

‘हमारे हिस्से का सूरज’ काव्य में दलित विमर्श

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दलित शब्द –आकाश, वेदना, पीडा, चुनन, घुटन, छटपटाहट आह का परिचायक है। शोषित, पीडित समुदाय की वेदना पीडा और छटपटाहट को व्यक्त करने वाला साहित्य दलित साहित्य है। आज दलित साहित्य जागृति और गुलामी से मुक्ति पाने का संदेश भी दे रहा है। दलित साहित्य में दलितों की समस्या, वेदना और व्यक्तिगत संघर्ष को अभिव्यक्त किया गया है।

हिंदी दलित कविता का प्राथम आठवें दशक से माना गया है। इससे पहले एन.सिंह संपादित काव्य संकलन ‘दर्द का दरतावेज’ प्रकाशित हो चुका था। आठवें दशक के प्रारंभिक दौर में माता प्रसाद, पुरुषोत्तम सत्यप्रेमी, सोहन लाल सुमनाक्षर, ओमप्रकाश वाल्मीकि, जयप्रकाश कदम, दयानंद बटोही, रमणीका गुप्ता, डा. सुशीला टाकमोरे आदि ने कई दलित काव्य संग्रहों का संकलन कर हिंदी दलित साहित्य को अपना उत्कृष्ट योगदान दिया है।

आप सब ने दलित समुदाय की पीडा को शोषण, अत्याचार, वर्ण भेद, ऊच-नीच, भेद-भाव, अश्लील गालिया आदि का विरोध करते हुए दलितों में उभरने वाले अस्मिता को अभिव्यक्त किया है। सुशीला जी ने दलित वर्ग के प्रति मानवीय वेदना का यथार्थ चित्रण अपने काव्य में चित्रित किया है। सदियों से दलित बिना आवाज उठाए सदणों का शोषण सहते आ रहे हैं। इसका चित्रण कवयित्री ने ‘स्वयं को पहचानो’ कविता में व्यक्त किया है –

हमारी जाति हगारा धर्म हमारा नयिष्य
हमारा कर्म ।
मनुस्मृति काल से आज तक अपनी जगह पर अटल ।
“(28)

कवयित्री कहती है मनुस्मृति के आधार पर ही दलित अपने अधिकारों से वंचित रह गए हैं। हमेशा समाज ने उनको हीन दृष्टि से देखा है। दलितों ने

कभी अपने बारे में नहीं सोचा है। आकाश कविता में सुशीला जी लिखती हैं–

“स्मृति काल से जो
उपेक्षित अमान्य माना गया
उसे आज तक क्या मिला?
सोचा कभी आपने।” (55)
मेरे पूर्वज । ब्राह्मणवादि युग
उत्तर वैदिक काल से दोते आए हैं
सदिया। एक बोज़ की तरह। (34)

जाति या वर्ण के आधार पर मूल्य अशिक्षा, आर्थिक विपन्नता आदि से घरत दलित समाज को डॉ. बाबासाहेब आंबेडकर नामक मसीहा मिले, उन्होंने दलितों के अधिकार व्रत जीवन में समता स्वतंत्र, बंधुता सामाजिक न्याय रूपी प्रकाश लाने के लिए अपना समग्र जीवन व्यतीत किया और वे सफल भी हुए। दलित की मूक यातना को, वेदना को शब्दों के माध्यम से सुशीला जी यातना के स्वर कविता में देख सकते हैं–

दलित– पीडित, अपाहिज पीडिया

न कुछ समझ पाई, ना कुछ कह पाई अपना
दुख दर्द अन्याय अत्याचार को समझते रहे जीवन का
यथाथ। (11)

वर्ण व्यवस्था के कारण सदियों से दलित अशिक्षित ही रहे। कभी प्रगति के पथ पर आगे बढ़ने की कोशिश नहीं किया। उनके प्रति संवेदना प्रकट करते हुए हमारे हिस्से का सूरज कविता में सुशीला जी लिखती हैं–

सदियों की गुलामी है
ऊपर देखने की आदत ही नहीं है
कैसे देखेंगे क्रातिसूर्य को
कैसे समझेंगे
जागृति और परिवर्तन को प्रकाश
को।”(9)



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भोगे हुए अनुभव को प्रामाणिक रूप से चित्रित करते हुए कवयित्री सामाजिक असमानता, आर्थिक विघ्नता, शिक्षा का अभाव, छुआछूत की समस्या, ऊच्च-नीच की भावना दलित समाज में जाति छुपाने की प्रवृत्ति आदि कई समस्याओं का चित्रण अपनी कविताओं में किया है। दलितों को स्वाभिमान प्रदान करने का महत्त्व कार्य डॉ बाबासाहेब आंबेडकर जी ने किया उन्हीं के मार्ग पर चलते हुए कवयित्री भी अपने समाज को जागृत करने का प्रयत्न किया है और दलित पीड़ा को अछूत कविता के माध्यम से अभिव्यक्त किया है।

इस तरह हमारे हिस्से का सूरज का रायह में लेखिका ने दलित समुदाय की पीड़ा, गुलाब शोषण यात्रा को शब्दों के माध्यम से काव्य रूप में प्रस्तुत किया है। उन्हें जागृत करने का प्रयास किया है और सामाजिक, राजनीतिक, आर्थिक स्थिति से लड़ते हुए आगे बढ़ने का संदेश भी दिया है।

संदर्भ पुस्तक

- हमारे हिस्से का सूरज - डा सुशीला टाकभारे, शरद प्रकाशन, नागपुर, 2005

वे अछूत है। उन्हें न हवा हिला सकती है
वे सब जगह है। घर में, गली में गाव में, शहर में,
जन्मी अजन्मी सोच में। उन्हें कोई छू नहीं सकता
सब जानते है। वह कौन है। पर सब चुप है। (22)

आगे वे दलित कविता में लिखती है-

हम दलित बरसों से
दया सहानुभूति के विथडों में
लिपटे हुए थे। पर उन
विथडों को हमने उतार फेंका है। (मह दलित 51)

डॉ बाबासाहेब आंबेडकर ने दलितों के उद्धार के लिए बहुत परिश्रम किया उन्हें स्फूर्ति, प्रेरणा नया जीवन नयी लक्ष्य प्रदान किया सुशीला जी "जयभीम" कविता में लिखती है-

अपित कर अपना जीवन
सबके लिए जिया है आपने
निर्बल को बल मूंग को हुकार
दलितों में घतना संचार किया है आपने। (95)

दलित समुदाय को अपनी स्थिति पहचान करवाते शिक्षा के पथ पर आगे बढ़ने का संदेश देते हुए 'दलित घतना' कविता में लिखती है-
'दलित उत्थान का लक्ष्य दलित आंदोलन की सफलता
हमारे हाथ में है।'

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Applications of Nanomaterials in Environmental science and medicine

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Abstract

Nanomaterials are at the leading edge of the speedily emerging field of nanotechnology. Their exclusive size-dependent possessions make these materials superior and essential in many spaces of human activity. This brief assessment efforts to summarise the most recent developments in the field of applied Nanomaterials, in individual their application in environmental science and medicine, and deliberates their commercialisation predictions.

Key words; nanoparticles, Nanomaterials, environment, Nano medicine, catalysis, cancer therapy, biomolecules, environmental science

Introduction

Nanotechnology is enabling technology that deals with nano-meter sized substances. It is projected that nanotechnology will be established at several levels: materials, devices and systems. The Nanomaterials level is the most innovative at present, both in scientific knowledge and in commercial applications. A decade ago, nanoparticles were deliberate because of their size-dependent physical and chemical properties Now they have entered a commercial exploration period .

Out of plethora of size-dependant physical properties available to someone who is interested in the practical side of Nanomaterials, optical and magnetic effects are the most used for biological applications.

The aim of this review is firstly to give reader a significant prospective of nanomaterial application to environmental science and medicine, secondly to review the most recent progresses in this field, and finally to discuss the hard road to commercialisation. Hybrid bio Nanomaterials can be applied to build novel electronic, optoelectronic and photonic devices. However, the safety and toxicity of these materials, this will not be discussed here and will be a subject of a separate article.

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Generally, Nanomaterials are currently classified as

- (i) metal-based ,
- (ii) carbonbased
- (iii) dendrimers, and
- (iv) Composites. Generally, carbon-based Nanomaterials contain carbon, and are found in morphologies such as hollow tubes, spheres ellipsoids. Metal-based Nanomaterials are metal based materials that we commonly regarded as, nano silver, nano gold and oxide dramatic dots, s with metal bases. Titanium dioxide is one such example. They are a focus of the pharmaceutical and biomedical industries.

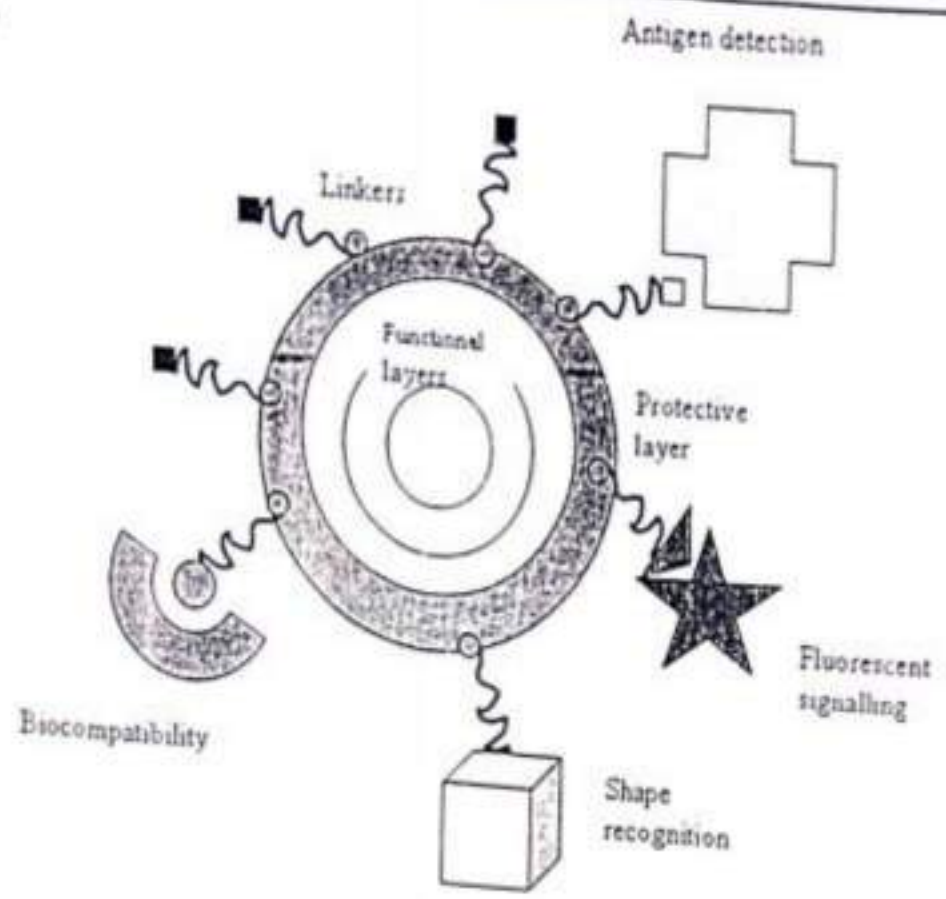
NANOPARTICLES AND NANOMATERIALS

Composites are combination of nanoparticles or nanoparticles and other materials. Nanoparticles, such as nano sized clays, are already being added to yields ranging from auto parts to packaging materials, to enhance mechanical, thermal, barrier, and flame-retardant properties. Although Ag, zinc oxide, copper oxide , cerium dioxide , titanium dioxide , iron oxide , fullerenes, carbon nanotubes , and a small number of others remain the most widely used and researched Nanomaterials , some newer Nanomaterials have been produced in recent years. The greatest interest and development has been in broad classes of materials including nano composites and nano hybrids.

Nano composites are Nanomaterials enclosed or encapsulated with other materials, which may not have nano scale features, whereas nano hybrids are the linking of 2 or more discrete NMs to give different functionality . Such NMs can be based on semiconductor substrates such as GaAs, CdSe, CdS, SiGe, and others, modified with shells and coatings, along with mixtures of carbon-carbon and carbon-metal or metal oxides

Applications

- Fluorescent natural labels Drug and gene conveyance
- Bio recognition of pathogens Detection of proteins Probing of DNA structure Muscle engineering Tumour destruction via heating (hyperthermia)
- Separation and sanitisation of biological fragments and compartments
- MRI distinction enhancement



configurations utilised in nano-bio materials applied to medical or biological problems.

Tissue work

Natural bone external is quite often contains features that are about 100 nm across. If the surface of an artificial bone implant were left smooth, the body would try to reject it. Because of that smooth surface is likely to cause production of a fibrous tissue covering the surface of the implant. This layer reduces the bone-implant contact, which may result in loosening of the implant and additional tenderness. It was established that by creating nano-sized features on the external of the hip or knee prosthesis one could reduce the chances of denial as well as to stimulate the making of osteoblasts. The osteoblasts are the cells responsible for the growth of the bone matrix and are found on the advancing surface of the developing bone.

The effect was demonstrated with polymeric, ceramic and, more recently, metal materials. More than 90% of the human bone cells from disruption adhered to the nanostructured metal surface, but only 50% in the control sample. In the end this findings would allow to design a more durable and longer lasting hip or knee replacements and to reduce the chances of the implant getting loose.

Titanium is a well-known bone repairing material widely used in orthopaedics and dentistry. It has a high fracture resistance, ductility and weight to strength ratio. Unfortunately, it suffers from the lack of bioactivity, as it does not support cell adhesion and growth well. Apatite coatings are known to be bioactive and to bond to the bone. Hence, several techniques were used in the past to produce an apatite

coating on titanium. Those coatings suffer from thickness non-uniformity, poor adhesion and low mechanical strength. In addition, a stable porous structure is required to support the nutrient transport through the cell growth.



It was shown that using a biomimetic approach – a slow growth of nanostructured apatite film from the simulated body fluid – resulted in the formation of a strongly adherent, uniform nanoporous layer. The layer was found to be built of 60 nm crystallites, and possess a stable nanoporous structure and bioactivity.

A real bone is a nanocomposite material, composed of hydroxyapatite crystallites in the organic matrix, which is mainly self-possessed of collagen. Thanks to that, the bone is mechanically tough and, at the same time, plastic, so it can recover from a mechanical damage. The actual nanoscale mechanism leading to this useful combination of properties is still debated.

An artificial hybrid material was prepared from 15–18 nm ceramic nanoparticles and poly (methyl methacrylate) copolymer. Using tribology approach, a viscoelastic performance (healing) of the human teeth was established. An investigated hybrid material, deposited as a coating on the tooth surface, improved scratch resistance as well as possessed a healing behaviour similar to that of the tooth.

Cancer therapy

Photodynamic cancer therapy is based on the destruction of the cancer cells by laser generated atomic oxygen, which is cytotoxic. A greater quantity of a special dye that is used to generate the atomic oxygen is taken in by the cancer cells when compared with a healthy tissue. Hence, only the cancer cells are destroyed then exposed to a laser radiation. Unfortunately, the remaining dye molecules migrate to the skin and the eyes and make the patient very sensitive to the daylight exposure. This effect can last for up to six weeks.

To avoid this side effect, the hydrophobic version of the dye molecule was enclosed inside a porous nanoparticle. The dye stayed trapped inside the Ormosil nanoparticle and did not spread to the other parts of the body. At the same time, its oxygen generating ability has not been affected and the pore size of about 1 nm freely allowed for the oxygen to diffuse out.

NANOMATERIALS ON THE ENVIRONMENT

The growing production and use of NMs in diverse industrial processes, construction, and medical and consumer products is resulting in increasing exposure of humans and the environment. Humans encounter Nanomaterials from many sources and exposure routes, including ingestion of food, direct dermal contact through consumer products and by inhalation of airborne Nanomaterials. The increasing use of Nanomaterials in our life or the customer productions has inevitably caused the accumulation exposure of the nanoparticles into the environment, yet the fate of these particles may greatly depend on their environmental medium, physical or chemical property.

Positive Impacts on the Environment Engineered Nanomaterials exhausted into the atmospheric environment tend to be exposed to sunlight and UV wavelengths at significantly higher degrees than those released into other compartments. This exposure is likely to increase the possible outcomes of photochemical changes to Nanomaterials.

Nanotechnology based detection systems vary in their mechanisms and designs but they share the same goal, that is, timely and accurate detection of trace pathogens or other contaminants [26]. Nanotechnology is of great use in many fields, in particular in the agrofood industry, where it is used primarily in: primary production, food processing and packaging and food supplements

Nanofertilizers have beneficial effects over conventional ones. This is the case of the use of zinc oxide nanoparticles in Zn fertilizers to increase their solubility [62; 63]. De la Rosa et al. [64] found that by applying zinc oxide nanoparticles through the foliar spray, growth and biomass of alfalfa, tomato, and cucumber can be increased

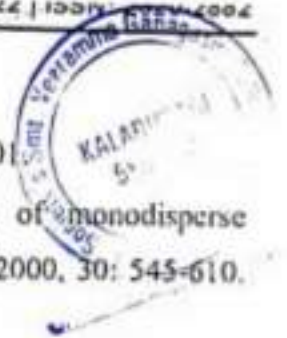
The presence of NMs was also demonstrated to exert low to high toxicity impacts on aquatic life. According to the toxicological investigations, Nanomaterials may affect unicellular aquatic organisms and creatures (e.g. fish and Daphnia). Several studies suggest that the toxicity of silver nanoparticles is attributed to their release of silver ions in cells as both silver nanoparticles and silver ions have been reported to have similar cytotoxicity.

CONCLUSION

The environment and on human beings. Accordingly, Nanomaterials can be compared as drugs because it is well known that they have both desired and undesirable effects. Until now, Nanomaterials have been explored for many different applications in diverse sectors including catalysis, sensing, photovoltaic, energy, environment, and biomedical. However, the level of Nanomaterials in the environment is consistently increasing.

The hazards of Nanomaterials to plants, animals and microbes have had an indirect effect on our humans. Increased attention needs to be directed towards the new Nanomaterials because the development of knowledge of these nanoparticles is still in its infancy. Since the shape, size and composition of nanoparticles can have both significant effects on their function and possible risks to human health, extensive research is needed to fully understand their synthesis, characterization, and possible toxicity.

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INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

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Principles and Applications of Green Chemistry

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Abstract:

The field of Green Chemistry had been inconceivable used towards detections and recognitions in science & technology by smearing twelve basic green chemistry ideologies. , we explained the attainments and developments of green chemistry by using Green Empathies. Each branch of Green Chemistry tree represents to corresponding each of the 12 ideologies, and plants represent the different areas of achievement relevant to that particular ideologies.

Keywords Green Chemistry, Green Chemistries, ideologies,

INTRODUCTION

Chemistry has indulge the beneficial things in the form of medicine, dyes, cosmetics, food products, nano particles, liquid crystal, polymers, paints, biomolecules, agrochemicals. Presently, various complex yields can be manufactured easily. Nevertheless, chemical progression not only yields the essential product but also the unwanted or undesired and harmful substance in large actions in the form of liquid, gases, and solid. Sustainability and Green chemistry go in one breath. Sustainable development is a process of reaching the requirements of the present era without negotiating the proficiency of unborn age group to complete their own needs. Its concepts inspire the designing of innovative processes and raw materials that minimizes the utilization of harmful substance and their manufacture This has become the enormous threat for the chemistry. So for the synthetic chemists the decrease of the chemical pollution has become the critical urgency.. Green chemistry's concepts stands for two most important components The concepts of Green chemistry are not new or unused rather it is new approach towards the sustainability.

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principles. Here, Each branch signify to each of the principle and leaves represent to the availability of the various techniques to the researchers employed in Green Chemistry research.



The Green ChemisTree importance the attainments

: Prevention: It is better to prevent the formation of waste than to treat it after it is formed. The various techniques corresponding to this principle include One-pot synthesis, circular economy, Process intensification, Self-Separation, Additive manufacturing, Combined processes, Excess as feedstock and Molecular home-made It is better to check the formation of waste than to treat it after it is formed.

The various techniques corresponding to this principle include One-pot synthesis, spherical economy, Process intensification, Self-Separation, Additive developed, Integrated processes, Waste as feedstock and Molecular self-assembly Less hazardous synthesis: "Wherever practicable, synthetic methods should be designed to use and generate substances that possess less or no toxicity to environment and human health".

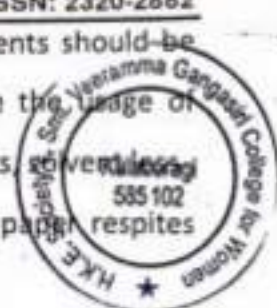
This principle cover Life cycle analysis, Green synthesis evaluation metrics, Non-metal catalysis, Energy efficiency metrics, Dialkyl carbonate reactions, Material efficiency metrics, C-H bond functionalization, Hazard and risk metrics,

: Atom condensed: Synthetic methods should be calculated in such a way that all the reactant materials combined in the process converted into products. Here, Each branch represent to each of the principle and plants represent to the availability of the various techniques to the researchers working in Green Chemistry research.

Degradable plan: Chemical products should be designed to innocuous degradable products and do not persist in the environment. The products which should be designed to innocuous degradable products are Benign metabolites, Read across, Green pharmaceuticals, , Degradable polymers, Reactivity parameters, Molecular triggers, Biodegradation databases, Metabolism, Prediction tools, Design guidelines. Incorporated in the process changed into products. The reactions came under this group are Grubbs metathesis, Reaction network optimization, Cycloaddition, Coupling reactions, Synthetic efficiency metrics, Rearrangement reactions, E-factor, Ring modification reactions and Aromatization reactions. **: Atom economy:** Synthetic methods should be designed in such a way that all the reactant materials

Safer chemicals: Chemical products should be designed to preserve efficacy whilst reducing toxicity. This principle explain the importance to design the benign chemicals. This principle propose the Enzymatic models, Read across, Modes of toxic action, , Reactivity parameters, , Design guidelines, Adverse outcome pathways and Metabolism ,

Harmless solvents: The usage of auxiliary substances like solvents and extrication agents should be made avoidable wherever possible and innocuous when used. This principle choose the range of important benign solvents such as Ionic liquids, Switchable solvents, Bio-sourced solvents, Greener surfactants, Water, Sub and supercritical liquids Concern of insides of this paper upon the authors and not upon the Editor & Publisher. and Gas-expanded liquids



Smart catalysis: The selective catalytic reagents are more superior than the stoichiometric reagents The selective catalytic reagents or processes were Nano catalysis, Solid acids and bases, Abundant metal catalysis, Clay/zeolites, Biocatalysis, Metalorganic frameworks, Enzyme engineering, Isolated enzymes, Ultra-low loadings, Control, Organo catalysis.

Energy efficiency: Energy requirements should be minimized and also conducted the synthetic methods at ambient temperature and pressure. The energy efficiency should be maintained by using Microwave irradiation, Electro catalysis, Mechano chemistry, Photo catalysis, Sono chemistry and Self-separation .

Renewable feedstocks: Wherever carefully and technically practicable then a raw material or feedstock should be renewable rather than draining. The usable Renewable feedstocks are Biofuels, Joined biorefinery, , Fermentation CO2 Biomass-to-chemical, Enzymatic progressions, Renewable platform chemicals, and New stage chemicals

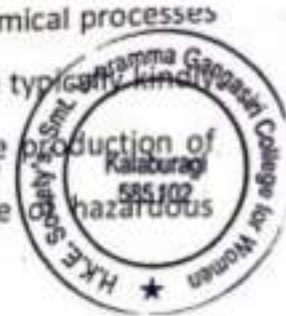
Reduce derivatives: Redundant derivatives should be avoided or minimized because such steps required additional reagents and can generate waste. The unnecessary derivatives should be removed by using Flow chemistry, Electro synthesis, Molecular chaperones, Click chemistry, Molecular self-assembly and Non-covalent derivatives

Smart catalysis: The selective catalytic reagents (Processes) are greater than the stoichiometric reagents (Processes). The selective catalytic reagents or processes were Nano catalysis, Solid acids and bases, Abundant metal catalysis, Clay/zeolites, Biocatalysts, Metalorganic frameworks, Enzyme engineering, Isolated enzymes, Ultra-low loadings, Immobilization, Organo catalysis ..

design: Chemical foodstuffs should be designed to innocent degradable harvests and do not continue in the air. The produces which should be designed to innocuous degradable products are Kind metabolites, Read across, Green pharmaceuticals, Degradable polymers, Reactivity limitations, Molecular triggers, Biodegradation records, Breakdown, Calculation tools, Enterprise guideline.

Real-time analysis for pollution inhibition: Real-time analytical procedures should be Responsibility of contents of this daily rests upon the authors and not upon the Editor & Publisher. developed to control the formation of hazardous residents. These Real-time analytical devices should be include Computational advances, Sensors, Spectroscopy, Continuous flow and investigation, Chromatography.

Hazardous and coincidence prevention: The chemical things and reagents used in chemical processes should be selected to minimize the risk for chemical accidents, explosion and fires. The typical green chemistry for coincidence prevention are Substitute the hazardous materials, On site production of hazardous materials, On-demand production of perilous materials and Reduced use of hazardous materials.



Applications

Metal organic frameworks cause the adsorptive elimination and panel of chemicals Removal of harmful chemicals and their parting from the atmosphere has become a vital issue. At present, adsorptive elimination is important for keep. Therefore, adsorption and separation of abundant nitrogen containing compounds, olefins, sulphur compounds and π -electron-rich vapours via π -complex expansion among an adsorbent and adsorbate molecules is very inexpensive. Absorbent metal-organic contexts are much knowledgeable in the adsorption or separation of different liquids and gases without damaging their dissimilar characteristics.

Production of carotenoids from natural sources The separation of Atisane-type diterpenoids are the principal essential of tetracyclic C20 -diterpenoids, widely inaccessible from the plant kingdom with changing grades of structural complexity and pharmacological activity. Different total synthesis is an active tactic to synthesize several artisans-type diterpenoids using physical interconversion from a common intermediate. They are also very helpful in production of carotenoids.

human bone standby with Coral skeletons Coral skeletons can redevelop replacement human bone in nonloadbearing exhumed skeletal locations. A combination of multiscale, interconnected pores and channels and highly bioactive surface chemistry has established corals as an important different to using healthy host bone substitutions.

. Liberal Omachineries in coral aquaculture and self-organization inorganic chemistry are serving to modify natural corals and create synthetic coral architectures able to accelerate bone improvement with proper host adding at more skeletal locations, modified to recent surgical methods and used to treat intrinsic emaciated abnormalities and metabolic conditions.

Sildenafil citrate: It is first drug which was effectively used for oral treatment for erectile dysfunction. -. The redesigned chemistry process proved to be beneficial for sildenafil citrate, as it increased the yield significantly. This process developed production, decreased the wastage of green solvents like ethyl acetate, water and tertiary Polymer

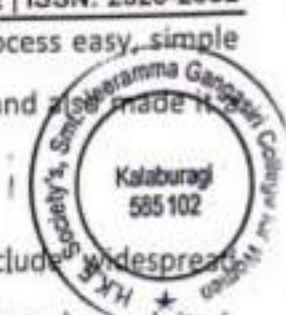
-butanol. According to the progress process ethyl acetate could be used over three fixed steps

i.e. a) Addition of hydrogen, b) Activation by acid, c) Acylation, which made the process easy, simple and eliminated the requirement of totally alteration solvents among entire steps, and a) most important energy saving and waste elimination solvent method.

Polysaccharide Polymers: They are an essential group of compounds that include packages. they have got their dangerous consequences. The big range of compounds can be exploited. Polysaccharide because the feedstock have to be used as opening materials due to the fact that it's far extra globally feedstock. Those are organic and have the benefit of being renewable or viable, in place of petroleum feedstock. On the opposite side these don't have any chronic toxicity to environment and health of humans Extraction of Carotenoids from Microalgae and Seaweeds The production of carotenoids from algal sources at large scale made it most famous topic of interest for productions and also for marketable level. Marine microalgae and seaweeds are the sustainable cause of several physically active substances. They are source for various natural carotenoids including, astaxanthin β -carotene, zeaxanthin, violaxanthin, lutein, and fucoxanthin. Conventional processing techniques serve simple procedure to isolate carotenoids. They suffer some, innate limits including low efficiency, consumption of solvent in large amount, its selectivity and time for long treatment, leading to new advancements in the search for inventive withdrawal machineries like green chemistry.

Conclusion:

The discussing the broad spectrum of Green Chemistry original investigation from review articles show not only the conventional developments used in academic examination, but also the performing of progressive procedures and progressive conservational benign methods in industry. Here, we can also explain the developments and achievements of green chemistry by using Green tree. Each branch of green chemis tree Polymer signifies to corresponding each of the twelve principles, and leafs represent the dissimilar areas of attainment related to t Reaction network optimization, Cycloaddition, Coupling reactions, Synthetic productivity metrics, Rearrangement reactions, E-factor, Ring adjustment reactions and Aromatization reactions . Remarkably essential to make the green chemistry ideas clear among students for better outcomes which initiated with pollution free raw material and detection no secondary product and does not need any solvents for purification, separation and chemical conversion.



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CYCLIC VOLTAMETRIC AND DNA CLEAVAGE STUDIES OF INDOLYL CARBOHYDRAZIDES

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ABSTRACT

The indole analogues were investigated for the electrochemical behavior using the glassy carbon electrode as the working electrode. In the present study electrochemical reduction or oxidation of indole analogues in sulphuric acid media was reported. We can see that the C-N functional group in the molecule is easily reduced at the glassy carbon electrode. These compounds were also subjected to DNA cleavage study. In this study Compounds Ia-c have shown highest activity and remaining compounds shown moderate activity. Compounds with halogen, methyl substitution at five positions and phenyl ring at third position of indole nucleus have exhibited very good activity when compared to standard.

Key words: Indole, Carbohydrazide, DNA Cleavage activity, Cyclic voltametry

INTRODUCTION

Synthesis of indole analogues have found great significance due to their wide spectrum of biological and pharmacological activities [1]. Indole derivatives were reported to have biological effects [2], anti-inflammatory [3], antitubercular [4] and antimicrobial [5] activities. Tri-indole derivatives possess antifungal [6], antimicrobial [7], antibacterial, analgesic [8, 9], anticonvulsant [10], antioxidant [11], antihypertensive [12], and antiviral agents [14]. For the synthesis of heterocyclic compounds carbohydrazides are well known as useful building. A large number of heterocyclic carbohydrazides derivatives are reported to exhibit significant biological activities [15,16]. Cyclic voltammetry (CV) is an widely used electroanalytical technique that allows studying redox processes of molecules particularly in organic and metal-organic systems, electrochemical behaviour of complex chemical and biochemical systems [17]. Indole analogues are well-known electro active compounds that are readily oxidized or reduced at carbon based electrodes, i.e. glassy carbon electrode [18-20]. Some new indole analogues with highly potent antioxidant, DNA cleavage, antimicrobial, anti-inflammatory, analgesic, CNS depressant, activities and cyclic voltametric studies [21-25], were described previously. As the indole derivatives exhibit broad spectrum of biological activities we thought of making molecules which are bioactive compounds.

EXPERIMENTAL

CYCLIC VOLTAMETRY STUDIES

INSTRUMENTATION

The electrochemical experiments were carried out using a model-660 Electrochemical Workstation (CHI660c). All experiments were carried out in a conventional three-electrode system. The electrode system contains a working Glassy Carbon electrode, a platinum wire as counter electrode and saturated calomel electrode as reference electrode (a reference electrode, typically Ag/AgCl). Experimentally, the potential of a working electrode is linearly scanned Vs a reference electrode from an initial value to a final value and back. Thus, forward and backwards electrochemical reactions can be studied. This is a typical cyclic voltammetric experiment of substrate (indole derivative), reaction mixture consisted of indole derivative solution, ethyl alcohol and sulphuric acid media was used for the electrostatic reduction. The three electrodes were connected to a computer controlled potentiostat and required potential scan rate, current sensitivity, initial potential and final potential were fixed and the resulting current measured as a function of applied potential.

Pre-treatment of glassy carbon electrode

Before each measurement, Glassy-carbon electrode is generally pre-treated either electrochemically or mechanically to obtain a reproducible electrode surface. Electrochemical pre-treatment is usually performed by cyclic scanning over a wide potential range. Mechanical polishing is generally performed by polishing the glassy-carbon electrode with alpha alumina powder (0.3µ) on rubbing pad and then rinsed with purified water until there were no visible markings or scratches. This procedure was repeated after each set of experiment.

DNA CLEAVAGE ACTIVITY

Preparation of culture media

DNA cleavage experiments were done according to the literature [26]. Nutrient broth [peptone, 10; yeast extract, 5; NaCl, 10; in (g/l)] was used for culturing of *Escherichia coli*. Fifty-milliliter media was prepared, autoclaved for 15min at 121°C under 15lb pressure. The autoclaved media were inoculated for 24h at 37°C.

Isolation of DNA

The fresh bacterial culture (1.5mL) was centrifuged to obtain the pellet which was then dissolved in 0.5mL of lysis buffer (100mM Tris pH 8.0, 50mM EDTA, 10% SDS). To this 0.5mL of saturated phenol was added and incubated at 55°C for 10min, then centrifuged at 10,000 rpm for 10min and to the supernatant, equal volume of chloroform: isoamyl alcohol (24:1) and 1/20th volume of 3M sodium acetate (pH 4.8) was added. Centrifuging at 10,000 rpm for 10min and to the supernatant, 3 volumes of chilled absolute alcohol were added. The precipitated DNA was separated by centrifugation and the pellet was dried and dissolved in TAE buffer (10mM Tris pH 8.0, 1mM EDTA) and stored in cold condition.

Agarose gel electrophoresis

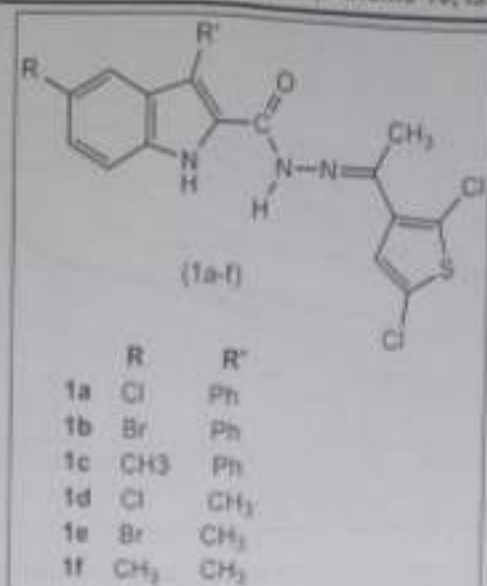
Cleavage products were analyzed by agarose gel electrophoresis method [27]. Test samples (1 µg/mL) were prepared in DMF. The samples (25µg) were added to the isolated DNA of *E. coli*. The samples were incubated for 2hr at 37°C and then 20mL of DNA sample (mixed with bromophenol blue dye at 1:1 ratio) was loaded carefully into the electrophoresis chamber wells along with standard DNA marker containing TAE buffer (4.84 g Tris base, pH 8.0, 0.5M EDTA/1L) and finally loaded on agarose gel and passed the constant 50V of electricity for 30min. Removing the gel and stained with 10.0 mg/mL ethidium bromide for 10-15min, the bands were observed under Vilber Lourmat Gel documentation system and then photographed to determine the extent of DNA cleavage. The results are compared with standard DNA marker.

RESULT AND DISCUSSION

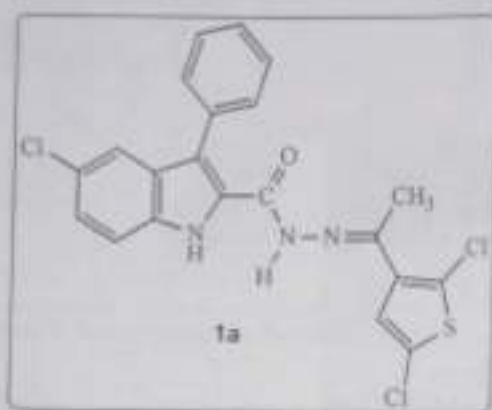
Cyclic Voltammetry Studies

Cyclic voltammetric studies of 3,5-Disubstituted-N-(1-(2,5-dichlorothiophen-3-yl)ethylidene)-1H-indole-2-carbohydrazide (1a-f). 3,5-Disubstituted-N-(1-(2,5-dichlorothiophen-3-yl)ethylidene)-1H-indole-2-carbohydrazide derivatives were synthesized by reported methods [23] scheme-1. Cyclic voltammogram and reduced structure of 5-chloro-N-(1-(2,5-dichlorothiophen-3-yl)ethylidene)-3-phenyl-1H-indole-2-carbohydrazide (1a) as shown in Scheme-2 (Fig. 01) at a glassy carbon electrode in 25mM sulphuric acid media at scan rates 100 mVs⁻¹. The compound showed a cathodic peak potential at -0.636 V for the reduction of the C=N moiety. The quasi-reversibility was confirmed by the presence of an anodic peak between the potential of -1.0 mV to -1.0 mV. The effect of scan rate was studied and cathodic peak current was proportional to the scan rate and the process is diffusion-controlled. From the Fig. 01, we can see that the C=N functional groups in the molecule is easily reduced at the glassy carbon electrode. The reduction potential value is -0.636V which has chloro substitution at five position of indole. Variation of scan rate from 50 mVs⁻¹ to 250 mVs⁻¹ is shown in Fig. 02. With the increase of scan rate, the quasi-reversibility becomes completely irreversible in nature and the absence of anodic peak in the reverse direction.

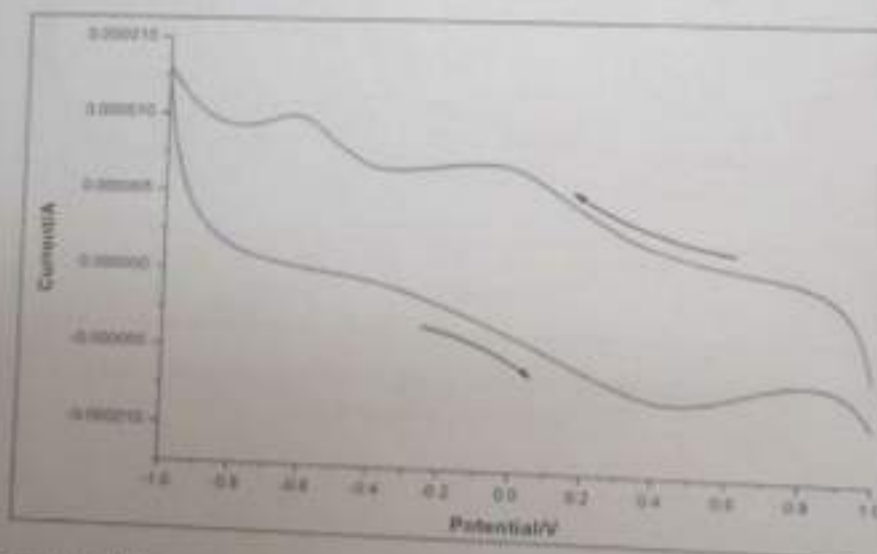
Cyclic voltammogram of (1-(2,5-dichlorothiophen-3-yl)ethylidene)-5-methyl-3-phenyl-1H-indole-2-carbohydrazide (80c) (Fig. 03) studied at a glassy carbon electrode in 25mM of sulphuric acid media at a scan rates of 100 mVs⁻¹. The compound showed a cathodic peak potential at -0.633 V for the reduction of the C=N function. The irreversibility was confirmed by the absence of an anodic peak between the potential of -0.8 mV to -1.0 mV. The effect of the scan rate was studied and the cathodic peak current was proportional to the scan rate and the process is diffusion-controlled. From Fig. 03 We can see that the C=N functional groups is easily reduced at the glassy carbon electrode. The reduction potential value is -0.633 V for methyl substituted at five position of indole. Variation of scan rate from 50 mVs⁻¹ to 300 mVs⁻¹ there is no change in the nature and remains irreversible as shown in Fig. 04.



Scheme 1. Schematic representation of indole analogues (1a-f).



Scheme 2. Probable structure of reduced compound 1a

Fig. 1. Cyclic Voltammogram of 80a at glassy carbon electrode in 25mM Sulfuric acid at scan rate 0.1Vs⁻¹ (1a)

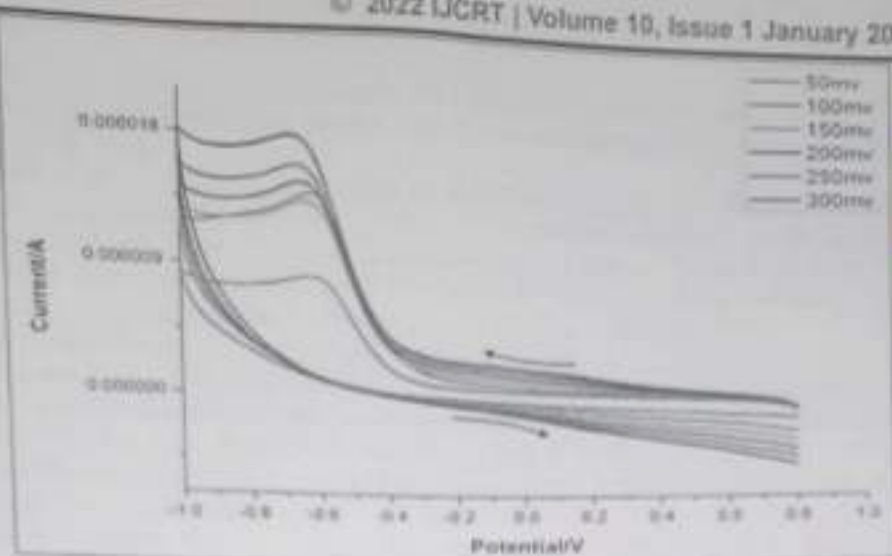


Fig. 4. Variation of scan rate from 50mVs^{-1} to 300mVs^{-1} (1a)

DNA CLEAVAGE ACTIVITY

Among the synthesized compounds have been subjected to DNA Cleavage studies. The DNA cleavage activity was determined using gel electrophoresis by Sambrook et.al [26]. The pictures of the gels are presented in Fig. 5. When the compound is made to interact with DNA could induce the breakage of DNA strands. The gel electrophoresis clearly reveal that, all the tested compounds did act on the DNA as little tailing in the bands can be observed in treated samples. The difference was observed in bands of all the compounds compared to the control DNA (C). This shows that the control DNA alone does not show any apparent cleavage as the compounds did. With this, it can be concluded that the compounds inhibits the growth of the pathogenic organism by cleaving the genome. Compounds 1a-c, have shown highest activity and remaining compounds shown moderate activity. Compounds with halogen and methyl substitution at five position and phenyl ring at third position of indole nucleus have exhibited very good activity when compared to standard.

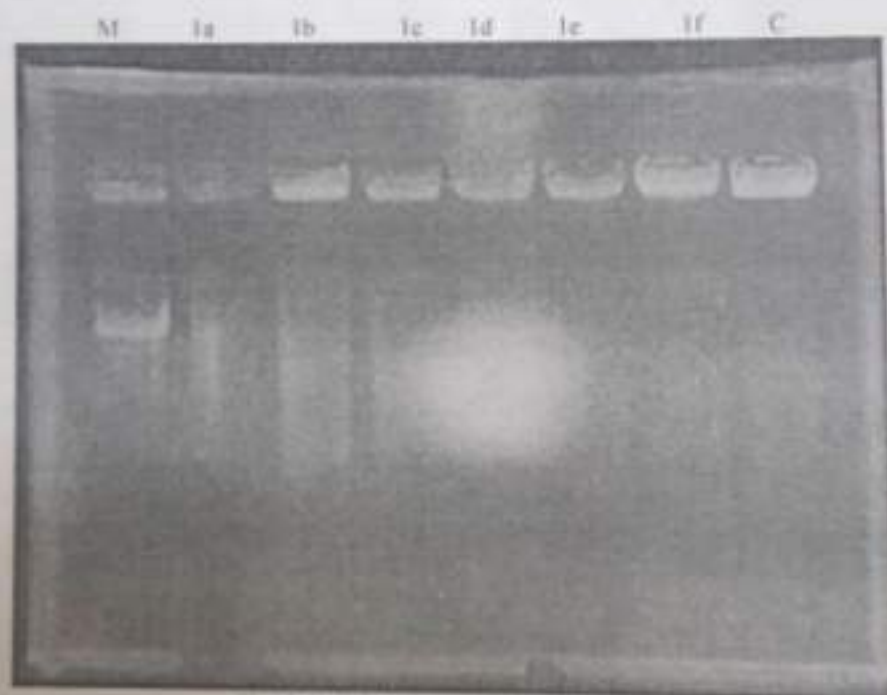


Fig. 5. DNA Cleavage Activity of (1a-f).

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Applications of Nanomaterials in Environmental science and medicine

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Abstract

Nanomaterials are at the leading edge of the speedily emerging field of nanotechnology. Their exclusive size-dependent possessions make these materials superior and essential in many spaces of human activity. This brief assessment efforts to summarise the most recent developments in the field of applied Nanomaterials, in individual their application in environmental science and medicine, and deliberates their commercialisation predictions.

Key words; nanoparticles, Nanomaterials, environment, Nano medicine, catalysis, cancer therapy, biomolecules, environmental science

Introduction

Nanotechnology is enabling technology that deals with nano-meter sized substances. It is projected that nanotechnology will be established at several levels: materials, devices and systems. The Nanomaterials level is the most innovative at present, both in scientific knowledge and in commercial applications. A decade ago, nanoparticles were deliberate because of their size-dependent physical and chemical properties Now they have entered a commercial exploration period .

Out of plethora of size-dependant physical properties available to someone who is interested in the practical side of Nanomaterials, optical and magnetic effects are the most used for biological applications.

The aim of this review is firstly to give reader a significant prospective of nanomaterial application to environmental science and medicine, secondly to overview the most recent progresses in this field, and finally to discuss the hard road to commercialisation. Hybrid bio Nanomaterials can be applied to build novel electronic, optoelectronics and communication devices (see S for details). Nevertheless, this will not be discussed here and will be a subject of a separate article.

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Generally, Nanomaterials are currently classified as

- (i) metal-based ,
- (ii) carbonbased
- (iii) dendrimers, and
- (iv) Composites. Generally, carbon-based Nanomaterials contain carbon, and are found in morphologies such as hollow tubes, spheres ellipsoids. Metal-based Nanomaterials are metal based materials that we commonly regarded as, nano silver, nano gold and oxide dramatic dots, s with metal bases. Titanium dioxide is one such example. They are a focus of the pharmaceutical and biomedical industries.

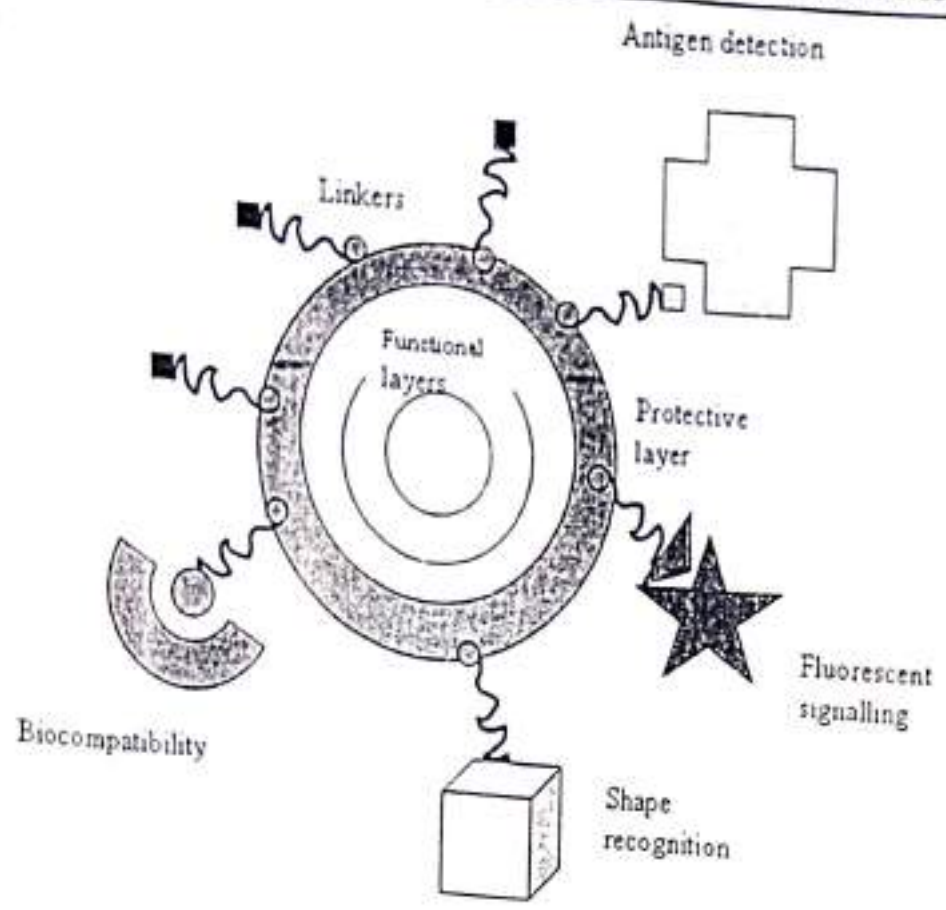
NANOPARTICLES AND NANOMATERIALS

Composites are combination of nanoparticles or nanoparticles and other materials. Nanoparticles, such as nano sized clays, are already being added to yields ranging from auto parts to packaging materials, to enhance mechanical, thermal, barrier, and flame-retardant properties. Although Ag, zinc oxide, copper oxide , cerium dioxide , titanium dioxide , iron oxide , fullerenes, carbon nanotubes , and a small number of others remain the most widely used and researched Nanomaterials , some newer Nanomaterials have been produced in recent years. The greatest interest and development has been in broad classes of materials including nano composites and nano hybrids.

Nano composites are Nanomaterials enclosed or encapsulated with other materials, which may not have nano scale features, whereas nano hybrids are the linking of 2 or more discrete NMs to give different functionality . Such NMs can be based on semiconductor substrates such as GaAs, CdSe, CdS, SiGe, and others, modified with shells and coatings, along with mixtures of carbon-carbon and carbon-metal or metal oxides

Applications

- Fluorescent natural labels Drug and gene conveyance
- Bio recognition of pathogens Detection of proteins Probing of DNA structure Muscle engineering Tumour destruction via heating (hyperthermia)
- Separation and sanitisation of biological fragments and compartments
- MRI distinction enhancement



configurations utilised in nano-bio materials applied to medical or biological problems.

Tissue work

Natural bone external is quite often contains features that are about 100 nm across. If the surface of an artificial bone implant were left smooth, the body would try to reject it. Because of that smooth surface is likely to cause production of a fibrous tissue covering the surface of the implant. This layer reduces the bone-implant contact, which may result in loosening of the implant and additional tenderness. It was established that by creating nano-sized features on the external of the hip or knee prosthesis one could reduce the chances of denial as well as to stimulate the making of osteoblasts. The osteoblasts are the cells responsible for the growth of the bone matrix and are found on the advancing surface of the developing bone.

The effect was demonstrated with polymeric, ceramic and, more recently, metal materials. More than 90% of the human bone cells from disruption adhered to the nanostructured metal surface, but only 50% in the control sample. In the end this findings would allow to design a more durable and longer lasting hip or knee replacements and to reduce the chances of the implant getting loose.

Titanium is a well-known bone repairing material widely used in orthopaedics and dentistry. It has a high fracture resistance, ductility and weight to strength ratio. Unfortunately, it suffers from the lack of bioactivity, as it does not support cell adhesion and growth well. Apatite coatings are known to be bioactive and to bond to the bone. Hence, several techniques were used in the past to produce an apatite

coating on titanium. Those coatings suffer from thickness non-uniformity, poor adhesion and low mechanical strength. In addition, a stable porous structure is required to support the nutrients transport through the cell growth.

It was shown that using a biomimetic approach – a slow growth of nanostructured apatite film from the simulated body fluid – resulted in the formation of a strongly adherent, uniform nanoporous layer. The layer was found to be built of 60 nm crystallites, and possess a stable nanoporous structure and bioactivity.

A real bone is a nanocomposite material, composed of hydroxyapatite crystallites in the organic matrix, which is mainly self-possessed of collagen. Thanks to that, the bone is mechanically tough and, at the same time, plastic, so it can recover from a mechanical damage. The actual nanoscale mechanism leading to this useful combination of properties is still debated.

An artificial hybrid material was prepared from 15–18 nm ceramic nanoparticles and poly (methyl methacrylate) copolymer. Using tribology approach, a viscoelastic performance (healing) of the human teeth was established. An investigated hybrid material, deposited as a coating on the tooth surface, improved scratch resistance as well as possessed a healing behaviour similar to that of the tooth.

Cancer therapy

Photodynamic cancer therapy is based on the destruction of the cancer cells by laser generated atomic oxygen, which is cytotoxic. A greater quantity of a special dye that is used to generate the atomic oxygen is taken in by the cancer cells when compared with a healthy tissue. Hence, only the cancer cells are destroyed then exposed to a laser radiation. Unfortunately, the remaining dye molecules migrate to the skin and the eyes and make the patient very sensitive to the daylight exposure. This effect can last for up to six weeks.

To avoid this side effect, the hydrophobic version of the dye molecule was enclosed inside a porous nanoparticle. The dye stayed trapped inside the Ormosil nanoparticle and did not spread to the other parts of the body. At the same time, its oxygen generating ability has not been affected and the pore size of about 1 nm freely allowed for the oxygen to diffuse out.

NANOMATERIALS ON THE ENVIRONMENT

The growing production and use of NMs in diverse industrial processes, construction, and medical and consumer products is resulting in increasing exposure of humans and the environment. Humans encounter Nanomaterials from many sources and exposure routes, including ingestion of food, direct dermal contact through consumer products and by inhalation of airborne Nanomaterials. The increasing use of Nanomaterials in our life or the customer productions has inevitably caused the accumulation exposure of the nanoparticles into the environment, yet the fate of these particles may greatly depend on their environmental mediums, physical or chemical property

Positive Impacts on the Environment Engineered Nanomaterials exhausted into the atmospheric environment tend to be exposed to sunlight and UV wavelengths at significantly higher degrees than those released into other compartments. This exposure is likely to increase the possible outcomes of photochemical changes to Nanomaterials.

Nanotechnology based detection systems vary in their mechanisms and designs but they share the same goal, that is, timely and accurate detection of trace pathogens or other contaminants [26]. Nanotechnology is of great use in many fields, in particular in the agrofood industry, where is it used primarily in: primary production, food processing and packaging and food supplements

Nanofertilizers have beneficial effects over conventional ones. This is the case of the use of zinc oxide nanoparticles in Zn fertilizers to increase their solubility [62; 63]. De la Rosa et al. [64] found that by applying zinc oxide nanoparticles through the foliar spray, growth and biomass of alfalfa, tomato, and cucumber can be increased

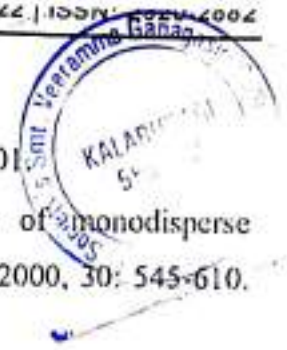
The presence of NMs was also demonstrated to exert low to high toxicity impacts on aquatic life. According to the toxicological investigations, Nanomaterials may affect unicellular aquatic organisms and creatures (e.g., fish and Daphnia). Several studies suggest that the toxicity of silver nanoparticles is attributed to their release of silver ions in cells as both silver nanoparticles and silver ions have been reported to have similar cytotoxicity.

CONCLUSION

The environment and on human beings. Accordingly, Nanomaterials can be compared as drugs because it is well known that they have both desired and undesirable effects. Until now, Nanomaterials have been explored for many different applications in diverse sectors including catalysis, sensing, photovoltaic, energy, environment, and biomedical. However, the level of Nanomaterials in the environment is consistently increasing.

The hazards of Nanomaterials to plants, animals and microbes have had an indirect effect on our humans. Increased attention needs to be directed towards the new Nanomaterials because the development of knowledge of these nanoparticles is still in its infancy. Since the shape, size and composition of nanoparticles can have both significant effects on their function and possible risks to human health, extensive research is needed to fully understand their synthesis, characterization, and possible toxicity.

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DESIGN, SYNTHESIS OF BISINDOLYLOXADIAZOLES AS POTENT ANTIMICROBIAL AGENTS

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ABSTRACT

A series of bisindolyl oxadiazoles were synthesized by reacting 3,5-disubstituted-indole-2-carboxyhydrazides with 3,5-disubstituted indol-2-carboxylic acids in the presence of phosphorus oxy chloride as the solvent. The products were obtained in good yields. The structures of the synthesized compounds were confirmed by IR, ¹HNMR, ¹³CNMR, mass and spectral analysis. The target compounds were evaluated for antimicrobial activities.

Keywords: Bisindole, Oxadiazole, Indole, Antimicrobial Activity, 3,5-disubstituted-indole-2-carboxyhydrazide, 3,5-disubstituted indol-2-carboxylic acids.

INTRODUCTION

The indole ring system is an important biologically active compound and is present in many natural products, pharmaceuticals and agrochemicals. The indole unit forms Bisindolylmethane and Trisindolyl methane structures. BIMs exhibit antimicrobial and antifungal activities, exhibit antibiotic activity and antibacterial activity [1], anticancer activity against several common cancer cell lines [2]

The discovery of privileged structures in drug discovery is an emerging trend in the field of medicinal chemistry. These structures represent a class of molecules capable of binding to multiple receptors with high affinity. This type of molecules let the medicinal chemist to discover biologically active compounds [3-5].

Recently reported the synthesis and the antitumor activity of bis-indolyl thiophene [6] pyrazoles [7] furans [8] and isoxazoles [8] that showed inhibitory activity against a wide range of human tumor cell lines, generally in the micro- and sub micromolar range. Even more recently bis-indolyl pyrroles [9] have exhibited concentration-dependent antitumor activity towards a panel of 42 human tumor cell lines, with mean IC50 values of 1.54 μ M and 0.67 μ M, respectively. Moreover, investigating human tumor xenografts in an *ex vivo* clonogenic assay revealed selective antitumor activity.

Oxadiazoles are important classes of heterocyclic compounds which have attracted attention due to their significant biological and pharmacological properties [10-18].

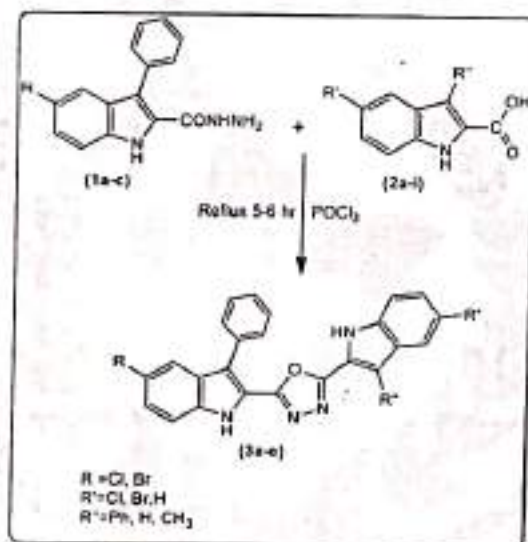
2, 5-disubstituted 1, 3, 4-oxadiazole attracted the considerable attention due to biological activity. The pharmaceutical compounds have also possess analgesic, anti-inflammatory, anticancer, anti-HIV agent, antiparkinsonian and antiproliferative agent [23-27]. 1,3,4-oxadiazole also have played a vital role in heterocyclic chemistry and also used in medicinal chemistry [28,29]. The

methods used in synthesis of 1,3,4-oxadiazole is condensation of hydrazide and its derivatives with substituted indole-2-carboxylic acid [30,31]. 2,5-disubstituted 1,3,4-oxadiazole can be conveniently synthesized by the treatment of pyridine-4-carboxylic acid with substituted indole-2-carboxylic acid in basic and acidic media [32,33]. The other method is pyridine-4-carboxylic acid which can be subsequently cyclized to 2,5-disubstituted 1,3,4-oxadiazole in the presence of reagent like phosphoryl chloride [34-36]. In our earlier approaches, we have synthesized some new derivatives of 1,3,4-oxadiazole with highly potent antioxidant, DNA cleavage and antimicrobial activities [37-40].

RESULT AND DISCUSSION

CHEMISTRY. Molecules were designed with the aim of exploring their antimicrobial activities. The target compounds were synthesized as outlined in (Scheme 1). A novel and efficient method for the synthesis of 2,5-bis(3,5-disubstituted-1H-indol-2-yl)-1,3,4-oxadiazoles (3a-e) by reacting 3,5-disubstituted-indole-2-carboxylic acid (2a-e) with 3,5-disubstituted indol-2-carboxylic acid (1a-c) in the presence of POCl₃ at reflux for 5-6 hr. The IR spectrum of 2-(5-chloro-3-phenyl-1H-indol-2-yl)-5-(1H-indol-2-yl)-1,3,4-oxadiazole 3a shown a strong absorption at 3374 cm⁻¹ and 3177 cm⁻¹ corresponds to indole NH and absorption at 1650 cm⁻¹ corresponds to C=N stretching respectively. The ¹H NMR spectrum of 3a has exhibited a singlets at δ 12.60 and δ 11.90 ppm is due to indole NH which are also D₂O exchangeable. A multiplet between δ 7.34-7.70 ppm corresponds to thirteen aromatic protons present in the molecule. The ¹³C NMR spectrum of 3a has displayed signal at δ 109, 112, 115, 115, 116, 120, 120, 122, 125, 128, 136, 158 and 159.

The mass spectrum of compound 3a has shown isotopic peaks at m/z 410 (100%), 412 (30%). The molecular ion has undergone into fragmentation to give fragment m₁ at m/z 375 (15%) by the loss of chlorine radical. This cation m₁ has lost C₆H₅ to give radical cation m₂ at m/z 298 (5%). The radical cation m₂ has lost C₆H₅N to give m₃ at m/z 182 (20%). This fragmentation pattern and above spectral data supports the formation of compound 3a.



Scheme-1

Table-01: Physical and analytical data of the 2-(5-chloro-3-phenyl-1H-indol-2-yl)-5-(1H-indol-2-yl)-1,3,4-oxadiazoles (3a-e).

Comp. No.	Substituents			M.P.	Yield (%)	Nature (Solvent)	Molecular Formula	Found (%) Calcd.		
	R	R'	R''					C	H	N
3a	Cl	H	H	252-54	65	Brown Crystals (Ethanol)	C ₂₄ H ₁₅ N ₄ ClO	70.13 (70.16)	03.40 (03.68)	13.55 (13.64)
3b	Cl	Br	Ph	280-82	75	Green solid (Ethanol)	C ₃₀ H ₁₅ N ₄ BrClO	63.63 (63.68)	03.19 (03.21)	09.84 (09.90)
3c	Cl	Cl	Ph	290-92	70	Green Solid (Ethanol)	C ₁₀ H ₁₅ N ₄ Cl ₂ O	69.03 (69.11)	03.42 (03.48)	10.67 (10.75)
3d	Br	H	H	210-12	60	Black solid (Ethanol)	C ₂₄ H ₁₅ N ₄ BrO	63.27 (63.31)	03.24 (03.32)	12.23 (12.31)
3e	Br	Br	CH ₃	258-60	70	Green Crystals (Ethanol)	C ₂₅ H ₁₆ N ₄ Br ₂ O	55.72 (54.77)	02.91 (02.94)	10.02 (10.22)

Table-02: Spectral data of the 2-(5-chloro-3-phenyl-1H-indol-2-yl)-5-(1H-indol-2-yl)-1,3,4-oxadiazoles(3a-e).

Comp. No.	IR (KBr, cm ⁻¹)			¹ HNMR and ¹³ CNMR
	C=N	Indole NH	Indole NH	
3a	1650	3177	3374	12.60 (s, 1H, Indole NH), 11.90 (s, 1H, Indole NH), 7.34-7.70 (m, 13H, Ar-H), 109, 112, 115, 115, 116, 120, 120, 122, 125, 128, 136, 158 & 159.
3b	1653	3061	3086	12.60(s, 1H, Indole NH), 11.24 (s, 1H, Indole NH), 7.35-7.89 (m, 16H, Ar-H).
3c	1622	3223	3261	12.53 (s, 1H, Indole NH), 11.02 (s, 1H, Indole NH), 7.28-7.58 (m, 16H, Ar-H).
3d	1637	3227	3296	12.65 (s, 1H, Indole NH), 12.12 (s, 1H, Indole NH), 7.35-7.92 (m, 13H, Ar-H).
3e	1654	3103	3151	12.55 (s, 1H, Indole NH), 12.54 (s, 1H, Indole NH), 7.36-7.66 (m, 12H, Ar-H), 2.20 (s, 3H, CH ₃).

BIOLOGICAL ACTIVITIES.**ANTIMICROBIAL ACTIVITY.****ANTIBACTERIAL ACTIVITY**

Applying the agar plate diffusion technique [41], series of analogues were screened for *in vitro* antibacterial activity against (Table 3) gram-negative bacteria *Escherichia coli* (*E. coli*) and *Klebsiella pneumoniae* (*K. pneumoniae*) and gram-positive bacteria *Staphylococcus aureus* (*S. aureus*) and Gentamycin was used as standard. The zone of inhibitions was measured in mm for each concentration. Amongst the compounds screened against *S. aureus*, compounds 3b-c and 3e have shown highest activity. Compounds 3a, 3d have shown moderate activity. Amongst the compounds tested against *E. coli* compounds 3b-c and 3e have shown very good activity. Compounds 3a and 3d are moderately active and compounds. Amongst the compounds screened against *K. pneumoniae*, 3b-c and 3e have shown highest activity. Compounds, 3a, have shown moderate inhibitory activity.

ANTIFUNGAL ACTIVITY

Antifungal activities of test compounds were compared with the activities of standard drug, fluconazole against *C. albicans* and *C. tropicalis* (Table-4). Amongst the compounds screened against *C. albicans*, compounds 3b-c and 3e have shown highest activity. Compounds 3a and 3d shown moderate inhibitory activity and remaining compounds have exhibited weak activities. Amongst the compounds tested against *C. tropicalis* compounds 3b-c and 3e have shown highest activity. Compounds 3a and 3d shown moderate inhibitory activity and remaining compounds have exhibited weak activities.

Table-03: Antibacterial activity results of synthesized compounds (3a-e).

Comp. No.	Substituent's			Antibacterial activity		
	R	R'	R''	<i>S. aureus</i>	<i>E. coli</i>	<i>K. Pneumoniae</i>
3a	Cl	H	H	11	12	13
3b	Cl	Br	Ph	15	16	15
3c	Cl	Cl	Ph	16	15	16
3d	Br	H	H	12	11	12
3e	Br	Br	CH ₃	16	14	15
Standard	-	-	-	16	18	17

Std. - Gentamycin.

Table-4: Antifungal activity results of synthesized compounds (3a-e).

Comp. No.	Substituents			Antifungal activity	
	R	R'	R''	<i>C. albicans</i>	<i>C. tropicalis</i>
3a	Cl	H	H	15	16
3b	Cl	Br	Ph	20	21
3c	Cl	Cl	Ph	21	20
3d	Br	H	H	15	16
3e	Br	Br	CH ₃	20	21
Standard	-	-	-	21	23

Std. - Fluconazole

EXPERIMENTAL

CHEMISTRY. All chemicals used in this investigation were analytical grade and were purified whenever necessary. Melting points of the synthesized compounds are measured in open capillaries and are uncorrected. Reactions are monitored by thin-layer chromatography (TLC) on silica gel 60 F254 aluminium sheets (MERCK). Iodine vapour was used as detecting agent. IR spectra are recorded in KBr on Perkin Elmer and FTIR spectrophotometer (Jmax in cm^{-1}). ^1H NMR and ^{13}C NMR spectra are recorded on BRUKER AVENE II 400-MHz NMR spectrometer (chemical shift in δ ppm down field from TMS as internal reference). The mass spectra are recorded on LC-MSD-Trap-SL instruments. The elemental analysis was determined on FLASH EA 1112 SERIES instrument.

General Procedure for the Synthesis of Compound (1a-e).

The precursors 3,5-disubstituted-indole-2-carboxyhydrazides (1a-c) and 3,5-disubstituted indol-2-carboxylic acid (2a-l) were obtained from 3,5-disubstituted indol-2-carboxylates by reported method [42].

2,5-bis(3,5-disubstituted-1H-indol-2-yl)-1,3,4-oxadiazoles (3a-e).

A mixture of 3,5-disubstituted indole-2-carboxyhydrazides(1a-c) (0.01mol) and appropriate 3,5-disubstitutedindol-2-carboxylic acids (2a-e) (0.01mol) were dissolved in phosphorus oxy chloride and refluxed for 5-6hrs. The mixture was then cooled and poured into ice cold water under constant stirring. The mass obtained was filtered and washed with water and recrystallized from suitable solvent to get bisindolyloxadiazoles (3a-e).

ANTIMICROBIAL ACTIVITY.

A series of novel bisindolyl analogues are tested for *in vitro* antimicrobial activity against gram-negative bacteria *Escherichia coli* and *Klebsiella Pneumoniae* and grampositive bacteria *Staphylococcus aureus* and antifungal activity against *Candida tropicalis* and *Candida albicans* by applying the agar plate diffusion technique [41]. The activity is compared with reference drugs Gentamycin for antibacterial and Fluconazole for antifungal activity. The zone of inhibition after 24 hr of incubation at 37°C, in case of antibacterial activity and 48 hr in case of antifungal activity, was compared with that of standards.

CONCLUSION

The novel method is employed for the synthesis of bisindolyl oxadiazole derivatives obtained in good to excellent yields and is one step synthesis approach highlighted the benefits of using this procedure. The target compounds were screened for antimicrobial activity. Amongst the compounds screened for antibacterial activity, compounds with halogen substitution at five positions and a phenyl ring at third position of indole ring have exhibited very good activity when compared standard. Compounds with halogen substitution at five positions and phenyl ring at third position of indole ring have exhibited very potent antifungal activity when compared standard.

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MULTICOMPONENT ONE-POT SYNTHESIS OF NOVEL INDOLE ANALOGUES AS POTENT ANTIOXIDANT AGENTS

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ABSTRACT

Objective: The purpose of this study was to design and synthesize innovative multicomponent one-pot indole analogues that would be effective antioxidants for the body.

Methods: A novel series of indolyl-pyrimidine derivatives were synthesized and characterized by spectrum analysis, and their antioxidant activity and DPPH, total antioxidant capacity, ferric reducing antioxidant power methods, and DNA cleavage activity were examined.

Results: Compound 6a displayed promising free radical scavenging and total antioxidant properties. Compound 6b has demonstrated excellent ferric reducing activity, which is due to the presence of a "CH₃" substitution at free position of indole. When compared to a standard DNA marker, compound 6a demonstrated the highest DNA cleavage activity at desired concentrations.

Conclusion: We have synthesized novel pyrimidine analogues containing an indole moiety to investigate drug-like molecules. We have devised that a method that is simple, multicomponent, has a short reaction time, and is ecologically benign.

Keywords: Indole, Multicomponent reaction, Antioxidant, DNA cleavage activities.

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INTRODUCTION

The concept of green chemistry has centered on multicomponent reactions (MCRs), in which at least three reactants react to produce a single product that allows the formation of several new bonds [1]. MCRs in organic synthesis have provided numerous interesting and novel modifications [2]. The MCR [3] is a reaction that occurs when three or more reactants combine in a single pot to produce a single product. There are a number of innovative compounds being synthesized using these reactions [4]. The microwave technique aids in the acceleration of reactions, the efficiency of heating, the absence of side reactions, the high purity of the product, and the environmental friendliness [5]. Synthesis of small molecules using microwave irradiation is a shorter time [6]. Heterocyclic compounds have a high degree of structural diversity and have proven to be broadly and cost-effectively useful as therapeutic agents [7]. Heterocycles have piqued the interest of many synthetic chemists due to their abundance in natural products, and medicinal chemistry is still developing new methods for their synthesis [8]. Indole derivatives have been discovered in a diverse range of natural products, including alkaloids, peptides, and a variety of synthetic compounds [9,10]. Indole alkaloids' recognition of the plant growth hormone, serotonin [11], and the essential amino acid tryptophan [12] as indole derivatives has boosted this research. Indole is a very weak base, because it is an electron-rich or -excessive system and the nitrogen atom contributes two electrons to the overall system [13]. Substituted indoles are biologically interesting compounds with antibacterial, antifungal, antiviral, and protein kinase inhibitory properties [14]. Pyrimidines are one of the most important heterocycles with remarkable pharmacological activities, because they are a necessary component of all cells and thus all living matter [15]. Pyrimidine derivatives have been reported to be antimicrobial [16], analgesic, antiviral, anti-inflammatory [17], anti-HIV [18], anti-tubercular [19], anti-tumor [20], anti-neoplastic [21], anti-malarial [22], and hypnotic drugs [23]. The ongoing search for novel

agents that target pathological processes in human carcinogenesis has resulted in the development of small molecules that may modulate cell cycle [24].

Free radicals are highly reactive chemical species that contain one or more unpaired electrons. It changes the chemical reactivity of an atom or molecule and is usually more reactive than the corresponding non-radical, and they act as electron acceptors. This loss of electrons is referred to as oxidation, and free radicals are referred to as oxidizing agents, because they cause other molecules to donate their electrons [25].

The hydroxyl radical (OH), superoxide radical (O₂⁻), and hydroperoxyl radical are examples of free radicals (RO₂). Antioxidants are compounds that prevent the oxidation of other molecules by delaying the initiation or propagation of oxidizing reactions [26]. Antioxidants act as "free radical scavengers," removing free radicals and inhibiting oxidation [27]. Oxygen free radicals, also known as reactive oxygen species (ROS), are byproducts of normal cellular metabolism [28]. As oxidative stress, ROS can cause damage to cell structure, including lipids and membranes, proteins, and nucleic acids [29]. Oxidative damage/stress, which is associated with ROS, is thought to be involved in a variety of pathological conditions such as diabetes, aging, atherosclerosis, inflammation, carcinogenesis [30,31], and neurodegenerative [32] disorders such as Parkinson's, Alzheimer's, and amyotrophic lateral sclerosis [33]. These literature reviews encourage us to synthesize novel indole analogues, and the development of simple, efficient, and environmentally friendly approaches for the synthesis of indole derivatives is highly desirable [34,35].

EXPERIMENTAL SECTION

Chemistry

Materials and Methods

All reagents were purchased commercially and purified further using conventional techniques. The melting points were determined using

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an uncorrected open capillary technique. Thin-layer chromatography with silica gel-G coated Al plates (Merck) was used to determine the purity of the compounds, and spots were observed by exposing the dried plates to iodine vapors. The IR (KBr pellet) spectra were acquired using an FT-IR spectrometer from Perkin-Elmer (Spectrum ONE). The ^1H and ^{13}C NMR (DMSO- d_6) spectra were acquired using Bruker NMR 500 and 125 MHz spectrometers, respectively, and the chemical shift values are presented in ppm (scale) using tetramethylsilane as an internal reference. Electron impact mass spectral measurements were performed at 70 eV on a JEOL GC/MS spectrometer. Flash EA 1112 series elemental analyzer was used to conduct the analyses.

Experimental

The precursors 3,5-disubstituted indol-2-carboxylic acids (**1**) were obtained from 3,5-disubstituted indol-2-carboxylates (**1a**) and 2,5-disubstituted indole-3-carboxaldehydes (**5a-c**) were synthesized by Vilsmeier-Black acylation reaction of 2,5-disubstituted indoles (**3**).

General Procedure for the synthesis of 2-(5-bromo-3-phenyl-1H-indole-2-carbonyl) hydrazinecarbothioamide (**3**)

To a solution of 5-bromo-3-phenyl-indol-2-carboxylic acid **1** (0.01 mol) in ethanol, ammonium thiocyanate **2** (0.01 mol) and few drops of hydrochloric acid are added to the reaction mixture. The mixture was refluxed 3-4 h. The completion of the reaction was monitored by TLC. After the completion, the reaction mixture was poured to a beaker containing 100 mL of ice-cold water, filtered, washed with water, and dried. The crude product was crystallized from ethanol.

General Procedure for the synthesis of Ethyl 1-(5-bromo-3-phenyl-1H-indole-2-carboxamido)-4-(5-chloro-2-phenyl-1H-indol-3-yl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**6a-c**)

Conventional method

After adding a solution of 2-(5-bromo-3-phenyl-1H-indole-2-carbonyl) hydrazinecarbothioamide **3** (0.01 mol), ethyl acetoacetate **4** (0.01 mol), substituted indole aldehyde **5** (0.05 mol), and a catalytic amount of MK10 Clay, the reaction mixture is refluxed for 6-8 h in ethanol as the solvent. TLC was used to monitor the reaction's conclusion. The reaction mixture was then poured into a beaker containing ice-cold water. The crude products obtained in this manner were filtered and crystallized to generate the named compounds, **6a-c**.

Microwave oven method

A solution of 2-(5-bromo-3-phenyl-1H-indole-2-carbonyl) hydrazinecarbothioamide **3** (0.01 mol), ethyl acetoacetate **4** (0.01 mol), substituted indole aldehyde **5** (0.05 mol), and a catalytic amount of MK10 Clay was added and mixed before being introduced into a borosil sample crucible. This was microwave irradiated for 8-10 min at 70% microwave intensity. Following completion of the TLC analysis, the reaction mixture was cooled to room temperature, washed with ethanol, and recrystallized to obtain the title compounds, **6a-c**.

Ethyl 1-(5-bromo-3-phenyl-1H-indole-2-carboxamido)-4-(5-chloro-2-phenyl-1H-indol-3-yl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**6a**)

Yield 66 and 85%, m.p. 265-67°C, FT-IR (KBr) (cm^{-1}): 3342 (NH), 3295 (NH), 3195 (NH), 3158 (CONH), 1730 (COOEt), 1620 (C=N), 1205 (C=S); ^1H NMR (DMSO- d_6) δ : 12.66, 12.32 (s, 1H, 2X indole-NH), 8.46 (s, 1H, Pyrimidin-NH D,O exchangeable), 8.46 (s, 1H, CONH D,O exchangeable), 6.89-7.86 (m, 7H, Ar-H), 4.43 (q, 2H, CH₂), 3.32 (t, 3H, CH₃), 2.15 (s, 3H, CH₃); ^{13}C -NMR (DMSO- d_6) δ : 104.3, 167.2, 161.9, 152.8. Aromatic carbons 144.6-111.8, 104.6, 61.8, 47.2, 14.2, 10.2; Mass: m/z 737 [M]⁺, 739 [M+2], 741 [M+4]; Anal. Calcd. for C₂₇H₂₄N₄O₅BrCl (737.086): C, 76.13, H, 3.95, N, 9.48. Found: C, 76.17, H, 3.92, N, 9.45%.

Ethyl 1-(5-bromo-3-phenyl-1H-indole-2-carboxamido)-4-(5-methyl-2-phenyl-1H-indol-3-yl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**6b**)

Yield 65 and 88%, m.p. 210-12°C; FT-IR (KBr) (cm^{-1}): 3344 (NH),

3292 (NH), 3198 (NH), 3155 (CONH), 1737 (COOEt), 1620 (C=N), 1204 (C=S); ^1H NMR (DMSO- d_6) δ : 12.68, 12.30 (s, 1H, 2X indole-NH), 8.47 (s, 1H, Pyrimidin-NH D,O exchangeable), 8.47 (s, 1H, CONH D,O exchangeable), 6.90-7.85 (m, 7H, Ar-H), 4.44 (q, 2H, CH₂), 3.29 (t, 3H, CH₃), 2.30 (s, 3H, CH₃), 2.01 (s, 3H, CH₃); ^{13}C -NMR (δ ppm): Mass: m/z 717 [M]⁺, 719 [M+2]; ^{13}C -NMR (DMSO- d_6) δ : 104.6, 167.1, 161.7, 152.9, 717 [M]⁺, 719 [M+2]; Anal. Calcd. for C₂₈H₂₆N₄O₅Br (717.141): C, 63.51, H, 4.49, N, 9.74. Found: C, 63.55, H, 4.44, N, 9.77%.

Ethyl 1-(5-bromo-3-phenyl-1H-indole-2-carboxamido)-4-(2-phenyl-1H-indol-3-yl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**6c**)

Yield 65 and 80%, m.p. 210-12°C, IR (cm^{-1}): 3342 (Indole-NH), 3295 (Indole-NH), 3195 (Pyrimidin-NH), 3158 (CONH), 1730 (Ester), 1620 (C=N), 1203 (C=S); ^1H NMR (δ ppm): 12.66, 12.32 (s, 1H, 2X indole-NH), 8.46 (s, 1H, Pyrimidin-NH D,O exchangeable), 8.46 (s, 1H, CONH D,O exchangeable), 6.89-7.86 (m, 7H, Ar-H), 4.43 (q, 2H, CH₂), 3.32 (t, 3H, CH₃), 2.15 (s, 3H, CH₃); ^{13}C -NMR (δ ppm): Mass: m/z 703 [M]⁺, 705 [M+2]; ^{13}C -NMR (DMSO- d_6) δ : 104.2, 167.8, 161.9, 152.7. Aromatic carbons 144.8-111.9, 104.6, 61.3, 47.7, 14.2, 10.2; Mass: m/z 703 [M]⁺, 705 [M+2]; Anal. Calcd. for C₂₉H₂₆N₄O₅Br (703.125): C, 63.07, H, 4.29, N, 9.94. Found: C, 63.09, H, 4.31, N, 9.99%.

Antioxidant activity

Free radical scavenging activity

The 2,2-diphenyl-1-picrylhydrazyl (DPPH) technique was used to assess free radical scavenging activity. Different concentrations of samples and butylated hydroxy anisole (BHA) were taken in separate test tubes (10 μg , 50 μg , and 100 μg). MeOH was added to get the volume to 100 μl . Five milliliters of 0.1 mM DPPH methanolic solution was added to each of these test tubes and vigorously shaken. For 20 min, the tubes were left to stand at 27°C. The control was prepared in the same manner as described above, but without samples. At 517 nm, the absorbances of the samples were determined. The activity of radical scavenging was determined using the following formula:

$$\% \text{Radical scavenging activity} = \left(\frac{[\text{Control OD} - \text{Sample OD}]}{[\text{Control OD}]} \right) \times 100$$

Total antioxidant capacity

Antioxidant capacity in total determined the total antioxidant capacity. A series of test tubes were filled with samples at various concentrations (10 μg , 50 μg , and 100 μg). This was followed by the addition of 1.9 mL of reagent solution (0.6 M sulfuric acid, 20 mM sodium phosphate, and 4 mM ammonium molybdate). The tubes were incubated for 90 min at 95°C and then allowed to cool. At 695 nm, the absorbance of each aqueous solution was determined in comparison to a blank. Antioxidant capacity is represented in ascorbic acid equivalents. Equivalents of ascorbic acid are computed using the standard graph of ascorbic acid. The data are presented in terms of ascorbic acid equivalents $\mu\text{g}/\text{mg}$ of samples.

Ferric reducing antioxidant power

The antioxidant activity of ferric reducing agents was determined according to samples at various concentrations (10 μg , 50 μg , and 100 μg) were combined with 2.5 mL of 200 mM/L sodium phosphate buffer (pH 6.4) and 2.5 mL of 1% potassium ferricyanide. For 20 min, the mixture was incubated at 50°C. Following that, 2.5 mL of 10% hydrochloric acid (w/v) was added. 5 mL of this solution was combined with 5 mL distilled water and 1 mL 0.1% ferric chloride, and the absorbance at 700 nm was determined spectrophotometrically. BHA was employed as a control.

DNA cleavage activity

Preparation of culture media

DNA cleavage experiments were done according to the literature [39]. Nutrient broth (peptone, 10; yeast extract, 5; NaCl, 10; in $\mu\text{g}/\text{ml}$) was used



for culturing of *Coli-gram*, 50 ml. media was prepared, autoclaved for 15 min at 121°C under 15 lb pressure. The autoclaved media were inoculated for 24 h at 37°C.

Isolation of DNA

The freshly prepared bacterial culture (1.5 ml.) was centrifuged to obtain the pellet which was then dissolved in 0.5 ml. of lysis buffer (100 mM Tris pH 8.0, 50mM EDTA, 10% SDS). To this 0.5 ml. of saturated phenol was added and incubated at 55°C for 10 min, then centrifuged at 10,000 rpm for 10 min and in the supernatant, equal volume of chloroform: isoamyl alcohol (24:1) and 1/20th volume of 1M sodium acetate (pH 4.8) were added. Centrifuging at 10,000 rpm for 10 min and to the supernatant, 3 volumes of chilled absolute alcohol were added. The precipitated DNA was separated by centrifugation and the pellet was dried and dissolved in TAE buffer (100mM Tris pH 8.0, 1mM EDTA) and stored in cold condition.

Agarose gel electrophoresis

Cleavage products were analyzed by agarose gel electrophoresis method. Test samples (1 µg/ml.) were prepared in DME. The samples (50 µg and 100 µg) were added to the isolated DNA of *Coli-gram*. The samples were incubated for 2 h at 37°C, and then, 20 ml. of DNA sample (mixed with bromophenol blue dye at 1:1 ratio) was loaded carefully into the electrophoresis chamber wells along with standard DNA marker containing TAE buffer (4.04 g Tris base, pH 8.0, 0.5M EDTA/1L) and finally loaded on agarose gel and passed the constant 50V of electricity for 30 min. Removing the gel and stained with 10.0 mg/ml. ethidium bromide for 10-15 min, the bands were observed under VilberLourmat Gel documentation system and then photographed to determine the extent of DNA cleavage. The results are compared with standard DNA marker.

RESULTS AND DISCUSSION

Chemistry

5-bromo-3-phenyl-indole-2-carboxylhydrazide **1** (0.01 mol), ammonium thiocyanate **2** (0.01 mol), and few drops of hydrochloric acid in ethanol to under reflux temperature to afford 2-(5-bromo-3-phenyl-1H-indole-2-carboxyl)hydrazinecarbothioamide **3a** (Scheme 1). The synthesis of ethyl 1-(5-bromo-3-phenyl-1H-indole-2-carboxamide)-4-(5-chloro-2-phenyl-1H-imidazol-3-yl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidin-5-carboxylate **6a-c** is carried out by both conventional and microwave method. In conventional method, the reaction of 2-(5-bromo-3-phenyl-1H-indole-2-carboxyl)hydrazinecarbothioamide **3** (0.01 mol), ethyl acetoacetate **4** (0.01 mol), and substituted indole aldehyde **5** (0.05 mol) and a catalytic amount of MK10 Clay is added and refluxed for 6-8 h in ethanol to yield the titled compound **6a-c** (Scheme 2). The same reaction is carried out by microwave method by the reaction of 2-(5-bromo-3-phenyl-1H-indole-2-carboxyl) hydrazine carbothioamide **3** (0.01 mol), ethyl acetoacetate **4** (0.01 mol), and substituted indole aldehyde **5** (0.05 mol) and a catalytic amount of MK10 Clay is mixed and irradiated for 8-10 min with 70% microwave power to yield the titled compounds. The formation of products was monitored by TLC. All the newly synthesized compounds were characterized by IR, ¹H NMR, and mass spectroscopic techniques (Table 1).

The IR spectrum of compound **6a** showed a strong absorption peak at 3342 cm⁻¹, 3295 cm⁻¹ corresponding to two indole NH, absorption peak at 3195 cm⁻¹, and 3150 cm⁻¹ corresponding to pyrimidine NH and CONH, absorption peak at 1730 cm⁻¹ corresponds to ester carbonyl and absorption at 1620 cm⁻¹ and 1203 cm⁻¹ which corresponding to C=N and C=S functions, respectively. The ¹H NMR spectrum of **6a**, the signal appeared as singlet at δ 12.66 ppm, 12.52 ppm due to two indole NH, singlet at δ 8.46 ppm and δ 8.43 ppm pyrimidine NH and CONH which are D,D exchangeable. Signal resonated as multiplet between δ 6.89 and 7.86 ppm which corresponds to seventeen aromatic protons. Signal appeared as a Quartet at δ 6.43 ppm is assigned for the CH₂ protons, a signal resonated as triplet at δ 3.32 ppm corresponds to methyl protons and singlet at δ 2.35 ppm assigned for methyl protons. The mass spectrum of compound **6a** has shown molecular ion peak at m/z 779

[M]⁺, 741[M+2], 743[M+4] which is corresponding to molecular weight and isotopic peak of the compound. These spectral data confirm the formation of the titled compound **6a**. Similarly, other compounds series were synthesized.

Biological evaluation

Antioxidant activity

Free radical scavenging activity

The DPPH technique was used to test the target compounds for free radical scavenging activity. The samples were prepared at concentrations of 10, 50, and 100 µg/100 µl, with BHA serving as the standard. In a methanolic solution, DPPH is a stable free radical, due to the unpaired electron in DPPH, it has a significant absorption maximum in the visible area at 517 nm (purple color). Among the substances studied, **6a** shown extremely promising free radical scavenging capability. The presence of halogen substitution at the low location of both indoles accounts for the reduce of activity. Compounds **6b** with a methyl group at another indole ring demonstrated moderate activity, while compounds **6c** shown the least activity when compared to the standard. Fig. 1 shows a bar graph representation of the proportion of free radical scavenging activity.

Total antioxidant capacity

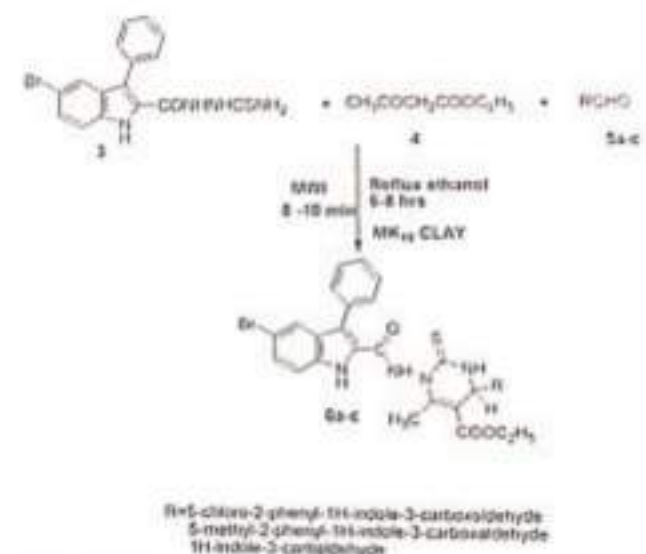
Total antioxidant activity was tested in the newly synthesized substances. Antioxidant capacity is measured in terms of ascorbic acid equivalents. Among the examined compounds, **6a**, which is halogen substituted at the fifth position of both indoles, demonstrated a very high overall antioxidant capacity. When compared to the standard, compounds having methyl substitution at the fifth position of the indole ring and no substitution at the second and fifth positions had the lowest overall antioxidant capacity. Fig. 2 depicts the overall antioxidant activity results.

Ferric reducing antioxidant power activity

The ferric reducing antioxidant activity of the new compounds was tested. The standard was BHA. Compound **6a** exhibits high ferric reduction antioxidant activity, whereas other indole counterparts exhibit moderate to low activity. The presence of a methyl group at



Scheme 1: Schematic route for the synthesis of compound **3**



Scheme 2: Schematic route for the synthesis of compounds (**6a-c**)

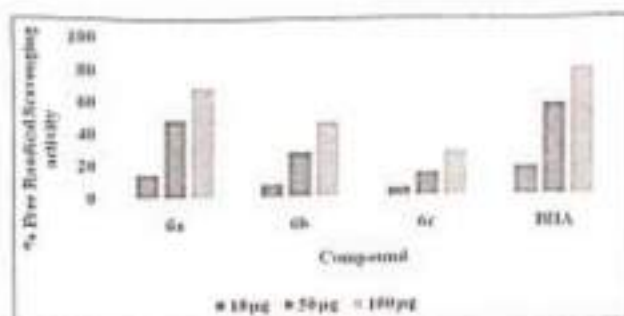


Fig. 1: Free radical scavenging activity of compounds 6a-c

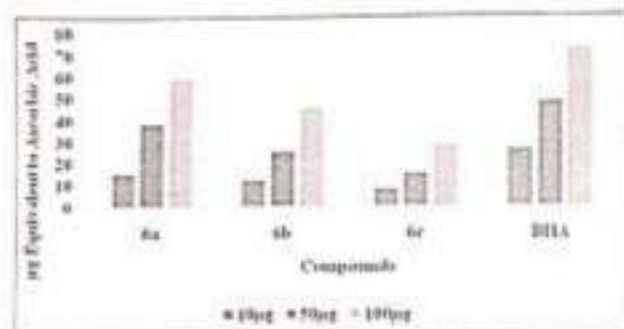


Fig. 2: Total antioxidant capacity of compounds 6a-c

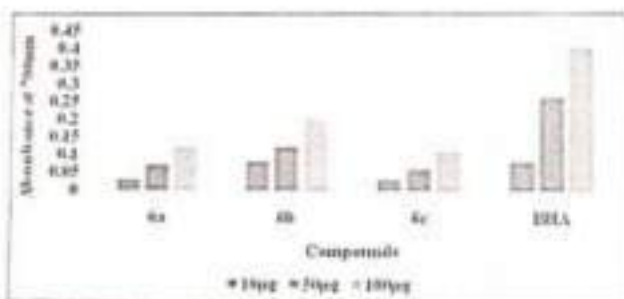


Fig. 3: Ferric reducing antioxidant power activity of compounds 6a-c

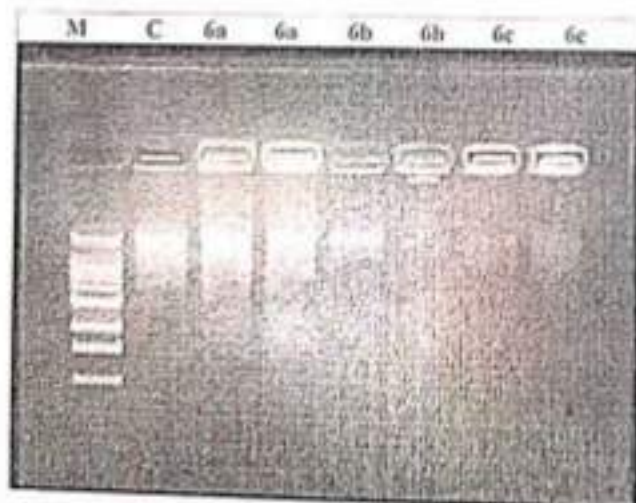


Fig. 4: DNA cleavage activity of compounds 6a-c

the fifth position of the indole ring acts as a superior electron donor, enhancing the compounds' reducing power activity. The results are shown in Fig. 2.

Table 1: Physical data of the target compound 6a-c

Comp. No.	M.P. (°C)	Yield (%)	
		Conventional method	Microwave method
6a	218-12	65	88
6b	265-67	68	85
6c	200-02	58	70

DNA cleavage activity

DNA cleavage tests have been performed on all of the new chemicals. Used gel electrophoresis to measure the DNA cleavage activity. Fig. 4 depicts images of the gels. When compared to a standard DNA marker, compound 6a demonstrated the maximum activity at 50 µg and 100 µg, whereas the remaining compounds demonstrated moderate activity at 50 µg and 100 µg.

CONCLUSION

In this study, we synthesized new pyrimidine analogues containing an indole moiety to investigate drug-like molecules. We created a simple, MCR with a short reaction time, an environmentally friendly technique, and an excellent yield of all produced chemicals. $MgCl_2$ Klay has proven to be an effective catalyst. When compared to the standard, compound 6a showed promising free radical scavenging and total antioxidant activity, with the maximum activity attributed to the presence of halogen at position five of the indole ring. Compound 6b has demonstrated strong ferric reducing activity, which is attributable to the presence of a "CH," substitution at five positions of indole. Compound 6a demonstrated the strongest DNA cleavage activity at both doses, whereas the remaining compounds demonstrated moderate activity.

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AUTHORS' CONTRIBUTIONS

Parveen R. is mainly involved in the design and execution; the experimental section, results and discussion, and analysis section were performed by Prabhakar W. Chavhan, who is the supervisor of the overall work. Dr. Jaisree B. and Dr. Prashant C. Hanamshetty were involved in biological screening and results.

CONFLICTS OF INTEREST

The authors state that they have no conflicts of interest.

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SYNTHESIS OF NOVEL ISATIN ANALOGUES AS POTENT ANTIMICROBIAL AGENTS

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Abstract

A series of isatin derivatives were systematically designed synthesized and evaluated for biological activities. Isatin has attracted a lot of attention due to its broad range of biological and pharmacological properties and are widely used as starting materials for the synthesis of a broad range of heterocyclic compounds and as precursor for drug synthesis. The intermediate 5-substituted-2-chloro isatin was prepared by reacting 5-substituted isatin with phosphorus pentachloride in dry benzene this is then made to react with sodium azide to get substituted tetrazole ring. The tetrazoles was treated with thiosemicarbazide to get the products. All these synthesized novel compounds were confirmed by IR, ¹HNMR and mass spectral analysis. Selected compounds were evaluated for antimicrobial agents. Among the tested compounds **3b** & **4b** have shown very good activity against all the three bacterial strains and **4b** exhibited significant antifungal activity.

Key words: Isatin, tetrazole, antibacterial agents, antifungal agents

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I. INTRODUCTION

Isatin (1H-indole-2,3-dione) and its derivatives is an versatile substrates and it can be used for the synthesis of a large variety of heterocyclic compounds, such as indoles and quinolones, and as raw material for drug synthesis.¹

Drugs containing the isatin skeleton are used to treat diseases such as epilepsy², tuberculosis³, and bulimia⁴. Therefore the need to create novel isatin derivatives for emerging drug targets is an active area of medicinal chemistry.

Isatins and its derivatives can suffer nucleophilic attack at positions C-2 and/or C-3. The chemoselectivity of these reactions depends on the nature of the nucleophile, on the nature of the substituent's attached to the isatin nucleus, and especially of those bonded to the nitrogen atom, as well as upon the solvent and temperature employed.

Isatin and 1-alkylisatins furnish condensation products at the C-3 position when reacted with hydrazine⁵, alkyl and arylhydrazines^{6,7} heteroarylhydrazines derived from pyrimidine⁸, pyrazine⁹, thiazole¹⁰, 1,2,4-triazine¹¹, quinazoline^{12,13}, benzimidazole¹⁴, benzothiazole¹⁵, phthalazine¹⁶ and triazines¹⁷, semicarbazines¹⁸ and thiosemicarbazides^{19,20,21}. The reaction of 1-methylisatin and semicarbazone yielded methisazone, a compound that found use in the treatment of variola, a viral disease that has now been eradicated²².

Isatin is considered as an important class of bioactive compounds exhibiting antibacterial, and antiproliferative activity²³, anticancer²⁴ antidepressant²⁵, antifungal²⁶, anti-HIV²⁷ and anti-inflammatory properties²⁸.

Organic azides are especially versatile functional groups. Tetrazoles are increasingly important heterocyclic compounds. Azides adjacent to a heteroaromatic nitrogen atom exist in equilibrium with the corresponding tetrazole.²⁹ Substituents on the heteroaromatic ring can influence the ratio of products at equilibrium,³⁰ but in most instances, the tetrazole is the predominant species present. In medicinal chemistry an enormous number of tetrazole-containing biologically active compounds are known in the literature.^{31,32} Tetrazoles have been studied extensively since they were first described in 1885 and have been used in a variety of synthetic and medicinal chemistry applications.³³ Apart from their use in medicinal chemistry, tetrazoles have found widespread application in a variety of fields including the areas of medicine and agriculture³⁴, antimicrobial, antioxidant^{35,36}, anti-inflammatory³⁷, antitumor³⁸, antiviral, antiallergic, anticonvulsant and anti-inflammatory properties³⁹.

II. EXPERIMENTAL PROCEDURE

Materials and Methods

All the reagents/chemicals were purchased commercially and used by further purification using standard procedures. Melting points were determined by an open capillary method and are uncorrected. The purity of all the newly synthesized compounds was checked by thin layer chromatography using silica gel-G coated Al plates (Merck), spots were visualized by exposing the dry plates in iodine vapors. The IR (KBr pellet) spectra were recorded on a Perkin-Elmer (Spectrum ONE) FT-IR Spectrometer. The Proton Nuclear Magnetic Resonance (1H-NMR) Nuclear Magnetic Resonance, Deuterated Dimethyl Sulfoxide (DMSO-d₆) spectra were recorded with a Bruker NMR 500 and 125 MHz spectrometers, and the chemical shift values are expressed in ppm (δ scale) using Tetramethylsilane (TMS) as an internal standard. The mass spectral measurements were carried out by Electron Impact method on JEOL GC mate spectrometer at 70 eV. Elemental analyses were performed on flash EA 1112 series elemental analyzer.

2-Chloroindol-3-one(2-chloroisatin)2a

Isatin (0.05 mole) was refluxed with phosphorous pentachloride (0.10 mole) refluxed with dry benzene for 5 hours. After cooling to room temperature, the resulting red crystals were filtered, recrystallized.

General procedure for the synthesis of Tetrazolo[1,5-a] indoline-3-one 3a,b: To a solution of 2-chloroindoline-3-one (0.001 mole) in acetonitrile (5ml), sodium azide was added (0.02 mole) and the mixture was stirred at room temperature for 2 hour, then the reaction mixture was refluxed for 5 hours. The reaction mixture was poured in ice-cold water and extracted from chloroform. After evaporation of the solvent dark red colored compound was obtained.

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[Signature]

Tetrazol[1,5-a]indoline-3-one 3a: Yield: 54%; M.p.: 184 °C; R_f 0.87 ethyl acetate: pet ether (1:1) mixture; FT-IR (KBr) (cm^{-1}): 1690 (C=O), 1596 (C=N), 1482 (C=N); $^1\text{H NMR}$ (DMSO- d_6): δ : 8.02-8.09 (m, 4H, Ar-H); $^{13}\text{C NMR}$ (DMSO- d_6): 186.3, 137.8, 136.7, 134.9, 130.4, 130.2, 125.3 & 124.1; MS (EI) m/z 172.039 (M^+); Anal. Calcd. for $\text{C}_8\text{H}_4\text{N}_4\text{O}$ (172.039), C, 55.82, H, 2.34, N, 32.55%. Found: C, 49.07, C, 55.82, H, 2.34, N, 32.55%.

5-Nitro-tetrazol[1,5-a]indoline-3-one 3b: Yield: 62%; M.p.: 194 °C; R_f 0.94 ethyl acetate: pet ether (1:1) mixture; FT-IR (KBr) (cm^{-1}): 1698 (C=O), 1602 (C=N), 1482 (C=N), 1413, 1244 (NO_2); $^1\text{H NMR}$ (DMSO- d_6): δ : 6.46-7.12 (m, 3H, Ar-H); $^{13}\text{C NMR}$ (DMSO- d_6): 187.6, 143.8, 136.7, 134.8, 130.6, 125.3 & 124.2; MS (EI) m/z 172.039 (M^+); Anal. Calcd. for $\text{C}_8\text{H}_3\text{N}_5\text{O}_3$ (217.024), C, 44.25, H, 1.39, N, 32.25%. Found: C, 49.07, C, 44.28, H, 1.33, N, 32.28%.

General procedure for the synthesis of 2-(9H-tetrazolo[1,5-a]indol-9-ylidene)hydrazine carbothioamide (4a,b): To a solution of compound 3a (0.001 mol) in absolute ethanol (10ml), thiosemicarbazide (0.002 mol) was added and it was refluxed for 5-6 hrs. The product thus obtained were filtered, dried and recrystallized from ethanol.

2-(9H-tetrazolo[1,5-a]indol-9-ylidene)hydrazine carbothioamide 4a: Yield: 48%; M.p.: 185-86 °C; R_f 0.90 ethyl acetate: pet ether (1:1) mixture; FT-IR (KBr) (cm^{-1}): 3214 (NH_2), 3098 (NH), 1601 (C=N), 1488 (N=N); $^1\text{H NMR}$ (DMSO- d_6): δ : 11.20 (s, 1H, NH), 9.18 (s, 2H, NH_2), 7.04-7.87 (m, 4H, Ar-H); $^{13}\text{C NMR}$ (DMSO- d_6): 180.2, 146.3, 140.1, 136.2, 130.3, 127.4 & 124.5; MS (EI) m/z 245.048 (M^+); Anal. Calcd. for $\text{C}_9\text{H}_7\text{N}_7\text{S}$ (245.048), C, 44.07, H, 2.88, N, 39.98%. Found: C, 44.09, H, 2.85, N, 39.97%.

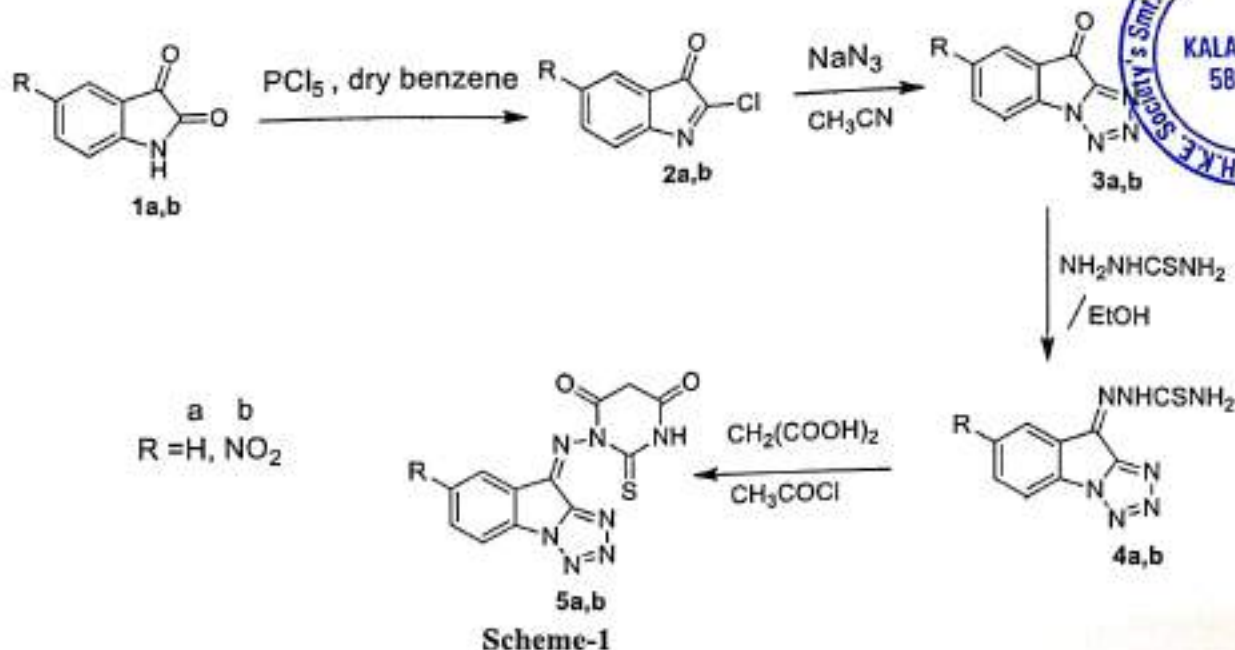
5-Nitro-2-(9H-tetrazolo[1,5-a]indol-9-ylidene)hydrazine carbothioamide 4b: Yield: 62%; M.p.: 202-4 °C; R_f 0.94 ethyl acetate: pet ether (1:1) mixture; FT-IR (KBr) (cm^{-1}): 3221 (NH_2), 3102 (NH), 1609 (C=N), 1487 (N=N), 1410, 1269 (NO_2); $^1\text{H NMR}$ (DMSO- d_6): δ : 11.12 (s, 1H, NH), 9.10 (s, 2H, NH_2), 7.01-7.80 (m, 3H, Ar-H); $^{13}\text{C NMR}$ (DMSO- d_6): 179.8, 145.9, 139.7, 136.3, 130.2, 127.0 & 124.1; MS (EI) m/z 245.048 (M^+); Anal. Calcd. for $\text{C}_9\text{H}_5\text{N}_8\text{O}_2\text{S}$ (290.261), C, 37.34, H, 2.08, N, 38.60%. Found: C, 37.34, H, 2.08, N, 38.60%.

III. Results and Discussion Chemistry

Reactions outlined in Scheme-1 were adopted to synthesize the desired compounds. The key intermediate the 5-Substituted-2-chloro isatin which was prepared by reacting substituted isatin with phosphorus pentachloride in dry benzene this was made to react with sodium azide to get tetrazole ring. The reaction was carried out in acetonitrile solvent at room temp for 2hr then refluxed for 5 hrs. Many reactions were reported to synthesize tetrazoles from DMSO and DMF as solvent. But in acetonitrile good yield was obtained. The tetrazole (3a, b) was treated with thiosemicarbazide in ethanol products (4a, b) obtained then it undergone cyclisation with malonic acid in acetyl chloride to give thiopyrimidinone derivative of isatin containing tetrazole moiety. All these synthesized new compounds were confirmed by IR, $^1\text{H NMR}$ and mass spectral data and spectral data were included in the experimental section.

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IV. Biological Activity
Antimicrobial Activity

The synthesised compounds were screened for *in-vitro* antibacterial activity against (Table I) gram-negative bacteria *Escherichia coli* (*E. coli*) and *Klebsiella pneumoniae* (*K. pneumoniae*) and gram-positive bacteria *Staphylococcus aureus* (*S. aureus*) at 25 µg/mL, 50 µg/mL, and 100 µg/mL concentrations, respectively. Gentamycin was used as standard. The zone of inhibitions was measured in mm for each concentration. Most of the screened compounds were found to have significant antibacterial activity.

Compounds 3b, 4b have shown very good activity against all the three bacterial strains, remaining compounds have shown moderate to least active. Antifungal screening of the compounds was carried out *in-vitro* against two fungi strains *Candida tropicalis* and *Candida albicans* at 25 µg/mL, 50 µg/mL, and 100 µg/mL concentrations using fluconazole as standard. Among the tested compounds 4b exhibited significant antifungal activity. The results of antifungal activity are shown in Table II.

Table I: Results of antibacterial activity of synthesised compounds (3a-b)& (4a-b)

Comp. No.	Antibacterial Activity								
	<i>S. aureus</i>			<i>E. coli</i>			<i>K. Pneumoniae</i>		
Concentrations	25	50	100	25	50	100	25	50	100
3a	05	08	12	08	04	06	03	05	11
3b	15	16	18	15	20	16	19	15	15
4a	07	08	11	05	05	06	05	06	06
4b	16	18	20	18	18	19	18	20	21
Std. Gentamycin	18	20	23	17	19	22	21	23	23

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Table II: Results of antifungal activity of synthesised compounds (3a-b) & (4a-b)

Comp. No.	Antifungal activity					
	C. tropicalis			C. albicans		
Concentrations	25	50	100	25	50	100
3a	10	11	13	09	08	10
3b	12	16	19	14	11	19
4a	06	06	08	07	08	09
4b	12	16	19	14	11	19
Std. Fluconazole	16	20	22	18	18	21

V. CONCLUSION

The key intermediate in scheme-1 is the 2-chloro isatin which is prepared by reacting isatin and 5-nitro isatin with phosphorus pentachloride in dry benzene. Since the chloro isatins were unstable they are made to react with sodium azide to get tetrazole ring. The reaction was carried out in acetonitrile solvent at room temp for 2hr then refluxed for 5 hrs. Many reactions were reported to synthesize tetrazoles from DMSO and DMF as solvent. But in acetonitrile it gave good yield. Compounds **3b**, **4b**, have shown very good activity against all the three bacterial strains and **4b** exhibited significant antifungal activity.

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MASS ATTENUATION COEFFICIENTS, EFFECTIVE ATOMIC NUMBER, ELECTRON DENSITY AND KERMA OF BBPD AND BBPO ORGANIC MOLECULES

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Abstract

The effective atomic numbers (Z_{eff}) and electron densities (N_{el}) of selected organic molecules containing C, H, N and O viz., 2-(4-*tert*-butylphenyl) -5(4 - biphenyl) -1, 3, 4-oxadiazole (BBPD) and 2, 5-bis(4 - biphenyl) -oxadiazole (BBPO) have been calculated for the total photon interactions in the wide energy range of 1 keV-100 GeV using WinXCom program. The kerma (K_a) also have been calculated for the organic molecules in the energy range of 0.001-20 MeV. The significant variation of Z_{eff} and N_{el} is due to the variation in the dominance of different interaction processes in that particular energy region. The maximum values of Z_{eff} and N_{el} are found in the low-energy range ($E < 0.01$ MeV), where photoelectric absorption is the main interaction process. The K_a values show peak due to the photoelectric absorption.

Keywords: Organic molecules, effective atomic numbers, electron density, Kerma WinXcom

Introduction

The study of photon atom interaction in different materials has gained importance in recent years. Since these interactions involve various compounds with different compositions. G. J. Hine has pointed out that in composite materials, for photon interactions, a single number cannot represent the atomic number uniquely across the entire energy region, as in the case of pure elements [1]. This number for composite materials is known as "effective atomic number" (Z_{eff}) and it varies with energy. Electron density is the measure of the probability of an electron being present at a specific location. In molecules, regions of electron density are usually found around the atom and its bonds. The energy absorption in a given medium can be calculated if certain constants are known. These necessary constants are Z_{eff} and N_{el} of the medium.

Knowledge of photon interaction with matter is essential in nuclear physics, radiation physics, radiation medicine, radiation measurement, radiation dosimetry, radiation biology, fluorescence studies, radiation shielding, nuclear technology and space research. The photons in the keV range are important in radiation biology as well as in medical diagnostics and therapy[2]. Photons in the MeV range are vital for radiography and medical imaging and photons in the GeV range are of interest in astrophysics and cosmology [3].

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The mass attenuation coefficients (μ/ρ), effective atomic number (Z_{eff}) and electron density (N_e) are the basic quantities required in determining the penetration of X-rays and gamma photons in matter. The mass attenuation is the key parameter in the primary physics and many applied fields. Mass attenuation coefficient is a measure of how strongly a substance absorbs or scatters radiation at a given wavelength per unit mass per unit area. Mass attenuation coefficients tend to increase with increasing atomic number at same photon energy, so the materials chosen to shield X-ray and gamma rays have high atomic numbers (with high mass attenuation coefficients) [4, 5].

Organic compounds are those that have carbon atoms. The presence of nitrogen, oxygen and other atoms adds variety to these carbon molecules. Organic molecules which are used in the present work have the property of fluorescence [6]. Many publications compiled the data of mass attenuation parameters for different materials. Berger et al developed XCom for estimating mass attenuation coefficient and photon interaction cross-section of any element, compound and mixture in the energy range from 1 keV to 100 GeV. XCom was transformed to the Windows platform by Gerward et al and this Windows version is called WinXCom [7, 8]. The mass attenuation coefficients of material at various energies are used for estimation of effective atomic number by ratio effective atomic cross-section to effective electronic cross-section. A similar program XmuDat also calculates mass attenuation coefficient, mass energy transfer, mass attenuation coefficients for elements, compounds, and mixtures in the energy range from 1 to 50 MeV photon energy range for the medical physics interest. Several researchers have studied photon interaction parameters like the Z_{eff} and N_e for various composite materials at photon energy. In the past R S Niranjana [9] and P D Govind [10], Shivalinge Gowda [11], Vishwanath P. Singh [12] D Yilmaz [13] and Manohara et al. [14] have reported effective atomic numbers for chemical compounds using WinXCom program.

In the present work, results reported on the effective atomic numbers Z_{eff} and electron densities N_e for selected organic molecules in the extended energy range from 1 keV to 100 GeV. The kerma relative to air has been calculated in the energy range 0.001- 20 MeV. The aim of this work is to investigate interaction of gamma rays with these molecules in this wide energy range and also the significant variation of Z_{eff} and N_e with energies.

Computational method and theoretical basis

Calculation of effective atomic number and electron density

When a beam of monoenergetic X-ray or gamma ray photons passes through a material medium, the intensity of the photons is reduced due to absorption and scattering of photons. The three principal modes of gamma rays interaction are photoelectric effect, Compton scattering and pair production are energy dependent. If I_0 and I are the incident and transmitted photons, then the decrease in the intensity of photons is given by Beer-Lambert's law,

$$(1)$$

where x is the mass per unit area (g/cm^2) and (μ/ρ) is the photon mass attenuation coefficient (cm^2/g) [15]. For a chemical compound or mixture, the total photon mass attenuation coefficient $(\mu/\rho)_{comp}$ has been estimated by the following 'mixture rule' with WinXCom program.

$$(2)$$

where $(\mu/\rho)_i$ and w_i are respectively the photon mass attenuation coefficient and weight fraction of the i th constituent element present in the given compound. For a material composed of multi elements the fraction by weight is given by

(3)

where A_i is the atomic weight of the i th element and n_i is the number of formula units of the i th element.

The total cross section (σ) and different partial cross-sections are related by the relation

(4)

where σ_{coh} and σ_{incoh} are coherent and incoherent scattering cross-sections, respectively. τ is the atomic photoelectric cross-section, κ is the positron electron pair production cross-section and $\sigma_{ph,n}$ is the photonuclear cross-section. The effective molecular cross section (σ_m) is estimated using the values of mass attenuation coefficients $(\mu/\rho)_{comp}$ by the following relation:

(5)

where N is the Avogadro's number, n_i and A_i are the total number of atoms and atomic weight of the i th element in a molecule respectively.

The effective atomic cross-section (σ_a) and effective molecular cross-section (σ_m) are related by the following equation:

(6)

Similarly, electronic cross-section (σ_e) is given by the following equation:

(7)

Where A_i and $f_i = n_i / \sum_i n_i$ are the atomic number and fractional abundance of the constituent element

Effective atomic number (Z_{eff}) is the ratio of the atomic and electronic cross-sections and it is given by

(8)

Equation (8) can be regarded as the definition of the effective atomic number. Essentially, it is assumed that the actual atoms of the molecule can be replaced by the same number of identical (average) atoms, each having Z_{eff} electrons.

Using the above equations Manohara et al (2008b) have shown that Z_{eff} is given by

(9)

here Z_i is the atomic number of the i th element present in a molecule.

The number of electrons per unit mass can be defined as the electron density (N_e) and is closely related to the effective interaction cross sections in the energy range from 1 keV to 100 GeV using WinXCOM. This program uses the same underlying cross-sectional database as the well-known tabulation of Hubbell and Seltzer (1995). WinXCom atomic number. The electron density for a compound is given by

(10)

In the present work, we have generated mass attenuation coefficients and photon makes it possible to export the cross-sectional data to a predefined MS Excel template, a feature that greatly facilitates the subsequent graphical and numerical data analysis [16, 17].

Computation of kerma relative to air

Kerma is an acronym for "kinetic energy released per unit mass", defined as the sum of the initial kinetic energies of all the charged particles liberated by uncharged ionizing radiation (i.e., indirectly ionizing radiation such as photons and neutrons) in a sample of matter, divided by the mass of the sample. Air Kerma is of importance in the practical calibration of instruments for photon measurement, where it is used for the traceable calibration of gamma instrument metrology facilities using a "free air" ion chamber to measure air kerma.

Kerma is applicable to photons (X-ray, gamma ray, bremsstrahlung etc) and neutrons and has the same unit, $\text{J kg}^{-1} = \text{Gy}$, as the absorbed dose. Kerma is directly related to photon fluency and likelihood of interacting medium.

To see the relationship with the mass energy-absorption coefficient μ_{en}/ρ , let ψ (J m^{-2}) be the energy fluency of mono-energetic photons passing normally through an area A in an absorber. The photon energy transferred to charged particles in a volume over a short distance dx behind the area is then $(\psi \mu_{\text{en}})A dx$. Since the mass in the volume with density ρ is $\rho A dx$, the kerma is

$$(11)$$

In order to compute the kerma relative to air -absorption coefficient μ_{en}/ρ , for air and organic molecules were calculated using the

$$(12)$$

Therefore, kerma is the product of the energy fluence and absorption coefficient. Kerma of a organic molecule relative to air can be expressed as following equation:

$$(13)$$

where w_i and $(\mu_{\text{en}}/\rho)_i$ are the weight fraction and the mass energy-absorption coefficient of the i th constituent element present in a molecule. The values of $(\mu_{\text{en}}/\rho)_i$ have been taken from the compilation of Hubbell and Seltzer.

Results and Discussion

Organic molecules with their chemical composition are shown in the Table 1. The selected organic molecules have the same behaviour since they consist of hydrogen, carbon, nitrogen and oxygen in about the same proportions. This is also evident from the fact that both molecules have a mean atomic number, $\langle Z \rangle$ of about 4.74. The value of average electron density $\langle N_{\text{el}} \rangle$, have been calculated and it is about 3.81. The average values of both the parameters have been calculated from Table 1 in the energy range 1 keV – 100 GeV.

The calculation of average values of Z_{eff} and N_{el} are carried out with the help of MS Excel to which cross sectional data was exported from WinXCom. These data shows that both the parameters depend upon chemical composition of the given molecule or compound.

Effects of chemical bonding

The present calculations are based on atomic photon-interaction cross sections. Therefore Z_{eff} (and N_{el}) have the same value for compounds having the same chemical formula. In the present approximation, Z_{eff} and N_{el} are independent of any effects due to chemical bonding. A much larger

and higher-dimensional database would be required to accommodate molecular and other matrix environments of the target atom. Careful experiments would be required to study any possible effect of chemical bonding on photon-interaction cross sections and Z_{eff} of organic molecules. Such studies should, however, stimulate further theoretical developments. Careful experiments would be required to study any possible effect of chemical bonding on photon-interaction.

Effective atomic number

Fig.1 shows the energy dependence of Z_{eff} for total photon interaction (with coherent). One can clearly distinguish three energy regions. Between these regions, there are transition ranges with a rapid variation of Z_{eff} .

Table 1. Organic molecules BBPD and BBPO in the present work. $\langle Z_{eff} \rangle$ is mean atomic number and $\langle N_{el} \rangle$ is the mean electron density calculated from the molecular formula. The effective atomic number (dimensionless) and electron densities (in units of 10^{23} electrons kg^{-1}) SN = sample number.

SN	Name	$\langle Z_{eff} \rangle$	$\langle N_{el} \rangle$
1	BBPD	4.66	3.88
2	BBPO	4.82	3.73

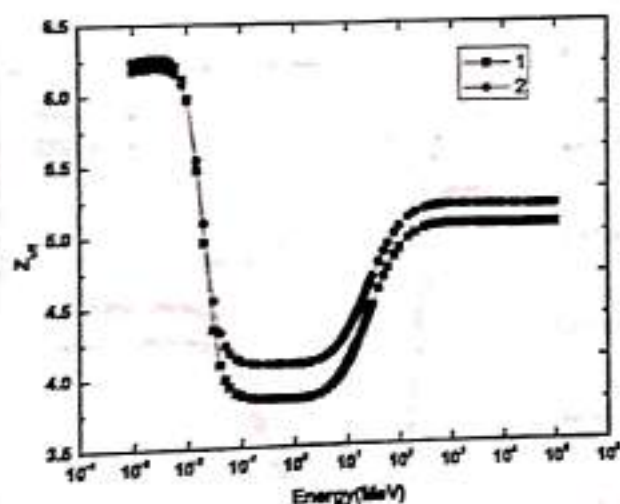


Fig. 1. Energy dependence of the effective atomic number of organic molecules for total photon interaction (with coherent).

At low-energies ($E < 0.01$ MeV), Photoelectric interaction is the main photon interaction process in the low-energy region. For a given molecules, the maximum value of Z_{eff} is found in this energy range, since the Z^4 dependence of the photoelectric absorption cross section gives a heavy weight to the element with the highest Z .

At intermediate energies ($0.05 < E < 5$ MeV), the Z_{eff} drops to a lower value in the transition region. In this energy region, incoherent or Compton scattering is the main interaction process, between about 0.05 MeV-5 MeV and after that energy range Z_{eff} is almost constant. In this energy range, Z_{eff} is close to the mean atomic number of the material, since the Compton scattering cross section of a given element is proportional to Z . For a given compound, the minimum value of Z_{eff} is found in this intermediate energy range. In the transition region from 5 MeV and 200 MeV, Z_{eff} increases with increasing energy as pair production gradually becomes dominant.

At high energies ($E > 200$ MeV), the Z_{eff} assumes an almost constant value determined by pair production. The value for Z_{eff} is smaller than that obtained for photoelectric absorption. This is due to the fact that the pair production cross section is proportional to Z^2 , giving less weight to the higher- Z elements than the photoelectric absorption cross section [20, 21].

Electron density

The energy dependence of the electron density N_e is shown in the figure 2, for total photon interaction (with coherent). Equation (10) gives the relation between Z_{eff} and N_e , where the behaviour is similar to that of the effective atomic number Z_{eff} [21, 22]. The maximum value of N_e occurs in the low-energy range determined by photoelectric absorption and the minimum value occurs intermediate energies, where Compton scattering is the main photon-interaction process. At high energies, pair production is the main interaction process. On comparison of Fig. 1 and Fig. 2, one can say that variation of N_e is similar to that of the Z_{eff} .

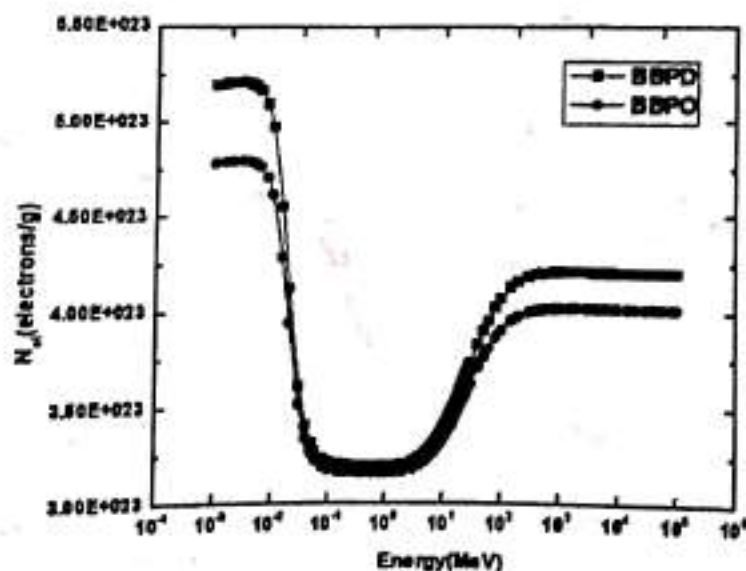


Fig. 2. Energy dependence of the effective electron density N_e , of organic molecules for total photon interaction (with coherent).

Kerma

The average kerma $\langle K_a \rangle$ have been calculated for the both the organic molecules and results are shown in the Table 2. The average values are calculated from the kerma values in the energy range 0.001-20 MeV. The variation of kerma relative to air (K_a) of the organic molecules for photon energy 0.001 keV to 20 MeV is shown in Fig. 3. The variation of kerma with photon energy represents variation of effective atomic numbers in partial photon interaction processes; photoelectric absorption, Compton scattering and pair production [9, 18]. The K_a values were estimated using equation (12) and values of the selected organic molecules vary from 0.63 to 1.24 below 100 MeV where photoelectric absorption is the dominating interaction process. It is to be noted that the K_a values of both the molecules were closely related and the variation of kerma as a function of energy is the same. From 0.1 MeV it starts decreasing up to 20 MeV. The K_a becomes maximum around 7.1 of about 0.08 MeV

Table 2. The $\langle K_a \rangle$ is the mean kerma calculated from the molecular formula.

SN	Name	Molecular formula	$\langle K_a \rangle$
1	BBPD	$C_{24}H_{22}N_2O$	2.25
2	BBPO	$C_{27}H_{19}NO$	2.22

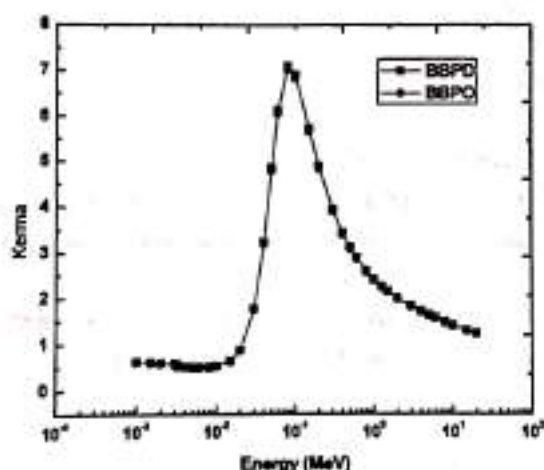


Fig. 3. Energy dependency of kerma relative to air of organic molecules.

Conclusions

The study has been undertaken to get information of the effective atomic number Z_{eff} and electron density N_{el} of selected organic molecules BBPD and BBPO in the energy range 1 keV to 100 GeV using WinXCom program and its underlying database of atomic photon interaction cross sections. The kerma values also have been calculated in the energy range 0.001-20 MeV. The variation of Z_{eff} and N_{el} can be distinguished in three energy regions as low, intermediate and high energies. The maximum value Z_{eff} and N_{el} are found at low-energy region where photoelectric effect is the main interaction process and minimum values at intermediate energies than higher-energy region.

- At low-energy region ($E < 0.01$ MeV), photoelectric absorption is the dominant process.

- At intermediate energies ($0.01 \text{ MeV} < E < 0.05 \text{ MeV}$), the Compton scattering is the dominant process.
- At high-energy region ($E < 200 \text{ MeV}$), pair production is the dominant process.
- Organic molecules which are used contain C, H, O, and N atoms. Therefore the calculated values of Z_{eff} and N_{el} of both the molecules the same.
- The K_{α} values shows peak due to photoelectric absorption.
- The comprehensive and consistent set of formulas which are used for calculating the N_{el} and Z_{eff} in the present work can be used for any other materials.

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COMPARATIVE STUDY OF NMR, IR, RAMAN SPECTROSCOPY, HOMO-LUMO SURFACES OF BENZOFURAN AND COUMARIN DERIVATIVE IN VACUUM AND METHANOL

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Abstract

The photophysical properties of benzofuran and coumarin derivative have been studied using computational methods. The NMR chemical shifts and vibrational modes of IR-Raman spectra have been analyzed by using B3LYP/6-311G (d) basis set in vacuum and methanol. ^1H and ^{13}C NMR chemical shifts obtained by using GIAO method at B3LYP/6-311G (d) basis set. The HOMO-LUMO surfaces have been studied in vacuum and methanol. TD-DFT method has also been used to study HOMO-LUMO surfaces at B3LYP/6-311G basis set. The HOMO-LUMO energy gap and chemical hardness have been calculated for both the molecule. The values of energy gap and chemical hardness have small values in vacuum and methanol from this we can predict that molecule is soft and easier for the electrons to move from HOMO to LUMO level. Because of the effect of solvent i.e methanol compared to that in vacuum, we have observed the variation in the chemical shifts, vibrational modes and HOMO-LUMO energies of the molecules.

Keywords: NMR, IR, Raman, HOMO-LUMO, Benzofuran and Coumarin derivative,

Introduction

Fluorescence probes represent the most important area of fluorescence spectroscopy [1]. Organic fluorescent molecules were the only choices for fluorophores. Various monographs and review articles provide detailed coverage of fluorescence spectroscopy. Fluorophores and fluorescent probes for readers who require further information predict the optical properties of fluorescent molecules by quantum calculation have been made in recent years. It may eventually be possible to combine organic and computational chemistry to obtain new fluorescent molecules with superior properties [2]. Some of the examples for fluorophores are derivatives of anthracene, acridine, benzofuran and coumarin etc [3]. In the present work, we have carried out computational studies on benzofuran and coumarine derivative viz., 5-((naphtho [2, 1-b] furan-1-

yl)-1,3,4-oxadiazole-2(3H)-thione (5NFMOT) and 4-[(5-amino-1,3,4-thiadiazol-2-ylthio) methyl]-7-methoxy-2H-chromen-2-one (4ATMMC) respectively, in vacuum and methanol.

Coumarin and their derivatives represent a class of well known laser dyes in the blue-green region. They are used as colorants, dye lasers, and non-linear optical fluorophores, because they exhibit fluorescence in the UV-Visible region. They are also used as optical brighteners, fluorescent indicators, biological and chemical sensors. Benzofuran is one of the most important heterocycle consisting of fused benzene and furan rings. It is frequently used as a building block in material science and in organic synthesis. Several recent reviews covered the investigation of benzofurans in natural products, bioactivity and synthesis. Both benzofuran and coumarin derivatives exhibit various biological activities including anti-inflammatory, antitumor, cytotoxic, antimicrobial, antitubercular, antioxidant, antiplasmodial, enzyme inhibitory, hepatitis C virus (HCV) inhibitory and human immunodeficiency virus (HIV) inhibitory activities [4-13].

From the above applications, it seems that 5NFMOT and 4ATMMC are significant molecules and till date no computational studies have been made from the literature survey. So it has motivated us to study spectroscopic properties by using Gaussian software. Gaussian 16 brings variety of new methods, property predictions and performance enhancements. Gauss View 6 provides support for all major Gaussian 16 features as well as offering additional modeling capabilities of its own. Gaussian 16 can predict a variety of spectra, in both the gas phase and in solution [14]. The UV-Visible spectra are related to the excited state geometries, several different methods to study the excited state systems. IR and Raman spectroscopy are another spectroscopic techniques used to study vibrational modes in a molecular system. Gaussian can compute the vibrational spectra of molecules, predicting the frequencies and intensities of spectral lines corresponding to nuclear vibrations comprising each of the molecules normal modes. One can also study various molecular properties such as mulliken charges, electron density, counter map, HOMO-LUMO and ESP map [15].

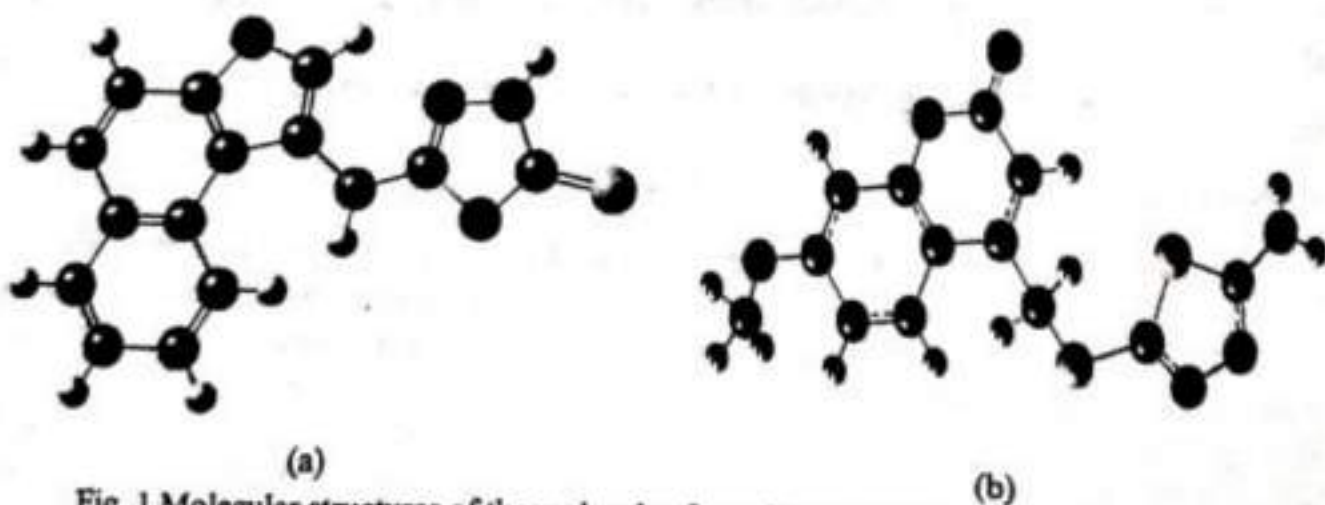


Fig. 1 Molecular structures of the molecules from Gauss view 6.

(a) 5-[(naphtho[2,1-b]furan-1-yl)methyl]-1,3,4-oxadiazole-2(3H)-thione

(b) 4-[(5-amino-1,3,4-thiadiazol-2-ylthio) methyl]-7-methoxy-2H-chromen-2-one



The present work focuses on the spectroscopic analysis of vibrational modes of Raman and NMR chemical shifts with the help of Gaussian program of the fluorophores in vacuum and methanol. The molecular structures of the selected molecules are shown in Fig. 1. The HOMO-LUMO energy gap and chemical hardness have been calculated in vacuum and methanol.

Computational methods

The spectroscopic properties have been studied using Gaussian program. Solvent effect was analyzed by using IEFPCM (Integral Equation Formalism Polarizable Continuum Model) [16]. The evaluation of IR (Infrared) and Raman activity were carried out using DFT method at B3LYP/6-311G (d) basis set [17]. The ^1H and ^{13}C NMR (Nuclear Magnetic Resonance) chemical shifts were studied using well known GIAO (Gauge Independent Atomic Orbital) approach. The Molecular orbital HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) were studied in gas phase and solution. In vacuum HOMO-LUMO surfaces obtained from Semi-empirical method for optimized geometry. In methanol both the surfaces obtained from TD-DFT (Time dependent Density functional theory method at B3LYP/6-311G basis set. The comparative study of HOMO-LUMO energies have been made from the results of Semi-empirical and TD-DFT methods [18].

Results and discussion

Analysis of NMR spectra by chemical shifts

GIAO method was one of the most common approaches for calculating isotropic nuclear magnetic shielding tensors. Application of the GIAO approach to molecular systems was significantly improved by an efficient application of the method to the *ab initio* SCF calculations, using techniques borrowed from analytic derivative methodologies. GIAO procedure is somewhat superior since it exhibits a faster convergence of the calculated properties upon extension of the basis set used. Taking into account the computational cost and the effectiveness of calculation, the GIAO method seems to be preferable from many aspects at the present state of this subject. On the other hand, the density functional methodologies offer an effective alternative to the conventional correlated methods, due to their significantly lower computational cost [19]. The ^1H and ^{13}C NMR chemical shifts of 5NFMOT and 4ATMMC were computed in combination with the B3LYP method from Gauge Atomic Independent Orbital (GAIO) theory using 6-311G (d) basis set in vacuum and methanol. The ^1H and ^{13}C NMR shielding values are shown in Fig. 2 and 3, and also the chemical shift values are given in Table 1 and 2. The chemical shift analysis is one of the most important techniques for the structural analysis for organic compounds [20, 21].

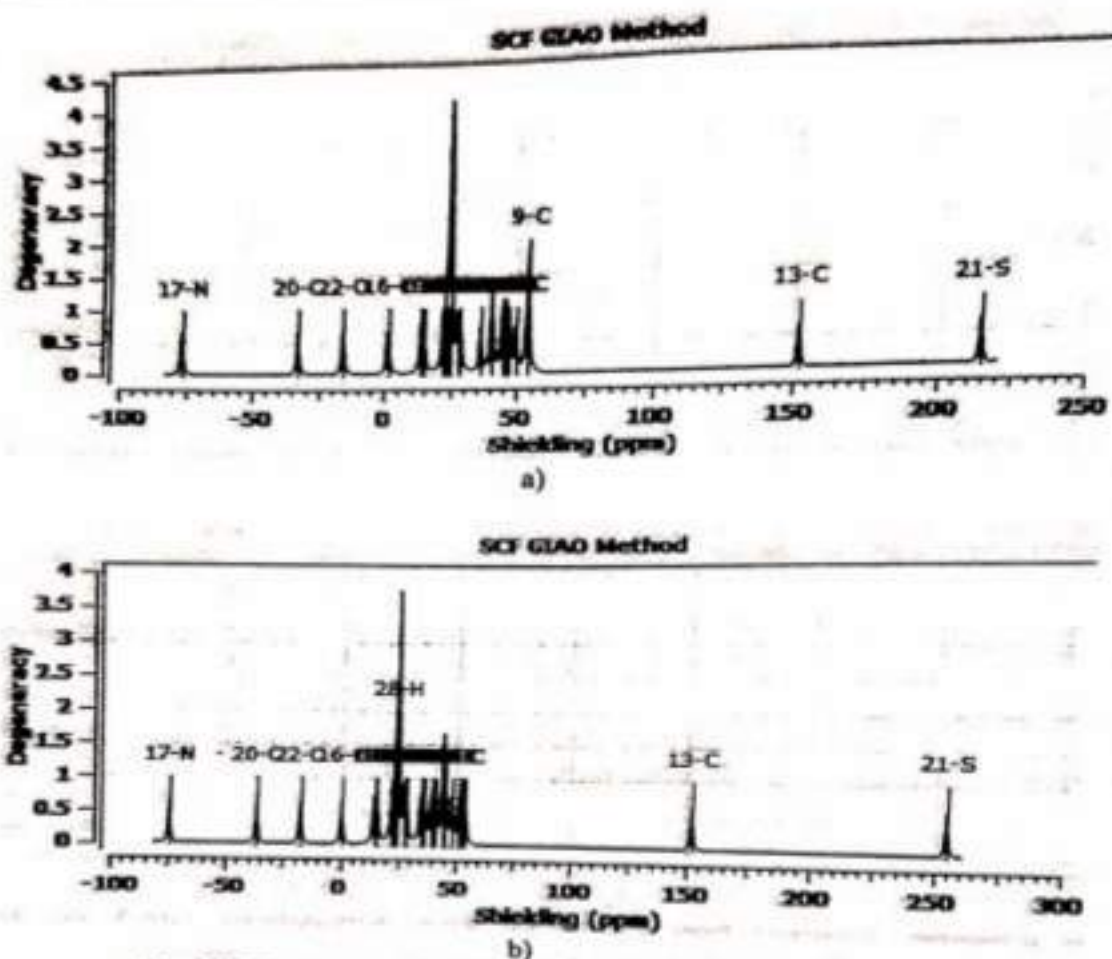


Fig. 2 NMR spectra of 5NFMOT in a) vacuum and b) methanol.

From observations ^{13}C NMR chemical shifts for 5NFMOT, the 6-C and 10-C have minimum value of chemical shifts because of bonding with Oxygen atoms. The atom 16-C have less value of chemical shifts which is bonding with nitrogen and sulphur atom. The atom 20-C has negative value of chemical shift because it shares bonding with nitrogen, oxygen and sulphur atoms. The carbon atoms present in benzene ring, 1-C, 2-C, 23-C, 3-C, 27-C, 24-C and 26-C, have chemical shifts between 36-55 ppm in vacuum and methanol. The maximum chemical shift for 13-C present in methylene group is about 152 ppm in both the phases.

The ^1H NMR chemical shifts for atoms 11-H, 29-H, 25-H, 7-H, 30-H, 28-H, 8-H, 19-H, 14-H and 15-H are in the range for vacuum 22-29ppm and for methanol 22-34ppm. Minimum value of chemical shift is for 11-H atom. The maximum value of chemical shift is for 15-H atom. The atoms 29-H, 25-H, 7-H, 30-H, 28-H and 8-H are attached to benzene ring. The atom 11-H is attached to Nitrogen atom where as 14-H and 15-H are present in methylene group.

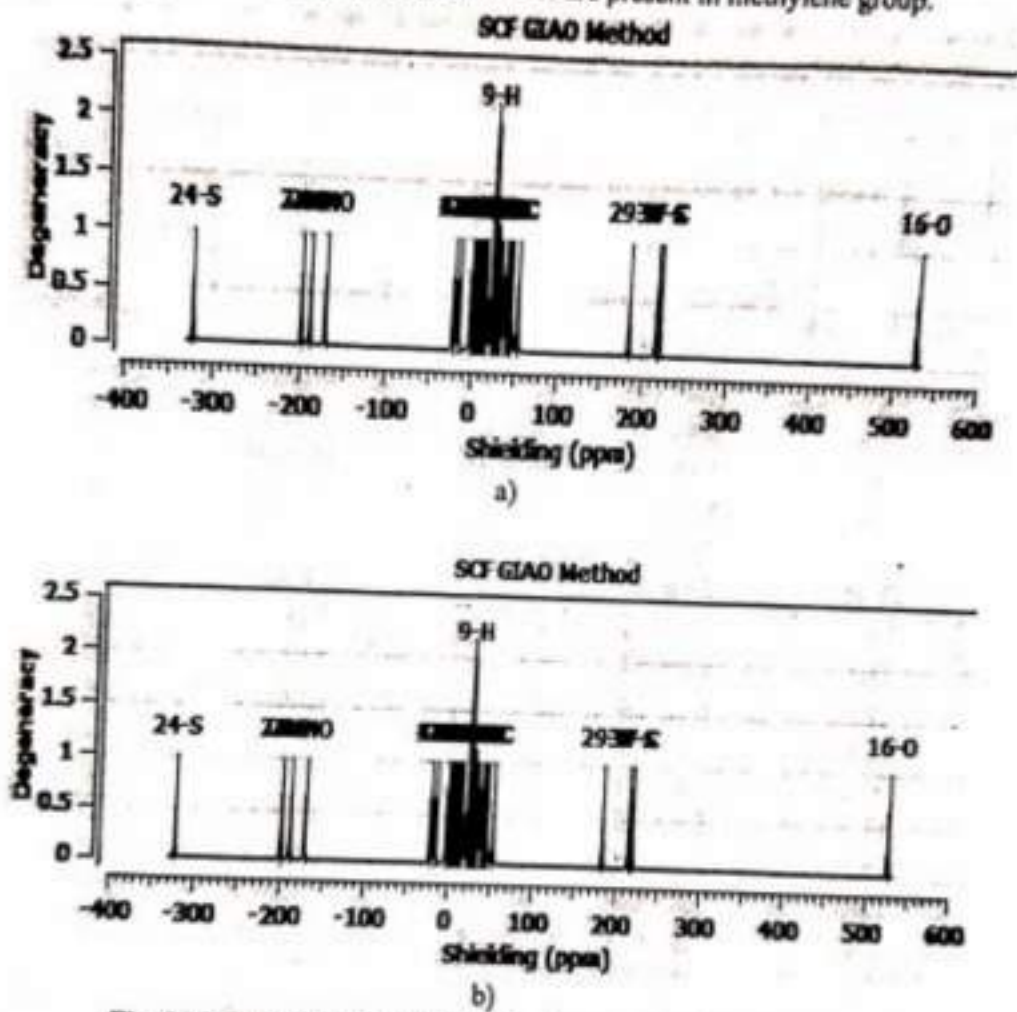


Fig. 3 NMR spectra of 4ATMMC in a) vacuum and b) methanol.

From observations for 4ATMMC, the 4-C, 11-C, 26-C and 25-C have lowest value of chemical shifts because of bonding with methylene group, Nitrogen and Sulphur atoms in vacuum and methanol. The atoms 1-C and 2-C have chemical shifts of 36ppm and 41ppm share bonding with nearest Oxygen atom. The atoms present in the coumarin molecule 3-C, 4-C, 5-C, 7-C, 8-C, 10-C, 11-C and 18-C, have chemical shifts between 34-54ppm and 43-64ppm in both the phases. The maximum ^{13}C NMR chemical shift for 17-C in both the phases is about 221ppm and 217ppm, is due to the bonding with nearest sulphur atom and coumarin molecule.

The ¹H NMR chemical shifts for atoms 13-H, 12-H, 6-H, 9-H, 22-H, 23-H, 31-H and 32-H are in the range 10-32ppm and 13-35ppm in vacuum and methanol. The minimum value of ¹H NMR chemical shift is for 19-H, 20-H and 21-H for methyl group hydrogens. The 13-H, 12-H and 6-H are attached to Benzene ring. The 9-H atom is attached to coumarin moiety. The hydrogen atoms in the coumarin molecule have almost same value of ppm and shift is very less. The 22-H and 23-H Hydrogen atoms are in methylene group, whereas 32-H and 31-H are in amino group. The hydrogen atoms in amino group have high value of ppm due to nitrogen atom and 22-H has highest value of ppm due to the nearest sulphur atom.

Table 1. Chemical shifts of 5NFMOT in vacuum and methanol.

Atom Position	Vacuum		Methanol	
	Chemical shifts (ppm)	Degeneracy	Chemical shifts (ppm)	Degeneracy
20-C	32.5492	1	36.4011	1
16-C	1.6271	1	0.3865	1
6-C	13.9922	1	14.6443	1
10-C	15.1680	1	15.9739	1
11-H	22.5210	1	22.4391	1
29-H	23.8500	1	23.6213	1
25-H	24.5412	1	24.4485	1
7-H	24.6981	1	24.5388	1
30-H	24.7526	1	24.6251	1
28-H	24.8459	1	24.6345	1
8-H	24.9273	1	24.7916	2
19-H	25.2007	1	27.8497	1
14-H	27.9915	1	28.5554	1
15-H	28.7834	1	34.5816	1
1-C	36.2835	1	36.5897	1
2-C	40.7252	1	41.1678	1
23-C	44.4627	1	44.2666	1
3-C	45.2263	1	44.4400	1
27-C	45.9139	1	44.9519	1
24-C	46.7997	1	45.6234	1
26-C	49.5391	1	48.6074	1
4-C	53.8926	2	51.4848	1
9-C	53.9230	2	53.6334	1
5-C	54.0645	1	54.2553	1
13-C	152.3770	1	152.2068	1

Table 2. Chemical shifts of 4ATMMC in vacuum and methanol.

Atom Position	Vacuum		Methanol	
	Chemical shifts (ppm)	Degeneracy	Chemical shifts (ppm)	Degeneracy
4-C	-20.6946	1	-24.0117	1
11-C	-15.0948	1	-16.0359	1
26-C	-0.8841	1	-6.2165	1
25-C	0.9146	1	-2.8091	1
1-C	5.614	1	2.8848	1
2-C	8.3251	1	9.841	1
19-H	10.9853	1	13.8219	1
20-H	13.8013	1	16.0244	1
21-H	16.4459	1	19.5194	1
13-H	24.3281	1	23.9499	1
12-H	24.7823	1	24.4396	1
6-H	24.9523	1	24.9742	1
9-H	24.9763	2	25.0111	2
23-H	26.592	1	26.7243	1
32-H	28.6465	1	28.2671	1
31-H	29.3488	1	28.6072	1
22-H	31.0753	1	35.4856	1
18-C	34.4906	1	41.9854	1
5-C	38.7745	1	43.8431	1
10-C	43.4539	1	43.987	1
3-C	44.0882	1	44.2168	1
8-C	45.5321	1	57.6484	1
7-C	54.4966	1	64.1282	1
17-C	221.3292	1	217.4942	1

IR and Raman activity spectra

Vibrational spectroscopy is utilized widely in organic chemistry where the identification of functional groups is important. It is also used for the study of molecular conformations, kinetics [22]. Structure of the molecule is nonlinear due to asymmetry in the charge distribution consisting of different atoms. The frequency of IR/Raman absorption depends on the mass of the atoms connected to a chemical bond, the strength of the chemical bond and the geometry of the molecule. Raman spectra results from the scattering of light from vibrating molecule and IR spectra results from absorption of light from vibrating molecule. There are two basic types of vibrations stretching and bending. The stretching vibrations may be symmetric or asymmetric. The bending vibrations are classified as, in plane bending (scissoring and rocking) and out of

plane bending (wagging and twisting). There will be $(3N - 6)$ vibrational modes in any molecule. Whereas N is the number of atoms present in the molecule with three rotational degrees of freedom. There are 30 atoms and 84 vibrational modes of frequency for 5NFMOT. There are 32 atoms and 90 vibrational modes of frequency for 4ATMMC. All the fundamental vibrations are active in both IR and Raman. In these active vibrational modes, there is no imaginary frequency which indicates the occurrence of true minimum at the potential surface. The plots of IR active vibrations are presented in Fig. 4 and Fig. 5 and Raman scattering activity are presented in Fig. 6 and Fig. 7 of 5NFMOT and 4ATMMC in vacuum and methanol. The Vibrational modes of IR and Raman spectra in vacuum and methanol [23] are given in Table 3. There is variation in the intensity, for same value of frequency, for IR and Raman spectra. The calculated frequency of each fundamental mode was scaled with the hybrid functional 6-311G (d)/B3LYP in the DFT approach. The vibrational bands observed in the infrared region are very sharp, broad and less intense. All these bands have been assigned in terms of various fundamental, overtone and combination vibrations. The molecule has different vibration types as C-H, CH₃, CH₂, C=N, C=O, NH₂ and ring etc. Therefore, when we investigated vibrations of the molecule, we discussed above mentioned vibration types in vacuum and methanol [24].

Vibrational modes of 5NFMOT

C-H vibrations

The spectral position of C-H stretching and bending vibrations of the methyl and methylene groups are also discussed at different frequencies along with the aromatic C-H ring stretching [25]. There are nine C-H bonds in the 5NFMOT molecule, six in the benzene ring, one in the ring attached to benzene containing Oxygen, where methylene has two C-H bonds. In vacuum, C-H stretching vibrations observed at 3202 cm⁻¹, 3181 cm⁻¹ and 3190 cm⁻¹ in the benzene ring. The methylene group, which show bending vibration at 3031 cm⁻¹ and between the range 968-548 cm⁻¹. The C-H bending vibrations were appeared in the benzene ring between the range 1665 cm⁻¹-1061 cm⁻¹.

In methanol 5NFMOT shows the following vibrations, C-H stretching vibrations occurred at 3310 cm⁻¹-3164 cm⁻¹ in the benzene ring. C-H bending vibrations assigned at 1565 cm⁻¹-1006 cm⁻¹ for the benzene ring. The bending vibrations found at 1263 cm⁻¹ for all the C-H bonds in the molecule. The vibrations also obtained at lower frequencies 497 cm⁻¹ and 433 cm⁻¹. The methylene group shows bending vibrations at 3052 cm⁻¹, 3031 cm⁻¹ and 1477 cm⁻¹.

C=C and C-O-C vibrations

The C-C stretching vibrations are more interesting if the double bond is in conjugation with the ring. In vacuum the 5NFMOT shows these vibrations, C=C bond stretching vibrations appeared for the frequencies 1665 cm⁻¹, 1599 cm⁻¹ 1405 cm⁻¹ and 1360 cm⁻¹ in the benzene ring. The vibrations also obtained in the coumarin moiety for 1311 cm⁻¹. The C-O-C stretching

vibrations observed at 1263 cm^{-1} , 1139 cm^{-1} and 876 cm^{-1} . The C=O bond stretching vibration assigned at 951 cm^{-1} .

In methanol SNFMOT shows these vibrations, C=C bond stretching vibrations generally give rise to bands for the frequency range 1626 cm^{-1} - 1006 cm^{-1} . The vibrations also arise at lower frequencies between 874 cm^{-1} - 433 cm^{-1} . The C=O bond stretching vibration observed at 1150 cm^{-1} and 1139 cm^{-1} . The C-O-C stretching bond vibrations located at 1150 cm^{-1} and 970 cm^{-1} .

N-N, N=C, N, N-H and C=S vibrations

In vacuum SNFMOT shows these vibrations, N-N bond stretching vibration appeared at 1075 cm^{-1} . The stretching vibration corresponds to N-H bond located at 3691 cm^{-1} . The identification of the N-C stretching vibration generally is very difficult to identify due to the fact that in this region several modes are mixed [26]. The stretching modes associated to N=C bond are found for the frequencies 1679 cm^{-1} and 1509 cm^{-1} . The S=C=N bond stretching vibrations observed at 1312 cm^{-1} .

In methanol stretching vibrations have been observed for both C=N and N-N bonds. The N-N bond vibrates located at 1078 cm^{-1} . The N=C bond vibrates obtained at 1674 cm^{-1} . The N-H bond stretching vibration appeared at 3668 cm^{-1} . It has been observed that the presence of N-H in various molecules may be correlated with a constant occurrence of absorption bands whose positions are slightly altered from one compound to another, this is because the atomic group vibrates independently of the other groups in the molecule and has its own frequency [27]. The stretching vibrations for both the bonds N-H and N=C appeared at 1509 cm^{-1} . The N-H stretching vibration frequencies are always higher than the other stretching vibrations and bond length is smaller than other molecules bond length [22].

Vibrational modes of 4ATMMC

C-H vibrations

In aromatic compounds, C-H stretching frequencies appear in the range of 3000 - 3100 cm^{-1} , C-H in-plane bending in the range of 1000 - 1300 cm^{-1} and C-H out-of-plane bending vibration in the range 750 - 1000 cm^{-1} [28]. The C-H stretching vibrations are occurred in the frequency range 3300 - 3000 cm^{-1} . There are nine C-H bonds in the 4ATMMC molecule, three in the benzene ring, one in the ring attached to benzene containing oxygen, other five in methyl and methylene group attached to coumarin molecule. The bands in the benzene and methylene are observed at 3214 cm^{-1} , 3157 cm^{-1} and 3093 cm^{-1} . These show all bonds are in the aromatic region. The vibrations observed for C-H at 3077 cm^{-1} and 3016 cm^{-1} for methyl group. The C-H vibrations observed in the benzene ring at 1468 cm^{-1} and 1421 cm^{-1} for high intensity. The methylene vibrates at the band 1233 cm^{-1} . Both methylene and methyl group show bands at 1209 cm^{-1} . All these vibrations are within the cited range for aromatic and aliphatic compounds [29].

In methanol, methyl group shows stretching vibrations at 3034 cm^{-1} and 3160 cm^{-1} . The C-H shows bending vibrations in the range 1652 cm^{-1} - 876 cm^{-1} . For frequencies 1493 cm^{-1} and 1202 cm^{-1} bending vibrations observed both in methylene and methyl group. The bending vibrations for methyl group appeared at 1321 cm^{-1} , 1544 cm^{-1} , 1512 cm^{-1} and 3210 cm^{-1} .

C=C, C=O and C-O-C vibrations

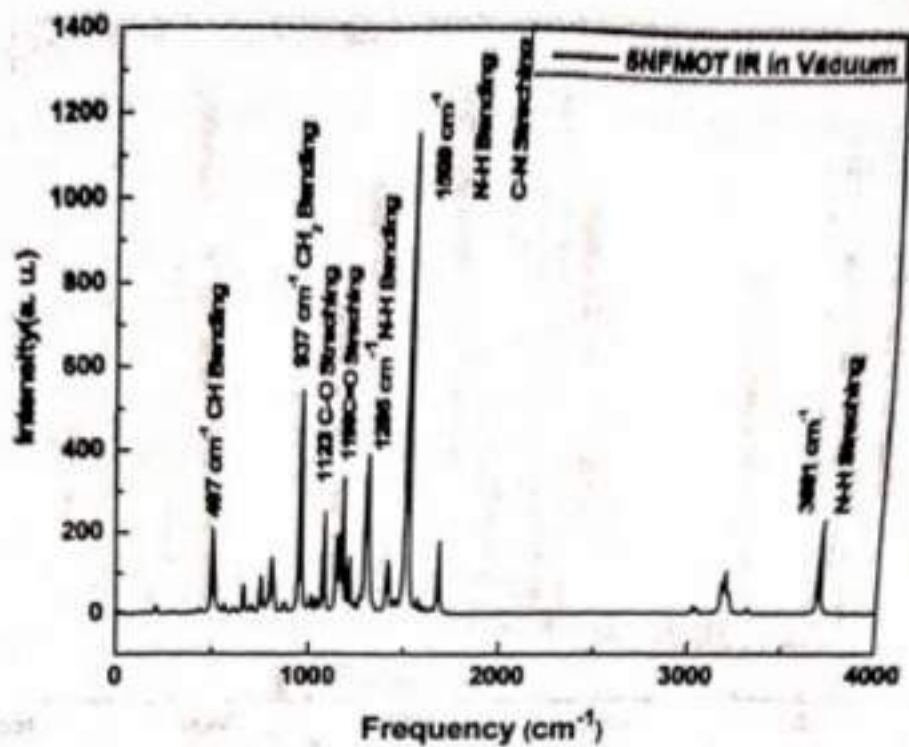
The ring stretching vibrations are much important for 4ATMMC coumarin derivative in the range 1650 cm^{-1} - 1550 cm^{-1} . The C=C vibration bands observed at 1657 cm^{-1} , 1585 cm^{-1} and 1545 cm^{-1} for coumarin molecule. The vibrations have also been observed at 1421 cm^{-1} . The C=C vibrations observed in the benzene ring at 1363 cm^{-1} . The stretching vibrations for C=O bond in the coumarin has been appeared at 1822 cm^{-1} , in which the position of C=O stretching band depends on the physical state, electronic and mass effects of neighboring substituents, conjugations and intramolecular and intermolecular hydrogen bonding [30]. The identification of C-N vibrations is a difficult task, since the mixing of vibration is possible in this region. However with the help of force field calculations, the C-N vibrations are identified and assigned in this study [31, 32]. The C-O-C bond in the coumarin molecule has stretching vibrations at 1144 cm^{-1} and also at lowest frequency 986 cm^{-1} .

In Methanol, the ring stretching vibrations of C=C bands are located for the frequencies 1652 cm^{-1} , 1643 cm^{-1} , 1577 cm^{-1} , 1544 cm^{-1} , 1462 cm^{-1} , 1422 cm^{-1} , 1360 cm^{-1} , 1202 cm^{-1} and 1075 cm^{-1} . The C=C stretching bond vibrations also observed for minimum frequency range 389 - 682 cm^{-1} . The C=C band vibrations are assigned at 448 cm^{-1} in coumarin moiety. For frequency 510 cm^{-1} , the C=C bond vibrations are occurred in the whole molecule. The C=O bond stretching vibrations observed at 1766 cm^{-1} .

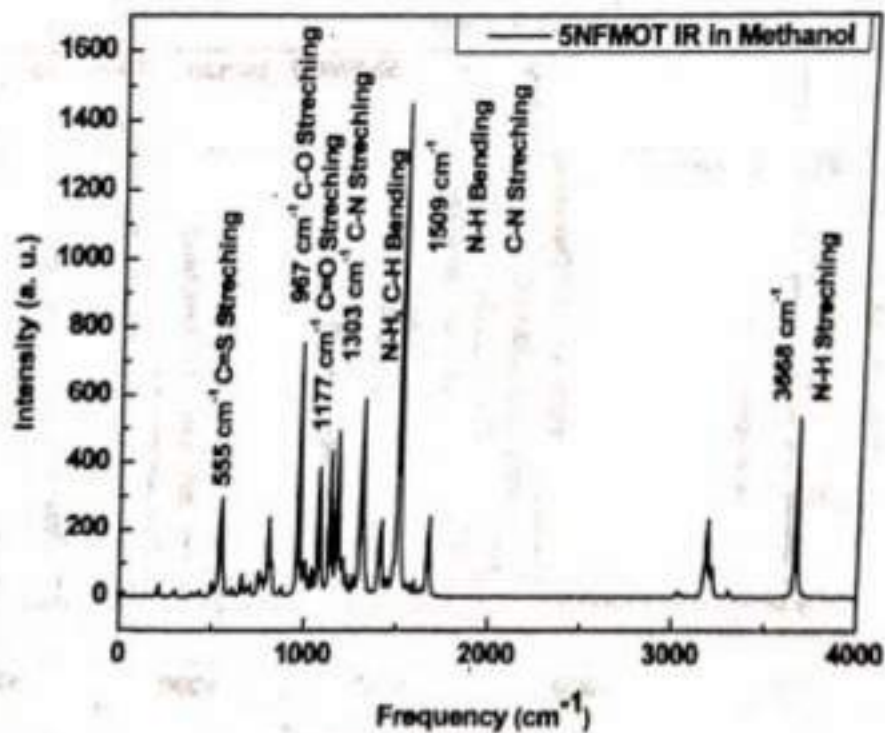
H-N-H, N=C and S-C-S vibrations

In Vacuum, the amino group vibrations are observed at 3557 cm^{-1} and 3659 cm^{-1} . The vibrations for amino group has also observed at 673 cm^{-1} . The C-S bond and amino group vibrates at 638 cm^{-1} . There are two N=C bonds in the title molecule. The ring containing C=N bonds vibrates at 1467 cm^{-1} . The amino group attached to carbon atom vibrates at 1333 cm^{-1} . The ring containing sulphur and nitrogen atoms vibrates at 765 cm^{-1} , this shows that the ring is not aromatic. Both amino group and N=C bond vibrates at 548 cm^{-1} which shows the values are pushed towards lower end of the range.

In methanol, the amino group stretching vibrations are occurred at 3576 cm^{-1} . The bending vibrations are observed at 3685 cm^{-1} , 1674 cm^{-1} , 1335 cm^{-1} , 482 cm^{-1} and 329 cm^{-1} . The N=C bond bending vibrations appeared at 1335 cm^{-1} , 1016 cm^{-1} and 765 cm^{-1} . The N-N stretching vibration located at 1162 cm^{-1} , N=C-S bending vibration located at 379 cm^{-1} .

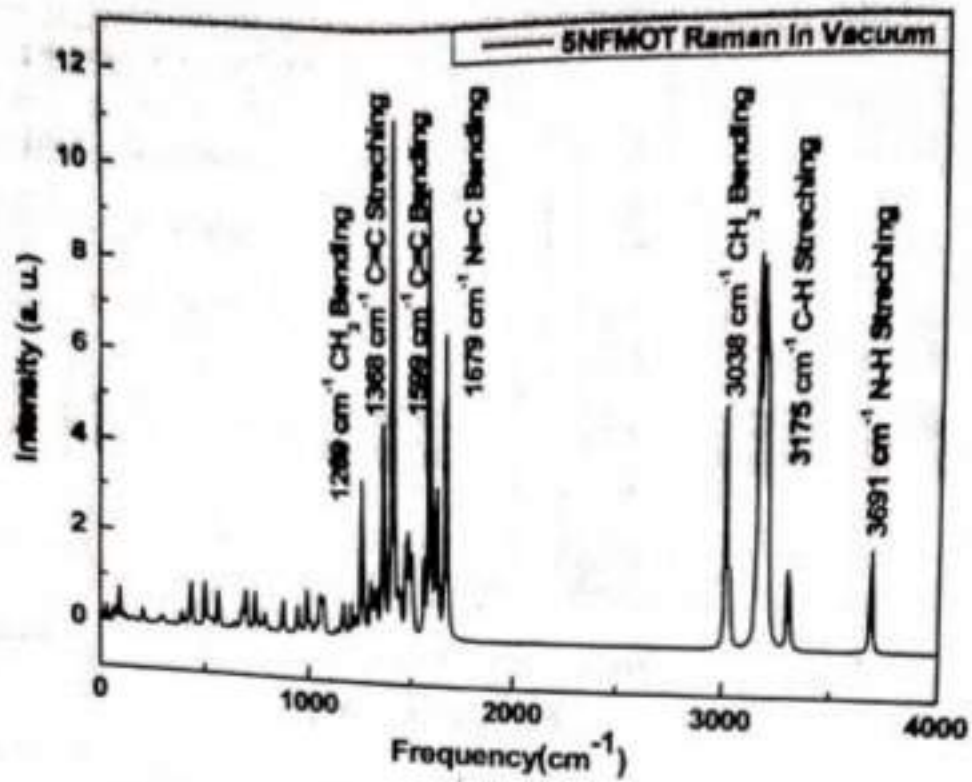


a)

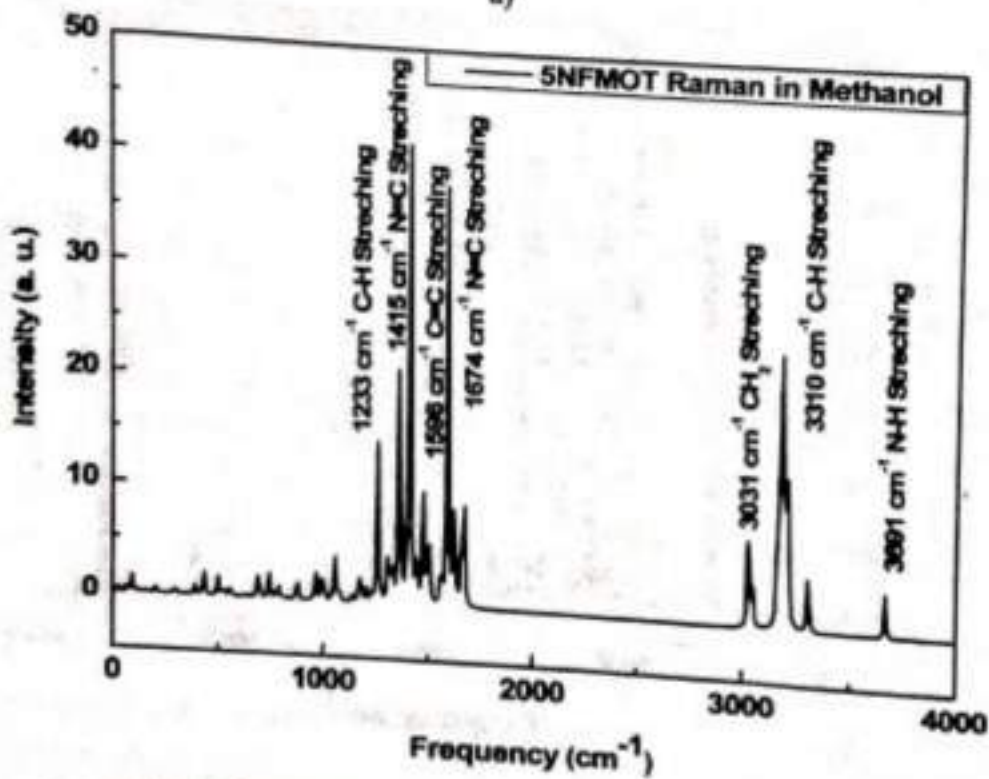


b)

Fig. 4 IR spectra of 5NFMOT in a) vacuum and b) methanol.

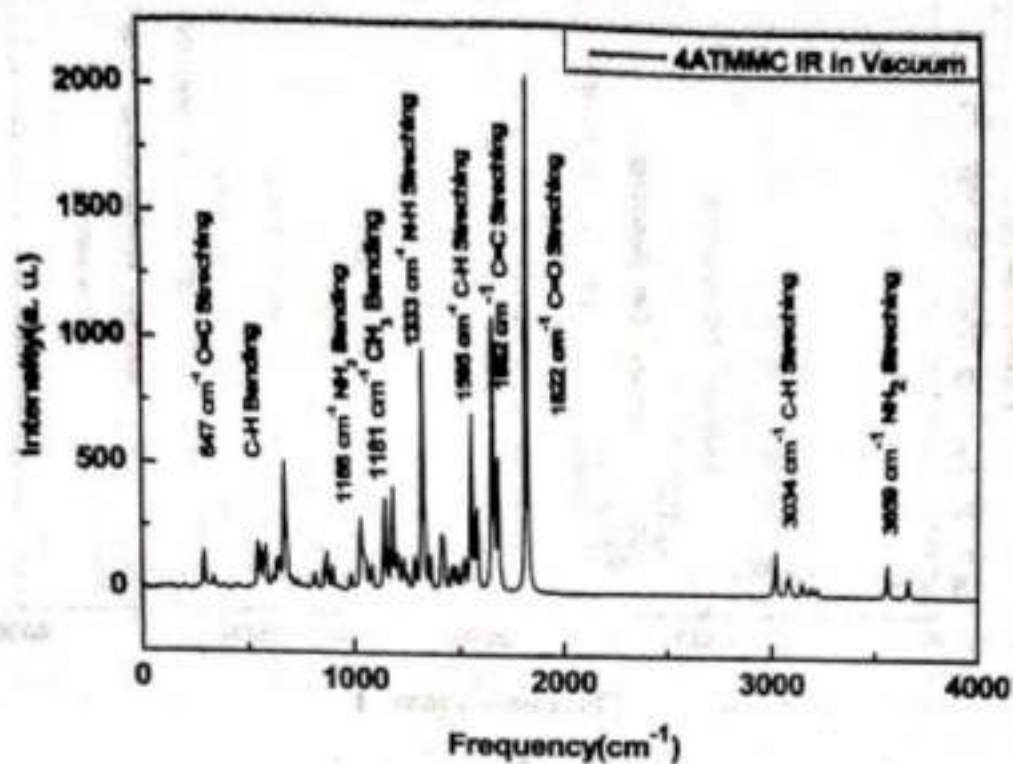


a)

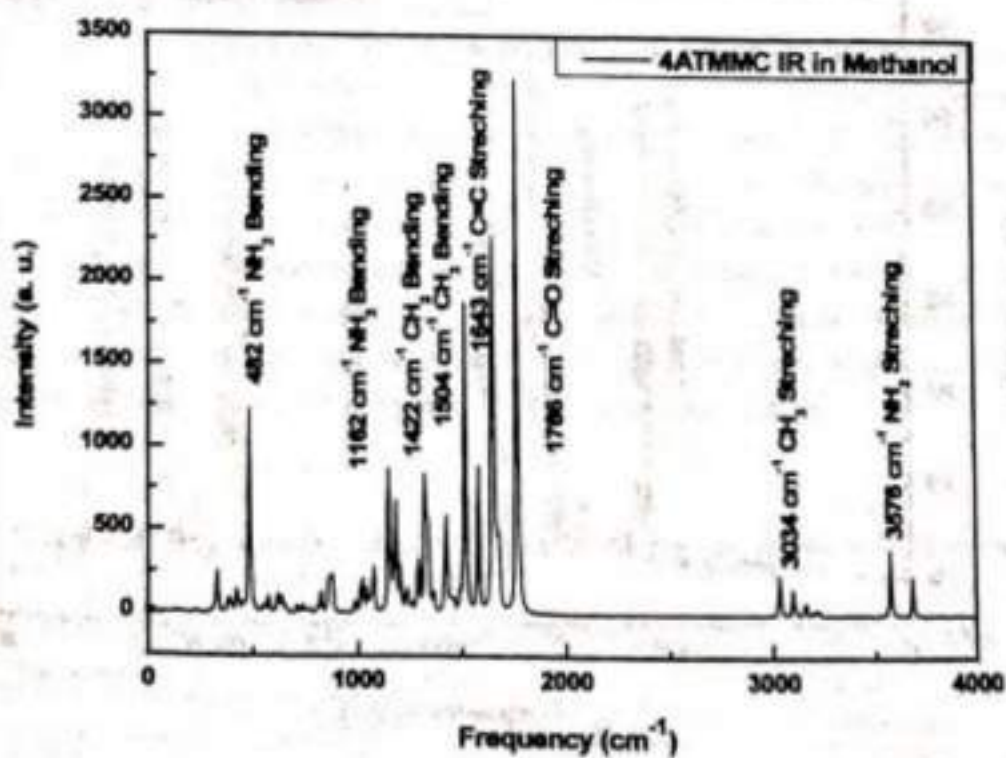


b)

Fig. 5 Raman spectra of 5NFMOT in a) vacuum and b) methanol.

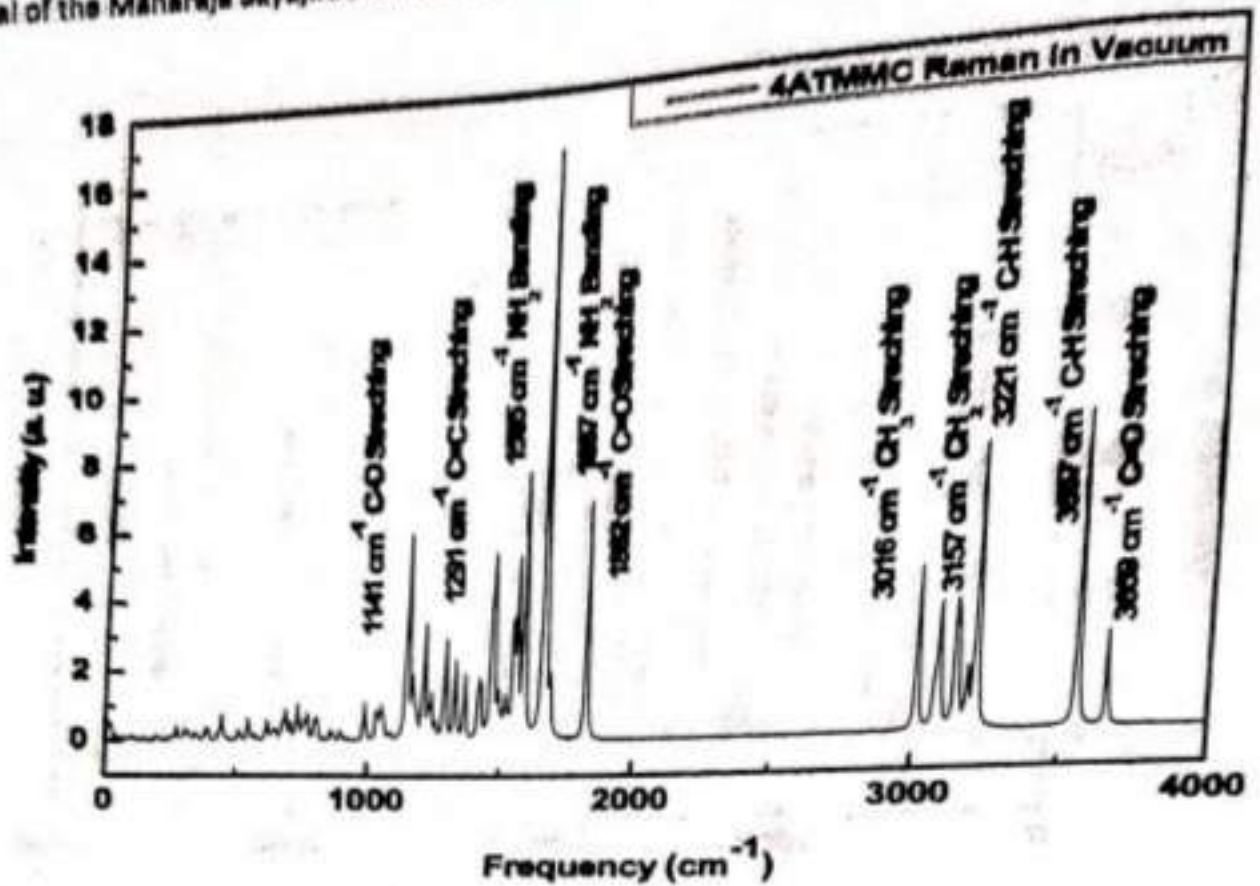


a)

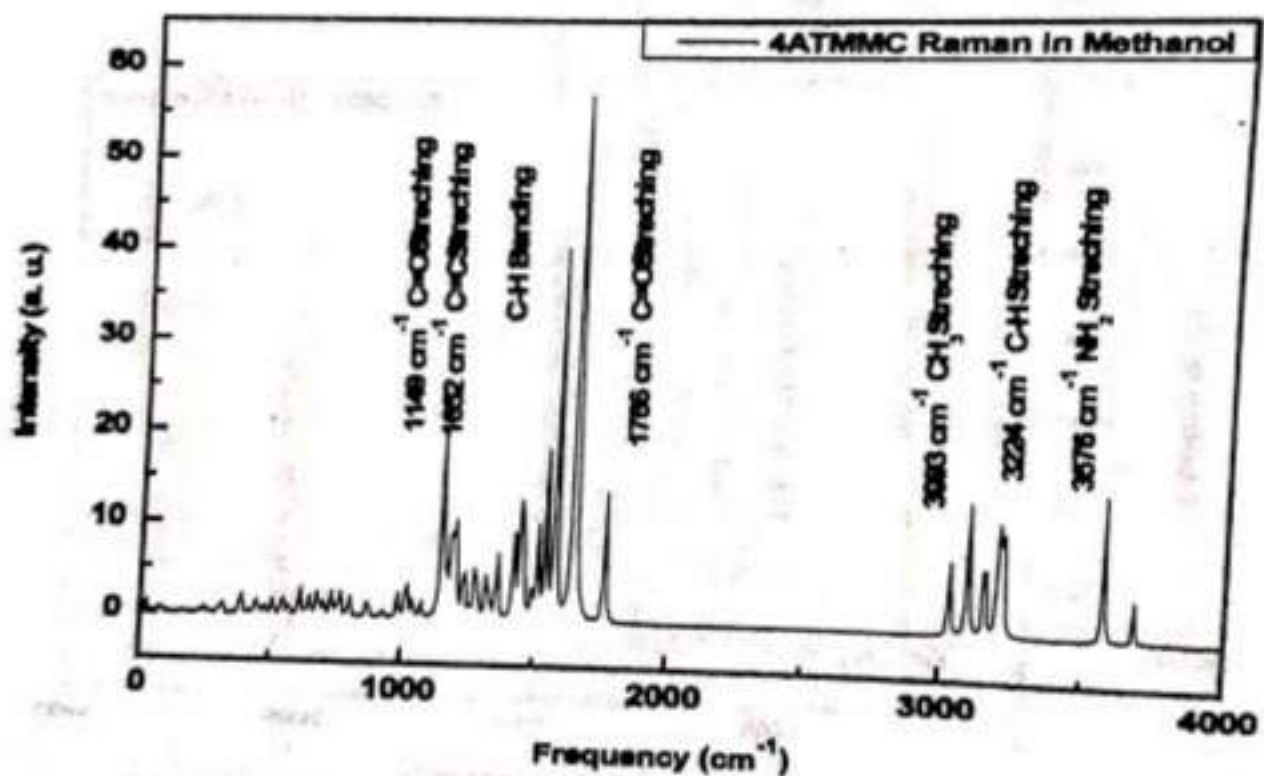


b)

Fig. 6 IR spectra of 4ATMMC in a) vacuum and b) methanol.



a)



b)

Fig. 7 Raman spectra of 4ATMMC in a) vacuum and b) methanol.

Table 3. IR and Raman Vibrational modes of two fluorophores in vacuum and methanol.

Molecule	Phases	IR		Raman	
		Frequency (cm ⁻¹)	Vibrational Modes	Frequency (cm ⁻¹)	Vibrational Modes
5NFMOT	Vacuum	937	CH ₂ Bending	1368	C=C Stretching
		1295	N-H Bending	1599	C=C Bending
		1509	N-H Bending	3175	C-H Stretching
	Methanol	967	C-O Stretching	1415	N=C Stretching
		1509	N-H Bending	1674	N=C Stretching
		3668	N-H Stretching	3310	C-H Stretching
4ATMMC	Vacuum	1333	N-H Stretching	1687	NH ₂ Bending
		1662	C=C Stretching	1882	C-O Stretching
		1822	C=O Stretching	3557	C-H Stretching
	Methanol	1504	CH ₃ Bending	1652	C=C Stretching
		1643	C=C Stretching	1766	C=O Stretching
		1766	C-O Stretching	3576	NH ₂ Stretching

HOMO-LUMO Surfaces

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are named as frontier molecular orbitals (FMOs). The HOMO-LUMO surfaces are shown in Fig. 8 and 9. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. Also, the FMOs play an important role in the optical and electric properties, as well as in quantum chemistry and UV-Vis spectra [33]. The UV-Visible absorption maxima of this molecule correspond to the electron transition from HOMO to LUMO as can be seen from the absorption maxima values obtained from TD-DFT method. Energy gap (ΔE) and chemical hardness (η) reflect chemical reactivity of the molecule. The chemical hardness is calculated from the following equation

$$\eta = \frac{Z - E}{2} \quad (1)$$

where $Z = E_{\text{HOMO}}$ and $E = E_{\text{LUMO}}$, the calculated values of energy gap chemical hardness are given in Table 4.

Table 4. HOMO-LUMO energy gap and chemical hardness of 5NFMOT and 4ATMMC

Parameters(eV)	5NFMOT		4ATMMC	
	Vacuum	Methanol	Vacuum	Methanol
HOMO	-0.332	-0.220	-0.033	-0.081
LUMO	-0.047	-0.055	-0.330	-0.219
Gap	-0.285	-0.165	-0.297	-0.138
Chemical Hardness	-0.142	-0.082	-0.148	-0.069

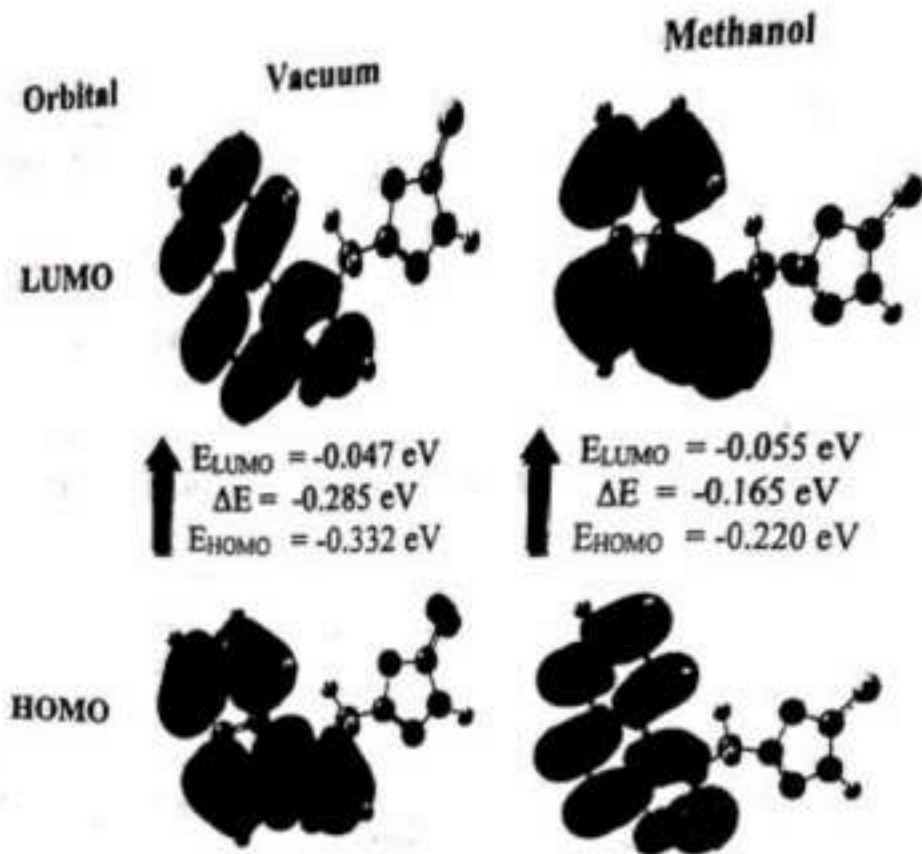


Fig. 8 HOMO-LUMO surfaces of 5NFMOT in vacuum and methanol.

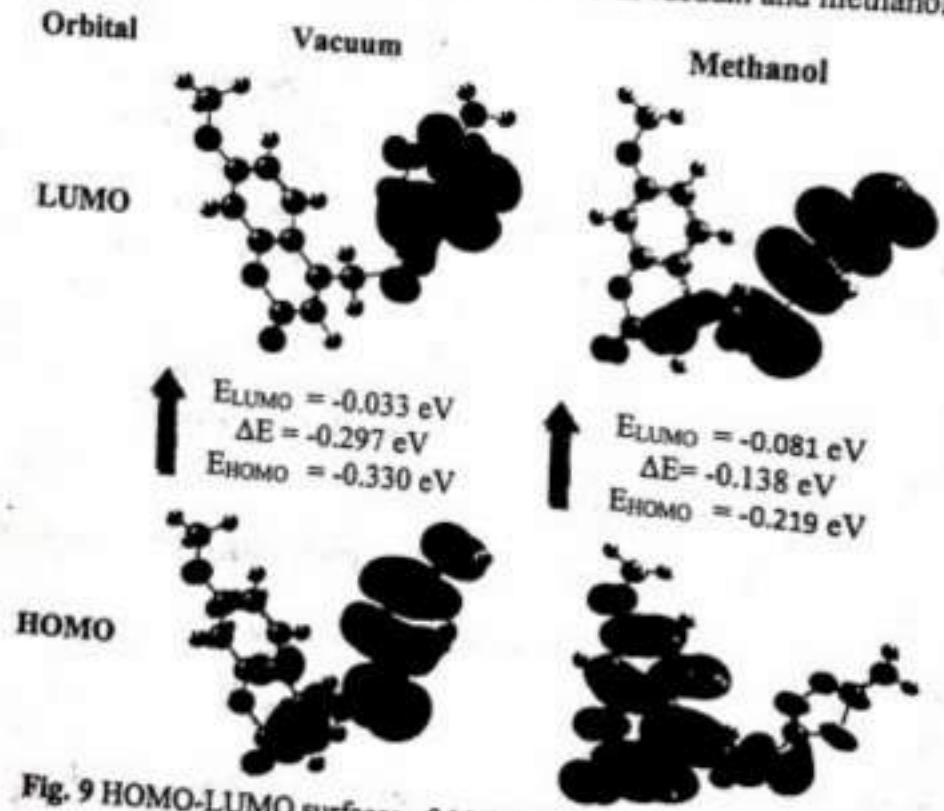


Fig. 9 HOMO-LUMO surfaces of 4ATMMC in vacuum and methanol.

The small values of energy gap for the molecule also support the observed higher values of excited-state dipole moments. The molecules possessing large HOMO-LUMO energy gap and chemical hardness are considered as hard, whereas molecules possessing small HOMO-LUMO energy gap and chemical hardness are considered as soft molecules. Soft systems are large and highly polarizable, while hard systems are relatively small and less polarizable[34-40].

Conclusions

The spectroscopic properties of benzofuran derivative 5-((naphtho [2, 1-b] furan-1-yl)-1,3,4-oxadiazole-2(3H)-thione and 4-((5-amino-1,3,4-thiadiazol-2-ylthio) methyl)-7-methoxy-2H-chromen-2-one such as NMR, IR and Raman activity spectra have been studied by using computational methods for optimized geometry in vacuum and methanol. The ^1H and ^{13}C NMR chemical shifts have been studied using GIAO method and stretching-bending vibration modes of IR and Raman have been studied in gas phase at B3LYP/6-311G (d, p) basis set. The ^1H and ^{13}C NMR chemical shifts provide a schematic approach for the structural prediction of large bio molecules. The strongest active vibrations observed at 1509 cm^{-1} for N-H bonds and 1599 cm^{-1} for C=C bonds in IR and Raman activity spectra respectively for 5NFMOT. The strongest active vibrations observed at 1766 cm^{-1} for C=O bonds and 1882 cm^{-1} for C-O bonds in IR and Raman activity spectra respectively for 4ATMMC. The HOMO and LUMO maps were obtained in vacuum and methanol. TD-DFT methods have been used to study HOMO-LUMO energies in solution. The HOMO-LUMO energy gap and chemical hardness in vacuum are -0.285 eV and 0.165 eV . The values of energy gap and chemical hardness have also small values in methanol which indicates that molecule is soft. Smaller the energy gap and chemical hardness values easier for HOMO electrons to be excited to LUMO levels.

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STRATEGIC ROLE OF LITERATURE IN FREEDOM STRUGGLE

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ABSTRACT:

The close reflective account of Indian Literature in English reveals the touching saga and tribulations of Indian freedom struggle. All the writers of pre-independent India including Mahatma Gandhi, Jawaharlal Nehru, Premchand, Tagore and several other writers in vernacular languages across the country, were busy in penning down their profound thoughts and emotions closely associated with securing the freedom for India. The literatures written during this period in unequivocal terms by all the writers were united and steadfast in their expressions with political stalwarts of the times. It may not be an exaggeration if said that all writers were rather frenzy in their vocal and written expressions as for as their expression are concerned towards mother India, especially with regard to their cherished love and pride for the country. In this joint paper we have tried to bring out how the literature of pre-independent India and the writers were greatly dominated by their strong impulse and commitment for the cause of freedom struggle. Indian literature demonstrated a new sensibility and emotional response through its themes in all its literary forms. During the times of freedom struggle nationalism, sense of devotion and sacrifice became the order of the milieu. All literary forms were pregnant with themes such as the love for the nation, patriotic fervor and a deep sense of unity. During this period the literature too played a significant role in national consciousness. When nationalist ideas began to emerge and literature enabled permeation of such ideas into different Indian languages. Many writers then began to write literature for sheer patriotic purpose.

Key Words: freedom, struggle, emotions, patriotism, tribulations, literature, nationalism, consciousness, devotion, sacrifice.

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The Indian Literature in English reveals the saga and tribulations of Indian freedom struggle. All the writers of pre-independent India including Mahatma Gandhi, Jawaharlal Nehru, Premchand, Tagore and several other writers in vernacular languages across the country, were busy in penning down their profound thoughts and emotions closely associated with securing the freedom for India. The literatures written during this period in unequivocal terms by all the writers were united and steadfast in their expressions with political stalwarts of the times. It may not be an exaggeration if said that all writers were rather frenzy in their vocal and written expressions as for as their expression are concerned towards mother India, especially with regard to their cherished love and pride for the country. In this joint paper we have tried to bring out how the literature of pre-independent India and the writers were greatly dominated by their strong impulse and commitment for the cause of freedom struggle. Indian literature demonstrated a new sensibility and emotional response through its themes in all its literary forms. During the times of freedom struggle nationalism, sense of devotion and sacrifice became the order of the milieu. All literary forms were pregnant with themes such as the love for the nation, patriotic fervor and a deep sense of unity. During this period the literature too played a significant role in national consciousness. When nationalist ideas began to emerge and literature enabled permeation of such ideas into different Indian languages. Many writers then began to write literature for sheer patriotic purpose.

The kind of environ our fellow Indians lived in, had infused among them the deep impulses of love for their mother land and this movement made the young generation to incline towards patriotism. Majority of the writers felt that it was their duty to create literature of a kind that contributed to their society, and paved the way for national liberation from the British regime.

As time passed there was a surge of people into the freedom movement and the demand for freedom became more persistent, luckily the role of literature strengthened the growing idealism of the people. It was literature that really made a remarkable impact on the psyche of the fellow Indians. In turn it stirred their hearts and emboldened them to make all kind of sacrifices for the cause of the country's release from the clutches of the foreign rule. The collective realization of the importance of freedom and realization of their well-being started to inspire and dawn upon them, and further it was coupled with influence of western ideas also.

The national consciousness influenced the Indian literature and paved the way for the production of the nationalist writers. The writers who were for pro-home-rule were bent upon in kindling the spirit of patriotism and make a mass movement. Especially Gandhiji with his peers created a mass movement through his and the writings of his peers, who in turn wrote about the nation in all its political hues and shades. It transformed the attitude of common citizens and also thinking of the political writers' in the country. "The idea of national identity emerged in Indian literature during nineteenth century. The Indian writing turned into voice of nationalism. The writers of nineteenth century expressed the feeling of nationalism, raised the question of why the British ruled over them, and the nature and extent of British exploitation of Indian people through their writing. They were bringing the message of patriotism and revolutionary thought." 1.

Like the leading writers of Hindi literature Bankim Chandra Chattajee and Bhartendu Harish Chandra, who raised the question against British, were well known for their patriotic writing, even in Kannada too many writers came on the scene, especially from the west, who made a substantial and pioneering contribution to Kannada literature and for its growth. It gave a new impetus to native Kannada writers at a later stage to plunge into literary horizon. It is said that the advent of printing press proved to be a catalyst to writing environ. "Among the several early Kannada publications, the first Kannada-English dictionary by Ferdinand Kittle from Dharwad (1894) is noteworthy.^[4] B. L. Rice edited and published ancient Kannada classics and compiled a brief history of Kannada literature, while J. H. Fleet compiled a collection of folk ballads including the well-known Sangoli Rayanna Dhanghe ("The Revolt of Sangolli Raya"). The most outstanding lyrical poet of this period, whose poems were reminiscent of the medieval mystic Kannada poetry, was Sisunala Sharief."² The contributions of Aluru Venkata Rao, who was the son of the soil (Bijapur) are noteworthy for his outstanding contributions for the unification of Kamataka, his services are indeed unique and cannot be forgotten, he was an eminent historian, writer, and an Indian revolutionary too.

History reveals that there are some factors that have a strong bearing on Indian literature to grow faster and reach a larger Indian audience. The chief among them happen to be the printing press, which carried literature far and wide and it enabled the communication of ideas faster. "A number 53 of newspapers and periodicals started. By the middle of the century journals were being brought out in a number of Indian languages, in different towns. The second factor was the

official introduction of English education in India in 1835, which opened new horizons of learning and thinking among those Indians who received English education and imbibed the ideas of western science and philosophy.”³.

It is a matter of great curiosity to observe that the revolt of 1857, though was not successful, yet it succeeded as far as literary horizon was considered, especially in producing a fire-brand poetry like folk poetry, which is a byproduct of colonial oppression and suppression of fellow Indians. The folk poetry became a torch bearer to whip the consciousness of those who were ready to plunge into freedom movement. The folk writers vehemently served for the cause of nation by composing folk poetry on patriots and it was in full song on revolt leaders. The poetry profusely sung the brave hearts like Jhansi Rani Laxmibai, and Nana Saheb Peshwa II, Tatyta Tope, Begum Hazrat Mahal, Mangal Pandey, Kunwar, Singh, Chandra Shekhar Azad and a host of others. In fact singing heroics of these stalwarts literature was produced in vernacular languages. The folk poetry instilled the patriotic fervor, and revolt of 1857 gave it a new impetus.

Further the English education empowered majority of Indian educated class to pen their views through writing books and articles, and “published newspapers to critically analyze the British policies, and develop consciousness among the masses.”⁴. “Writing in India acquired a strong nationalistic overtone and included love for the mother tongue. Each literature looked to its own past tradition and its historical antecedents, in order to create for its patrons a strong sense of identity/regional and culture.”⁵. In all the writings they could infuse love for the motherland and the unique importance of self sacrifice. Nothing permeated into their minds but only nation and nation and its freedom struggle.

A scholar named Sisir Kumar commenting on the state of affairs in the Indian literary field of twentieth century, has this to say “Indian literature of the twentieth century is a memorable record of the triumph and tragedy of Indian people involved in most significant engagement in their history- the struggle for independence and the challenges that followed the achievement of that goal tragedy.”⁶. Basically we can witness that the literary writers were engrossed in attempting to give their tumultuous experiences in the country as all of them were one with the freedom movement, hence the themes echoed the day today problems of life and the prevailing situations in the country. The writers were happy and eager to express their sense of pride in attempting to write on their chosen themes. Most of the writings were dominated by the themes



of political affairs. ""Indian literature began to negotiate with the changes in the literary community from the nineteenth century that witnessed the introduction of the printing press, the rise of a new middle class under a new educational dispensation, and slow decline of the old tradition system. The greater writers of this period had expressed a nostalgic feeling for the past glories of India. They had passion for social reform, and urge for rational inquire and a quest for new value." ibid

When it comes to Kalyan Karnataka we have a good number of stalwarts who worked tirelessly till their last breath for the country's emancipation, whether it was through writing and publication of their literature or through establishment of libraries, and in turn through them they could create awareness of freedom and its importance by providing literature which could influence and inspire them. The important freedom fighters from Kalaburagi include Poojya Doddappa Appaji, Kalyan Shetty of Maregou, Chandrashekar Patil, who became a minister later in the Karnataka government; Ramananda Theerta, Sardar Sharan Gonda Imandar, Vidhyadhar Guruji, who lived for more than 100 years passed away very recently, he was the Member of Karnataka Legislative Asembly. There are a good number of folk songs available in Kannada praising the heroic deeds of Sharanagouda Inamdar, he is the most respected freedom fighter along with others, and even today rural folk sing of his adventurous deeds and his efforts made during the freedom struggle. Personally, I had an opportunity to meet him on a couple of occasions when he was invited to our Godutai Women's College, Kalaburagi as the Chief Guest to hoist the national flag on the occasion of the Independence Day celebrations. When I was the principal of the college I had the honors to host him when he visited it on another occasion. I still remember that glowing face of Sharanagoudaji, he was truly handsome in his fair complexion, and he wore white attire with a neat turban over his head. He had indeed a magnetic personality both in his physic and in his spirits. He spoke of his adventurous life and the epic struggle he made for the cause of freedom and the deep and abiding love he held for the countrymen. But all these freedom fighters still remain as the unsung heroes. In addition to them, we have a galaxy of intellectuals including Suvarna Prathap Reddy, Hardekar Manjappa, Vittalrao Devulganwkar, Poojya Doddappa Appa, Pandit Taranath and others that spearheaded the freedom movement.



As we all know the Hyderabad Nizam kept the Kalyan Karnataka region under political disturbances, economic exploitation and religious atrocities. The Klyan Karnataka people had to struggle for independence even after India got independence. Nationalism was at its peak in the minds and hearts of the people during that period. It is said that as many as 30 camps were set up by the freedom fighters of Kalyan-Karnataka region along the borders of Raichur and Kalaburgi to wage an armed struggle against the Razaakars and to liberate their region from Nizam's rule. Sardar Vallabhai the then Home Minister made Nizam of Hyderabad surrenders and join India instead of Pakistan (against the wish of Nizam) after the Police Action. "Against the political odds created by the Nizam's government, the nationalists of this region struggled successfully to establish five national schools. In the history of the Hyderabad struggle, the founding of Hyderabad State Congress and the entry of the Swamy Ramananda Tirtha coincided not by an accident, but as a result of a series of seemingly non-political movements meant for the political preparedness of the people of Kalyana Karnataka (Hyderabad Karnataka) to launch direct action against the autocratic rule of the Nizam. This helped develop political consciousness and national spirit among the Kannadigas of Bidar, Gulbarga and Raichur districts. The Police Action was a historic event in the history of independence movement in Hyderabad state. To restore law and order and to grant the responsible government and to integrate the state with the union of India, a Police Action became imperative." 7.

The scholar Somanath C.H. further quotes from memoirs of Swamy Ramananda Tirtha. In his memoirs of Hyderabad Freedom Struggle, Swamy Ramananda Tirtha states that the Muslim fanatics treated the Hindus as slaves. The life of the people was controlled by the Muslim oligarchy. Muslims were allowed to use weapons. Much discrimination was shown in the application of law against the Hindus, whereas, Muslims enjoyed special treatment in the administration of justice. Private enterprise in education was almost forbidden and it was looked upon with disfavor. Kannada language and culture were reeling under the influence of Urdu, the official language of the state. The press, which is the mirror of public opinion, did not enjoy the freedom to publish articles on nationalism and liberty.

Poojya Dodappa Appaji the seventh Mahadasoha Peethadipathi played a pivotal role in this part of the country in the freedom struggle. The Samsthana of Sharanabasaveshwara was attacked by the Razakars when the freedom struggle was at its peak flaring up the tension in Kalaburgi.



During this time when the All India Congress convention was held in Belgaum, Mahatma Gandhiji who was present in it, was shocked to hear the news of Sharanabasaveashwara Temple being attacked by the fanatics. Hence the father of nation Mahatma Gandhiji paid a visit to Sharanabasaveshwara Samsthana and met Poojya Dodappa Appaji in order to de-stress the situation prevailing then in Gulbarga. Gandhiji paid his honor and respects to Sharanabasaveshwara and also donated for the cause of freedom struggle. Even Poojya Appaji the present Peethadipathi who was just eight years old then had come from Sholapur to Kalaburagi during this time to perform the daily worshipping of Sharanabasaveshwara. This way he too was able to contribute in his own way to his revered father Poojya Dodappa Appa. The Sharanabasaveshwara temple was the centre of all activities related to freedom moment in Gulbarga. The public used to gather secretly in the sanctum sanatorium and devise the activities to be initiated the next day or the week after. The oldest English daily like *The Hindu* has reported this in its news item. Doddappa Appaji also created awareness of freedom and its importance through the establishment of the library in Kalaburagi along with his educational institutions and their services for the country by creating a right fervor for the country's freedom struggle.

Along with the literary contributions, the contributions made by Library Movement in Hyderabad- Karnataka region are very unique. The local press and national schools played a crucial role in bringing wakefulness and responsiveness on Library Movements among the people of Hyderabad-Karnataka. It is reported that the library movement was closely associated with national movement. In 1918 Dodappa Appa started the Sharana Basveshwar Kannada Library. The main aim of this was to take an active part in the national movement and create national awareness among the people. "In 1930 the founder of N V School, Vittalarao Devalganwakar established National Library Association, in 1931 Bartha Library was established at Chincholli. With the support of Pandit Taranath, Jaganath Rao Fadnavis, R. G. Joshi and others established Bharath and Jayalakshmi Libraries in Raichur, Jagannath Desai established Dasappa Library at Kanakagiri of Ganagavathi Taluk. In 1932 advocate Uday Banu and Gopal Dev Shastri established Arya Samaj Library at Basavakalayana, Shirur Virabhadrapa opened Vishwanath Library at Adur in 1932. In the same year Basaweshwar Libraries were established at Itagi, Yalburga, Rajuri. Kannada Sahitya Sangha library started at Gulbarga. In the freedom movement of H-K, libraries played very important role in bringing awareness about the



freedom to the masses. Former MP of Bidar Ramachandra Veerappa, Sardar Sharangouda Patil of Jewargi, M. Nagappa of Raichur, Shivakumaraswamy Alavandi, who later became the Lok Sabha member from Koppal, Bheemanna Khandre of Bhalki, Jayateerth Rajpurohit of Kanakagiri, Kolar Mallappa of Yadagir, Benakal Bheemasenrao of Karatagi, were some of the heroes who led the struggle from these camps. The Gorta village in Basavakalyana taluk bore the brunt of Razaakar attack.”

We know India's freedom fighters fought a long and hard struggle for the country's independence from the British. And, for years their words have inspired us. It is time that we should preserve it at any cost and build the nation. India has celebrated its 75th Independence Day on August 15, 2021, across the country amid the corona virus pandemic. To celebrate 75 years of independence and commemorate it as 'Azadi Ka Amrut Mahotsav', the Government of India has called upon people to submit videos of them singing the national anthem. The government will be organizing year-long celebrations across India to mark the 75 years of the nation's Independence. Let us all be part of it and pay our respects to the motherland. Who can forget the immortal declaration of Bal Gangadhar Tilak: "Swaraj is my birthright and I shall have it" and let us occlude the paper by quoting the famous poem by Tagore, the national poet, which inspired millions and millions of Indians.

Rabindranath Tagore heralds the message of freedom in the following way:

“Where the mind is without fear

and the head is held high,

where knowledge is free.

Where the world has not been broken up into fragments by narrow domestic walls.

Where words come out from the depth of truth,

where tireless striving stretches its arms toward perfection.

Where the clear stream of reason has not lost its way

into the dreary desert sand of dead habit.

Where the mind is led forward by thee”

Rabindranath Tagore indeed longed for an India of such kind of spirit as demonstrated in the above lines, which were dearer to his heart.



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GREEN ISSUES IN ENGLISH LITERATURE

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ABSTRACT:

From environmental history we have learnt that a simple alteration in environment has possibility to imbalance the world. It may have far reaching consequences in a long run. It can cost the environment very dearly, leading to a severe effect on living and nonliving beings. The destruction of one species can lead to the extinction of other species. Therefore, we must stop harming environment so that we can make it a better place to live in. As days have passed, we have learnt how nature works with the help of ecology. It is reported that in order to form one inch of soil on the surface of earth 600 years are required. We have not realized how much harm we are doing to soil by using chemicals, we are also deserting and making it unfertile. In India plans are in offing to educate people in this direction. The Karnataka state forest area will be increased from its present 25% to 30% area in the next few years says the Government of Karnataka.

This paper makes an attempt to study how things have started falling apart, when nature is neglected and how man's greed has landed him into a most difficult time in the history of mankind. Some poetry of English literature, especially stressing on Wordsworth, is taken for study. Green issues are the most widely debated issues across the world. Eco-criticism is taking a stock of the situation prevailing in nature and studies how the literary writers responded and expressed their eco-sensibility. On the other hand, the word criticism is derived from the Greek word which means judgment, we know that in criticism is a free play of mind, any work of literature can come under its scrutiny and criticism examines the excellences and defects in the work of art. The eco-criticism is also known by other names or nomenclatures like green studies, echo poetics, environmental literary criticism, literary ecology or echo theory. However eco-criticism is a recent branch of study, still it is trying to find its feet in different disciplines, but certainly it offers a very broad vision of life and our place in nature too. However, there are several writers in English literature who have penned their responses in different forms. But in the present paper I have taken only Wordsworth's poetry that seems to be adequate.

Key Words: *eco-criticism, nature, environment, ecology, pollution, global warming*

Introduction:

Eco-criticism is defined as "the study of the relationship between literature and physical environment" William Ruckert "Eco-criticism is an application of ecology and ecological

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concept to study of literature, because, ecology has greatest relevance to the present and future of world "It is a literary discipline which seeks to examine the intersections of culture, literature and ecology" Features of eco-criticism include, synthesis of literary criticism and environmental issues by focusing on the literary analysis of the representation of nature in literary texts. It also gives a call to literature to connect to issues of today's environmental crisis, so, it is concerned with both nature and the environment. It is basically earth-centered study as earth is the center of study. Eco-criticism as perceived, not only tries to save the environment, but also tries to change the way we see and interpret the world around us. Man and nature coexist since centuries and both are dependent on each other. Man being a rational and intelligent one made advancement in terms of knowledge and skills. This has made man's life better than the other animals in the nature. But in the long run, this led to serious problems of environmental issues. The rampant and unscrupulous exploitative activities of human beings, made the nature bald and then man began to understand the terrible crime he made against nature. Realizing his folly he began to pay attention to it. But, man realized its implications only recently. Now the scientists, environmentalists, nature lovers, poets, thinkers, artists, media personnel and others began to give further impetus to green issues and bring governments across the globe to the negotiating table to frame policies in order to seize the over-exploitation of nature and foster it at any cost. Hence, the poets have celebrated this concept in a most beautiful way in their own style, in their literary form and philosophy.

The exploitation of nature has created crisis, as its consequences are most devastating and have led to a global warming. Further, it led to a condition wherein extinction of some species, depletion of water level and creation of drinking water scarcity have taken place. Migratory birds and insects are made to go thirsty, compelling the farmers to dig bore-wells to deeper parts of the earth for the agricultural activities.

The unscientific irrigation systems, unpredictable behavior of seasons, farmer's increased interest in multiplying their produce, has made them to exploit the earth and compelling them to go for multi crops annually. This has created many more problems like deforestation and depletion of water level. Building of dams also resulted into encroachment of vast land by back water have all together compelled us to find a solution for a better living of human beings. In fact that has become a paramount issue for all of us; therefore there is an urgent need for all of us to deliberate upon these issues, as the students of English literature. We have to make efforts to trace in literature how the writers, thinkers and poets have raised issues of environment and nature. It is time that we must express our gratitude to these visionaries for undertaking such vital issues in their literary works in the best interest of mankind.

Eco-criticism in English Literature:

For a healthy living of people on earth, there is a necessity of creating awareness on green issues, especially among the general public. Already efforts have been made by different organizations, associations, forums, national and international bodies in this direction and are



even continuing now. There was a sincere effort by United Nations, which conducted a conference on Environment and Development UNCED at Rio de Janeiro in 1992. This conference is popularly known as Earth Summit. It was indeed a milestone that the conference decided to have equitable distribution of natural resources between the present and future generations. The conference took critical note on the contributions of British writers like William Wordsworth, Robert Frost and others. The conference was attended by the scholars from Britain, America, India and other countries. Presently, we all need a healthy environment for a happy living, which necessitates conservation of our environment.

It is always humanity that triumphs from the extraordinary contributions made by writers, philosophers, thinkers, visionaries, even artists like musicians, painters or an architect. When we look at the world-masters in these spheres, we come across and learn what great services these masters have rendered to all of us, without considering geographical, linguistic and other constraints.

The writers be it American, British or Indian, especially the poets, who write in English, have shown genuine concern for environmental issues in their creative works. We must basically remember that we have to pay our debt to this mother-earth as we have been from our day one of birth, till the last breath of our life, are nurtured and sustained by it. We are enlivened and fed, given enough oxygen by it. Right from childhood we have been walking on it, we ride and drive on it a, rather all our life-sustaining activities are carried, on this planet. When our own kith and Kin on several occasions fail to take care of us and are more likely to be deserted, the nature on the contrary, without any discrimination takes care of us, nurtures and sustains us. So, this makes us to think that any amount of services we render to this mother-earth is not enough to clear our debts for its gratitude, and all the help it has made to us. Hence, the writers have begun to generate that indebtedness to Nature among the fellow human beings. Writers are creating the awareness as presently massive unscrupulous activities are going on across the globe to explore and exploit the natural resources deep within the earth, as well as on the surface of this earth, thus, man demonstrating his callousness towards nature for his greed.

Presently the world is driven by commercial considerations and the nature is the casualty of such exploitation. Many business firms and organizations have indulged in rampant exploitation of nature, which must be immediately seized and the pristine beauty of nature must be regained. Otherwise the future generation will be compelled to pay very dearly and heavily. We, being the 21st century people of this planet-earth, having been exposed to its devastating effects, must immediately plunge into action, and at any cost save this nature for posterity as well as for our own healthy living.

Robert Frost, an American poet has made most subtle, memorable, heart and soul touching rendition in English poetry, especially in his poems like *The Road Not Taken*, *Stopping*



by *Woods on a Snowy Evening* and other poems, the poet vividly describes the nature which was near and dear to his heart. The most intimate and moving personal experiences of the poet are very sensitively and exquisitely rendered in his poetry. Robert Frost, a great lover of nature like William Wordsworth, has beautifully described the valleys, the hills, the rivers, the forests, flowers, plants, trees, even animals, birds and micro insects as well. He very touchingly describes the changes that take place in the nature. His concern for Nature is really appreciable. Matthew Arnold, Thomas Hardy, John Ruskin, Thomas Carlyle and others have also deeply felt for nature and expressed their concern for nature in their writings. On the other hand they have deeply lamented over the destruction of environment, which was the byproduct of industrialization. Wordsworth a high priest of nature, who's DNA was made up of profound love and reverence for nature is the notable poet. He nurtured a profound faith in healing power of the nature and the same spirit he infused in his poetry and created this awareness among the readers across the globe.

Nature is another name for peace and tranquility; it can bring profound peace in man. Nature offers perpetual joy, the poem like *Daffodils* swells the poet's heart with joy and he expresses his gratefulness to nature. Even in Wordsworth's poems like *Resolution and Independence/Leech Gatherer, We are seven* and other poems, he luxuriously celebrates the close intimacy between man and nature. Wordsworth was a strong critic of materialistic life as he believed, the world is too much with us, that's how he believed and celebrated the beauty and mystery of nature in his poems. He advocated retaining pristine beauty of nature; *The World is too much with us*, speaks how people are busy in wealth creation and accumulation of it. They fail to get any interest in the beautiful objects in nature. That is really unacceptable, they are insensitive to the beautiful moonlight and the fragrance of flowers. All beautiful things go unnoticed by people. Like Wordsworth W.H. Davies is another great poet who very touchingly depicts his concern for nature in his poem like *Leisure* and other poems.

Those living in the lap of nature know the value of green environment, green leaves, green trees, green issues, green phraseology, and Green wars, green that is there everywhere. The sight of greenery would excite and fill them with joy in their heart and soul. The green initiatives can fill them with joy and happiness, as green alone could sooth the human soul and nothing else. Because greenery is our life, green alone sustains us and ultimately green is all.

It is very essential to know that man who is known as the home-sapiens cannot be excluded from nature, man is a part and parcel of this nature, and nature means all that lives on this planet earth. It includes plants, trees, birds, animals, insects, rivers, oceans, even human beings. Together they constitute nature. The perception of nature doesn't mean only the environment around us, the forest around us or only the rivers around us. We simply cannot segregate ourselves from nature, so what we study in eco-criticism is nothing but our own study, it is the study of what we were; what we have done and what we are expected to do. This severe

onslaught on nature and its impact is the sum and substance of environment. Therefore, it is not the study of physical geography or geology or the study of species that we undertake here. Here it is an integrated approach of study that never looks at human beings as a separate entity: they are born, brought up, and sustained. It is also the same planet where all of us are born, once the life goes off and the mortal remains are also consigned here. Therefore every activity that goes on here is directly or indirectly related to our life. We are not supposed to treat the environmental issues as non-concerned to us or a separate branch of study as our bond with nature is too deep. We human beings are born in this nature, started our lives here, the bond over the years with it began to develop, now it is high time that how we human beings on this planet earth pay back for all what nature has done to us. It is not time to ask questions, instead of asking what Nature has done to us; we should ask what we have done to Nature. Otherwise our life will be deprived of the basic needs we are getting at this juncture, if not immediately, it might be in the near future.

The Deserted Village by Oliver Goldsmith, The Prelude by William Wordsworth, and Leaves of the Grass by Walt Whitman are the best Green poetry in literature. Peace is always beautiful says Whitman. After all green literature promotes nature and protects it from being exploited. The green color in literature is used symbolizing as nature and relaxation. As a part of our study let us quote some lines from Oliver Goldsmith's

The deserted village:

"How often have I paused on every charm,
The sheltered cot, the cultivated farm,
The never-failing brook, the busy mill,
The decent church that topt the neighbouring hill,
The hawthorn bush, with seats beneath the shade,
For talking age and whispering lovers made!
How often have I blest the coming day,"

In this poem the poet recollects his reminiscences of village life and how life has changed beyond recognition, all that he had imprinted in his mind comes here alive, and he brings it vividly and paints it. He also instilled this idealization of English rural life with the simplicity. He mingles his idealized scenes with memories of his own careless youth in Ireland. Goldsmith had a serious concern, that of the effects of the agricultural revolution, which resulted in the enclosure of arable land, often to form private parks. The Enclosure Acts caused pain to small farmers whose families had earned their living from the land for generations, were made to lose everything.

The Prelude: Wordsworth

"—Was it for this
That one, the fairest of all Rivers, lov'd
To blend his murmurs with my Nurse's song,
And from his alder shades and rocky falls,

And from his fords and shallows, sent a voice
That flow'd along my dreams? For this, didst Thou,
O Derwent! travelling over the green Plains
Near my 'sweet Birthplace', didst thou, beauteous Stream
Make ceaseless music through the night and day”

“ I had melancholy thoughts...
a strangeness in my mind,
A feeling that I was not for that hour,
Nor for that place.”

It is very significant to notice that human beings are an alter ego of nature, because all elements present in nature are also found in us. “ Human being is a part of the natural world. Scientifically speaking, he is made of various elements like carbon, water and cellular material, therefore we possess all elements found in nature; therefore we are a part of nature..... Humans have always been intimately linked with rivers, lakes and wetlands for water, food, fiber, medicines and places for habitation.” The process of urbanization, construction of dams and intensified agriculture, along with navigation has led to excessive use of water.

Wordsworth emphasized on emotional and spiritual values as well as his deep engagement with nature, hence romanticism is found to be well-engraved in the soul of Wordsworth. It is a landmark in the history of English poetry, which has gifted us very strong nature poetry. Some of the lines from his poems like Prelude and Tintern Abbey are quoted here for their messages, as these lines speak of nature's power and its impact on the poet.

Tintern Abbey

“How oft, in spirit, have I turned to thee,
O sylvan Wye! thou wanderer thro' the woods'
How often has my spirit turned to thee!”

This poem of Wordsworth written in 1798 is in form of a ode, the poem is situated in a small place called Tinton village on the west bank of the river Wye, what Wordsworth has tried to channelize in this poem is his profound philosophy on the nature and its beauty . The readers are really touched by his intimate relationship with this place and lovely bond he had with it.

Ode: Intimations of Immortality

‘Turn wheresoe'er I may,
By night or day,
The things which I have seen
I now can see no more.’



In this magnificent ode, the poet has explored his divine relationship with nature and how his personality has been molded under its benevolence and grace. He brings out in this poem the deep relationship between himself when he was a child with mother-nature. But the poet also brings out how he lost that experience as he is deprived of the divine vision and company of that nature. But he assured himself that he can recollect it and relive those past glorious memories with nature and still sustain his relationship with that glorious nature by his poetic power.

The Solitary Reaper

"I listened, motionless and still;
 And as I mounted up the hill,
 The music in my heart I bore
 Long after it was heard no more."

In this ballad Wordsworth echoes his inner thoughts on nature, how a young girl is reaping in the fields and how majestically she is singing a song and how she has totally fused with the loveliness of nature, and her song is so alluring, so captivating to the poet that he feels he is really mesmerized by the beautiful rendering of this song. But the poet is least interested to disturb this young girl and he even asks the passers-by to wait and listen to the reapers song rather than disturbing this young girl. In this poem the poet tries to bring the beautiful harmony that exists between man and nature, and how the nature is enjoying the company of man and so also the man enjoying the company of nature. There is a perfect synchrony between them, each is complimentary to the other, the beauty of this nature without the human habitation would have really looked meaningless, dull and useless. But when there is a human habitation, the charm, the glory of the place gets multiplied. That is what I perceive that he might be speaking in this poem about the perfect harmony that exists between man and nature.

Daffodils

"or aft, when on my couch I lie
 In vacant or in pensive mood,
 They flash upon that inward eye Which is the bliss of solitude;
 And then my heart with pleasure fills,
 And dances with the daffodils."

This is a most celebrated poem of Wordsworth, it heralds the quintessence of romantic poetry. This poem brings out how the poet's heart was filled with joy when he saw daffodils without number on a field. The daffodils were really countless in number; he saw them while walking with his sister Dorothy. This poem brings out poet's close intimacy and how joyous he is in the company of daffodils as they are here, they were there, and they were everywhere. A

poet feels profoundly blessed in the company of nature. He instantly becomes a great worshipper of nature on such occasions; he feels as if like a child and indulges in squeezing the exquisite inner beauty of nature. The poet's soul swells with pride. The poet totally forgets the rest of the world, when he is in the company of daffodils.

Composed upon Westminster Bridge

Never did sun more beautifully sleep
In his first splendour valley, rock, or hill
Ne'er saw I, never felt, a calm so deep!
That river glideth at his own sweet will:
Dear God! the very houses seem asleep:
And all that mighty heart is lying still!"

Again this is the most celebrated sonnet and also frequently anthologized across the globe. In this poem the poet is depicting the beauty of London city in early morning. Let us be clear that the city is the part of the nature, human habitation in towns, the cottages, the multistory buildings are all part of this grand design of God, and are part of the nature. Therefore, the poet is bewitched in the early morning by the majestic beauty of this city, which is attracting people across the globe. He is standing on the Westminster Bridge and looking at the serenity that has donned early in the morning in the entire surroundings. The poet says that the mighty heart that is the city is still sleeping. But soon he laments that this beauty is going to fade, once this morning aura and serenity come to an end. So the poet being the great lover of nature takes aid of his inner eyes and looks at the charming beauty that the London city is radiating in the morning.

Conclusion:

The writers in general and poets in particular have dealt on several issues pertaining to nature, though its appreciation dominates in their creative writings, yet it does not escape from their eyes the man's perennial exploitation of nature. A small impact on environment has a potential to imbalance the whole planet, it may have far reaching consequences. It can cost the environment very dearly. Truly the destruction of one species leads to the extinction of other species. Therefore, we must stop harming environment so that we can make it a worthy place for our domicile, which has been amply displayed by the literary writers through their inspired works. We have done much to harm the soil by using chemicals, and making it not worthy for cultivation. This paper makes an attempt to study how things have scattered when nature is neglected. Green issues are the most widely debated issues across the world. Eco-criticism is taking a stock of the situation prevailing in nature and studies how the literary writers like Wordsworth, Goldsmith, Robert Frost and others have responded and expressed their eco-sensibility in English literature. Only when all is well that ends well, otherwise everything will not be all right.

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