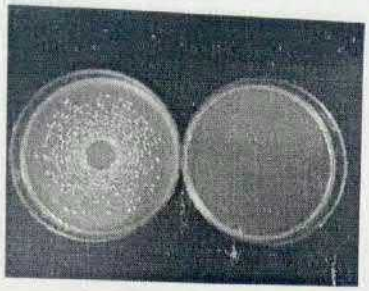
**Neutralizer Validation :**

| Validation Test | | |
|---|---|---|
| **Test Organism** | **Viable count in Saline (CFU/ml)** | **Viable Count in Neutraliser** |
| Staphylococcus aureus | 78 | 80 |
| Streptococcus mutans | 45 | 46 |
| Escherichia | 53 | 52 |
| Psedomonas aeruginosa | 80 | 78 |
| Candida albicans | 32 | 30 |

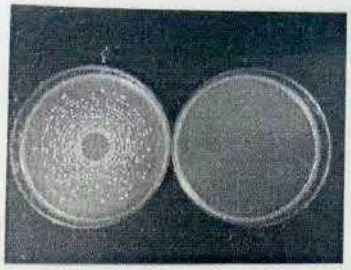
## Results :

| Sample Identification | Test Organism | Exposure Time | Count of Test Organism | | | Antimicrobial Activity | |
|---|---|---|---|---|---|---|---|
| | | | Initial Count | After Exposure | | Log Reduction | Percentage Reduction |
| | | | | CFU/ml | Log | | |
| Aloevera Gel Tooth Paste | Staph. Aureus | 30 Sec | $1.45x10^5$ | <10 | <1 | >4.16 | >99.99 |
| | | 60 Sec | CFU/ms | <10 | <1 | >4.16 | >99.99 |
| | | 2 Min | L = 5.16 | <10 | <1 | >4.16 | >99.99 |
| Bright Tooth Paste | | 30 Sec | $1.41x10^5$ | <10 | <1 | >4.14 | >99.99 |
| | | 60 Sec | CFU/ms | <10 | <1 | >4.14 | >99.99 |
| | | 2 Min | L = 5.14 | <10 | <1 | >4.14 | >99.99 |
| Aloevera Gel Tooth Paste | Steptococcus Mutans | 30 Sec | $1.35x10^5$ | $9.50x10^4$ | 4.97 | 0.16 | 29.62 |
| | | 60 Sec | CFU/ml | $1.00x10^4$ | 4.0 | 1.13 | 92.59 |
| | | 2 Min | L = 5.13 | <10 | <1 | >4.13 | >99.99 |
| Bright Tooth Paste | | 30 Sec | $3.50x10^5$ | <10 | <1 | >4.54 | >99.99 |
| | | 60 Sec | CFU/ml | <10 | <1 | >4.54 | >99.99 |
| | | 2 Min | L = 5.54 | <10 | <1 | >4.54 | >99.99 |
| Aloevera Gel Tooth Paste | Escherichia Coli | 30 Sec | $1.08x10^5$ | <10 | <1 | >4.16 | 29.62 |
| | | 60 Sec | CFU/ml | <10 | <1 | >4.16 | 92.59 |
| | | 2 Min | L = 5.03 | <10 | <1 | >4.16 | >99.99 |
| Bright Tooth Paste | | 30 Sec | $1.10x10^5$ | <10 | <1 | >4.16 | >99.99 |
| | | 60 Sec | CFU/ml | <10 | <1 | >4.16 | >99.99 |
| | | 2 Min | L = 5.04 | <10 | <1 | >4.16 | >99.99 |
| Aloevera Gel Tooth Paste | Pseudomonas aeruginosa | 30 Sec | $1.09x10^5$ | <10 | <i | >4.16 | >99.99 |
| | | 60 Sec | CFU/ml | <10 | <1 | >4.16 | >99.99 |
| | | 2 Min | L = 5.03 | <10 | <1 | >4.16 | >99.99 |
| Bright Tooth Paste | | 30 Sec | $1.15x10^5$ | $>1.00x10^6$ | >6.0 | < 1 | 0.00 |
| | | 60 Sec | CFU/ml | $>1.00x10^6$ | >6.0 | < 1 | 0.00 |
| | | 2 Min | L = 5.06 | $>1.00x10^6$ | >6.0 | < 1 | 0.00 |
| Aloevera Gel Tooth Paste | Candida albicans | 30 Sec | $4.60x10^5$ | <10 | <1 | >4.66 | >99.99 |
| | | 60 Sec | CFU/ml | <10 | <1 | >4.66 | >99.99 |
| | | 2 Min | L = 5.66 | <10 | <1 | >4.66 | >99.99 |
| Bright Tooth Paste | | 30 Sec | $2.60x10^5$ | <10 | <1 | >4.41 | >99.99 |
| | | 60 Sec | CFU/ml | <10 | <1 | >4.41 | >99.99 |
| | | 2 Min | L = 5.41 | <10 | <1 | >4.41 | >99.99 |

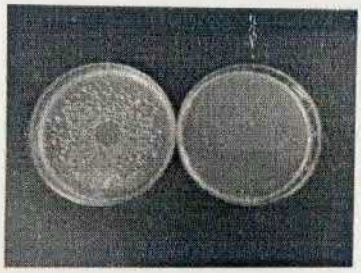
Percentage Reduction of Microorganism = 100 (Initial – After Exposure)/ Initial
Log Reduction = Log Initial – Log after Exposure



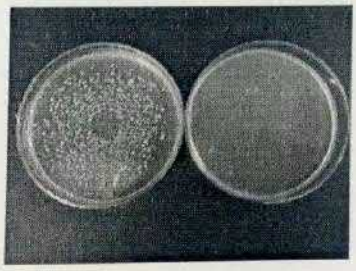
Candida_Aloe_2_mins



Candida_Bright_L_control and_right_2_min



S_mutans_Aloe_L_control_ and_right_2_mi



S_mutans_Bright_L_control_ and_right 2_min

## Conclusion :

Test Product named as Alovera Tooth Gel has shown >99.99% reduction of test bacteria viz Staphyllacoccus aureus, Streptococcus mutans, Escherichia coli, Pseudomonas aeruginosa and Candida albicans in 30 sec, 60 cec and 2 minutes, Bright Tooth Paste has shown >99.99% reduction of test bacteria viz Staphylococcus aureus, Streptococcus mutans, Escherichia coli in 30 sec, 60 sec and 2 minutes, and Bright Tooth Paste has shown no reduction of Pseudomonas aeruginosa in 30 sec, 60 sec and 2 minutes when analysed as per ASTM E 2315 – 03 (Re. 2008) Method.

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# FORMULATION AND EVALUATION OF ALOE-VERA GEL WITH ACTIVE SALT AND ALUM : AS A NEW DENTIFRICE

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**Abstract:** Aloe vera is well known for its marvellous medicinal properties. These plants are one of the richest sources of health for human beings coming from nature. It has been grown as an ornamental plant widely. Products of the plant are used in the treatment of various ailments. Various parts of the plant have different effects on the body. Aloe vera is an ancient, natural ingredient that would be hailed as a major scientific breakthrough if it came out of a modern drug lab. It coats, soothes and can even heal ulcers and irritations. Proven in multiple clinical studies, Aloe vera has been used in dentistry for its wound-healing effects, gingivitis, plaque control & curing oral mucosal lesions. Aloe vera may also reduce the pain and duration of oral ulcers while speeding healing. The dentists should use Aloe vera at a level high enough to maximize its therapeutic benefit.

**Keywords:** Aloe tooth, *Escherichia coli, Candida albicans,* zone of inhibition, natural antimicrobial agents.

## Introduction :

The Aloe vera plant has been known and used for centuries for its health, beauty, medicinal and skin care properties. The name Aloe vera derives from the Arabic word –Alloeh meaning –shining bitter substance, while –vera in Latin means –true. 2000 years ago, the Greek scientists regarded Aloe vera as the universal panacea. The Egyptians called Aloe –the plant of immortality. Aloe barbadensis Miller (Aloe vera) belong to the liliaceal family, of which there are about 360 species. The use of natural products in the prevention and treatment of oral conditions has increased recently and

could be of benefit to low socioeconomic level in urban and rural communities. Among the various currently available herbal agents the most popular and currently receiving a lot of scientific attention is Aloe vera. It is a perennial succulent xerophyte, which develops water-storage tissue in the leaves to survive in dry areas of low or erratic rainfall [1]. The plant has stiff grey-green lance-shaped leaves containing clear gel in a central mucilaginous pulp. Benefits associated with Aloe vera have been attributed to the polysaccharides contained in the gel of the leaves. It is a cactus like plant that grows in hot and dry climates. Numerous studies on Aloe vera are being done to demonstrate the antiviral, antibacterial, analgesic, antiinflammatory & wound healing properties. The Aloe barbadensis plant consists of two different parts, each of which produces substances with completely different compositions and therapeutic properties. The parenchymal tissue makes up the inner portion of the aloe leaves and produces the Aloe vera gel (or mucilage), a clear, thin, tasteless, jelly-like material. This tissue is recovered from the leaf by separating the gel from the inner cellular debris. The other part of the plant is a group of specialized cells known as the pericyclic tubules, which occur just beneath the outer green ring of the leaf. These cells produce an exudate that consists of bitter yellow latex with powerful laxative-like actions [2].

History: The plant Aloe-vera has a history dating back to biblical times. Aloe vera has been used for medicinal purposes in several cultures for millennia: Greece, Egypt, India, Mexico, Japan and China. Egyptian queens Nefertiti and Cleopatra used it as part of their regular beauty regimes. Alexander the Great, and Christopher Columbus used it to treat soldiers' wounds. The first reference to Aloe vera in English was a translation by John Goodyew in A.D. 1655 of Dioscorides Medical treatise De Materia Medica [3].

**The Components or Elements in Aloe vera are** [4]. Lignins, Saponins, Glycosides, Anthraquinones, Minerals. Vitamins, Mono and Polysaccharides and Amino Acids.

**Mechanism of Action:**

a) **Anti-Inflammatory Effects:** It inhibits the cyclooxygenase pathway and reduces prostaglandin E2.
b) **Antifungal Property:** A processed Aloe vera gel preparation reportedly inhibited the growth of Candida albicans [7].

c) **Antiviral Property:** This action may be direct and indirect; i.e. indirect due to stimulation of immune system, and direct due to aloe emodin.

d) **Immunomodulating Effects:** Aloe vera, a great immune stimulant, contains 90% rhodium and iridium (trace minerals) in the acemannan which is one of the polysaccharides which dramatically increases the white blood cells or macrophages and T cells.

e) **Antioxidant Property:** Aloe vera has very strong antioxidant nutrients. Glutathione peroxide activity, superoxide dismutase enzymes and a phenolic antioxidant were found to be present in Aloe vera gel, which may be responsible for these antioxidant effects.

f) **Antitumor Effect:** The two fractions from Aloes that are claimed to have anticancer effects include glycoproteins (lectins) and polysaccharides.

g) **Dental Implants:** Aloe vera gel placed around dental implants is found effective to reduce inflammation. Aloe vera reduces inflammation by its antimicrobial & antiinflammatory effects.

## Materials and Methods:

Different concentrations of viscosity enhancer Carrageenam gum were tried and finally gel that showed good spreadability and consistency was selected for dentifrice property of herbal gel of Aloe vera, active salt and alum.

Carrageenam gum was purchased from Sarin Industries Pvt Ltd., Mumbai (India), precipitated and hydrated silica from Madhu Silica Pvt. Ltd (Gujrat), Methyl Paraben, Propyl Paraben, Sodium Chloride was Purchased from Titan Biotech Ltd. Rajasthan (India) and colours from Neelicon food dyes and chemicals ltd, Mumbai. Aloe vera (Aloe barbadensis) plant was obtained from Herbal Garden, Vidyabharti Pharmacy College – Amravati.

## EXPERIMENTAL WORK

### Analysis of Aloe – vera extract :

Complete analysis of Aloe – vera extract was done according to specification.

Thick succulent leaves of Aloe vera (*Aloe barbadensis*) plant obtained from Herbal Garden, Vidyabharti college of Pharmacy-Amravati, were used. To obtain Aloe vera extract, the mucilaginous jelly obtained from the centre (the parenchyma) of the plant

leaf of Aloe vera, the leaves of Aloe vera were collected, washed with water and a mild chlorine solution and were finally cut transversely into pieces. With a vegetable peeler, the thick epidermis was selectively removed and the inner gel-like pulp in the center of the leaf was separated with a spoon, minced, and homogenized in a mixer.

**Selection, Optimization and Preparation of Aloe-Vera tooth gel :**

One of the main ingredients of the formulation is the gelling agent. The concentration of viscosity enhancer or gel former is of immense value as a less concentration will lead to simple solution or lotion with very low consistency, while high concentration may lead to formation of gels with high viscosity leading to non-uniform distribution of drug and problem with handling of gel. Different gel formers were tried in order to select the best gelling agent.

So in order to optimize the concentration of gelling agent to achieve proper consistency of the gel formulations were prepared with different gel formers, Sodium Carboxy methylcellulose, Carbomer 934, 974, Carrageenam gum in different concentration of viscosity enhancer vis. 1.0, 2.0, 3.0 and 4.0 % were tried.

Gels containing aloe vera juice extract and Sodium CMC showed phase separation and were rejected. Aloe vera gels containing 1.0 % of carbomer 934 form a very thin gel that liquefies within 6h of preparation. With 2.0% gelling agent somewhat better gel was obtained but the problem of liquification after 24h was observed. Gel containing 3.0% of carbomer 934 formed uniform and smooth gel that does not liquefy upon keeping. At 4.0 % of carbomer gel was very thick and more sticky that could not be properly spread out. With carbopol974 the gels formed are poor in consistency and very thick as indicated by spreadability and extrudability values. Thus, 0.55% of carrageenam was selected as the optimized concentration of gelling agent.

**Table 1: Formulation of Aloe-Vera Gel dentifrice**

| S. N. | Ingredients | % (w/w) |
|---|---|---|
| 1 | Sorbitol | 65.00 |
| 2 | VTP Gum ( Carrageenan gum) | 0.55 |
| 3 | F - Sil 100 ( Abbrasive Silica ) | 13.5 |
| 4 | M - Fil 100 ( Hydrated Silica ) | 6.5 |
| 5 | Poly ethylene glycol 400 | 0.5 |
| 6 | Sodium Saccharin | 0.3 |
| 7 | Sodium fluoride | 0.22 |
| 8 | Sodium lauryl sulphate | 2.5 |
| 9 | Methyl Paraben | 0.1 |
| 10 | Propyl Paraben | 0.01 |
| 11 | Colour | 0.1 |
| 12 | Flavour | 0.5 |
| 13 | Water | 0.92 |
| 14 | Aloe – vera gel | 9.0 |
| 15 | Sodium salt | 0.2 |
| 16 | Alum | 0.1 |

Finalized base formulation for gel tooth paste with aloe – vera extract , salt and alum as an active ingredients with other common ingredients of gel dentifrice.

**Procedure :**

Weigh all the ingredients. Take sufficient quantity of water . Add sodium saccharin, Sodium fluoride , preservatives , colour, Sodium salt, alum in it . Mix it properly. Then warm the water up to 45 – 50°c . Then at this temperature add VTP gum. Then add sorbitol, Poly-ethylene glycol. Then add both silica powder i.e. abrasive silica & hydrated silica to it. Mix it 15 minutes. The add Aloe – vera gel & flavour to it and mix it 10 -15 minutes properly. Lastly add sodium lauryl sulphate to the formulation by making a slurry. Slight amount of foam will generate. Remove air by vacuum.

## Evaluation of Aloe-vera Tooth Gel

### pH

1.0 g gel was accurately weighed and dispersed in 100 ml purified water. The *p*H of the dispersion was measured using digital pH meter, which was calibrated before use with standard buffer solution at 4.0, 7.0 and 9.0. The measurements of *p*H were done in triplicate and average values were calculated.

### Spreadability

One of the criteria for a topical formulation to meet the ideal qualities is that it should possess good spreadability. It is the term expressed to denote the extent of area to which formulation readily spreads on application to skin or affected part. The therapeutic efficacy of a formulation also depends upon its spreading value. To determine the spreadability of formulation, 0.5 g of gel was placed within a circle of 1 cm diameter pre-marked on a glass plate of 20 × 20 cm, over which a second glass plate was placed. A weight of 500 g was allowed to rest on the upper glass plate for 5 min. The increase in the diameter due to gel spreading was noted.

### Extrudability

To determine extrudability a closed collapsible tube containing formulation was pressed firmly at the crimped end. When the cap was removed, formulation extruded until the pressure dissipated. Weight in grams required to extrude a 0.5 cm ribbon of the formulation in 10 sec was determined. The average extrusion pressure in gms was reported.

### Viscosity

The viscosity of the formulations was determined as such without dilution by R/S CPS Plus Rheometer (Brookfield Engineerring Laboratorie, Inc., Middleboro, MA, USA) using spindle No. 6, 50-1 having diameter of 50 mm using software RHEO3000.

**Homogeneity**

The developed formulations were tested for homogeneity by visual inspection after the gel had been filled in the container. They were tested for their appearance and presence of any aggregates.

**Analysis of dentifrice Capacity as per IS6356:2001:**

The formulated Aloe vera tooth gel sample was tested as per IS 6356 : 2001

( Specification for tooth paste.)

**Antimicrobial Analysis of Aloe-vera Tooth Gel :**

This in-vitro study was carried out to determine Antimicrobial efficacy of Aloe-vera tooth gel against oral pathogens. In order to study in their effectiveness against the test microorganisms , Escherichia coli, S. aureus S. mutans and Candida albicans were selected as test microorganisms ,against which the antimicrobial assay by modified agar well diffusion method as per NCCLS guide lines 2005 was performed.

- **Name of Test :** Anitibacterial property of test product by well diffusion method as NCCLS guidelines 2005

**Test Inoculum :**

1. Staphylococcus aureus ATCC 6538
2. Streptococcus mutans ATCC 25175 bacteria
3. Escherichia coli ATCC 10536
4. Candida albicans ATCC 10231

**Test Procedure :**

The test organisms diluted approx. $10^7$-$10^8$ CFU/ml were individually spread by a sterile swab evenly over the face of Soyabean Casein digest agar. Using cork borer a well of 8 mm diameter was punched in the medium. Test material-as it is in 100 ul quantity was then applied to each well. Control plant comprised of 100 ul distilled water solution. The plates incubated at $37^0$C/$28^0$C for 24/72 hrs. Zone of inhibition were measured by calibrated ruler.

## Results and Discussion:

### Analysis of Aloe-vera Extract:

| Sr.No. | Parameter | Specification | Result |
|---|---|---|---|
| 1 | Botanical Source | Aloe Barbadensis Miller | Complies |
| 2 | Appearance | Colourless and Transparent | Complies |
| 3 | Solubility in Water | Soluble | Soluble 100% |
| 4 | Odor | Characteristic | Characteristic |
| 5 | pH | 4.0 – 8.0 | 6.28 |
| 6 | Specific Gravity @ 25 deg C. | 1 to 1.1 | 1.0090 |
| 7 | Refractive Index @ 20 deg. C. | 1.3 to 1.5 | 1.3932 |
| 8 | Loss on drying | About 97 -98% | Complies |
| 9 | Heavy Metals | 10 ppm Max. | Less than 2 ppm |
| 10 | Arsenic | 10 ppm Max.<br>LT : NMT 10 ppm | Complies |
| 10 | Microbial Limits :<br>Total Bacterial Count<br>Yeast and Mold Count<br>S. Aureus<br>E Coli/g<br>Salmonella/g<br>Pseudomonas | 100 cfu/gram Max.<br>NMP 50 cfu/g | <br>Complies<br>Complies<br>Absent<br>Absent<br>Absent<br>Absent |

The pH of the formulation was determined in order to be sure that the formulation can be used without the risk of irritancy to the oral cavity. The *p*H was found to be 6.28 for gel which was very near to the neutral *p*H, thus the formulation can be used without the risk of irritancy to the oral cavity. This also indicated that the selected ingredients of the formulation did not alter the *p*H of the formulation.

The Spreadability of formulations was found to decrease with increasing the concentration of gelling agent. The value of Spreadability for optimized gel was found out to be 8.6 cm indicating that the gel easily spreadable by small amount of shear.

**Table 3: Evaluation of Aloe Tooth Gel as per IS: 6356 : 2001 (Specification for tooth paste)**

| S.No. | Description | Standard | Results |
|---|---|---|---|
| 1. | Fineness | | |
| i) | 150 Micron | Lt : Max.10% | 0.004% |
| ii) | 75 Micron | Lt : Max 2.5% | 0.004% |
| 2. | pH of Aqueous Suspension | 5.5 to 10.5 | 6.60 |
| 3. | Foaming power | Lt : Min. 50ml | 200ml. |
| 4. | Heavy metals | Lt : Max 20ppm | Test Passes |
| 5. | Arsenic | Lt : Max 2 ppm | Test Passes |
| 6. | Viscosity | 42000 to 60000 | 48,900 cps. |
| 7. | Hard and sharp edge particles | To pass the test | No hard & sharp edge particles observed |
| 8. | Spreadability | To pass the test | Test passes |
| 9 | Extrudability | To pass the test | 20.3 |
| 10 | Homogeniety | To pass the test | Homogenous |

**Results of anti-microbial Assay:**

- Name of Test :
  Anitibacterial property of test product by well diffusion method as NCCLS guidelines 2005

**Test Inoculum :**

Staphylococcus aureus ATCC 6538
Streptococcus mutans ATCC 25175 bacteria
Escherichia coli ATCC 10536
Candida albicans ATCC 10231

The test organisms diluted approx. $10^7$-$10^8$ CFU/ml were individually spread by a sterile swab evenly over the face of Soyabean Casein digest agar. Using cork borer a

well of 8 mm diameter was punched in the medium. Test material-as it is in 100 ul quantity was then applied to each well. Control plant comprised of 100 ul distilled water solution. The plates incubated at 37°C/28°C for 24/72 hrs. Zone of inhibition were measured by calibrated ruler.

**Table 4: Antimicrobial Assay of Aloe-Vera tooth gel**

| Sample Identification | Test organism | Zone of Inhibition in mm (average) | | | | |
|---|---|---|---|---|---|---|
| | | 1 : 1 | 1 : 2 | 1 : 4 | 1 : 8 | 1 : 16 |
| Aloe vera gel T.P. | Staph. Aureus | 21.6 mm | 21mm | 16.6 mm | 15.3 Mm | 14. 5 mm |
| Bright T.P | | 21 mm | 20.3 mm | 19.6 mm | 14 mm | 13 mm |
| Aloe vera gel T.P. | Strep. Mutans | 20 mm | 13 mm | 17 mm | No. Zone | No. Zone |
| Bright T.P | | 25.3 mm | 21.3 mm | 18 mm | 15. mm | 13.2 mm |
| Aloe vera gel T.P. | Esch. Coli | No. Zone | No. Zone | No. Zone | No. Zone | No. Zone |
| Bright T.P | | No. Zone | No. Zone | No. Zone | No. Zone | No. Zone |
| Aloe vera gel T.P. | can. albicans | 29 mm | 27 mm | 24.6 mm | 16 mm | 15 mm |
| Bright T.P | | 30 mm | 25 mm | 23.2 mm | 20 mm | 12 mm |

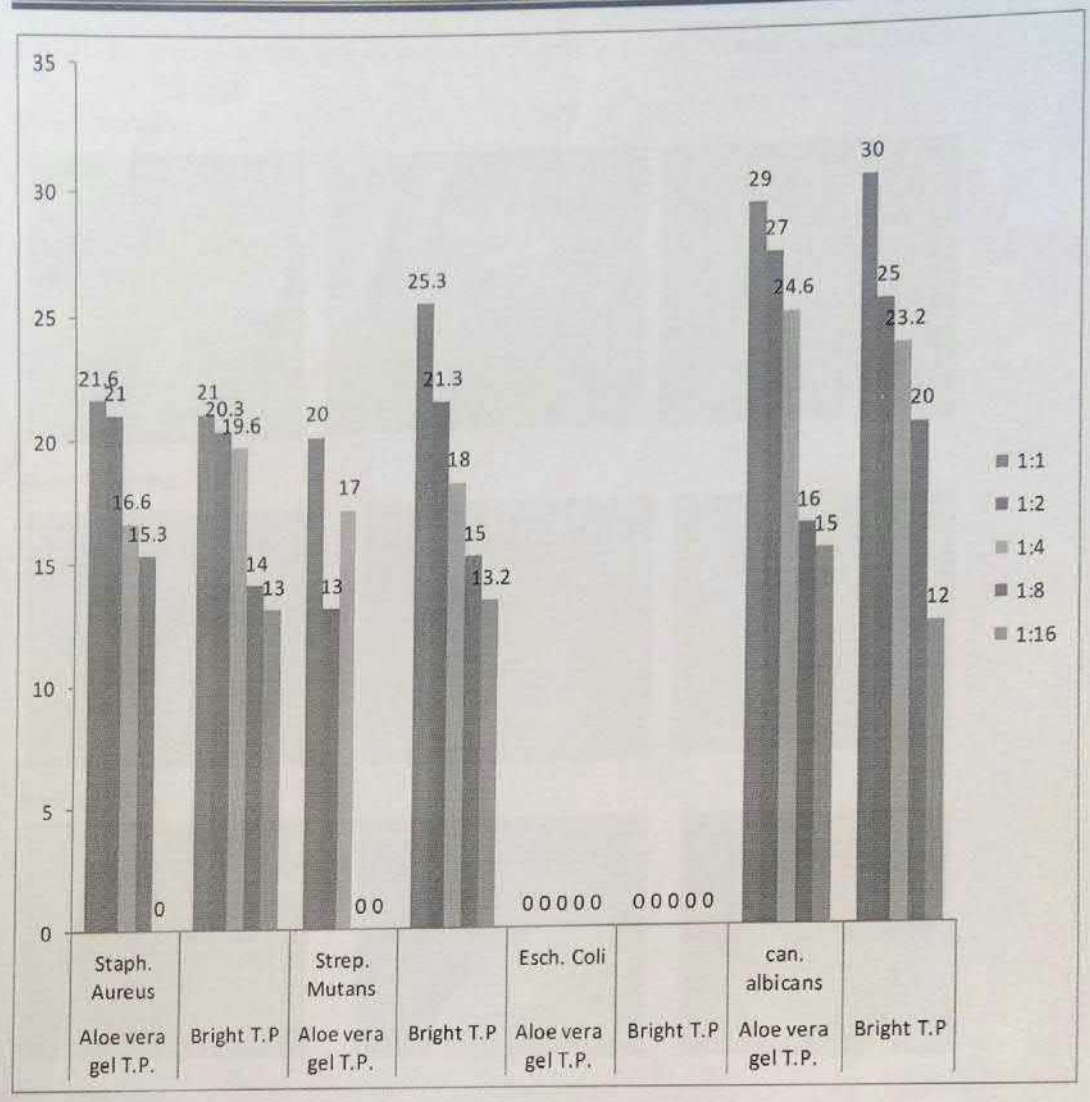



**Figure no. 1: Biological indicator verses zone of inhibition of Aloe-Vera Tooth Gel**

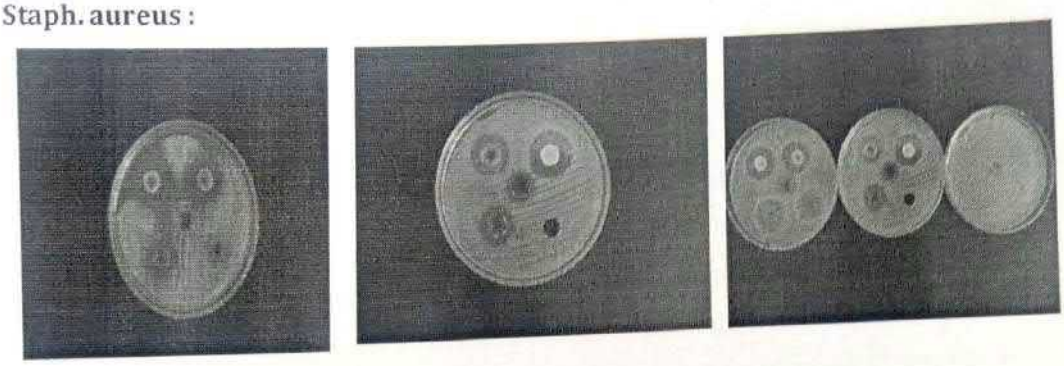
**Graphical Representation of Result of Anti-microbial Analysis of Aloe Tooth Gel having active salt and alum.**

**Note :**

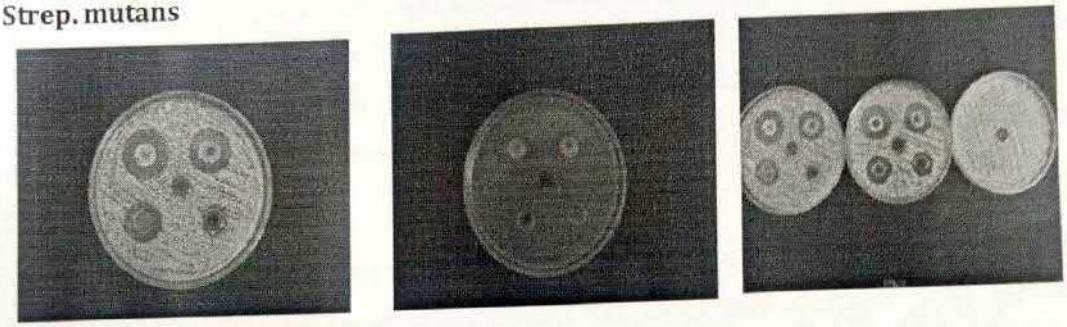
1. 100 ul was used per well
2. Presence on Antibacterial substance in Formulation is indicated by zone of Inhibition.
3. Larger the zone size more is the concentration of Antibacterial substance.

4. No. Zone of inhibition is no antibacterial activity unless material is non diffusible.

Staph. aureus :



Strep. mutans



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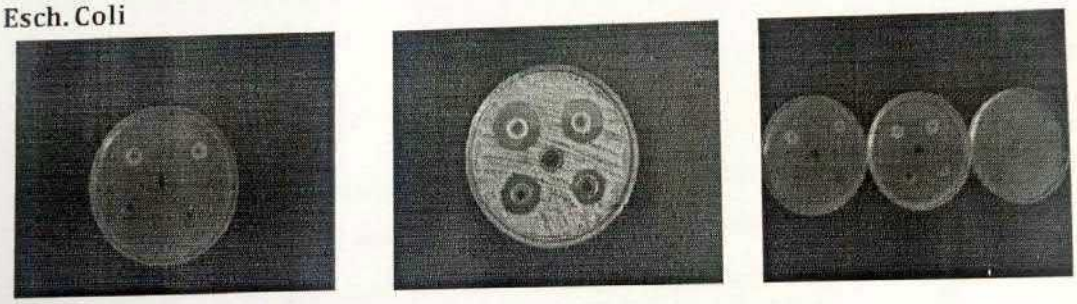

Can. Albicans

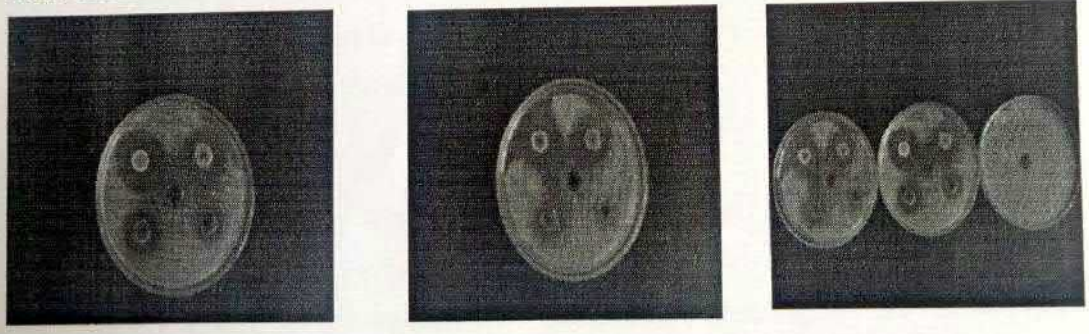

**Figure : Photographs of Antimicrobial Assay**

The greater part of the world's population relies on traditional medicine for their health care. This is also the case in the treatment of teeth. In developing countries, formulations prepared from plants have been widely used for the treatment of dentifrice by medical personnel trained in western medicine as well as by traditional practitioners. Wound relating with teeth healing is a dynamic response to injury that results in wound contraction, wound closure and restoration of the functional barrier.[14] It has three overlapping phases: inflammation, granulation tissue formation and remodeling. During the wound healing process, especially the transition from granulation tissue to scar tissue formation, collagen remodeling occurs, which involves the degradation of collagen with the formation of larger collagen bundles and an increase in the number of intermolecular cross-linkages. This process is controlled by matrix metalloproteinases. They are proteolytic enzymes discharged by fibroblasts, macrophages, epidermal cells and endothelial cells. The tensile strength of a teeth can be related to its collagen formation and maturation.

The prepared Aloe-Vera Tooth Gel has promising effect on the teeth. Further studies need to be performed to understand the exact mechanism of teeth wound healing by Aloe vera gel.

## CONCLUSION :

From all experiments conclusions can be drawn that Aloe-vera gel tooth paste were successfully prepared along with active sodium salt and alum. According to result of analysis, prepared gel dentifrice formulation is capable of reducing the bad odour, reduces plague, gives whitening effect to the teeth. Also the formulation is potentially effective against various micro- organisms like S. aureus, S. mutans, Candia albicans. Thus, it is a best formulation for dental care.

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# RESEARCH BULLETIN

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## CONTENT

# THE NOVELS OF NADINE GORDIMER: A THEMATIC STUDY

**Mr. V.P. Shekokar.**

Assistant Professor

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erature is a mirror to its society. It expresses the country's social, political and cultural ages most effectively. African literature received world wide acclaim nowadays. The writers Chinua Achebe,Dorris lessing, Ngugi, Nadine Gordimer and Wole Soyinka are the pioneers African literature. Nadine Gordimer says about African writing "done in any language by ans themselves and by others of whatever skin colour. They denote the African culture and ty throughout their writing. The most imperative phase of African literature is that olonial writing. The major themes of the literature are about identity crises, cultural acement and tyranny.

ine Gordimer is a South African novelist. She was awarded with Novel Prize in 1991 for her ing. Her work is mainly about Apartheid and the suffering of black citizens of South Africa. is on a top place among the white South African writers. In this paper, an effort has been to reach out the substance of the major novels written by Nadine Gordimer. Her work is with moral and social issues, particularly apartheid in South Africa.

mes are the dynamic force of the novels. Gordimer gave new thematic dimensions to the h African novels. Her themes have loaded and wide-ranging interpretations. The novels like s People, My Son's Story, Burger's Daughter and The Pickup, she tries to state reality. dimer tells the stories of common people, revealing moral ambiguities and choices. Another el My Son's Story was published in 1990. The novel depicts a family disturb by illicit love, itical struggle and Apartheid.. This novel was considered as a milestone in Gordimer's rary career as she was awarded the Noble Prize for the same. This novel depicts the active olvement of black citizens in the freedom movement.

novel Burger's Daughter is published in 1979. It is a political and historical novel. It deals a group of white anti-apartheid activists in South Africa. The novel is set in the history of anti-apartheid struggle and references to actual events and people from that period including son Mandela. The novel was well received by critics. A reviewer for The New York Time l that Burger's Daughter is Gordimer's most political and most moving novel. A critic in The lson Review had mixed feelings about the book, saying that it "gives scarcely and pleasure in ing but which one is pleased to have real nonetheless". Gordimer wrote in an easy in "What

Happened to Burger's Daughter" that the theme of my novel is human conflict between the desire to live a personal, private life and the rival claims of social responsibility to one's follow men". Her works have explored the impact of apartheid on individual in South Africa. It is also very true with the novel Burger's Daughter. It is story of a woman analysing her relationship with her father, a martyr to the anti-apartheid movement. The child of two communist and anti-apartheid revolutionaries, Rosa Burger finds herself drawn into political activism as well. Written in the aftermath of the Soweto uprising, the novel was shortly thereafter banned by the South African government. Gordimer described the novel as a coded homage to Bram Fischer, the lawyer who defended Nelson Mandela and other anti-apartheid activists. The main theme in this novel is Rosa's search for her identity. Rosa tries to understand the father's efforts to unite the black and the white as they belong to the same country. The novel is an attempt to recollect Rosa's life and the influences on her when her parents were alive. Her father and mother died in the jail during anti-apartheid movement. The most effective incident of her life was with Baasie, her childhood friend. His anger and bitterness changed the current of her life. She decide to return to South Africa and continue to fight against the plight the oppressed and depressed. Baasie remanded her that the suffering in South Africa still exists. She understands sacrifice and struggle for her father. Rosa came to know that she could not reject totally her father and his work. She was now read to accept the effect of being Lionel Burger's Daughter. She once again returns to her job in the Hospital. Due to her friend and relatives she understands her life. Gordimer's through her work, she tried to search new ways to understand the political world. She was in search of the solution that the black and the white might be united as citizens from the same country.

July's People is published in 1981. Gordimer imagines a bloody South African revolution, in which white people are hunted and murdered after black citizen's revolt against the apartheid government. Nadine Gordimer was South African novelists who write about the subjugation of the South African people under the Apartheid system. In this novel Maureen and Bamford Smales, and educated white couple, compel to live with July, their former black servant. The story examines how people deal with the terrible choices forced on them by violence, race hatred and the state. Black citizen were dehumanized by the state. It is a major theme in her novels. In this novel the writer tries to expose in its main characters how the white felt more greater than the black citizens as they has to endure the obstacles and misery in their life. Through the character she tried to display how the South African black citizens tried to end Apartheid. In July's People, the novelist tried to show how the revolution replaces the power of

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family and their calm in their city home. It also depict how July, the servant shares modern facilities. All that happens in this novel is because of shifting of power from black. July's brave venture by risking his own life gives him ability. The Smales family to leave their home. Thus the novel displays the subversion of power of the whites of the black revolution. The Smales family faces the new life and they have to adapt the ronment. The family feels a sense of interference.

was an attempt to discuss the some major novels of the writer. Gordimer is as prominent voice of South African situation. Thus the novels of Nadine Gordimer with the themes and issues that depict the sufferings and problems of South African

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## ANYASI : FREEDOM IN THE MIDST OF THINGS, FORMS AND PURPOSE

Assist. Prof. **Shyam M. Gedam**
Shri Shivaji Arts, Commerce and Science College, Akot

### ODUCTION:

*Sanyasi*that was published in the year 1889 is the first major play of Tagore, bearing mpses of his mystical attitude. Tagore regards it as an "introduction to all his future because its essence represents his-fundamental conviction of the "the joy of attaining the within the finite". Regarding its theme, Tagore asserts; "..... the great is to be found in all, the infinite within the bounds of form, and the eternal freedom of soul in love.[2] The pression gathered from the play is that Tagore wants to establish his concept of rian mysticism. It consists in the faith that humanity leads to divinity and salvation

# TRAINING ENGLISH LANGUAGES TEACHERS: A NEED BASED APPROACH (PROBLEMS & REMEDIES)

ASHWINI N. TONDRE, DR. PRADNYA S. YENKAR

**Abstract:** Today's economy is globalized; it means many of us are interacting across cultures. The importance of learning English as a second language becomes self-evident. Learning a second language helps you to communicate across world, where you may never have previously considered potential teach. Here trained teachers play a crucial role. It is said that, "Great teachers help create great students" In fact, an inspiring and informed teacher is the most important school-related factor influencing student achievements, so it is essential to pay close attention to how we train and support both new and experienced educators. The research paper focuses on the need of trained teachers to teach the second language. It also briefly discusses the problems faced teachers. And attempt has been made to provide remedies to the problems.

**Keywords:** Globalization, culture, learning, teacher, problems, remedies

**Introduction:**University courses prepare students to become academically eligible for the labour market. In higher education language teaching has a huge share to achieve this goal. Increasing internationalization and developments in technology, societies and working life have changed the environment to such an extent that English language learning has become the need of the day. The primary aim of language and communication studies is to enable students and staff to become convincingly communicating experts in their own fields and to be able to cope with international; in other words and intercultural contexts. And for this purpose the demand of the trained and efficient language teachers need to be satisfied. Considering this the researcher has used the following research methodology for the research purpose

1.1 **Research methodology:**The study is based on secondary data which is collected from various books, National and International journals and publication from various websites which focused on importance of language teaching teachers. Descriptive Research was used for the research purpose

1.3 **Teacher training:**The best teacher-preparation programs highlight subject-matter mastery and provide many opportunities for student teachers to spend time in real classrooms under the supervision of an experienced mentor. Just as professionals in medicine, architecture, and law have opportunities to learn through examining case studies, learning best practices, and participating in internships, such teacher-preparation programs allow teacher to apply their learning in the context of practical teaching in a real classroom sessions.

1.4 **Importance of Language Teacher training:**

Teacher training is an important aspect in the dome of English Language Teaching. Teachers need to be trained to improvise their knowledge on the professional ground and enhance their teaching capabilities. Training is, even, more important when curriculum, teaching approach or methods or course books are changed or modified as teachers need to cope up with the changes and to apply new approach effectively in the classroom. Teacher training programmes are always aimed at the improvement of the quality of teaching and learning and developing the ability in teachers to teach effectively. With a view to enhancing the quality of English language teaching and learning, Communicative approach was introduced. Accordingly English teachers have been trained to equip them with the new approach. But question is about the implementation of the training in the classroom. This study aims to find out the rate of implementation as well as spotting different kinds of problems that may hinder the implementation of training in the classroom with a view to suggest possible ways to overcome from them.

Non trained teachers are often assigned to the most challenging schools and classes with little supervision and support. Most of the teachers are dissatisfied with their jobs and couldn't perform at the expected level, so more attention should be paid to provide them with early and adequate support, especially if they are assigned to demanding school environments. Mentoring and coaching from veteran colleagues is necessary to the successful development of a new

teaches. Great induction programs create opportunities for beginner teachers to learn from best practices and analyse on their teaching.

**1.5 English as a Lingua Franca:** The world has become a global village. English has become necessary for mobility and social and economic success in the world today. The approach of the people towards English language has changed now. There is a great demand of education of English in English and through English throughout the country. English the same time it has become a status symbol. English has become a status symbol and a student without a reasonable command over English is perhaps not very comfortable with attainment of any educational goal. Similarly, teaching of English holds the key position in the entire curriculum of education. Teachers of English, in this context, take the responsibility to enable the learners to achieve the educational goals in general and language aim in particular. Hence the teaching of English language is required to be strengthened and problems need to be reduced with the best efforts of government and educationists and researchers. For this purpose teacher must be well trained but on the contrary this question remains unanswered, **Are our English teachers adequately trained to face this challenge and make the students competent enough to face the world?**

Let's look at the problems in teaching and learning English language.

**1.6 Problems in Teaching and Learning English Language:** Around the world and in the country like India, many people learn English. While some could get the fluency within a few years, lots of students encounter problems and challenges along the way. Some of these pertain to learning English in particular, due to the language's diverse roots, large amount of irregular verbs and profound regional variations. Some of the common problems in learning are as stated below.

**1.6.1. Pronunciation, Vocabulary and Grammar:**

Almost all English learners encounter following problems:

1) Challenges with pronunciation
2) Issues with vocabulary
3) Grammar

**1.6.2Selection of Appropriate Techniques:** earning English requires different techniques for different types of learners. Some people require more time to reflect on concepts before diving into dialogs and presentations. Others need to speak to reinforce new information. Music, rhymes, chants, poems and games provide additional reinforcement

**1.7 Conventional English Language Teaching:** In the past, students were introduced to English only in their fifth or sixth standard. Students learned English just as another subject like Physics and Mathematics with lot of burden and used to get little opportunities to use it within as well as outside the school premises. Only in convent schools students used to get the opportunities to use this language. Fortunately well trained teachers were available in such premises. But in other schools there has always been a scarcity of such well trained language teachers. They used inappropriate methods to teach English as a second language.

The above context was appropriate for the use of methods that did not focus much on communicative competence. Language teachers usually adopted and followed different methodologies such as

**1. Grammar Translation Method:**
**2. Bilingual Method:**
**3. Direct Method:**

But use of such methods was not of that much use to check the communicative status of candidate. Because teaching of English subject was treated like other subjects and the importance of this was always neglected.

**1.8 English is simply treated as a subject:** Students learned English only as a subject rather than as language. They are unable to put their learning into practice due to lack of a favorable environment. In addition to the given constraints, teachers have to manage with the limited teaching hours which is not enough to teach the language in detail.

Another limitation seen in Indian teachers is that some of the English teachers are not familiar with the latest developments in ELT pedagogy. The situation is no better even at the college level as Robert Bellarmine observes, "The most serious problem in the teaching of English in our country is the appallingly small quantity and atrociously poor quality of English to which our learners are exposed." Teaching of English in India is examination-oriented only.

**1.9 Challenges in Teaching English Today:** Challenges before the English Language teachers in India are huge and obvious. They should be able to provide to the practical needs of learners, to make them competent enough to interact with one another and also to retrieve information all over the world.

English has a base in several countries and is considered as the most suitable and convenient tool for International Communication. The people who

have proficiency in this language could access large number of jobs and also were seen holding high positions in many National and International Organizations.

In the earlier days English was just like a Library language, but now that notion has changed totally. At present the challenges visible before the English language teachers in India are diverse and it is necessary for them to shape up accordingly to meet the demands of the day.

**1.10 Methods to be Adopted to Improve Spoken Skills:**

1. **Group Discussions:** Due to the world wide growing trend in English, teachers give more emphasis to communicative approach rather than the lecture mode. Their main goal is to make the students communicative in English language.

To achieve this, they involve the students to participate more in classroom activities so that they will acquire adequate command over speaking skills. To create this environment, teachers can conduct group discussions, where students are supposed to speak only in English. Here, they can give their views, ideas and thoughts in English due to which they develop the habit of speaking fluently in English like they do in their mother tongue.

Various types of discussions also help students to improve their general awareness and understanding about current affairs. It gives a lot of scope for good imagination and deep thoughts. This type of discussions help the students to listen to the views of fellow students which in turn helps them to gain knowledge and enrich the vocabulary also.

2. **Debates:** Debates too play an important role to improve the speaking ability of the students both at school and at higher level. Debates not only make the students to speak boldly and fluently but also help them to take one stand and be firm and consistent on that. Along with this advantage of reasoning, it gives students some experience to control their emotions without losing their temper. This also helps them to organize their thoughts and ideas in a specific way while speaking.

3. **Role Plays:** Role-plays are another important task that can improve the basic colloquial English of the learners. In role plays, the students assume themselves as one of the characters and behave and speak accordingly involving in the given character completely. In these types of activities teachers have to play a vital role as instructors and guide the students properly so that they can act appropriately to meet the situation. They should help the students now and then to understand and take up the role given to get a grip on the tone of voice.

4. **Language Lab Learning:** Now-a-days computer has become a part and parcel of our day to day life. It plays a vital role in the process of teaching and learning. It can be used to learn a foreign language like English. Language lab software has made language learning easy and also made the language learning process interesting and enjoyable for both teacher and student in this technical world.

**1.10 English for Specific Purposes:** As English has emerged as a global language, it also plays a vital part in every profession with respect its importance and demand. Every profession has its own professional terminology which is used frequently in that particular profession. For example, certain terms used by the doctors, lawyers, et al. are quite different from those of other professionals. So, to benefit these professionals, English for specific purposes is introduced so that specific English words related to that particular profession can be taught by those professionals. Jargon related to one profession is different from the other. Hence every professional is taught in a particular manner that fits in well with his professional demands.

**1.11 Teaching Language through Visual Aids:** One of the innovative methods used by the teacher to teach language in class room is visual aids. The teacher distributes visual aids to students by dividing them into various groups. The students are then given stipulated time to extract relevant information on the given aids. After that, those learners are supposed to speak about the visual aids given to them. This method expands the analyzing capacity of the students. By looking at the picture, the learner should think and come out with innovative thoughts which also help in learning language by creating fun-filled environment around them. The teacher acts as facilitator who motivates the students to talk freely. As each person gets their own unique thinking it helps to sharpen their thinking process.

**1.12 Conclusion:** The goal of this paper was to convey the importance of teacher training which is the need of the day. As the complexities of living conditions demand skilled persons in various dimensions of life. All the skills have their own significance so is the teaching of English as a language. Hence, the teaching of English language is required to be strengthened and problems need to be reduced with the best efforts of government and educationists and researchers. Instead of conventional language teaching new technical methods need to be adopted for the better result of language learning and teaching. Teaching English language is a challenge today especially before non trained teachers so they should be properly trained to get the positive result. Use of new technology changes the class room environment from a boring one to a positive environment where students would be concentrating and participating in various activities selected by teachers. Trained teachers of English, in this context, should take the responsibility to enable the learners

to achieve the educational goals in general and language aim in particular.

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प्रति,

* अम-१/६-१५/५-१६
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शेगाव-रहाटगाव रोड, २२
कैवल कॉलनी, अमरावती-४

प्रेषक
संपादक अक्षरदेवी
जनसाहित्य भवन
गणेश कॉलनी,
अमरावती.
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शोधनिबंध

# रमेश पाटील यांच्या कथेतील दलित आशयविश्व

डॉ.गजानन बनसोड

मराठी विभाग, विद्याभारती महाविद्यालय, कॅम्प, अमरावती.भ्रमणभाष-९७३०४१९१५९

रमेश पाटील यांचे 'निखाऱ्यातील फुले', 'सावलीची बहीण' व 'भूक' हे तीन कथासंग्रह प्रसिद्ध आहेत. त्यांच्या कथा वाचताना कथालेखनाची उत्तम शैली जाणवते. अत्यंत खुबीने कथेमध्ये शब्दांची निवड ते करतात. सहज सोपी वाक्यरचना, ओघवती निवेदनशैली व अफाट शब्दसामर्थ्य त्यांच्याजवळ आहे. त्यातूनच त्यांच्या कथेमधील सलगता व एकसंधता भावते. फार प्रसिद्धीच्या झोतात नसलेले रमेश पाटील हे सातत्याने गेल्या चार दशकांपासून कथालेखन करतात. अनेक दिवाळी अंकांसह 'अस्मितादर्श', 'अक्षरवैदर्भी' व 'लोकानुकंपा' या नियतकालिकांतून त्यांची कथा वाचकांपर्यंत पोहोचली आहे. समकालीन वास्तवातून व समाजभानातून त्यांनी आपल्या अनुभवालाला कथारूप प्राप्त करून दिले आहे. समाजातील भेदक वास्तव कलात्मकतेने कथेतून अधोरेखित केले आहे. ग्रामीण व दलित माणसांची सुखदुःखे, व्यथावेदना त्यांनी कथेतून मुखर केली आहेत. परिवर्तनवादी विचाराचा पुरस्कार करीत गंभीरपणे ते कथालेखन करतात.

**(१) रमेश पाटील यांच्या कथेचे स्वरूप-**

डॉ.बाबासाहेब आंबेडकर यांनी दिलेल्या धम्मदीक्षेनंतर पूर्वाश्रमीच्या अस्पृश्यांच्या व धर्मांतरित नवबौद्धांच्या जीवनाशी दलित साहित्य सीमित झाले होते. त्याच काळात शहरीकरणामुळे आणि काहीशा औद्योगिकीकरणामुळे ग्रामीण परिसर बदलू लागला. ग्रामीण जीवन परिसरात नवा राजकीय वर्ग उदयास आला. शंकरराव खरात, बाबुराव बागूल, केशव मेश्राम, वामन होवाळ, योगीराज वाघमारे यांच्या कथासाहित्यातून दलितांच्या शोषणाचे व त्यांच्या व्यथावेदनांचे पडसाद उमटत होते. नकार आणि विद्रोह ही भूमिका घेऊन अवतीर्ण झालेल्या दलित साहित्याचे निराळेपंण जाणवू लागले होते. दलितांचे दाहक-विदारक अनुभव कधी कळवळून, कधी आव्हान देऊन कधी रागाने तर कधी त्वेषाने व्यक्त होत होते. डॉ.आंबेडकरांच्या विचारांनी पूर्वीश्रमीचा अस्पृश्य जागृत होऊ लागला होता. त्याला आत्मभान प्राप्त झाले होते. दलितांच्या जीवनात, सामाजिक संबंधात स्थित्यंतरे होऊ लागली याची स्पंदने

कथेत उमटली आहेत.

'निखाऱ्यातील फुले' या कथासंग्रहाच्या प्रस्तावनेत डॉ.यशवंत मनोहर म्हणतात, 'रमेश पाटील यांची कथा मराठी कथा समीक्षेपुढे एक नवे वाङ्मयीन वास्तव उभे करीत आहे. एक नवा उजेड पुरवीत आहे. ही कथा ग्रामीणही आहे. पण दलित कथा असल्याने ग्रामीण जीवनातील दलित केंद्र ही कथा आपले मध्यवर्ती केंद्र मानते. त्यामुळे इतर ग्रामीण लेखकांप्रमाणे ही कथा ग्रामीण राहात नाही. इतर दलित लेखकांप्रमाणे ही कथा दलितही असत नाही, ग्रामीणता येते म्हणून ती दलित लेखकांपेक्षा निराळी ठरते आणि दलित जाणिवेची उपस्थिती तिच्यात असल्याने ती विद्यमान ग्रामीण लेखकांच्या पुढे जाते. दलितांच्या ग्रामीण कथेची एक नवी आकृती, आंबेडकर जाणिवेने सिद्ध केलेली ग्रामीण आशयाची एक नवी प्रकृती येते साकार होते. हा सिंथेसिसच रमेश पाटील यांच्या कथेला वेगळे स्वरूप प्राप्त करून देतो.'[१] डॉ.मनोहर यांच्या विवेचनातून रमेश पाटील यांच्या कथेचे स्वरूप अधिक स्पष्ट होते. सामाजिक अनुभवातून व सूक्ष्म निरीक्षणातून पाटील यांची कथा समृद्ध झाली आहे. कथेतून सुशिक्षित बेकारापासून तर कष्टकरी, श्रमजीवी व पोटासाठी भीक मागणाऱ्या माणसांची व्यथा बोलकी केली आहे. समकालीन दलित कथेचे अभ्यासक डॉ.मनोहर सुरवाडे यांच्या मतानुसार 'दलित कथा सुरुवातीची असो की आजची; तिचा हेतू स्पष्ट असून दलितत्वातून आलेल्या व्यथा-वेदनांना ती मुखर करते. जीवनवादी भूमिकेतून अवतीर्ण होते. हे दलित जीवन ज्या व्यवस्थेतून वाट्याला आले त्या व्यवस्थेला नाकारून माणसाच्या अस्तित्वाची जाणीव करून देते. पायाभूत सुविधांपासून ज्यांना उपेक्षित ठेवले गेले, अशा मनांचे आक्रंदन या कथेतून येते. समताधिष्ठित सामाजिक जीवनाची मागणी ही कथा करताना दिसते.'[२] वरील भाष्यातून अलिकडच्या काळातील दलित कथेचे स्वरूप उजागर होते. आजच्या सामाजिक वास्तवाला कवेत घेण्याचा प्रयत्न रमेश पाटील यांची कथा करते.

**(२) कथेतील दलित आशयविश्व-**

प्रा.रमेश पाटील यांनी दलितांचे प्रखर-भेदक वास्तव कथेतून मांडले आहे. त्यांच्या अनुभवाचे क्षेत्र व्यापक आहे. दलित माणसांचे जीवन व त्याच्या मनाची होत असलेली घुसमट ते कथेत टिपतात. प्रस्थापित व्यवस्थेमध्ये दलितांवर येणाऱ्या मानसिक दडपणाचा वेधही त्यांनी कथेत घेतला आहे. 'एका सूडाचा प्रवास' या कथेत विठोबा या अस्पृश्य माणसाच्या मुलीने खंडू पाटलाच्या श्रीकांतशी आंतरजातीय विवाह केला, त्या विठोबाला पाटील घरी बोलावून मारझोड करतो. 'विठू महाराला पाटील मारीत आहे. ही वार्ता हां हां म्हणता वाऱ्यासारखी महारपुऱ्यात



घराघरात घुसली आणि सारे धावत चावडीकडे आले. त्यांनी पुढे होऊन विठूला सोडवून घेतले. विठूची पाठ हिरवी-निळी झाली होती!'[१] वरील प्रसंगातून खंडू पाटलाच्या अन्यायाला बळी पडलेल्या सोशिक विठूचे वर्णन आहे. कथेला शब्दबंबाळ होऊ न देता नेमक्या वाक्यांत अत्यंत संयतपणे दलितांचे जीवन ते कथेत उजागर करतात.

पारंपरिक केरसुण्या बनविणारा पिऱ्या मांग आपल्या पोरीला शाळेत घालतो हे गावातील भदू पाटलाला बघवत नाही. तो पिऱ्याच्या घरी येतो व म्हणतो, 'त्याला शिकून काय करणार- बालिस्टर की वकील? मग असं कर- दे उद्यापासून तुह्या पोराले माह्या ढोराकडं पाठून! माह्या प्रश्न मिटंल, तुही बी कडकी दूर व्हईल. चाल आताच घरी. चार पायली ज्वारी घेऊन जा. मिरची ने.'[४] वरील प्रसंगांत शिवाची शाळा बंद करण्यासाठी भदू पाटलाने केलेली क्लृप्ती लक्षात राहाण्यासारखी आहे. सवर्णीय असणारा सुभाष बेकारीत असणाऱ्या अशोकची टिंगल करताना म्हणतो, 'अरे आहे रे, पण ती झाली प्रायव्हेटच ना! तुला काय गव्हरमेंट नोकरी लागेल. तू बॅकलॉगचा माणूस. सरकारनं बॅगलॉग भरण्याची मोहीमच काढली आहे, एका झटक्यात लागून जाशील.'[५] विप्लवशी आंतरजातीय विवाह करायला निघालेली अंजू म्हणते, 'तेवढा जातीचा वीक पॉईंट सोडला तर तो वाईट नाही बाबा.'[६]

गावामध्ये समाजकार्य करणाऱ्या व स्वाभिमानी वृत्तीने जगणाऱ्या रघूवर वासुदेव पाटील व नाना मेंढे चोरीचा आळ घेतात व त्याला कारागृहात पाठवितात. 'खालच्या आळीतला हाय साहेब तो. मलेबी त्याच्यावर संशोय हाये साहेब. झाकटीतच थो पेटी घिऊनशानी सांधनीनं जाताना दिसला व्हता. खोटं कायले सांगाव? पाटील माहे काही नातलग नाई आन रघ्याबी माहा दुश्मन नाई. खरं हाय थे सांगतो. मंग थे पेटी त्यानं कुटूनशानी आणली हे मातर मले ठाव नाई.'[७] युगानुयुगे सवर्ण लोक गावातील बहुसंख्याक गरीब, कष्टकरी, श्रमजीवी, आदिवासी लोकांचे दमन करीत आले. त्यांच्या अज्ञानाचा फायदा घेऊन गावातील मोक्याच्या जागा बळकावत राहिले. त्याविषयी 'हक्क' या कथेतील नव्या उमेदीच्या राहुलने पुकारलेला यल्गार पुढील प्रसंगात व्यक्त झाला आहे. 'बुहसंख्येनं आपण आपल्या गावात असून सुद्धा एकही वर्ष दलित, आदिवासी मनुष्य ग्रामपंचायतीचं सरपंचपद भोगू शकत नाही ह्याचा विचार आता आपण करायला पाहिजे. जिल्हा परिषदमध्ये आपला एकही उमेदवार निवडला जात नाही. राखीव मतदारसंघातून जो उमेदवार निवडला जातो तोही नंदीबैल असतो- त्यांच्या इशाऱ्यावर मान डोलावणारा! आता आपण सर्वांनी एकमतानं ठरवून दिलेल्याच उमेदवाराला निवडून देऊ. कुणाच्याही दबावाला आपण बळी पडणार नाही, अशी शपथ घेऊन आजची मिटींग संपली असं मी जाहीर करतो.'[८]

बदलणाऱ्या दलित अंतर्विश्वासंबंधी व त्यांच्या सामाजिक, सांस्कृतिक जीवनासंबंधी भाष्य करताना डॉ.अविनाश डोळस म्हणतात की, 'आज मानसिकदृष्ट्या बौद्ध मंडळी पुष्कळशी पुढारलेली आहेत. देव, धर्म, कर्मकांड त्याचबरोबर जात, वंश, पापपुण्य, पूर्वजन्म, आत्मा या रहाटगाड्यातून बाहेर पडली आहेत. वैज्ञानिक दृष्टिकोन त्यांनी अंगीकारला आहे. जातिव्यवस्थेच्या विरोधात ते ठामपणे उभे आहेत. विलक्षण गती त्यांच्या जीवनाला आली आहे. आपल्या कार्यात, व्यवहारात त्यांनी जातिअंतासाठी पूरक ठरणाऱ्या गोष्टींचा पाठपुरावा केला आहे. भाषणातून, लिखाणातून ते नव्या विचारांचा आग्रह धरताहेत.'[९] वरील विवेचनातून बदलत्या जीवनाचा वेध डॉ.डोळसांनी घेतला आहे.

**(३) अभावग्रस्तांच्या भूकेचे चित्रण–**

दरिद्री जीवनात भूक ही केंद्रवर्ती असून अपमान, अवहेलना, मारहाण, शिव्याशाप या गोष्टी तिच्याभोवती घिरट्या घालतात. दलितांना उपजीविकेसाठी दररोज कामधंदा मिळत नाही. त्यामुळे पोटाची खळगी भरायची कशी? खायचे काय? हा प्रश्न त्यांच्यासमोर उभा ठाकतो. भीक मागून, उष्टेखरकटे, शिळेपाळे जे काही मिळेल तेवढेच पोटात ढकलायचे याशिवाय दुसरा इलाज नाही, अभावग्रस्तांच्या भुकेचे वर्णन रमेश पाटील 'भूक' या कथासंग्रहात करतात. दुष्काळामुळे गुराढोरांचे व माणसाचे हाल होत असताना धोंडीबाची मुले बाहेरगावी काम करण्यासाठी निघून गेली होती. उपाशीतापाशी घरादारांची राखण धोंडीबा करत होता. 'दिलावरपूरच्या बद्रीसेठ मारवाड्याच्या तेरवीचा कार्यक्रम आज होणार होता, हे त्याला माहित झालं होतं या तेरवीच्या कार्यक्रमात मिष्टान्नाचं जेवण मिळणार होतं या लालसेनं धोंडीबा चार कोस पायी तुडवत गेला होता. तो दोन दिवसांपासून उपाशीच होता. घरात जमा केलेली मोहाची सुकलेली फुलं खाऊन तो आपलं मुटकुळं अंग टाकून घराची राखण करत होता.'[१०] पोटात भूक असताना सारंग शाळेत जातो पण त्याचे चित्त शाळेत नसते. तो स्वप्नात हरवतो. 'आईनं कसंबसं समजावून त्याला शाळेत पाठवलं होतं. शाळेतून येताच तुझ्यासाठी भाकरी करून ठेवतो म्हणून सांगितलं होतं. ह्याच तिच्या शब्दाच्या आशेवर त्यानं पाटी-दप्तर घेऊन शाळेची वाट धरली होती! पण उपाशीपोटी असल्याने मास्तर शिकवत असलेले सारे शब्द वाऱ्यावर उडून जात होते. त्याच्या पोटात भुकेचा आगडोंब पेटला होता. चेहरा म्लान झाला होता. शरीर गळलं होतं. त्याचा जीव भुकेनं अधिकाधिक कासावीस होत होता आणि त्याचं मन घरात भाकरी थापत असलेल्या आईजवळ चुलीपाशी जाऊन बसलं. जाळ पेटला होता तवा चुलीवर तापत होता. आई भाकरीचं पीठ मळत होती. हाती उंडा घेत होती गरगर हातावर चक्र फिरत होतं. भाकरीनं



आकार घेतला होता आणि चन् चन् असा आवाज निघून भाकर तव्यात पडली तशी पुकडीची चपराक त्याच्या गालावर बसली.'[११] वरील प्रसंगातून रमेश पाटील यांनी शाळकरी मुलाच्या भुकेची दाहकता व्यक्त केली आहे.

**(४) कथेतील आंबेडकरी विचारसूत्र–**

'शिका, संघटित व्हा आणि संघर्ष करा'– या त्रिसूत्रीतून बाबासाहेबांनी विचारसरणी प्रकट होते. भारतातील विषमतावादी जातीव्यवस्था शोषण करणारी असून माणसाना अज्ञान व अंधश्रद्धेत ढकलणारी आहे याची जाणीव त्यांनी आपल्या अनुयायांना करून दिली. त्यासाठी त्यांनी मानवमुक्तीचा लढा उभारला व मानसिक गुलामगिरीतून पूर्वाश्रमीच्या अस्पृश्यांना बाहेर काढले. 'स्वातंत्र्य, बंधुत्व व न्याय' ही मानवतावादी मूल्ये रुजविण्यासाठी संपूर्ण आयुष्य खर्ची घातले, त्याच आंबेडकरी विचाराची सूत्रे रमेश पाटील यांच्या कथेत उमटली आहेत. 'दिशा' या कथेत ते सांगतात, शिक्षणाशिवाय माणसाचा उद्धार होणार नाही. आपल्यासारख्या सहिबांनी शिक्षणाचीच आस धरली पाहिजे. आठवले सर त्यांना शिक्षणाचं महत्व पटवून देऊ लागले. शिक्षणामुळेच बाबासाहेब लोकप्रिय झाले. दलितांचे उद्धारकर्ते झाले.'[१२] वरील विवेचन बोधकारक आहे.

दंगलीमध्ये मारल्या गेलेल्या माणसाबद्दल अनेकांच्या कूपमंडूक ढोकबाजू निघालेल्या प्रतिक्रयेवर 'एका माणसाची कविता' या कथेत संविधान व नायकाची प्रतिक्रिया अत्यंत बोलकी आहे, तो म्हणतो–

*'माणूस माणसापासून दूर जात आहे.*
*आणि स्मशानाचा पाठलाग चालू आहे*
*माणूस मेला, गोड झाला*
*पण आमच्या लेखी तो*
*हिंदू, मुसलमान, ख्रिश्चन, बौद्ध की अधिक कोणी*
*सिद्ध झाला नाही*
*आम्ही पाहातो आमची जात*
*आमचा धर्म.*
*आणि वगळून टाकतो आमचं कर्म*
*माणसानं माणसासाठी झटावं*
*हे आमच्या तत्त्वात बसत नाही*
*अरे, कोणीच कसा त्याला*

*आपला म्हणून ओळखत नाही?*
*अरे, सारे तर्कवितर्क सोडून*
*'माणूस' मेला, फक्त माणूस! त्याला तुम्ही*
*कां बरं स्वीकारत नाही?'*[१३]

संविधान हा माणसाच्या कवितेतून आंबेडकरी विचार लोकांच्या हृदयापर्यंत पोहोचवितो. रमेश पाटील यांनी आपल्या कथेतून निवेदन व संवादामध्ये आंबेडकरी विचारांची मांडणी केली आहे.

(५) निष्कर्ष–

(१) प्रा.रमेश पाटील यांची कथा समकालीन समाजवास्तवाच्या भेदक अनुभवातून साकारली आहे.

(२) दलित मनाच्या सुखदुःखाची स्पंदने त्यांच्या कथेत उमटली आहेत.

(३) रमेश पाटील यांची कथा ग्रामीण जीवनातील दलित केंद्र आपले मध्यवर्ती केंद्र मानते.

(४) दलित व ग्रामीण आशयाची नवी प्रकृती त्यांच्या कथेत साकारते.

(५) दलित माणसांच्या मनाची घुसमट या कथेत टिपली आहे.

(६) रमेश पाटील यांनी सुशिक्षित बेकारापासून तर कष्टकरी, श्रमजीवी व पोटासाठी भीक मागणाऱ्या माणसाची व्यथा कथेतून बोलकी केली आहे.

(७) दलित अंतर्विश्वातील सामाजिक, सांस्कृतिक जीवनाचा आशय या कथेत आहे.

(८) 'भूक' या कथासंग्रहात विविधांगी पद्धतीने कलात्मकतेने भुकेचे चित्रण केले आहे.

(९) डॉ.बाबासाहेब आंबेडकरांनी दिलेल्या धम्म–दीक्षेनंतर झालेल्या मूल्यांतराचे पडसाद 'दिशा', 'हक्क', 'संघर्ष', 'एका माणसाची कविता' इ.कथांत उमटलेले आहेत.

संदर्भ टीपा–

(१) निखाऱ्यातील फुले, रमेश पाटील, संघमित्रा प्रकाशन, गौतमनगर, नागपूर, 'प्रस्तावना' (२) समकालीन दलित कथा, डॉ.मनोहर सुरवाडे, अन्वय प्रकाशन, पुणे, पृ.८१. (३) निखाऱ्यातील फुले, पृ.६. (४) निखाऱ्यातील फुले, पृ.२३,२४. (५) सावलीची बहीण, रमेश पाटील, अक्षर मानव प्रकाशन, पुणे, पृ.८. (६) सावलीची बहीण, पृ.५९. (७) सावलीची बहीण, पृ.६४. (८) सावलीची बहीण, पृ.११२. (९) आंबेडकरी चळवळ : सामाजिक संदर्भ, अविनाश डोळस, सुगावा प्रकाशन, पुणे, पृ.२४. (१०) भूक, रमेश पाटील, अक्षर मानव प्रकाशन, पुणे, पृ.२२. (११) भूक, पृ.६४. (१२) सावलीची बहीण, पृ.७७. (१३) सावलीची बहीण, पृ.९९.

**Article**

# Bianchi Type V Viscous Fluid Cosmology with Linear Equation of State & Hybrid Scale Factor

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**Abstract**

The paper deals with the study of Bianchi Type V cosmological model filled with viscous fluid governed by the linear equation of state $p=(\gamma-1)\rho,\ 0\le\gamma\le 2$ has been studied in the framework of general theory of relativity. The exact solutions of the Einstein's field equations are obtained under the assumption of Hybrid Expansion Law (HEL) for the average scale factor that yields power law and exponential law cosmologies in its special cases. Different solutions are discussed with constant and time varying cosmological constant together with variable and constant bulk viscosity. The physical and kinematical properties are also discussed.

**Keywords:** Bianchi Type V, spacetime, linear equation, hybrid scale factor, cosmology.

## 1. Introduction

Dissipative effects involving both the bulk and shear viscosity play a significant role in the early evolution of the universe. The inclusion of dissipative terms in the energy-momentum tensor of cosmic fluid seems to be the best motivated generalization of the matter term of the gravitational field equations. It has been argued for a long time that the dissipative process in early stages of cosmic expansion may well account for the high degree of isotropy we observe today. Eckart [1] developed the first relativistic theory of nonequilibrium thermodynamics to the effect of bulk viscosity. The effect of bulk viscosity on the cosmological evolution has been investigated by a number of authors namely, Kandalkar [2] Saha [3–5], Singh et al.[6], Sahni and Starobinsky [7], Peebles and Ratra [8], Bali and Pradhan[9], Bali and Kumawat [10], and Bali [11].Romano and Pav´on [12] have investigated the evolution of Bianchi type I universe with viscous fluid.

A wide range of observations suggest that universe possesses a non-zero cosmological constant. Recently Barrow and Shaw[13] suggested that cosmological term corresponds to a very small value of the order $10^{-122}$ when applied to Friedmann universe. Linde [14] has investigated that

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$\Lambda$ is a function of temperature and is related to the spontaneous symmetry-breaking process. A number of cosmological models in which $\Lambda$ decays with time have been investigated by, Bertolami[15], Beesham [16], Berman [17], Singh and Desikan [18], Abdussattar and Vishwakarma [19], Bronnikov et al. [20], Bali and Singh [21], and Ram and Verma [22].

The phenomenon of accelerated expansion of the Universe came into picture in the last decade, and by now it has been confirmed by different data sets of complimentary nature such as type Ia supernovae (SN Ia), baryon oscillations, galaxy clustering, cosmic microwave background (CMB) and weak lensing [23]. But this has posed a challenging problem- what is driving the accelerated expansion of the Universe. In fact, power-law and exponential law cosmologies can be used only to describe epoch based evolution of the Universe because of the constancy of deceleration parameter. For instance, these cosmologies do not exhibit the transition of the Universe from deceleration to acceleration. Padmanabhan and Chitre [24] pointed out that the presence of bulk viscosity leads to inflationary-like situations in general relativity.

In this paper, we considered the anastz [25] for the scale factor of the Universe. We confronted the hybrid scale factor cosmology with the latest observational data from H(z) and SN Ia compilations, and then studied the kinematics and dynamics of the hybrid scale factor Universe in detail.

## 2. Metric and Field Equations

We consider the spatially homogeneous and anisotropic Bianchi type V space time is described by the line element

$$ds^2 = -dt^2 + A^2dx^2 + B^2\exp(-2mx)dy^2 + C^2\exp(-2mx)dz^2 \tag{1}$$

where $A$, $B$, $C$ are the metric functions of cosmic time $t$ and $m$ is constant.

We consider the matter component of source field to be viscous fluid described by the energy momentum tensor

$$T_{ij}^M = (\rho + \bar{p})v_i v_j + \bar{p}g_{ij} - 2\eta\sigma_{ij} \tag{2}$$

Where $\bar{p}$ is the effective pressure related to the equilibrium pressure $p$ by

$$\bar{p} = p - \varsigma v^i{}_{;i} \tag{3}$$

Here $\rho$ is the energy density of matter, $\eta \geq 0$ and $\varsigma \geq 0$ are coefficient of shear and bulk viscosity respectively and $v^i$ is the four velocity vector of the fluid satisfying the relations $v_i v^j = -1$. $\theta$ is the expansion scalar and $\sigma_{ij}$ is the shear tensor defined by

$$\theta = v^i{}_{;i}$$

$$\sigma_{ij} = \frac{1}{2}\left(v_{i;k}h_j^k + v_{j;k}h_i^k\right) - \frac{1}{3}\theta h_{ij} \tag{4}$$

where $h_{ij} = g_{ij} + v_i v_j$ is the projection tensor.

The shear viscosity characterizes a change in shape of a fixed volume of the fluid, whereas the bulk viscosity characterizes a change in volume of the fluid of a fixed shape.

The equation of state is taken to be of usual form

$$p=(\gamma-1)\rho, \quad (0\le\gamma\le 2) \tag{5}$$

We choose gravitational units such that $8\pi G=c=1$.

Since the vaccum has the symmetry of the background, its energy momentum tensor has the form $T_{ij}^{M}=\Lambda g_{ij}$, where $\Lambda$ is a function of time in a homogeneous space.
In commoving coordinate system $(v^i=\delta_4^i)$it corresponds to a perfect fluid with energy density $\rho_\Lambda=\Lambda$ and pressure $p_\Lambda=-\Lambda$.

The Einstein's field equations with viscous matter and vacuum energy are given by

$$R_{ij}-\frac{1}{2}R_k^k g_{ij}=-T_{ij}^{total} \tag{6}$$

where $T_{ij}^{total}=T_{ij}^{M}+T_{ij}^{\Lambda}=(\rho_t+p_t)v_iv_j+p_t g_{ij}$
with $\rho_t=\rho+\Lambda,\ p_t=p-\Lambda$ are total energy density and total pressure, respectively.
The Bianchi identities require that $T_{ij}^{total}$ has a vanishing divergence.

The surviving components of the field equations (6) for the Bianchi type V metric are

$$-\frac{\ddot{B}}{B}-\frac{\ddot{C}}{C}-\frac{\dot{B}\dot{C}}{BC}+2\eta\frac{\dot{A}}{A}+\frac{m^2}{A^2}=p-\left[\varsigma-\frac{2}{3}\eta\right]\theta-\Lambda \tag{7}$$

$$-\frac{\ddot{A}}{A}-\frac{\ddot{C}}{C}-\frac{\dot{A}\dot{C}}{AC}+2\eta\frac{\dot{B}}{B}+\frac{m^2}{A^2}=p-\left[\varsigma-\frac{2}{3}\eta\right]\theta-\Lambda \tag{8}$$

$$-\frac{\ddot{A}}{A}-\frac{\ddot{B}}{B}-\frac{\dot{A}\dot{B}}{AB}+2\eta\frac{\dot{C}}{C}+\frac{m^2}{A^2}=p-\left[\varsigma-\frac{2}{3}\eta\right]\theta-\Lambda \tag{9}$$

$$\frac{\dot{A}\dot{B}}{AB}+\frac{\dot{B}\dot{C}}{BC}+\frac{\dot{A}\dot{C}}{AC}-\frac{3m^2}{A^2}=\rho+\Lambda \tag{10}$$

$$2\frac{\dot{A}}{A}-\frac{\dot{B}}{B}-\frac{\dot{C}}{C}=0 \tag{11}$$

Here and henceforth an overhead dot (.) denotes ordinary derivative with respect to cosmic time t and semicolon (;) stands for covariant derivative.

We define average scale factor $R$ for Bianchi type V space time as

$$R^3 = ABC \tag{12}$$

Generalized Hubble parameter $H$ and generalized deceleration parameter $q$ are defined as

$$H = \frac{\dot{R}}{R} = \frac{1}{3}\left(H_1 + H_2 + H_3\right)$$

$$q = -\frac{R\ddot{R}}{\dot{R}^2} = -\frac{\dot{H}^2}{H^2} - 1 \tag{13}$$

where $H_1 = \frac{\dot{A}}{A}$, $H_2 = \frac{\dot{B}}{B}$, $H_3 = \frac{\dot{C}}{C}$ are directional Hubble factors along $x$, $y$ & $z$ directions respectively.

For Bianchi Type V metric expressions for volume expansion scalar $\theta$ and shear tensor $\sigma_{ij}$ come out to be

$$\theta = 3H$$

$$\sigma_1^1 = H_1 - H, \quad \sigma_2^2 = H_2 - H, \quad \sigma_3^3 = H_3 - H, \quad \sigma_4^4 = 0 \tag{14}$$

Magnitude $\sigma$ of the shear tensor $\sigma_{ij}$ is given by

$$\sigma^2 = \frac{1}{2}\sigma_{ij}\sigma^{ij} = \frac{1}{6}\left[\left(H_1 - H_2\right)^2 + \left(H_2 - H_3\right)^2 + \left(H_3 - H_1\right)^2\right] \tag{15}$$

From (6)-(8), we obtain the following two equations after integration

$$\frac{\dot{A}}{A} - \frac{\dot{B}}{B} = \frac{d_1}{R^3} e^{-2\int \eta dt}$$

$$\frac{\dot{B}}{B} - \frac{\dot{C}}{C} = \frac{d_2}{R^3} e^{-2\int \eta dt} \tag{16}$$

Using (11), from equation (16), we obtain that

$$\frac{\dot{A}}{A} = \frac{\dot{R}}{R} + \frac{\left(2d_1 + d_2\right)}{3R^3} e^{-2\int \eta dt} \tag{17}$$

$$\frac{\dot{B}}{B}=\frac{\dot{R}}{R}+\frac{\left(d_2-d_1\right)}{3R^3}e^{-2\int\eta dt} \tag{18}$$

$$\frac{\dot{C}}{C}=\frac{\dot{R}}{R}-\frac{\left(d_1+2d_2\right)}{3R^3}e^{-2\int\eta dt} \tag{19}$$

We consider the shear viscosity $\eta$ scaling with the expansion scalar $\theta$, that is

$$\eta=3\eta_0\frac{\dot{R}}{R} \tag{20}$$

$\eta_0$ being constant.

Using (20) in (17)-(19), we obtain

$$\frac{\dot{A}}{A}=\frac{\dot{R}}{R}+\frac{\left(2d_1+d_2\right)}{3R^{3+6\eta_0}} \tag{21}$$

$$\frac{\dot{B}}{B}=\frac{\dot{R}}{R}+\frac{\left(d_2-d_1\right)}{3R^{3+6\eta_0}} \tag{22}$$

$$\frac{\dot{C}}{C}=\frac{\dot{R}}{R}-\frac{\left(d_1+2d_2\right)}{3R^{3+6\eta_0}} \tag{23}$$

## 3. Solution of Field equations

To solve the equations (21)-(23), we use the following ansatz [25] for the scale factor

$$R=a_1t^{\alpha}e^{\beta t} \tag{24}$$

where $a_1>0,\ \alpha\geq 0\ \ and\ \beta\geq 0$ are constants.

We referred this generalized form of scale factor to as the Hybrid Expansion Law (HEL). This scale factor has two factors: one factor behaving like exponential expansion and the other factor behaving like power law expansion. One may immediately observe that the (HEL) leads to power law cosmology for $\beta=0$ and the exponential cosmology for $\alpha=0$. In other words the

power law and exponential law cosmologies are the special cases of HEL cosmology. Therefore the case $\alpha > 0 \;\; and \, \beta > 0$ leads to a new cosmology arising from the HEL.

From equations (21)-(23), the metric functions can be explicitly written in terms of the average scale factor $R$ as

$$A = k_1 R \exp\left[\frac{(2d_1 + d_2)}{-3(2+6\eta_0)R^{2+6\eta_0}}\right] \tag{25}$$

$$B = k_2 R \exp\left[\frac{(d_2 - d_1)}{-3(2+6\eta_0)R^{2+6\eta_0}}\right] \tag{26}$$

$$C = k_3 R \exp\left[\frac{(d_1 + 2d_2)}{3(2+6\eta_0)R^{2+6\eta_0}}\right] \tag{27}$$

where $k_1$, $k_2$, $k_3$ are constants of integration.

Using (24), we find the metric functions explicitly in terms of $t$ as follows.

$$A = (k_1 a_1) t^{\alpha} \exp\left[\beta t + \frac{m_1}{(2+6\eta_0)\left(a_1 t^{\alpha} e^{\beta t}\right)^{2+6\eta_0}}\right] \tag{28}$$

$$B = (k_2 a_1) t^{\alpha} \exp\left[\beta t + \frac{m_2}{(2+6\eta_0)\left(a_1 t^{\alpha} e^{\beta t}\right)^{2+6\eta_0}}\right] \tag{29}$$

$$C = (k_3 a_1) t^{\alpha} \exp\left[\beta t + \frac{m_3}{(2+6\eta_0)\left(a_1 t^{\alpha} e^{\beta t}\right)^{2+6\eta_0}}\right] \tag{30}$$

where $m_1 = \frac{(2d_1 + d_2)}{-3}$, $m_2 = \frac{(d_2 - d_1)}{-3}$, $m_3 = \frac{(d_1 + 2d_2)}{3}$.

The pressure and energy density are given by

$$p - \left[\varsigma - 2\eta_0\left(\beta + \frac{\alpha}{t}\right)\right]3\left(\beta + \frac{\alpha}{t}\right) - \Lambda = 2\frac{\alpha}{t^2} + 3\left(\beta + \frac{\alpha}{t}\right)^2 + \frac{(m_1 + m_2)(6+6\eta_0)}{\left(a_1 t^{\alpha} e^{\beta t}\right)^{3+6\eta_0}}\left(\beta + \frac{\alpha}{t}\right)$$

$$- \frac{\left(m_2^2 + m_3^2 + m_2 m_3\right)}{\left(a_1 t^{\alpha} e^{\beta t}\right)^{6+12\eta_0}} + 6\eta_0\left(\beta + \frac{\alpha}{t}\right)\left[\beta + \frac{\alpha}{t} + \frac{m_1}{\left(a_1 t^{\alpha} e^{\beta t}\right)^{3+6\eta_0}}\right]$$

$$+\frac{m^2}{(k_1a_1)^2 t^{2\alpha}\exp 2\left[\beta t+\frac{m_1}{(2+6\eta_0)\left(a_1t^{\alpha}e^{\beta t}\right)^{2+6\eta_0}}\right]} \tag{31}$$

$$\rho=\left[3\left(\beta+\frac{\alpha}{t}\right)^2+\frac{(m_1m_2+m_2m_3+m_1m_3)}{\left(a_1t^{\alpha}e^{\beta t}\right)^{6+12\eta_0}}\right]-\frac{3m^2}{(k_1a_1)^2 t^{2\alpha}\exp 2\left[\beta t+\frac{m_1}{(2+6\eta_0)\left(a_1t^{\alpha}e^{\beta t}\right)^{2+6\eta_0}}\right]}-\Lambda \tag{32}$$

One may observe that (28)-(32) represents exact solutions of the Einstein's field equations (7)-(11).

Now we find expressions for some other cosmological parameters of the model

$$\text{The Anisotropy parameter } \overline{A}=\frac{1}{3}\sum_{i=1}^{3}\left[\frac{H_i-H}{H}\right]^2 \tag{33}$$

The directional Hubble factors $H_i$ $(i=1,\ 2,\ 3)$ as defined are given by

$$H_i=\left(\beta+\frac{\alpha}{t}\right)+\frac{m_i}{\left(a_1t^{\alpha}e^{\beta t}\right)^{3+6\eta_0}} \tag{34}$$

The expansion scalar is given by

$$\theta=3H=3\left(\beta+\frac{\alpha}{t}\right) \tag{35}$$

Using (34) and (35) into (33), we obtain

$$\overline{A}=\frac{1}{27\left(\beta+\frac{\alpha}{t}\right)^2}\left[3\left(\beta+\frac{\alpha}{t}\right)^2+\frac{\left(m_1^2+m_2^2+m_3^2\right)}{9\left(a_1t^{\alpha}e^{\beta t}\right)^{6+12\eta_0}}\right] \tag{36}$$

The volume and shear scalar of the model are given by

$$R^3 = \left(a_1 t^{\alpha} e^{\beta t}\right)^3 \tag{37}$$

$$2\sigma^2 = \left[\frac{\left(m_1 m_2 + m_2 m_3 + m_1 m_3\right)}{\left(a_1 t^{\alpha} e^{\beta t}\right)^{6+12\eta_0}}\right] \tag{38}$$

### 4.1.1. Model with constant $\Lambda$ term and $\varsigma(t)$

In this case equations (31), (32) together with (5) yield the expressions for energy density, isotropic pressure and bulk viscosity are respectively given by

$$\rho = \left[3\left(\beta + \frac{\alpha}{t}\right)^2 + \frac{\left(m_1 m_2 + m_2 m_3 + m_1 m_3\right)}{\left(a_1 t^{\alpha} e^{\beta t}\right)^{6+12\eta_0}}\right] - \frac{3m^2}{\left(k_1 a_1\right)^2 t^{2\alpha} \exp 2\left[\beta t + \frac{m_1}{\left(2+6\eta_0\right)\left(a_1 t^{\alpha} e^{\beta t}\right)^{2+6\eta_0}}\right]} - \Lambda \tag{39}$$

$$p = \left(\gamma - 1\right)\left\{\left[3\left(\beta + \frac{\alpha}{t}\right)^2 + \frac{\left(m_1 m_2 + m_2 m_3 + m_1 m_3\right)}{\left(a_1 t^{\alpha} e^{\beta t}\right)^{6+12\eta_0}}\right] - \frac{3m^2}{\left(k_1 a_1\right)^2 t^{2\alpha} \exp 2\left[\beta t + \frac{m_1}{\left(2+6\eta_0\right)\left(a_1 t^{\alpha} e^{\beta t}\right)^{2+6\eta_0}}\right]} - \Lambda\right\} \tag{40}$$

$$\varsigma = \left(\gamma + 2\eta_0 - 1\right)\left(\beta + \frac{\alpha}{t}\right) + \frac{\left(m_1 m_2 + m_2 m_3 + m_1 m_3\right)\gamma}{3\left(a_1 t^{\alpha} e^{\beta t}\right)^{6+12\eta_0}\left(\beta + \frac{\alpha}{t}\right)} - \frac{\left(3\gamma + 1\right)m^2}{3\left(\beta + \frac{\alpha}{t}\right)\left(k_1 a_1\right)^2 t^{2\alpha} \exp 2\left[\beta t + \frac{m_1}{\left(2+6\eta_0\right)\left(a_1 t^{\alpha} e^{\beta t}\right)^{2+6\eta_0}}\right]}$$

$$- \frac{2\alpha}{3\left(\beta + \frac{\alpha}{t}\right)t^2} - \frac{\left(m_2 + m_3\right)\left(2+2\eta_0\right)}{\left(a_1 t^{\alpha} e^{\beta t}\right)^{3+6\eta_0}} + \frac{\left(m_2^2 + m_3^2 + m_2 m_3\right)\left(2+2\eta_0\right)}{3\left(a_1 t^{\alpha} e^{\beta t}\right)^{6+12\eta_0}\left(\beta + \frac{\alpha}{t}\right)}$$

$$- 2\eta_0\left(\beta + \frac{\alpha}{t} + \frac{m_1}{\left(a_1 t^{\alpha} e^{\beta t}\right)^{3+6\eta_0}}\right) - \frac{\left(1+\gamma\right)\Lambda}{3\left(\beta + \frac{\alpha}{t}\right)} \tag{41}$$

It is observed that the solutions are singular at $t = 0$. At late times the energy density converges to $3\beta^2 - \Lambda$. Positivity of $\rho$ is ensured only for $3\beta^2 > \Lambda$. As $t \to \infty$ then $p \to \left(\gamma - 1\right)\left(3\beta^2 - \Lambda\right)$,

$\varsigma \to (\gamma + 2\eta_0 - 1)\beta - 2\eta_0\beta - \dfrac{(1+\gamma)\Lambda}{3\beta}$ this shows that the pressure and bulk viscosity is constant as $t \to \infty$ .

### 4.1.2. Model with variable $\Lambda$ term and constant $\varsigma(t)$

Assuming the coefficient of bulk viscosity is constant $\varsigma(t) = \varsigma_0 = Cons\tan t$ , then (31), (32) together with (5) yield the following expressions for energy density, pressure and cosmological constant are given by

$$\rho = \frac{1}{\gamma}\left[6\left(\beta + \frac{\alpha}{t}\right)^2 + \frac{2\alpha}{t^2} + \frac{\left(m_1m_2 + m_1m_3 - m_2^2 - m_3^2\right)}{\left(a_1t^\alpha e^{\beta t}\right)^{6+12\eta_0}}\right] + 3\varsigma_0\left(\beta + \frac{\alpha}{t}\right)$$

$$- \frac{2m^2}{(k_1a_1)^2 t^{2\alpha}\exp 2\left[\beta t + \dfrac{m_1}{(2+6\eta_0)\left(a_1t^\alpha e^{\beta t}\right)^{2+6\eta_0}}\right]} + \frac{(m_2+m_3)(6+6\eta_0)}{\left(a_1t^\alpha e^{\beta t}\right)^{3+6\eta_0}}\left(\beta + \frac{\alpha}{t}\right)$$

$$- 6\eta_0\left(\beta + \frac{\alpha}{t}\right)\left(\beta + \frac{\alpha}{t} + \frac{m_1}{\left(a_1t^\alpha e^{\beta t}\right)^{3+6\eta_0}}\right) - 6\eta_0\left(\beta + \frac{\alpha}{t}\right)^2 \tag{42}$$

$$p = \frac{(\gamma-1)}{\gamma}\left\{\left[6\left(\beta + \frac{\alpha}{t}\right)^2 + \frac{2\alpha}{t^2} + \frac{\left(m_1m_2 + m_1m_3 - m_2^2 - m_3^2\right)}{\left(a_1t^\alpha e^{\beta t}\right)^{6+12\eta_0}}\right] + 3\varsigma_0\left(\beta + \frac{\alpha}{t}\right)\right.$$

$$- \frac{2m^2}{(k_1a_1)^2 t^{2\alpha}\exp 2\left[\beta t + \dfrac{m_1}{(2+6\eta_0)\left(a_1t^\alpha e^{\beta t}\right)^{2+6\eta_0}}\right]} + \frac{(m_2+m_3)(6+6\eta_0)}{\left(a_1t^\alpha e^{\beta t}\right)^{3+6\eta_0}}\left(\beta + \frac{\alpha}{t}\right)$$

$$\left. - 6\eta_0\left(\beta + \frac{\alpha}{t}\right)\left(\frac{m_1}{\left(a_1t^\alpha e^{\beta t}\right)^{3+6\eta_0}}\right)\right\} \tag{43}$$

$$\Lambda = \left(3 - \frac{6}{\gamma}\right)\left(\beta + \frac{\alpha}{t}\right)^2 + \left[\left(m_1m_2 + m_2m_3 + m_1m_3\right) - \frac{\left(m_1m_2 + m_1m_3 - m_2^2 - m_3^2\right)}{\gamma}\right]\frac{1}{\left(a_1t^\alpha e^{\beta t}\right)^{6+12\eta_0}}$$

$$+\left(\frac{2}{\gamma}-3\right)\frac{2m^2}{(k_1a_1)^2t^{2\alpha}\exp 2\left[\beta t+\frac{m_1}{(2+6\eta_0)\left(a_1t^{\alpha}e^{\beta t}\right)^{2+6\eta_0}}\right]}-\frac{2\alpha}{\gamma t^2}+\frac{3\varsigma_0}{\gamma}\left(\beta+\frac{\alpha}{t}\right)$$

$$-\frac{(m_2+m_3)(6+6\eta_0)}{\gamma\left(a_1t^{\alpha}e^{\beta t}\right)^{3+6\eta_0}}\left(\beta+\frac{\alpha}{t}\right)-\frac{6\eta_0}{\gamma}\left(\beta+\frac{\alpha}{t}\right)\frac{m_1}{\left(a_1t^{\alpha}e^{\beta t}\right)^{3+6\eta_0}} \quad (44)$$

The quantities diverge at $t=0$. As the evolution progress, the energy density, pressure and cosmological constant decreases. As $t\to\infty$ then $\rho\to\frac{3\beta}{\gamma}(2\beta+\varsigma_0)-12\eta_0\beta^2$ ,

$p\to\frac{(\gamma-1)}{\gamma}6\beta^2+3\varsigma_0\beta-6\eta_0\beta$, $\Lambda\to\left(3-\frac{6}{\gamma}\right)\beta^2+\frac{3\varsigma_0}{\gamma}\beta$, It means pressure, density and cosmological constant are constants at t tends to infinity.

### 4.1.2. Model with variable $\Lambda$ term and constant $\varsigma\ \alpha\ \rho$

Let us assume that $\varsigma(t)=\varsigma_0\rho$, then from equations (31) and (32) together with (5) we obtain the expressions for energy density, pressure bulk viscosity and cosmological constant are as follows

$$\rho=\frac{1}{\left[\gamma-3\varsigma_0\left(\beta+\frac{\alpha}{t}\right)\right]}\left\{\left[6\left(\beta+\frac{\alpha}{t}\right)^2+\frac{2\alpha}{t^2}+\frac{(m_1m_2+m_1m_3-m_2^2-m_3^2)}{\left(a_1t^{\alpha}e^{\beta t}\right)^{6+12\eta_0}}\right]\right.$$

$$-\frac{2m^2}{(k_1a_1)^2t^{2\alpha}\exp 2\left[\beta t+\frac{m_1}{(2+6\eta_0)\left(a_1t^{\alpha}e^{\beta t}\right)^{2+6\eta_0}}\right]}+\frac{(m_2+m_3)(6+6\eta_0)}{\left(a_1t^{\alpha}e^{\beta t}\right)^{3+6\eta_0}}\left(\beta+\frac{\alpha}{t}\right)$$

$$\left.+6\eta_0\left(\beta+\frac{\alpha}{t}\right)\left(\frac{m_1}{\left(a_1t^{\alpha}e^{\beta t}\right)^{3+6\eta_0}}\right)\right\} \quad (45)$$

$$p=\frac{(\gamma-1)}{\left[\gamma-3\varsigma_0\left(\beta+\frac{\alpha}{t}\right)\right]}\left\{\left[6\left(\beta+\frac{\alpha}{t}\right)^2+\frac{2\alpha}{t^2}+\frac{\left(m_1m_2+m_1m_3-m_2^2-m_3^2\right)}{\left(a_1t^\alpha e^{\beta t}\right)^{6+12\eta_0}}\right]\right.$$

$$-\frac{2m^2}{(k_1a_1)^2t^{2\alpha}\exp 2\left[\beta t+\frac{m_1}{(2+6\eta_0)\left(a_1t^\alpha e^{\beta t}\right)^{2+6\eta_0}}\right]}+\frac{(m_2+m_3)(6+6\eta_0)}{\left(a_1t^\alpha e^{\beta t}\right)^{3+6\eta_0}}\left(\beta+\frac{\alpha}{t}\right)$$

$$\left.+6\eta_0\left(\beta+\frac{\alpha}{t}\right)\left(\frac{m_1}{\left(a_1t^\alpha e^{\beta t}\right)^{3+6\eta_0}}\right)\right\} \tag{46}$$

$$\varsigma=\frac{\varsigma_0}{\left[\gamma-3\varsigma_0\left(\beta+\frac{\alpha}{t}\right)\right]}\left\{6\left(\beta+\frac{\alpha}{t}\right)^2+\frac{2\alpha}{t^2}+\frac{\left(m_1m_2+m_1m_3-m_2^2-m_3^2\right)}{\left(a_1t^\alpha e^{\beta t}\right)^{6+12\eta_0}}\right.$$

$$-\frac{2m^2}{(k_1a_1)^2t^{2\alpha}\exp 2\left[\beta t+\frac{m_1}{(2+6\eta_0)\left(a_1t^\alpha e^{\beta t}\right)^{2+6\eta_0}}\right]}+\frac{(m_2+m_3)(6+6\eta_0)}{\left(a_1t^\alpha e^{\beta t}\right)^{3+6\eta_0}}\left(\beta+\frac{\alpha}{t}\right)$$

$$\left.+6\eta_0\left(\beta+\frac{\alpha}{t}\right)\left(\frac{m_1}{\left(a_1t^\alpha e^{\beta t}\right)^{3+6\eta_0}}\right)\right\} \tag{47}$$

$$\Lambda=\left(3-\frac{6}{\gamma-3\varsigma_0\left(\beta+\frac{\alpha}{t}\right)}\right)\left(\beta+\frac{\alpha}{t}\right)^2+\left[\left(m_1m_2+m_2m_3+m_1m_3\right)-\frac{\left(m_1m_2+m_1m_3-m_2^2-m_3^2\right)}{\gamma-3\varsigma_0\left(\beta+\frac{\alpha}{t}\right)}\right]\frac{1}{\left(a_1t^\alpha e^{\beta t}\right)^{6+12\eta_0}}$$

$$-\frac{2\alpha}{\left[\gamma-3\varsigma_0\left(\beta+\frac{\alpha}{t}\right)\right]t^2}+\left(\frac{2}{\gamma-3\varsigma_0\left(\beta+\frac{\alpha}{t}\right)}-3\right)\frac{m^2}{(k_1a_1)^2t^{2\alpha}\exp 2\left[\beta t+\frac{m_1}{(2+6\eta_0)\left(a_1t^\alpha e^{\beta t}\right)^{2+6\eta_0}}\right]}$$

$$-\frac{(m_2+m_3)(6+6\eta_0)}{\left[\gamma-3\varsigma_0\left(\beta+\frac{\alpha}{t}\right)\right]\left(a_1t^\alpha e^{\beta t}\right)^{3+6\eta_0}}\left(\beta+\frac{\alpha}{t}\right)-\frac{6\eta_0}{\left[\gamma-3\varsigma_0\left(\beta+\frac{\alpha}{t}\right)\right]}\left(\beta+\frac{\alpha}{t}\right)\frac{m_1}{\left(a_1t^\alpha e^{\beta t}\right)^{3+6\eta_0}} \tag{48}$$

We observe that the energy density $\rho$, cosmological constant $\Lambda$ decreases very sharply. As $t \to \infty$ then $\rho \to \frac{1}{[\gamma - 3\varsigma_0\beta]} 6\beta^2$, $p \to \frac{(\gamma - 1)}{[\gamma - 3\varsigma_0\beta]} 6\beta^2, \Lambda \to \left(3 - \frac{6}{\gamma - 3\varsigma_0\beta}\right)\beta$.

## 5. Conclusion

In the present work, we have constructed viscous fluid distribution in the background of homogeneous anisotropic Bianchi type V space-time with a cosmological term $\Lambda$, which scales with Hubble parameter *H*. Coefficient of shear viscosity $\eta$ is assumed to vary as expansion scalar $\theta$. The spatial volume is zero at $t = 0$ and expansion scalar is infinite, which shows that the universe starts evolving with zero volume at $t = 0$ with a big bang. The Hubble factors and shear scalar diverge at $t = 0$. The anisotropy parameter tend to infinity at the initial epoch. As $t$ increases, the scale factors and spatial volume increase but the expansion scalar decreases. As $t \to \infty$ scale factors and volume become infinite whereas $H_i \to \beta$, $\theta \to 3\beta$, $\bar{A} \to \frac{1}{9}, \sigma^2 \to 0$. We have determined the Bianchi-V space-time by considering hybrid scale factor for the average scale factor that yields power law and exponential-law cosmologies in its special cases. We find that the hybrid scale factor exhibits transition from deceleration to acceleration which is an essential feature of dynamic evolution of the Universe. The resulting model evolves with decelerating expansion in the initial epoch followed by a late time accelerated expansion. The use of a hybrid scale factor significantly changes the behavior of the cosmic fluid. The Bianchi-V hybrid scale factor Universe begins with high anisotropy but becomes isotropic at the later stages of the evolution. If we take $\beta = 0$ we retrieve the power law solution and if we take $\alpha = 0$ we retrieve exponential solution obtained in earlier work (Kandalkar 2012).

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# Synthesis and Structural Properties of Nanocomposite of PANI/ZnO by *in – Situ* polymerization

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## Abstract

***Hybrid PANI/ZnO synthesized by typical oxidative polymerization. This nanocomposite of PANI/ ZnO has been investigated for their structural properties because of hybrid structures. This adopted synthesis method is calledin –situ polymerization. XRD patterns of pure zinc oxide, pure polyaniline and nanocomposites PANI/ZnO gives confirmation of elements were present in compound. SEM micrographs shownanocomposite material PANI/ZnO nanotube formation PANI and in situ deposition of ZnO. EDX gives confirmation of nanocomposites material PANI/ZnO. This nanotube structures enhances the active and passive properties.***

**Keywords:** Nanostructure Pure PANI, ZnO, ***in –situ polymerization*** of PANI/ZnO, XRD, SEM, EDX.

## Introduction

Now days, All polymers are thought to be excellent insulating materials until the l970's, when Hideshishirakawaand their associates reported the high conductance of polyacetylene doped with $AsF_5$[1-3]. Sincethen, broad research has been carried out on conducting polymers because of theirexcellent electrical and optical properties. These materials have broad application in areasranging from anticorrosion coatings, to chemical sensors and biosensors, light-emittingdevices, and solar cells, as well as many others[4]. Among the variety of conducting polymers due to unique electrical properties, stability and easy fabrication process polyaniline is one of the most attractive materials. Because of these interesting properties, polyaniline has been a potential candidate in sensor applications[5,6]. However, the difficulties with these conducting polymers are their low processing ability, poor chemical stability and mechanical strength[7]. As an option, there are a plenty of space to fabricate hetero junctions, to enhancement of the sensor characteristics and mechanical strength. By usingpolymerization, polyaniline and its nanocomposite have been synthesized in a bulk form.

Polyaniline which can besynthesized either by chemical oxidization polymerization[8-10] or electro polymerization[11]. Conventional chemical polymerization is conducted by polymerizing aniline monomersin the presence of a free radical activator. Polyaniline, prepared via chemicalpolymerization with a protonic acid, is typically called doped polyaniline or ernemldinesalt. Generally, conventional bulk chemical synthesis produces only bull-likepolyaniline. One dimensional (1D) nanostructures of conducting polymers such as nanowires, nanofibers, and nanotubes, have been intensively investigated because theypossess superior properties due to their high surface area-to-volume ratio. In past twodecades, a variety of methods have been used to synthesize polyaniline nanofibers, including electrospinning[12], interfacial polymerization[13] rapid- mixing[14], nanofibers seeding[15] templates[16] and surfactants[17] or oligomer-assisted polymerization[18].

Among the various semiconductor oxides materials, Zinc Oxide (ZnO) has been chosen as the key sensing material. Zinc Oxide is among the extensively studied metal oxide outstandingbecause of their unique properties and important characteristics for example low cost, easy availability and wide range of applications. Several researchers have studied this Zinc Oxide either individually or along with some dopant. Metal oxide ZnO is usually semiconductor.Zinc oxide has received forceful attention due to its significant combination of physical and optical properties among the group of II-VI compound semiconductors. Its wide band gap, high exciton binding energy (60 meV), and its assorted growth morphologies make ZnO a key material in the fields of nanotechnology.

There are growing interests to combine both organic and inorganic materials for applications in electro-optic[19]. Combination of nanosized metal oxides and polyaniline has the potential to enhance the property of the conducting polymer. Such composites can operate at room temperature due to its optimized volume to surface ratio of nanosized metal oxides. The properties of nanocomposite materials depend not only on the properties of their constituents but also on their combined morphology and interfacial characteristics[20].

In present work ZnO and PANI nanoparticles synthesized and structural properties were studied.The choice of materials in any research work is an extremely crucial issue which, in turn, is governed by several theoretical as well as practical

considerations such as their suitability and compatibility under the given laboratory conditions.

## Methodology

**Synthesis of Conducting Polymer: Polyaniline:** In present work, use International Union of Pure Applied Chemistry (IUPAC) method is used prepare polyaniline in which aniline hydrochloride (5.18gm) is dissolved in 100 ml distilled water to make up volume. Ammonium peroxydisulphate (11.42gm) is dissolved in 100 ml distilled $H_2O$ in a volumetric flask. The solutions are kept for 1 hour at room temperature. The above solutions are mixed together in equally proportion with constant stirring.

This solution kept under Ultrasonic wave treatment (Sonication process) for period of 10 minutes at room temperature. The precipitated is collected by filtration and washed with 0.2 M HCl, to remove all residual monomers, oxidant and its decomposing products. Finally it is washed with acetone to removes low –molecular-weight organic intermediates and oligomers. It also prevents the aggregation of PANI precipitated during drying. The precipitated is dried at $60^0$C for 12 hours.The resultant material is a polyemeraldine salt.

**Synthesis of Nanomaterial Metal Oxide: Zinc Oxide:** All the chemicals used in this study were of GR grade purchase from Sd-Fine, India (purity 99%). The chemicals are used without any further purification. Synthesis method adopted from S.D. Charpe***etal***liquid –phase method. Finally we get product of ZnO nanoparticles.

**Synthesis of Nanocomposite (PANI/ZnO):** In this synthesis we used ***in –situ polymerization*** method[21-22] to prepare nanocomposite PANI/ZnO. First we prepare 1 M HCl solution in distilled water. Here we used Zinc Oxide which prepared in steps II.

In preparation we add Zinc Oxide (ZnO) in 1M HCl solution to achieved 0.1 M gel solution of Zinc Oxide then this solution under treatment of sonication for 1 hour. Now prepared 100 ml 0.1 M Aniline hydrochloride Solution then add 10 ml sonicated ZnO solution. Again go for sonication for 10 minutes then add 100 ml Ammonium peroxydisulphate (APS) solution slowly with continues stirring, after 3 hours we achieved polymerization. This type polymerization is called as ***in-situ Polymerization***.

After 3 hours filter, washed above solution with 1 M HCl solution and dried under vacuum for 12 hours. Final we get nanocomposite of PANI/ ZnO.

## Results and Discussion

**X-Ray Diffraction Studies: Polyaniline (PANI):** The polycrystalline structure of the nano polyaniline (PANI) was characterized by powder X-ray diffraction (Rigaku X-ray diffractometer) with Cu-α source and $2\theta$ range of 10° - 90°. Figure1show XRD pattern of synthesized polyaniline (PANI) which confirmed that PANI has polycrystalline nature which showsthat ithasamorphousnature.

**Zinc Oxide (ZnO):** The crystallographic structure of the synthesized ZnO nanostructure was characterized by powder XRD.Figure 2show XRD pattern of ZnO. The corresponding X-ray diffraction peak for (100), (002), (101), (102) (110), (103), (200), (112), (201), (004), (202) and (104) planes confirm the formation of hexagonal wurtzite structure of ZnO (DB card no.-2300013).Hence XRD pattern confirmed that synthesized ZnO are highly crystalline in nature. The domain size of the crystal can be estimated by Scherrer form. The average particle size was calculated from (101) peak ZnO is found to be 35nm.Fromsoftware analysis it is confirm that prepared zinc oxide powder contains Zn and O elements only, not any impurity[23].

**PANI/ZnO Composite:** The semi-crystalline structure of the synthesized nanocomposite of Polyaniline (PANI) and Zinc Oxide (PANI/ ZnO) was characterized by XRD. The recorded XRD pattern confirmed that synthesized composite of Polyaniline (PANI)/Zinc Oxide (ZnO) is polycrystalline that is semi amorphous in nature. Figure 3 shows XRD pattern of zinc oxide nanoparticles and that of various nanocomposites showed similar peak patterns, therefore, it may be assumed that presence of polyaniline did not cause any change in crystal structure of zinc oxide or negligible change which may be ignored[24,25].

These results show that polyaniline present in nanomatrix is amorphous in nature which supports the previous reports. Moreover above discussion also supports that the incorporation of supporting polymer into polyaniline does not affect the crystal structure of ZnO. However, presence of such polymers seems to cause the decrease in the size of ZnO nanoparticles this is due to formation of polymer-Zn complex on the surface of ZnOnanoparticles present within/on the surface. This superficial property of the nanocomposites as has also been suggested by Tang***et al***[26] in the study of x-rays patterns of Polymethylmethacrylate (PMMA) and zinc oxide composites.

**Scanning Electron Microscopy Studies: SEM of Polyaniline (PANI):** Scanning Electron Microscope (SEM) images of selected sample was obtained using SEM-JEOL 840 A. The surface morphology of nano size Polyaniline by SEM and its micrographsare shown in figure 4 (a,b). From SEM image PANI is more porous in nature. Due to small pores size, its surface area is more which helps to enhance properties.

**SEM of Pure Zinc Oxide (ZnO):** Figure-5 (a, b) shows SEM micrograph of the pure ZnO. From micrograph it is observed that there is randomly distribution of nanospheres ZnO. Due to such a distribution of nanospheres, surface to volume ratio of the ZnO may be increase.

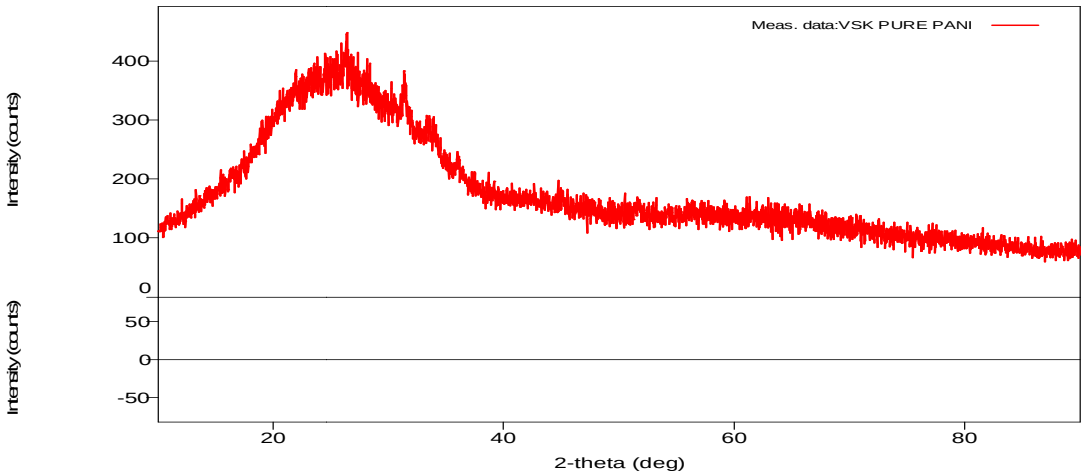


**Figure-1**
**XRD of Pure Nanostructure PANI**

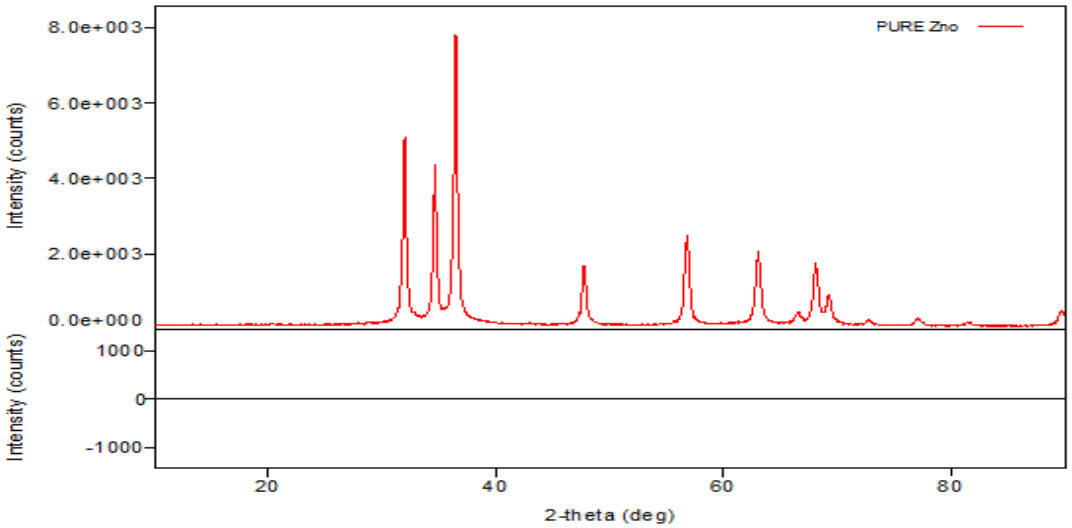


**Figure-2**
**XRD Pattern of Pure Nanostructured ZnO**

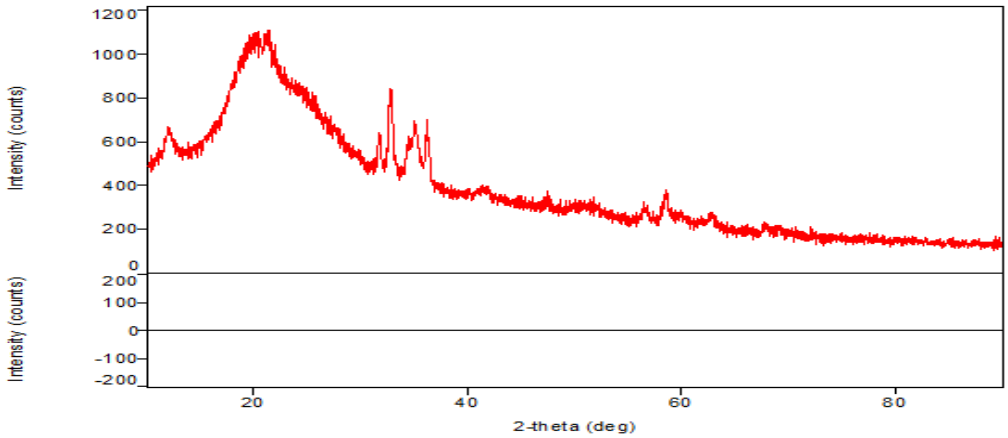


**Figure-3**
**XRD Pattern of Nanocomposite of PANI/ ZnO**

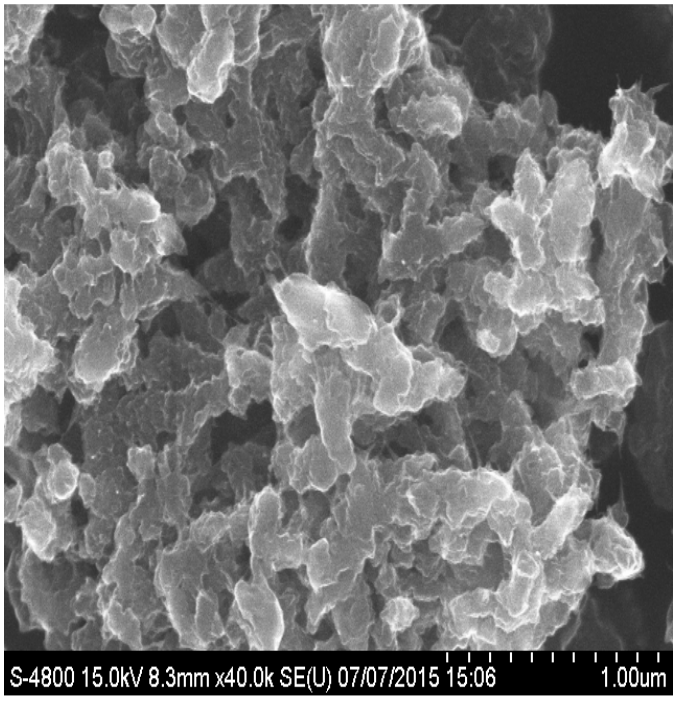


**Figure-4(a)**
**SEM micrograph of PANI**

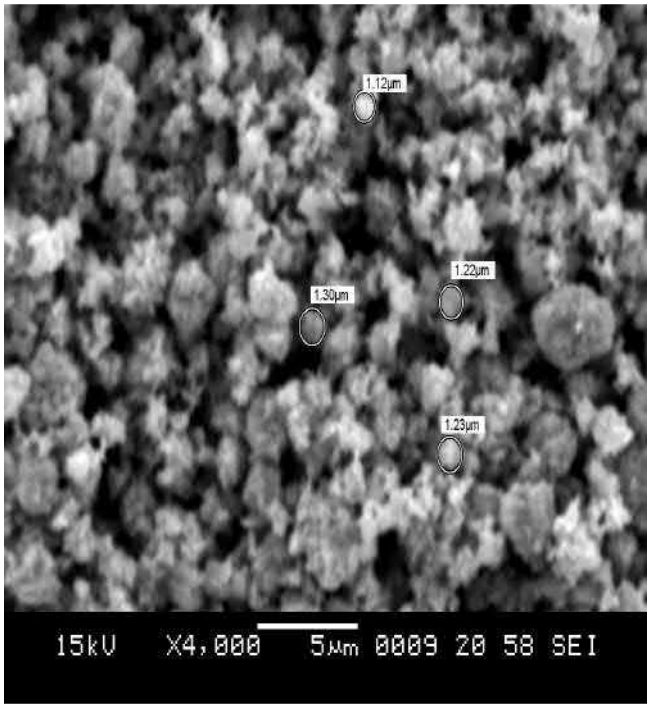


**Figure-5(a)**
**SEM micrograph of ZnO**

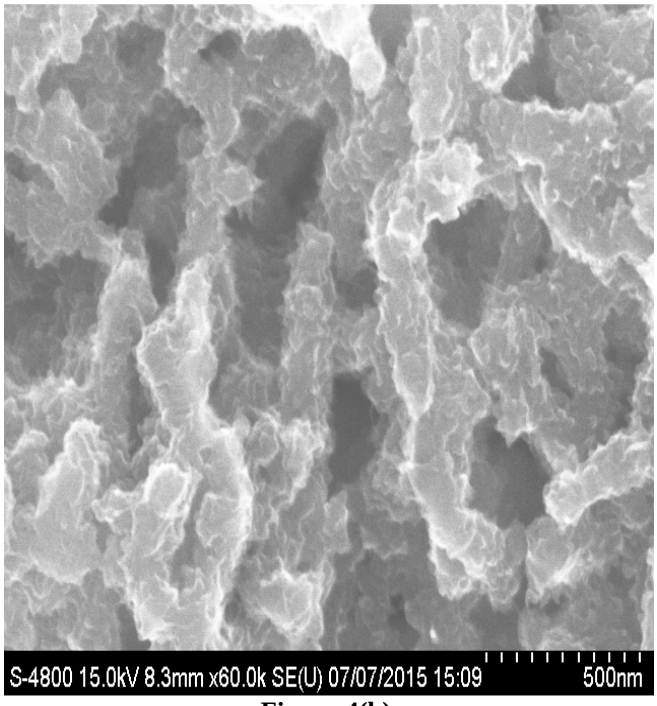


**Figure-4(b)**
**SEM micrograph of PANI**

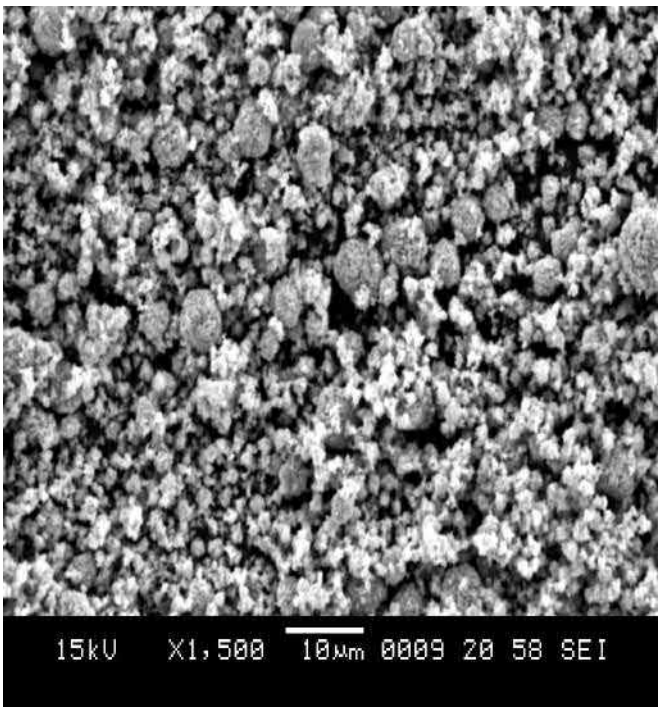


**Figure-5(b)**
**SEM micrograph of ZnO**

**SEM of Nanocomposite PANI/ZnO:** Figure-6 (a,b,c,d) shows SEM micrograph of nanocomposite of polyaniline and zinc oxide.From micrographs it is cleared that there were formation of nanotubes of nanocomposite material PANI/ZnO. It is observed that from image 6 (aand d) on head of polyaniline nanotube there is decomposition of nanosized Zinc Oxide. This is evidencefor ***in –situ polymerization***method of PANI and ZnO to synthesis nanocomposite of PANI/ZnO.

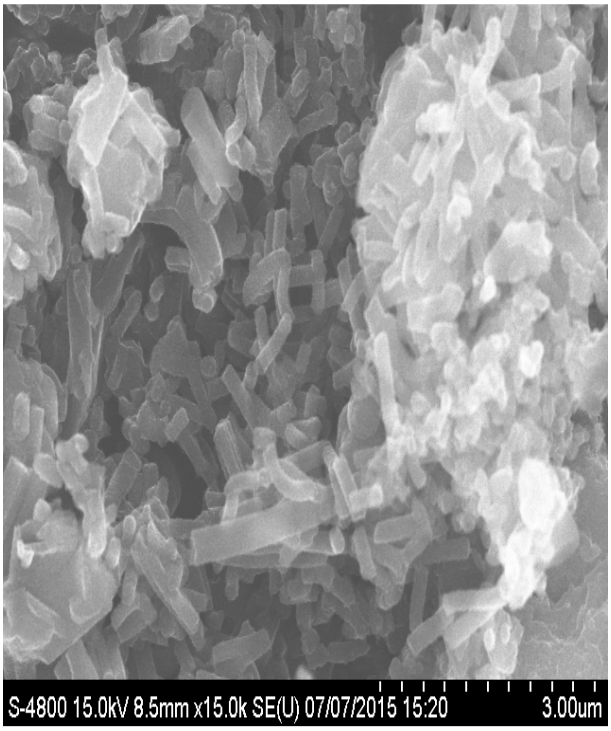


**Figure-6(a)**
**SEM micrograph of PANI/ZnO**

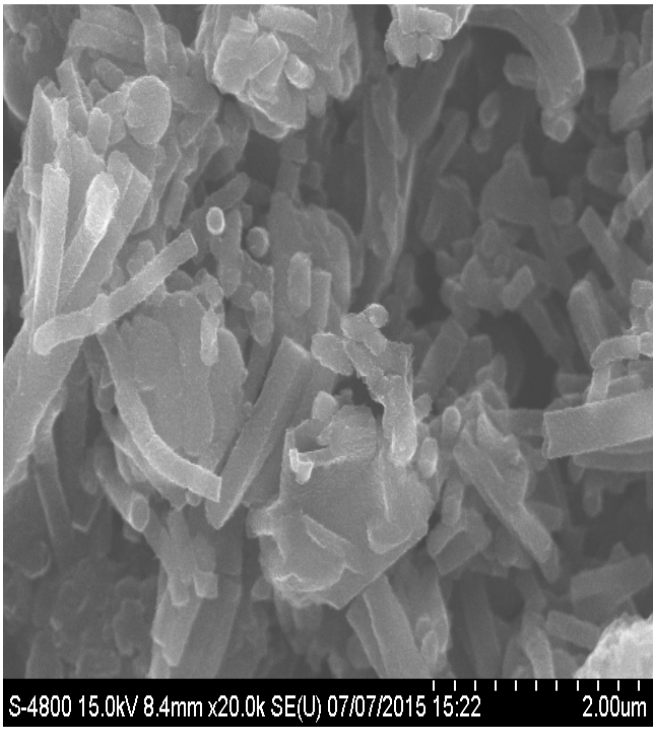


**Figure-6(c)**
**SEM micrograph of PANI/ZnO**

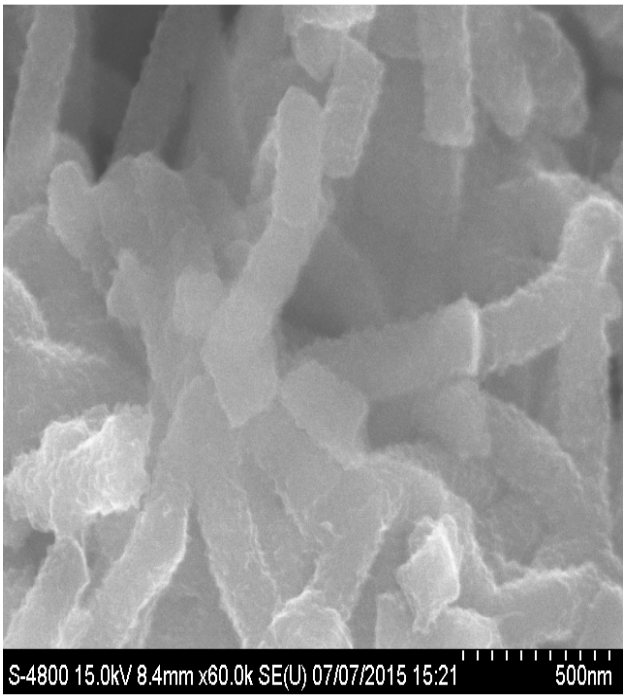


**Figure-6(b)**
**SEM micrograph of PANI/ZnO**

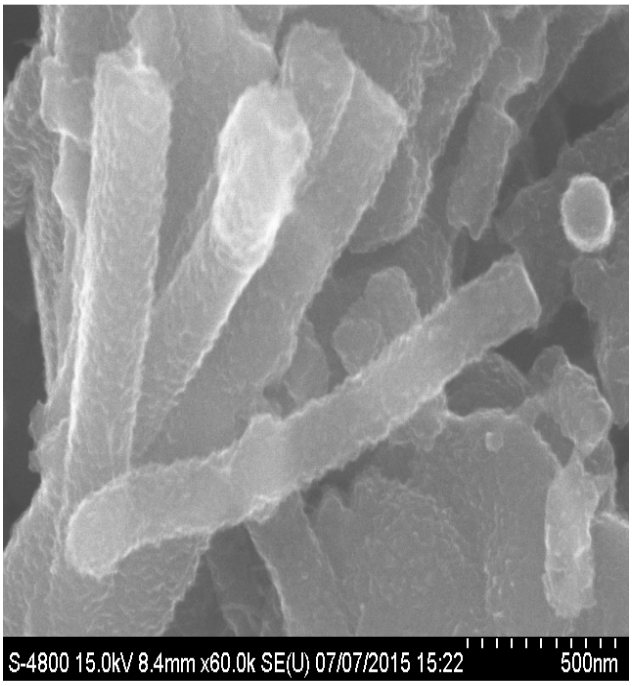


**Figure-6(d)**
**SEM micrograph of PANI/ZnO**

**EDX of Nanocomposite of PANI/ZnO:** An energy dispersive Spectroscopy (EDX) image of selected sample wasobtained using SEM-JEOL 840 A. Elemental compositions of PANI/ZnO from spectrum: 4417 are given in Table-1. From table is cleared that no other elements were present in given sample of nanocomposite PANI/ZnO.

**Table-1**
**EDX of Nanocomposite of PANI/ZnO**

| Sr.No | Element | Atomic Number | Weight by % | Atomic Weight by % |
|---|---|---|---|---|
| 1 | C | 6 | 57.47 | 64.50 |
| 2 | N | 7 | 19.95 | 19.20 |
| 3 | O | 8 | 15.61 | 13.15 |
| 4 | Na | 11 | 2.83 | 1.66 |
| 5 | S | 16 | 2.97 | 1.25 |
| 6 | Zn | 30 | 1.17 | 0.24 |
| Total | | | 100 | 100 |

## Conclusion

The Pure Zinc Oxide, Pure Polyaniline andPANI/ZnO nanocomposites have been successfully synthesized. PANI nanotubes were successfully covered with PANI byprocess of '***in situ'*** chemical oxidative polymerization of aniline. Due to interfacial interactions between nanocomposite ZnO and PANI, there is formation of PANI and ZnO matrix. This type of hybridmaterialwill use in many applications.

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I pay respect and express indebtedness to Dr. V.S. Kalymwar because of their guidance, consistent supervision as well as suggestions at every phase of this thesis work that made it possible to materialize. Authors would like to thanks University Grant Commission (UGC), New Delhi (India) and UGC DAE CSR Indore for financial support.

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Original article

# Diversity of Saurian fauna in the Buldhana district, Maharashtra, India

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ABSTRACT

The present report provides knowledge about the diversity of Saurian fauna in the Buldhana district of the Indian state of Maharashtra as a model geographic area to promote conservation management. The presented study is based on the field work carried out in the study sites during February 2014 to January 2015. The study revealed the presence of 14 Saurian species belonging to 5 families dominated by Gekkonidae (43.05%), Scincidae (29.15%), Agamidae (21.35%), Varanidae (6.1%), and Chamaeleonidae (0.35%). The relative dominance of species varied with different months, apparently indicating that the Buldhana district has a healthy environmental and demographic setup that accommodates rich Saurian diversity.



## Introduction

The biological diversity of the earth and its origins has long been a source of amazement and curiosity (Tantarpale 2015). The study of biological diversity encompasses both the intrinsic and anthropocentric values associated with it. The values of the biological elements are recognized in correspondence to the perceived importance by the human being, which is realized in terms of the ecosystem services (Daily 1997; Baumgartner 2007). Biological diversity is the base for upholding the ecosystems and the functional aspects of the species that provide goods and services for human well-being. Monitoring of species diversity of a region enables estimation of the prospective functional roles of the species. In any ecosystems, monitoring species diversity can be used as a tool to reduce human mismanagement and pollution in urbanized, industrial, rural, and other managed areas (Wilson 1997). Extending this view, studies on species diversity in any ecosystems are necessary to understand the effect of anthropocentric development on the integrity and sustenance of an ecosystem.

The diversity of reptiles has been emphasized in many studies owing to their dominance in the terrestrial and aquatic ecosystems and provision of ecosystem services such as pest control and ecological maintenance (Joshi 2014). Among reptiles, saurian fauna is a diverse group that changes from the primitive to the specialized, phylogenetically, and their structural modifications exhibit greater variations than any other group of reptiles (Smith 1935). Lizards are members of the suborder Sauria which is one of the two suborders of the order Squamata (Class: Reptilia). They are poikilothermous, insectivorous, and oviparous to ovoviviparous (Matthew 2007). Presently, lizards are one of the most diversified groups of vertebrates that have ever lived on earth over the past 250 million years. Over 5,000 species of lizards have lived on earth, inhabiting a variety of habitats ranging from the highest mountainous peak to the low-lying terrestrial and aquatic habitats (Lalmuchhawa et al. 2015). South Asia, including the Indian subcontinent, is the home for herpetological diversities in the tropical region with India harboring 228 Saurian species in different biophysical zones (Sengupta 2010).

In this context, the conservation of lizards is necessary to sustain varied kinds of ecosystem services for human well-being. In view of the essential ecosystem services rendered by lizards and to promote conservation management, the present study was aimed at the estimation of the saurian diversity in the Buldhana District, Maharashtra, India. The results of the study are expected to supplement the necessary information on the conservation management and enhance the ecological roles of the saurian species in the Buldhana District and similar geographical regions.

## Materials and methods

### Study area

The Buldhana district (Figure 1) is one of the most diversified regions in Maharashtra State of India, with respect to biodiversity.

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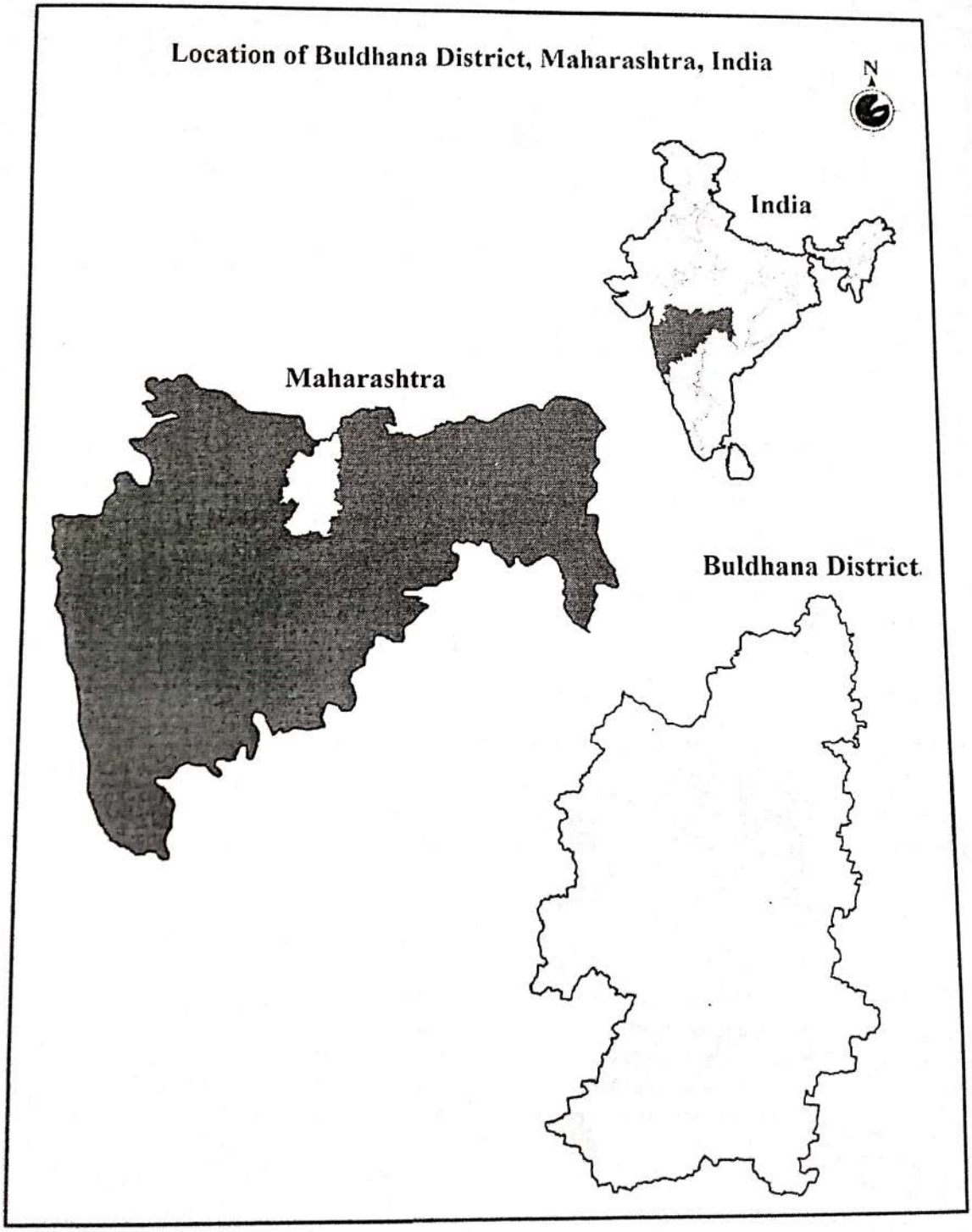


**Figure 1.** Buldhana District, Maharashtra, India.

**Table 1.** Diversity of Saurian fauna during February 2014 to January 2015 in the Buldhana district, Maharashtra, India.

| Family | Scientific name | Common name | No. of individuals | IUCN national | Local status |
|---|---|---|---|---|---|
| Agamidae | *Calotes versicolor* (Daudin, 1803) | Indian garden lizard | 42 | NE | Abundant |
| | *Calotes rouxii* (Dumeril and Bibron, 1844) | Indian forest lizards | 16 | NT | Occasional |
| | *Psammophilus blanfordanus* (Stoliczka, 1871) | Blanford's rock agama | 5 | NE | Rare |
| Chamaeleonidae | *Chamaeleo zeylanicus* (Stoliczka, 1872) | Indian Chamaeleon | 01 | NE | Rare |
| Gekkonidae | *Hemidactylus brookii* (Gray, 1930) | Brook's house gecko | 12 | LC | Rare |
| | *Hemidactylus flaviviridis* (Murray, 1886) | Yellow-green House Gecko | 35 | LC | Common |
| | *Hemidactylus frenatus* (Dumeril and Bibron, 1844) | Asian house gecko | 25 | LC | Frequent |
| | *Hemidactylus giganteus* (Stoliczka, 1871) | Giant Indian gecko | 03 | NE | Occasional |
| | *Hemidactylus leschenaultii* (Dumeril and Bibron, 1844) | Common bark gecko | 42 | LC | Abundant |
| | *Hemidactylus triedrus* (Daudin, 1802) | Termite hill gecko | 10 | NT | Rare |
| Scincidae | *Eutropis carinata* (Schneider, 1799) | Keeled grass skink | 34 | NT | Common |
| | *Eutropis macularia* (Blyth, 1853) | Bronze grass skink | 40 | LC | Abundant |
| | *Lygosoma punctatus* (Gmelin, 1799) | Spotted supple skink | 12 | NT | Rare |
| Varanidae | *Varanus bengalensis* (Daudin, 1803) | Bengal monitor lizard | 18 | VU | Frequent |

LC = least concern; NE = not evaluated; NT = nearly threatened; VU = vulnerable.

Its healthy climate, mountainous terrain, rugged configuration, and sudden fall in elevation are phenomenal (Joshi et al 2015). It is in the Amravati division of Maharashtra state in Western India. It is situated at the westernmost border of the Vidarbha region of Maharashtra, and is 500 km from the state capital, Mumbai. It lies between 19°51′ N and 21°17′ N latitude and 75°57′ E and 76°59′ E longitude. It has a total area of 9,745 km$^2$ (3,761 square miles). The climatic condition of this district is characterized by a hot summer, well-distributed rainfall during the south-west monsoon season, and generally dry weather during the rest of the year. The cold season is from December to February. The average annual rainfall in the district is 796.6 mm (31.37 inches). During summer, the mean daily maximum temperature was 42.3°C and the minimum was 27.4°C, and it decreased toward winter with a mean daily maximum temperature of 27.6°C and a minimum of 15.1°C (Buldhana Gazetteer 2015).

### *Survey methods*

The present study is based on the field work carried out in the study sites during February 2014 to January 2015. During the survey, an efficient protocol was adopted. The survey was made using a "visual encounter survey" method (Doan 2003) as well as by employing randomized walking (Whitaker 2006). The selected area

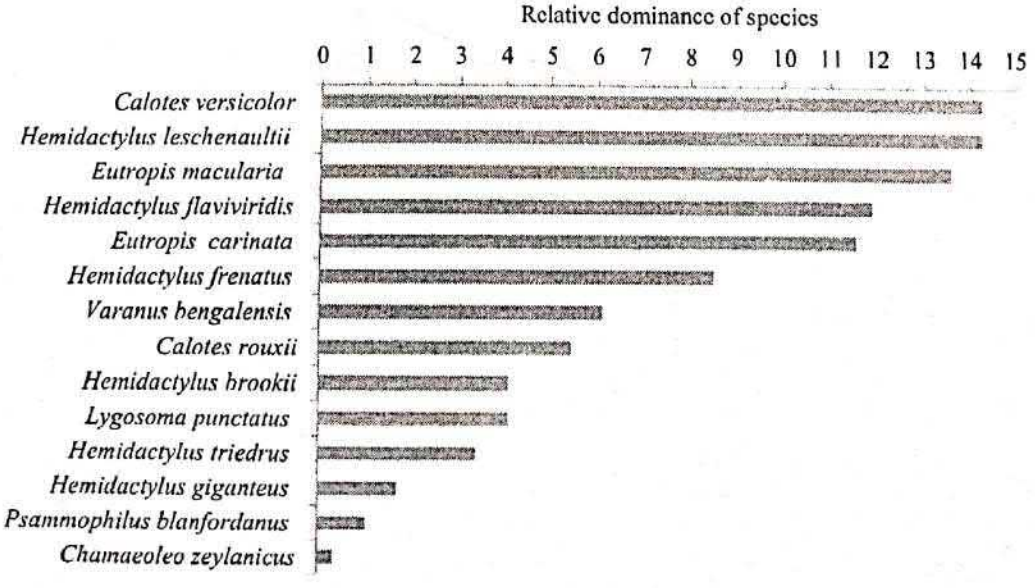


**Figure 2.** Relative abundance of saurian species in the Buldhana district, Maharashtra, India.

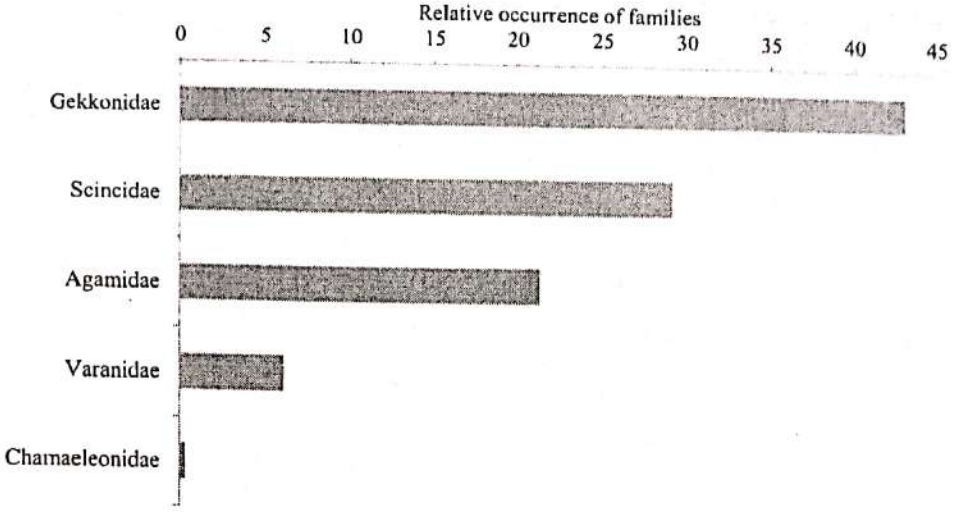


**Figure 3.** Relative dominance of saurian families in the Buldhana district, Maharashtra, India.

was randomly explored on the basis of habitat structure and the possibility of availability of species.

*Species identification*

After detection, a specimen was identified with the help of visible structural features. For identification and comparative studies of observed specimens, keys and methods suggested by Daniel (2002), Das (2002), and Ahmed et al (2009) were adopted. The International Union for Conservation of Nature (IUCN) status of each encountered species was categorized on the basis of Molur et al (1998), Kumbhar et al (2013), and Alexandar and Jayakumar (2014).

*Data analysis*

Species occurrence analysis was carried out by using the following formulas. Relative dominance (RD) of species was calculated as [RD = Ni × 100/Nt], where Ni is the number of individuals of species and Nt is the total number of individuals of all

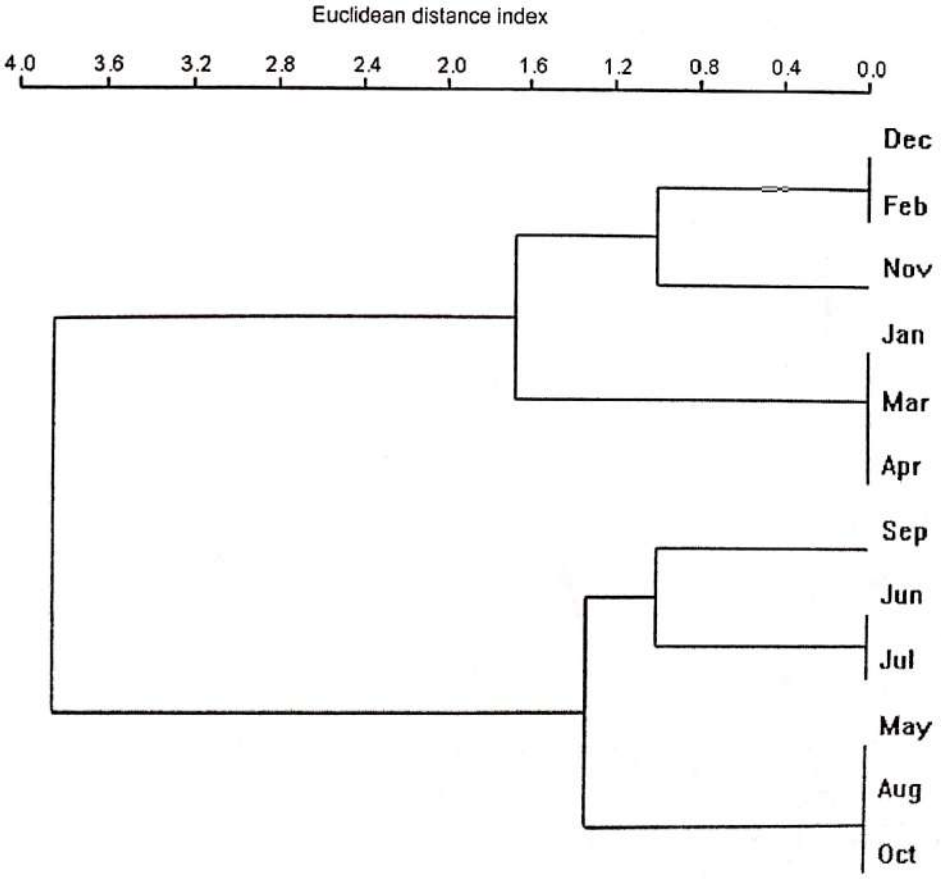


**Figure 4.** Dendrogram showing similarity in number of saurian species composition among the studied month during February 2014 to January 2015.

species (Basavarajappa 2006; Joshi 2014). Relative occurrence (RO) of the family was calculated as [RO = Ns × 100/Nt] where Ns is the number of species of each family and Nt is the total number of all species (Basavarajappa 2006; Joshi 2014). Mean percent occurrence (M%) for a month was calculated as [M% = Nm × 100/Nt] where Nm is the number of individuals in each month and Nt is the total number of individuals during the complete study tenure (Basavarajappa 2006; Joshi 2014). The mean values of the pooled species occurrence data were used to calculate the monthly diversity of and to categorize the local status of species.

The diversity assessment enabled highlighting the observed species richness pattern of the saurian species. The diversity indices were quantified with the help of PAST Version 1.60 software (Palaeontological Asso., Norway; Hammer et al 2001). The species diversity was calculated using the Shannon diversity index that calculated [$H' = -\sum_{i=1}^{R} Pi \log Pi$], where $Pi$ is the proportion of the first species which is given by $Pi = ni/N$, where ni is number of individual in particular month and N is total number of species; species richness was obtained by using the Margalef equation [R = (S-1)/log N], where R is the index of species richness, S is total number of species and N is the total number of individuals (Magurran 1988); while species equitability was determined by the equation of Pielou [$J = N_1/N_0$] where $N_1$ is the number of abundant species in the sample and $N_0$ is the number of species in the sample (Hammer et al 2001). The similarity association matrix upon which the cluster was based was computed using the nearest neighbor pair linkage algorithm of Euclidean distance index for the presence and absence data (Hammer et al 2001).

The differences between the diversity and evenness indices among different study months were statistically analyzed using analysis of variance. The statistical analyses were performed following Zar (1996) using the SPSS version 10 (SPSS Inc., Chicago, IL, USA; Kinnear and Gray 2000).

## Results

During the study, a total of 295 individuals of 14 saurian species belonging to 5 families were identified (Table 1). From the observed species, 3 were abundant, 2 were common, 2 were frequent, 2 were occasional, and 5 were rare. The maximum abundance was shown by *Calotes versicolor* followed by *Hemidactylus leschenaultii* and *Eutropis macularia*, while *Chamaeleo zeylanicus* was the most rarely observed with least abundance (Figure 2). During the study, the Gekkonidae family was observed to be more dominant over the Scincidae, Agamidae, Varanidae, and Chamaeleonidae families (Figure 3).

A monthly comparison of saurian species occurrence showed the highest number of species during June to September and the lowest during February to May. A dendrogram developed by Euclidean distance cluster analysis was observed to be multifaceted and showed variation in the level of similarity in the number of saurian species in 12 months. The months with the minimum to moderate number of species belong to one cluster, whereas the rest of the months with moderate to maximum number of species formed another cluster (Figure 4).

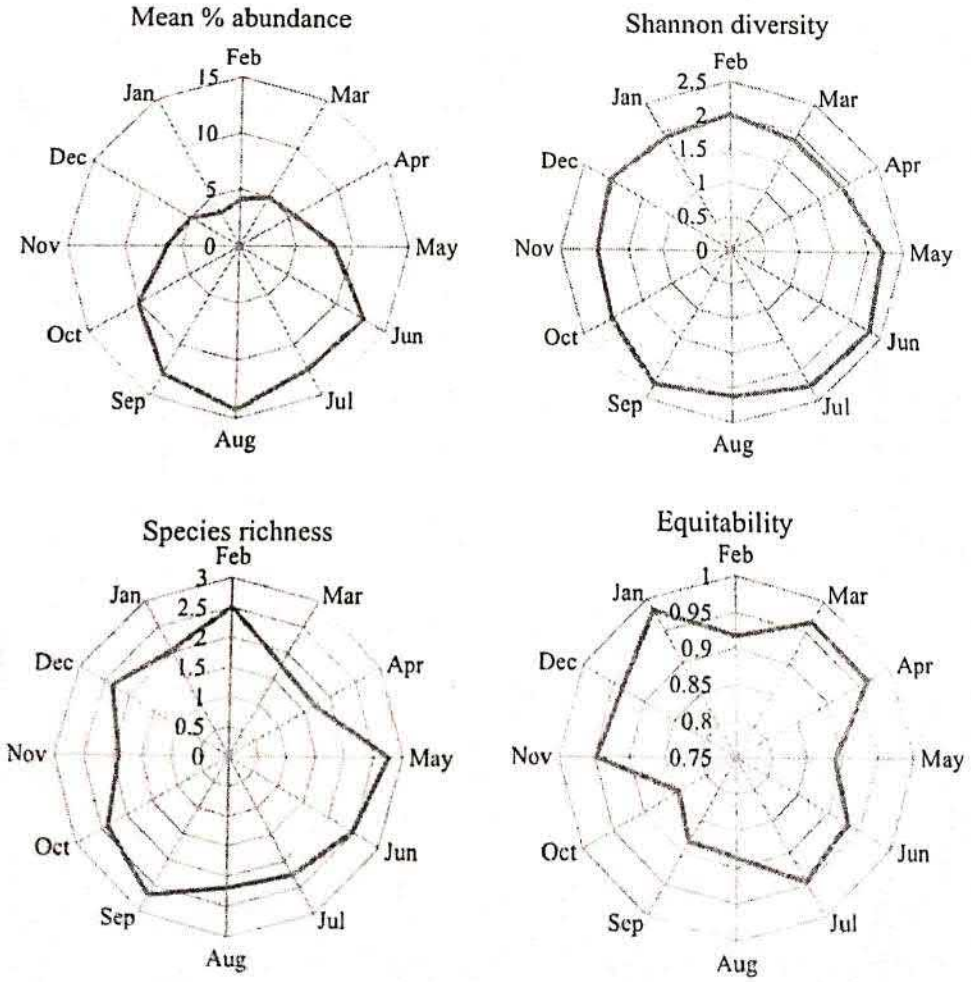


**Figure 5.** The values of the diversity indices in different months observed through the random sampling of the Saurian fauna in the Buldhana District, Maharashtra, India.

A monthly comparison of species diversity attributed to saurian fauna in the studied area revealed that faunal diversity was highest during June to September while lowest during February to May. Mean percent abundance of saurian fauna was significantly different ($F = 30.314$, $df = 11$, $p < 0.05$); Shannon diversity values of saurian fauna were significantly different ($F = 3.813$, $df = 11$, $p < 0.05$); species evenness among different months was significantly different ($F = 16.824$, $df = 11$, $p < 0.05$) while species richness among the study months was not significantly different ($F = 1.529$, $df = 11$, $p > 0.05$) showing a contradictory pattern. A trend in mean % abundance was noted to be nearly similar to that of Shannon diversity although species richness and species equitability showed contradictory patterns (Figure 5).

## Discussion

The utility of saurian species as indicators of environmental conditions is a basis for studying seasonal saurian diversity. Observations on the saurian diversity provided information about the variations in the species richness and the abundance shaped by the seasons. The differences in the diversity can be attributed to the monthly changes in the climatic conditions. In the present context, a monthly comparison of saurian species occurrence showed the highest number of species during June to September and the lowest during February to May.

The possible cause behind their minimum diversity in the winter months to early summer months is the cold-blooded nature of reptiles. Lizards preferred to hibernate in their burrows or resting places during winter to early summer. Species were generally observed more during monsoon months. According to Pal et al (2012) and Joshi (2014), due to favorable environmental conditions, the monsoon season is the breeding season for most of the reptiles, which leads to their maximum abundance in rainy months. Earlier studies on the saurian diversity in various parts of Maharashtra show consistency with the present observations (Wadekar 2003, Deshpande et al 2012; Kumbhar et al 2013, Pandhurkar et al 2015).

As revealed through the present study, at least 14 saurian species belonging to 5 families were recorded during all the studied months. In the observations, characters of the studied species were found to be almost the same as per existing records of Daniel (2002) and Ahmed et al (2009). The maximum abundance was shown by *Calotes versicolor* followed by *Hemidactylus leschenaultia* and *Eutropis macularius*, while *Chamaeleo zeylanicus* was the most rarely observed with the least abundance. During the study, the Gekkonidae family was observed to be more dominant over Scincidae, Agamidae, Varanidae, and Chamaeleonidae.

In parity with the species diversity observed in the Buldhana district, it may be assumed that the saurian species carry out diverse functional roles for the sustenance of the ecosystems. The availability of the green space and the heterogeneity of the habitats in terms of the available vegetation and allied factors that render stability to the population and species assemblages in the landscapes are possibly important contributors to the observed variations in the saurian species observed in the present study. The present diversity study is confined to a limited area and selected habitats. There is, in the future, a chance of more species being reported because of few pockets and habitats in the studied area requiring more extensive exploration.

## Acknowledgements

The authors are thankful to Dr. S.M. Kulkarni, Former Vice Chancellor, Swami Ramanand Tirtha Marathwada University, Nanded, India and Former Director, Higher Education, Government of Maharashtra, Pune, India, for creative guidance during conduct of this study.

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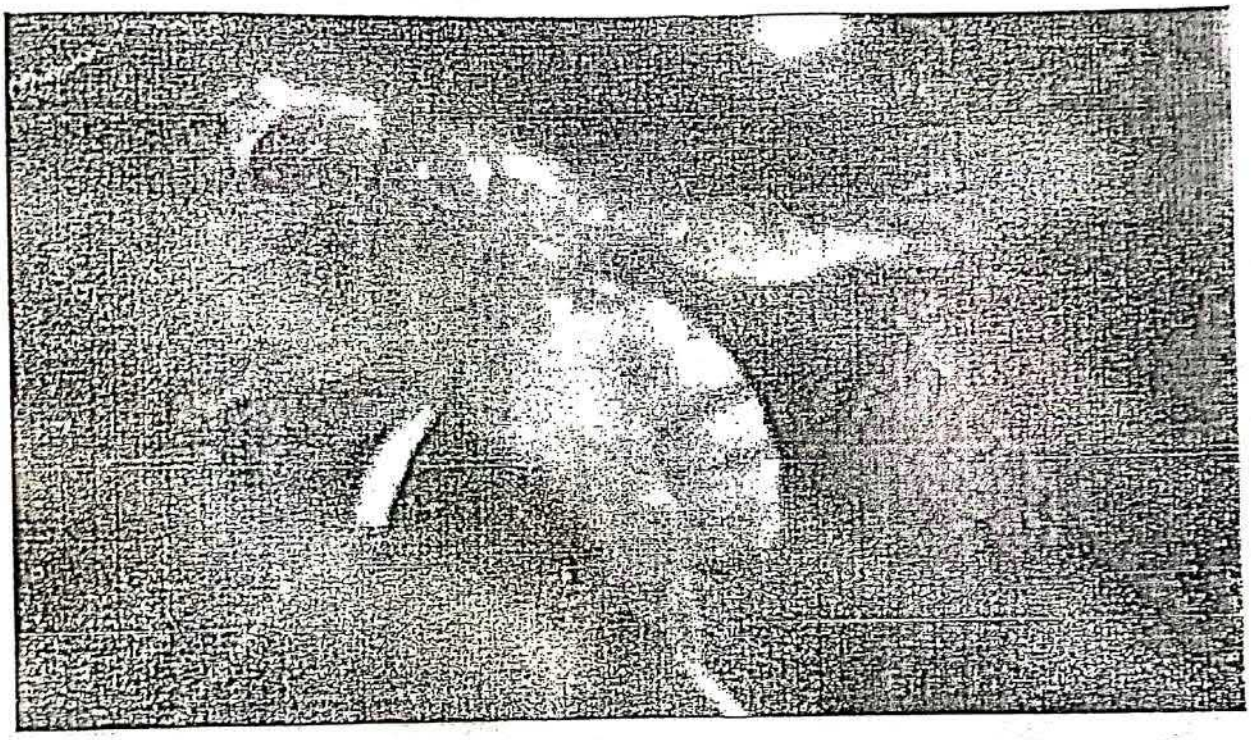
# EFFECT OF AZADIRACHTIN ON THE PHENOTYPE OF DIFFERENT DEVELOPMENTAL STAGES OF *DROSOPHILA MELANOGASTER*



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**ABSTRACT:**

In the present study we have studied the effect of azadirachtin on insect model *Drosophila melanogaster. Drosophila melanogaster* is a small, common fly and exhibit complete metamorphism. *Drosophila melanogaster* captured from rotten food, ripped banana and kitchen. They were cultured in controlled culture media and also kept separate normal culture one. After the development of each stages various parameter have been taken place and statically compared the controlled and normal flies, and eventually we have observed decrease in the size of flies which were fed on controlled culture media.

KEY WORDS: *Drosophila melanogaster*, Azadirachtin.

## INTRODUCTION:

A drug includes all chemicals other than food that affect living processes. If this effect helps the body than drug is acting as a medicine but if a drug causes a harmful effect on the body the drug is acting as a poison. To investigate about the drug effect on the human body the drug is not directly applied to the human body but various tests is done on various other organism, so far several studies have mainly been done on rat or mouse animal model and rarely with other animals like monkey, cat, dog, rabbit etc.

Regarding the various reason like more proliferation and low price scientist have focused on insect models. *Drosophila melanogaster* is a small, common fly found near unripe and rotted fruit. Drosophila is very valuable in terms of four pairs of chromosomes for genetic researchers, due to its small size, ease of culture and short generation time. There are several reason to be taken *Drosophila* as an experimental animal because they can be easily handled, anesthetized and manipulated individuals with very unsophisticated equipment. *Drosophila* are sexually dimorphic (males and females are different), making it is quite easy to differentiate the sexes. It is easy to obtain virgin males and females, as virgins are physically distinctive from mature adults. Flies have a short generation time (10-12 days) and do well at room temperature. The care and culture requires little equipment, is low in cost and uses little space even for large cultures.

*Drosophila melanogaster* exhibits complete metamorphism, meaning the life cycle includes an egg, larval (worm-like) form, pupa and finally emergence (enclosure) as a flying adult. This is the same as the well-known metamorphosis of butterflies and many other insects. The larval stage has three instars, or molts. After the third instars, larvae will begin to migrate up the culture vial in order to pupate.

Azadirachtin, a botanical pesticide derived from the neem tree, *Azadirachta indica* is one of the most promising natural compounds (Winkaler *et al.*, 2007), where it is less harmful to the environment than the synthetic pesticides (Sundaram, 1996).

Azadirachtin is structurally similar to that of insect hormone known as ecdysones. The insect hormone ecdysone plays an important role during growth of insect when passing from larva to adult. As Azadirachtin is similar to ecdysone it controls the process of metamorphosis by affecting on corpus cardiacum (an organ which secrete hormone in insects) means controls the secretion of hormone.

## MATERIALS & METHODS

**Collection of *Drosophila* flies:** - Fruit fly has cosmopolitan distribution, and flies were easily collected on ripe banana or fruit. Ripe banana was put in a Petridis in one place then, the fruit flies were attracted and feed on ripe banana and the flies were transferred to a conical flask in the lab, we cover to the opening of the flask with a Maslin cloth the flies were easily collected with a brush.

**Preparation of *Drosophila* culture media**

**Material required**

**Potato, sugar, Propionic acid, yeast.**

| | | |
|---|---|---|
| Potato | - | 100g |
| Agar | - | 1.09 g |
| Water | - | 100 ml |
| Dextrose | - | 1 gm |
| Propionic acid | - | 0.8 ml |
| Yeast | - | 0.5 gm |

Boil the potato and clean it then weight up to 100 g. then add 1.09 g agar, 100 ml of $H_2O$ added in it and I gm dextrose. Homogenize the mixture and make a fine paste. After formation of paste autoclave it at 15 IP for 10-15 min.

Cool the media up to 60°C. Then add 0.8 ml propionic acid put the culture media up to 40°C add 0.59 gm yeast in it by dissolving it in distilled water then sterilize it in autoclave at 15 IP.

**Preparation of culture vials:** - After sterilization of culture vials, transferred the culture, medium in ordered manner. First label the four cultured vials as A,B,C,D and then the vials with culture media. Arrange the vials at different azadirachtin concentrations.

| | | | |
|---|---|---|---|
| Vials | A | - | 75 µl |
| | B | - | 35 µl |
| | C | - | 18 µl |
| | D | - | Control |

**Transfer of *Drosophila* flies into culture vials:-**

*Drosophila* flies were collected in collection bottle, the transfer 10-15 fruit flies into culture vials (half male and half female) and close the mouth of vials. Different concentration of drug was added to the culture as mentioned in the experimental set-up. These flies laid eggs in culture, hatch and completed their life cycle within 10-15 days. After completion of life cycle, various stages of the flies were collected and proceed for the measurement. The life cycle of Drosophila melanogaster were studied in these culture vials.

**Observation of various stages:** - Male and female copulate after 2-3 hours of copulation, female lay fertilized eggs. After 24 hrs of fertilization eggs hatches into first instars larva. First instar larvae change into second instars larvae, after 3-days. After the fifth day second instar larvae changes into third instar larvae and in sixth day third instars larvae changes into pupa. The sizes of larvae changes in all stages were found to be shrinkage than in normal condition in case of azadirachtin fed larvae.

**Collection of adult flies:** - The pupa changes in adult fly. After the development of adults, flies were collected for the observation and measurement of various parameters. First etherized them and collected in Petridis.

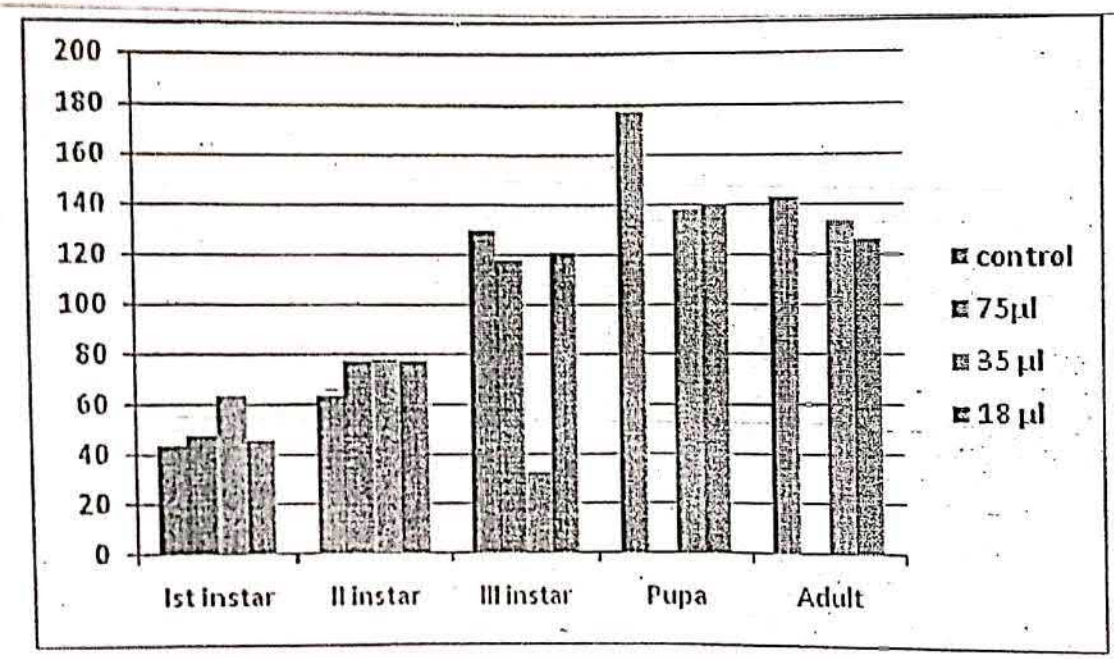
**Measurement of various parameters:** - The measurement of different developmental stages of the flies was done in under the microscope. These observations made under 10 x magnifications by using occulometer having scale given in micrometer (um).

## OBSERVATIONS AND RESULT

In our present work we observed the effect of azadirachtin on the molting of the flies and we found the inhibition of the molting with the increased dosages of azadirachtin, at higher doses (1ml, 0.5ml, 0.01ml) we observed the total mortality which shows the highly toxicity of azadirachtin. But at (18µl, 35µl, 75µl) respectively we noticed the development of 3rd instar larvae into pupa and adult incase of azadirachtin (18µl and 35µl) but at (75µl) no 3rd instar larvae developed into pupa thus the pupae development was inhibited or we may say the moulting was inhibited.

| Sr. No. | Devpt.-stage / Concentration | I$^{st}$ Instar (µm) | II$^{nd}$ Instar (µm) | III$^{st}$ Instar (µm) | Pupa (µm) | Adult (µm) |
|---|---|---|---|---|---|---|
| 1 | Control | 42.83±5.15 | 63.5±6.80 | 130.16±15.38 | 177.83±4.99 | 143.16±9.6 |
| 2 | 75µl | 48±4.73$^{NS}$ (10.77) | 77.66±4.45$^{**}$ (18.23) | 118.5±3.44$^{NS}$ (9.83) | | |
| 3 | 35µl | 63.83±4.30$^{**}$ (32.89) | 78.5±15.01$^{*}$ (19.10) | 32.5±4.27$^{NS}$ (1.76) | 138.5±13.18$^{**}$ (28.39) | 134.16±10.12$^{*}$ (13.16) |
| 4 | 18µl | 46±7.48$^{NS}$ (6.89) | 77.66±5.31$^{**}$ (6.20) | 120.83±6.64$^{NS}$ (7.72) | 140.5±6.09$^{**}$ (26.56) | 126.5±6.44$^{*}$ (7.90) |

Values are mean ± SD of six observations, * p<0.05>, ** p<0.01 & NS- Not Significant. Values are in paranthesis indicate the percent change in size over the control.




**Graph- Effect of azadirachtin on the size of different developmental stages *of Drosophila melenogaster.***

## DISCUSSION AND CONCLUSION

Paul B. Tanzubil and Alan R. M. Caffery (1990) studied the treatment of larvae of the African armyworm (*Spodoptera exempta*) with azadirachtin and aqueous neem seed extracts produced a range of adverse effects that were dose dependent. High doses of up to 10 µg per larva of azadirachtin resulted in 100% larval mortality, but this effect was delayed and prolonged. At lower doses of azadirachtin, however, inhibition and disruption of molting was observed and larval-pupal intermediates or abnormal pupae were commonly found. Similar results were obtained with the aquebus extracts of neem seeds. The few pupae obtained from larvae treated with lower doses of the extracts (0.01 and 0.1 µg per larva) either failed to develop further or developed into adults that died during eclosion, or had frizzled, curled wings.

Low doses of azadirachtin merely prolonged the inter-moult stage, apparently due to a delayed

ecdysteroid peak. Medium and high doses suppressed adult ecdysis, and the larvae became permanent larvae, the longevity of which increased with rising doses. Although medium doses prevent ecdysis, apolysis and secretion of adult cuticle were taking place. The ecdysteroid peak was further delayed in these larvae and was somewhat lower than in controls. Permanent larvae induced by high azadirachtin doses showed neither ecdysis nor apolysis. Larvae also showed an ecdysteroid peak, which was considerably delayed and distinctly lower than in the controls. Thus, treatment with different azadirachtin doses allowed some dissection of the molting cycle into different steps, in which the hormonal regulation could be studied independently.

Menakshi Bhat et al (2011) in their study using invivo diabetic murine model, *AZadiracta indica* and *Bougainvillea spectabilis* chloroform, methanolic and aqueous extracts were investigated for the biochemical parameters important for controlling diabetes. It was found that *A. indica* chloroform extract and *B. spectabilis* aqueous, methanolic extracts showed a good oral glucose tolerance and significantly reduced the intestinal glucosidase activity. Interestingly, *A. indica* chloroform and B. spectabilis aqueous extracts showed significant increase in glucose-6-phosphate dehydrogenase activity and hepatic, skeletal muscle glycogen content after 21 days of treatment. In immunohistochemical analysis, they observed a regeneration of insulin-producing cells and corresponding increase in the plasma insulin and c-peptide levels with the treatment of *A. indica* chloroform and *B. spectabilis* aqueous, methanolic extracts.

A. J. Mordue et al (2008) studied the biological effect of azadirachtin on fifth instars nymphs of *Locusta migratoria migratorioides*. Azadirachtin injection at the beginning of the instar resulted in a dose-dependent range of developmental aberrations. Low concentrations (c. 1.7/µg/g body weight) resulted in adults with curled wing tips and reduced longevity; higher concentrations (c. 2.9µg/g) resulted in death during the imaginal molt; doses of c. 6.5µg/g cause death immediately prior to the molt; and doses of c. 7.3µg/g induce a greatly extended instar. Such doses were related to a proportionately slower growth rate of the insect and a significantly reduced food intake, as assessed by wet weight and faeces production. Doses of 80µg/g resulted in death within 24 h. Experiments *in vivo* and *in vitro* demonstrate a significant reduction with azadirachtin treatment in the rate of passage of food through the gut, and in gut motility. The significance of that direct effect on gut motility was discussed in relation to the mode of action of azadirachtin on growth and molting.

In our study *Drosophila melanogasters* were fed on culture containing different concentration of azadirachtin as at (0.01ml, 0.5ml, 0.01ml) we found the total death of the feeding drosophila that is the total mortality was observed the mortality hence may be attributed to the pesticidal effect of azadiractin and also concluded that azadirachtin responsible for decreasing the size of *Drosophila melanogaster.*

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# Synthesis, Characterisation and Screening of newly synthesised analogues of Imidazolo-Thiazoles and their Impact on growth of *Oyster mushroom spp.* (*Pleurotus sajor-caju*)

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## Abstract

***The majority of farmers and mushroom growers in tropical region of country (Central India) has been experimenting with Oyster mushroom cultivation and are very worried about the very high temperature and susceptibility of mushroom crops towards the pathogens responsible for common crop diseases. This is the main constraint in the large scale cultivation of edible mushrooms like Oysters in this part of the country. As a consequence, ultimate yield of Oyster mushroom in Central India is adversely affected. Whenever, the crops fall prey to diseases, farmers try to control them by spraying some fungicides on them but in many cases they do not succeed. Basic understanding about the disease is a prior strategy to manage them. To safeguard the crop by various preventive and controlling measures which were elaborated by several workers with some basic aspects based on their research activity. Literature survey reveals that, the utility of imidazole substituted azoles in the fields of agricultural science and medicinal chemistry is ever-increasing. Owing to their importance in the field of agriculture as plant protecting and growth regulating agents, we thought it worthwhile to study the efficacy of newly synthesised heterocycles viz. 2-phenylamino-4-benzoyl-5-(2-hydroxy-5-chlorophenyl)-1,3-thiazole, 2-N-phenyl-N-[(2-hydroxy-5-chloro-phenyl)ethanonylamino]-4-benzoyl-5-(2'-hydroxy-5'-chlorophenyl)-1,3-thiazole, 2-[2-phenylthio-4-(2-hydroxy-5-chlorophenyl)imidazolo]-4-benzoyl-5-(2'-hydroxy-5'-chlorophenyl)-1,3-thiazole and 2-[2-phenylthio-4-(2-acetyloxy-5-chloro-phenyl)imidazolo]-4-benzoyl-5-(2'-acetyloxy-5'-chlorophenyl)-1,3-thiazole in the light of their significance towards growth promoting and disease controlling impact on Oyster mushroom crop. The results obtained in the present study are very encouraging.***

**Keywords:** Phenylthiazole, Ethanonylamino-1,3-thiazole, Imidazolo-1,3-thiazole, Acetyloxy-imidazolo-1,3-thiazole, Antimicrobial activity, ***Pleurotus sajor-caju.***.

## Introduction

The ring system of five membered heterocyclic compounds contain heteroatoms at 1,3-positions are designated as ***1,3-azoles.*** In such rings, when both positions are occupied by nitrogen, then they are referred as ***imidazole*** and in case, nitrogen and sulphur are present at 1,3-positions they are called as ***thiazoles.***

Together with the other derivatives of 1,2 and 1,3-azoles, the thiazoles soon constituted an important part of heterocyclic chemistry. Some substituted thiazoles were reported to have antibacterial[1], anti-cancer[2], antimicrobial[3], antioxidant[4], antihelmintic, insecticidal, antitumor[5], anticonvulsant, antifungal[6], cytotoxic[7] and anti-inflammatory[8] activities.

In the tropical region of our country (Central India), the majority of farmers and mushroom growers have been engaged in the production of ***Oyster mushroom*** crop but the yield they have produced did not commensurate with their efforts and investment since mushroom crop easily fall prey to infections caused by crop pathogens ***viz. Gliocladium roseum (Link) Bainier***, ***Verticillium fungicola, Pseudomonas stutzeri***, ***Pseudomonas alcaligens, Pseudomonas fluorescene, Burkholderia gladioli*** and thus became a major problem in the cultivation.

Literature survey reveals that imidazole blended thiazoles have great importance in the field of agriculture. Most of the pesticides have imidazoles analogue of thiazole as an active ingredients in their composition.

Besides these imidazole blends of azoles there are some compounds such as methyl-1-(2-methylthioethyl-carbamoyl)benzimidazol-2-yl- carbamate, 2-(3,5-dimethylpyrazol-1-yl) -benzimidazole, {(***RS***)-2-[3-(4-chlorophenyl)propyl]-2,4,4-trimethyl-1,3-oxazolidin-3-yl}-(imidazol-1-yl)-methanone and 2-(1,3-thiazol-4-yl)-benzimidazole are reported as major constituents of many pesticides and plant growth regulatory agents[9-11].

Owing to the importance of azoles in the field of agricultural sector as plant protecting and growth regulating agents, we thought it worthwhile to synthesise and study the efficacy of some 1,3-thiazoles ***viz***. 2-phenylamino-4-benzoyl-5-(2-hydroxy-5-chlorophenyl) -1,3-thiazole, 2-N-phenyl -N- [(2-hydroxy-5-chlorophenyl) ethanonylamino] -4-benzoyl-5- (2'-hydroxy-5'-chlorophenyl) -1,3-thiazole, 2-[2-phenylthio- 4-(2-hydroxy-5-chlorophenyl) -imidazolo] -4-benzoyl-5- (2'-hydroxy-5'-chlorophenyl) -1,3-thiazole and 2-[2-phenylthio-4-(2-acetyloxy-5-chloro-phenyl) imidazolo] -4-benzoyl-5- (2'-acetyloxy-5'-chlorophenyl) -1,3-thiazole with special reference to their use as growth promoting and disease controlling agents for ***Oyster mushroom spp.*** viz**.** ***Pleurotus sajor-caju***.

## Methodology

The structures of all the newly synthesised compounds were confirmed on the basis of their elemental analysis, chemical properties and spectral data. UV-Vis spectra were recorded in ethanol solvent. IR spectra were recorded in KBr pellets. $^1$H NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard. The melting points were recorded by capillary method in paraffin using Thiele's apparatus and all are uncorrected. The purity of newly synthesized compounds was tested by TLC using different solvent combination.

**Preparation of 1-(2-hydroxy-5-chlorophenyl)-2-bromo-3-phenylpropane-1,3-dione (2):** 1-(2-Hydroxy-5-chlorophenyl)-3-phenylpropane-1,3-dione (1) (0.01M) was treated with bromine in glacial acetic acid reagent (6.4 ml). After complete addition of reagent, the reaction mixture was kept at room temperature for about 30 minutes. The solid product, thus separated, was filtered and washed with a little petroleum ether to get the compound (2). (m.p. 73$^o$C, yield: 78 %).

**Molecular Formula $C_{15}H_{10}O_3ClBr$ (2):** Yellowish brown amorphous solid, m.p. 73$^o$C, yield 78 %, Elemental analysis (%): **C** 50.91/50.95; **H** 2.82/2.85; **O** 13.55/13.57; **Cl** 09.98/10.03; **Br** 22.57/22.60. **UV** (ethanol): $\lambda_{max}$ 520 nm, n→ π* transition. **IR** (KBr) (cm$^{-1}$): 3222.46 (-OH stret.), 3070.46 (Ar. C-H stret.), 1958.66 & 1906.65 (Overtone bands), 1701.30 (C=O stret.), 1626.19 (C=O stret.), 771.81 (C-Cl stret.), 698.00 (C-Br stret.). **$^1$H NMR** (δ ppm): 5.12 (s, 1H, -CO-C**H**Br-CO-), 7.0-8.2 (m, 8H, Ar-**H**), 11.04 (s, 1H, Ar-O**H**), 6.7 (s, 1H, -C**H**=C-OH), 4.4 & 4.5 (s, 1H, -CH=C-O**H)**

**Preparation of 2-phenylamino-4-benzoyl-5-(2-hydroxy-5-chlorophenyl)-1,3-thiazole (3):** A mixture of 1-(2-Hydroxy-5-chlorophenyl)-2-bromo-3-phenylpropane-1,3-dione (2) (0.01M) and phenylthiourea (0.01M) was dissolved in ethanol (25 ml). To this aqueous potassium hydroxide solution (0.02M) was added and refluxed for 2.5 hours. After cooling, it was diluted with water and acidified with conc. HCl. The product, thus separated, was filtered and crystallized from ethanol to get the compound 3 (mp. 68 $^o$C, yield: 77 %).

**Molecular Formula $C_{22}H_{15}N_2O_2SCl$ (3):** Pale yellow crystalline shiny solid**,** m.p. 68$^o$C, yield 77 %, Elemental analysis (%): **C** 64.92/64.94; **H** 3.69/3.72; **N** 6.84/6.88; **O** 7.83/7.86; **Cl** 8.68/8.71; **S** 7.85/7.88. **UV** (ethanol): $\lambda_{max}$ 495 nm, n→ π* transition. **IR** (KBr) (cm$^{-1}$): 3600-2400 (-OH stret.), 3421.55 (-NH stret.), 3175.53 (Ar. C-H stret.), 1668.54 (C=O stret.), 1605.49 (C=N stret.), 1200.49 (C-O stret.), 804.54 (C-Cl stret.), 685.51 (C-Cl stret.). **$^1$H NMR** (δ ppm): 2.18 (s, 2H, -N**H**-Ph), 6.2 (h, 1H, -O**H**), 6.9-8.3 (m, 13H, Ar-**H**).

**Preparation of 2-N-phenyl-N-[(2-hydroxy-5-chlorophenyl) ethanonylamino]-4-benzoyl-5-(2'-hydroxy-5'-chlorophenyl)-1,3-thiazole (4):** A mixture of 2-Phenylamino-4-benzoyl-5-(2-hydroxy-5-chlorophenyl)-1,3-thiazole (3) (0.01M) and 1-(2-hydroxy-5-chlorophenyl)-2-bromo-ethanone (2b) (0.01M) refluxed in ethanol for about 1 hour. After cooling, the reaction mixture was decomposed in ice-cold water. The product, thus separated, was filtered and crystallized in ethanol to yield the compound 4 (m.p.152 $^o$C, yield: 68 %).

**Molecular Formula $C_{30}H_{20}N_2O_4SCl_2$ (4):** Yellow solid, m.p. 152$^o$C, yield 68 %, Elemental analysis (%): **C** 62.56/62.61; **H** 3.44/3.50; **N** 4.82/4.87; **O** 11.07/11.12; **Cl** 12.27/12.32; **S** 5.55/5.57. **UV** (ethanol): $\lambda_{max}$ 370 nm, n→ π* transition. **IR** (KBr) (cm$^{-1}$): 3500-2600 (-OH stret.), 3085.21 (Ar. C-H stret.), 2915.21 & 2848.21 (Ali. C-H stret.), 1645.14 (C=O stret.), 1614.15 (C=N stret.), 1560.15 (C=C stret.), 823.13 & 673.14 (C-Cl stret.). **$^1$H NMR** (δ ppm): 1.2 (s, 2H, -C**H**$_2$), 6.82 (s, 1H, C**H=C**-OH), 7.2-8.1 (m, 11H, Ar-**H**).

**Preparation of 2- [2-phenylthio -4- (2-hydroxy -5-chlorophenyl) imidazolo] -4-benzoyl-5- (2'-hydroxy-5'-chlorophenyl) -1,3-thiazole (5):** 2-N-phenyl-N-[(2-hydroxy-5-chlorophenyl) ethanonylamino] -4-benzoyl-5- (2'-hydroxy-5'-chlorophenyl)-1,3-thiazole (4) (0.01M) dissolved in glacial acetic acid (20 ml) was refluxed with potassium thiocyanate (0.01M) for about 4 hours. After cooling, the reaction mixture was poured in ice-cold water. The product, thus separated, was filtered and crystallized from ethanol to get the compound 5 (m.p.168 $^o$C, yield: 67 %).

**Molecular Formula $C_{31}H_{19}N_3O_3S_2Cl_2$ (5):** Yellow amorphous solid, m.p. 168 $^o$C, yield 67 %, Elemental analysis (%): **C** 60.35/60.39; **H** 3.10/3.11; **N** 6.79/6.82; **O** 7.76/7.79; **S** 10.37/10.40; **Cl** 11.45/11.50. **UV** (ethanol): $\lambda_{max}$ 345 nm, n→ π* transition. **IR** (KBr) (cm$^{-1}$): 3600-2800 (-OH stret.), 3085.68 (Ar. C-H stret.), 2916.69 (Ali. C-H stret.), 1650.49 (C=O stret.), 1600.59 (C=N stret.), 1566.61 (C=C stret.), 771.57 (C-Cl stret.), 682.61 (C-Cl stret.). **$^1$H NMR** (δ ppm): 6.8 (s, 1H, Ar-O**H**), 7.5-8.1 (m, 17H, Ar-**H**).

**Preparation of 2-[2-phenylthio -4- (2-acetyloxy -5-chlorophenyl) imidazolo] -4-benzoyl-5- (2'-acetyloxy-5'-chlorophenyl)-1,3-thiazole (6):** 2-[2-Phenylthio-4-(2-hydroxy-5-chlorophenyl) imidazolo] -4-benzoyl-5- (2'-hydroxy-5'-chlorophenyl) -1,3-thiazole (5) (0.01M) was refluxed with

acetic anhydride for about 45 min. in glacial acetic acid. After cooling, the reaction mixture was decomposed in water and product, thus separated, was filtered and crystallized from ethanol to get the compound 6 (m.p. 107 $^{o}$C, yield: 80 %).

**Molecular Formula $C_{35}H_{23}N_3O_5S_2Cl_2$ (6):** Yellowish crystalline solid, m.p. 107 $^{o}$C, yield 80 %, Elemental analysis (%): **C** 59.93/60.00; **H** 3.27/3.31; **N** 5.94/6.00; **O** 11.37/11.42; **S** 9.09/9.15; **Cl** 10.07/10.12. **UV** (ethanol): $\lambda_{max}$ 530 nm, n→ π* transition. **IR** (KBr) (cm$^{-1}$): 3500-2800 (-OH stret.), 2974.37 (Ali. C-H stret.), 1653.25 (C=O stret.), 1645.78 (C=N stret.), 804.54 (C-Cl stret.). **$^{1}$H NMR** (δ ppm): 6.8 (s, 2H, C-**H**), 7.1-8.1 (m, 12H, Ar-**H**).

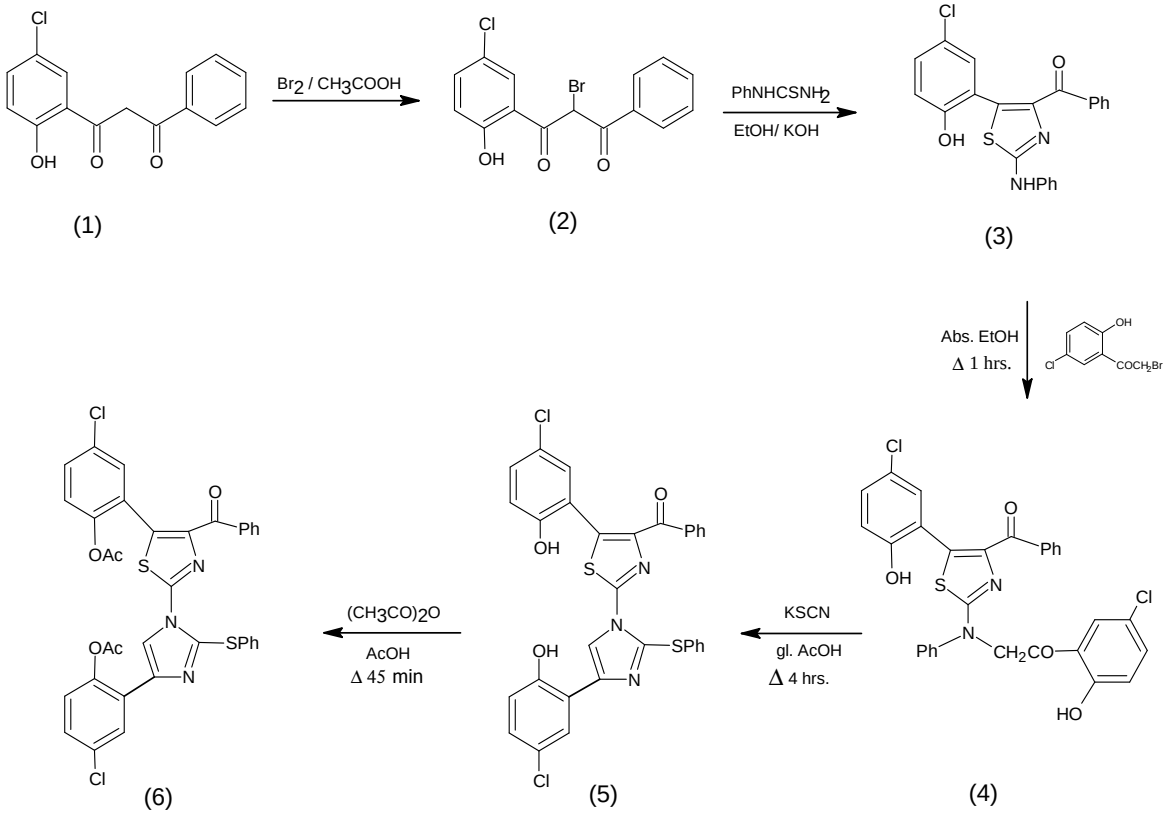
**Antimicrobial Screening:** The newly synthesised titled compounds 2, 3, 4, 5 and 6 were screened for their antifungal and antibacterial activity by cup plate method against causative organisms which are responsible for ***Oyster mushroom*** crop diseases ***viz. Gliocladium roseum (Link) Bainier***, ***Verticillium fungicola, Pseudomonas stutzeri***, ***Pseudomonas alcaligens, Pseudomonas fluorescene*** and ***Burkholderia gladioli.*** The inhibitory effects of compounds against these organisms are given in Table-1.

**Impact of titled compounds on growth of Oyster mushroom:** ***Pleurotus sajor-caju:*** The experiment was conducted at the ICAR affiliated Krushi Vidyan Kendra, Durgapur (Badnera) Dist. Amravati. A species of Oyster mushroom ***Pleurotus sajor-caju*** ie ***P. pulmonarius*** has been selected and cultivated in the specially made house.

The experimental setup was divided into two parts. **Part-A:** In this case the beds of control group crop spawns were inoculated and cultivated by the conventional method. **Part-B:** The beds of this group were treated with the solutions of test compounds.
**Spawn treatment:** The spawns of mushroom species were treated with the test compounds solution before inoculation in the respective beds.

**Field treatment:** The uniform size beds/packets of substrate (soybean straw) were prepared. The equal quantity spawns treated with the solutions of titled compounds were inoculated in the beds. The mouths of packets were tighten with threads and bags were incubated for mycelium growth on or below 25$^{o}$C.

After the completion of mycelium growth, the spawn packets were transferred to cultivation house and opened, also irrigated as per the need. When the first primordial initiated, the test compounds were sprayed with specific interval of time. Mushroom crop was harvested before the fruiting body showed any splitting on the edges. The yields of mushroom crop from various bags with different parameters viz length, diameter, thickness, weight and colour were recorded (Table-2).




**Scheme-1**

**Table-1**
**Antimicrobial screening of titled compounds against *Oyster mushroom* crop pathogens**

| Compounds | Zone of inhibition (mm) | | | | | |
|---|---|---|---|---|---|---|
| | Fungal pathogens | | Bacterial pathogens | | | |
| | G. roseum | V. fungicola | P. stutzeri | P. alcaligens | P. fluorescene | B. gladioli |
| 2 | 08 | 09 | 07 | 09 | 09 | 08 |
| 3 | 12 | 13 | 10 | 13 | 15 | 12 |
| 4 | 10 | 13 | 13.5 | 12 | 17 | 11 |
| 5 | 18 | 21 | 20.5 | 19 | 24 | 17 |
| 6 | 12 | 19 | 16.5 | 15 | 21 | 21 |
| Carbendizium | 09 | 09 | NA | NA | NA | NA |
| Gentamycine | NA | NA | 08 | 08 | 08 | 08 |

**Table-2**
**Impact of titled compounds on growth of Oyster mushroom: *P. sajor-caju***

| Treated bags | Compo-unds | D(cm) | T(cm) | L(cm) | Weight of Dry Bags (gm) (After Harvesting) | Total Weight (gm) | | Colour |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Fresh | Dry | |
| 1 | 2 | 8.1 | 0.4 | 6.0 | 0.992 | 189 | 18.20 | Grey |
| 2 | 3 | 9.5 | 0.6 | 6.4 | 0.867 | 228 | 22.95 | Grey |
| 3 | 4 | 8.8 | 0.5 | 6.2 | 0.923 | 210 | 19.88 | White |
| 4 | 5 | 11.4 | 0.6 | 7.0 | 0.988 | 239 | 24.37 | Creamy |
| 5 | 6 | 10.0 | 0.6 | 7.1 | 0.990 | 207 | 18.70 | Grey |
| 6 | 1,4-Dioxane | 6.0 | 0.4 | 6.1 | 0.990 | 176 | 19.13 | White |
| 7 | Control | 6.8 | 0.3 | 5.5 | 0.853 | 204 | 20.00 | White |
| D = Diameter ; T = Thickness ; L = Length | | | | | | | | |

## Results and Discussion

In the present study the titled compounds 2, 3, 4, 5 and 6 were screened for their antimicrobial activity against some mushroom crop damaging pathogens**.** From the results it has been observed that the titled compounds showed good to moderate antifungal and antibacterial activity.

The impact of the titled compounds on the growth of ***Pleurotus sajor-caju*** was also studied. When the treated and control species of mushroom was compared with reference to their morphological characters, it was interesting to note that imidazole bends of azoles were found more effective in the enhancement of diameter and thickness of the cap as well as lengthening of stipe. However, the more vigorous observation reveals that the mushrooms treated with blends showed increase in the value of crude fibre percentage as compared to other treated compounds. As a consequence, there was increase in the yields.

## Conclusion

On the basis of chemical analysis and spectral data, it is concluded that, the synthesis of titled compound were achieved successfully. The newly synthesised titled compounds are capable to cramp the growth of fungal and bacterial pathogens. The treated species shows significant growth in morphological characters that reflects the curative and growth promoting properties of the titled compounds. However, further investigation and a systematic approach in the light of agricultural science would certainly prove to be a potential tool for the growth promoting and creating an ecofriendly environment for mushroom cultivation in tropical belt of India.

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# THE PH METRIC STUDY OF SYNTHESIZED HETEROCYCLIC COMPOUND ISOXAZOLIN WITH Cu (II) AND Fe (III) METAL IONS

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## ABSTRACT

In the present study the five membered heterocyclic compound i.e. isoxazolines have been synthesized by reported method, their structure have been confirmed on the basis of the chemical test and spectral analysis. The interaction of the metal ions Cu (II) and Fe (III) with isoxazolines have been studied pH metrically, Proton-ligand stability constant (pK) and metal- ligand stability constant (logK) at 0.1 M ionic strength has been determined at $30^0$C in 70% dioxane-water mixture. The above study shows the 1:1 and 1:2 complex formation take place.

**KEYWORDS:** Heterocyclic compounds, isoxazoline, pH metric.

## INTRODUCTION

The literature survey shows that derivatives of the pyrazoline and isoxazoline possess broad spectrum of pharmacological activities[1-7] such as antimicrobial[8-10], antidepressant[11], anticonvulsant[12], antimalarial[13], antifungal[14], antitumor[15], anti-inflammatory[16], anti diabetic[17] and pesticidal.[18] These five membered heterocyclic compounds possess good complexing capacity because of presence of the oxygen as a donor atom in their structure. From the literature survey it is reveals that the pH metric studies of complexes have been carried by many researchers.[19-23] The study of 4-amino-3-naphthol-sulphonic acid and 6-amino-5-naphtholsulphonicacid with transition metal ions and calculation proton-ligand and metal-ligand stability constants is done by Deosarkar S. D. And Narwade M. L.[24]

The PKa value of phenolic compounds in acetonitrile-water mixture by using spectrophotomteric technique have been estimated by Aktas *et al.*[25]

**Experimental:** The ligand i.e. 2-Hydroxy isoxazoline have been prepared by known reported method. Systronic make pH-meter with accuracy ±0.01 unit with combined glass electrode and saturated calomel was used for the measuring pH. The instrument was calibrated by using buffer solution of pH 4.00 and 9.20 at 30$^{o}$C.

The following ligands have been used for the study

1. **$L_1$**= 3-(2-Hydroxy-3, 5-dichlorophenyl)-5-(2, 4-dichloro phenyl) isoxazoline (HDPI-B)

2. **$L_2$** = 3-(2-Hydroxy-3, 5-dichlorophenyl)-5-( 4-chloro phenyl) isoxazoline (HCPI-A)

The following reagents were used for the experiment

i) Nitric acid :- (0.1M) A. R. grade

ii) Potassium nitrate (1M):- A. R. grade

iii) Sodium hydroxide (0.1N):- A. R. grade

iv) Oxalic acid(0.1M) :-A. R. grade

v) Metal ions solutions**:-**Cu (II) and Fe(III) nitrates were used to prepare 0.01 m solutions. All solutions were prepared by dissolving requisite amount of substances in distilled water. 0.01m solutions of the ligands were prepared in Dioxane.

**Titrations:-** The procedure of the experiment is involved following titration

1. Free acid titration
2. Free acid and ligand titration.
3. Free acid, ligand and metal ion titration against standard NaOH solution

The above titrations were carried out in 100 ml Pyrex glass beaker maintained at constant of 30$^{0}$C temperature in 70% Dioxane-water at 0.1M ionic strength. Nitrogen gas was slowly bubbled through the solution to remove the oxygen gas and $CO_2$.The reading of the pH meter was recorded at every addition of 0.2ml NaOH solution from the burette with constant stirring.

The graph of pH against volume of alkali added were plotted as

1. Acid curve(A)
2. Ligand titration curve(A+L)
3. Metal ligand titration curve(M+L+M)

**Method for the determination of the stability constants**

i) Calculation of proton-ligand stability constant (pK values)

The proton-ligand stability constant (pK) is defined as the pH at which half of the amount (concentration) of the ligand is ionized i.e conc. of ionized and unionized forms of the ligand are equal.The value of pK for various ligands are estimated by half integral method by calculating the value of proton-ligand formation number **($\eta^-_A$)** at various pH by using Irving and Rossotii equation.

$\eta^-_A = \gamma - [(E^o + N)\,\Delta V/(V_o + V_1)\,T^o_L]$ --------- (1)

Where

$V_0$ = Initial volume of solution

N = Normality of sodium hydroxide

$T^o_L$ = Concentration of ligand in the solution

$E^0$ = Initial con. of free acid ($HNO_3$)

$\gamma$ = number of dissociable protons from ligand

$(V_2-V_1)$ = $\Delta V$= Difference in volumes of alkali consumed by acid and ligand on the same p H.

The proton-ligand formation curve was drawn by plotting graph of $\eta^-_A$ against pH. The pH at which $\eta^-_A$ = 0.50 gave value of proton-ligand stability constant (pk) of the ligand. The robustness of these values were confirmed by calculating the average pK value by point-wise calculation in the $\eta^-_A$ range of 0.2 to 0.8, using the following equation.

$pK - pH = \log \eta^-_A / 1 - \eta^-_A$ ----------(2)

Where $\eta^-_A$ value corresponds to given pH. The values of pK calculated by point-wise calculation are presented in table 1, 2

ii) Calculation of metal-ligand stability constant (log k value). This calculation, first involves calculation of metal-ligand formation number at various pH, from the equation.

$\eta^- = (N + E^0)\,\Delta v / (V_0 + V_2)\;\eta^-_A\,Tm^0$ ----------(3)

Where $V_0$ = Initial volume of solution

N = Normality of NaOH

$T^0_M$ = Conc. of metal ions

$\eta^-_A$ = Proton-ligand formation no.

$E_0$ = Initial conc. of free acid ($HNO_3$)

$(V_3-V_2)$ = $\Delta V$ = Difference in volumes of NaOH consumed by ligand and metal ions at the same pH

The metal-ligand formation curve was constructed by plotting $\eta^-$ values against pH.

The free ligand concentration (pL) at $\eta^- = 0.5$ and 1.5 gives the values of metal ligand stability constant $\log k_1$ and $\log k_2$ respectively. The PL values were calculated by using Irving-Rossotti equation.

$PL = \text{Log } K = \log [ H^+ / (K. ( T^o_L - T_m{}^o \times n^-) \times V_o + V_3 / V_o]$

Where $[H^+]$ = Concentration of the hydrogen ion at $\boldsymbol{\eta^-} = 0.5$ or 1.5

K = Ionization constant of the ligand

$\eta^-$ = Metal-ligand formation numbers

## RESULT AND DISCUSSION

**Table 1: pH metric Titration data**

| Volume of NaOH(ml) | Free Acid Titration (A) pH | Ligand Titration (A+L) pH | Metal-Ligand Titration (A+L+$Cu^{+2}$) pH | Metal-Ligand Titration (A+L+$Fe^{+3}$) pH |
|---|---|---|---|---|
| 0.0 | 0.77 | 0.68 | 0.83 | 0.83 |
| 0.05 | 0.81 | 0.72 | 0.84 | 0.84 |
| 1.00 | 0.85 | 0.76 | 0.87 | 0.87 |
| 1.5 | 0.89 | 0.80 | 0.89 | 0.89 |
| 2.0 | 0.93 | 0.84 | 0.94 | 0.94 |
| 2.5 | 0.98 | 0.89 | 0.97 | 0.97 |
| 3.0 | 1.03 | 0.94 | 1.00 | 1.02 |
| 3.5 | 1.09 | 0.99 | 1.05 | 1.04 |
| 4.0 | 1.14 | 1.05 | 1.10 | 1.09 |
| 4.5 | 1.21 | 1.10 | 1.15 | 1.12 |
| 5.0 | 1.27 | 1.17 | 1.21 | 1.20 |
| 5.5 | 1.35 | 1.23 | 1.28 | 1.26 |
| 6.0 | 1.45 | 1.32 | 1.35 | 1.34 |
| 6.5 | 1.53 | 1.40 | 1.44 | 1.42 |
| 7.0 | 1.62 | 1.55 | 1.55 | 1.52 |
| 7.5 | 1.74 | 1.62 | 1.63 | 1.63 |
| 8.0 | 1.86 | 1.74 | 1.77 | 1.74 |
| 8.5 | 2.00 | 1.89 | 1.92 | 1.90 |
| 9.0 | 2.19 | 2.05 | 2.10 | 2.05 |
| 9.5 | 2.42 | 2.28 | 2.24 | 2.20 |
| 10.0 | 2.70 | 2.60 | 2.46 | 2.38 |
| 10.5 | 3.40 | 3.03 | 2.82 | 2.75 |
| 11 | 4.44 | 3.99 | 3.36 | 3.30 |
| 11.5 | 5.77 | 5.02 | 4.40 | 4.36 |
| 12.0 | 9.10 | 8.24 | 5.56 | 5.48 |

| | | | | |
|---|---|---|---|---|
| 12.5 | 10.62 | 9.69 | 8.00 | 7.85 |
| 13.0 | 11.84 | 10.85 | 9.72 | 9.60 |
| 13.5 | 12.21 | 10.96 | 11.36 | 11.28 |
| 14.0 | 12.43 | 11.49 | 11.80 | 11.70 |
| 14.5 | 12.58 | 11.96 | 12.02 | 11.89 |
| 15.0 | 12.70 | 12.22 | 12.12 | 12.06 |
| 15.5 | 12.78 | 12.41 | 12.26 | 12.18 |
| 16.0 | 12.85 | 12.50 | 12.40 | 12.35 |
| 16.5 | 12.95 | 12.64 | 12.52 | 12.32 |
| 17.0 | 13.01 | 12.70 | 12.60 | 12.50 |

System (HDPI-B) ($L_1$) Volume= 50 ml

$E^0$ = 1.00 x $10^{-2}$ M N = 0.1 M

Medium: - 70% 1, 4-Dioxane -Water Temperature:-30 $^0$C±0.1

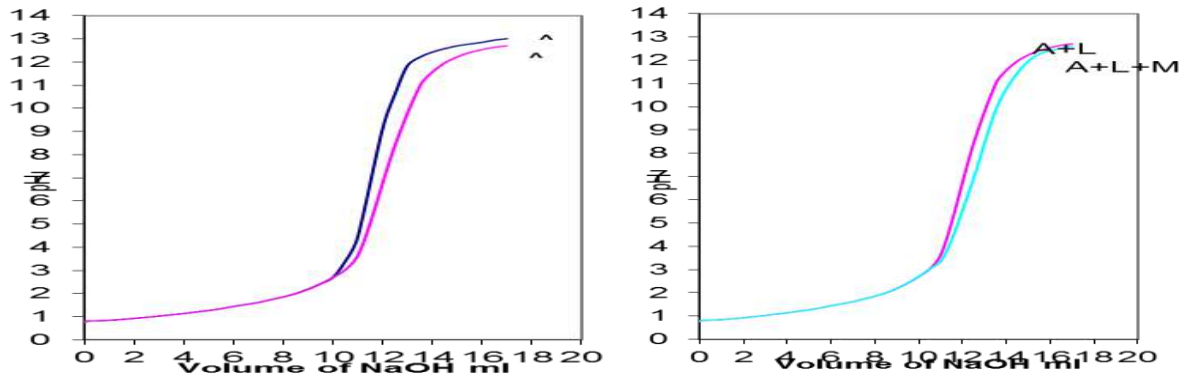



**Fig.1 Titration graph of free acid, free acid + ligand And free acid + ligand +metal ion for $L_1$**

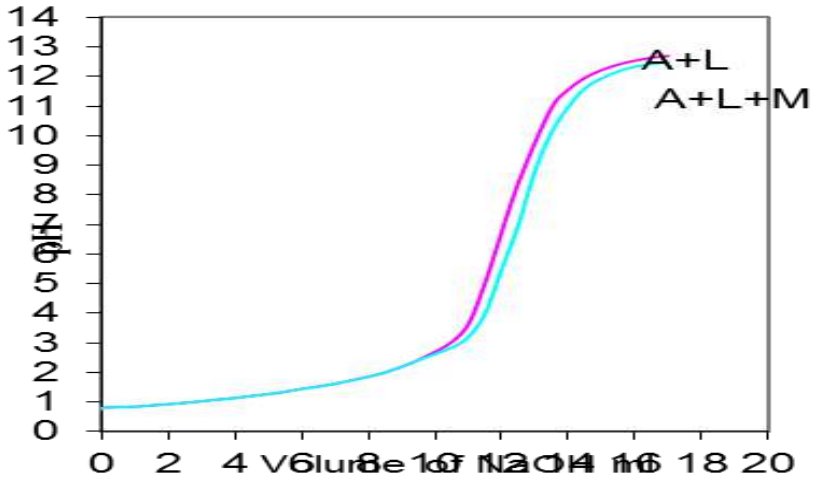



**Table 2 pH- metric Titration Data**

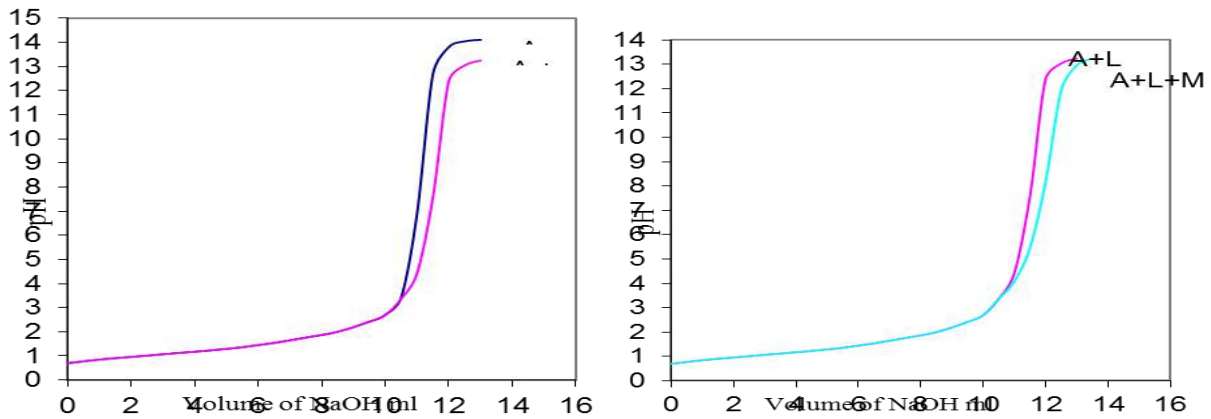
System (HDPI-A) ($L_2$) Volume=50 ml

$E^0$ = 1.00 x $10^{-2}$ M N = 0.1 M

Medium:- 70% 1,4-Dioxane -Water Temperature:-30 $^0$C ±0.1

**Table-2**

| Volume of NaOH(ml) | Free Acid Titration (A) pH | Ligand Titration (A+L) pH | Metal-Ligand Titration (A+L+$Cu^{+2}$) pH | Metal-Ligand Titration (A+L+$Fe^{+3}$) pH |
|---|---|---|---|---|
| 0.0 | 0.66 | 0.70 | 0.77 | 0.80 |
| 0.5 | 0.77 | 0.80 | 0.83 | 0.85 |
| 1.00 | 0.81 | 0.85 | 0.86 | 0.90 |
| 1.5 | 0.86 | 0.90 | 0.91 | 0.96 |
| 2.0 | 0.90 | 0.96 | 0.95 | 1.00 |
| 2.5 | 0.96 | 1.00 | 1.00 | 1.02 |
| 3.0 | 1.03 | 1.07 | 1.03 | 1.04 |
| 3.5 | 1.11 | 1.08 | 1.08 | 1.07 |
| 4.0 | 1.18 | 1.16 | 1.13 | 1.18 |
| 4.5 | 1.27 | 1.23 | 1.20 | 1.23 |
| 5.0 | 1.31 | 1.28 | 1.26 | 1.28 |
| 5.5 | 1.40 | 1.36 | 1.34 | 1.36 |
| 6.0 | 1.47 | 1.40 | 1.42 | 1.46 |
| 6.5 | 1.56 | 1.54 | 1.53 | 1.53 |
| 7.0 | 1.65 | 1.61 | 1.60 | 1.60 |
| 7.5 | 1.77 | 1.76 | 1.74 | 1.70 |
| 8.0 | 1.90 | 1.88 | 1.86 | 1.84 |
| 8.5 | 2.04 | 2.00 | 2.04 | 1.90 |
| 9.0 | 2.17 | 2.16 | 2.21 | 2.18 |
| 9.5 | 2.42 | 2.42 | 2.45 | 2.40 |
| 10.0 | 2.66 | 2.70 | 2.72 | 2.70 |
| 10.5 | 3.42 | 3.37 | 3.38 | 3.06 |
| 11 | 6.92 | 4.43 | 4.50 | 3.77 |
| 11.5 | 12.70 | 11.64 | 9.76 | 7.03 |
| 12.0 | 13.80 | 12.63 | 11.58 | 10.00 |
| 12.5 | 14.04 | 13.04 | 12.70 | 12.02 |
| 13.0 | 14.10 | 13.24 | 12.96 | 12.35 |
| 13.5 | | | 13.24 | 12.63 |
| 14.0 | | | | 12.78 |
| 14.5 | | | | 12.95 |
| 15.00 | | | | 13.02 |



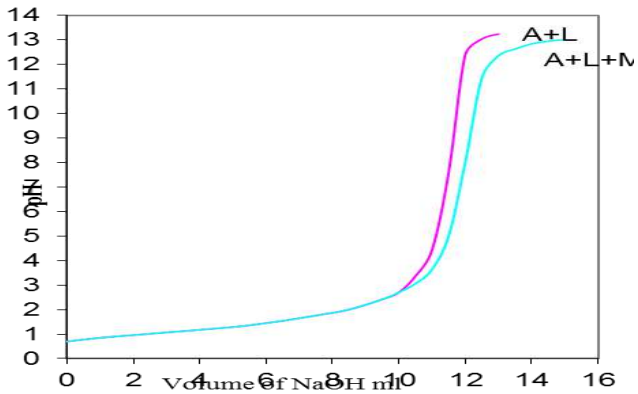



**Fig.2 Titration graph of free acid, free acid+ligand And free acid + ligand +metal ion for $L_2$**

**Table 3 pK value and Log K values of Metal-ligand complexes.**

| Ligands | pK | Metal ion | $logK_1$ | $logK_2$ |
|---|---|---|---|---|
| $L_1$ | 10.75 | Cu(II) | 8.2646 | 7.2765 |
| | | Fe(III) | 10.3577 | 9.2197 |
| $L_2$ | 12.10 | Cu(II) | 8.347 | 6.0245 |
| | | Fe(III) | 10.9332 | 9.8029 |

## CONCLUSION

The metal-ligand stability constant have been calculated by half integral method and the metal ligand formation number value indicates that the formation of 1:1 and 1:2 complexes in solution. These ligands contain phenolic –OH group, normally phenolic –OH dissociates in the pH range of 9 to 10[26]. In the present study pK of $L_1$ is found to be 10.75 the slightly higher value may be due to presence of weak electron withdrawing effect of chlorine atoms. The pK value 12.10 of $L_2$ is quite high and this might be due to electron withdrawing effect of one more chlorine atom in its structure. Due to high pK value, at stomach pH of 2.0 and intestine pH of 6.0 both ligands are 99% unionized and hence are easily absorbed by stomach and intestine indicating their high lipophilic character. Both ligands form stable complexes with Cu (II) and Fe (III)ion as seen from their high logK value The Fe(III) ion due to its higher charge and lower ionic size forms more stable complex with both ligands than Cu (III)ions.

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# A Study On The Ultrasonic Behaviour Of Some Chalcones And Their Mixtures

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***ABSTRACT***

*Ion-solvent or solvent-solvent interaction involved in a binary mixture system can be studied by various methods.Ultrasonic studies in organic liquids and their binary mixtures have been of considerable research interest during the last few decades. A liquid mixture is said to show ideal behaviour if the variations in density and sound velocity etc., with mole fraction of the solute are linear. Ultrasonic velocity and adiabatic compressibility, which can be measured accurately. Thermodynamic parameters like molar volume, adiabatic compressibility, appar molal volume, molar adiabatic compressibility acoustic impedance and adiabatic bulk modulus have been evaluated from the measured values of ultrasonic velocity and density for pure dielectric liquids of Chalcone of P-Chlorobezaldehyde,Salicylaldehyde,& Benzaldeyde and also their mixtures. It is observed that apparent molal volume, molar adiabatic compressibility increase with increasing the concentration of ligands & adiabatic compressibility decrease with decreasing the concentration of ligands.*

## 1. INTRODUCTION

Ion-solvent or solvent-solvent interaction involved in a binary mixture system can be studied by various methods.There are three techniques which are generally used for the measurement of ultrasonic velocity viz.optical diffraction technique,Echo pulse technique & interferometric technique. Ultrasonic studies in organic liquids and their binary mixtures have been of considerable research interest during the last few decades. A liquid mixture is said to show ideal behaviour if the variations in density and sound velocity etc., with mole fraction of the solute are linear. Ultrasonic velocity and adiabatic compressibility, which can be measured accurately. Chalcone of P - Chlorobezaldehyde, Salicylaldehyde, & Benzaldeyde have been chosen for ultrasonic study .ultrasonic velocity, density,measurements have been made and some acoustical parameters like adiabatic compressibility, appear molal volume,molar adiabatic compressibility ,intermolecular free length (Lf), etc., are evaluated. Ultrasonics is the branch of physics dealing with the study and applications of sound waves having frequencies which are beyond the range

## 2.Principle of Interferometric Technique

There are the three techniques which are the generally used for the measurement of ultrasonic velocity viz. optical diffraction technique,Echo pulse technique, Interferometric Technique.In the present study , Interferometric Technique has been used for the determination of ultrasonic velocity.The principle used in the measurement of velocity (v) in the based on accurate determination of wavelength ($\lambda$) in the medium ultrasonic waves of known frequency ($f$) are the produced by quartz crystal fix at the bottom of cell.The interferometer is an instrument for exact measurement of wavelength of any wave motion. One of the most accurate ways of measuring ultrasonic constants in fluids or gasses is, to set up stationary wave resonances. This is usually done in a column at one end of which the source is located and at the other end of which is placed a reflector. This is known as single interferometer and was originally proposed by Perrin.

## 3.MATERIALS AND METHODS

Commercially available AR grade DMSO & chalcone of various compound were used as such. Densities were measured with the help of bicapillary pyknometer. All the weighings were made using single pan digital balance. The binary mixtures were prepared by volume, by mixing selected volumes of liquid components in air tight glass bottles. A 10 ml. specific gravity bottle and electronic balance were used for the determination of density measurements.To prepare concentration of various molar solutions.& calculate the various parameters :-

1]To calculate the adiabatic compressilbility :-

$$\beta=1/V^2 \times d$$

2. To calculate the Apparent molal volume:-

$$\Phi v= 1000(do-ds)/c.ds.do +m/ds$$

3. To calculate the molar adiabatic compressilbility:-

$$\Phi k =1000(\beta s.do- \beta 0.ds)/ c.ds.do + \beta s.m/ ds$$

## 4. RESULTS AND DISCUSSTION

The values of molar refraction and polarizability constants of some ligand systems at different concentrations are presented in Table. It is observed that adibatic compressibility, appar molal volume, molar adiabatic compressibility increase with increasing the concentration of ligands & adiabatic compressibility decrease with decreasing the concentration of ligands .The values different concentrations of ligands in different percentage of ethanol- mixtures are presented in following tables:-

**Table 1: concentration Vs** apparent molal volume **Of various chalcones at different concentration**

| Conc. | Ligand A | Ligand B | Ligand C |
|---|---|---|---|
| 0.7 | 4.84 | 6.325 | 5.826 |
| 0.54 | 3.63 | 5.362 | 4.562 |
| 0.4 | 2.365 | 4.253 | 3.256 |
| 0.3 | 1.236 | 3.05 | 2.356 |

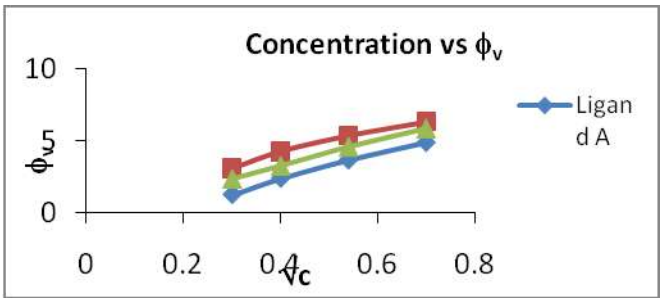
**Table 2: concentration Vs** adiabatic compressilbility **Of various chalcones at different concentration**

| | Ligand A | Ligand B | Ligand C |
|---|---|---|---|
| 0.7 | 6.0679 | 2.536 | 4.326 |
| 0.54 | 8.365 | 4.365 | 6.326 |
| 0.4 | 10.236 | 6.325 | 8.365 |
| 0.3 | 12.624 | 8.236 | 10.358 |

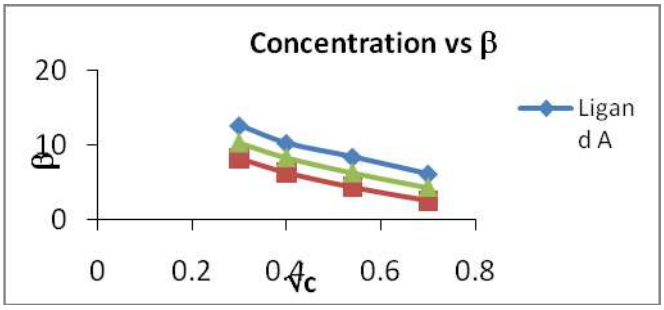
**Table 3: concentration Vs** molar adiabatic compressilbility **of various chalcones at different concentration**

| Conc. | Ligand A | Ligand B | Ligand C |
|---|---|---|---|
| 0.7 | -14466 | -10615 | -12200 |
| 0.54 | -15634 | -11616 | -13400 |
| 0.4 | -16363 | -13563 | -14910 |
| 0.3 | -17896 | -14791 | -16420 |

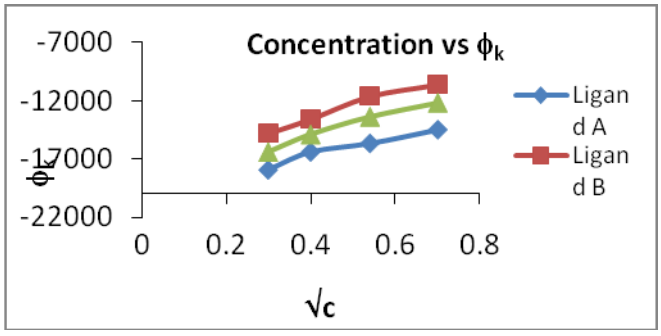
**Graph 1**




**Graph 2**




**Graph 3**




## 6. CONCLUSION

Thermodynamic parameters like molar volume, adiabatic compressibility, appar molal volume, molar adiabatic compressibility acoustic impedance and adiabatic bulk modulus have been evaluated from the measured values

of ultrasonic velocity and density for pure dielectric liquids of Chalcone of P-Chlorobezaldehyde, Salicylaldehyde, & Benzaldeyde and also their mixtures. Some acoustical parameters like adiabatic compressibility Intermolecular Free length (Lf) are evaluated for the chosen materials and their mixtures

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# Molecular structure investigation and biological evaluation of Michael adducts derived from dimedone

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**Abstract** Trimolecular salt Michael adducts **2a–c** were synthesized in excellent yields up to 92 % via one-pot multicomponent reactions in an aqueous medium. The chemical structures of compounds **2a–c** were characterized by X-ray single-crystal diffraction techniques. Calculations of the density functional theory for the synthesized compound were performed. The stability of the products was deduced by TGA analysis. Compounds **2a–c** were screened in vitro for different bio-assays such as thymidine phosphorylase inhibition assay, urease inhibition assay, $\beta$-glucuronidase inhibition assays and cytotoxicity against PC-3 and HeLa cell lines.

**Keywords** Michael adduct · Dimedone · Thymidine phosphorylase assay · Urease inhibition assay · $\beta$-Glucuronidase inhibition assay

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## Introduction

5,5-Dimethylcyclohexane-1,3-dione, commonly known as dimedone, belongs to the family of cyclic 1,3-diketones –class of organic compounds. A wide range of applications of dimedones includes its use as reagent for various analytical techniques [1, 2], as well as a versatile synthon for synthesis of several *spiro* and heterocyclic compounds [3], such as xanthene derivatives, which have emerged as an important class of compound because of their industrial importance [4] and other synthetic applications [5].

The versatile chemistry [6–10] and ready availability of cyclohexane-1,3-diones [11–13] and its derivatives make them suitable precursors for the preparation of divergent organic compounds, for example chromene derivatives, which possess anticancer, antioxidant, spasmolytic, anti-anaphylactic, anti-HIV and anti-bacterial activities [14, 15], oxozolidinones with antibacterial activity [16–19], substituted xanthene derivatives with several uses in dyes [20, 21], laser technology [22], fluorescent compounds [23], and more importantly, have been reported to show a variety of biological activity [24–26]. Additionally, acridine and its derivatives display antimalarial, anticancer, antibacterial, and mutagenic properties, while phenylbutazones exhibit unique pharmacological uses for pain treatment associated with Tietze's syndrome and rheumatoid arthritis [27].

On the other hand, with the increasing environmental concerns, green chemistry has attracted major scientific and commercial interest in recent years. Multicomponent one-pot reactions are an efficient and economical procedure, with wide uses in the preparation of heterocycles molecules [28–30]. On the other hand, organic transformation takes place in aqueous media gives a clean, environmentally safe, and cost-effective approach. Recently, Barakat and coworkers reported examples for MCR (one-pot fission) for example reaction of substituted cyclohexanedione with alkanal mediated by diethylamine in water [31–36].

In the current study, the structure of salt Michael adducts **2a–c** were elucidated by X-ray single-crystal diffraction and TGA study. In addition, density functional theory (DFT) using B3LYP/6-311G(d,p) method were used to study different structural aspects of the compounds. Also, the synthesized compounds **2a–c** were evaluated for a set of in vitro biochemical assays.

## Experimental

### General

Chemical reagents were purchased from Fluka, Sigma-Aldrich, Aldrich, etc., and were used without further purification, unless otherwise stated. The crystal data were collected on a Bruker APEX-II CCD area diffractometer, crystallographic data for the compounds, **2a**, **2b** and **2c** are deposited with the CCDC-993141, 993142, and 993140 respectively.

*Diethylammonium 2-((4-bromophenyl)(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)methyl)-5,5-dimethyl-3-oxocyclohex-1-enolate (**2a**)*

Compound **2a** was synthesized from dimedone and *p*-bromobenzaldehyde **1a** as a white crystal. The structure of **2a** was unambiguously deduced by X-ray diffraction analysis. A suitable colorless cubic crystal of **2a** was grown in $CHCl_3/Et_2O$ at rt after 48 h.

*Diethylammonium 2-((3-bromophenyl)(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)methyl)-5,5-dimethyl-3-oxocyclohex-1-enolate (**2b**)*

Compound **2b** was synthesized from dimedone and *m*-bromobenzaldehyde **1b** as a crystalline compound. Colorless cubic crystals of compound **2**, found suitable for X-ray analysis, were grown in $CH_2Cl_2$/pet. ether at rt after standing for 24 h.

*Diethylammonium 2-((2,4-dichlorophenyl)(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)methyl)-5,5-dimethyl-3-oxocyclohex-1-enolate (**2c**)*

Compound **2c** was synthesized from dimedone and 2,4-dichlorobenzaldehyde (**1c**) as a colorless cubical crystals in $CH_2Cl_2$/pet. ether at rt. The crystals suitable for X-ray analysis were obtained after 3 days.

## DFT calculations

In the present work, DFT calculations using the B3LYP method, together with local or non-local functionals, were performed that unites the Becke's three-parameter exchange functional (B3) with the Lee, Yang, and Parr correlation functional (LYP). The density functional theory (DFT) calculations were carried out utilizing GAMESS program. The input geometry of the synthesized compounds were optimized using at B3LYP/6-311G(d,p) basis set for C, O, N, and H atoms without imposing any external constraint on the potential energy surfaces.

## Biological assay

The *p*-nitrophenyl-*β*-D-glucuronide (N-1627) and *β*-glucuronidase (E.C. 3.2.1.31, from bovine liver, G-0251) were purchased from Sigma Chemical Co. (U.S.A.). $Na_2CO_3$ anhydrous and all other reagents of standard grade were getting from E. Merck. The anhydrous EtOH and $CHCl_3$were used in experiment and these were dried by using the standard methods. All other solvents and reagents were of standard grade like the benzoyl chloride.

## *β*-D-glucuronidase assay

*β*-D-glucuronidase inhibition assay was performed as described by Khan et al. [37].

### Urease assay and inhibition

The assay was performed as described by Khan et al. [38] and Weatherburn et al. [39].

### Thymidine phosphorylase assay protocol

The assay was performed as described by Krenitsky et al. [40].

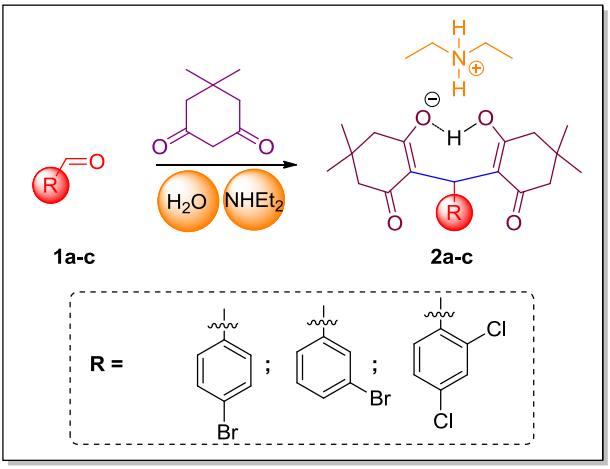
### Cytotoxic activity

The assay was performed as described by Mosmann et al. [41].

## Results and discussion

### Synthesis of the salt of Michael adduct

Recently, there has been a lot of interest in the development of highly efficient transformations for the synthesis of biologically active organic molecules, with potential utilities in agrochemical or pharmaceutical industries. There is also interest in discovering new, strategically important protocols, which are efficient and environmentally benign, and lead to the complex structural variations with simple work-up procedures in high yields [32–35]. During the current study, diethylamine in aqueous medium mediated the one-pot two-component Aldol-Michael addition of 5,5-dimethylcyclohexane-1,3-dione (dimedone), with different arylaldehyde **2a–c** in 2:1 molar ratio to provide trimolecular Michael adducts **2a–c** in excellent yields up to 92 % (Scheme 1) [31].




**Scheme 1** Synthetic protocol used in the present work

## X-ray crystal structures

The chemical structures of the final adduct **2a–c** were unambiguously deduced by single-crystal X-ray diffraction technique (Fig. 1a–c). Tables 1, 2, 3 and 4 display the crystal data and main geometrical parameters of the compounds.

Slow evaporation of compounds **2a** ($CHCl_3/Et_2O$, 3 days), **2b** (DCM/pet. ether, 24 h), and **2c** (DCM/pet. ether, 2 days), at room temperature yielded pure crystals of **2a–c**. Crystals of dimensions 0.38 × 0.37 × 0.24 (**2a**), 0.47 × 0.42 × 0.14 (**2b**) and 0.31 × 0.21 × 0.20 (**2c**) mm were selected for X-ray diffraction analysis on a

**Table 1** The crystal data of **2a–c**

| | **2a** | **2b** | **2c** |
|---|---|---|---|
| Empirical formula | $C_{27}H_{37}BrNO_4$ | $C_{27}H_{37}BrNO_4$ | $C_{27}H_{36}Cl_2NO_4$ |
| Formula weight | 519.49 | 519.41 | 509.47 |
| Temperature | 273 (2) | 273 (2) | 273 K |
| Wavelength | 0.71073 Å | 0.71073 Å | 0.71073 Å |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/c$ | $P2_1/n$ |
| A | 10.2861 (11) Å | 12.6829 (13) Å | 10.3400 (10) Å |
| B | 18.1701 (19) Å | 12.2729 (13) A | 18.2984 (18) Å |
| C | 15.6171 (16) Å | 18.5831 (19) Å | 15.0374 (15) Å |
| $\alpha$ | 90° | 90° | 90° |
| $\beta$ | 106.5 (2)° | 108.283 (3)° | 98.257 (2)° |
| $\gamma$ | 90° | 90° | 90° |
| Volume | 2798.5 (5) $A^3$ | 2746.5 (5) $A^3$ | 2815.7 (5) $A^3$ |
| $Z$ | 4 | 4 | 4 |
| Calculated density | 1.233 $mgm^{-3}$ | 1.256 $mgm^{-3}$ | 1.202 $mgm^{-3}$ |
| Absorption coefficient | 1.498 $mm^{-1}$ | 1.527 $mm^{-1}$ | 0.261 $mm^{-1}$ |
| F(000) | 1092 | 1092 | 1084 |
| Crystal size | 0.38 × 0.37 × 0.24 mm | 0.47 × 0.42 × 0.14 mm | 0.31 × 0.21 × 0.20 mm |
| $\theta$ range | 1.76–25.50° | 1.69–25.50° | 1.76–28.37° |
| Reflections collected | 16,291 | 15,992 | 20,357 |
| Reflections unique | 5202 | 5050 | 7014 |
| ($R_{int}$) | 0.0384 | 0.0597 | 0.0442 |
| $R_1$ with $I > 2\sigma(I)$ | 0.0553 | 0.0518 | 0.0605 |
| $R_2$ with $I > 2\sigma(I)$ | 0.1273 | 0.1142 | 0.1358 |
| $R_1$ for all data | 0.1068 | 0.1192 | 0.1092 |
| $R_2$ for all data | 0.1528 | 0.1438 | 0.1609 |
| Goodness of fit | 1.081 | 0.972 | 1.017 |
| Max/min $\rho$ $e^{-3}$Å | 0.567 and −0.730 | 0.326 and −0.258 | 0.474 and −0.225 |
| CCDC | 993,141 | 993,142 | 993,140 |

**Table 2** Geometric parameters (Å, °) of **2a** (selected)

| Bond | Experimental | Calculated |
|---|---|---|
| Br1–C3 | 1.902 (4) | 1.8905 |
| O2–C13 | 1.286 (4) | 1.2595 |
| O4–C19 | 1.334 (4) | 1.3831 |
| N1–C26 | 1.481 (6) | 1.4785 |
| N1–C25 | 1.492 (6) | 1.4786 |
| C8–C13 | 1.388 (4) | 1.3831 |
| C14–C19 | 1.353 (4) | 1.3558 |
| Bond angle | Experimental | Calculated |
| C26—N1—C25 | 114.5 (4) | 117.6644 |
| O2—C13—C8 | 122.2 (3) | 122.5294 |
| O2—C13—C12 | 115.4 (3) | 111.9032 |
| O4—C19—C14 | 124.3 (3) | 127.8520 |
| CO4—C19—C18 | 110.9 (3) | 113.9985 |
| N1—C26—C27 | 110.3 (4) | 109.9599 |
| C24—C25—N1 | 111.7 (5) | 111.5620 |

**Table 3** Geometric parameters (Å, °) of **2b** (selected)

| Bond | Experimental | Calculated |
|---|---|---|
| Br1–C2 | 1.897 (4) | 1.8930 |
| O1–C9 | 1.329 (4) | 1.2650 |
| O3–C17 | 1.290 (3) | 1.2301 |
| N1–C25 | 1.467 (4) | 1.4768 s |
| N1–C26 | 1.501 (5) | 1.4770 |
| C8–C9 | 1.358 (4) | 1.3560 |
| C16–C17 | 1.386 (4) | 1.3646 |
| Bond angle | Experimental | Calculated |
| C25—N1—C26 | 112.2 (3) | 117.6644 |
| O1—C9—C8 | 124.6 (3) | 121.5499 |
| O1—C9—C10 | 111.4 (3) | 119.5021 |
| O3—C17—C16 | 122.6 (3) | 121.3063 |
| O3— C17— C18 | 116.2 (3) | 111.9032 |
| C24— C25— N1 | 112.8 (3) | 111.5620 |
| C27—C26—N1 | 111.9 (4) | 109.9599 |

Bruker Smart Apex II diffractometer, equipped with CCD detector and graphite monochromatic MoKα radiations ($\lambda = 0.71073$ Å) at 293 (2) K. Cell refinement and data reduction were carried out by Bruker SAINT [14]. The chemical structure

**Table 4** Geometric parameters (Å, °) of **2c** (selected)

| Bond | Experimental | Calculated |
|---|---|---|
| Cl1–C9 | 1.741(2) | 1.7354 |
| C12–C11 | 1.736(3) | 1.7207 |
| O2–C5 | 1.299(2) | 1.2307 |
| O4–C19 | 1.329(3) | 1.2639 |
| N1–C26 | 1.472(4) | 1.4774 |
| N1–C25 | 1.482(4) | 1.4775 |
| C4–C5 | 1.508(3) | 1.5113 |
| C14–C19 | 1.360(3) | 1.3646 |
| Bond angle | Experimental | Calculated |
| O2–C5–C6 | 121.97(19) | 121.9985 |
| O2–C5–C4 | 115.08(18) | 118.2618 |
| O4–C19–C14 | 125.1(2) | 120.7989 |
| O4–C19–C18 | 110.92(19) | 119.0782 |
| C8–C9–Cl1 | 120.03(19) | 119.9182 |
| C11–C10–C9 | 118.8(2) | 119.8890 |
| C12–C11–C10 | 120.0(2) | 120.1922 |
| C12–C11–Cl2 | 120.1(2) | 119.9325 |
| N1–C26–C27 | 110.9(3) | 110.2876 |
| C24–C25–N1 | 112.1(3) | 110.1151 |

was solved by using SHELXS-97 [15, 16]. The listed crystallographic parameters in Table 1 indicate that compounds **2a**, **2b**, and **2c** were crystallized in monoclinic crystal system with space group $P2_1/n$ for **2a** and **2c** and $P2_1/c$ for **2b**. The crystal structures **2a**, **2b**, and **2c** (Fig. 1a) were finally refined with R factor of 5.5, 5.1, and 6.0 %, respectively. The molecule of diethyl amine solvate played an important role to stabilize the structures in crystal lattice through intermolecular hydrogen bondings (Fig. S7–S9; Table S1–S3; see supplementary material).

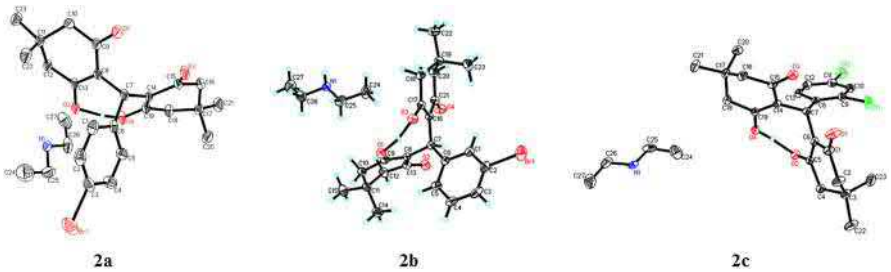



**Fig. 1** The structure of **2a–c** (ORTEP diagrams)

## DFT calculations

*Optimized molecular geometry*

From our XRD data, it is clear that compounds **2a, 2b**, and **2c** possess monoclinic crystal structures. The cell dimensions and other data are presented in Table 1. Selected values of calculated DFT and experimental geometric parameters for the synthesized molecules were found to be in good agreement, and are listed in Tables 2, 3 and 4. Figures 2 and 3 depict the optimized structures and HOMO–LUMO for compounds **2a, 2b**, and **2c**.

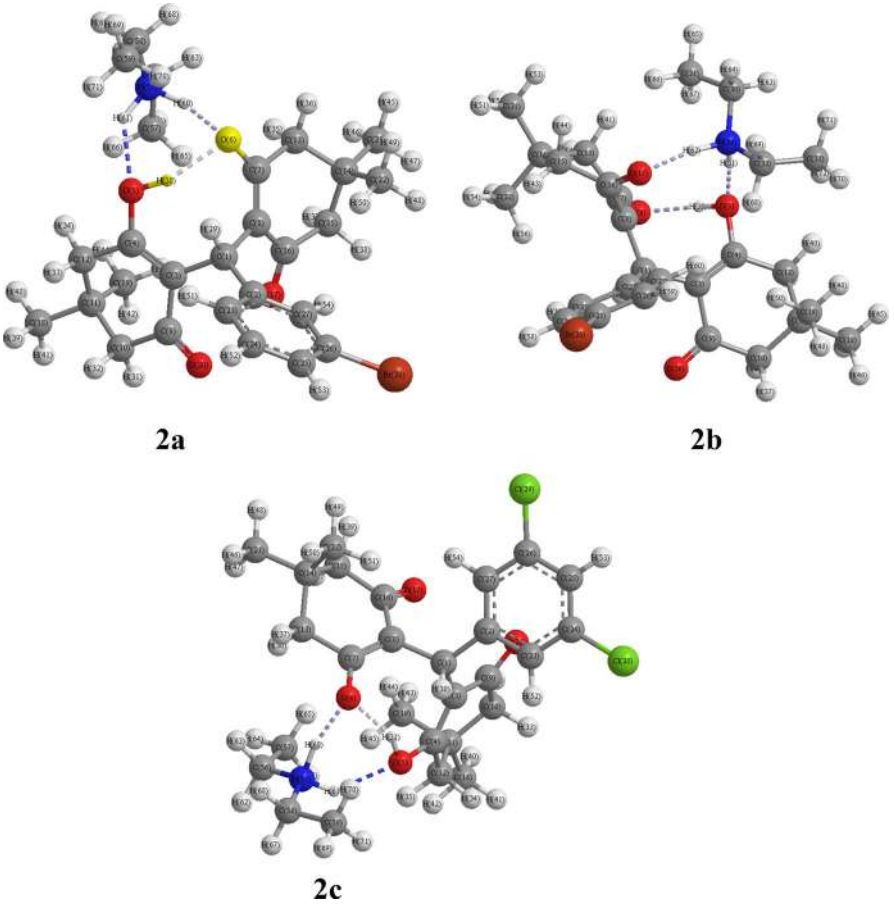



**Fig. 2** Optimized molecular structures of compounds **2a, 2b**, and **2c**

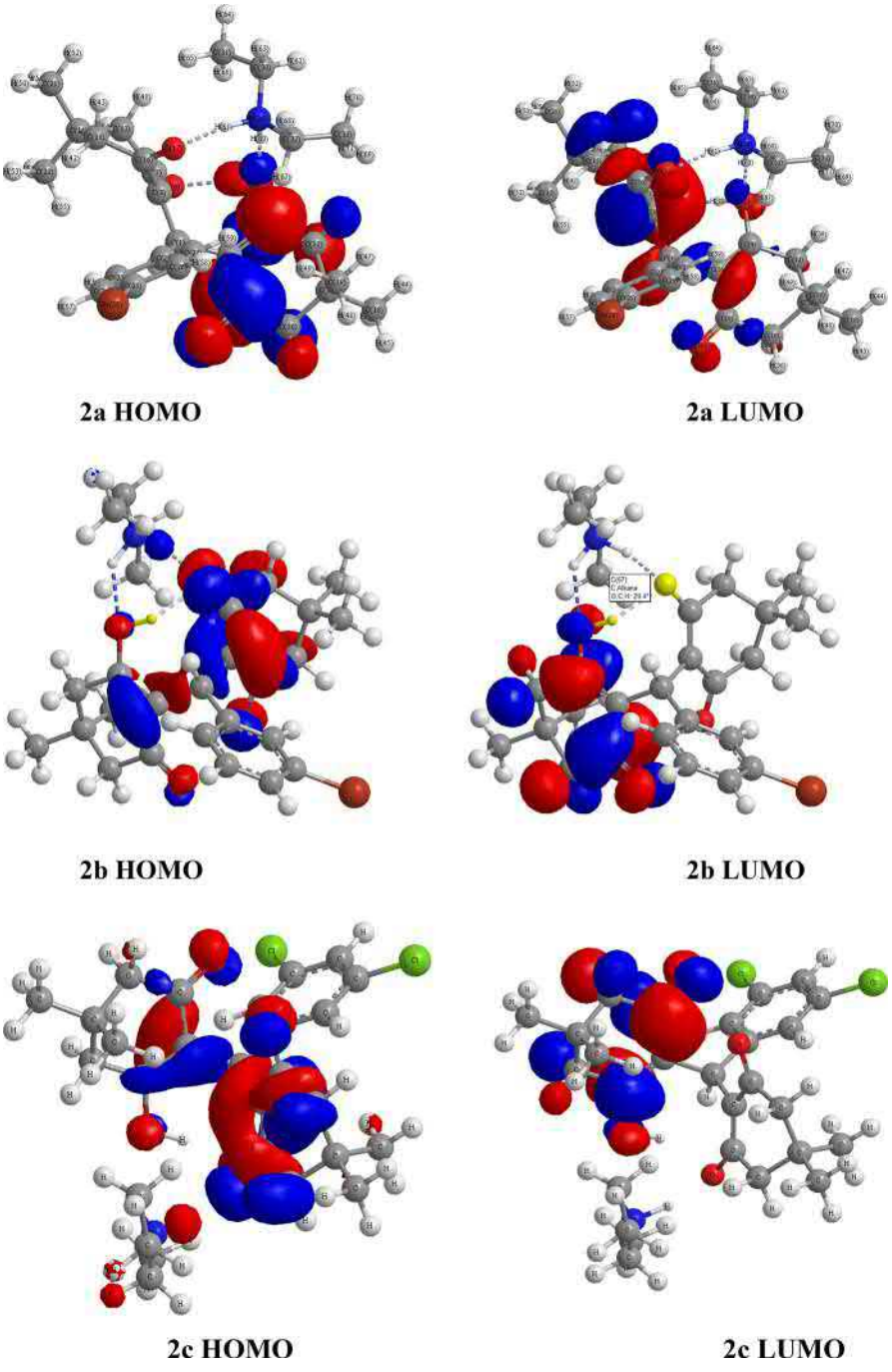



**Fig. 3** HOMO and LUMO for compounds **2a, 2b**, and **2c**

*Thermal gravimetric analysis (TGA)*

Thermal stability of the synthesized compounds was investigated by thermogravimetric analysis (TGA). All the samples were made under nitrogen atmosphere in the temperature ranges between 0 and 800 °C with a heating ramp rate of 10 °C per min (Table 5). It has shown that all the synthesized compounds demonstrated thermal stability up to 200 °C, with a percentage weight loss of 31.45, 22.42, and 16.12 for the compounds **2a**, **2b**, and **2c**, respectively. When the temperature was further raised to 300 °C, dramatic percentage weight loss of up to 98.9, 97.3, and 97.7 for the compounds **2a**, **2b**, and **2c** respectively. Hence, it can be said that the synthetic compounds are thermally stable up to 200 °C, and from there on a rapid degradation occur (Fig. 4).

*Biological activity evaluation*

Compounds **2a–c** were screened in vitro for different bio-assays such as thymidine phosphorylase, urease, and $\beta$-glucuronidase inhibition assays. These compounds

**Table 5** Weight loss of synthesized molecules with temperature

| Temperature | Weight loss (%) | | |
|---|---|---|---|
| | **2a** | **2b** | **2c** |
| 100 | 0.07 | 0.24 | 0 |
| 200 | 31.45 | 22.42 | 16.12 |
| 300 | 98.907 | 97.301 | 97.794 |
| 400 | 99.5205 | 98.977 | 98.17 |
| 500 | 99.8727 | 99.318 | 98.212 |
| 600 | 99.6842 | 99.621 | 98.045 |
| 700 | 99.6564 | 99.4393 | 97.682 |
| 800 | 99.8236 | 99.088 | 97.215 |

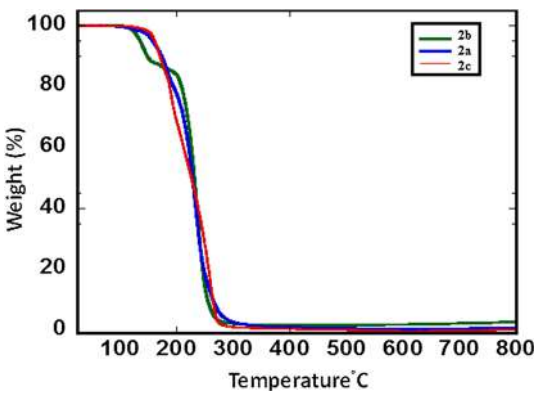



**Fig. 4** The TGA curve of the studied compounds **2a**, **2b** and **2c**

**Table 6** Results of biological activity of the synthesized compounds **2a–c**

| Compounds | Cytotoxicity (PC-3 cell line) | Cytotoxicity (HeLa cell line) | Thymidine phosphorylase inhibition $IC_{50} \pm SEM$ (μM) | Urease inhibition $IC_{50} \pm SEM$ (μM) | β-glucuronidase inhibition $IC_{50} \pm SEM$ (μM) |
|---|---|---|---|---|---|
| **2a** | NA | NA | NA | 154.8 ± 1.33 | 351.6 ± 4.12 |
| **2b** | >30 | >30 | 283.3 ± 0.7 | 75.4 ± 1.46 | NA |
| **2c** | >30 | >30 | 243.3 ± 1.5 | 108.2 ± 1.3 | NA |
| Std. | Doxorubicin 0.912 ± 0.12 | Doxorubicin 0.506 ± 0.15 | 7-Deazaxanthine 41 ± 1.64 | Thiourea 21.2 ± 1.3 | D-Saccharic acid 1-4 lactone 45.75 ± 2.16 |

were also evaluated for their cytotoxic effect against PC-3 and HeLa cell lines. Results are summarized in Table 6.

Compounds **2b, c** showed a varying degree of thymidine phosphorylase inhibition with $IC_{50}$ values 283.3 ± 0.7 and 243.3 ± 1.5 μM, respectively, against the tested standard drug 7-deazaxanthine ($IC_{50} = 41 \pm 1.64$ μM). Compound **2a** found to be inactive (Table 6).

The tested compound **2a–c** ($IC_{50} = 154.8 \pm 1.33$, 75.4 ± 1.46, and 108.2 ± 1.3 μM) showed weak urease inhibition activity against the standard compound thiourea ($IC_{50} = 21.2 \pm 1.3$ μM). Michael adducts **2a–c** were also evaluated for their in vitro $\beta$ -glucuronidase inhibitory potential and compound **2a** ($IC_{50} = 351.6 \pm 4.12$ μM) showed weak inhibition of $\beta$-glucuronidase enzyme in comparison to the standard drug D-saccharic acid 1-4 lactone ($IC_{50} = 45.75 \pm 2.16$ μM). Michael adducts **2b** and **2c** found to be inactive.

Michael adducts **2b–c** were found to be non cytotoxic against of PC-3 normal and HeLa cancer cell lines, and showed >30 % inhibition while compound **2a** was found to be inactive against PC-3 normal and HeLa cancer cell lines (Table 6).

## Conclusions

In the present study, three Michael adducts were synthesized by using a simple, high-yielding, and economical synthetic scheme. The structures were established with the help of physico-chemical properties and single-crystal X-ray diffraction technique. Single-crystal X-ray analysis and DFT calculations revealed that H-bonding plays a crucial role in stability of the molecules. It was observed that all the synthesized compounds demonstrated a thermal stability up to 200 °C. Compounds **2a–c** were also evaluated for their biological activities in various in vitro biological assays.

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RESEARCH ARTICLE

# Virtual Screening Techniques to Probe the Antimalarial Activity of some Traditionally Used Phytochemicals

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**Abstract:** Malaria parasites show resistance to most of the antimalarial drugs and hence developing antimalarials which can act on multitargets rather than a single target will be a promising strategy of drug design. Here we report a new approach by which virtual screening of 292 unique phytochemicals present in 72 traditionally important herbs is used for finding out inhibitors of plasmepsin-2 and falcipain-2 for antimalarial activity against *P. falciparum*. Initial screenings of the selected molecules by Random Forest algorithm model of Weka using the bioassay datasets AID 504850 and AID 2302 screened 120 out of the total 292 phytochemicals to be active against the targets. Toxtree scan cautioned 21 compounds to be either carcinogenic or mutagenic and were thus removed for further analysis. Out of the remaining 99 compounds, only 46 compounds offered drug-likeness as per the 'rule of five' criteria. Out of ten antimalarial drug targets, only two target proteins such as 3BPF and 3PNR of falcipain-2 and 1PFZ and 2BJU of plasmepsin-2 are selected as targets. The potential binding of the selected 46 compounds to the active sites of these four targets was analyzed using MOE software. The docked conformations and the interactions with the binding pocket residues of the target proteins were understood by 'Ligplot' analysis. It has been found that 8 compounds are dual inhibitors of falcipain-2 and plasmepsin-2, with the best binding energies. Compound 117 (6aR, 12aS)-12a-Hydroxy-9-methoxy-2,3-dimethylenedioxy-8-prenylrotenone (Usaratenoid C) present in the plant *Millettia usaramensis* showed maximum molecular docking score.

**Keywords:** Malaria, *Plasmodium falciparum,* virtual screening, weka, ADME, molecular operating environment, molecular docking.

## INTRODUCTION

The spread of malaria is a major health problem, inspite of the various methods adopted to control it. The malady is a key obstruction to social and economic development in areas of Sub-Sahara Africa, Southeast Asia, and Latin America [1, 2]. According to recent reports, approximately 3 billion people are prone to malarial attack [3]. In humans, Malaria is caused by one of the five species of plasmodium parasites out of which *Plasmodium falciparum* (*P. falciparum*) is responsible for the majority of morbidity and mortality. Since *P. falciparum* has developed resistance to many of the clinically available drugs, there is an urgent need to find novel and effective drugs for the cure of malaria. Consequently, a new strategy is essential to find out the availability of effective antimalarials. Plasmodium parasites exhibit a high resistance to most of the newly introduced medicines. This necessitates the development of new antimalarial agents, the resistance of which can subdue the potential of the parasites [4, 5].

To stop the spread of multidrug resistance, the World Health Organization (WHO) recommended Artemisinin-based Combination Therapies (ACTs). But this strategy is now in danger of extinction by the emergence of the parasites with decreased sensitivity and resistance to artemisinin. Hence, the development of antimalarial drugs against new targets is an urgent priority. Consequently, development of novel antimalarial drugs directed against new targets, especially acting on multi-targets, is imperative. Malaria proteases have been subjected to wide and profound study for the development of gorgeous antimalarial drugs.

Computational methods revealed the presence of five major classes of proteases like aspartic, cysteine, metallo, serine and threonine in *P. falciparum* parasite genome [6]. Among these, cysteine (Falcipain-2) and aspartic (plasmepsin-2) proteases bring about the degradation of heamoglobin (Hb). This feature enhances the rate of food assimilation of the parasites resulting in the increase of malarial parasite within the infected red blood cells [7]. Hence the obstruction of falcipain-2 and/or plasmepsin-2 offers a notable measure against the growth of malaria [8].

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Recent reports illustrate that falcipain-2 and plasmepsin-2 can act cooperatively in the hydrolysis of hemoglobin [9-11].

In the lead identification and drug discovery process, natural products occupy the uppermost position. [12-14]. Antimalarial drugs like quinine, isolated from *Cinchona succiruba* and artemisinin from *Artemisia annua*, are some apt examples of natural product derived drugs [15]. Herbal remedies have several potential advantages, as they are readily available and affordable. Currently, *in silico* methods are central to the progress of the development and understanding of the interactions of drugs with the target molecule [16, 17]. It is one of the more efficient ways better than the traditional approval of drug discovery.

But it is difficult to find out an excellent chemical component from the phytoconstituents for the treatment and prevention of malaria using conventional methods. So we have developed computational strategies which include Machine learning (ML), Adsorption Distribution, Metabolism and Excretion (ADME) studies, virtual screening and molecular docking studies to identify potential phytochemicals present in herbs which can effectively bind the selected protein targets. Based on the ML, ADME, RO5 and molecular docking studies, we then identified 8 Lead phytochemical compounds (Fig. **1**).

## MATERIALS AND METHODS

### Ligands Selected for the Study

A thorough survey of literatures revealed the genuineness of 72 herbs especially found in Africa, China and Asia as effective antimalarials. These were considered as the parent plants for our study (Table **1**). The various phytochemicals reported to be present in these herbs were screened and those compounds which are unique were selected (Supplementary Table **2**: Structures of the selected phytochemicals from 72 herbs). The 3D structure drawing and geometry cleaning of the ligands were carried out using ChemDraw. Energy minimization of the compounds was performed using MOE 2007.09 software by applying MMFF94x force field.

### Data Source

The datasets [AID: 504850 and AID: 2302] were downloaded from PubChem Bioassay [18]. Since the inconclusive and unspecified compounds show uncertainty in the biological activity, they were not included in the study. The active and inactive compounds were used for the generation of descriptors using PowerMV [19].

### WEKA

Classification, association and clustering were the methods adopted in Machine Learning approach. For classification and regression, Artificial Neutral Network (ANN), K-Nearest Neighbour (KNN), Radial Basis Function Neutral Network (RBFNN) and Random Forest (RF) were chosen.

In Machine learning approach, artificial intelligence was made use of to predict a set of outcomes. This was achieved by observing the known properties of a dataset, usually known as training set. Random Forest, first described by Leo Breiman [20] is a method based on decision trees, and is considered to be one of the best classfiers [21, 22]. The algorithm implemented in it makes distinction between the active compounds and other molecules based on a set of generated descriptors.

It helps to distinguish the features which are mutually shared by the different subsets of active compounds and accordingly filters out compounds within the target dataset which do not have these features. It is one of the most precise classifiers accessible.

### Prediction of Toxicity

The objective of lead enhancement is to improve the viability of the introductory hit compounds from the screening process. Toxtree v1.60 was utilized to find out compounds which can be carcinogenic and/or mutagenic. For carcinogenicity and mutagenicity prediction Benigni-

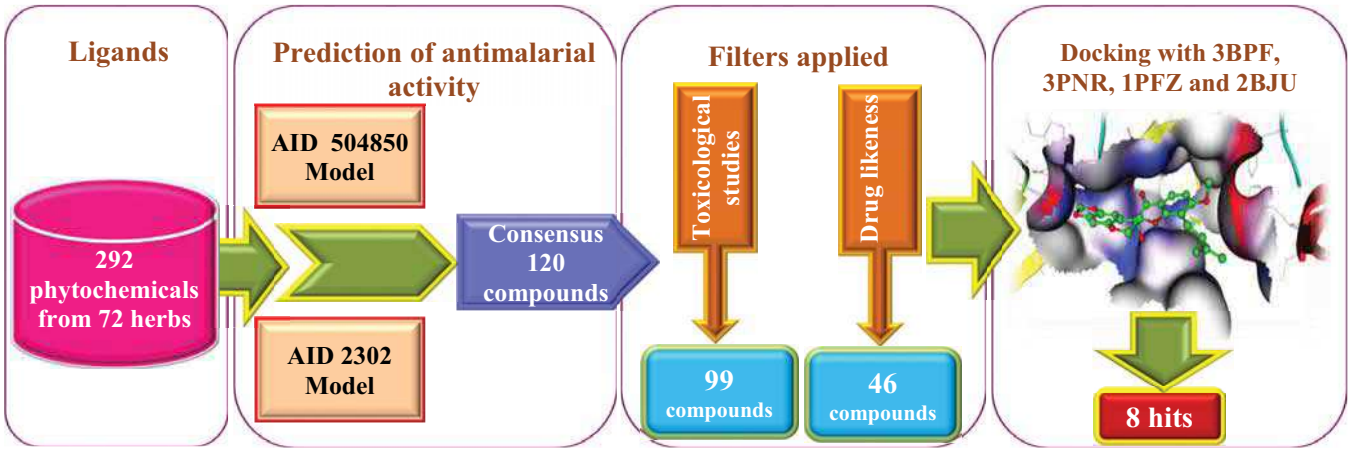


**Fig. (1).** Virtual screening protocol for the identification of novel antimalarial lead compounds.

**Table 1. Details of selected antimalarial herbs.**

| Sl. No | Scientific names of the selected herbs |
|---|---|
| 1 | *Caesalpinia crista* |
| 2 | *Campnosperm apanamense* |
| 3 | *Artocarpus champeden* |
| 4 | *Artocarpusaltilis* |
| 5 | *Erythrina fusca* |
| 6 | *Cannabis sativa* |
| 7 | *Dorstenia barteri var* |
| 8 | *Allanblackia monticola* |
| 9 | *Cratoxylum cochinchinense* |
| 10 | *Symphonia globulifera Linn f* |
| 11 | *Garcinia polyantha Olv* |
| 12 | *Holostylis reniformis* |
| 13 | *Kniphofia foliosa* |
| 14 | *Albizia gummifera* |
| 15 | *Triclisia sacleuxii* |
| 16 | *Polygonum senegalense* |
| 17 | *Erythrina abyssinica* |
| 18 | *Psorospermum glaberrimum* |
| 19 | *Harungana madagascariensis* |
| 20 | *Pycnanthus angolensis* |
| 21 | *Millettia usaramensis* |
| 22 | *Zanthoxylum simulans* |
| 23 | *Artemisia annua* |
| 24 | *Alstonia angustifolia* |
| 25 | *Brucea javanica* |
| 26 | *Simaba guianensis* |
| 27 | *Eurycoma longifolia* |
| 28 | *Quassia indica* |
| 29 | *Achillea millefolium* |
| 30 | *Anthemis nobilis* |
| 31 | *Garcinia cowa* |
| 32 | *Garcinia dulcis* |
| 33 | *Aspidosperma pyrifolium* |
| 34 | *Thalictrum alpinum* |
| 35 | *Berberis valdiviana* |
| 36 | *Hernandia peltata* |
| 37 | *Thalictrum faberi* |
| 38 | *Strychnos species* |
| 39 | *Peschiera fuchsiaefolia* |
| 40 | *Geissospermum sericeum* |
| 41 | *Galipea officinalis* |
| 42 | *Nepenthes thorelii* |
| 43 | *Tabebuia ochraceassp. Neochrysantha* |
| 44 | *Neurolaena lobata* |
| 45 | *Nardostachys chinensis* |
| 46 | *Vernonia brasiliana* |
| 47 | *Betula Utilis* |
| 48 | *Cedrela odorata* |
| 49 | *Hernandia voyronii* |
| 50 | *Sparattanthelium amazonum* |
| 51 | *Duguetia hadrantha* |
| 52 | *Cryptolepis sanguinolenta* |
| 53 | *Strychnos myrtoides* |
| 54 | *Pseudopterogorgia elisabethae* |
| 55 | *Octocoral Muricea austere* |
| 56 | *Pseudopterogorgia bipinnata* |
| 57 | *Ancistrocladus likoko* |
| 58 | *Ancistrocladus korupensis* |
| 59 | *Ancistrocladus tanzaniensis* |
| 60 | *Stephania rotunda* |
| 61 | *Cyclea atjehensis* |
| 62 | *Cyclea barbata* |
| 63 | *Saracha punctata* |
| 64 | *Bauhinia malabarica Roxb* |
| 65 | *Caribbean sponge Plakortissp* |
| 66 | *Plakortis halichondrioides* |
| 67 | *Distephanus angulifolius* |
| 68 | *Ekebergia capensis* |
| 69 | *Chisocheton ceramicus* |
| 70 | *Morinda morindoides* |
| 71 | *Ciocalapata sp* |
| 72 | *Sclerotinia homoeocarpa* |

Bossa rule was used [23]. The structural alerts (SAs) were separated into genotoxic and nongenotoxic, without difference between carcinogenicity and mutagenicity [24]. The list of SAs is available in the literature [25].

## Drug-Likeness Assessment

The selected 99 antimalarial compounds were subjected to Lipinski's rule of five in order to access the drug likeness of the compounds [26]. The “drug-likeness” test was carried out using Lipinski’s RO5. Molecular weight (MW), number of hydrogen bond acceptors (HBA), lipophilicity (log P) and number of hydrogen bond donors (HBD) of the compounds were considered as the basis for accessing the drug-likeness of the selected 99 antimalarial compounds.

## Target Analysis

Falcipain-2 is transcendently communicated in trophozoites, is amassed in food vacuoles and is in charge of

**Table 2. Primary structure characterization for target proteins.**

| PDB ID | pI | Half-life hours | Instability index | Aliphatic | GRAVY |
|---|---|---|---|---|---|
| 1YVB | 5.02 | 0.8 | 42.00 (unstable) | 79.49 | -0.396 |
| 2GHU | 4.95 | 0.8 | 35.83 (stable) | 77.26 | -0.388 |
| 2OUL | 4.95 | 0.8 | 35.83 (stable) | 77.26 | -0.388 |
| **3BPF** | 4.95 | 0.8 | 35.83 (stable) | 77.26 | -0.388 |
| **3PNR** | 4.95 | 30 | 33.59 (stable) | 78.00 | -0.378 |
| 1LF2 | 4.67 | 5.5 | 44.10 (unstable) | 90.03 | -0.062 |
| 1LYB | 5.64 | 30 | 41.33 (unstable) | 75.26 | -0.192 |
| 1ME6 | 4.67 | 1.9 | 44.31 (unstable) | 89.39 | -0.065 |
| **1PFZ** | 5.23 | 30 | 38.48 (stable) | 89.45 | -0.138 |
| **2BJU** | 5.42 | 30 | 37.40 (stable) | 89.43 | -0.164 |

no less than 93% of trophozoite solvent cysteine protease movement. Disturbance of the falcipain-2 quality causes trophozoites to amass undegraded hemoglobin in the parasite nourishment vacuole. 1YVB, 2GHU, 2OUL, 3BPF and 3PNR are retrieved from PDB. Plasmepsin-2 is produced as a zymogen (an inactive precursor), known as proplasmepsin-2. The X-ray crystallography structure of the proteins 1LF2, 1LYB, 1ME6, 1PFZ and 2BJU for Plasmepsin-2 was obtained from PDB which is present in *P. falciparum*.

### Primary and Secondary Structure Prediction

For physiochemical characterization, molecular weight, total number of positive and negative residues, theoretical isoelectric point (pI), instability index, extinction coefficient, aliphatic index and Grand Average Value of Hydropathicity (GRAVY) of the 10 selected proteins for falcipain-2 and plasmepsin-2 inhibitors were computed using the Expasy ProtParam server. Secondary structure prediction was carried out using Self Optimized Prediction Method with Alignment (SOPMA).

### Energy Minimization and Validation

The energy of the protein molecules was minimized using Molecular Operating Environment (MOE 2007.09) tool. The minimized structures were used as template for molecular docking. The Triangle Matcher was used as a placement technique and for rescoring purposes London dG scoring function was utilized. Ramachandran plot was used to check the backbone conformation of the energy minimized protein molecules using MOE 2007.09.

### Molecular Docking

The active site of the receptor molecule was found by using "site finder" module implemented in MOE 2007.09. For selecting one site, the specific site was isolated from the rest of the molecule. MOE docking system with default parameters was utilized to comprehend the binding nature of 46 phytochemicals chosen with the receptor protein. The right conformity of the ligand was understood in order to get least vitality structure. The molecular docking of the selected 46 phytochemicals were performed utilizing the default parameters. After molecular docking, the best pose with good molecular docking score was analyzed for the binding interactions using Ligplot

### ADME Prediction

The molecular properties which describes Adsorption Distribution, Metabolism and Excretion (ADME) were predicted using the online software PreADMET (http://preadmet.bmdrc.org/).

## RESULT AND DISCUSSION

### Model Building Using WEKA

Bioassay datasets AID 504850 and AID 2302 were downloaded from PubChem Bioassay. The bioassay contained compounds in AID: 504850 have the potential to inhibit the malarial parasite Plasmodium. The dataset 504850 contained a total of 2304 compounds. Compounds in AID: 504850 were described taking into account of the 'PubChem Activity Score'. Compounds having an activity score between 40 and 100 were considered as active (1172), all compounds with a score of 0 were inactives (344) and the ones having a score between 1 and 39 were marked as uncertain (788). The assay AID: 2302 uses levels of *P. falciparum* lactate dehydrogenase as surrogate of parasite growth. Inhibition of Dd2 growth by compounds has been determined in this assay. In AID 2302 assay the numbers of compounds tested and identified as actives and in-actives were 7921 and 5461, respectively.

Using PowerMV software, 179 molecular descriptors were computed for each dataset, which included 147 pharmacophore fingerprints, 24 weighted burden number and 8 property descriptors. The active and inactive compounds were merged to create a new file. The data sets were randomized. The datasets were split into 20% test set and 80% training-cum-validation set. Random forest algorithm based on decision trees was used for the present study to screen 292 phytochemicals with both the datasets. The

training set was imported in Weka for classification. Tenfold cross validation was utilized for training the dataset.

For AID 504850, the specificity and sensitivity of the built model were 72.4% and 66.3%, respectively. The true positive (TP) rate and false positive (FP) rate of the model were respectively predicted as 76.5% and 66.3%. The overall accuracy (Q) of the model was found to be 76.49%, which depicts that the results are accurate. ROC area was 72.5%.

For AID 2302, the specificity and sensitivity of the built model were 72.4% and 72%, respectively. The true positive (TP) rate and false positive (FP) rate of the model were respectively predicted as 72.4% and 34.4%. The overall accuracy (Q) of the model was found to be 72.37%, which depicts that the results are accurate. ROC area was 77%.

The AID 504850 and AID 2302 models predicted 246 compounds and 147 compounds respectively as potentially active anti-malarias. Of these molecules, a total of 120 compounds were predicted potential actives by both the models based on molecular descriptors and were considered for further analysis.

### Toxtree

The toxic properties were checked using Toxtree. For carcinogenicity and mutagenicity, 35 SAs were obtained based on Benigni/Bossa rule. By analyzing the result, it was found that out of 120 phytochemicals selected from data mining, 21 compounds were found to be carcinogenic or mutagenic. Thus, finally 99 compounds were selected for further studies.

### Rule of Five (Ro5) Analysis

Lipinski's criteria, generally referred to as the "Rule of Five" (ro5), have been utilized as a part of the assessment of presumable oral accessibility of the compounds selected. Thus, the drug-likeness of selected phytochemical compounds was accessed by calculating the Lipinski's ro5descriptors. Out of 99 compounds, over 46 of the compounds satisfied all RO5 criteria. Thus selected 46 compounds were used for further studies.

## MOLECULAR DOCKING

### Primary and Secondary Structure Prediction

Primary structure prediction of the selected proteins 1YVB, 2GHU, 2OUL, 3BPF, 3PNR of falcipain-2 and proteins 1LF2, 1LYB, 1ME6, 1PFZ, 2BJU of plasmepsin-2 show that except for proteins 1YVB, 1LF2, 1LYB and 1ME6, all other target molecules have high structural stability, which was supported by instability index less than 40 (Table **2**). The high thermodynamic stability of the preferred protein molecules was confirmed by the aliphatic index value which varies from 75 to 90.

All the chosen target molecules showed negative values for GRAVY which supports the hydrophilic nature of these proteins. Out of these 10 proteins, we selected 3BPF, 3PNR, 1PFZ and 2BJU proteins as they showed higher half-life period, lower instability index below 40 and good aliphatic index. The secondary structure of a protein gives information about the amino acids present in helix, strand or coil.

It was predicted that in protein 3BPF, 24.07% were α helices, 18.67% were extended strand, 6.64% were β turns and 50.62% were random coils. In protein 3PNR, 26.25% were α helices, 18.75% were extended strand, 9.17% were β turns and 45.83% were random coils. In protein 1PFZ, 17.37% were α helices, 31.58% were extended strand, 6.32% were β turns and 44.74% were random coils. In protein 2BJU, 20.09% were α helices, 33.33% were extended strand, 4.86% were β turns and 41.72% were random coils.

### Secondary Structure Prediction of the Proteins

3BPF, 3PNR, 1PFZ and 2BJU using SOPMA show low percentage of β turn and high percentage of α helix which confirms the structural stability.

### Validation

The quality of the proteins 3BPF, 3PNR, 1PFZ and 2BJU was evaluated using Ramachandran plot obtained from MOE 2007.09 (Fig. **2**). The 3D structures of the proteins are shown in Fig. **3**. The output of the result showed that the protein 3BPF has two outlier amino acids Ser108 and Lys59.

The number of residues in the core, allowed and outlier region was 89.66%, 9.48% and 0.86%, respectively. 3PNR also had two outlier aminoacids Tyr22 and Ser108. The number of residues in the core, allowed and outlier region was 91.17%, 7.98% and 0.84%, respectively. 1PFZ protein had no outlier amino acids. The number of residues in the core and allowed region was 95.36% and 4.64%, respectively. 2BJU protein showed one outlier amino acid Ser2. The number of residues in the core, allowed and outlier region was 92.35%, 7.33% and 0.30%, respectively. Thus, the protein molecules of Falcipain-2 and Plasmepsin-2 have good quality for molecular docking analysis.

### Molecular Docking

In order to find out binding interactions of the selected 46 ligands, molecular docking studies were carried out using MOE-dock with most of the default parameters. For each ligand, 30 conformations were generated. The top ranked conformation of each ligand was used for detailed study of binding mode. The docked conformation of compounds exposed that they interacted with the binding site of the target proteins through interactions like sidechain and backbone hydrogen bonding, polar and weak van der Waals interactions.

### Ligand-target interactions

The molecular docking results of the selected phytochemicals into the protein molecules are represented in Table **3**. In 3BPF and 1PFZ protein, four chains A, B, C and D were present. For docking studies, we selected chain A. In protein 2BJU and 3PNR, only chain A was present. So it was selected for the molecular docking.

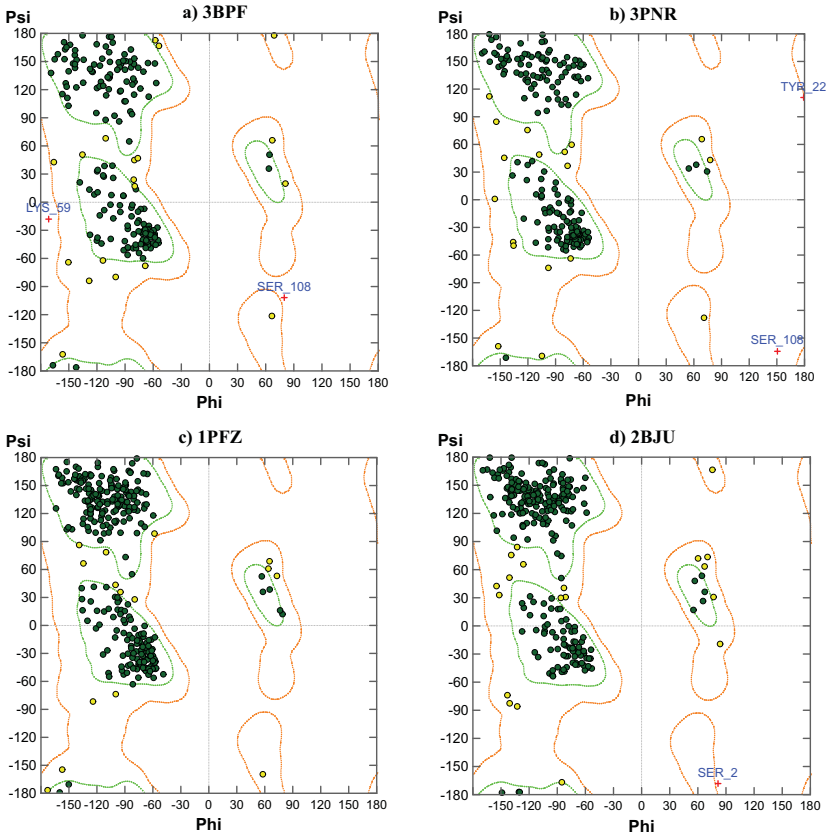


**Fig. (2).** Ramachandran Plot of the proteins (**a**) 3BPF; (**b**) 3PNR; (**c**) 1PFZ and (**d**) 2BJU after energy and residue optimization.

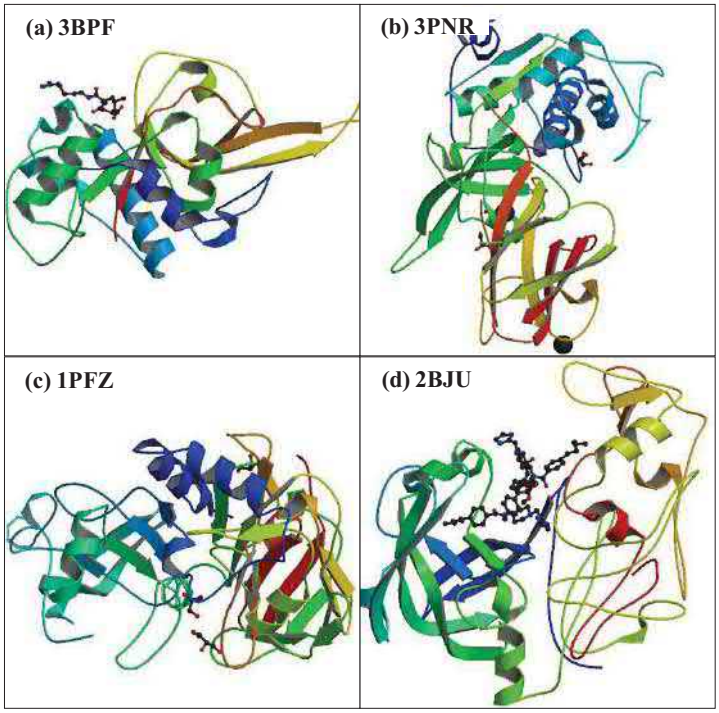


**Fig. (3).** 3D structure of the proteins (**a**) 3BPF; (**b**) 3PNR; (**c**) 1PFZ and (**d**) 2BJU.

## Binding Interactions of the Ligands with Protein 1PFZ

The binding modes of compounds were analyzed using MOE 2007.09. The active site of the protein 1PFZ are Thr31 Pro32 Val33 Lys34 Ala42 Phe45 Ser46 Gly49 Glu52 Glu67 Ala175 Val176 Met177 Lys203 Asn204 and Ser205.

The 2D and molecular docking pose of the 8 active compounds with the protein 1PFZ are shown in Fig. **4** and

**Table 3. Docking results of selected phytochemicals into the protein molecules using MOE.**

| Compounds | 3BPF (kcal/mole) | 3PNR (kcal/mole) | 1PFZ (kcal/mole) | 2BJU (kcal/mole) | 1LYB (kcal/mole) |
|---|---|---|---|---|---|
| 86 | -11.8514 | -11.9314 | -13.4654 | -11.9459 | -10.9471 |
| 91 | -12.3248 | -12.9719 | -13.1297 | -12.8768 | -12.0978 |
| 109 | -13.2418 | -11.5913 | -13.3854 | -11.9399 | -12.0894 |
| 110 | -10.1978 | -11.4718 | -13.8708 | -11.3379 | -9.7255 |
| 114 | -10.2059 | -11.4195 | -13.6768 | -11.0904 | -10.9509 |
| 117 | -9.7797 | -12.1637 | -14.0148 | -12.8001 | -10.0102 |
| 210 | -11.1213 | -12.2491 | -13.1906 | -11.2783 | -9.6652 |
| 239 | -11.0207 | -12.9072 | -11.7203 | -14.7910 | -11.3817 |

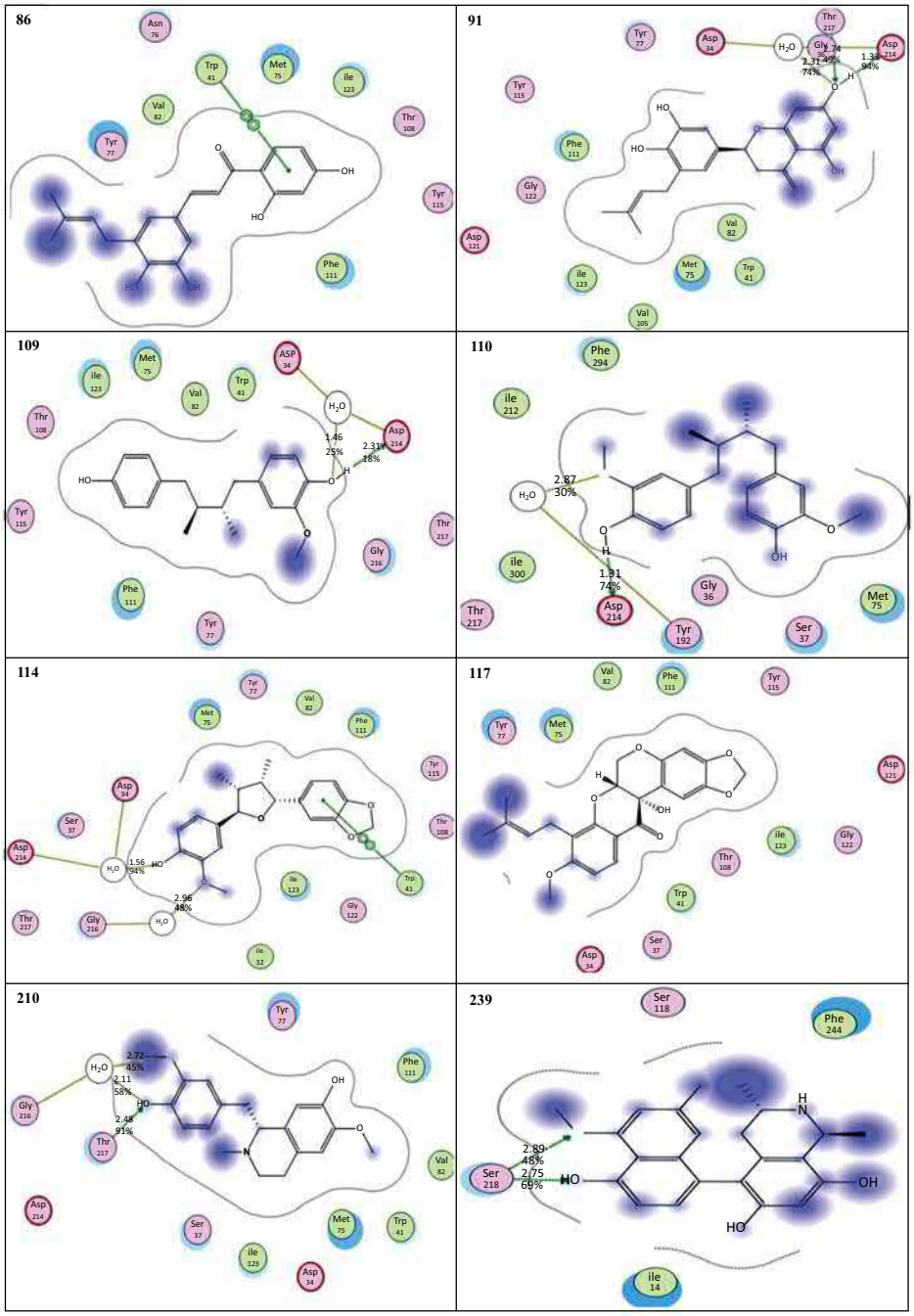


**Fig. (4).** 2D interaction graph of the active compounds with 1PFZ.

Fig. **5**. Compound 86 formed backbone hydrogen bonding interaction between polar residue Leu33 and two hydroxyl groups (1.49 Å; 2.69 Å). Both the interactions had very low bond strength (23%; 11%). One of the hydroxyl groups formed indirect hydrogen bonding interactions with amino acids Thr35, Asp34 and Asp214 through bridged water molecule. The hydroxyl group attached to the phenol ring formed backbone hydrogen bonding interaction with Val9 (1.6 Å) with moderate bond strength (61%). The methylbutene group has high solvent exposure. The hydroxyl group also showed high solvent exposure and it is also indirectly interacted with the acidic residue Glu87. It showed a molecular docking score of -13.4654 kcal/mole. The binding mode observed for the compound 91 showed that both the hydroxyl groups attached to the dihydrochromenone ring showed sidechain hydrogen bonding interactions with residues Gln12 (1.6 Å, 20%) and Asp34 (1.36 Å, 51%), respectively. One of the hydroxyl groups attached to the dihydrochromenone ring showed indirect hydrogen bonding interactions with residues Thr35 and Asp214. The hydroxyl group attached to the methylbutenylphenol ring formed backbone hydrogen bonding interaction with the residue Val9 (1.37 Å, 35%). The proximity contour showed that the molecule was very closely hemmed-in by the active site. The molecular docking score was found to be -13.1297 kcal/mole. Molecular docking of compound l09 with molecular docking score -13.3854 kcal/mole showed a backbone hydrogen bonding interaction between the hydroxyl group of the benzene ring and Gly36 (1.68Å, 32%). The hydroxyl group attached to the methoxy benzene ring showed a sidechain hydrogen bonding interaction with Gln12 (1.41Å, 15%). It also showed indirect hydrogen bonding interactions with the residues Gln12, Asp214 and Thr35 through bridging water molecules. The methoxy group also showed indirect hydrogen bonding interaction with the alike residues Gln12, Asp214 and Thr35. The proximity contour showed that the phenol ring was very closely hemmed-in by the active site. In case of compound 110, a large number of interactions were present. It was observed that the hydroxyl group attached to the methoxy benzene ring showed both backbone hydrogen bonding interaction with Leu33 (1.43 Å, 50%) and indirect interaction with the residues Leu33 and Met15. The methoxy group showed indirect hydrogen bonding interaction with residues Asp234, Gln12 and Thr35. The hydroxyl group attached to the other end of the molecule showed sidechain hydrogen bonding interaction with the acidic residue Glu87 (1.63 Å, 85%). The methoxy group also showed an indirect interaction with the same residue Asp87. The molecular docking score of the compound 23 was - 13.8708 kcal/mole. The binding mode observed for compound 114 showed a molecular docking score -13.6768 kcal/mole. The oxygen atom attached to the benzodioxole ring showed indirect interaction with the residues Gln12 and Asp214. The methoxygroup attached to the phenol ring showed interaction with Asn13 through bridged water molecule. One side of the molecule was very closely hemmed-in by the active site which was indicated by the proxy contour while the other side had very high solvent accessible surface area.

From the molecular docking analysis, it is clear that amino acids Asp214, Gln12, Asp34, Thr35, etc interact effectively with the compound 117.

A sidechain hydrogen bonding interaction was observed between the oxygen atom of the benzodioxo ring and Thr35 (2.9 Å, 42%). Both the oxygen atoms of the benzodioxole ring showed hydrogen bonding interactions with the residues Thr35, Trp193, Asp214 and Gln12 through the bridging water molecules. The hydroxyl group showed sidechain hydrogen bonding interaction with the residue Gln12 (1.94 Å, 37%). The molecular docking score observed was -14.0148 kcal/mole. The binding mode observed for compound 210 showed that it binds within the binding pocket with a molecular docking score -13.1906 kcal/mole. The hydroxyl group attached to the methoxy benzene ring showed both back bone hydrogen bonding interaction with Thr35 (2.75 Å, 85%) and sidechain hydrogen bonding interaction with Asp234 (1.44 Å, 75%). Both the hydroxyl and methoxy groups show hydrogen bonding interactions with the residues Asp234, Thr35 and Asn13. The methylpiperidine ring had solvent accessible surface area. The binding mode observed for the compound 239 showed that both the hydroxyl groups attached to the dimethyl tetrahydroisoquinoline ring showed hydrogen bonding interactions with the residues Gln12, Asn13, Asp34, Asp234 and Thr35. Both the alkyl groups of this ring have solvent accessible surface area. The molecule bonds within the binding pocket with a molecular docking score -11.7203 kcal/mole.

**Binding Interactions of the Ligands with Protein 2BJU**

The binding modes of compounds were analyzed using MOE 2007.09. The active site of the protein 2BJU in chain A are Ile 14, Met 15, Ile 32, Asp 34, Met 75, Tyr 77, Phe 111, Tyr 115, Ser 118, Asp 121, Tyr 192, Asp 214, Gly 216, Thr 217 and Ile 300.

The 2D interactions of the 8 active compounds with the protein 2BJU are shown in the Fig. **6** and Fig. **7**. The binding mode observed for compound 86 showed that it binds within the binding pocket with a molecular docking score -11.9459 kcal/mole. An arene-arene interaction was observed between the benzene ring and polar amino acid Trp41. Hydrophobic interactions were observed between benzene-1,3-diol ring and the sandwich of the backbone atoms of Met75, Ile123, Thr108, Tyr115 and Phe111. The proximity contour showed that the molecule was very closely hemmed in by the active site. Compound 91 forms sidechain acceptor interaction between polar Gly36 and –OH group attached to the dihydrochromenone ring. Dihydrochromenone ring showed hydrophobic interactions with residues Gly36, Thr217 and acidic Asp214. The OH group attached to the dihydrochromenone ring forms sidechain donor interaction with acidic amino acid Asp214 (1.33 Å). The polar bond has very high bond strength (94%). It also forms indirect H-bonding interactions with residue Asp34 through bridged water molecule. The molecular docking top ranking score was -12.8768 kcal/mole. The (methylbutenyl) benzenediol ring formed hydrophobic interactions with the residues Tyr77, Phe111, Gly122, Asp121, Ile123, Val105, Met75, Trp41 and Val82. The binding mode observed for the compound 109 showed that the phenol ring is located in a hydrophobic pocket surrounded by Val82, Met75, Ile123, Thr108, Tyr112, Phe111 and Tyr77. The molecular docking interaction of compound 109 showed sidechain donor

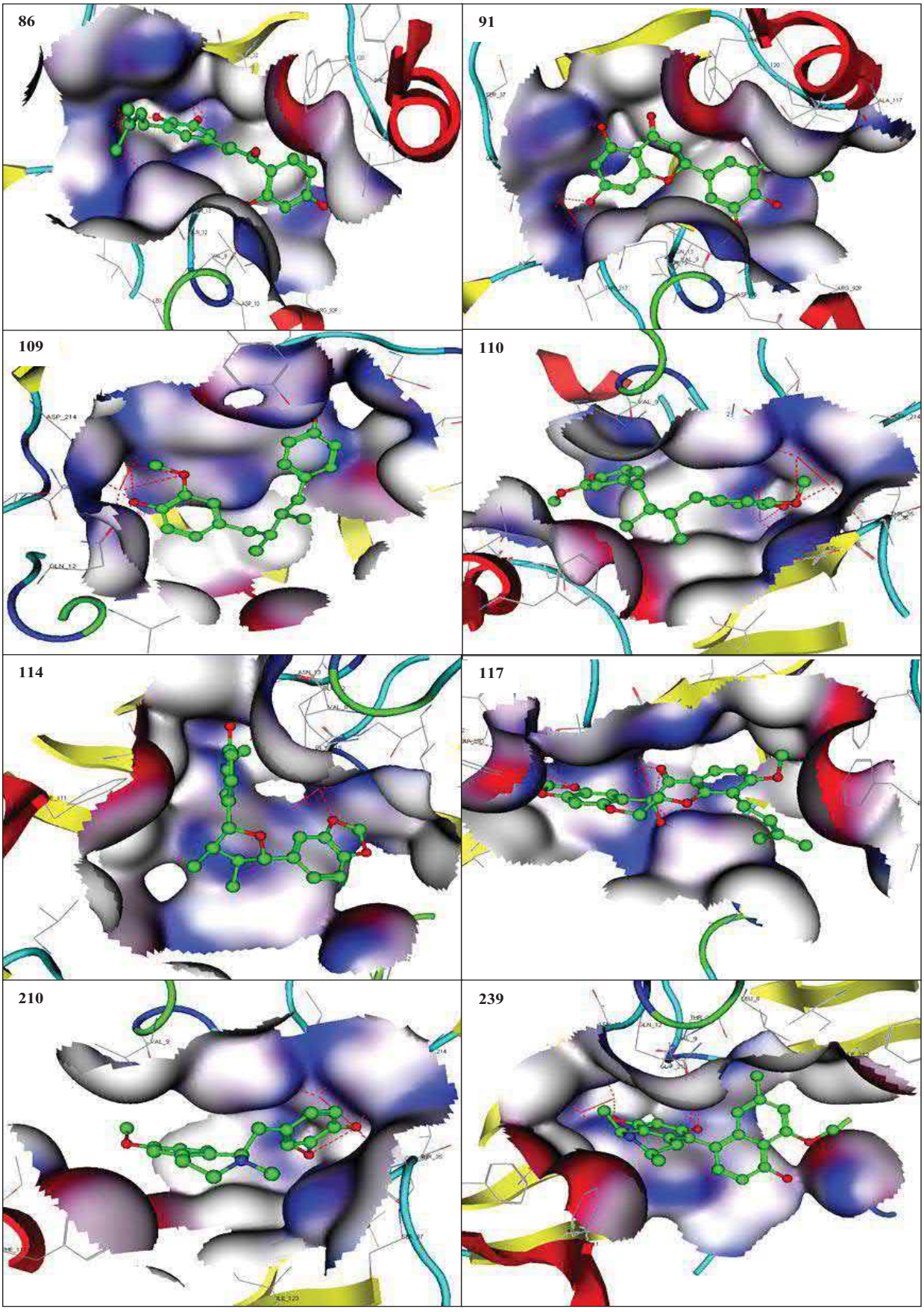


**Fig. (5).** Molecular docking pose of the active compounds with protein 1PFZ.

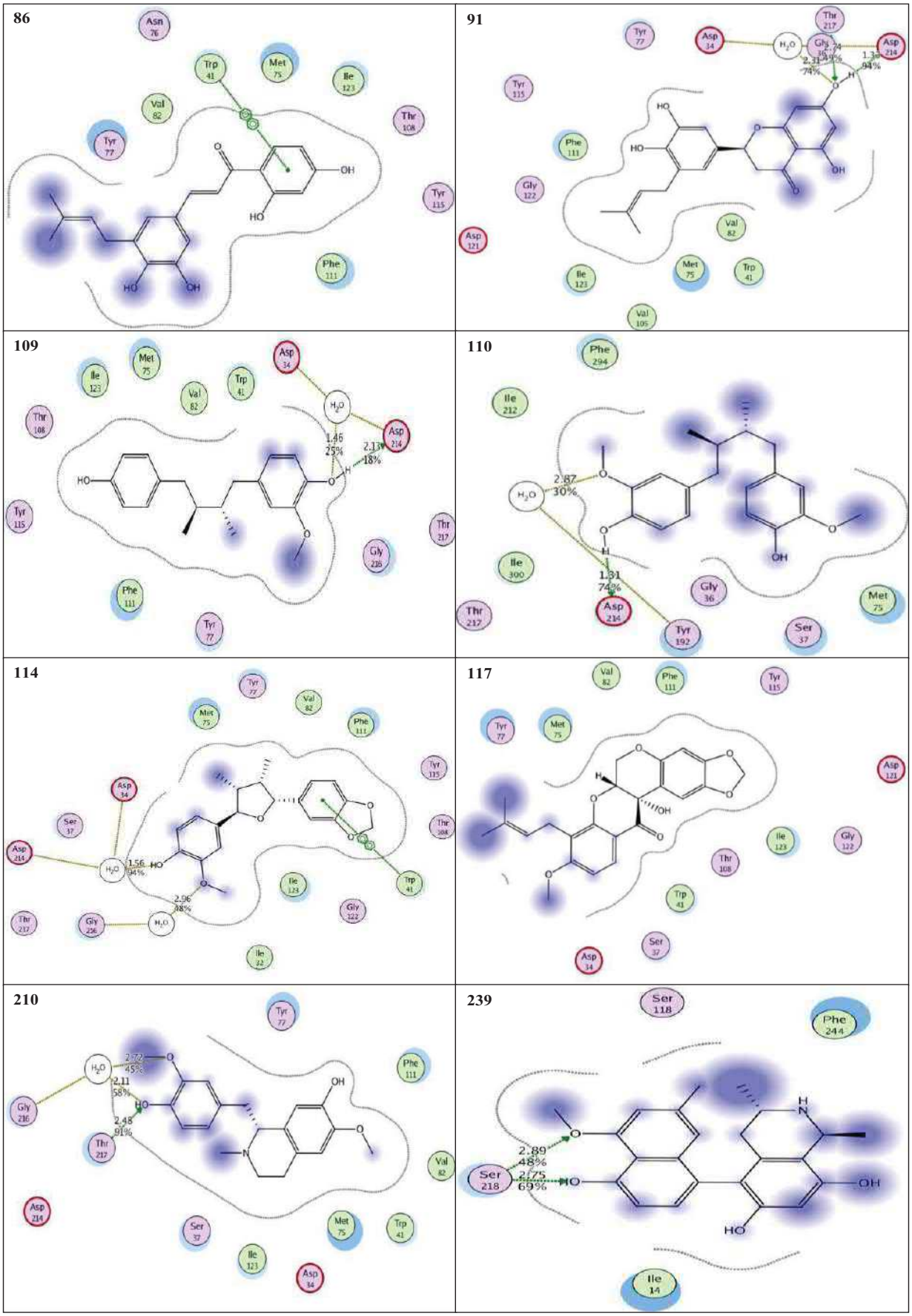


**Fig. (6).** 2D interaction graph of the active compounds with 2BJU.

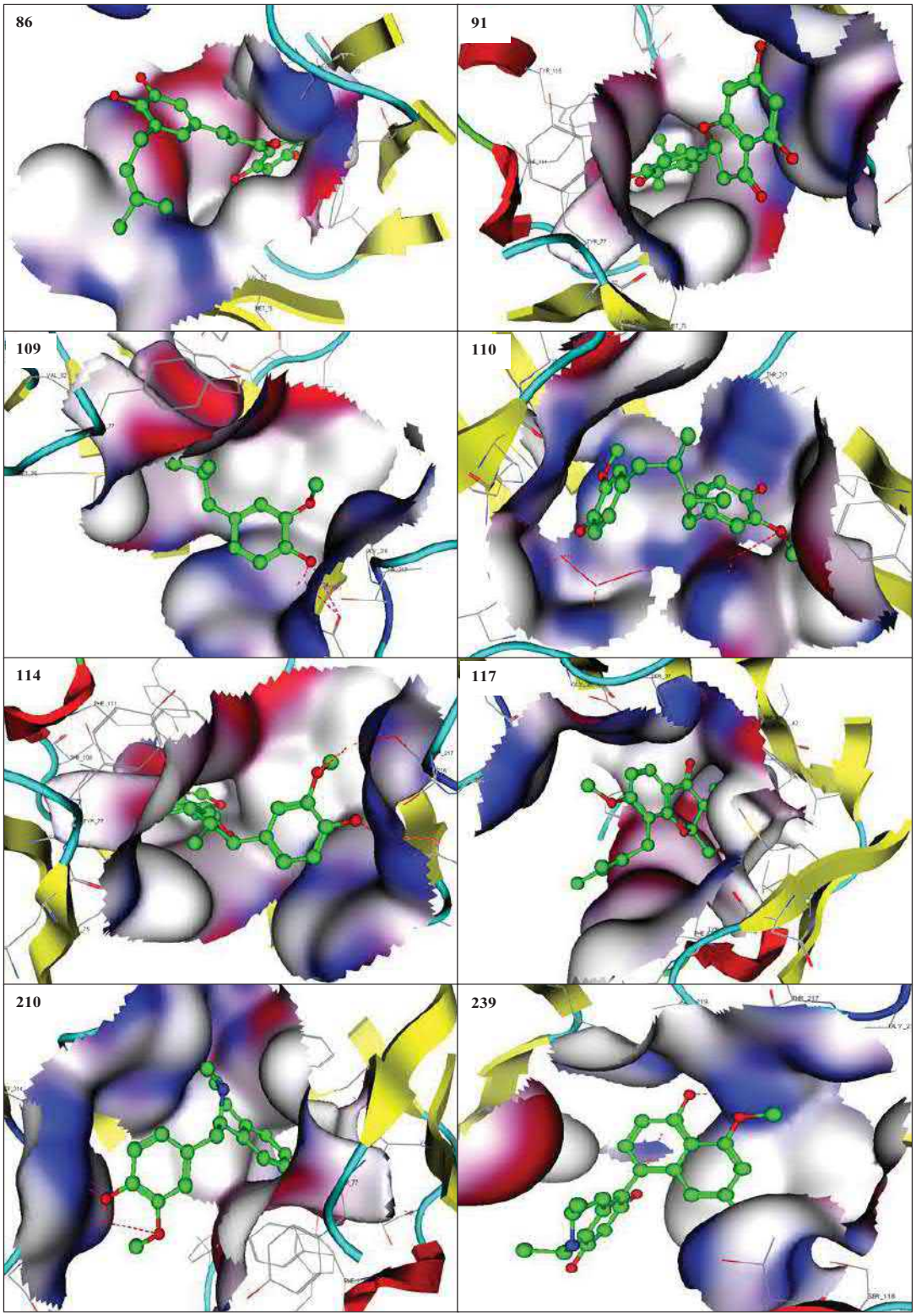


**Fig. (7).** Molecular docking pose of the active compounds with protein 2BJU.

interaction with the –OH group attached to the methoxybenzene ring and acidic Asp214 (2.13 Å) with very low bond strength 18%. The proximity contour showed that the molecule is very closely hemmed-in by the active site. The molecular docking score is found to be -11.9399 kcal/mole. Molecular docking of compound l10 with molecular docking score -11.3379 kcal/mole showed an acidic sidechain donor interaction between O atom of the hydroxyl group attached to the methoxybenzene ring (1.31Å, 74%). The methoxy group attached to the benzene ring showed an indirect H-bonding interaction with the residue Tyr192. Both methoxyphenol ring show hydrophobic

interactions with residues Ile212, Ile300, Thr217, Asp214, Tyr192, Gly36, Ser37 and Met75. In case of compound 114, a large number of interactions were present. It was observed that the benzene ring of the benzodioxole ring formed an arene-arene interaction with polar residue Trp41. Hydrophobic interactions between benzodioxole ring and Val82, Phe111, Tyr115, Thr108, Trp41, Gly122, Ile123 as well as the methoxyphenol ring with Asp34, Ser37, Asp214, Thr217 and Gly216 appeared to constrain the molecule in close proximity with the amino acids. The –OH group attached to the methoxy benzene ring showed an indirect H-bonding interaction with the acidic residues Asp34 and Asp214. The O atom of the methoxy group attached to the benzene ring also showed an indirect interaction through the bridged water molecule with the polar residue Gly216. The proximity contour showed that the compound 23 was very closely hemmed-in by the active site. The molecular docking score of the compound 23 was -11.0904 kcal/mole.

No prominent interactions were observed in compound 117 at the active site of the target protein 2BJU. The molecular docking score of the compound 23 is -12.8001 kcal/mole. The binding mode observed for compound 210 showed that most of the interactions present were concentrated on the methoxyphenol ring with a molecular docking score -11.2783 kcal/mole. A sidechain acceptor interaction was observed between polar Thr217 and hydroxyl group of the compound 117 (2.48 Å) with very high bond strength 91%. The proximity contour showed that the methoxy methyl tetrahydroisoquinolinol group was very closely hemmed in by the active site.

Molecular docking results reveals that Ser218 is the residue that make compound 239 a potent inhibitor. Both the hydroxyl and methoxy group attached to the naphthalene ring showed sidechain acceptor interactions with the polar residue Ser218 (2.75 Å, 69%, 2.89 Å, 48%). The molecular docking score observed was -14.7910 kcal/mole.

### Binding Interactions of the Ligands with Protein 3BPF

The binding modes of compounds were analyzed using MOE 2007.09. The active site of the protein 3BPF in chain A are Gln 36, Gly 40, Ser 41, Cys 42, Trp 43, Tyr 78, Asn 81, Gly 82, Gly 83, Leu 84, His 174, Ala 175 and Gln 209.

The 2D interactions of the 8 active compounds with the protein 3BPF are shown in the Fig. **8** and Fig. **9**. The binding mode observed for compound 86 showed that it binds within the binding pocket with a molecular docking score -11.8514 kcal/mole. The hydroxyl group attached to phenol moiety formed backbone hydrogen bonding interaction with polar residue Leu172 (1.51 Å), with moderate bond strength (48%). No prominent interactions were present in compound 91 with the protein 3BPF. The molecular docking score of the compound was found to be -12.3248 kcal/mole. Compound 109 forms bidirectional hydrogen bond interaction between polar residue Asn86 and hydroxyl group (2.51 Å, 38%; 3.36 Å, 16%). Ile85 had a backbone hydrogen bonding interaction to the connected methoxy group. The molecular docking top ranking score is -13.2418 kcal/mole. The binding mode observed for the compound 110 showed that the hydroxyl group showed sidechain hydrogen bonding interaction with the polar Ser130 residue with very high bond strength (2.51 Å, 99%). The molecular docking score was found to be -10.1978 kcal/mole. Molecular docking of compound 114 with molecular docking score -10.2059 kcal/mole showed a sidechain hydrogen bonding interaction between hydroxyl group and polar Asn86 (1.68Å, 36%). Compound 117 had no hydrogen bonding interactions with the protein, but it was buried quite deep with the protein 3BPF. The molecular docking score of the compound was -9.7797 kcal/mole In case of compound 210, it was observed that the hydroxyl group formed sidechain H-bonding interactions with residueLeu172 (1.71Å, 46%). The molecular docking score of the compound 210 was -11.1213 kcal/mole. Compound 239 has no hydrogen bonding interactions with the protein 3BPF. The molecular docking score is found to be - 11.0207 kcal/mole.

### Binding Interactions of the Ligands with Protein 3PNR

The binding modes of compounds were analyzed using MOE 2007.09. The active site of the protein 3PNR are Ala151 Gly169 Asp170 Gln171 Cys229 and Gly230.

The 2D interactions of the 8 active compounds with the protein 3PNR are shown in the Fig. **10** and Fig. **11**. Compound 86 formed sidechain hydrogen bonding interaction with acidic Asp234 and hydroxyl group (1.22 Å). The polar bond had moderate bond strength (54%). The hydroxyl group attached to the (methylbutenyl) phenol ring formed indirect hydrogen bonding interactions with the residues His174 and Gln36 through bridged water molecules. The molecular docking top ranking score was -11.9314 kcal/mole. The binding mode observed for the compound 91 showed that the carbonyl group showed a sidechain hydrogen bonding interaction with the residue Gln36 (2.53 Å, 30%). The hydroxyl group showed a back bone hydrogen bonding interaction with amino acid Asn81. This molecule showed good solvent exposure. The molecular docking score was -12.9719 kcal/mole. Molecular docking of compound l09 with docking score -11.5913 kcal/mole showed a sidechain hydrogen bonding interaction between hydroxyl group and His174 (2.95Å, 14%). The hydroxyl group attached to the other end also showed a sidechain hydrogen bonding interaction with acidic residue Asp234 (1.27), with low bond strength (39%). The molecule had solvent accessible surface area. In case of compound 110, it was observed that the two oxygen atoms of methoxyphenol ring formed H-bond interactions with residues Gln36 and His174 through bridged water molecule. The hydroxyl group formed backbone hydrogen bonding interaction with the residue Gly4 (1.82 Å, 39%). The hydroxyl group attached to the other end of the molecule formed a sidechain hydrogen bonding interaction with the acidic residue Asp234 (1.28 Å, 86%). The molecule had high solvent accessible surface area. The molecular docking score of the compound 110 was found to be -11.4718 kcal/mole. The binding mode observed for compound 114 showed a molecular docking score -11.4195 kcal/mole. The hydroxyl group of the molecule formed a sidechain hydrogen bonding interaction with the residue Asn86 (1.53 Å, 49%). The oxygen atom of the dimethyl tetrahydrofuran ring formed hydrogen bonding interaction with Asp234 through bridged water molecule. The methyl groups had high solvent accessible surface area. The binding mode observed for compound 117 showed that

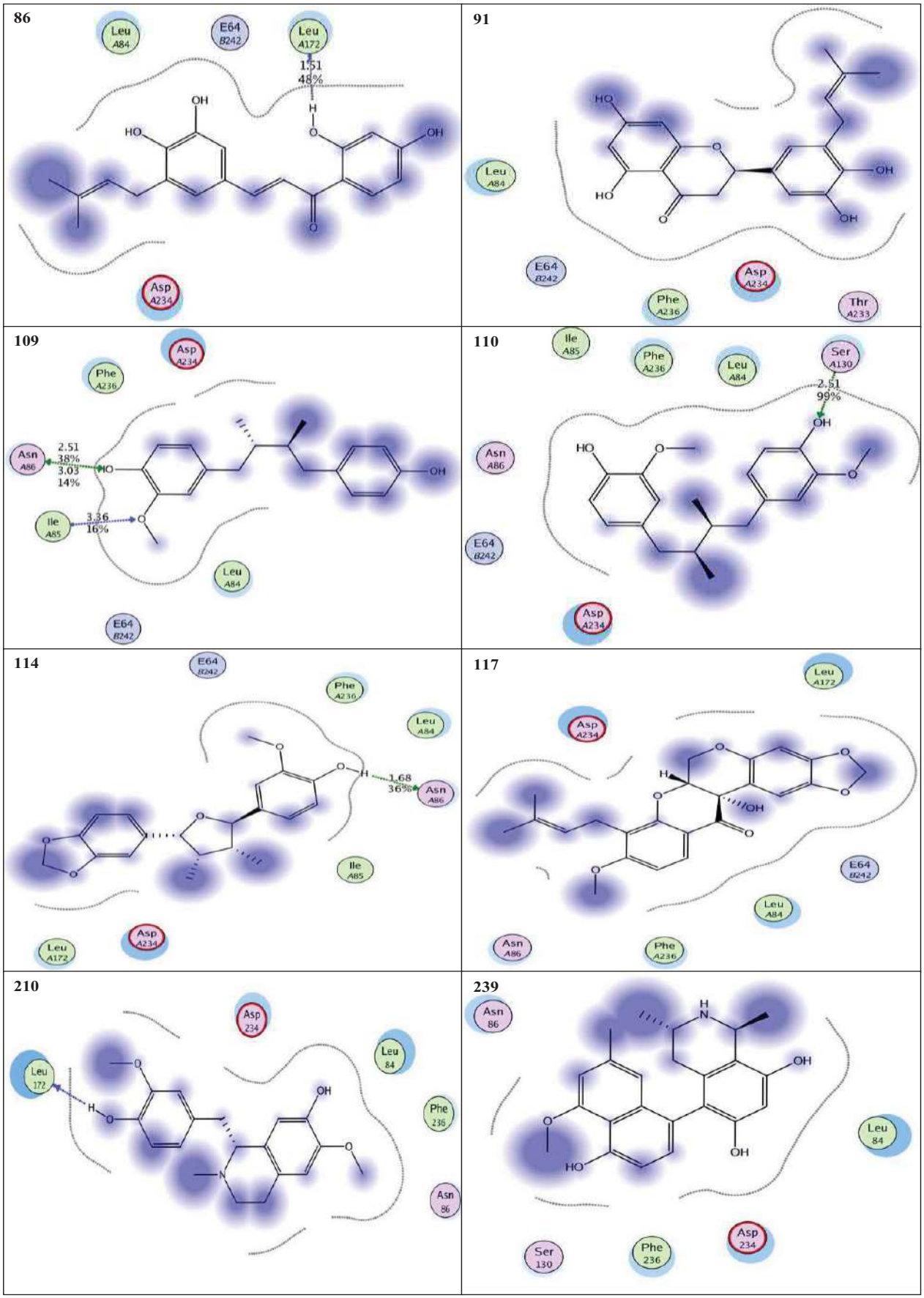


**Fig. (8).** 2D interaction graph of the active compounds with 3BPF.

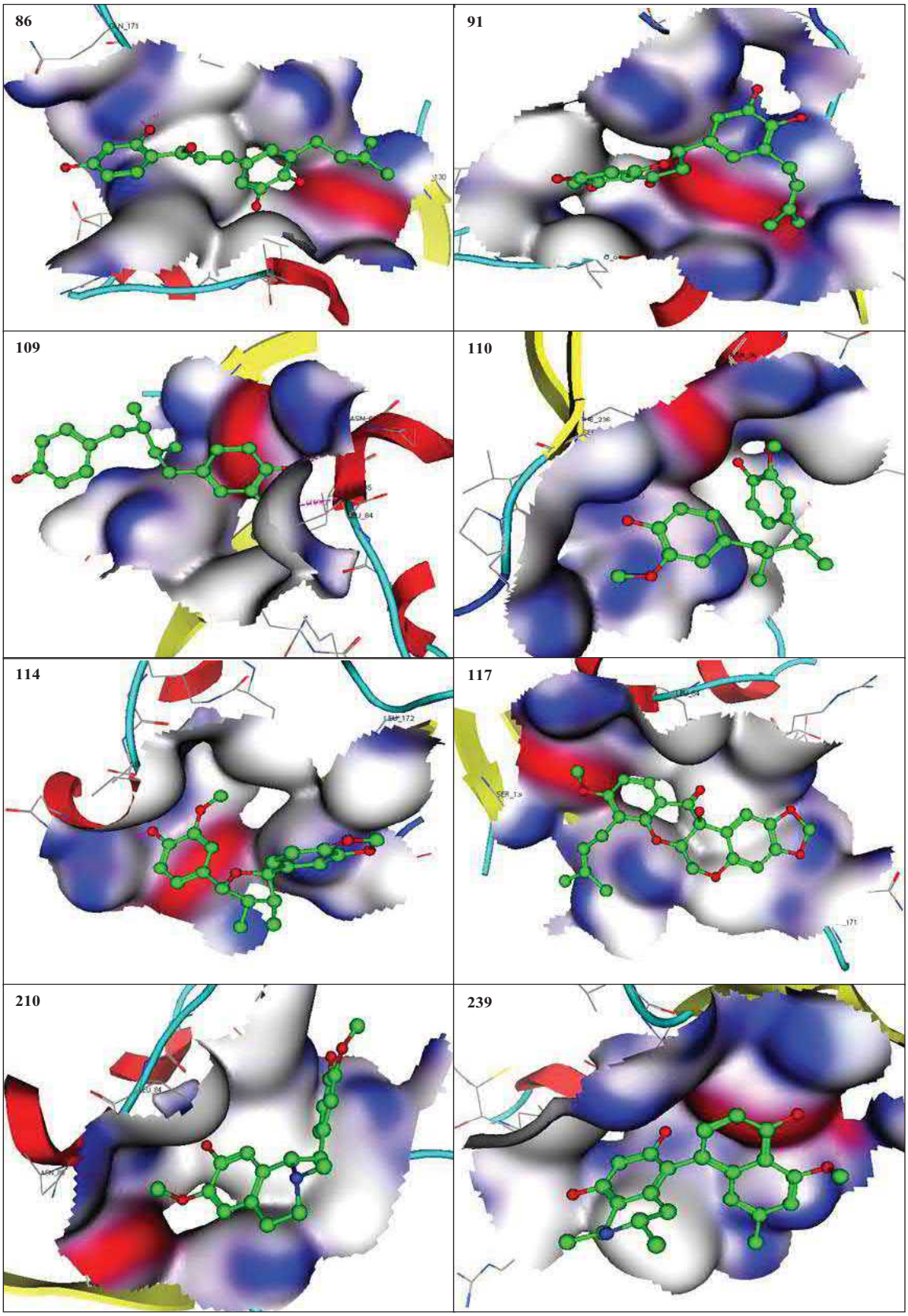


**Fig. (9).** Molecular docking pose of the active compounds with protein 3BPF.

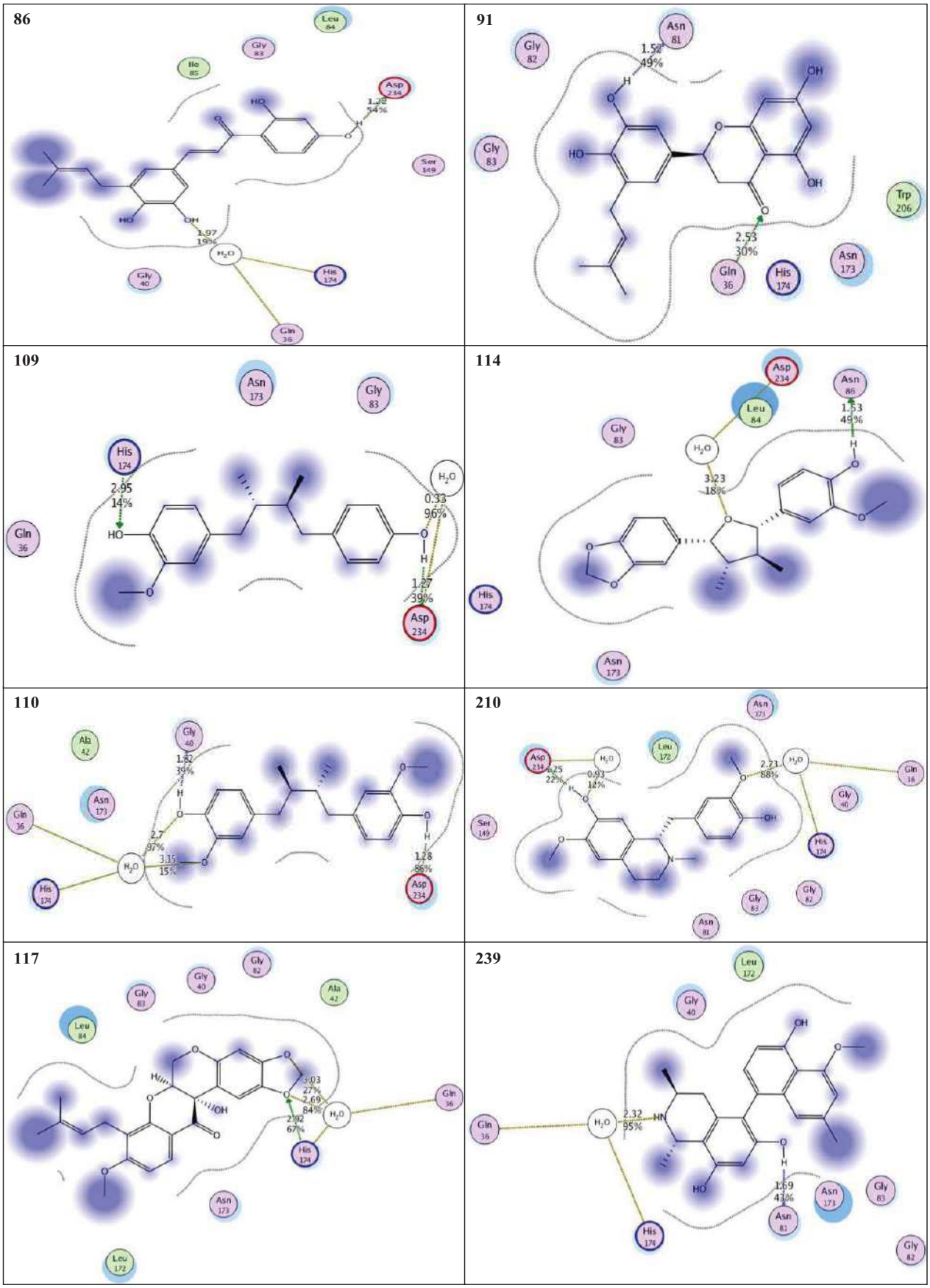


**Fig. (10).** 2D interaction graph of the active compounds with 3PNR.

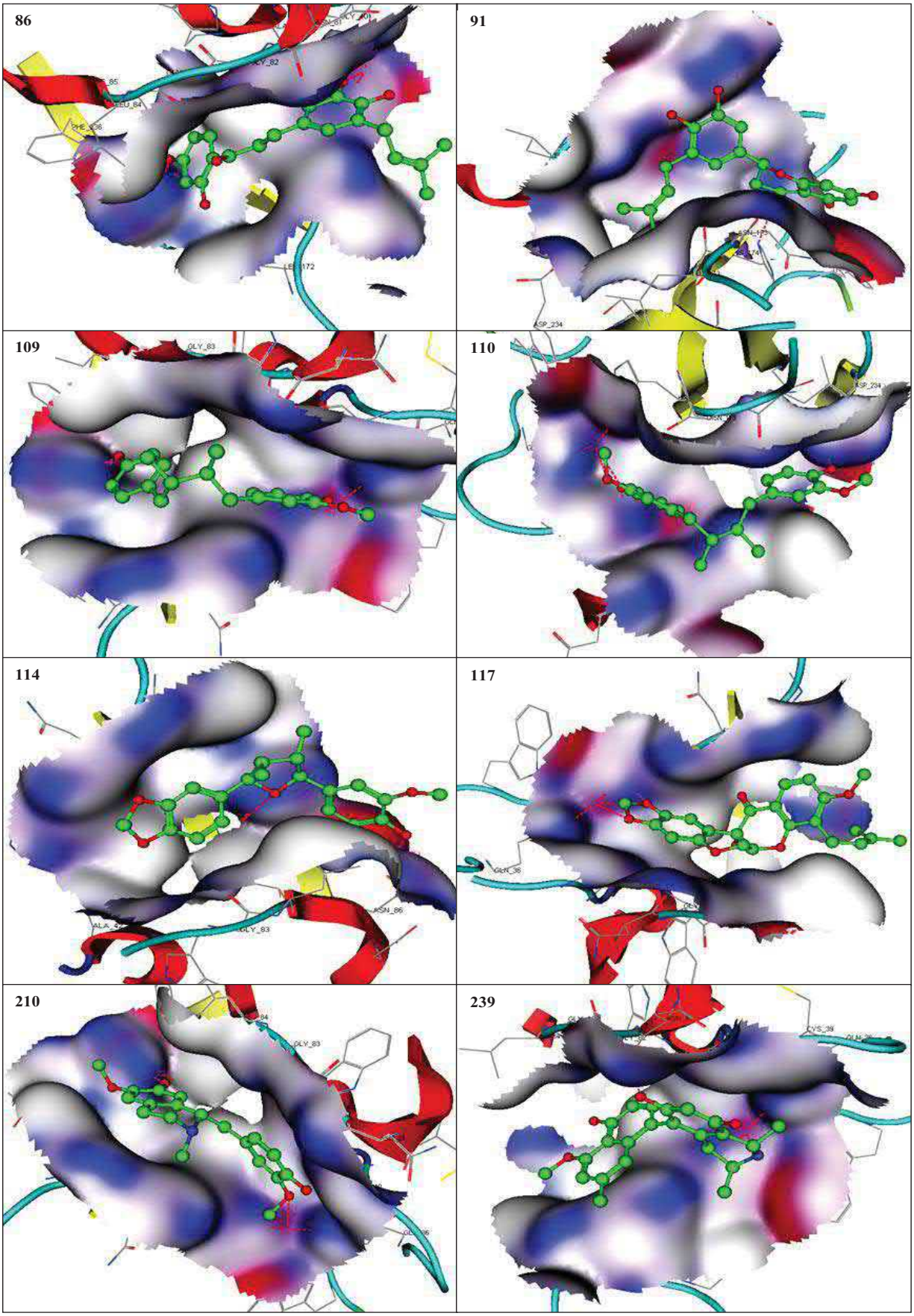


**Fig. (11).** Molecular docking pose of the active compounds with protein 3PNR.

it binds within the binding pocket with a molecular docking score -12.1637 kcal/mole. The oxygen atom of the benzodioxole ring formed a sidechain hydrogen bonding interaction with the residue His174 (2.92 Å), with moderate bond strength (67%). Both the oxygen atoms formed hydrogen bonding interactions with the residues His174 and Gln36. The binding mode observed for the compound 210 showed that the hydroxyl group of the molecule formed a sidechain hydrogen bonding interaction with the residue Asp234 (1.25Å, 22%). It also formed an indirect hydrogen bonding interaction with the same the residue Asp234. The methoxy group attached to the other side of the molecule also forms interaction with residues His174 and Gln36. The binding mode observed for compound 210 showed that it binds within the binding pocket with a molecular docking score -12.2491 kcal/mole. In case of compound 239, it was observed that the hydroxylgroup forms back bone hydrogen bonding interaction with the residue Asn173 (1.69, 43%). The –NH formed hydrogen bonding interaction with the residues Gln36 and His174. The molecular docking score of the compound 239 was -12.9072 kcal/mole. On comparing the molecular docking results with respect to the four target proteins the compounds with highest molecular docking score such as compound 86, 91, 109, 110, 114, 117, 210 and 239 were selected as the lead compounds. When the molecular docking scores of the compounds were evaluated, it is established that the compounds 86, 91, 109, 110, 114, 117, 210 and 239 (Fig. **12**) demonstrated maximum docking score with the protein 1PFZ as it showed highest interactions with the compounds. The compounds showed only few interactions with the active site of the proteins 2BJU and 3PNR. Consequently the proteins showed comparatively low docking score than 1PFZ.

In order to validate the molecular docking of the compounds into the active site of the proteins we have redocked the natural cofactor of the proteins. The results show that the natural ligand E64 in the protein 3BPF showed a molecular docking score of -10.3634 kcal/mole and the natural ligand IH4 in the protein 2BJU showed a molecular docking score of -11.9120 kcal/mole.

## Binding Interactions of the Ligands with Protein 1LYB

In order to find out the difference in selectivity for *P. falciparum* protein and human cathepsin D protein we carried out the molecular docking studies of the selected 8 natural compounds with the human cathepsin D protein. The result showed that most of the compounds show lesser interactions with human cathepsin D than the P. falciparum protein.

The binding modes of compounds were analyzed using MOE 2007.09. The 2D interactions of the 8 active compounds with the protein 1LYB are shown in the Fig. **13**.

The docking pose of the compound 86 showed that it binds within the binding pocket with a molecular docking score -10.9471 kcal/mole. The three hydroxyl groups attached to the compound showed one sidechain and two backbone hydrogen bonding interactions. One of the hydroxyl groups of the benzene diol ring showed a backbone hydrogen bonding interaction with polar residue Gly233 (3.31 Å). The other hydroxyl group showed a sidechain hydrogen bonding interaction with the residue Asp323 with moderate bond strength (57%). The hydroxyl group attached to the other end of the compound showed a backbone hydrogen bonding interaction with the residue Asp172 (1.41 Å, 25%). Compound 91 showed one prominent backbone hydrogen bonding interaction with a docking score of -12.0978 kcal/mole with the residue Thr291 (1.33 Å, 27%). Compound 109 forms a sidechain hydrogen bonding interaction between polar residue Glu260 and hydroxyl group (1.29 Å, 34%). Most of the groups in the molecule were highly exposed to the solvent. The docking score of the compound was found to be -12.0894 kcal/mole. Compound 110 showed a backbone hydrogen bonding interaction to the

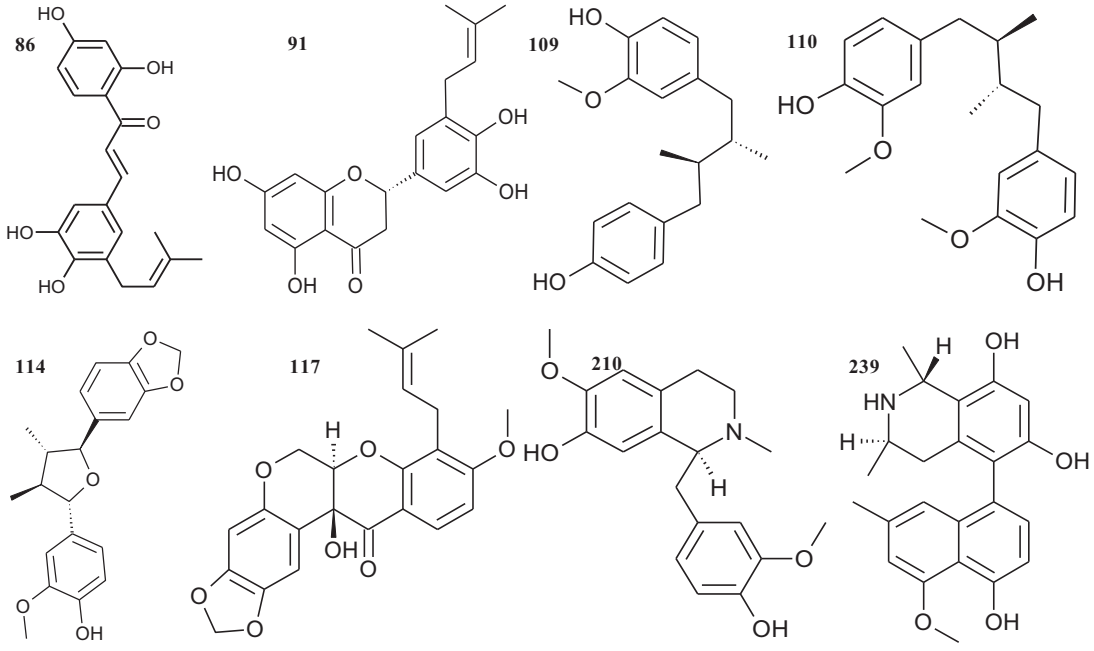


**Fig. (12).** Structures of the lead compounds.

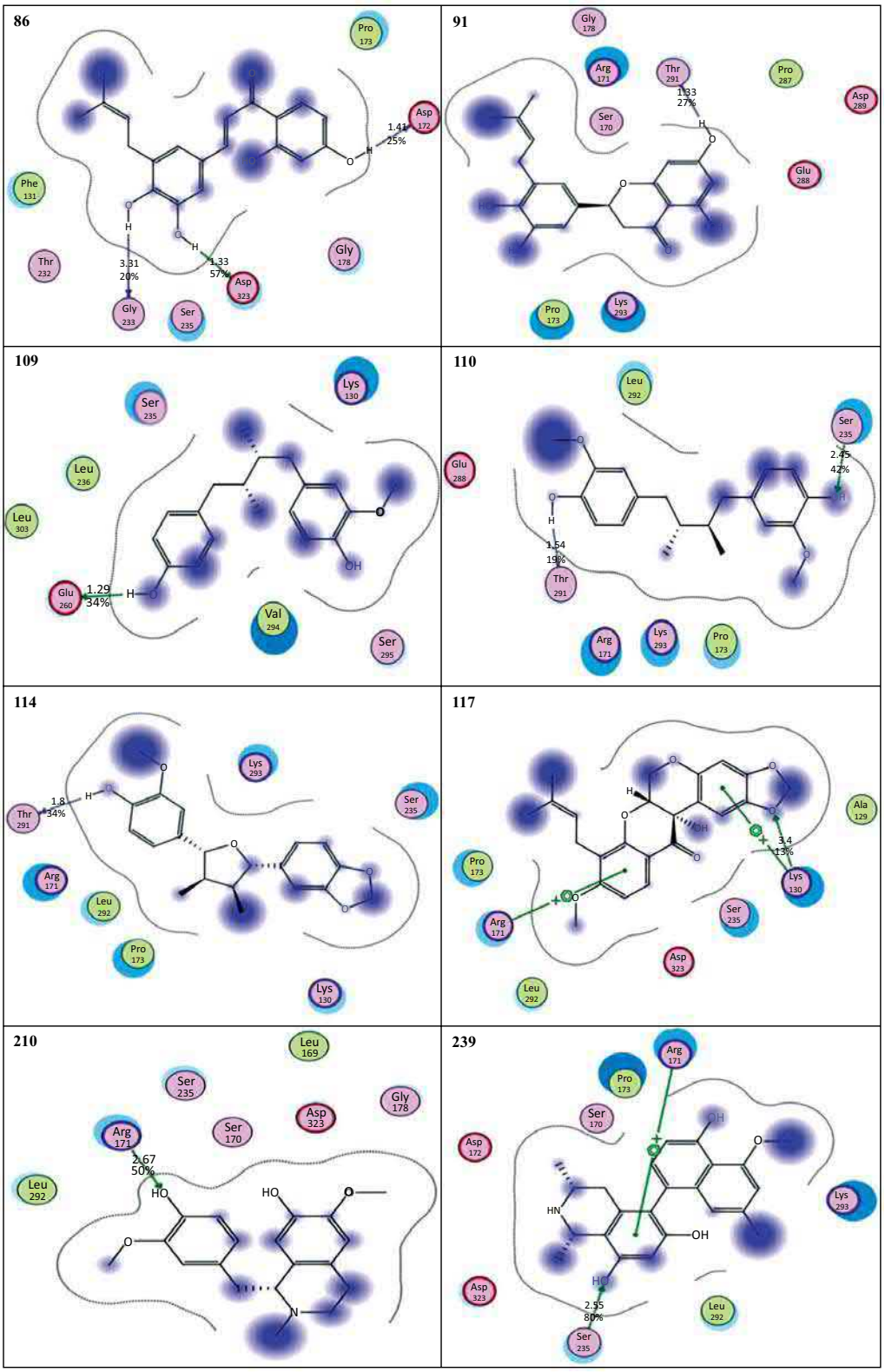


**Fig. (13).** 2D interaction graph of the active compounds with 1LYB

residue Thr291 through the hydroxyl group connected to the methoxy benzene group. The hydroxyl group attached to the other end of the compound showed a sidechain hydrogen bonding interaction with the residue Ser235 (2.45 Å, 19%). The compound showed a docking score of 9.7255 kcal/mole.

The binding mode observed for the compound **114** showed that the hydroxyl group attached to the methoxy benzene ring showed backbone hydrogen bonding interaction with the polar Arg171 residue. The molecular docking score was found to be -10.9509 kcal/mole. The

methyl group and the methoxy group of the compound was highly exposed to the solvent.

Molecular docking of compound **117** with molecular docking score -10.0102 kcal/mole showed an arene-cation hydrogen bonding interaction between the benzene ring and polar Asn86 (1.68Å, 36%). The benzene ring at the other end of the molecule showed another arene-cation interaction with the residue Lys130. The same residue also showed a sidechain hydrogen bonding interaction with one of the oxygen atoms attached to the benzodioxole ring (3.40 Å, 13%).

Compound 210 showed only one hydrogen bonding interactions with the protein, but it was buried quite deep within the protein 1LYB. The molecular docking score of the compound was -9.6652 kcal/mole. It showed a sidechain hydrogen bonding interaction between the hydroxyl group and Arg171 with moderate bond strength (2.67 Å, 50%).

In case of compound 239, it was observed that the hydroxyl group formed sidechain H-bonding interactions with residue Ser235 (2.55Å, 80%). The molecular docking score of the compound 239 is - 11.3817 kcal/mole. The benzene ring showed an arene-cation interaction with the residue Arg 171 (2.55Å, 80%).

Rumsh *et al*. have reported that two synthesized inhibitors exhibited a pronounced selectivity to plasmepsin 2 (Ki = 5.5 and 5 nM) in comparison with that of cathepsin D (Ki = 230 and 3000 nM, respectively) [27]

### ADME Properties Calculation

The finally selected eight compounds were subjected to ADME prediction using preADMET tool. Table **4** demonstrates the relative ADME profiles of the selected eight candidate molecules. The ADME calculation gave details such as human intestinal absorption (%); in vitro Caco-2 cell permeability (nm/s), in vitro MDCK cell permeability (nm/s), in vitro skin permeability (logKp·cm/h), in vitro plasma protein binding (%) and in vivo blood brain barrier penetration (c.blood/c.brain).

The HIA (Human Intestinal Absorption) results demonstrate the best absorption of all the eight compounds into human intestine. They showed moderate cellular permeability against Caco-2 cells. BBB (Blood-Brain Barrier) penetration values help to know whether the compounds are able to pass across the blood-brain barrier or not. This parameter expresses the BBB penetration capacity and absorption rate of compound to CNS (Central Nervous System). All the compounds were observed to be having very moderate absorption to CNS. All the selected lead compounds were found to be inhibitors of the protein CYP3A4, which demonstrates that they metabolize very easily. The PPB indicates the plasma protein binding of the drug and predicts its stay in the system and resultant clearance too. The PPB value of the compounds **86**, **91**, **109**, and **110** was highest among the selected eight molecules.

## CONCLUSION

In summary, this study evaluates the anti-malarial activities and molecular docking properties of some important phytochemicals present in herbs which are widely used for the treatment of malaria. The findings of the present work indicate that eight compounds possessed significant antimalarial properties. The inferences from the present study indirectly confirm the wide use of medicinal plants which are traditionally important. The following eight compounds such as compound 86- (2E)-3-[3,4-dihydroxy-5-(3-methylbut-2-en-1-yl)phenyl]-1-(2,4-dihydroxyphenyl) prop-2-en-1-one and compound 91-(2S)-2-[3,4-dihydroxy-5-(3-methylbut-2-en-1-yl)phenyl]-5,7-dihydroxy-3,4-dihydro-2H-1-benzopyran-4-one from the plant *Erythrina abyssinica*, compound 109-4-[(2S,3R)-3- [(4-hydroxyphenyl)methyl]-2-methylbutyl]-2-methoxyphenol, compound 110-4-[(2R,3S)-3-[(4-hydroxy-3- methoxyphenyl)methyl]-2-methylbutyl]-2-methoxyphenol and compound 114-4-[(2S,3S,4S,5S)-5-(1,3-benzodioxol-5-yl)-3,4-dimethyltetrahydrofuran-2-yl]-2-methoxyphenol from the plant *Pycnanthus angolensis*, compound 117-(6aR, 12aS)-12a-Hydroxy-9-methoxy-2,3-dimethylenedioxy-8-prenylrotenone from the plant *Millettia usaramensis*, compound 210-(1S)-1-[(4-hydroxy-3-methoxyphenyl)methyl]-6-methoxy-2-methyl-1,2,3,4-tetrahydroisoquinolin-7-ol from the plant *Hernandia voyronii* and compound 239-(1R,3R)-5-(4-hydroxy-5-methoxy-7-methylnaphthalen-1-yl)-1,3-dimethyl-1,2,3,4- tetrahydroisoquinolin-6,8-diol from the plant *Ancistrocladus korupensis* were screened through machine learning, ADMET screening, drug-likeness analysis and molecular docking studies. For further studies the screened lead compounds can be used. Apart from this, this study gave a noteworthy approach in distinguishing proof of novel and intense antimalarial compounds from herbs, and can be utilized as a lead for future studies for screening and outlining the fundamentally differing compounds from the herbs.

**Table 4. The tabulated ADME properties obtained from PreADMET server.**

| Properties | 86 | 91 | 109 | 110 | 114 | 117 | 210 | 239 |
|---|---|---|---|---|---|---|---|---|
| BBB | 2.304 | 1.486 | 7.645 | 5.283 | 0.253 | 0.061 | 0.963 | 0.541 |
| Caco2 | 19.403 | 11.176 | 31.011 | 35.177 | 47.193 | 29.6261 | 19.0216 | 16.892 |
| CYP_3A4_inhibition | Inhibitor | Inhibitor | Inhibitor | Inhibitor | Inhibitor | Inhibitor | Inhibitor | Inhibitor |
| HIA | 86.055 | 84.264 | 93.190 | 93.359 | 95.677 | 97.045 | 93.264 | 90.605 |
| MDCK | 0.103 | 0.7194 | 60.124 | 57.647 | 1.953 | 0.296 | 116.026 | 85.099 |
| PPB | 100 | 100 | 100 | 100 | 98.349 | 89.259 | 84.788 | 88.475 |

## CONFLICT OF INTEREST

The authors confirm that contents of this article have no conflict of interests.

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## SUPPLEMENTARY MATERIAL

Supplementary material is available on the publishers website along with the published article.

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# Synthesis and Evaluation of Compounds Containing 4-Arylpiperazinyl Moieties Linked to a 2-(Pyridin-3-yl)-1H-Benzimidazole as...

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# Synthesis and Evaluation of Compounds Containing 4-arylpiperazinyl Moieties Linked to a 2-(pyridin-3-yl)-1H-benzimidazole as p38 MAP Kinase Inhibitors

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**Abstract:** A series of novel ethyl 1-(2-(4-(2-amino-5-(ethoxycarbonyl) phenyl) piperazin-1-yl) ethyl)-2-(2-(substituted) pyridin-3-yl)-1H-benzo[d]imidazole-5-carboxylate analogues were synthesized and screened as p38 MAP kinase inhibitors. The 4-chlorophenoxy substitution in the 2nd position of the pyridyl moiety (**5i**) gave effective inhibition of p38α with $IC_{50}$ 17μM. Moreover, the synthesized benzimidazole derivatives possess a significant antiproliferative activity against blood-leukemia (CCRF-CEM), colon (HCT-116) and breast (MDA-MB-468) cancer cell lines. Based on the report, we discussed structure-activity relationship (SAR) study of synthesized benzimidazole derivatives. Molecular modelling performed for the identification of most active compounds by using three dimensional crystal structures of MAPK p38, provide a disclosed binding template of these inhibitors in the active site of their respective enzyme.

**Keywords**: Benzimidazole, pyridine, MAPK p38, Leukemia, Colon cancer, Breast cancer.

## INTRODUCTION

The mitogen-activated protein kinases (MAPKs) are major components and controlling pathways of embryogenesis, cell differentiation, cell proliferation and cell death [1]. p38 mitogen-activated protein kinases (MAPK) are 38-kDa intracellular signal transduction proteins comprising four variants, that are p38 α, β, γ, and δ joined with c-Jun amino-terminal kinase and p42/44 MAPK, p38 MAPK develops a MAPK family [2]. The p38 MAP kinase is over expressed in severe invasive breast cancers and its regulates cytokine biosynthesis (IL-1 and TNFα), which is associated with various side effects like rheumatoid arthritis, Crohn's disease, and inflammatory bowel syndrome [3-5]. The p38 group in mammals are represented as isoforms p38α, p38β, p38γ and p38δ with overlapping and distinct physiological roles [4]. Among four isoforms, p38α is the best and characterized isoform. Recent studies highlighted that, Retinoids, Cisplantin and also other chemotherapeutic agents initiate cancer cell apoptosis through the activation of p38 MAP kinase. It was observed that, the p38 MAP kinase activation is necessary for cancer cell death initiated by various anti-cancer agents [6-9]. The p38 MAPK signaling cascade is involved in various biological responses like cell proliferation, differentiation, apoptosis, invasion and inflammation. The p38 MAPK inhibitors such as (AMG548, AS1940477, CBS3830, FR-167653, JLU1124, LASSBio-998, Losmapimod (GW856553), LY2228820, LY3007113, ML3403, Pamapimod, PD-169316, PH-797804, R-130823, RO3201-195, RPR-200765A, RPR-203494, RWJ-67657, SB-202190, SB-203580, SB-239063, SB-242235, SCIO-323, SD-282, Semapimod|CNI-1493, Soblidotin|TZT-1027, TAK-715, TalmapimodSCIO-469, UO126, UR-13756, VX-702, VX-745) are widely used in many recently published research papers [10-13]. In continuation of our efforts in drug design and especially in the area of anti-cancer agents developement, we are interested in synthesis of benzimidazole derivatives as MAPK inhibitors. Benzimidazole and substituted benzimidazoles are an important class of heterocycle analogues that exhibit a broad spectrum of pharmacological properties [14-22]. In heterocyclic compounds, imidazole

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nucleus possess wide interest because of their diverse biological and clinical applications. In our life cycle, DNA plays a major role in the process of biological synthesis of proteins and enzyme through the replication and transcription of genetic information. The knowledge about drug-DNA interactions is a promising approach to develope biologically active compounds and plays a key role in pharmacology today. In view of the diverse biological applications of benzimidazole and its derivatives, they represent a good lead in developing new drugs for anticancer chemotherapy. Hence, in this investigation designed benzimidazole scaffold as a starting point for the inhibition of p38α by using molecular modelling to explore the plausible binding mode in the ATP-binding site of p38α. In continuation of our research work, we wish to report herein the synthesis and design of new class of benzimidazole derivatives as potential p38α inhibitors.

## MATERIALS AND METHOD

### Materials

Synthetic starting material, reagents, and solvents were of analytical grade or of the highest quality commercially available. The chemicals were purchased from E.Merck (Germany) and S.D fine chemicals (India). The melting points were determined by open tube capillary method and are uncorrected. Purity of the compounds was checked on thin layer chromatography (TLC) plates (silica gel G) in the solvent system toluene-ethyl ecetate-formic acid (5:4:1) and benzene-methanol (8:2), the spots were located under iodine vapours or UV light. IR spectrums were obtained on a Perkin-Elmer 1720 FT-IR spectrometer (KBr Pellets). $^1$H NMR were performed on Bruker Avance 300 ($^1$H: 300 MHz) spectrometer in DMSO/$CDCl_3$, using TMS as an internal standard. Mass spectra were recorded on Varian 320-MS TQ LC/MS using ESI and elemental analyses performed on Perkin Elmer 2400 Series II CHN Elemental Analyzer.

### Preparation of Ethyl-4-fluoro-3-nitrobenzoate

The 4-fluoro-3-nitrobenzoic acid (5 g, 27 mmol) in ethanol (50 mL) and concentrated $H_2SO_4$ (2 mL) were heated under reflux for 8 h. Based on evidence from TLC, after completion of reaction the solvent was evaporated under reduced pressure. The aqueous layer was extracted with ethyl acetate (25 mL x 3). The organic layer was dried over $Na_2SO_4$, concentrated under reduced pressure and the product was separated by using vacuum filtration to yield Ethyl-4-fluoro-3-nitrobenzoate [23, 24].

### Preparation of Ethyl 3-amino-4-(4-(2-((4-(ethoxycarbonyl)-2-nitrophenyl) amino) ethyl) Piperazin-1-yl) Benzoate

The reaction mixture ethyl-4-fluoro-3-nitrobenzoate, (0.5 g, 2.34 mmol), N-(2-aminoethyl) piperazine (0.15 mL, 1.16 mmol) and N,N-diisopropylethylamine, DIPEA (0.49 mL, 2.78 mmol) was mixed in dichloromethane (10 mL) and this mixture was stirred overnight at room temperature. Based on evidence from TLC, after completion of reaction the reaction mixture was washed with water (10 mL x 2) followed by 10% $Na_2CO_3$ solution (10 mL). The organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure to yield ethyl 3-amino-4-(4-(2-((4-(ethoxycarbonyl)-2-nitrophenyl)amino)ethyl)piperazin-1-yl)benzoate as brown oil.

### Preparation of Ethyl 3-amino-4-(4-(2-((2-amino-4-(ethoxycarbonyl) phenyl) Amino) Ethyl) Piperazin-1-yl) Benzoate

The reaction mixture ethyl 3-amino-4-(4-(2-((4-(ethoxy carbonyl)-2-nitro phenyl)amino)ethyl) piperazin-1-yl) benzoate, (0.486 g, 1 mmol), ammonium formate (0.378 g, 6 mmol) and Pd/C (50 mg) was mixed in ethanol (10 mL). The reaction mixture was refluxed until solution turned colourless then filtered through Celite 545 and filtrate was evaporated under reduced pressure. It was resuspended in ethyl acetate and washed with water, dried over $Na_2SO_4$ and evaporated to dryness to yield (70%).

### Preparation of Sodium Bisulfite Adducts of 4-substituted Benzaldehyde

The appropriate substituted pyridine aldehyde (10 mmol) was dissolved in ethanol (20 mL) and sodium metabisulfite (15 mmol) in 5 mL water was added in portion over 5 minutes. The reaction mixture was stirred at room temperature for 1 h, and subsequently stirred at 4$^o$C overnight and the formed precipitate was filtered and dried to get sodium bisulfite adducts.

### Preparation of Ethyl 1-(2-(4-(2-amino-4-(ethoxycarbonyl) phenyl) Piperazin-1-yl) ethyl)-2-(2-(sub) Pyridine-3-yl)-1*H*-benzo*[d]*imidazole-5-carboxylate Derivatives

The reaction mixture Ethyl 3-amino-4-(4-(2-((2-amino-4-(ethoxy carbonyl) phenyl) amino) ethyl) piperazin-1-yl) benzoate, (1 mmol) and various substituted pyridine sodium bisulfite adducts, (1.5 mmol) were dissolved in water (5 mL) and this mixture was stirred at RT under $N_2$ atmosphere for 2-3 h. Based on evidence from TLC, the reaction mixture was diluted in ethyl acetate (25 mL) and washed with water (10 mL x 3). The organic layer was collected, dried over $Na_2SO_4$ and evaporated under reduced pressure to get compounds in 63-90% yields.

Ethyl 1-(2-(4-(2-amino-5-(ethoxycarbonyl) phenyl) piperazin-1-yl) ethyl)-2-(2-chloropyridin-3-yl)-1H-benzo[d] imidazole-5-carboxylate (5a): $^1$H NMR: 1.36 (3H, t, J = 7.2 Hz), 1.42 (3H, t, J = 7.2 Hz), 2.51 (4H, t, J = 4.8 Hz), 2.82 (2H, t, J = 6.9 Hz), 3.91 (4H, t, J = 4.8 Hz), 4.36 (2H, q, J = 7.2 Hz), 4.41 (2H, t, J = 6.9 Hz), 4.44 (2H, q, J = 7.2 Hz), 6.92 - 8.26 (9H, m), 8.77 (2H,s); $C_{30}H_{33}ClN_6O_4$, C: 62.44 (62.46), H: 5.76 (5.74), N: 14.56 (14.53).

Ethyl 1-(2-(4-(2-amino-5-(ethoxycarbonyl) phenyl) piperazin-1-yl) ethyl)-2-(2-dimethylamino pyridin-3-yl)-1H-benzo[d]imidazole-5-carboxylate (5b): $^1$H NMR: 1.29 (6H,s), 1.36 (3H, t, J = 7.2 Hz), 1.49 (3H, t, J = 7.2 Hz), 2.58 (4H, t, J = 4.8 Hz), 2.87 (2H, t, J = 6.9 Hz), 3.91 (4H, t, J = 4.8 Hz), 4.31 (2H, q, J = 7.2 Hz), 4.49 (2H, t, J = 6.9 Hz), 4.42 (2H, q, J = 7.2 Hz), 6.92 - 8.29 (9H, m), 8.79 (2H,s); $C_{32}H_{39}N_7O_4$, C: 65.62 (65.66), H: 6.71 (6.74), N: 16.74 (16.73).

Ethyl 1-(2-(4-(2-amino-5-(ethoxycarbonyl) phenyl) piperazin-1-yl) ethyl)-2-(2-bromopyridin-3-yl)-1H-benzo[d] imidazole-5-carboxylate (5c): $^1$H NMR: 1.39 (3H, t, J = 7.2 Hz), 1.43 (3H, t, J = 7.2 Hz), 2.56 (4H, t, J = 4.8 Hz), 2.81 (2H, t, J = 6.9 Hz), 3.95 (4H, t, J = 4.8 Hz), 4.32 (2H, q, J = 7.2 Hz), 4.45 (2H, t, J = 6.9 Hz), 4.54 (2H, q, J = 7.2 Hz), 6.95 - 8.21 (9H, m), 8.82 (2H,s); $C_{30}H_{33}BrN_6O_4$, C: 57.97 (57.96), H: 5.35 (5.37), N: 13.52 (13.58).

Ethyl 1-(2-(4-(2-amino-5-(ethoxycarbonyl) phenyl) piperazin-1-yl) ethyl)-2-(2-methylpyridin-3-yl)-1H-benzo[d] imidazole-5-carboxylate (5d): $^1$H NMR: 1.21 (3H,s), 1.39 (3H, t, J = 7.2 Hz), 1.47 (3H, t, J = 7.2 Hz), 2.54 (4H, t, J = 4.8 Hz), 2.85 (2H, t, J = 6.9 Hz), 3.93 (4H, t, J = 4.8 Hz), 4.32 (2H, q, J = 7.2 Hz), 4.45 (2H, t, J = 6.9 Hz), 4.46 (2H, q, J = 7.2 Hz), 6.90 - 8.20 (9H, m), 8.70 (2H,s); $C_{31}H_{36}N_6O_4$, C: 66.89 (66.86), H: 6.52 (6.14), N: 15.10 (15.13).

Ethyl 1-(2-(4-(2-amino-5-(ethoxycarbonyl) phenyl) piperazin-1-yl) ethyl)-2-(2-trifluromethyl pyridin-3-yl)-1H-benzo [d]imidazole-5-carboxylate (5e): $^1$H NMR: 1.39 (3H, t, J = 7.2 Hz), 1.41 (3H, t, J = 7.2 Hz), 2.57 (4H, t, J = 4.8 Hz), 2.86 (2H, t, J = 6.9 Hz), 3.97 (4H, t, J = 4.8 Hz), 4.34 (2H, q, J = 7.2 Hz), 4.44 (2H, t, J = 6.9 Hz), 4.47 (2H, q, J = 7.2 Hz), 6.98 - 8.21 (9H, m), 8.79 (2H,s); $C_{30}H_{33}F_3N_6O_4$, C: 60.98 (60.96), H: 5.45 (5.41), N: 13.76 (13.73).

Ethyl 1-(2-(4-(2-amino-5-(ethoxycarbonyl) phenyl) piperazin-1-yl) ethyl)-2-(2-methoxypyridin-3-yl)-1H-benzo [d] imidazole-5-carboxylate (5f): $^1$H NMR: 1.29 (3H, t, J = 7.2 Hz), 1.34 (3H,s), 1.49 (3H, t, J = 7.2 Hz), 2.51 (4H, t, J = 4.8 Hz), 2.81 (2H, t, J = 6.9 Hz), 3.96 (4H, t, J = 4.8 Hz), 4.34 (2H, q, J = 7.2 Hz), 4.41 (2H, t, J = 6.9 Hz), 4.47 (2H, q, J = 7.2 Hz), 6.92 - 8.32 (9H, m), 8.87 (2H,s); $C_{31}H_{36}N_6O_5$, C: 65.02 (65.07), H: 6.34 (6.39), N: 14.68 (14.63).

Ethyl 1-(2-(4-(2-amino-5-(ethoxycarbonyl) phenyl) piperazin-1-yl) ethyl)-2-(2-thiophenyl pyridin-3-yl)-1H-benzo[d] imidazole-5-carboxylate (5g): $^1$H NMR: 1.32 (3H, t, J = 7.2 Hz), 1.43 (3H, t, J = 7.2 Hz), 2.24 (2H, s,) 2.59 (4H, t, J = 4.8 Hz), 2.79 (2H, t, J = 6.9 Hz), 3.97 (4H, t, J = 4.8 Hz), 4.36 (2H, q, J = 7.2 Hz), 4.46 (2H, t, J = 6.9 Hz), 4.49 (2H, q, J = 7.2 Hz), 6.87 - 8.16 (12H, m), 8.89 (2H,s); $C_{36}H_{38}N_6O_4S$, C: 66.44 (66.46), H: 5.89 (6.84), N: 12.91 (12.93).

Ethyl 1-(2-(4-(2-amino-5-(ethoxycarbonyl) phenyl) piperazin-1-yl) ethyl)-2-(2-cyclohexyloxy pyridin-3-yl)-1H-benzo[d]imidazole-5-carboxylate (5h): $^1$H NMR: 1.08 (8H,m), 1.47 (3H, t, J = 7.2 Hz), 1.54 (3H, t, J = 7.2 Hz), 2.62 (4H, t, J = 4.8 Hz), 2.85 (2H, t, J = 6.9 Hz), 3.91 (4H, t, J = 4.8 Hz), 4.47 (2H, q, J = 7.2 Hz), 4.56 (2H, t, J = 6.9 Hz), 4.65 (2H, q, J = 7.2 Hz), 7.12 - 8.16 (9H, m), 8.89 (2H,s); $C_{35}H_{42}N_6O_5$, C: 67.07 (67.09), H: 6.75 (6.72), N: 13.41 (13.46).

Ethyl 1-(2-(4-(2-amino-5-(ethoxycarbonyl) phenyl) piperazin-1-yl) ethyl)-2-(2-thiomorpholino pyridin-3-yl)-1H-benzo[d]imidazole-5-carboxylate (5i): $^1$H NMR: 1.37 (8H,m), 1.44 (3H, t, J = 7.2 Hz), 1.52 (3H, t, J = 7.2 Hz), 2.61 (4H, t, J = 4.8 Hz), 2.89 (2H, t, J = 6.9 Hz), 3.99 (4H, t, J = 4.8 Hz), 4.41 (2H, q, J = 7.2 Hz), 4.57 (2H, t, J = 6.9 Hz), 4.66 (2H, q, J = 7.2 Hz), 7.12 - 8.37 (9H, m), 8.92 (2H,s); $C_{34}H_{41}N_7O_4S$, C: 63.43 (63.49), H: 6.42 (6.44), N: 15.23 (15.26).

Ethyl 1-(2-(4-(2-amino-5-(ethoxycarbonyl) phenyl) piperazin-1-yl) ethyl)-2-(2-(4-chloro phenoxy) pyridin-3-yl)-1H-benzo[d]imidazole-5-carboxylate (5j): $^1$H NMR: 1.32 (3H, t, J = 7.2 Hz), 1.44 (3H, t, J = 7.2 Hz), 2.58 (4H, t, J = 4.8 Hz), 2.87 (2H, t, J = 6.9 Hz), 3.92 (4H, t, J = 4.8 Hz), 4.32 (2H, q, J = 7.2 Hz), 4.46 (2H, t, J = 6.9 Hz), 4.57 (2H, q, J = 7.2 Hz), 6.78 - 8.43 (13H, m), 8.82 (2H,s); $C_{36}H_{37}ClN_6O_5$, C: 64.62 (64.66), H: 5.57 (5.51), N: 12.56 (12.53).

Ethyl 1-(2-(4-(2-amino-5-(ethoxycarbonyl) phenyl) piperazin-1-yl) ethyl)-2-(2-pyrrolidinyl pyridin-3-yl)-1H-benzo [d]imidazole-5-carboxylate (5k): $^1$H NMR: 1.27 (8H,m), 1.34 (3H, t, J = 7.2 Hz), 1.53 (3H, t, J = 7.2 Hz), 2.66 (4H, t, J = 4.8 Hz), 2.81 (2H, t, J = 6.9 Hz), 3.97 (4H, t, J = 4.8 Hz), 4.49 (2H, q, J = 7.2 Hz), 4.58 (2H, t, J = 6.9 Hz), 4.69 (2H, q, J = 7.2 Hz), 7.18 - 8.17 (9H, m), 8.85 (2H,s); $C_{34}H_{41}N_7O_5$, C: 66.76 (66.79), H: 6.76 (6.74), N: 16.03 (16.06).

Ethyl 1-(2-(4-(2-amino-5-(ethoxycarbonyl) phenyl) piperazin-1-yl) ethyl)-2-(2-(4-chloro phenyl) pyridin-3-yl)-1H-benzo[d]imidazole-5-carboxylate (5l): $^1$H NMR: 1.25 (3H, t, J = 7.2 Hz), 1.42 (3H, t, J = 7.2 Hz), 2.53 (4H, t, J = 4.8 Hz), 2.82 (2H, t, J = 6.9 Hz), 3.97 (4H, t, J = 4.8 Hz), 4.37 (2H, q, J = 7.2 Hz), 4.48 (2H, t, J = 6.9 Hz), 4.59 (2H, q, J = 7.2 Hz), 6.82 - 8.49 (13H, m), 8.82 (2H,s); $C_{36}H_{37}ClN_6O_4$, C: 66.20 (66.26), H: 5.71 (5.74), N: 12.87 (12.90).

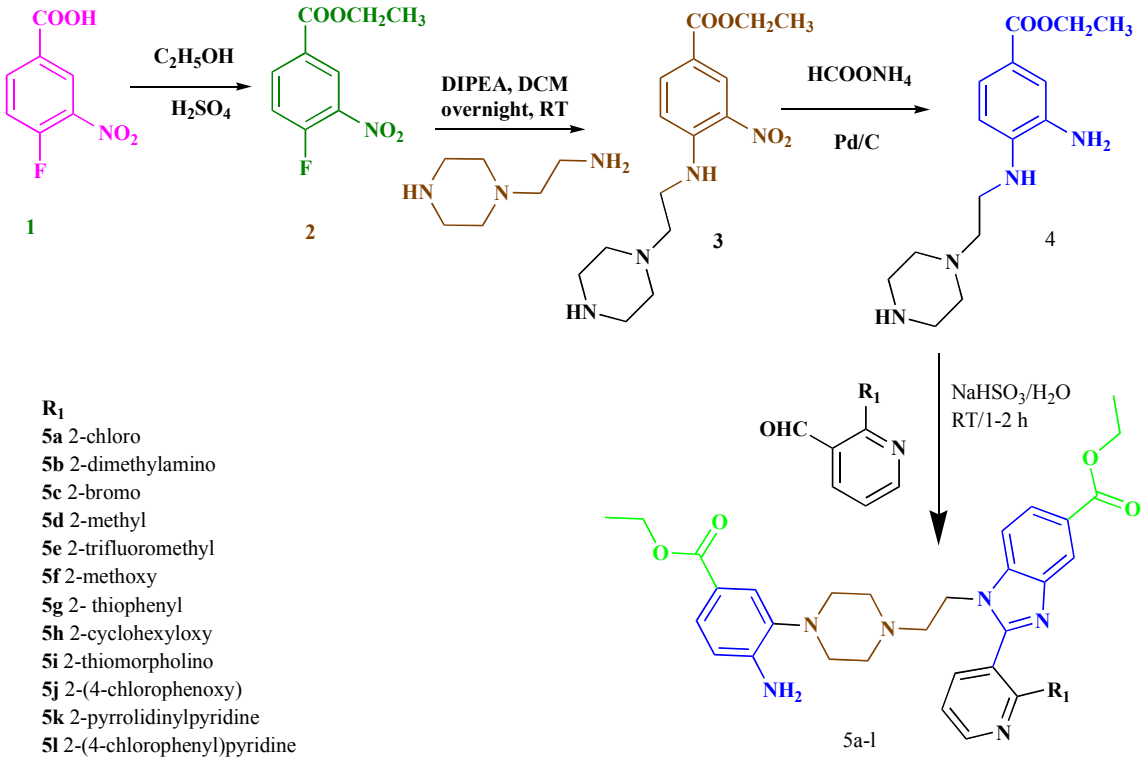
## BIOLOGY

**Cell Proliferation Assay**: The activity of the synthesized compounds was tested against cancer cell lines and obtained from the American Type Culture Collection (Rockville, MD). The cells were seeded in 96-well plates at a density of 5_103 per well and treated with 50 μM of selected compounds allowed to adhere for 72 h. According to the manufacturer's instructions, the proliferative activity was determined by 3-(4,5-dimethyl thiazol- 2-yl)-5-(3-carboxy methoxy phenyl)-2-(4-sulfo phenyl)-2H-tetrazolium, inner salt assay (Cell Titer 96 Non-Radioactive Cell Proliferation Assay; Promega, Madison, WI) to monitor the number of viable cells. Briefly, inner salt solution was added at 20 lL/well, and then 1 h of incubation at 37°C in a humidified 5% $CO_2$ atmosphere, the conversion of, inner salt to formazan was measured in a plate reader at 490 nm. All experiments were done in triplicate, and the proliferation rate was calculated as the ratio of absorbance under each experimental condition to that of the control nontransfectant.

## RESULTS AND DISCUSSION

### Chemistry

The series of heterocycles was synthesized by using aminoethyl ester and various 2-substituted pyridine aldehyde and sodium metabisulfite to yield final compounds in the range of 76-90% Scheme (**1**). The NMR and CHN spectral datas show that the synthesized compounds were in full agreement with the proposed structures. In $^1$H NMR spectrum the chemical shifts, multiplicities and coupling constants, and signals of the respective protons were verified to conform synthesized compounds. The $^1$H NMR spectrum, of




**Scheme (1).**

benzimidazole **5a** showed a triplet at δ 1.36, 1.42 ppm due to the ester methyl group, *N*-methylene protons from the imidazole side chain also appeared as a triplet at δ 4.36-4.41 ppm. The *o*-methylene protons (from the ester group) appeared as a quartet at δ 4.44 ppm, δ 6.92-8.26 due to aromatic protons and pyrimidine ring protons Similar $^{1}$H patterns were obtained for other substituted benzimidazoles derivatives **5a-l**.

## PHARMACOLOGY

The inhibitory potency of **5a-l** was evaluated using radiometric p38α assay performed by Millipore KinaseProfiler$^{TM}$.[13] The results was summarized in Table **1**, and it shows that all the compounds exhibited moderate to good inhibitory activity against p38α. Among all the compounds, **5i** showed excellent inhibitory activity. However, the inhibitory activity was greatly affected when the substitution was replaced at 2$^{nd}$ position of the pyridyl moiety, 4-chlorophenoxy group at *ortho* substitution in pyridine ring shows the excellent inhibitory activity as compare to other substitutions. This clearly show that, the inhibitory effect changed when another group was added to the pyridine ring. Most active compounds in terms of inhibitory activity followed by 4-chlorophenoxy substitution at ($IC_{50}$ = 17μM) were thiophenyl substitution at ($IC_{50}$ = 24μM), 2-chloro group substation $IC_{50}$ = <31μM), thiomorpholino $IC_{50}$ = <38μM), dimethylamnino $IC_{50}$ = <88μM), whereas other compounds showed moderate to good inhibitory activity. Interestingly, part is substituted *p*-chloro phenyl and trifluoromethyl substituted derivatives also showed inhibitory activities. A simple, structure-activity relationship of synthesized compounds was concluded from the observed results. Interestingly, the presence of 4-chlorophenoxy and thiophene group at the 2$^{nd}$ position of substituent (**5i**) and (**5g**) as well as the presence of electron withdrawing group at the 2$^{nd}$ position greatly enhanced inhibitory activity and we also observed that, the changing of substituents at the pyridine ring influenced on inhibitory activity. Some other factors to electron donating or withdrawing characteristics of substituent's need to be sought and further modification on the chemical structures are required. The electron withdrawing properties of the other substitution leading to less efficient hydrogen acceptor property of the pyridine nitrogen resulted in negative effect on the inhibitory activity (Table **1**).

The synthesized compounds **5i**, **5g** and **5c** were evaluated for their effect on proliferation of human ovarian adenocarcinoma (SK-OV-3), breast adenocarcinoma (MDA-MB-231), and leukemia adenocarcinoma (CCRF-CEM). Doxorubicin (Dox) and DMSO were used as positive and negative controls, respectively. Compounds **5i** inhibited the cell proliferation of used cancer cell line human ovarian adenocarcinoma (SK-OV-3), breast adenocarcinoma (MDA-MB-231), and leukemia adenocarcinoma (CCRF-CEM) cells by 82-92%. Compounds with 4-chlorophenoxy ring at pyridine 2$^{nd}$ positions exhibited excellent inhibitory activity in all used cell lines. Compound **5i** showed higher antiproliferative activity in MDA-MB-231 (92% inhibition) than CCRF-CEM and SK-OV-3 cells and other two compounds **5g** and **5c** showed 76-80% and 84-90% antiproliferective activity, respectively. Thus, this class of compounds has potential to be investigated as lead compounds in cancer studies (Table **2**).

**Table 1. Biological Activity of 5a-l against the p38 MAP Kinase.**

| Compound | $R_1$ | $IC_{50}$ p38α [a,b,c](μm) | Yield (%) | Melting point |
|---|---|---|---|---|
| 5a | 2-chloro pyridine | 174 | 77 | 164 |
| 5b | 2-dimethylaminopyridine | 88 | 82 | 141 |
| 5c | 2-bromo pyridine | 31 | 68 | 172 |
| 5d | 2-methyl pyridine | 115 | 80 | 162 |
| 5e | 2-trifluromethylpyridine | 183 | 86 | 184 |
| 5f | 2-methoxypryidine | 28 | 75 | 172 |
| 5g | 2-thiophenyl pyridine | 24 | 92 | 128 |
| 5h | 2-cyclohexyloxy pyridine | 345 | 90 | 154 |
| 5i | 2-thiomorpholino pyridine | 38 | 82 | 143 |
| 5j | 2(4-chlorophenoxy) pyridine | 17 | 75 | 189 |
| 5k | 2-pyrrolidinylpyridine | 265 | 84 | 194 |
| 5l | 2-(4-chloro phenyl)pyridine | 312 | 72 | 132 |

[a]The concentration required to inhibit the growth of the cells by 50% expressed as $IC_{50}$ (μM). [b]Values given represent the mean obtained from three consecutive experiments. [c]SEM represents the standard Error Mean.

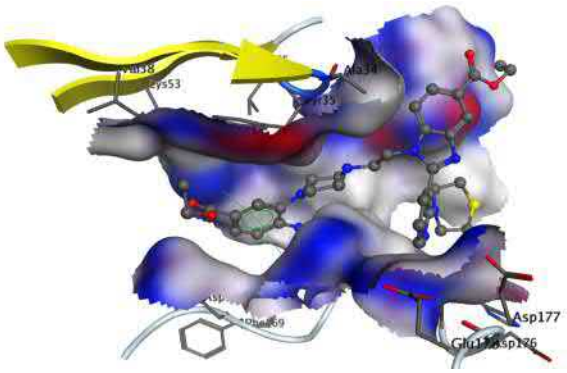
**Table 2. Anti-proliferative Activities of Selected Benzimidazole Derivatives Against CCRF-CEM, MDA-MB-231and SK-OV-3 Cancer Cell Lines.**

| Compound | Cell Inhibition (%) at 50 μM | | |
|---|---|---|---|
| | CCRF-CEM | MDA-MB-231 | SK-OV-3 |
| 5c | 76% | 82% | 80% |
| 5g | 84% | 90% | 85% |
| 5i | 92% | 82% | 84% |

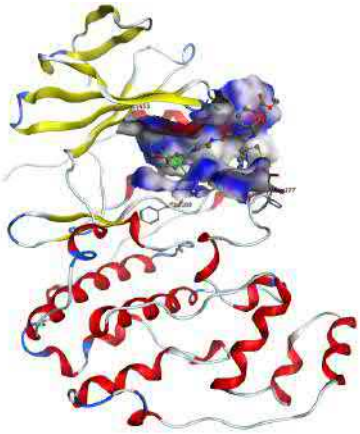
## MOLECULAR DOCKING

Molecular docking studies were performed by using the default procedure to determine the structural features that steer the bio-activity against MAPK p38. For the convenience representation, herein, we reported the docking pose for one of the most active compounds **(5g)**. It showed that, the residues Ile116, Leu122, His126, Val158, and Cys162 constitute the hydrophobic part, termed as ΦA site, of the binding pocket of MAPK-p38 for kinase interaction motif (KIM), whereas ΦB site is formed by Ala111, Ile116 and Glu160. Here, ΦA and ΦB represent the hydrophobic residues. The ΦB+1 site is enclosed by the side chains of Ala111, Ile116, Asn115 and Cys119. The residue Leu407, at ΦA-2 site, is present very close to hydrophobic pocket formed by His126, Phe129, Cys162 and Tyr311.

From Fig. (**1**), it is clear that, compound **5g** interacts with Tyr35, Lys53, Gln60, His64, Arg67, Asp168, Arg173, His174, and Glu178 residues of the receptor. The phenyl




(**a**) Close view



(**b**) Distant view

**Fig. (1)**. Docking pose for **5g** active compound in the active site of receptor along with the eletrostatic surface map of the receptor (Blue; H-bonding, Red: Mild polar and White: Hydrophobic region)

ring directly attached to piperazine moiety is responsible for the arene-charge interaction with the Lys53 and Arg173, these residues are basic cationically charged. A possible reason for close proximity of the phenyl ring to positively charged nitrogen of guinidine part in Arg173 could be due to the ester group, where as the $-NH_2$ group (electron rich) on same phenyl ring helps in establishing close contact with the positively charged nitrogen in side chain kkmn of Lys53. The phenyl ring attached to piperazine moiety is able to penetrate well inside the binding site due to the additional flexibility because of the $-CH_2-CH_2-$ linkage between piperazine and benzimidazole moiety and due to comparatively slender piperazine-phenyl-ester moieties. The bulkier benzimidazole, pyridine and ester part inhibit the further entrance of the compound in the active site. Therefore, the future modifications in $-CH_2-CH_2-$ linkage between piperazine and benzimidazole moieties, $-NH_2$ and ester groups on phenyl ring attached to piperazine and diminishing the bulkiness on benzimidazole moiety could be very useful.

## CONCLUSION

In conclusion, the current study revealed that, most of the benzimidazole derivatives showed moderate to good inhibitory activity against P38α enzyme. As evident from the list, **5i** showed sthe good antiproliferative activity against MDA-MB-231, CCRF-CEM, and SK-OV-3. In view of the above findings, **5i** of the benzimidazole derivatives showed higher antiproliferative activity in used cancer cell line. These lead compounds have electronic effects and have potential as antiproliferative agents after further optimization.

## CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

## ACKNOWLEDGEMENTS

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# A PARADIGM SHIFT IN SERVICE SECTOR IN INDIAN ECCONOMY – A REVIEW

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**Abstract**
The rising India has a very strong service base that contributes more than 50% to national Gross Domestic Product (GDP). It resulted out of paradigm shift that has taken place with the major structural changes in Indian economy since 1991. This was the watershed year in Indian economic history when major economic changes in terms of liberalization, privatization and globalization (LPG) were brought in Indian economic regulations by the 'the then finance minister' (**Dr. Manmohan Singh**). The revolution brought new technologies, new companies, new concepts and new customers to Indian market. India's unilateral liberalization and deregulation and shift in economic paradigm towards integration with the world economy have contributed to a favorable environment for the boom in service sector. It is now equipped with better technologies, better reach to overseas market and improved methods and processes. The study advocates the paradigm shifts in the service sector with new perspectives. The general objective of this paper is to provide an overview of the Indian Services sector. However, to be specific this paper provides an overview of the growth of Services sector and its components in India, focusing on its contribution to Gross Domestic Product (GDP)

**Introduction:**

Services sector is the lifeline for the socio-economic growth of a country. It is today the largest and fastest growing sector globally contributing more to the global output and employing more people than any other sector. In alignment with global trend, the Indian Services sector has witnessed a major boom and is one of the major contributors to both employment and national income in recent time. Services sector in India today accounts for more than half of India's GDP. Since independence, there has been a marked acceleration in Services sector growth in India.

In India, growth in services sector has been linked to the liberalization and reforms of the 1990s. In the first three decades (1950s to 1970s) after India's independence in 1947, GDP grew at an average decadal growth rate of less than four per cent. India was largely an agrarian economy. The share of services sector was small and a large number of services were government monopolies. Services sector started to grow in the mid-1980s but growth accelerated in the 1990s when India initiated a series of economic reforms after the country faced a severe balance of payment crisis. Reforms in the services sector were a part of the overall reform process, which led to privatization, removal of FDI restrictions and streamlining of the approval procedures, among others.

Existing studies show that liberalisation and reforms is one of the important factors contributing to the growth of services sector in India. With economic growth and rise in per capita income, there is a change in demand pattern from necessary to discretionary consumptions like education and personal and health care services. High income elasticity of demand for services has contributed to the high growth of this sector. Technological progress and availability of high skilled manpower has led to growth of services like information technology (IT) and IT enabled services. Developed countries outsource its services to developing countries like India leading to a rise in demand for services from the developing market. High government expenditure on certain services like community, social and personal services has also led to high growth of services.

## Reasons For Growth in Service Sector

India's service sector is the 12th largest in the world by nominal GDP and 4th largest when purchasing power is taken into account. The service sector provides employment to 27% of the population. Let us look into the factors that have led to the growth of the service sector in India:

### Economic Affluence

The Indian society is characterized by an increasing middle class. In addition the liberalization of the Indian economy has had a positive impact on the Indian households. Their income and expenditure has been pushed up fostering the demand for goods and services;

### Changing Role of Women

Earlier women were a neglected lot, who only had to carry out household chores. But with time there has been a change in the way of thinking. Women are educated and allowed to work. They are employed in several erstwhile male dominated services such as defense services, police services, postal services, software services, health services etc. An increase in the number of working women has led to the creation of a market for a number of products and services.

### Changing Culture

The traditionally common joint family system is slowly disintegrating and making way for a nuclear family way of living. This has been accompanied by an increased demand for a number of services like education, health care, entertainment, tourism etc. There has also been a marked change in a person's way of thinking with respect to investment, recreation and time perception leading to increased demand for services.

### Growth of IT Sector

In India information technology and business outsourcing are amongst the fastest growing sectors having a cumulative growth rate of revenue.

The growth of IT sector can be attributed to several factors such as increased specialization and availability of a large pool of low cost, highly skilled educated and fluent English speaking workers. This supply is matched by increased demand from foreign customers who are interested in India's service exports or those looking to outsource their operation.

### Development of Markets

Both the urban and the rural areas have witnessed wide spread retailing and whole selling. In fact retailing has even extended to remote rural areas.

### Health Care Consciousness

The present generations are becoming more and more diet and health conscious. They are resorting to services of gymnasiums and fitness clubs to maintain their physical and mental health.

### Economic Liberalization

The opening up of the Indian economy in 1991 was followed by a policy of disinvestment. This facilitated the entry of multinational Corporations leading to its accompanying increase in demands. This acted as a spurt for the development of the service sector.

### Migration from Rural to Urban Areas

With rapid industrialization and other developments in this era of globalization, there takes place large scale migration from the rural to the urban areas. This changes the life-style and enhances the demand for services.

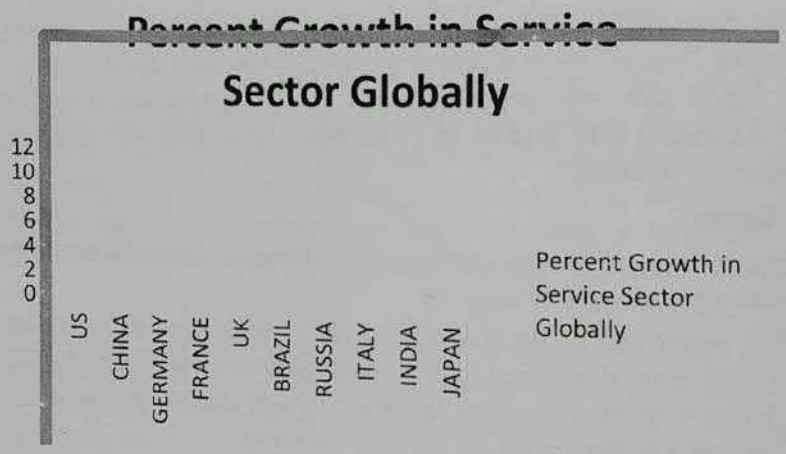
### Export Potential

The services offered by India to various parts of the world include banking, insurance, transportation, company data services, education, software services, tourism etc. In fact tourism and software services are among the major foreign exchange earners of the country.

**Service Tax**

The coverage of this tax has been extended. The tax net covers hotels and restaurants, transport, storage and commercialization, financial services, real estate, business services and social/personal services.

India has the second fastest growing services sector with its compound annual growth rate at nine per cent, just below China's 10.9 per cent, during the last 11-year period from 2001 to 2012, the Economic Survey for 2013-14 said. Russia at 5.4 per cent is a distant third. Among the world's top 15 countries in terms of GDP, India ranked 10th in terms of overall GDP and 12th in terms of services GDP in 2012, it said, adding that services share in world GDP was 65.9 per cent but its share in employment was only 44 per cent in 2012. As per the survey, in India, the growth of services-sector GDP has been higher than that of overall GDP between the period FY 2001- FY 2014. Services constitute a major portion of India's GDP with a 57 per cent share in GDP at factor cost (at current prices) in 2013-14, an increase of 6 percentage points over 2000-01.




**(Source: The Hindu- Business-budget-New Delhi July 9, 2014)**

In fact the growth rate of 6.8 per cent for the sector is marginally lower than in 2012-13. "This is due to deceleration in the growth rate of the combined category of trade, hotels, and restaurants and transport, storage, and communications to 3 per cent from 5.1 per cent in 2012-13," the survey said. On the other hand, robust growth was seen in financing, insurance, real estate, and business services at 12.9 per cent. FDI inflows to the services sector (top five sectors including construction) declined sharply by 37.6 per cent to USD 6.4 billion compared to an overall growth in FDI inflows at 6.1 per cent. India's share in world services exports, which increased from 0.6 per cent in 1990 to 1.1 per cent in 2000 and further to 3.3 per cent in 2013, has been increasing faster than its share in world merchandise exports, according to the survey. While exports of software services, accounting for 46 per cent of India's total services exports, decelerated to 5.4 per cent in 2013-14 from 5.9 per cent in 2012-13, travel, accounting for a nearly 12 per cent share, witnessed negative growth of 0.4 per cent. However, moving in tandem with global exports of financial services, India's exports of financial services registered a high growth of 34.4 per cent in 2013-14.

**Sector-wise contribution of GDP of India**

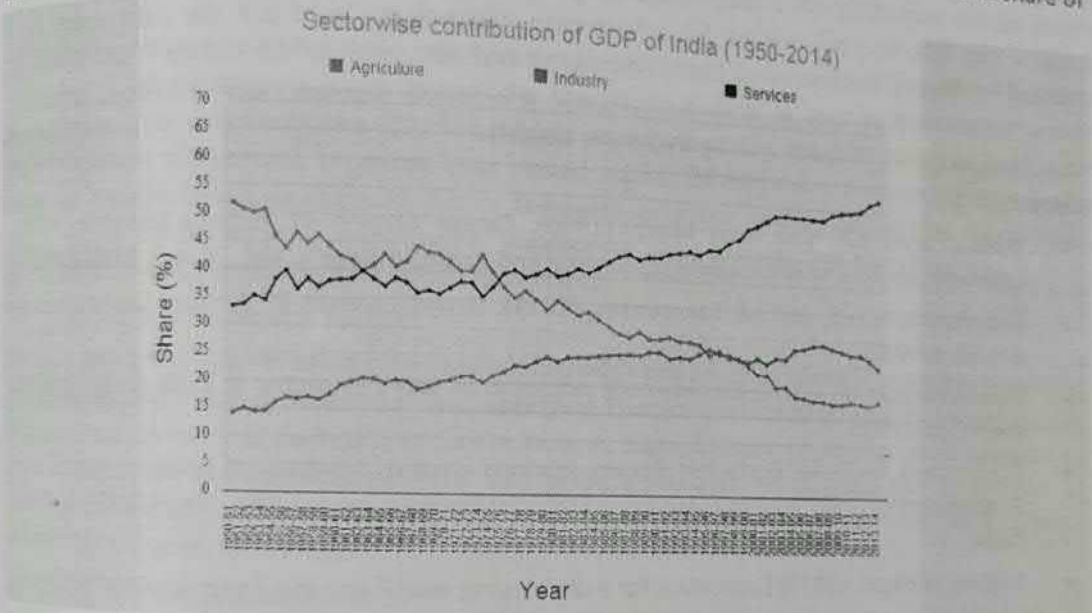
Indian economy is classified in three sectors — Agriculture and allied, Industry and Services. Agriculture sector includes Agriculture (Agriculture proper & Livestock), Forestry & Logging, Fishing and related activities. Industry includes Manufacturing (Registered & Unregistered), Electricity, Gas, Water supply, and Construction. Services sector includes Trade, repair, hotels and restaurants, Transport, storage, communication & services related to broadcasting, Financial, real estate & professional services, Community, social & personal services.

Services sector is the largest sector of India. Gross Value Added (GVA) at current prices for Services sector is estimated at 61.18 lakh crore INR in 2014-15. Services sector accounts for 52.97% of total India's GVA of 115.50 lakh crore Indian rupees. With GVA of Rs. 34.67 lakh crore, Industry sector contributes 30.02%. While, Agriculture and allied sector shares 17.01% and GVA is around of 19.65 lakh crore INR.

At 2011-12 prices, composition of Agriculture & allied, Industry, and Services sector are 16.11%, 31.37%, and 52.52%, respectively.

According to CIA Fackbook sector wise Indian GDP composition in 2014 are as follows : Agriculture (17.9%), Industry (24.2%) and Services (57.9%). Total production of agriculture sector is $366.92 billion. India is 2nd larger producer of agriculture product. India accounts for 7.68 percent of total global agricultural output. GDP of Industry sector is $495.62 billion and world rank is 12. In Services sector, India world rank is 11 and GDP is $1185.79 billion. Contribution of Agriculture sector in Indian economy is much higher than world's average (6.1%). Contribution of Industry and Services sector is lower than world's average 30.5% for Industry sector and 63.5% for Services sector.

At previous methodology, composition of Agriculture & allied, Industry, and Services sector was 51.81%, 14.16%, and 33.25%, respectively at current prices in 1950-51. Share of Agriculture & allied sector has declined at 18.20% in 2013-14. Share of Services sector has improved to 57.03%. Share of Industry sector has also increased to 24.77%




(Source : Planning Commission, Government of India)

## Future Prospects

Indian economy which was growing at an accelerated rate from 1998 to 2010 had a setback of sorts in 2012. The economy however is gradually picking up and moving in the right path. This will lead undoubtedly to increase the Per Capita Income of the high and middle income groups, while simultaneously striving to reduce the number of people below the poverty line.

The entire process would have stimulating effect with an increase in the literacy level. India has to her credit one of the youngest populations in the world. The cumulative effects of all this will be an increase in the demand for services like education, health, hotels, restaurants etc.

According to the Planning Commission India's service sector is expected to grow at the rate of 10% per annum in the period between 2012 and 2017.

India also ranks high in international trade accounting for 3.34% of exports and 3.31% of imports of services. It is in addition among the top 10 rankers of WTO members as regards export and import of services.

## Conclusions

As we have discussed the service sector is the fastest growing sector in India, contributing significantly to the GDP and is projected to rise even further. However, the increase in employment is not in keeping with the share of the sector in the GDP and even among those employed the big question is how many of these work in the organized service sector?

India has a number of problems which are socio economic in nature. Poverty and accelerated population growth are major constraints, thereby depriving several people of access to basic health and education.

A number of obstacles hamper the progress of this sector and its contribution to inclusive growth. Bureaucratic inertia, multiple government bodies having their own sets of rules and regulations, rampant corruption and absence of a uniform concrete policy have an adverse effect on the system. Slow reform process, restrictions on foreign direct investment, poor infrastructural facilities, absence of uniformity in the quality and standard of education, in spite of having renowned Brain Power and the existence of unemployable educated youth are all limiting factors.

India, however, has vast potential for promotion of service economy. This is attributed to factors such as emergence of a new middle class with increasing aspirations, opening of the economy leading to the availability of a wide range of goods and services, growing retail and improving domestic and international market for Information Technology. With just the right policy mix, propelled further by the revival of the US economy and the potential for India's IT and Business Process outsourcing sectors in different parts of the world together with increased domestic demand will no doubt take our country to greater heights.

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# IMPACT OF SOCIAL NETWORKING SITES ON THE ACADEMIC PERFORMANCE OF SENIOR COMMERCE COLLEGE STUDENTS.

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**Abstract:**

There is no doubt that Social media has gained wider acceptability and usability and is also becoming probably the most important communication tools among students especially at the higher level of educational pursuit. As much as social media is viewed as having bridged the gap in communication that existed. Within the social media Facebook, Twitter, Watsapp and others are now gaining more and more patronage.

This study attempts to obtain students' perceptions on how social networking sites impact their academic performance. In this paper a survey was conducted by distributing 200 questionnaires to selected students from the Faculty of Commerce in Amravati city. The purpose was to obtain respondents' opinion on the use of social networking sites and its influence on their academic performance. The study confirmed that most of the students are engage in the use of SNSs mainly for socializing activities rather than for academic purpose. However, most of the students do feel that the SNSs have more positive impact on their academic performance through collaborative learning.

## Introduction

The world has been changed rapidly by the evolution of technology; this has resulted into the use of technology as the best medium to explore the wide area of knowledge. The evolution of internet technology has led to its use as the best medium for communication. Whereby, two-third of the world's internet population visits social networking or blogging sites, thus serving as a communication and connection tool. The use of Internet has increased drastically between the year 2000 and 2007. According to Markey and Well during the year 2000 the number of people with access globally was estimated to be around 400 million. This number grew to 600 million in 2002. Internet is a tool that is used for different things by different people. It is used by employees of various organizations to search for information and to also exchange information with other people. At home the internet is used as means to chat to other people and to get news that affect the world in general. Some people make use of it to do business transactions through e-banking facility. The benefit that often come with the use of the internet such as obtaining useful information, chatting with friends, discussing and gaining knowledge on all sort of topics etc, have persuaded the college students. And access of social networking sites on internet has become a major attraction to these students.

The social media has become one of the most important communication means in recent times. However, social networking exist so as to provide communication among people regardless of the distance, making it open to people easily share information, files and pictures and videos, create blogs and send messages, and conduct real-time conversations. These systems are referred to as social, simply because they allow communication with buddies and co-workers so easily and effectively. It also strengthens the ties between people of those systems. The favorite in the realm of internet sites are Facebook, Twitter and others. These websites and social forums are way of communication directly with other people socially and in media. They are playing a large and influential role decision-making in the occasions from the global world economically, politically, socially and educationally. The driving factors for adoption of social media are the progressively ubiquitous access, convenience, functionality, and flexibility of social technologies. It has been

contended that, poor greater education, social technologies supports social constructivist techniques to learning they potentially have to improve students' construction of understanding and promote student interaction. An additional benefit of social technologies provided on the internet is that they are frequently free or require marginal investment, eliminating a potential barrier to adoption. There has been various overview and opinions which recognized four major advantages of social media use in higher education. These include, enhancing relationship, improving learning motivation, offering personalized course material, and developing collaborative abilities. This means that social networking activities have the possibility of enhancing student contact and is used to improve their participation in class, particularly where introverted students are involved. Students can function in online group learning, with less or no anxiety of needing to raise questions before peers at school.

## Review of Literature

Different researchers have conducted research to ascertain the influence of social media on users; for example, Moon (2011) in a study on "impact of facebook on undergraduate academic performance", averred that social media have negative impact on students. According to the result, the more students use facebook, the more it affects their academic performance. Similarly, Oye (2012) notes that most of the younger students use social networking sites mainly for socialising activities, rather than for academic purpose. Oye (2012) further observed that most of the students do feel that social networking sites have more positive impact on their academic performance. In another study conducted by Shana (2012), it was revealed that students use social network mainly for making friends and chatting. The result showed that only 26 percent of the students (respondents) indicated that they use social media for academic purpose. Seo (2004) corroborates Jeong's assertion when he opined that the negative influence of internet is only on excessive users and not on all users.

## Statement of Problem

The expansion in technology has also affected internet software, thus leading to chatting sites known by the name "social media". However the study will evaluate the impact of social networking on academic performance of college students.

## Need & Purpose of the study

It is a common scene to see a youth chatting in sensitive and highly organized places like church, mosque and lecture venues. Some are so carried away that even as they are walking along the highway, they keep chatting and put their lives in danger. The manufacturing and distribution of equally sophisticated cellular phones has complicated the situation, as youths no longer need to visit a cybercafé before they send and receive messages. Attention has been shifted from visible to invisible friends, while important ventures like studying and writing are affected in the process. This phenomenon has become a source of worry to many who believe in knowledge and skill acquisition.

The emergence of social media as a result of advancement in technology and expansion in internet software has raised eye brows among academics on its (social media) impacts on studies. Students at all levels of learning now have divided attention to studies, as a result of available opportunities to be harnessed from social media. Whether these opportunities promote studies is a question that needs to be answered. Thus, the study investigated the "Impact of social networking on the academic performance of senior college students."

## Objectives of the study.

- To analyse the time spent by the students on internet daily.
- To evaluate the students perception towards usage of social networking sites.
- To study the daily pattern of college attendance, tuitions and study time spent by students.
- To analyse the length of time since the student is using internet on mobile.
- To study whether the student is aspired to check social networking sites during studies.
- To evaluate how the use of internet have improved the learning pattern of students.

- To analyse whether it has been assumed that the use of social networking sites has become a status symbol among students.

**Hypothesis:**

Ho: There is no relationship between the use of social networking site and the academic performance of senior college students.

**Data collection:**

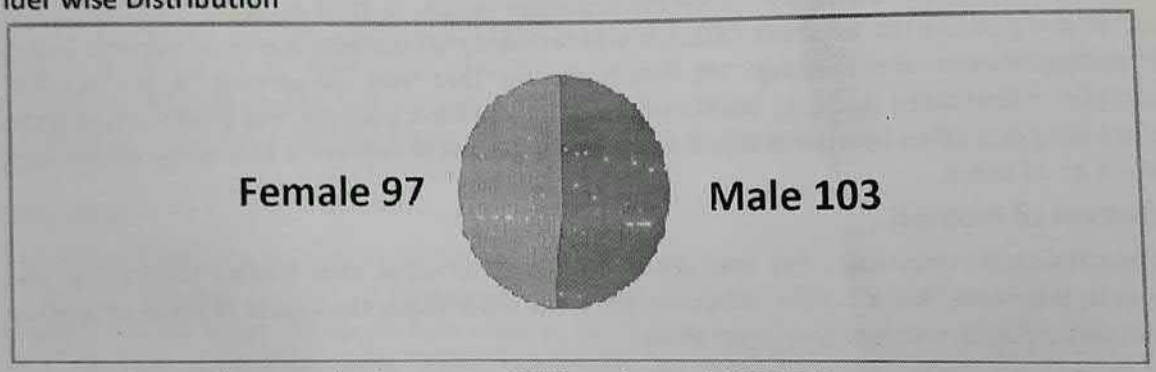
- Primary data was collected through questionnaire mailed through electronic media.
- Secondary data was collected from magazines, books and internet.

**Sampling:**

- Universe: Area was selected from Amravati city with the help of cluster sampling, the traditional senior colleges of commerce in the cluster.
- Size: 200 respondents.
- Sampling method: Disproportionate stratified random sampling method.

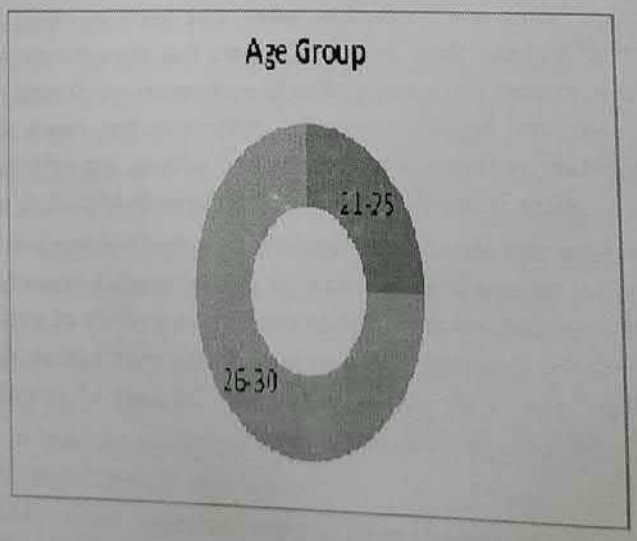
**Analysis and Interpretation**

**ender wise Distribution**



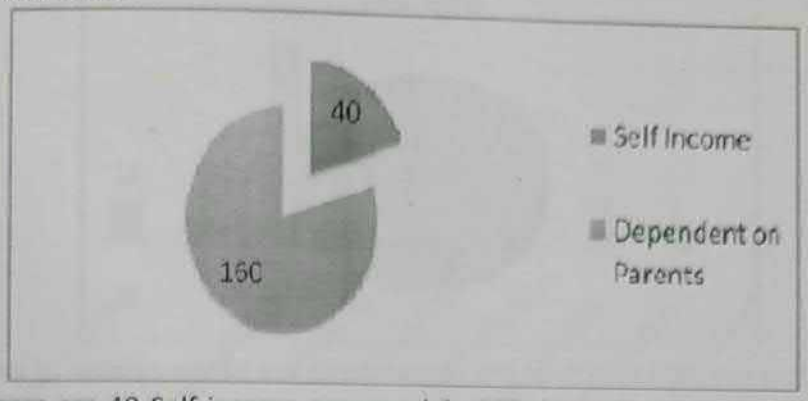

**Interpretation: In the sample there were 97 Females and 103 Male.**

**Age wise Distribution**



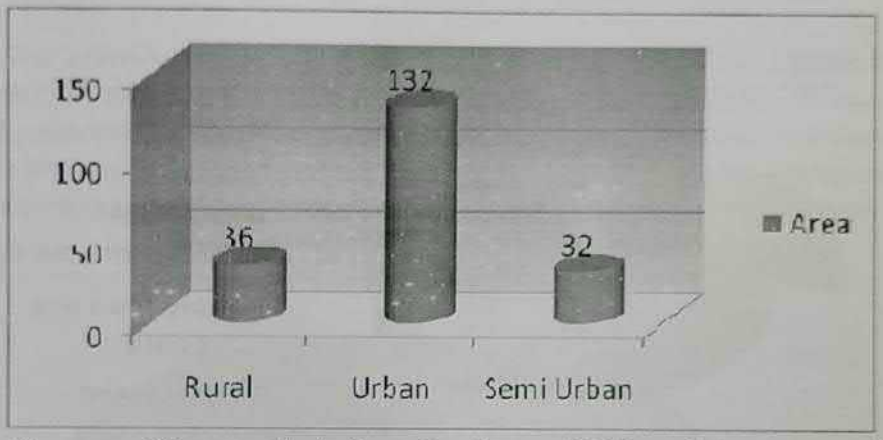
**Interpretation:** There are 150 respondents who are of the age group of 26-30 and 50 respondents are of 21-25 age group.

**Income wise Distribution**



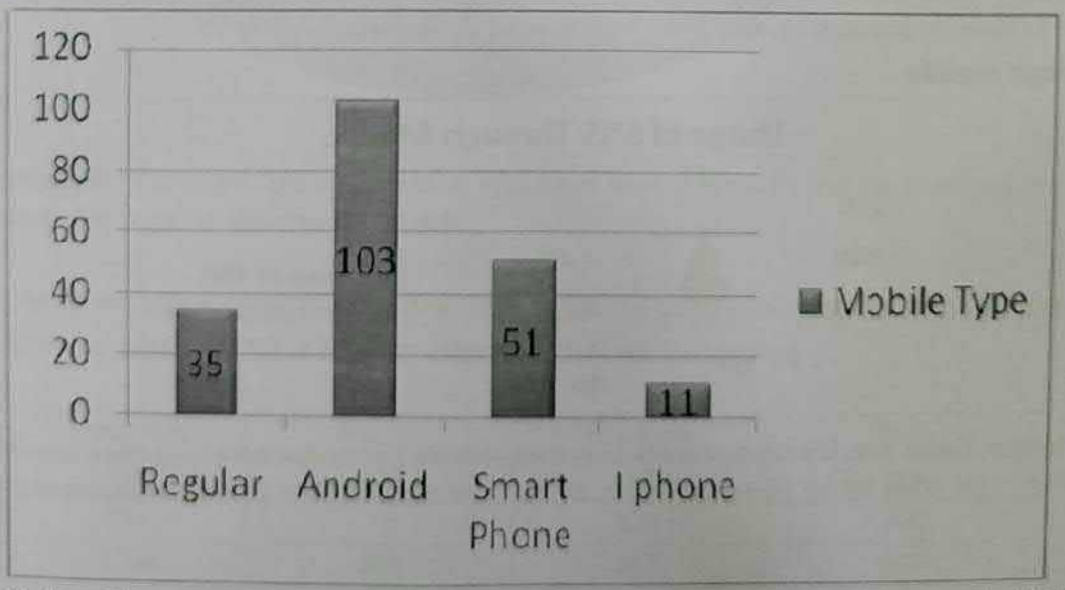

**Interpretation:** There are 40 Self income earner while 160 dependent on parents for their income source.

**Area Wise Distribution**



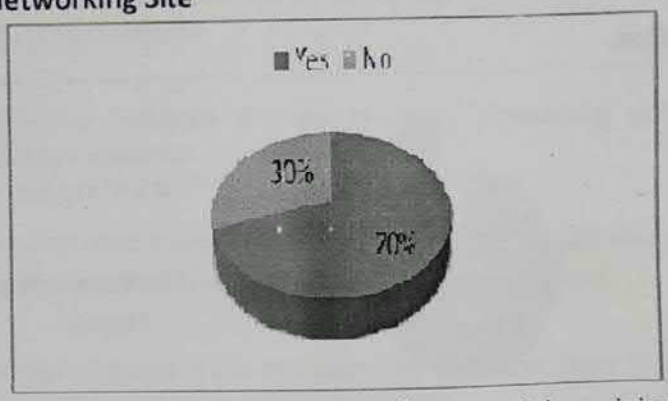

**Interpretation:** There are 36 respondents from Rural area, 132 from Urban area and 32 from Semi Urban area.

**Type of Mobile**



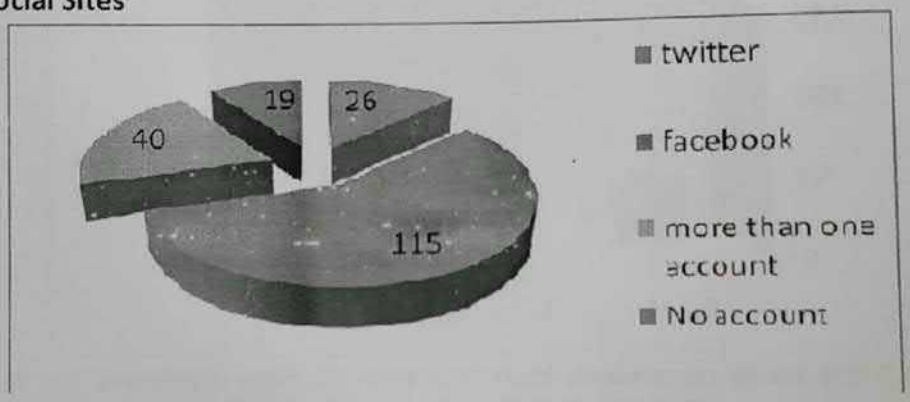

**Interpretation:** There are 35 respondents who have Regular Mobile, 103 who have Android Mobile, 51 who have Smart Phones and 11 who have I phones.

**Necessity of Social Networking Site**



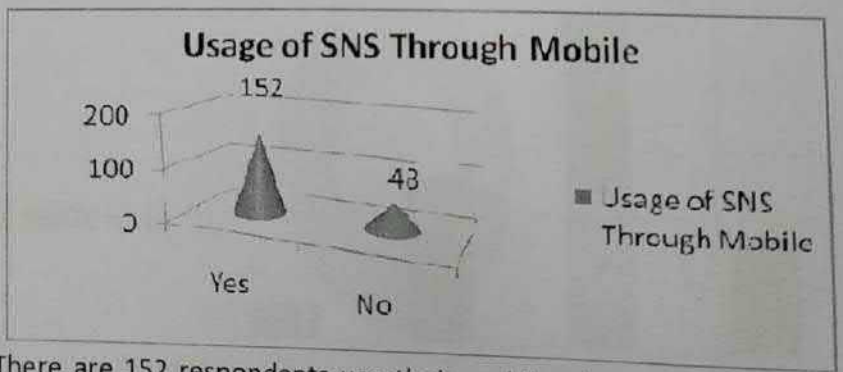

**Interpretation:** There are140 i.e. 70% of the respondents are of the opinion of having an account on SNSs while 60 i.e. 30% of the respondents feel that there is no need of opening or having an account on these sites. Therefore it may be said that having an account on these sites have become necessary among students for collaborative learning as well as have become status symbol among students.

**Preferred Social Sites**



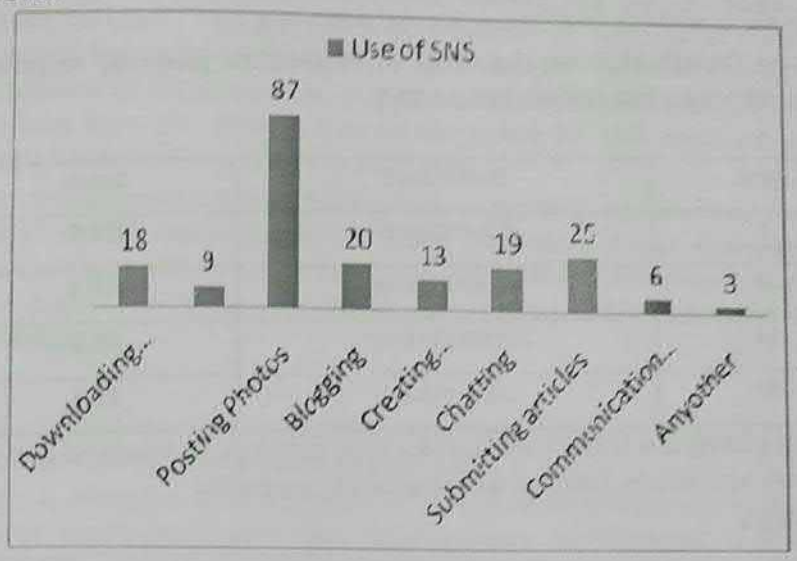

**Interpretation:** There are 26 respondents out of 200 who prefer twitter account, 115 respondents have facebook account, 40 respondents prefer more than one account on these sites while 19 respondents have no account on any of the social networking sites.

**SNS through mobile**



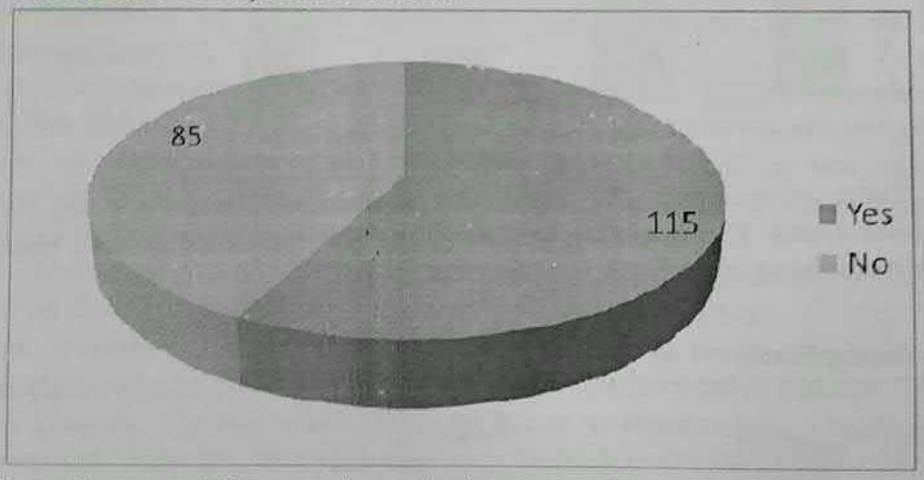

**Interpretation:** There are 152 respondents use their mobile phone for accessing their account on social networking sites while 48 respondents do not use their mobile phone for operating these sites.

**Primary use of SNS**




**Interpretation**: The primary use of SNS is for posting photos responded by 87 respondents, 25 respondents use it for submitting articles, 20 respondents use it for blogging, 19 respondents use it for chatting, 18 respondents use it for downloading music/videos, 13 respondents use it for creating polls/quizzes or surveys, 9 respondents use it for uploading music/videos, 6 respondents use it for communication with teachers/class fellow, 3 respondents use it for any other purpose.

**Friends on SNS are more compared to real life**




**Interpretation:** There are 115 respondents who have more friends in real life than real life and 85 respondents don't agree with this statement.

Testing of Hypothesis through Chi Square for proving SNS to be an effective tool for E-learning

**Hypothesis for testing: SNS is NOT an effective tool for E-learning**

| E-learning | Friends | Teachers | Total |
|---|---|---|---|
| Yes | 128 | 72 | 200 |
| No | 72 | 128 | 200 |
| Total | 200 | 200 | 400 |

**Conclusion:**

The calculated value is 31.36 which is greater than the table value 3.841. Hence, our hypothesis that SNS is not an effective tool for e-learning is proved wrong.

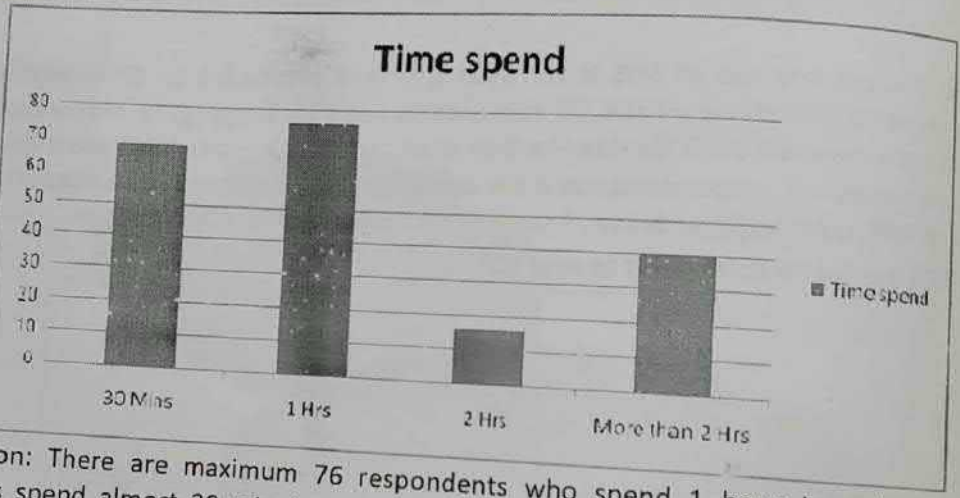
Therefore, we can say that SNS is an effective tool for e-learning

**Weighted Average Distribution on the basis of Preference given by respondents on the choice of community they join/subscribe on SNS.**

| Rank | Particulars | Score |
|---|---|---|
| I | Educational | 59.6 |
| II | Informational | 52.4 |
| III | Entertainment | 50.8 |
| IV | Any other | 32.4 |

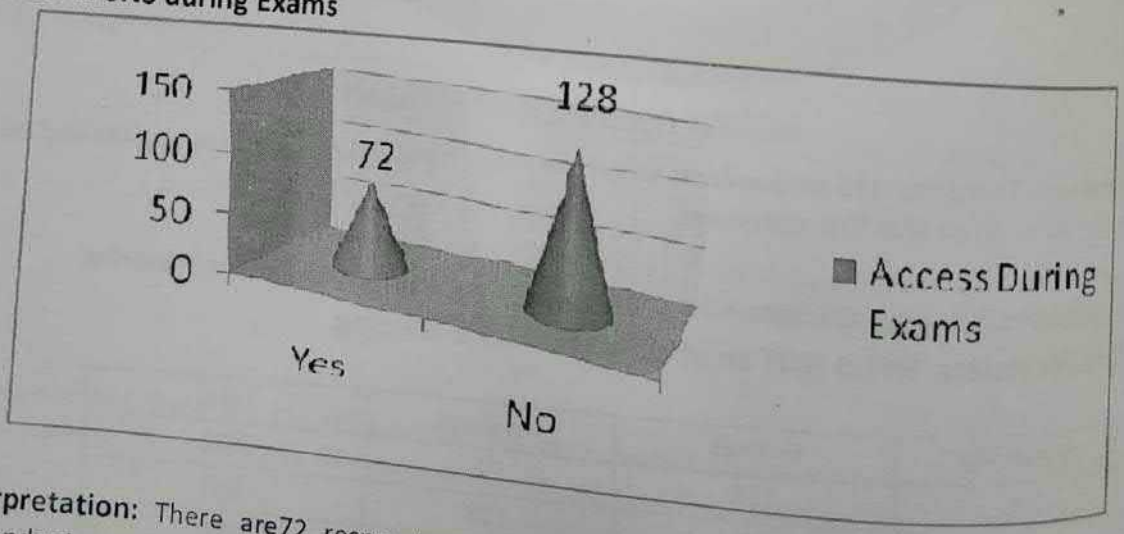
**NOTE:** Respondents stating any other communities were asked as to reasoned that they subscribe communities for marriage, sports, hobbies, astrological etc. purposes.

**Time spend on SNS's**




Interpretation: There are maximum 76 respondents who spend 1 hour in a day on SNS, 68 respondents spend almost 30 minutes on SNS whereas, 16 respondents spend 2 hours and 40 respondents for more than 2 hours a day.

**Access of SNS during Exams**




**Interpretation:** There are72 respondents accesss their SNS account during exams while 128 respondents are matured enough and don't access their account during exams.

**Findings:**

Positive perceptions obtained from users of social networking sites i.e. effective learning which has resulted in an easy learning climate among students. Through the study it has been explored that

how social networking sites encourage friendliness through the use of Facebook, Twitter and watsapp. The study concluded that numerous approaches can be used to encourage amiability among students which leads to a positive effect from SNSs user's point of view. It has been found that Facebook networking site is used by students more frequently and also faculty members. Recent data obtained from net, showed that approximately 297,000 users are university faculty members, although there are pros and cons in each case.

It has been found that internet is advantageous to both students and teachers if used as a tool of knowledge creation and dissemination. In the study conducted, it was observed that maximum students spent almost 1 hour daily on these sites as well as there are maximum of 128 out of 200 respondents who don't access these sites during exam which on the other hand don't affect their academic performance.

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