

Harmonising Chemical and Biological Sciences for Sustainable Development

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Harmonising Chemical and Biological Sciences for Sustainable Development

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A Satyam Roychowdhury initiative



Foreword

The book, “*Harmonising Chemical and Biological Sciences for Sustainable Development*” presents an extraordinary collection of articles that explore the innovative and synergistic interplay between chemical and biological sciences, demonstrating how their integration is not only advancing research but also providing tangible solutions for a more sustainable world.

As we confront global challenges such as climate change, resource depletion, and pollution, it becomes clear that the solutions lie in the convergence of disciplines. Chemistry and biology, traditionally viewed as distinct fields, are now recognized as interconnected disciplines essential for driving sustainable development. This book serves as a testament to the power of interdisciplinary research and its ability to generate breakthrough solutions for everyday issues.

The articles compiled here cover a wide range of exciting topics, from the latest advancements in nano-photocatalysis for consumer products to the development of heterogeneous catalysts for sustainable CO₂ transformations. These contributions not only enrich our comprehension of chemical processes geared toward a greener and more sustainable future but also underscore the indispensable role of biological sciences in ensuring that such advancements are safe, efficacious, and in harmony with the natural world.

I sincerely hope that the perspectives presented in this volume will ignite curiosity and drive among researchers, policymakers, and students to further delve into the immense possibilities offered by this interdisciplinary pattern. As I strive to build a more sustainable world, the integration of chemical and biological sciences will undoubtedly be a critical force in achieving long-lasting and meaningful change.

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Preface

In this new volume entitled, “Harmonising Chemical and Biological Sciences for Sustainable Development” the authors offer fresh insights and innovative frameworks for reinterpreting sustainable development in the context of global development. The book delves into potential strategies for addressing the complex interplay between energy, environmental sustainability. It explores the intersection of chemistry and biology in addressing the pressing challenges of sustainability bringing together cutting-edge research that delves into the transformative potential of science in creating eco-friendly solutions. By examining various applications, from green solvents and organic synthesis to the role of antioxidants in human health, the contributors provide a comprehensive overview of how harmonising these fields can lead to innovative, sustainable technologies and practices.

The first article delves into the promising applications of nano-photocatalysis in solving global challenges such as energy scarcity and environmental pollution. By utilising nanomaterials like TiO_2 , ZnO , and various metal nanoparticles, the article explores their use in a wide range of consumer products, including self-cleaning surfaces, UV-protective textiles, and medical devices.

This article entitled “Heterogeneous Catalysts for CO_2 Chemical Transformations in Sustainable Pathways” presents a comprehensive overview of the use of heterogeneous catalysts in the chemical transformation of carbon dioxide (CO_2) into value-added products. The focus is on catalytic cycloaddition reactions that utilise CO_2 to synthesise cyclic carbonates and other chemicals, highlighting their applications in industrial processes.

Moumita Roy in her article explores the significant role of indium-based catalysts in green organic transformations, emphasising their sustainability and recyclability. The study outlines various techniques for enhancing the catalytic efficiency of indium salts by immobilizing them onto functionalised polymers and metal-organic frameworks (MOFs).

The article “Ornamental Fish diversity of Mridangabhangha River - A distributaries of River Ganga” delves into the rich biodiversity of ornamental fishes in the Mridangabhangha River, a distributary of the River Ganga. Through seasonal assessments, the study identifies 49 species of ornamental fish, shedding light on their distribution, ecological roles, and the environmental pressures they face. This study is vital for understanding how human activities and natural environmental factors interact, and it advocates for the preservation of these valuable resources.

In the article “Thermal Stability and Swelling Behaviour in Aqueous Medium of Acrylamide-Based Hydrogels”, the authors examine the thermal stability and swelling Behaviour of acrylamide-based hydrogels in various aqueous environments. The study highlights the relationship between crosslinking and swelling Behaviour, demonstrating that the hydrogels' swelling characteristics are influenced by temperature and network structure.

Sobhana Palit (Paul) in her study investigates the bioaccumulation of heavy metals in

the muscle tissues of two commercially important prawn species from the Hooghly estuarine system. By analysing concentrations of metals such as copper, lead, and cadmium, the research highlights the potential health risks associated with consuming contaminated seafood.

Suman Mandal in his article explores the synthesis of copper nanoparticles (CuNPs) using different non-ionic surfactants, particularly polysorbates, and their morphological changes under varying conditions. Through a combination of techniques like transmission electron microscopy (TEM), dynamic light scattering (DLS), and UV-visible spectroscopy, the study provides insights into how surfactant concentration and type affect the size and shape of CuNPs.

The article “The Future of Zinc Implant: Its Revolutionary Effects in Modern Advancements” discusses the emerging field of zinc-based biodegradable implants as alternatives to traditional non-biodegradable materials used in orthopaedic surgeries. Focusing on zinc alloys such as Zn-Mg and Zn-Mn, the article highlights their mechanical properties, biocompatibility, and potential for reducing post-surgical complications.

The article, authored by Dipasree Roychowdhury, presents a comprehensive review of the pharmacological properties of guava (*Psidium guajava* L.), focusing on its medicinal benefits. The fruit and various plant parts of guava have been used traditionally to treat a wide range of ailments, including diabetes, diarrhoea, and inflammation. Recent studies support these traditional uses, with evidence of the plant's anti-diabetic, antimicrobial, anti-inflammatory, and antioxidant activities.

The article “Physico-Chemical Parameters for Checking Drinking Water Quality: A Review” provides a critical review of the physico-chemical parameters used to assess the quality of drinking water, emphasising the importance of these parameters in ensuring public health. The study outlines the various characteristics of water, such as pH, electrical conductivity, total dissolved solids, hardness, and levels of contaminants like chloride and sulphate, which are key indicators of water quality.

Another article authored by Debarati Dey, investigates the impact of external magnetic fields on electron transfer reactions, with a particular focus on homogeneous mediums. The study delves into the role of spin correlation and the mechanisms underlying photoinduced electron transfer (PET) processes, providing insights into how magnetic fields affect the dynamics of these reactions.

The article “Functional Molecules for Organic Light-Emitting Diodes (OLEDs)” addresses the crucial role of functional organic molecules in the development of organic light-emitting diodes (OLEDs). With a focus on amorphous molecular materials, the study reviews key components such as hole- and electron-transporting materials, charge-blocking layers, and emissive substances.

The article “Assessment of Total Flavonoid Content and Antioxidant Activity of Mango Pulp Extracts” presents an in-depth assessment of the flavonoid content and antioxidant activity of mango pulp extracts. Utilising various extraction techniques, including microwave-assisted extraction, the study compares the efficacy of different solvents in extracting bioactive compounds from mango pulp. The findings highlight

the potential health benefits of mango pulp due to its high flavonoid content and antioxidant properties, which are essential in combating free radical-related diseases.

In another article, Chandan Kumar explores the growing applications of ionic liquids (ILs) as alternative solvents in organic synthesis. Characterised by low vapour pressure and excellent thermal stability, ILs are considered green solvents and have gained significant attention for their eco-friendly properties. The article provides a detailed examination of the use of ILs in catalysis, nanoparticle synthesis, and other chemical reactions.

Another article, *Advancing Sustainable Chemical Processes through the Use of Green Solvents and Reaction Media*, emphasises the critical role of environmentally benign solvents in modern chemical synthesis. It explores emerging green alternatives, their benefits, and practical applications in sustainable chemistry. This work contributes to the global shift toward eco-friendly practices, offering valuable insights for researchers and industries focused on reducing the environmental impact of chemical processes.

The article, authored by Shib Shankar Biswas and colleagues, explores cutting-edge advancements in nano-engineered materials for defence applications. It provides a comprehensive review of processing methods, integration challenges, and transformative applications in stealth, armour, and energy systems. Emphasizing interdisciplinary innovation, the work highlights nanotechnology's critical role in enhancing operational efficiency, resilience, and protective capabilities in modern defence systems.

Rupankar Paira presents a comprehensive overview of recent advances in cobalt-catalysed C–H activation reactions involving alkynes, allenes, and arenes in his article. Highlighting cobalt's potential as a cost-effective and sustainable alternative to noble metals, the work underscores key developments in synthesis and selectivity that contribute significantly to modern organic chemistry.

This volume stands as a testament to the transformative power of integrating chemical and biological sciences in pursuit of a more sustainable and equitable future. By aligning with the United Nations Sustainable Development Goals—particularly SDG 12: Responsible Consumption and Production and SDG 3: Good Health and Well-being—the contributions within this book highlight innovative strategies to reduce environmental impact, promote efficient resource use, and enhance public health through science-driven solutions. This work not only advances academic inquiry but also inspires meaningful action toward responsible innovation and improved quality of life for communities around the world. We hope this book will serve not only to enrich scholarly discourse but also to catalyse tangible progress in responsible innovation, ultimately enhancing the well-being of communities worldwide.

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Recent Developments in Nanophotocatalysis for Everyday Applications and Consumer Products

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ABSTRACT

Nano-photocatalysis is one of the greatest beneficial technologies where both photo-energy even solar-energy and nano-sized catalyst materials have been used to solve two major problems facing world, day-to-day demand for energy sources and increasing pollution with advancement of human activities/civilisation. Nowadays, this interesting technology has been incorporated into different industrial sectors and everyday consumer products to revolutionise and improve product efficiencies and performances across various domains. In the field of agriculture, food safety, water purification, pharmacy, cosmetics, personal care, etc., nano-sized man-made engineered materials have been utilised which exhibit unique properties that differ from natural bulk materials. Several suitable photocatalyst nanomaterials, such as TiO_2 , ZnO , Ag_2O , CuO , Fe_3O_4 , ZnS , CdS , plasmonic Au , Ag , Cu , metal nanoparticles, some metal-free carbon-based Graphene, Graphene Oxide (GO), Carbon Nanotubes (CNTs), and Carbon Quantum Dots (CQDs), Nanoparticles (NPs) etc., and their composites have been successfully explored and exhibit outstanding performance towards some catalysis-chemical reactions for multifunctional photocatalysis applications. Integration of such a nano-photocatalysis mechanism into different consumer products such as UV-protective textiles, personal care products, self-cleaning building construction materials, roof tiles, glazed ceramic tiles, concrete, paint, and transports; anti-bacterial medical textiles, clothing, food packaging; anti-fogging and anti-reflective glasses, mirrors, solar panels, etc., has ushered in a new era of innovation and enhanced product efficiencies and performances. Another important problem regarding the gradual waning stage of natural fuel sources has been solved through the production of alternative renewable and non-fossil hydrogen fuel using this nanophotocatalysis technology. Even some semiconducting nanomaterials have been developed in such a way that it can absorb unlimited and free solar-light energy, and the performance for photo-catalytic reactions has been increased much more. In this chapter, it has been expounded how light energy, even solar energy, can be used to drive intriguing technologies to be utilised in daily life.

Keywords: *Air Purification; Hydrogen-Fuel; Light-Driven Chemical Reactions; Photo-Catalysis; Self-Cleaning; Semiconducting Nano-Materials; Waste-Water Treatment*

Introduction

Photocatalysis is one of the greatest beneficial technologies where photoenergy has been utilised to conduct a chemical reaction. Very recent nano-photocatalysis technology, i.e., nanotechnology-based photocatalysis, has been developed where

small semiconductor materials having a few nanometre sizes have been utilised as catalyst materials and have been integrated into many industrial sectors and everyday consumer products to revolutionise and improve product efficiencies and performances across various domains. Several research works have demonstrated that nanophotocatalyst materials have some unique properties different from those of bulk material (Long, Evans & Halliwell, 1999). As the dimension of a nanomaterial is so small, some new fascinating properties have been generated inside the material, such as interesting chemical and physical properties, a large specific surface-to-volume ratio and high catalyst-loading capacity (Dutta *et al.*, 2012; Maji *et al.*, 2012). In the presence of both photoenergy and nanosized semiconductor materials, chemical reaction speed is generally increased much more. Here, the light energy is the driving force for conducting a chemical reaction (Ge *et al.*, 2018). Light is an outstanding source of energy; it can give life to plants as well as power to human bodies. When solar energy is utilised in a photochemical reaction, it will be most useful alternative sustainable energy source, as the abundance is virtually unlimited and free. So, focus needs to be done on improving environmentally friendly, low-energy and cost-effective technologies for fully utilising this powerful unlimited resource for the sake of society. Nowadays, with tremendous development of science and technology, so many photo-catalysis research works have been devoted to the innovation and development of interesting technologies to be utilised in daily life. In the field of environmental wastewater treatment and air purification, the photocatalysis process has already been utilised worldwide for complete degradation of organic pollutants in the presence of nanocatalyst materials under light illumination (Dutta, Maji & Adhikary, 2014). Very recently, photocatalysis has been widely applied for hydrogen fuel production as an alternative non-carbon energy source (Banerjee *et al.*, 2021). In the field of environmental pollution, the nanophotocatalysis technology provides excellent support towards decomposition of numerous organic pollutants under solar and visible light illumination and has been successfully utilised in wastewater treatment, agricultural pesticide residue treatment, and air purification. Photocatalytic nanofiber membrane-based filtration processes have been successfully employed in commercial water purification systems to provide safe drinking water.

Integration of such a mechanism of nanophotocatalysis technology into different consumer products such as agriculture, food safety, medicine, pharmacy, cosmetics, personal care products, etc., has a new era of innovation and enhancing product efficiencies and performances (Festus-Ikhuoria *et al.*, 2024). The use of Titanium dioxide (TiO₂) and Zinc oxide (ZnO) semiconducting nanomaterials in Sunscreen, offer superior UV and Sun-protection through the creation of an efficient barrier that blocks harmful UV rays, ensuring better skin protection (Rajasekar *et al.*, 2024). Nano-titanium pigments have been integrated into paints, plastics, surface coatings, papers, personal-care products, and food additives to mediate excellent photoactive properties. Nano-photocatalytic self-cleaning surface coatings have widely been used in exterior building construction materials, tent materials, transport cars, trains, planes, etc. in which solar light

or indoor light has been used to decompose pollutants that can be washed away with rain/water (Padmanabhan & John, 2020). Some commercial painting materials, when mixed with photo-catalytic materials, have been widely utilised for improving the air quality and eliminating bad odours through degradation of carbon monoxide (CO) and nitrogen and sulphur-containing organic compounds (NO_x), and even Volatile Organic Compounds (VOCs) and Inorganic Pollutant and converted to harmless substances under solar or indoor light irradiation that come into contact with the surface of them (Zhao & Yang, 2003). Again, in the case of indoor air pollution caused by different sources like the adhesives and building material's discharge and the ignition (fire) processes in addition to the use of household products, furniture, and electric and electronic devices, VOCs can encourage damages to organs and metabolic systems or asthma and cardiovascular diseases. Nowadays, some wall paints, mixed with photocatalytic materials, have been widely applied for improving the indoor air quality. Nano-catalyst thin-film coatings on roof tiles, glazed ceramic tiles, concrete, glass windows, anti-fogging and anti-reflecting glasses, and mirrors can prevent the accumulation of deposited dust, dirt or contaminant particles on their surfaces, keeping them clean.

For medical applications, nano-photocatalytic coatings and solutions are widely commercialised to improve anti-bacterial, anti-viral, anti-microbial, and anti-fungal action to protect against infections from different viruses, bacteria, and even the COVID-19 and SARS-CoV-2 viruses. Face masks, surgical cloths, and wound dressing material with nano-catalysis coating can protect against bacterial growth, spread of contagious disease, and wound infections and can sterilise rooms, instruments, etc. through degradation of the cell wall and cytoplasmic membrane of micro-organisms and viruses that survive on surfaces for a long time (Prakash, Cho & Mishra, 2022). This type of photocatalytic disinfection has broadly been applied to protect against healthcare-associated infections in hospitals, public areas like bathrooms and train stations, and cleaning areas in the food industry. In the textile industry, nanophotocatalysis technology provides us UV-protective, heat-resistant fire-fighter's suits, coffee-red wine stains-resistant garments, etc. TiO₂ and ZnO-type semiconducting materials can absorb ultraviolet radiation and can protect the textile fabric from the harmful effect of UV rays and also act as a self-cleaning agent by photo-catalytic degradation of various colour stains (Shah *et al.*, 2022). In the year of 1972, Prof. Fujishima and Honda of Tokyo University of Science, Japan, first exposed that in photo-catalysis technology, similar types of photo-chemical reactions that occur during the natural photo-synthesis process in plant leaves have been carried out under light illuminations. Since their successful research, so many nanotechnology-based photocatalysis research works have widely been devoted to the development of interesting technologies such as hydrogen fuel generation as an alternative energy source from water splitting, carbon dioxide reduction to hydrocarbon fuels, environmental pollution remediation through degradation of pollutants, air purification, UV protection and self-cleaning on textile clothing, etc., in the presence of a catalyst material under light illumination for the sake of society (Hoffmann *et al.*, 1995).

General mechanism of Photo-catalysis

In the nano-photocatalysis process, metal oxides and metal sulphide-based NPs are so chosen as heterogeneous nano-photocatalyst materials because they are semiconductor materials and possess appropriate band-gap energy and flat band-potential levels with filled valance-band (VB) and vacant conduction-band (CB) (Figure 1). TiO₂ NPs has been chosen as a reference material to validate general photocatalytic reactions on semiconductor nanomaterial's surface. It is generally accepted that the main reaction responsible for nano-photocatalysis is the interfacial redox reaction of carriers generated when a certain amount of energy is absorbed by the semiconductor catalyst. If The band gap energy of the catalyst is equivalent to or less than the energy of the incident light, the electrons residing in VB will absorb the photon and be promoted to the CB, thus leaving behind a hole in VB of the semiconducting nanomaterials (Figure 3). As a result, electron/hole pairs (e⁻/h⁺) are generated. Many of them have a possibility for recombination, but some could be separated at the surface of the semiconductor, and that electrons are able to react with electron acceptors (O₂) and holes can accept electrons from water bodies to generate hydroxyl radicals (OH•) and other reactive oxygen species (ROS) (Al-Ekabi *et al.*, 1989). These radicals actually convey the photochemical reactions.

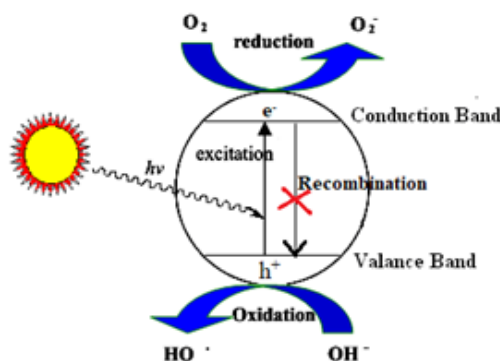
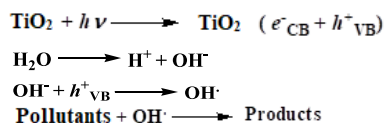
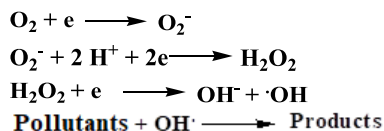


Figure 1: Illustration of Photo-Catalytic Mechanism

The complete photo-chemical reactions are represented as follows



The organic pollutants have been further degraded by O₂⁻ active species and superoxide radicals (O₂⁻), which were produced on the proposed nanomaterial's surface according to following mechanisms.



As a whole, both O_2^- and OH^- are responsible for photochemical reactions.

If that band-gap energy between VB and CB becomes tremendously low, the lifetime of the produced electron/hole pairs (e^-/h^+) also becomes short, and there is a possibility of the recombination of electron–hole pairs, and hence the photocatalytic performance of the material is decreased. In that case, different modifications on that nano-catalyst's surface have been carried out, such as amalgamation of semiconductors with other components by ion-doping, hetero-structure fabrication, noble-metal loading, morphology or size modulation, defect engineering, tuning of active crystal facets, etc., for enhancing the catalytic performances.

Defect engineering and surface modification generally have been used to modify a semiconductor's band structure for better light absorption and electron-hole pair separation, which can boost photo-chemical reactions. Also, in a hetero-nanostructure (Figure 2), lattice mismatch arises in the junction area due to the presence of different lattice spacing between two semiconductors and causes lattice defects as a whole. Actually, vacancy defects can enhance the catalytic efficiency of the semiconductors through changing its electronic structure and generate defective energy levels near the conduction-band (CB) or near the valence-band (VB) in case of n -type or p -type semiconductors, respectively. The newly formed energy level (Fermi level) in semiconductors can effectively prohibit the electron–hole pair recombination, can effectively promote light absorption or improve visible light harvesting, promote charge carrier separation (photo-induced carrier separation) and photo-electron transfer, which really extends the carrier lifetime, increases conductivity, and reduces the energy barriers for efficient multiple nanophotocatalytic applications.

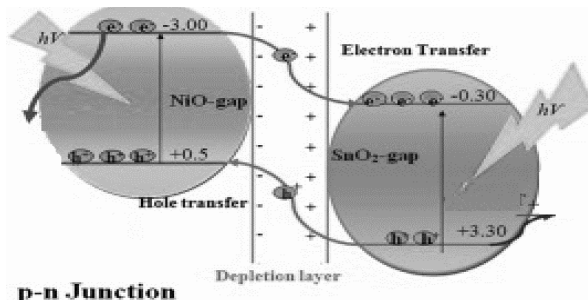


Figure 2: Synergistic-Effect Diagram on Charge Transference Towards Photo-Catalytic Reaction (Dutta, Maji & Adhikary, 2014)

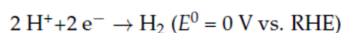
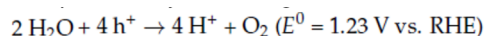
Very recent combinations of carbon-based materials, such as graphene, graphene oxide (GO), rGO nano-sheet, CNT, Carbon QDs, polymeric graphite carbon nitride (g-

C₃N₄) with semiconductor nano-catalysts, become more promising strategies to enhance catalytic performance and the solar or visible-light-driven response because carbon acts as a photosensitiser and can tune photocatalytic activity in the visible region (Wang *et al.*, 2009). Owing to possessing a wide band-gap energy, the TiO₂ or ZnS NPs are inactive under visible light; then graphene helps as a photosensitiser to absorb visible light and generate charge carriers, which get transferred to the CB of TiO₂ or ZnS NPs, making that wide band-gap semiconductor visible-light active (Zhang *et al.*, 2012).

Nano-Photocatalytic hydrogen-fuel production

Recently, nanophotocatalysis has been widely applied for hydrogen fuel production as an alternative non-carbon energy source. This is the low-cost method and does not evaluate harmful CO₂ gas, like natural fossil fuels (coal, oil, natural gas, etc.), which makes a serious impact on the environment with global warming. Inspirational from the first research work of Fujishima and Honda (1972) on water-splitting technology in a photoelectrochemical (PEC) setup using a TiO₂ electrode under light irradiation, nowadays, so many research groups have paid substantial attention to increasing hydrogen manufacturing efficiency in a large-scale way using efficient catalyst material even under natural solar light illumination.

Similar to the general mechanism of photocatalysis discussed above, photocatalytic hydrogen production occurs through water splitting into H₂ and O₂ over a heterogeneous semiconductor nanophotocatalyst under light illumination and mild conditions according to equation.



The photochemical reactions basically start from incident light energy activating semiconducting nanocatalysts, followed by free electron-hole pair (e⁻/h⁺) formation. That (e⁻/h⁺) have been transferred to the active sites of the semiconductor nano-catalyst's surface; after that, they will act as reducing/oxidising agents to drive reduction/oxidation reactions. In water splitting process, water molecules are reduced by the photo-induced electrons to form H₂ and are oxidised by the photo-induced holes to form O₂, i.e., the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The hydrogen gas produced was collected using a gas-tight syringe and analysed by gas chromatography.

Several research groups have proved that to pursue the complete water splitting process, nano-catalyst material must possess bottom level of the conduction band (CB) position more negative than the redox potential of H⁺/H₂ (0 V vs. NHE) and the top level of the valences band (VB) position more positive than the standard reduction potential of O₂/H₂O (1.23 V vs. NHE). Figure 3 represents the band potential positions of several metal chalcogenide semiconductors, which can proficiently split water to produce hydrogen. For TiO₂, its band gap is large enough to split water (3.0 eV vs. 1.23 eV for the

formation of H_2 and O_2), and also its band structure matches well with redox potentials of water splitting (Qiao *et al.*, 2018).

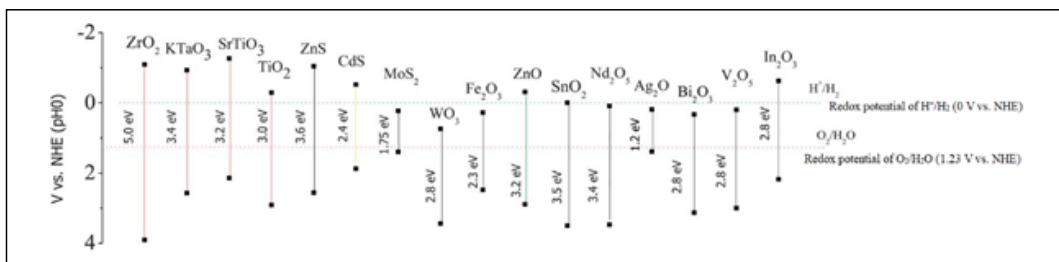


Figure 3: Band Potential Situation of Numerous Metal Chalcogenides NPs (Qiao *et al.*, 2018).

Some research groups have noticed another problem that after formation of hydrogen, some backward reaction of H_2 and O_2 to H_2O occurs and numerous effective strategies have been explored to increase hydrogen production efficiency using different efficient nanocatalysts, such as metal oxides, carbon nitrides, polymers, and heterostructures. When some semiconductors (TiO_2) are coupled with highly conductive supports such as metallic Silver, Gold, Pd, Pt or bimetallic PdPt NPs, they can strongly prevent the recombination of photogenerated electrons of the semiconductor, enhance the electron-transport behaviour and improve their photoelectrocatalysis performances towards water-splitting (da Silva *et al.*, 2020). ZnS nanostructure has excellent potential in solar-energy-driven hydrogen formation because of its ability to quickly generate photo-induced carriers. Again, zinc vacancies can modulate the electronic energy level of ZnS and affect the CB and VB position in such a way that it can decrease the oxidation capacity of the holes, protecting the Zn-deficient ZnS from photo-corrosion, leading to long-term photo-catalytic stability and exhibiting an outstanding light-energy-driven hydrogen productivity of $\sim 338 \mu\text{mol/h/g}$. Very recently, to effectively utilise sunlight, various near-infrared (NIR) and long-wavelength light (highest 49% contribution in the entire solar spectrum) harvesting systems have been developed which can efficiently harvest solar light, optimise the redox process and exhibit high solar-to-hydrogen (STH) conversion efficiency (Kim *et al.*, 2015).

Nano-Photocatalysis in Agriculture

Organic Pesticides are widely used in agriculture, but their unnecessary usage may generate hazards to both humans and the environment. DDT has been used extensively as a pesticide for agricultural purposes, but it does not degrade under natural conditions since it is lipophilic. Its poisonous effect has been persisting for long time in water bodies, making severe adversative influences on life and the environment of the planet, and it tends to bioaccumulate in fatty tissues and is biomagnified up the food chain. Considering their high solubility in water and low biodegradability, complete removal from wastewater is vital, and treatment of that wastewater is often being made

difficult by conventional methods. So, pesticide residues require effective treatment like wastewater due to their toxicity, high chemical Stability and low biodegradability.

Similar to wastewater treatment, nanophotocatalysis technology is a promising approach to solve the pesticide residue problem. Using the most effective and useful TiO_2 photocatalyst, pesticide particles have been easily degraded into H_2O , CO_2 and other less harmful compounds through a photocatalytic oxidation process under light illumination. Sarkar *et al.* (2016) had reported that, using Bi_2S_3 NPs as nano-photocatalyst, the rate of degradation of highly toxic dichlorodiphenyltrichloroethane (DDT) has been found to be much better compared to that exhibited by commercial WO_3 , and through aromatic ring cleavage, after degradation, it produces less harmful para-chlorotoluene and, at last, chloro-benzene (Figure 4).

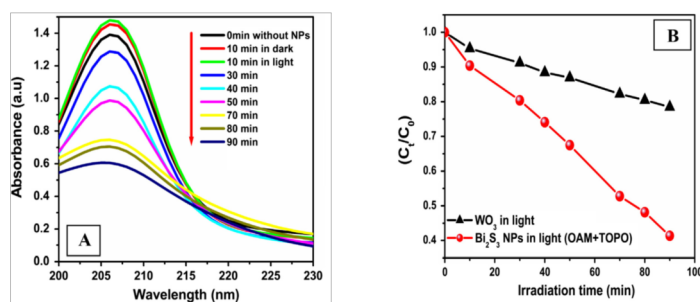


Figure 4: (A) Time Dependent UV-vis Spectral Change of DDT Solution (2×10^{-5} M) Using 20 mg Nano-Photocatalyst, Bi_2S_3 NPs, Under Visible Light Illumination (B) C_t/C_0 vs Time (t) Plot of DDT Decomposition Process (Sarkar *et al.*, 2016).

Another Common pesticide, 2,4-dichlorophenoxyacetic acid, has been reported to be decomposed in the presence of highly effective photocatalyst Ag-TiO_2 NPs under visible light illumination.

Nano-photocatalytic air purification

Nowadays, several air-purifier devices have been developed to be utilised in daily life based on nanophotocatalysis technology, where air pollutants are converted to harmless substances in the presence of a nanocatalyst under solar or indoor light irradiation. In these devices, photocatalytic oxidation (PCO) has been incorporated to purify air where nanocatalyst material can oxidise the gaseous compounds such as carbon monoxide, nitrogen oxides, volatile organic compounds (VOCs), other inorganic gases, etc., that come into contact with the surface of them (Zhao & Yang, 2003). In case of indoor air pollution caused by different sources like the adhesives and building materials' emissions and the combustion processes as well as the use of household products, furniture, electric and electronic devices, VOCs can encourage damages to organs and metabolic systems or asthma and cardiovascular diseases. Very recently, numerous carbon-based materials such as 2D graphene, graphene oxide (GO), rGO nano-sheets, CNT, Carbon QDs, polymeric graphite carbon nitride ($\text{g-C}_3\text{N}_4$) supported semiconductor composites have been fabricated to enhance PCO technology and used

in air purification technology that utilises light energy to break down pollutants and bacteria, remove VOCs (VOCs mineralization) and improve air quality. Again, some wall paints mixed with photocatalytic materials have been widely applied for improving the air quality through degradation of volatile organic and inorganic pollutants present in air or deposited on paint surfaces. Some TiO_2 (Titania)-based nanomaterials as a thin film coating on a piece of glass or ceramic or aluminium metal substrate have been used as photocatalysts. Similar to radical mechanism of photocatalysis, electrons that are released on the TiO_2 surface upon UV light irradiation interact with water molecules in the air to generate reactive oxygen species (ROS) such as hydroxyl radicals ($\text{OH}\cdot$), superoxide radicals (O_2^-), and hydrogen peroxide radicals ($\text{OOH}\cdot$), which can actually occur in the oxidation process to reduce contaminants. In the case of VOCs, a photocatalytic degradation process has been carried out similar to organic dye degradation in wastewater treatment, and the bigger carbon-based organic pollutant molecules break down into the harmless Substances CO_2 and H_2O . In comparison to air cleaner technology through simple filtration or trapping pollutants, photocatalytic air treatment shows a big advantage, where all harmful molecules (exhaust fumes) have been completely decomposed and effectively destroyed. Even in case of indoor air pollutants such as volatile organic compounds (formaldehyde, acetaldehyde) evaporating from paints, hairsprays, etc., photocatalytic chemical decomposition is the best route instead of removing them completely by sucking air-polluted particles and blowing clean out.

Nano-Photocatalytic UV-protection

With the help of superior photocatalytic and UV-light absorption properties of some semiconducting nanomaterials, protection of the wearer against the weather and the sun's harmful rays has been developed. Nano-titania or ZnO embedded sunscreen, textiles and clothing offer superior UV and Sun-protection through the creation of an efficient barrier that blocks harmful UV rays, ensuring better skin protection (Rajasekar *et al.*, 2024). Compared to traditional organic UV-blocking agents, ZnO NPs are more stable and have intense absorption in the UV region. UV-blocking characteristics of the textile's fabric have been improved by the incorporation of nano- ZnO and provide cost-effective UV-protective suits to the society in which transmission of the ultraviolet radiation to the skin through the fabric is blocked.

Very recently, some cosmetic products containing inorganic nano-sized UV filters have been developed in the form of creams, lotions, gels, sprays, and sticks and exhibit different protection mechanisms, sometimes absorbing or scattering and/or reflecting UV radiation. Nano-titania or ZnO are the most commonly used and have been included in cosmetic product formulations and exhibit a high sun protection factor (SPF). Occasionally, silver-based nanomaterials such as Ag_2O , Ag_2S , etc., have been incorporated into cosmetic product formulations due to the presence of well-known anti-microbial properties and also serve as photo-sensitisers in the photo-catalysis process.

Unlike traditional organic UV filters, the nanomaterials are more photostable and can enhance the durability of skin protection, prevent penetration of UV radiation into the deeper skin layers, decrease the release of ROS, which can start different photochemical reactions on skin. The nanomaterials are environmentally friendly, non-toxic and have a lower potential to produce skin irritation. Nano-sized particles make the products lightweight and transparent (Rajasekar *et al.*, 2024).

Nano-Photocatalytic self-cleaning

Following radical mechanism of photocatalysis, the photocatalytic self-cleaning process of deposited dirt or contaminant particles from any surface has become very popularised and commercialised through the decomposition of that dirt particles under solar-light or indoor-light irradiation. The photoexcited electron and valence band hole (h^+v_B) on the nanocatalyst surface can generate reactive oxygen species (ROS) that can convert dirt organic matter into CO₂ and water, resulting in the cleaning of the surface. This type of self-cleaning infused with nanophotocatalysis technology has been incorporated in different sections, including biomedical, healthcare, electronics, tissue engineering, packaging, clothing, first aid, surface disinfectants, dietary supplements, etc.

Especially in the textile industry, self-cleaning, stain-resistant, dirt-repellent clothing has been introduced through the incorporation of nanophotocatalysis technology. Traditional cotton-silk fabrics, rayon yarn, etc., finished with photocatalytic and antibacterial nanomaterials, provide effective protection against various colour stains and bacteria. Nano-titania or ZnO embedded textile clothing, when exposed to ultraviolet or visible light, the photocatalytic characteristic of the semiconducting nanoparticle allows it to act as a self-cleaning agent by photocatalytic degradation of various colour stains. Even the photocatalytic self-cleaning ability has been retained after several cycles of home washing. Silver-based nanomaterials, which have well-known anti-microbial and photo-sensitiser properties, have been immobilised to develop sun-light-driven cleaning and anti-bacterial characteristics, and fabrics of socks, inner wear, etc. embedded with silver nanoparticles can protect against odour and infection. Nowadays, with tremendous development of science and technology, so many research works have been devoted to the innovation and development of textile material with more features like more comfort, durable, hygienic, anti-odour, anti-microbial, anti-static, breathability, improved softness, better tear strength, water/spill repellence and wrinkle resistance but without altering the inherent properties of the textiles, including flexibility and washability (Tania, Ali & Akter, 2022).

Another nano-textile research work develops nano-fibres with diameters in the few nm range, which have been directly used to weave a cloth. Nano-fibres have been generated from different nano-sized polymeric materials. They are lightweight, low-density and have a controllable pore structure with a high surface-to-volume ratio. Textile-garments using nano-fibre yarn can enhance comfort, breathability, moisture

management, and anti-bacterial properties. Like the surface of a lotus leaf, nanofibre-made cloths show excellent water-repellent activity, i.e., they are resistant to water or liquids, and droplets bead up into spheres and easily roll off due to the presence of superhydrophobic surface morphologies with contact angles $>150^\circ$. Nano-photocatalytic self-cleaning nano-fibre-based surfaces also utilise sunlight or indoor light to break down deposited dirt or contaminant particles and easily be washed away with rain/water. Sporting goods, swimming suits, even PPE kits, face masks, surgical goods, etc., using nano-fibre yarn have benefitted from photocatalytic self-cleaning. The self-cleaning efficiency with super-hydrophilic (WCA less than 5°) nanomaterials-based surface coating can spread water droplets to form a film throughout itself and utilise solar light or indoor light to decompose any adsorbed organic contaminants such as oil and dirt. After that, the contaminants are washed away with the help of water flow.

Nano-photocatalytic Anti-microbial and Self-sterilising

Using these self-cleaning surface coating phenomena, photocatalytic disinfection has broadly been applied to protect against healthcare-associated infections in hospitals, public areas like washrooms, transport stations, cleaning areas in the food industry, etc. Similar to well-known anti-microbial Silver-based medicines, photocatalyst nanomaterials can degrade the cell-wall and cytoplasmic membrane of micro-organisms and viruses, that survive on surfaces for a long time, through the production of reactive oxygen species (ROS) such as hydroxyl radicals and hydrogen peroxide (Manke, Wang & Rojanasakul, 2013).

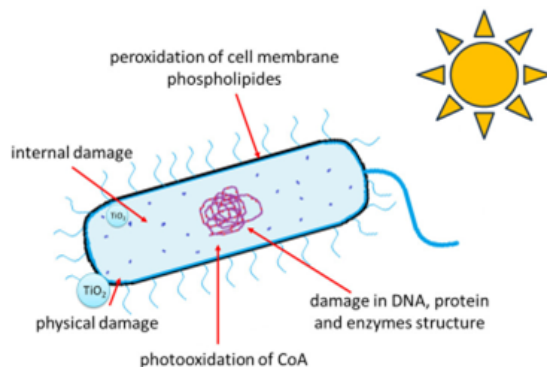


Figure 5: Mechanisms of Photocatalytic Bacterial Inactivation (Chae, Watanabe & Wiesner, 2011)

The unique photochemical and electrical properties of engineered nanomaterials induce oxidative stress response through the generation of ROS in bacterial cells and cause inflammation, genetic damage, inhibition of cell division, and cell death. Photocatalytic bacterial mineralisation has been carried out through reduction or complete termination of bacterial growth, photo-oxidation of Coenzyme A (CoA), leading to bacterial cell death. During interactions between the photocatalyst and

bacterial cells, the ROS, which is generated on the photocatalyst's surface, can induce the oxidative interference of proteins, metabolic activities, or damage in bacterial DNA and enzyme structures (Figure 5) (Chae, Watanabe & Wiesner, 2011).

That is why face masks, surgical cloths, and wound-dressing material with nano-catalysis coating have been widely commercialised, which can protect against bacterial growth, the spread of contagious disease, and wound infections and can sterilise rooms, instruments, etc. Silver (Ag), gold (Au) nanoparticles and even metal oxides nanoparticles (ZnO, TiO₂, CuO, Ag₂O, etc.) generally possess outstanding antibacterial and antimicrobial activity. Imparting these nanomaterials on cotton fabric can protect against bacterial growth and be effective against a wide range of micro-organisms.

Nano-photocatalysis in Cancer Treatment

During the development of Cancer treatment, heterogeneous nano-photocatalysis has been employed to provide advantage of catalysis chemical reaction on growing tumour cells and to accelerate depletion of metabolism of cancer cells. Owing to being extremely small in size, nanomaterials can be easily absorbed by the cells in a biological system and easily travel into blood vessels and organs within the body. Following the nano-photocatalytic mechanism, nanomaterials can encourage photodynamic therapy (PDT), where they act as photosensitisers and can generate reactive oxygen species (ROS) upon exposure to light. That ROS causes apoptotic and necrotic cell death and triggers oxidative damage of the amino acids of proteins, fatty acids in lipids and the nucleobases in DNA of tumour cells. Again, a photosensitiser can transfer the light energy to the surrounding oxygen molecules and generate Singlet oxygen that interacts with adjacent cancer tissues to induce apoptosis, necrosis-related cell death.

Mesoporous-structured nanomaterials with functionalised surfaces can act as carriers to transport anti-cancer drugs to tumour tissues. Unlike very common carriers like liposomes, dendrimers, micelles, etc., nanocarriers have high drug-loading capacity, improved stability, bio-compatibility, enhanced permeability-retention effect, precise targeting, and good pharmacokinetics, which can induce an anti-cancer drug's accumulation into tumour tissues. Nowadays, red-light-emitting carbon nanoparticles with high fluorescence quantum yield, NIR-light-harvesting N-doped carbon dots, plasmonic gold nanoparticles (AuNPs), etc., have been used in cancer treatment. In this case, bio-nanomedicine and photo-catalysis have been merged to provide the advantages of both bio-imaging markers and photo-dynamic agents.

Upon exposure to NIR radiation, the carbon-based nanoparticles can enhance photocatalytic response towards ROS generation and destroy the cancerous cell's structure. Simultaneously, the deep penetration power and photothermal effect of NIR light raises the temperature of tumours and accelerates photothermal therapy (PTT), where light-to-heat conversion efficiency kills cancer cells. It has been noted that the cancer cells are more heat sensitive than normal cells and the cancer cells die at the temperature

above about 45°C. Again, the NIR region is regarded as a biologically transparent window as the normal biological molecules, cells, etc. do not absorb in the NIR region, and NIR light possesses the optimum wavelength for penetration into deep tissues for cancer treatment.

Similarly, upon exposure to light, plasmonic gold nanoparticles (AuNPs) exhibit interesting Surface Plasmon Resonance from free surface electron oscillation and dipole oscillation along the direction of the electric vector of the light and can rapidly convert the absorbed light energy into the localised heat energy, and the temperature may rise to 330 K. When those AuNPs have been properly biofunctionalised at their surfaces so that they can be received preferentially by the target cancer cell receptors and preferentially accumulated into the cancer cells, then produce the localised heat energy upon irradiation with an NIR beam, which can easily destroy the heat-sensitive cancer cells.

Nano-photocatalytic Waste-water Treatment

Nowadays, photocatalytic nanofibre-based membranes are often used in the removal of micro-pollutants and finer contaminants from water bodies. Analogous to 'Safe Drinking Water Foundation, Canada', the Department of Science and Technology, Govt of India, has implemented 'Nano Mission' to convey collaborative research and development projects for nanotechnology-based water purification process. When nano-photocatalysis technology is incorporated into membrane-based filtration process, i.e., the filtration-photocatalysis integrated method both separation and decomposition of unwanted pollutants are carried out simultaneously and provide high-quality drinking water to millions of people in developing countries. Very similar to reverse osmosis (RO) purification, the nanofiber membrane-based filtration process has been successfully employed in commercial water purification system and has been extensively used for the softening of water and the removal of both physical, chemical and biological contaminants, leading to the formation of safe drinking water. When contaminated wastewater has been passed across the nanofiltration membrane under pressure, the membranes are capable of separating larger multivalent ions such as calcium sulphate while allowing smaller monovalent ions such as sodium chloride to pass through it. Also, some dissolved solids, even smaller molecules such as dissolved organics, pesticides, herbicides, agricultural chemicals phenols, polyaromatic hydrocarbons, etc., have easily been separated. Moreover, the Photo-generated ROS on the nano-fibre membrane's surface can effectively do the photo-degradation process of the unwanted pollutants, organic chemicals, and microbial species in water, as well as the self-cleaning properties (photocatalytic and anti-microbial) of membrane surfaces, which can significantly reduce blockage of its surface pores due to continuous deposition or adsorption of macro-molecules and make the membrane cost-effective, re-cyclable and reusable. Incorporation of photocatalytic Ag, Cu, Zn, activated carbon granules or Graphene into these nanofibre membranes can enhance photocatalytic

disinfection through effective killing of a wide range of micro-organisms such as viruses, bacteria, parasites, algae, and pathogens and provide improved water filtration (Singha & Mishrab, 2020). In this way, these photocatalytic nanofiltration membranes can retain healthy minerals, maintain healthy total dissolved solids (TDS) as per WHO, and provide long-lasting water purification of up to 14,000+ litres.

Too much research work has been focused on the development of hybrid water-treatment process involving photocatalysis and membrane technology through the fabrication of photocatalytic and antimicrobial nanomaterials onto traditional polymeric membranes such as polystyrene (PS), polyethersulfone (PES), Polyester, polyacrylonitrile (PAN), etc. Electrospinning of PES nanofiber membranes infused with TiO_2 nanomaterials has been reported for simultaneous separation and photodegradation of water pollutants. Electrospun PAN layers coated with ZnO NPs can easily achieve both photocatalytic and antibacterial properties for water treatment. Some research groups have paid great attention to developing activated carbon-based nanofibre membranes because activated carbon granules have been widely used in water filtration process over the past three decades. Carbon-based nanomaterials are highly porous materials, and due to the presence of different functional groups on a single sheet surface, these nanomaterials act as versatile absorbents used for the removal of heavy metals, lead, fluoride, chlorine and inorganic contaminants. Simultaneously, its good reducing properties can do bacterial reduction, chlorine-toxic chemical reduction and improve the taste and odour of drinking water, providing point-of-use (POU) water purification for domestic use.

Conclusion

This chapter aims to outline the diverse nanophotocatalysis applications in daily life. Nowadays, in the presence of light energy, some catalysis-chemical reactions provide outstanding support that can be utilised in everyday consumer products. Several innovative catalyst materials, especially nano-sized inorganic materials, have been developed worldwide for multi-functional photocatalysis applications. Some environmentally friendly, cost-effective nanomaterials, such as TiO_2 , ZnO, CuO, Fe_3O_4 , FeS, ZnS, CdS NPs, etc., and their composites, have been successfully industrialised and established as effective heterogeneous recyclable catalysts for conducting several photochemical reactions. More cost-effective metal-free carbon-based π -conjugated semiconductor nanomaterials have been successfully developed as organic photocatalysts. Recently, to achieve more complete utilisation of solar light, full-spectrum photocatalytic activity, i.e., full spectral-range (320-800 nm) light-driven photocatalysis, has been achieved with the help of carbon-based quantum dots (CQDs) and carbon dots (CDs), which can effectively accelerate the electron transfer, facilitating the effective utilisation of those photo-induced charge carriers in the nano-photocatalysis process. The catalytic capabilities of the NPs have also been effectively enhanced using nano-engineering technology, i.e., different modifications on the nano-

catalyst's surface, electronic energy structure through tuning shape, size, morphology and band-gap energy during the synthesis process. The nanomaterials have been widely explored as an efficient photocatalyst for the degradation of various organic pollutants under solar and visible light illumination. The possible photocatalytic decomposition mechanism has also been deliberated through the detection of reactive oxygen species (ROS) such as hydroxyl radical (OH), superoxide radicals (O_2^-), and hydrogen peroxide radical (OOH). These photocatalytic self-cleaning materials can also be used in many applications, including anti-bacterial, anti-fogging, and anti-reflective coatings and can provide a solution to the growing problem of environmental pollution. By improving interaction between nanomaterials and biological systems, the nanotechnology-based therapy has now broadly been applied in the biomedical and biotechnology fields. The proposed nanomaterials have been successfully commercialised in other different fields, such as hydrogen fuel generation as an alternative energy source from water splitting, self-cleaning air purification, etc. Finally, environmentally friendly, cost-effective technologies have been developed for solar-light-driven photocatalysis so that most of the solar spectrum and light energies can be utilised in the society for large-scale application.

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References

- Al-Ekabi, H., Serpone, N., Pelizzetti, E., Minero, C., Fox, M. A., & Draper, R. B. (1989). Kinetic studies in heterogeneous photocatalysis. 2. Titania-mediated degradation of 4-chlorophenol alone and in a three-component mixture of 4-chlorophenol, 2, 4-dichlorophenol, and 2, 4, 5-trichlorophenol in air-equilibrated aqueous media. *Langmuir*, 5(1), 250-255. <https://doi.org/10.1021/la00085a048>
- Banerjee, R., Pal, A., Ghosh, D., Ghosh, A. B., Nandi, M., & Biswas, P. (2021). Improved photocurrent response, photostability and photocatalytic hydrogen generation ability of CdS nanoparticles in presence of mesoporous carbon. *Materials Research Bulletin*, 134. <https://doi.org/10.1016/j.materresbull.2020.111085>
- Chae, S. R., Watanabe, Y., & Wiesner, M. R. (2011). Comparative photochemical reactivity of spherical and tubular fullerene nanoparticles in water under ultraviolet (UV) irradiation. *Water Research*, 45(1), 308-314. <https://doi.org/10.1016/j.watres.2010.07.067>
- Dutta, A. K., Maji, S. K., Srivastava, D. N., Mondal, A., Biswas, P., Paul, P., & Adhikary, B.

- (2012). Synthesis of FeS and FeSe nanoparticles from a single source precursor: a study of their photocatalytic activity, peroxidase-like behavior, and electrochemical sensing of H₂O₂. *ACS Applied Materials & Interfaces*, 4(4), 1919-1927. <https://doi.org/10.1021/am300408r>
- Dutta, A. K., Maji, S. K., & Adhikary, B. (2014). γ -Fe₂O₃ nanoparticles: an easily recoverable effective photo-catalyst for the degradation of rose bengal and methylene blue dyes in the waste-water treatment plant. *Materials Research Bulletin*, 49, 28-34. <http://dx.doi.org/10.1016/j.materresbull.2013.08.024>
- da Silva, A. G., Fernandes, C. G., Hood, Z. D., Peng, R., Wu, Z., Dourado, A. H. B., ... & Torresi, S. I. C. D. (2020). PdPt-TiO₂ nanowires: correlating composition, electronic effects and Ovacancies with activities towards water splitting and oxygen reduction. *Applied Catalysis B*, 277, 1-10. <https://doi.org/10.1016/j.apcatb.2020.119177>
- Fujishima, A., & Honda, K. (1972). Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 238(5358), 37-38. <https://doi.org/10.1038/238037a0>
- Festus-Ikhuoria, I. C., Obiuto, N. C., Adebayo, R. A., & Olajiga, O. K. (2024). Nanotechnology in consumer products: A review of applications and safety considerations. *World Journal of Advanced Research and Reviews*, 21(3), 2050-2059. <https://doi.org/10.30574/wjarr.2024.21.3.0923>
- Ge, L., Peng, Z., Wang, W., Tan, F., Wang, X., Su, B., ... & Wong, P. K. (2018). gC₃N₄/MgO nanosheets: light-independent, metal-poisoning-free catalysts for the activation of hydrogen peroxide to degrade organics. *Journal of Materials Chemistry A*, 6(34), 16421-16429. <http://dx.doi.org/10.1039/C8TA05488F>
- Hoffmann, M. R., Martin, S. T., Choi, W., & Bahnemann, D. W. (1995). Environmental applications of semiconductor photocatalysis. *Chemical Reviews*, 95(1), 69-96. <https://doi.org/10.1021/cr00033a004>
- Kim, T. W., Ping, Y., Galli, G. A., & Choi, K. S. (2015). Simultaneous enhancements in photon absorption and charge transport of bismuth vanadate photoanodes for solar water splitting. *Nature Communications*, 6(1), 8769. <https://doi.org/10.1038/ncomms9769>
- Long, L. H., Evans, P. J., & Halliwell, B. (1999). Hydrogen peroxide in human urine: implications for antioxidant defense and redox regulation. *Biochemical and Biophysical Research Communications*, 262(3), 605-609. <https://doi.org/10.1006/bbrc.1999.1263>
- Maji, S. K., Dutta, A. K., Biswas, P., Srivastava, D. N., Paul, P., Mondal, A., & Adhikary, B. (2012). Synthesis and characterization of FeS nanoparticles obtained from a dithiocarboxylate precursor complex and their photocatalytic, electrocatalytic and biomimic peroxidase behavior. *Applied Catalysis A: General*, 419, 170-177. <http://dx.doi.org/10.1016/j.apcata.2012.01.025>
- Manke, A., Wang, L., & Rojanasakul, Y. (2013). Mechanisms of nanoparticle-induced oxidative stress and toxicity. *BioMed Research International*, 2013(1), 942916.

<http://dx.doi.org/10.1155/2013/942916>

- Padmanabhan, N. T., & John, H. (2020). Titanium dioxide based self-cleaning smart surfaces: A short review. *Journal of Environmental Chemical Engineering*, 8(5), 104211. <https://doi.org/10.1016/j.jece.2020.104211>
- Prakash, J., Cho, J., & Mishra, Y. K. (2022). Photocatalytic TiO₂ nanomaterials as potential antimicrobial and antiviral agents: Scope against blocking the SARS-COV-2 spread. *Micro and Nano Engineering*, 14. <http://dx.doi.org/10.1016/j.mne.2021.100100>
- Qiao, M., Liu, J., Wang, Y., Li, Y., & Chen, Z. (2018). PdSeO₃ monolayer: promising inorganic 2D photocatalyst for direct overall water splitting without using sacrificial reagents and cocatalysts. *Journal of the American Chemical Society*, 140(38), 12256-12262. <https://doi.org/10.1021/jacs.8b07855>
- Rajasekar, M., Mary, J., Sivakumar, M., & Selvam, M. (2024). Recent developments in sunscreens based on chromophore compounds and nanoparticles. *RSC Advances*, 14(4), 2529-2563. <https://doi.org/10.1039/D3RA08178H>
- Sarkar, A., Ghosh, A. B., Saha, N., Srivastava, D. N., Paul, P., & Adhikary, B. (2016). Enhanced photocatalytic performance of morphologically tuned Bi₂S₃ NPs in the degradation of organic pollutants under visible light irradiation. *Journal of Colloid and Interface Science*, 483, 49-59. <https://doi.org/10.1016/j.jcis.2016.08.023>
- Shah, M. A., Pirzada, B. M., Price, G., Shibiru, A. L., & Qurashi, A. (2022). Applications of nanotechnology in smart textile industry: A critical review. *Journal of Advanced Research*, 38, 55-75. <https://doi.org/10.1016/j.jare.2022.01.008>

Heterogeneous Catalysts for CO₂ Chemical Transformations in Sustainable Pathways

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ABSTRACT

The increasing demand for green and sustainable fuel and industrial practices has emerged as a crucial issue in the past year, particularly within the chemical industry. Most of them, the capture and utilisation of carbon dioxide (CO₂) by porous heterogeneous material, particularly COF, into value-added products is a promising approach to address the sustainable energy crisis and control the reduction of the atmospheric CO₂ content for environmental remediation. Nowadays, catalytic cycloaddition of carbon dioxide into various cyclic carbonates like α -alkylidene and 2-oxazolidinones cyclic carbonates via CO₂ fixation reaction has focused on the creation of low-cost, environmentally friendly, and efficient catalysts. Looking ahead, this chapter offers a visionary viewpoint on harnessing heterogeneous materials for the sustainable capture and conversion of CO₂, which is a promising sustainable reaction.

Keywords: CO₂ Fixation; Cycloaddition; Green Pathway; Heterogeneous Catalysis

Introduction

Due to increased human activities, the manufacturing revolution, and such widespread activities as deforestation, fossil fuel consumption and industrialisation, carbon dioxide emissions have histrionically increased, which is a significant impact on climate change. The use of chemicals from industry has increasingly demonstrated significant scientific and economic value, garnering widespread attention. Through the development of efficient catalytic technology, researchers are going through a new phase in the twenty-first century regarding an ever-growing demand for new, proficient and green methods to carry out chemical reactions (Du, Ouyang & Tan, 2021). Although the synthetic strategies were related with some disadvantages, such as low selectivity, low functional group tolerance, hazardous reaction conditions, and finally recyclable deficiency, etc. To overcome these problems, production of new synthetic pathways is highly demanding. For this reason, During the past two decades, various categories of porous materials, specifically porous carbons and newly developed metal–organic frameworks (MOF) and porous organic polymers (POP) more one covalent organic framework (COF), owning their periodic framework and having a tuneable porosity, highly crystalline materials and high surface area, have been widely applied for capture and utilisation of CO₂. Due to these merits, nowadays some COF materials show numerous applications in nanotechnology, including electrocatalysis, organic catalytic transformations, and

photocatalysis. On the other hand, due to the huge amount of CO₂ emissions, the normal temperature of the earth has been altered in recent times, and as a result, global warming is gaining attention. In this respect, numerous studies to suppress CO₂ emissions or adsorption (carbon capture and storage, CCS) have been conducted (Park *et al.*, 2022). In the past researchers focused on limiting fossil fuels but mainly used sources of CO₂ emissions and emerging alternative energy systems. From a sustainability perspective, in a recent study, different protocols for the carbon dioxide fixation into different organic substrates have been used (Karishma *et al.*, 2024; Chen *et al.*, 2024). The production of cyclic carbonates is fully atom-efficient, economically viable, and has a wide range of industrial applications, including use as electrolytes in lithium-ion batteries, fuel additives, intermediates in pharmaceutical manufacturing, and in the production of lubricants and polymers. Numerous heterogeneous catalytic systems – particularly those based on transition metals – have been developed and extensively investigated for carbon dioxide cycloaddition into fine chemicals. Because of CO₂ itself being both thermodynamically stable and kinetically inert, converting it efficiently and selectively typically demands extreme reaction conditions. Covalent organic frameworks (COFs), with their distinctive structural features, stand out as highly adaptable materials suitable for applications such as heterogeneous catalysis, gas capture and storage, sensing technologies, and optoelectronic devices. The role and function of the supported materials over the mediated sustainable liquid phase reactions, like cyclic carbonate synthesis reactions, 2-oxazolidinones, α -alkylidene cyclic carbonates, etc., under CO₂ absorption.

Literature Review

Application of Heterogeneous Catalysts Over Some Organic Transformations in Presence of CO₂

Cyclic Carbonate Synthesis from Epoxide

Because of the ecological and economical concerns and CO₂ being nontoxic, cheap, and abundant, the researchers give more attention to chemical CO₂ fixation into valuable chemicals (Pal, De & Bharadwaj, 2022). One of the most powerful synthetic methods utilising CO₂ for the production of five-membered cyclic carbonates from epoxide is demonstrated in Figure 1. Various other value-added chemicals like carbamates, glycols, dialkyl carbonates and pyrimidines can be prepared from cyclic carbonate. For the production of cyclic carbonates, the conventional technique uses poisonous and hazardous materials. Therefore, synthetic chemists discover greener pathways where epoxide and CO₂ combine to offer cyclic carbonate. Yano *et al.* (1997) firstly reported metal oxide-catalysed cyclic carbonate synthesis. MgO, which is easily available in the market, catalysed the cycloaddition of carbon dioxide with epoxides to provide cyclic carbonates. But in that case at 2 MPa of carbon dioxide pressure and 135 °C temperature for 12 h in a DMF solvent medium, only 60 % yields of styrene carbonate were obtained. Further on for the reaction, Yamaguchi *et al.* (1999) reported a bimetallic oxide-based catalyst at 0.5 MPa CO₂ pressure and 100-120 °C temperature in DMF for 15-24 h (Then some researchers have developed more superior and effective catalytic systems for the

cyclic carbonate synthesis under solvent-free conditions, which is a much greener and cost-effective route). Various Co-catalysts like TBAB, TBAI, KI etc. were utilised for the ring-opening reaction of epoxides via nucleophilic attack in most of the cases. Several metals, such as Al, Cr, Co and Sn, supported porphyrin-based catalysts that were well known for this reaction. However, in maximum cases the catalyst either required high CO₂ pressure or they are homogeneous in nature. Both the reaction conditions were not suitable. As a result, Al complex was anchored on Merrifield resin for five-membered cyclic carbonate synthesis under atmospheric pressure, and it was first reported as a heterogeneous catalyst that could catalyse the reactions at 1 atmospheric pressure (He *et al.*, 2023; Wang *et al.*, 2023). A variety of metal-free catalytic systems were reported just to avoid the contamination of metal with product (Sarkar, Ghosh & Islam, 2022). Since then, many researchers developed much more perfect and greener catalytic systems under the green pathway (Singh, Prakash & Nagaraja, 2023; Sarkar, Ghosh & Islam, 2022).

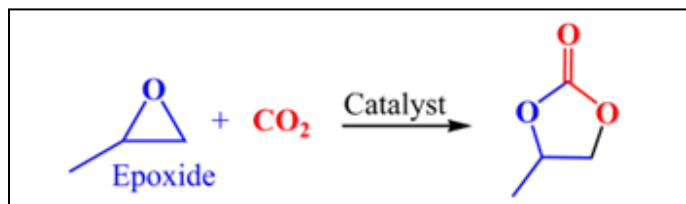


Figure 1: Scheme for Cycloaddition Involving CO₂ and a Terminal Epoxide

The following steps are involved in the process of synthesising a cyclic carbonate's reaction from CO₂ and epoxides catalysed by a bifunctional catalytic system. Metal centre acts as lewis acid centre, and the halide ion acts as a nucleophile in this bifunctional catalytic system. In the initial step, halide ions disconnected from the cocatalyst, and at the same time, the oxygen centre of the epoxide produced a coordination to raise the electrophilic character of the carbon atom where nucleophile halide ion attacks to give an alkoxide intermediate. Alkoxide intermediate with a negative charge will react with the carbon atom of carbon dioxide to produce a linear carbonate structure (Figure 2). Then the cyclic carbonate is formed via an intramolecular ring-closing nucleophilic reaction.

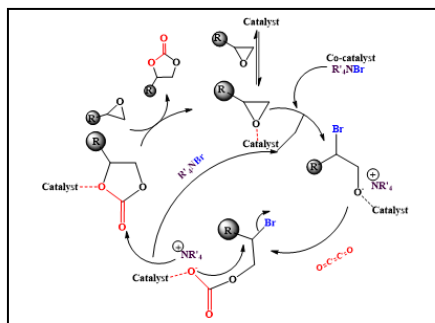


Figure 2: Plausible Reaction Mechanism for Cyclic Carbonate Synthesis Based on Literature

α -Alkylidene cyclic carbonates from propargylic alcohol

The CO₂ fixation reaction is greatly attractive and essential in the vision of environmental as well as economic issues, as it is the most important greenhouse gas but also a cheap, abundant, easily available C1 resource and renewable. Various methods have been promoted to CO₂ into several high value chemical but one of them most promotive synthetic path of α -Alkylidene cyclic carbonates is the carboxylative cyclization of easily obtainable propargyl alcohols and CO₂ (1atom). The cyclisation reaction of propargyl alcohols and CO₂ was developed by a transition metal, phosphine and carbene as the efficient catalyst.

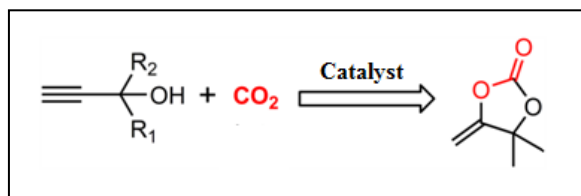


Figure 3: Scheme for the Synthesis of α -Alkylidene-Substituted Cyclic Carbonates

α -alkylidene cyclic carbonates have been extensively utilised as the intermediates of pesticide, pharmaceutical, and fine chemical production. These cyclic carbonates are also very useful for a variety of organic transformations. Numerous materials have been efficiently used for the production of cycloaddition of carbon dioxide via this carboxylative cyclisation process. Few of them – phosphines, alkoxide-functionalised imidazolium betaines/CO₂ adducts, bicyclic guanidines, N-heterocyclic olefin/CO₂ adducts, azole-anion-based aprotic ionic liquids, and N-heterocyclic carbene/CO₂ adducts, etc. – have been employed as metal-free catalysts for the cyclisation. Moreover, these reaction conditions are highly problematic, like high temperature and CO₂ pressure. Hence, the improvement of well-organized catalyst for the CO₂ fixation reaction under sustainable conditions are still highly valued and actively pursued. Researchers promoted more and more ideal and greener catalytic systems for the synthesis of α -alkylidene cyclic carbonates with time. Recently, Giri and his group (2024) developed Cu NP-embedded MOF (Cu-NPs/MOF) which has high catalytic performance for α -alkylidene cyclic carbonates by CO₂ coupling with propargylic amines and alcohols. Moreover, Yang *et al.* (2024) demonstrated carboxylative cyclisation of propargyl alcohols with CO₂ at room temperature using by Silver Nanoparticles on Porphyrinic Triazine-Based Frameworks.

In Figure 4, a probable mechanism is demonstrated for the synthesis of α -alkylidene cyclic carbonates in the presence of a catalyst (Hu *et al.*, 2016). It is believed that the CO₂ incorporation into propargyl alcohols proceeds through the following reaction pathway:

Firstly, the catalyst (1) activates the propargyl alcohol, followed by the base facilitating CO₂ activation, leading to the formation of a carbonate intermediate salt. The catalyst interacts with the triple bond, promoting the formation of intermediate 2 by facilitating

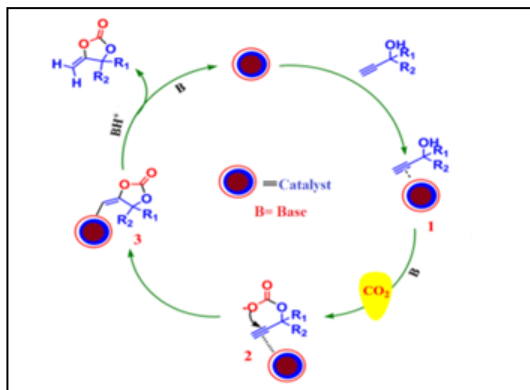


Figure 4: Probable Reaction Mechanism for α -Alkylidene Cyclic Carbonates Synthesis

the bonding between the adjacent oxygen atom and the internal carbon of the $\text{C}\equiv\text{C}$ group. Subsequently, a five-membered exo-trig cyclisation (3) takes place, followed by proton abstraction from BH^+ , leading to the formation of the target product and regeneration of the catalyst under optimised conditions. For activation of the *alkyne*, the catalyst played important parts to provide a driving force for the annulation reaction.

2-Oxazolidinones Synthesis

2-Oxazolidinones are saturated five-membered cyclic carbamates (Figure 5) that have extensive uses as chiral auxiliaries, chemical intermediates and antibacterial pharmaceuticals in medicinal and synthetic chemistry (Giri *et al.*, 2024). Near the beginning, the synthesis of oxazolidinones was performed via the reactions of 1,2-amino alcohols and phosgene or its derivatives or amino alcohols with CO_2 under high pressure (Arshadi *et al.*, 2019). Later on, various techniques have been promoted to manufacture oxazolidinones, including the reaction of CO_2 with propargylamines or ethyleneimines, the cycloaddition reaction of epoxides with isocyanates, and the carbonylation reaction of β -amino alcohols with CO_2 or dialkyl carbonates. But, in recent times, propargylic amine cyclisation with CO_2 has concerned much attention to get 2-oxazolidinones. In this route CO_2 is utilised as a highly suitable C1 resource to obtain various organic compounds. Various catalytic systems for the carboxylative cyclisation of propargylic amines with CO_2 have been promoted, which covers transition metal-based catalysts such as Pd, Ru, Ag, Cu, Au, and organocatalysts like N-heterocyclic carbene, superbases, and protic ionic liquids. Particularly, Yamada *et al.* have confirmed that AgOAc is an effective catalyst for the reaction of various propargylic amines and carbon dioxide into 2-oxazolidinones under mild conditions (Yoshida *et al.*, 2009). Recently Mondal and his team (2025) are going on the synthesis of oxazolidinones in the presence of a highly active 2D imine-linked covalent organic framework (Ag@TPT-TP COF) under mild conditions. Moreover, Srinivasappa and his team (2023) explored the selective one-pot strategy for CO_2 fixation into “oxazolidinone” by using stable porous trimetallic oxide foam (PTOF) as a new

catalyst. Thanks to its distinctive synthesis method and the unique combination and proportion of metal oxides, the PTOF catalyst displayed highly interconnected porous channels along with uniformly distributed active sites on its surface. Well ahead, the PTOF catalyst was screened for the fixation of CO₂ into oxazolidinone

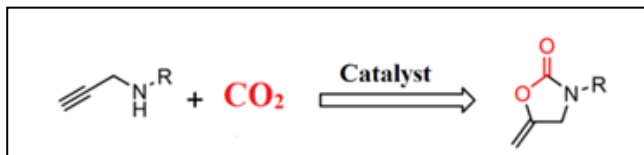


Figure 5: Scheme for the Synthesis of 2-Oxazolidinones

Most of the protocols for the synthesis of oxazolidinone have certain limitations, such as long reaction times, utilisation of high-pressure CO₂, limited substrate scope, harsh reaction conditions and requiring toxic reagents. But nowadays, therefore, a convenient, green, low-cost, large-range substrate-scope protocol which works under moderate reaction conditions will be particularly favoured. Therefore, designing highly efficient heterogeneous catalysts with densely packed basic and catalytic sites holds great potential for the effective capture and conversion of CO₂ into 2-oxazolidinones under ambient conditions. Thus, developing highly efficient heterogeneous catalysts with concentrated basic and catalytic sites is crucial for the effective capture and conversion of CO₂ into 2-oxazolidinones under ambient conditions (Rani, Das & Nagaraja, 2025).

Conclusion

In this view it is concluded the current status and major challenges and opportunities in the conversion of CO₂ into more valuable chemicals using chemical catalysis are more highlighted. This process can be effectively endorsed by various kinds of newly synthesised porous heterogeneous catalysts with Lewis acidic and nucleophilic sites. Moreover, Covalent Organic Frameworks (COFs) are indeed a promising class of materials due to their organic composition and flexibility in structure. The key advantages mentioned, such as their low cost and readily available monomer units, make them highly attractive compared to metal-containing inorganic catalysts or Metal-Organic Frameworks (MOFs), which can be more expensive and sometimes harder to synthesise or scale. The ability to tailor the electronic and steric properties of COFs by selecting different monomer units is one of their most notable features. This fine-tuning capability allows researchers to design COFs with specific functionalities, such as optimised surface areas, porosity, and chemical reactivity, which are essential for applications like CO₂ capture and reduction. The structural tunability of COFs can also enhance their selectivity and efficiency in these reactions, enabling better performance in energy conversion and storage technologies, like carbon capture or catalysis for the production of valuable chemicals. These materials combine the structural advantages of COFs with the enhanced catalytic properties provided by metal centres to create a

hybrid material that can be tailored for a range of important reactions, including coupling reactions, carbonylation reactions, and CO₂ fixation reactions. Their catalytic activity was observed in coupling reaction for the synthesis of cyclic acetals and dicoumarol, carbonylation reaction for the preparation of α -ketoamides and finally carbon dioxide fixation reaction for the production of cyclic carbonate from epoxide, α -alkylidene cyclic carbonates from propargylic alcohol and 2-oxazolidinones. The reaction conditions were optimised by varying several solvents, catalyst amount, temperature etc. to obtain the highest yield of the desired products. These catalytic systems are highly stable and recyclable. This chapter judges a significant development in the field of porous polymeric network-based heterogeneous catalysis and gives high inspiration for the synthesis of reusable and recyclable heterogeneous material for diverse CO₂ conversions into value-added fine chemicals.

Acknowledgment

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References

- Arshadi, S., Banaei, A., Ebrahimiasl, S., Monfared, A., & Vessally, E. (2019). Solvent-free incorporation of CO₂ into 2-oxazolidinones: a review. *RSC Advances*, 9(34), 19465-19482. <https://doi.org/10.1039/C9RA00551J>
- Chen, X., Liu, Y., Wang, G., Zhang, L., Kuang, Y., Tao, H., ... & Lv, X. (2024). Progress of CO₂ fixation using cycloaddition reaction. *Environmental Functional Materials*, 3(1), 13-24. <https://doi.org/10.1016/j.efmat.2024.07.001>
- Du, J., Ouyang, H., & Tan, B. (2021). Porous organic polymers for catalytic conversion of carbon dioxide. *Chemistry—An Asian Journal*, 16(23), 3833-3850. <https://doi.org/10.1002/asia.202100991>
- Giri, P. K., Parihar, V., Kumar, S., & Nagaraja, C. M. (2024). Copper nanoparticles anchored on the metal–organic framework as recyclable catalyst for CO₂ fixation to high-value compounds. *ACS Applied Nano Materials*, 7(13), 15488-15497. <https://doi.org/10.1021/acsanm.4c02393>
- He, M., Fang, Z., Wang, P., You, Y., & Li, Z. (2023). Recent progress in photocatalytic chemical fixation of carbon dioxide. *ACS Sustainable Chemistry & Engineering*, 11(33), 12194-12217. <https://doi.org/10.1021/acssuschemeng.3c01994>
- Hu, J., Ma, J., Zhu, Q., Qian, Q., Han, H., Mei, Q., & Han, B. (2016). Zinc (II)-catalyzed reactions of carbon dioxide and propargylic alcohols to carbonates at room temperature. *Green Chemistry*, 18(2), 382-385. <https://doi.org/10.1039/C5GC01870F>
- Karishma, S., Kamalesh, R., Saravanan, A., Deivayanai, V. C., Yaashikaa, P. R., & Vickram,

- A. S. (2024). A review on recent advancements in biochemical fixation and transformation of CO₂ into constructive products. *Biochemical Engineering Journal*, 208. <https://doi.org/10.1016/j.bej.2024.109366>
- Mondal, T., Sarkar, P., Islam, M. S., Dahlous, K. A., & Manirul Islam, S. (2025). Silver Nanoparticles Incorporated Covalent Organic Framework Catalyzed Sustainable Synthesis of Cyclic Carbonates and Oxazolidinones Under Atmospheric CO₂ Pressure: A Novel Approach of CO₂ Utilization. *ChemistrySelect*, 10(3), e202403353. <https://doi.org/10.1002/slct.202403353>
- Pal, T. K., De, D., & Bharadwaj, P. K. (2022). Metal-organic frameworks as heterogeneous catalysts for the chemical conversion of carbon dioxide. *Fuel*, 320. <https://doi.org/10.1016/j.fuel.2022.123904>
- Park, J. H., Yang, J., Kim, D., Gim, H., Choi, W. Y., & Lee, J. W. (2022). Review of recent technologies for transforming carbon dioxide to carbon materials. *Chemical Engineering Journal*, 427. <https://doi.org/10.1016/j.cej.2021.130980>
- Rani, P., Das, R., & Nagaraja, C. M. (2025). A review on framework (MOF/COF/POP)-based materials for efficient conversion of CO₂ to bio-active oxazolidinones. *Inorganic Chemistry Frontiers*, 12(2), 430-478. <https://doi.org/10.1039/D4QI02101K>
- Sarkar, S., Ghosh, S., & Islam, S. M. (2022). A Zn (II)-functionalized COF as a recyclable catalyst for the sustainable synthesis of cyclic carbonates and cyclic carbamates from atmospheric CO₂. *Organic & Biomolecular Chemistry*, 20(8), 1707-1722. <https://doi.org/10.1039/D1OB01938D>
- Singh, G., Prakash, K., & Nagaraja, C. M. (2023). Fe (III)-anchored porphyrin-based nanoporous covalent organic frameworks for green synthesis of cyclic carbonates from olefins and CO₂ under atmospheric pressure conditions. *Inorganic Chemistry*, 62(32), 13058-13068. <https://doi.org/10.1021/acs.inorgchem.3c01899>
- Srinivasappa, P. M., Prasad, D., Chaudhari, N. K., Samal, A. K., Thapa, R., Siddharthan, E. E., & Jadhav, A. H. (2023). Trimetallic Oxide Foam as an Efficient Catalyst for Fixation of CO₂ into Oxazolidinone: An Experimental and Theoretical Approach. *ACS Applied Materials & Interfaces*, 15(18), 21994-22011. <https://doi.org/10.1021/acsami.2c23019>
- Wang, Q., Chen, P., Li, X., Liang, Y., & Pan, Y. (2023). Chemical fixation of carbon dioxide into cyclic carbonates catalyzed by porous materials. *Asian Journal of Organic Chemistry*, 12(8). <https://doi.org/10.1002/ajoc.202300308>
- Yamaguchi, K., Ebitani, K., Yoshida, T., Yoshida, H., & Kaneda, K. (1999). Mg– Al mixed oxides as highly active acid– base catalysts for cycloaddition of carbon dioxide to epoxides. *Journal of the American Chemical Society*, 121(18), 4526-4527. <https://doi.org/10.1021/ja9902165>
- Yang, Y., Li, Y., Zhang, Z., Chen, K., & Luo, R. (2023). In situ anchoring of small-sized silver nanoparticles on porphyrinic triazine-based frameworks for the conversion of CO₂ into α -alkylidene cyclic carbonates with outstanding catalytic activities under ambient

conditions. *ACS Applied Materials & Interfaces*, 16(1), 411-424. <https://doi.org/10.1021/acsami.3c10521>

Yano, T., Matsui, H., Koike, T., Ishiguro, H., Fujihara, H., Yoshihara, M., & Maeshima, T. (1997). Magnesium oxide-catalysed reaction of carbon dioxide with an epoxide with retention of stereochemistry. *Chemical Communications*, (12), 1129-1130. <https://doi.org/10.1039/A608102I>

Yoshida, S., Fukui, K., Kikuchi, S., & Yamada, T. (2009). Silver-catalyzed preparation of oxazolidinones from carbon dioxide and propargylic amines. *Chemistry Letters*, 38(8), 786-787. <https://doi.org/10.1246/cl.2009.786>

Advancing Sustainability: Reusable Indium Catalysts for Green Organic Transformations

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ABSTRACT

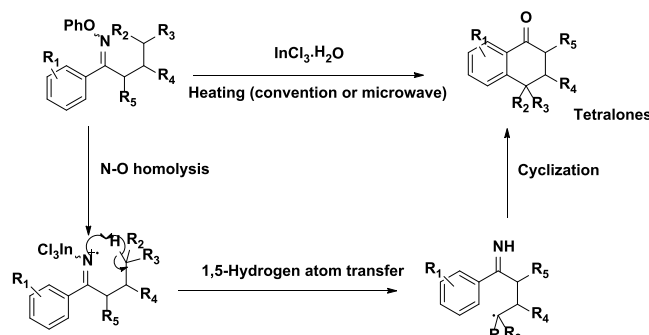
Sustainable chemistry aims to minimise environmental impact by designing efficient, eco-friendly processes, with catalysis playing a crucial role. Reusable catalysts enhance sustainability by allowing recovery, regeneration, and repeated use, which reduces resource depletion and operational costs. This chapter explores different methods for attaching homogeneous indium salts, e.g., ionic bonding with an ionic liquid, complexation with functionalised polymers like polyaniline, and integration into metal-organic frameworks (MOFs). Additionally, it provides a detailed discussion on the application of indium-based reusable catalysts in various organic transformations, along with their recovery and recyclability.

Keywords: A3-Coupling; Aza-Michael Reaction; Indium Catalysis; Ionic Liquid; Metal-Organic Framework; Polyaniline; Strecker Reaction

Introduction

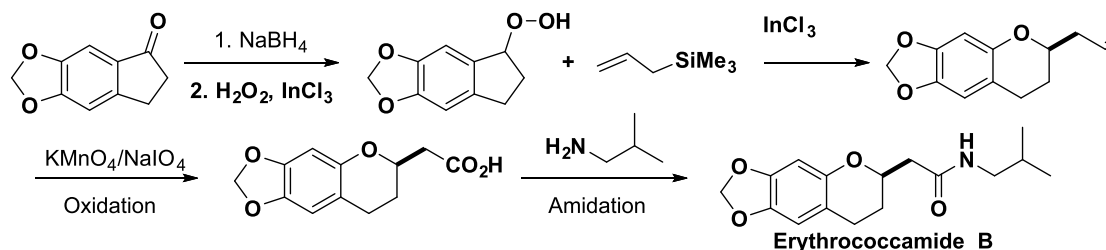
Catalytic reactions by indium salts are of immense importance in synthesising organic molecules of importance (Datta, 2021; Singh & Raghuvanshi, 2012). A vast range of organic transformations is reported using homogeneous Indium catalysts as indium chloride is equally compatible with water and organic solvents. Moreover, Indium salts are stable in the presence of oxygen and nitrogen-containing nucleophiles (Cintas, 1995).

Recently, Jones *et al.* (2025) reported the synthesis of diversified tetralones, which is an important class of organic compounds via InCl_3 -catalysed N-O homolysis-1,5-hydrogen atom transfer-cyclisation from O-phenyloximes (Scheme 1).



Scheme 1: Synthesis of Tetralones

In 2023, Bosnidou *et al.* reported “Tandem InCl_3 -Promoted Hydroperoxide Rearrangements and Nucleophilic Additions” as a strategy to synthesise different benzoxacycles such as erythrococcamide B (Scheme 2).



Scheme 2: Synthesis of Erythrococcamide B

Recent developments of indium chloride-catalysed synthesis of heterocycles are well depicted in the recent ACS Omega review by Mahato *et al.* (2020). Figure 1 summarises the wide application of InCl_3 in the synthesis of heterocycles.

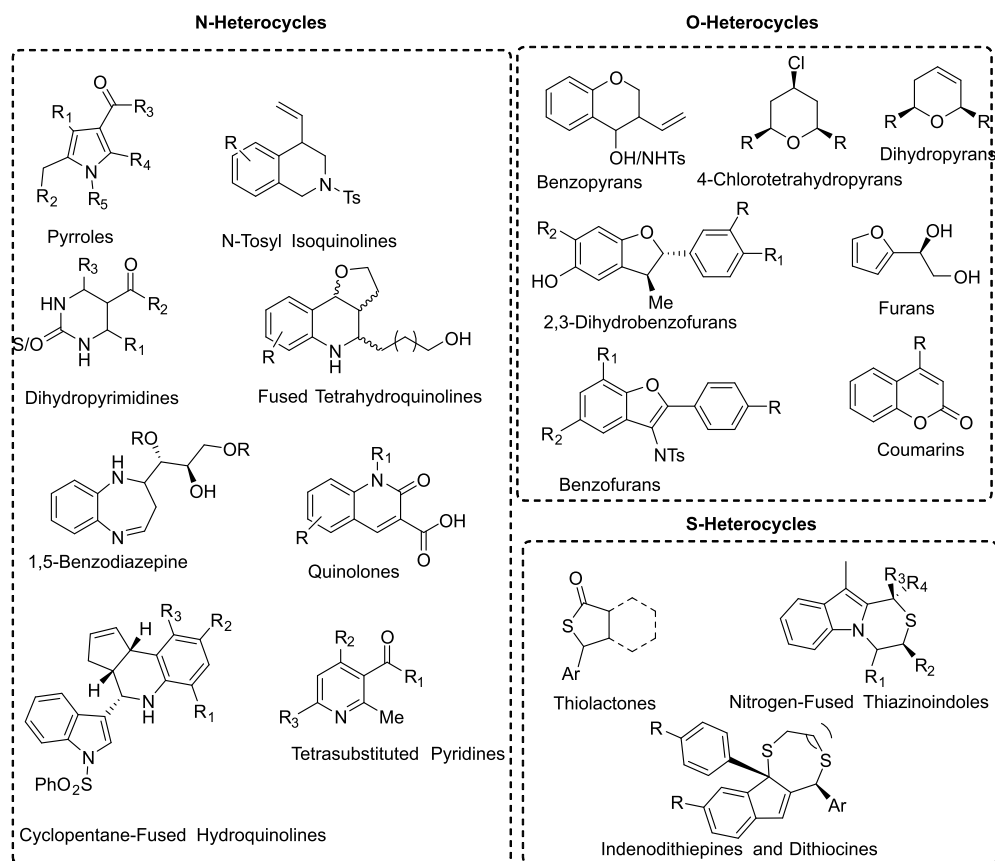


Figure 1: Selected Application of Indium Catalysis in the Synthesis of Heterocycles

As discussed, InCl_3 is a versatile catalyst and has found widespread application and acceptance among the organic synthetic community (Table 1).

Table 1: Representative Examples of the Homogeneous Indium Catalysis

Sl. No	Reaction Type	Reference
1	Aza-Diels alder reaction	1. Sridharan <i>et al.</i> , 2007 2. Li, Zhang & Li, 2003.
2	Aza-Michael reaction	Selvi & Velmathi, 2018
3	Strecker reaction	Shen, Ji & Loh, 2008
4	Mannich reaction	Loh & Wei, 1998
5	Sakurai reaction	Pinet, Figadère & Ferrière, 2020
6	Meyer-Schuster rearrangement of propargylic alcohols	Francos <i>et al.</i> , 2015
7	Glycosylation	Yang <i>et al.</i> , 2025
8	Thiolysis of α,β -Epoxy-carboxylic Acids	Fringuelli <i>et al.</i> , 2005
9	Cyclotrimerization of Alkynes	Xu <i>et al.</i> , 2011
10	Selective Reduction of the α,β -Carbon–Carbon Double Bond in Highly Activated $\alpha,\beta,\gamma,\delta$ -Unsaturated Alkenes	Ranu & Samanta, 2003

For sustainability and green chemistry, reusable catalysts are preferable to their homogeneous counterparts due to their obvious advantages, such as reduced waste and lower cost.

Reusable Indium Catalysis

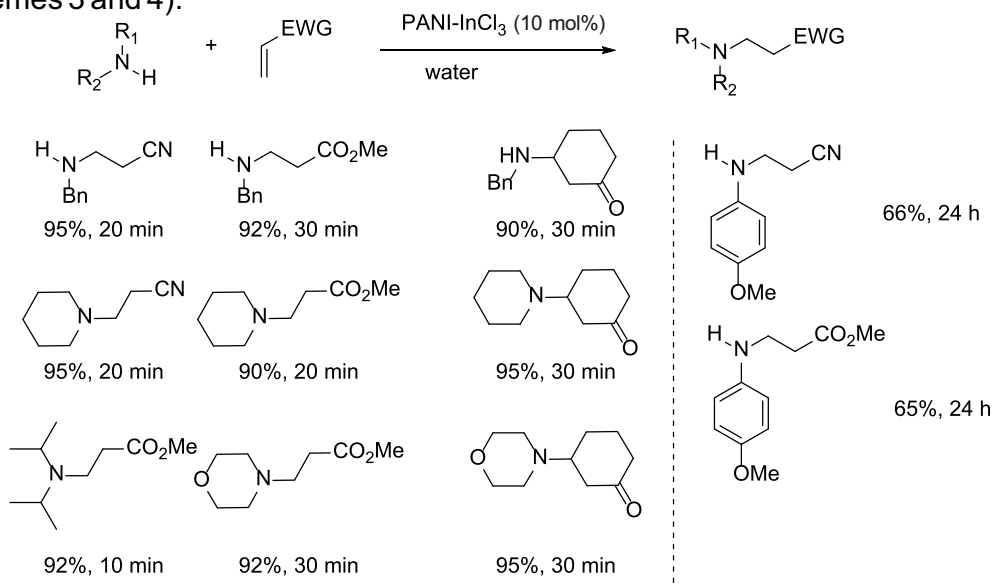
Immobilized Indium Catalyst on Polyaniline Support and Used in Aza-Michael and Aza-Diels-Alder Reaction

Aza-Michael and aza-Diels-Alder reactions are efficient tools for organic chemists to synthesise complex molecules. In his two important reviews on the aza-Michael reaction, Rulev (2011, 2023) aptly captured the development and use of the aza-Michael reaction. Aza-Diels alder reaction is an equally important method for accessing biologically important molecules (Cao, Green & Xu, 2017).

The immobilisation of metal salts onto a functionalised polymer is a well-established strategy to prepare new heterogeneous catalysts. Kantam *et al.* (2007) used an indium chloride solution in acetonitrile and polyaniline base to prepare a polyaniline-supported indium catalyst (PANI-In). It has been extensively characterised by FTIR, XPS, scanning electron microscopy–energy dispersive X-ray spectroscopy, and inductively coupled plasma atomic emission spectroscopy. FTIR showed a new peak at 1136 cm^{-1} , indicating the complexation of indium with polyaniline. X-ray photoelectron spectroscopy clearly showed the presence of Indium and Chlorine as revealed by a peak In 3d_{5/2} at 445.17 eV and Cl 2p at 198.58 eV. Scanning electron microscopy (SEM) analysis showed a very low deformation of the polymeric structure of the polyaniline backbone. Energy dispersive X-ray and inductively coupled plasma-atomic emission spectroscopy were used to analyse the indium content, which was $\sim 0.67\text{ mmol/g}$.

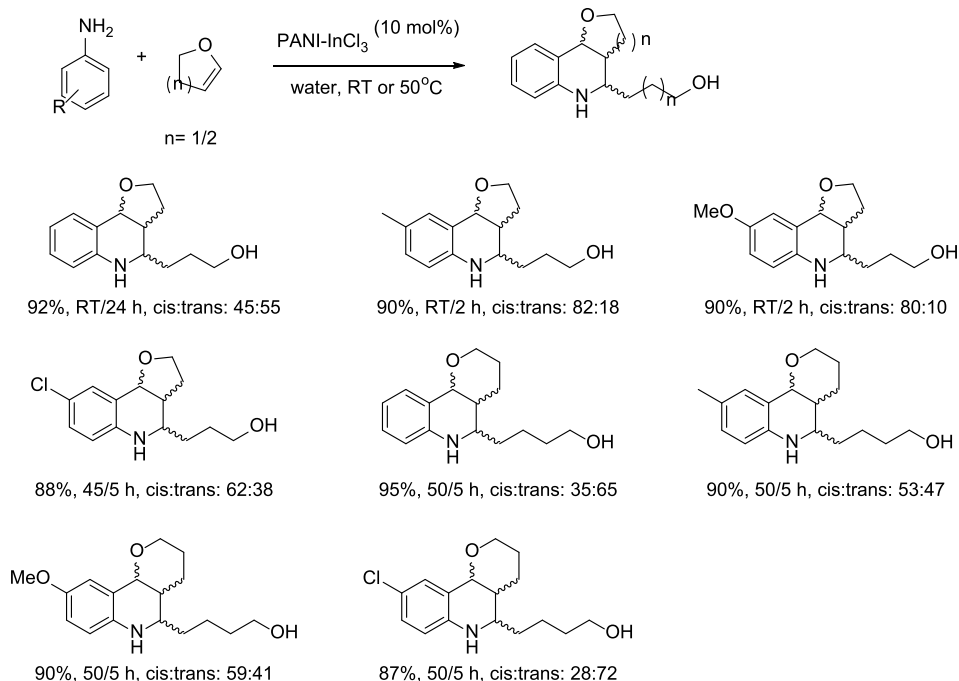
The as-synthesised PANI-In catalyst was explored in two different organic

transformations: the Aza-Michael reaction and the aza-Diels-Alder reaction in water (Schemes 3 and 4).



Scheme 3: Aza-Michael Reaction Catalyzed by PANI-In

Aza-Michael reaction of aliphatic amines was quicker in comparison with aromatic amines, and mono-selectivity was very high wherever applicable.



Scheme 4: Aza-Diels-Alder Reaction Catalyzed by PANI-In

Reusable Indium Catalysts for Green Transformations

The Aza-Diels-Alder reaction of substituted anilines with dihydrofuran or dihydropyran efficiently yielded tetrahydroquinolines in high yield.

Reusability

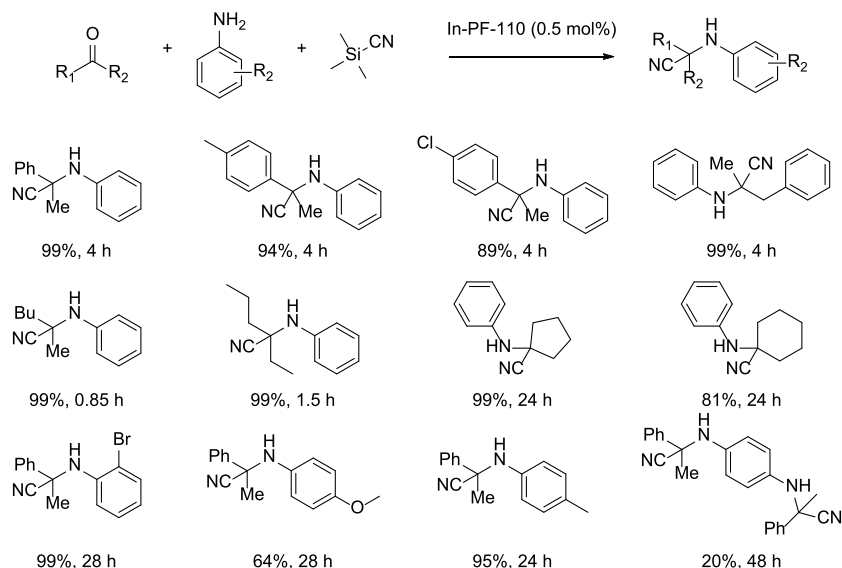
PANI-In was recovered by filtration and reused multiple times with minimal loss activity in both the aza-Michael and aza-Diels-Alder reactions (Table 2).

Table 2: Recyclability of PANI-In Catalysts

Aza-Michael		Aza-Diels-Alder	
Cycle	Yield (%)	Cycle	Yield (%)
1	95	1	90
6	92	6	87

Indium-Based Metal-Organic Framework (MOF) Catalysts for Organic Transformations

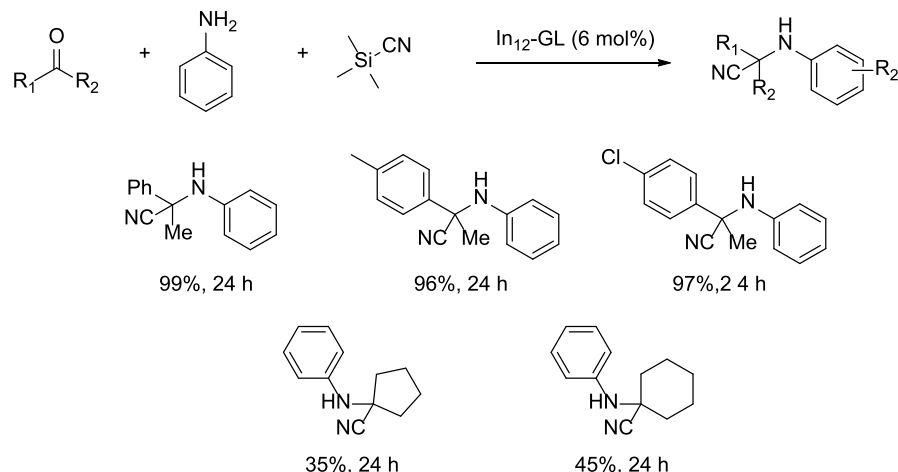
Recently, MOFs are getting considerable attention for their unique properties and catalytic activities. Reinares-Fisac *et al.* (2016) synthesised indium-based MOF and showed its excellent catalytic activity in the Strecker reaction of ketones. Strecker synthesis provides easy access to α -aminonitriles, which are important intermediates for the synthesis of many organic compounds, mainly amino acid derivatives. The catalyst was prepared from $\text{In}(\text{NO}_3)_3$ and 1,3,5-tris(4-carboxyphenyl) benzene, and it was denoted as InPF-110 (indium polymeric framework). It was well characterised by XRD and TPD for Brunauer–Emmett–Teller surface area. It is mesoporous in nature. The catalyst was employed in the Strecker reaction of ketones (Scheme 5).



Scheme 5: Strecker Reaction Using InPF-110

α -Aminonitriles were afforded in good yield. The catalyst was filtered off and recycled 10 times in the reaction of acetophenone, aniline, and trimethylsilyl cyanide. Very consistent yield was obtained even after the 10th cycle (1st: 98%; 2nd: 98%; 3rd: 97%, 4th: 98%; 5th: 99%, 6th: 99%, 7th: 99%, 8th: 95%, 9th: 94%, 10th: 91%).

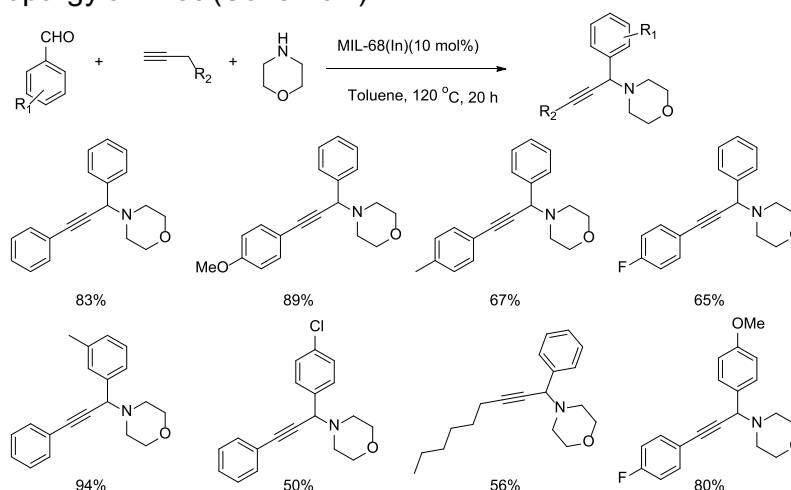
Liang *et al.* (2020) prepared another indium-based MOF In12-GL, and used the catalyst for the Strecker synthesis. Details are captured in Scheme 6.



Scheme 6: Strecker Reaction Using In12-GL Catalyst

In12-GL exhibited minimal reduction in activity even after five cycles in the Strecker reaction involving aniline, acetophenone, and TMS-CN.

Lam *et al.* (2016) investigated another indium-based MOF, MIL-68(In), for its application in propargylamine synthesis. Propargylamines are a significant class of building blocks. MIL-68(In) facilitated the coupling of aldehydes, alkynes, and amines to produce propargylamines (Scheme 7).



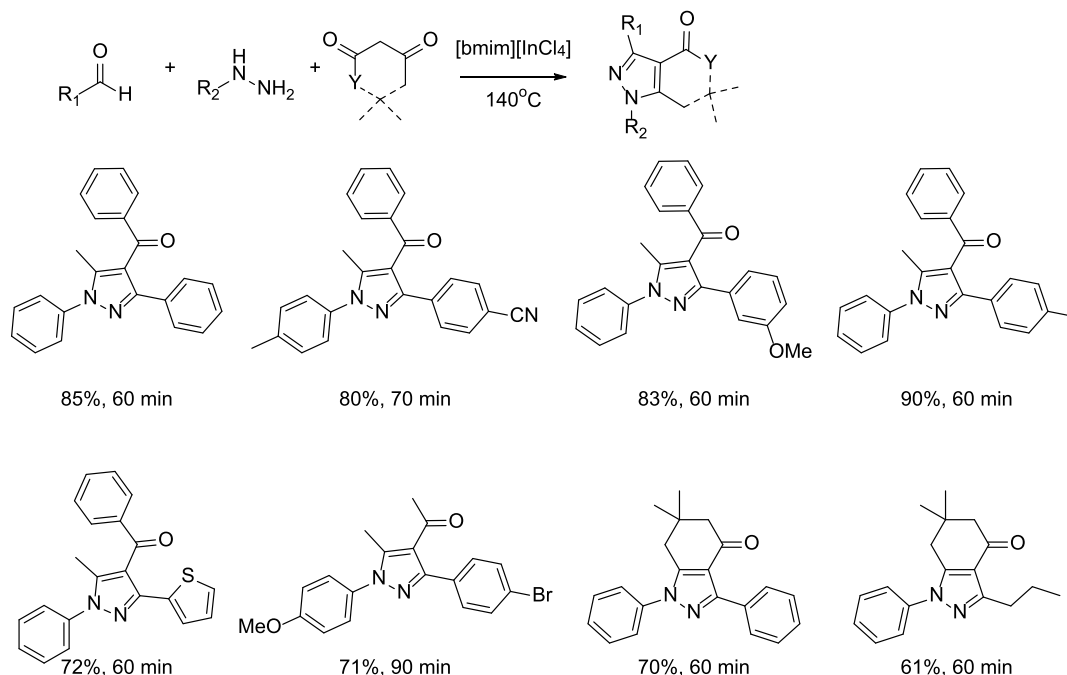
Scheme 7: Synthesis of Propargylamines Using MIL-68(In) Catalyst

Reusable Indium Catalysts for Green Transformations

MIL-68(In) catalyst was recovered by filtration and reused for seven cycles in the coupling of phenylacetylene, benzaldehyde, and morpholine with similar catalytic efficiency.

Ionic Liquid-Anchored Indium Catalysts

Ionic liquid gained considerable attention for its efficient recovery and solubility for many catalytic systems. Safaei *et al.* (2013) reported a tetrachloroindate-based ionic liquid catalysed efficient and regioselective formation of pyrazoles.



Scheme 8: Synthesis of Substituted Pyrazoles Using $[bmim][InCl_4]$ Catalyst

Details are presented in Scheme 8. The authors demonstrated that a room-temperature ionic liquid containing an indium catalyst provided superior regioselectivity compared to the homogeneous $InCl_3$ catalyst (100:0 vs. 80:20). Furthermore, the catalyst was efficiently recovered by adding water to the reaction mixture, precipitating the product, and subsequently removing water under reduced pressure. Notably, the catalyst retained its activity over three cycles without any loss.

Conclusion

This review highlights the significance of indium catalysis in organic synthesis and its progression toward sustainability through the development of easily recoverable and recyclable indium catalysts. It discusses three distinct classes of heterogeneous indium catalysis, categorised based on their efficiency and recyclability. This insight is expected to serve as a valuable guide for future advancements in the field of indium catalysis.

Acknowledgement

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References

- Bosnidou, A. E., Fayet, A., Cheibas, C., Gayraud, O., Bourcier, S., Frison, G., & Nay, B. (2023). Tandem InCl₃-Promoted Hydroperoxide Rearrangements and Nucleophilic Additions: A Straightforward Entry to Benzoxacycles. *The Journal of Organic Chemistry*, 88(13), 9277-9282. <https://doi.org/10.1021/acs.joc.3c00845>
- Cao, M. H., Green, N. J., & Xu, S. Z. (2017). Application of the aza-Diels–Alder reaction in the synthesis of natural products. *Organic & Biomolecular Chemistry*, 15(15), 3105-3129. <https://doi.org/10.1039/C6OB02761J>
- Cintas, P. (1995). Synthetic organoindium chemistry: What makes indium so appealing?. *Synlett*, 1995(11), 1087-1096. <https://doi.org/10.1055/s-1995-5192>
- Datta, M. (2021). Recent advances of indium (III) chloride catalyzed reactions in organic synthesis. *ChemistrySelect*, 6(2), 187-216. <https://doi.org/10.1002/slct.202003828>
- Franco, J., Borge, J., Díez, J., García-Garrido, S. E., & Cadierno, V. (2015). Easy entry to donor/acceptor butadiene dyes through a MW-assisted InCl₃-catalyzed coupling of propargylic alcohols with indan-1, 3-dione in water. *Catalysis Communications*, 63, 10-14. <https://doi.org/10.1016/j.catcom.2014.07.028>
- Fringuelli, F., Pizzo, F., Tortoioli, S., & Vaccaro, L. (2005). InCl₃-catalyzed regio- and stereoselective thiolysis of α , β -epoxycarboxylic acids in water. *Organic Letters*, 7(20), 4411-4414. <https://doi.org/10.1021/ol051582y>
- Jones, S. A., Botello, J. A., Singh, J., Damstedt, G. L., Payne, J. C., Griffin, E. D., ... & Castle, S. L. (2025). Microwave-Promoted Synthesis of 1-Tetralones via Iminyl Radical-Mediated 1, 5-Hydrogen Atom Transfer. *The Journal of Organic Chemistry*, 90(6), 2547–2552. <https://doi.org/10.1021/acs.joc.4c02887>
- Kantam, M. L., Roy, M., Roy, S., Subhas, M. S., Sreedhar, B., Choudary, B. M., & De, R. L. (2007). Polyaniline supported indium chloride: A reusable catalyst for organic transformations in water. *Journal of Molecular Catalysis A: Chemical*, 265(1-2), 244-249. <https://doi.org/10.1016/j.molcata.2006.10.021>
- Lam, H. N., Nguyen, N. B., Dang, G. H., Truong, T., & Phan, N. T. (2016). Three-component coupling of aldehyde, alkyne, and amine via C–H bond activation using indium-based metal–organic framework MIL-68 (In) as a recyclable heterogeneous catalyst. *Catalysis Letters*, 146, 2087-2097. <https://doi.org/10.1007/s10562-016-1805-7>
- Li, Z., Zhang, J., & Li, C. J. (2003). InCl₃-catalyzed reaction of aromatic amines with cyclic hemiacetals in water: facile synthesis of 1, 2, 3, 4-tetrahydroquinoline derivatives. *Tetrahedron Letters*, 44(1), 153-156. [https://doi.org/10.1016/S0040-4039\(02\)02450-4](https://doi.org/10.1016/S0040-4039(02)02450-4)
- Liang, G. M., Xiong, P., Azam, K., Ni, Q. L., Zeng, J. Q., Gui, L. C., & Wang, X. J. (2020). A

- discrete tetrahedral indium cage as an efficient heterogeneous catalyst for the fixation of CO₂ and the strecker reaction of ketones. *Inorganic Chemistry*, 59(3), 1653-1659. <https://doi.org/10.1021/acs.inorgchem.9b02763>
- Loh, T. P., & Wei, L. L. (1998). Novel one-pot Mannich-type reaction in water: Indium trichloride-catalyzed condensation of aldehydes, amines and silyl enol ethers for the synthesis of β -amino ketones and esters. *Tetrahedron Letters*, 39(3-4), 323-326. [https://doi.org/10.1016/S0040-4039\(97\)10478-6](https://doi.org/10.1016/S0040-4039(97)10478-6)
- Mahato, S. K., Acharya, C., Wellington, K. W., Bhattacharjee, P., & Jaisankar, P. (2020). InCl₃: A versatile catalyst for synthesizing a broad spectrum of heterocycles. *ACS Omega*, 5(6), 2503-2519. <https://doi.org/10.1021/acsomega.9b03686>
- Pinet, A., Figadère, B., & Ferrié, L. (2020). Access to Functionalized 3, 5-Disubstituted 1, 2-Dioxolanes under Mild Conditions through Indium (III) Chloride/Trimethylsilyl Chloride or Scandium (III) Triflate Catalysis. *Advanced Synthesis & Catalysis*, 362(5), 1190-1194. <https://doi.org/10.1002/adsc.201901145>
- Ranu, B. C., & Samanta, S. (2003). Remarkably selective reduction of the α , β -carbon-carbon double bond in highly activated α , β , γ , δ -unsaturated alkenes by the InCl₃-NaBH₄ reagent System. *The Journal of Organic Chemistry*, 68(18), 7130-7132. <https://doi.org/10.1021/jo0347821>
- Reinares-Fisac, D., Aguirre-Díaz, L. M., Iglesias, M., Snejko, N., Gutiérrez-Puebla, E., Monge, M. Á., & Gándara, F. (2016). A mesoporous indium metal-organic framework: remarkable advances in catalytic activity for strecker reaction of ketones. *Journal of the American Chemical Society*, 138(29), 9089-9092. <https://doi.org/10.1021/jacs.6b05706>
- Rulev, A. Y. (2011). Aza-Michael reaction: achievements and prospects. *Russian Chemical Reviews*, 80(3), 197-218. <https://doi.org/10.1070/RC2011v080n03ABEH004162>
- Rulev, A. Y. (2023). Aza-Michael Reaction: A Decade Later-Is the Research Over?. *European Journal of Organic Chemistry*, 26(26). <https://doi.org/10.1002/ejoc.202300451>
- Safaei, S., Mohammadpoor-Baltork, I., Khosropour, A. R., Moghadam, M., Tangestaninejad, S., Mirkhani, V., & Khavasi, H. R. (2013). [Bmim][InCl₄]-Catalyzed Addition of Hydrazones to β -Diketones: An Efficient Regioselective Synthesis of Pyrazoles and Pyrazole-Fused Cyclohexanones. *Synlett*, 24(09), 1086-1090. <https://doi.org/10.1055/s-0032-1316900>
- Selvi, T., & Velmathi, S. (2018). Indium (III) triflate-catalyzed reactions of aza-Michael adducts of chalcones with aromatic amines: Retro-Michael addition versus quinoline formation. *The Journal of Organic Chemistry*, 83(7), 4087-4091. <https://doi.org/10.1021/acs.joc.7b03151>
- Shen, Z. L., Ji, S. J., & Loh, T. P. (2008). Indium (III) iodide-mediated Strecker reaction in water: an efficient and environmentally friendly approach for the synthesis of α -aminonitrile via a three-component condensation. *Tetrahedron*, 64(35), 8159-8163. <https://doi.org/10.1016/j.tet.2008.06.047>
- Singh, M. S., & Raghuvanshi, K. (2012). Recent advances in InCl₃-catalyzed one-pot organic

- synthesis. *Tetrahedron*, 68(42), 8683-8697. <https://doi.org/10.1016/j.tet.2012.06.099>
- Sridharan, V., Perumal, P. T., Avendano, C., & Menéndez, J. C. (2007). The first aza Diels–Alder reaction involving an α , β -unsaturated hydrazone as the dienophile: stereoselective synthesis of C-4 functionalized 1, 2, 3, 4-tetrahydroquinolines containing a quaternary stereocenter. *Organic & Biomolecular Chemistry*, 5(9), 1351-1353. <https://doi.org/10.1039/B703083E>
- Xu, Y. L., Pan, Y. M., Wu, Q., Wang, H. S., & Liu, P. Z. (2011). Regioselective synthesis of 1, 3, 5-substituted benzenes via the InCl_3 /2-iodophenol-catalyzed cyclotrimerization of alkynes. *The Journal of Organic Chemistry*, 76(20), 8472-8476. <https://doi.org/10.1021/jo201010d>
- Yang, L., Qiu, Y., Pan, L., Zhou, Z., Tan, Y., Li, M., ... & Tao, H. (2025). In (OTf) 3-Only-Catalyzed Glycosylation via Activation of an Alkyne Appended with an Amide Auxiliary Group. *Organic Letters*, 27(7), 1735–1740. <https://doi.org/10.1021/acs.orglett.5c00219>

Ornamental Fish Diversity of Mridangabhanga River- A Distributaries of River Ganga

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ABSTRACT

The present study was conducted to assess the distribution of ornamental fishes of the Mridangabhanga River and investigated the core threats to the ichthyofaunal community to ensure conservational strategies to protect the River and its biota. The study was conducted in the pre-monsoon and post-monsoon seasons at five sites: S1. Kadamtala, S2. Purbo Dwarakapur, S3. Brojoballavpur, S4. Kedarpur, S5. Bolerhat during the study period. During the study a total of 49 fish species were identified as ornamental fishes belonging to 31 genera, 20 families and 6 orders. The maximum number of fish species was from Order Cypriniformes (35%). The Mridangabhanga River is home to these fish species; furthermore, the ovulating females among them serve as a valuable source that could contribute to the growth of their population in the river.

Keywords: *Ichthyofaunal Diversity; Indigenous; Mridangabhanga River; Ornamental Fishery*

Introduction

The anthropogenic activity has drastically changed the river ecosystem, which has created adverse effects on aquatic flora and fauna. The ichthyofaunal composition of all aquatic bodies is in stress due to this adversity. Moreover, unfavourable environmental effects like heavy storms and severe droughts were added adversity to the manmade lethal influences. This area during every monsoon season experiences a high tidal effect, and the embankment area always gets collapsed due to it (Chakraborty & Adhikary, 2014). The only way to protect the existing ichthyofaunal diversity of this river is to go through sustainable exploitation. Periodic assessment of the ichthyofaunal population is essential (Sheikh & Goswami, 2014). Siligato and Bohmer (2001), in their extensive study, depicted that fish as an indicator in the assessment of water quality was the best option due to easy availability and being economy friendly. Sarkar (2021) identified ninety fish species from Mridangabhanga River from three study sites, but the present study intended to identify the ornamental fishes which are native to this River. The Ornamental fishes are the most special fishes, which are gifted with beautiful colouration with spots on the body, tail, or fins. they are unique in behavior some had special feeding habits (Allison *et al.*, 1998; Brooks *et al.*, 2002; Chakraborty *et al.*, 2021). Most of these fish species could be easily bred in captivity, and the population could be increased according to market value (Bhattacharjya, Sugunan & Choudhury, 2000). This research work intended to identify those species of ornamental fishes which are indigenous and easily available in this Mridangabhanga River (Table 1). The Fishermen

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community as well as local people who exploit river wealth for their livelihood, might take the opportunity to manage and conserve these aquatic jewels for the betterment of their life status.

Table 1: List of Ornamental Fishes of Mridangabhanga Rivere water level in the U-tube just touches and wets the sintered glass at the beginning.

SL.NO.	CLASS	ORDER	FAMILY	SUB FAMILY	NAME OF THE FISH	STATUS
1	Actinopterygii	Kurtiformes	Kurtidae		<i>Kurtus indicus</i>	NE
2	Actinopterygii	Perciformes	Ambessidae		<i>Ambassis kopsii</i>	NE
3	Actinopterygii	Perciformes	Ambessidae		<i>Chanda nama</i>	LC
4	Actinopterygii	Perciformes	Ambessidae		<i>Parambassis baculis</i>	LC
5	Actinopterygii	Perciformes	Ambessidae		<i>Parambassis ranga</i>	LC
6	Actinopterygii	Anabantiformes	Badidae		<i>Badis badis</i>	LC
7	Actinopterygii	Anabantiformes	Nandidae		<i>Nandus nandus</i>	LC
8	Actinopterygii	Anabantiformes	Osphronemidae		<i>Trichogaster fasciata</i>	LC
9	Actinopterygii	Anabantiformes	Osphronemidae		<i>Trichogaster lalius</i>	LC
10	Actinopterygii	Anabantiformes	Osphronemidae		<i>Trichogaster chuna</i>	LC
11	Actinopterygii	Anabantiformes	Channidae		<i>Channa orientalis</i>	VU
12	Actinopterygii	Anabantiformes	Channidae		<i>Channa punctate</i>	LC
13	Actinopterygii	Anabantiformes	Channidae		<i>Channa striata</i>	LC
14	Actinopterygii	Beloniformes	Belonidae		<i>Xenentodon cancila</i>	LC
15	Actinopterygii	Clupeiformes	Clupeidae		<i>Corica soborna</i>	LC
16	Actinopterygii	Clupeiformes	Clupeidae		<i>Nematalosa galathea</i>	LC
17	Actinopterygii	Clupeiformes	Engraulidae		<i>Setipinna tenuifilis</i>	DD
18	Actinopterygii	Cypriniformes	Danionidae		<i>Parluciosoma daniconius</i>	LC
19	Actinopterygii	Cypriniformes	Cyprinidae		<i>Amblypharyngodon mola</i>	LC
20	Actinopterygii	Cypriniformes	Cyprinidae		<i>Esumusdanricus</i>	LC
21	Actinopterygii	Cypriniformes	Cyprinidae		<i>Laubuka fasciata</i>	NT
22	Actinopterygii	Cypriniformes	Cyprinidae		<i>Labeo angara</i>	LC
23	Actinopterygii	Cypriniformes	Cyprinidae		<i>Puntius chola</i>	LC
24	Actinopterygii	Cypriniformes	Cyprinidae		<i>Puntius conchoni</i>	LC
25	Actinopterygii	Cypriniformes	Cyprinidae		<i>Puntius amphibious</i>	DD
26	Actinopterygii	Cypriniformes	Cyprinidae		<i>Puntius binotatus</i>	LC
27	Actinopterygii	Cypriniformes	Cyprinidae		<i>Puntius puntio</i>	NE
28	Actinopterygii	Cypriniformes	Cyprinidae		<i>Puntius phutunio</i>	LC
29	Actinopterygii	Cypriniformes	Cyprinidae		<i>Puntius sophore</i>	LC
30	Actinopterygii	Cypriniformes	Cyprinidae		<i>Puntius terio</i>	LC
31	Actinopterygii	Cypriniformes	Cyprinidae		<i>Puntius ticto</i>	LC
32	Actinopterygii	Cypriniformes	Cyprinidae	Danionidae	<i>Rasbora daniconius</i>	LC
33	Actinopterygii	Cypriniformes	Cyprinidae	Danionidae	<i>Danio rerio</i>	LC
34	Actinopterygii	Cypriniformes	Cyprinidae	Danionidae	<i>Danio aequipinnatus</i>	LC
35	Actinopterygii	Cypriniformes	Cyprinidae	Barbinae	<i>Pethiacon choni</i>	LC
36	Actinopterygii	Cypriniformes	Cobitidae		<i>Lepidocephalichthys guntea</i>	LC
37	Actinopterygii	Siluriformes	Siluridae		<i>Wallago attu</i>	VU
38	Actinopterygii	Siluriformes	Bagridae		<i>Mystus bleekeri</i>	LC

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39	Actinopterygii	Siluriformes	Bagridae		<i>Mystus cavasius</i>	LC
40	Actinopterygii	Siluriformes	Bagridae		<i>Mystus gulio</i>	LC
41	Actinopterygii	Siluriformes	Bagridae		<i>Mystus vittatus</i>	LC
42	Actinopterygii	Siluriformes	Bagridae		<i>Silonia silondia</i>	LC
43	Actinopterygii	Siluriformes	Pangasilidae		<i>Pangasius pangasius</i>	LC
44	Actinopterygii	Siluriformes	Clariidae		<i>Clarias batrachus</i>	LC
45	Actinopterygii	Mugiliformes	Mugilidae		<i>Rhinomugil corsula</i>	LC
46	Actinopterygii	Gobiiformes	Oxudercidae		<i>Glossogobius giuris</i>	LC
47	Actinopterygii	Synbranchiformes	Mastacembelidae		<i>Macrognathus pancalus</i>	LC
48	Actinopterygii	Synbranchiformes	Mastacembelidae		<i>Mastacembelus armatus</i>	LC
49	Actinopterygii	Osteoglossiformes	Notopteridae		<i>Notopterus notopterus</i>	LC

LC: Least concerned category; NT: Nearly Threatened; NE: Not Evaluated ; VC: vulnerable category; DD : Data deficit; ED: Endangered species

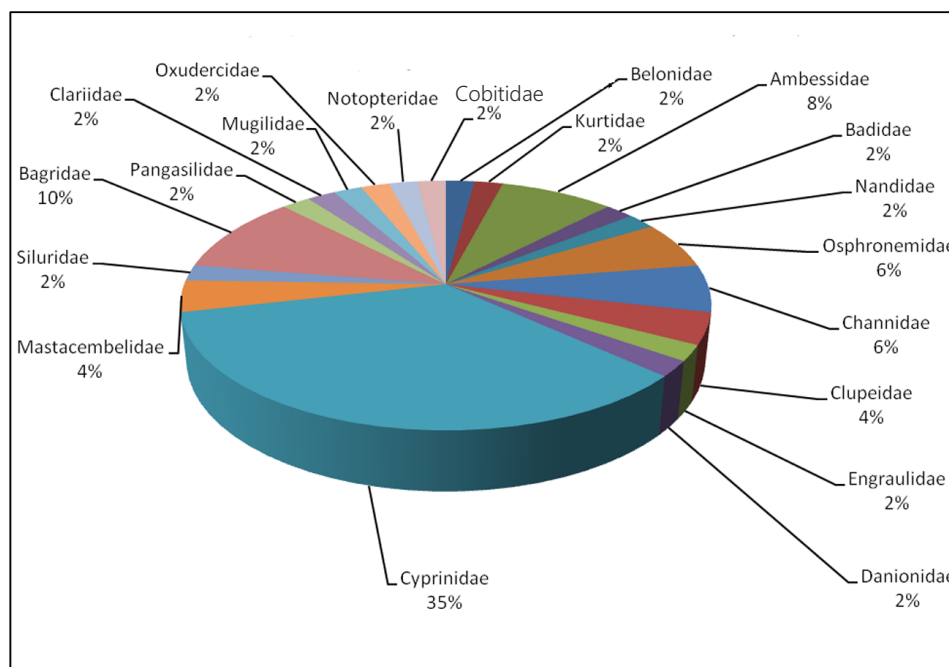


Figure 1: Ornamental Fish Diversity of Mridangabhanga River According to Orders

Methodology

All through three consecutive years (2022, 2023 and 2024) study of ornamental fishes of the Mridangabhanga River was done in three seasons: premonsoon, monsoon, and postmonsoon. The study was conducted in the pre-monsoon and post-monsoon seasons at five sites: S1. Kadamtala, S2. Purbo Dwarakapur, S3. Brojoballavpur, S4. Kedarpur, S5. Bolerhat (Figure 1). Two among the five study sites (S3. Brojoballavpur, S4. Kedarpur) were selected on the basis of presence of fish farms on the river bank, and the fifth (S5. Bolerhat) was selected as it has a large fish landing station the first

and second study sites (S1. Kadamtala, S2. Purbo Dwarakapur), are undisturbed and have less human infiltration. The fish farms on the river bank at S2. Purbo Dwarakapur, S3. Brojoballavpur for their culture solely depended on the fish seed collected from the Mridangabhanga River. Different fishing gears and crafts were engaged, and also fishermen were engaged in all collection sites for the stipulated time in three seasons. Identification up upto Species level was done following Day (1888), Talwar and Jhingran (1991) and Jayaram (1999).

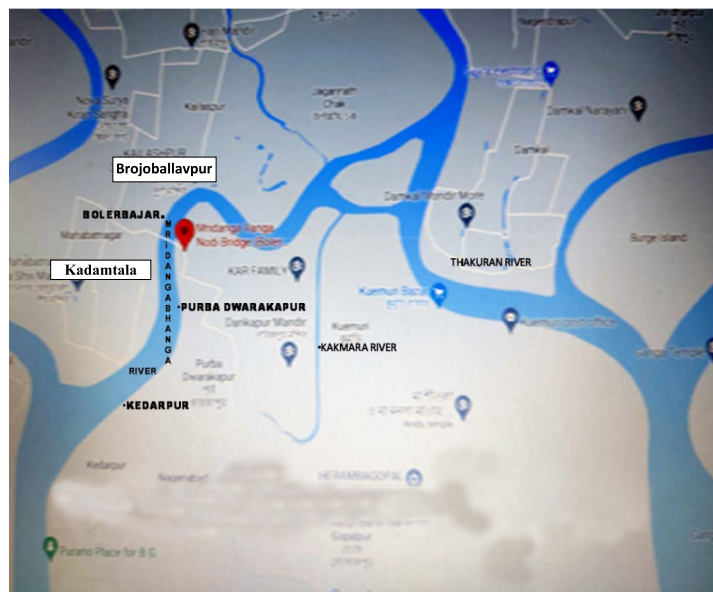


Figure 2: Map Showing Study Sites at Mridanga Bhanga River

During the study fish sampling was done throughout the day (7 a.m. to 6 p.m.) using Kheplajal mesh size (1.5 cm × 1.5 cm and 2 cm × 2 cm). For extensive fish catch, most of the local fishermen were engaged at all the study sites for fishing. The sites that were within one kilometre were included during netting. Initial identification was done in the field, keeping all the catch in a large, water-filled tub kept on the catch site then oozing female and juveniles were released immediately in river water at the catch site. Further detailed identification was done in the laboratory for those fishes which were preserved in 20% formalin solution (Sarkar & Banerjee, 2010). The hydrological parameters analyzed-alkalinity, pH, temperature, dissolved oxygen, transparency, and salinity-were measured using standard procedures outlined by the American Public Health Association (1999).

Discussion

The study of ornamental fishes of the Mridangabhanga river reveals a rich diversity of freshwater, estuarine and marine fishes. During the study a total of 49 Fish species were identified as ornamental fishes belonging to 6 Orders, a list of fishes indicating

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their systematics was shown in Table 2. The study reveals that Cyprinidae was the most dominant family, consisting of 35% of the total fish population, followed by the Bagridae (10%), Ambessidae (8%), Osphronemidae and Channidae 6%, Mastacembelidae and Clupeidae (4%), the other 13 families Belonidae; Kurtidae; Badidae; Nandidae; Engraulidae; Danionidae; Siluridae; Pangasilidae, Clariidae; Mugilidae; Oxudercidae; Notopteridae; Cobitidae contributes only (1%) represents of the diversity of fish fauna Figure depicts the pie chart that indicated the family-wise percentage data of the total fish catch.

Table 2: Shows the fish species diversity of Mridangabhanga at S1. Kadamtala, S2. Purbo Dwarakapur, S3. Brojoballavpur, S4. Kedarpur, S5. Bolerhat Bolerhat during the study period

		January 2021 to December 2021	January 2022 to December 2022	January 2023 to December 2023	January 2024 to December 2024
S1	Species Richness	49	49	49	49
	Margalef Index	11.15254	5.601416	5.698451	8.69789
	Shannon Wiener Index	4.085332	4.087129	4.094669	4.125793
S2	Species Richness	49	49	49	49
	Margalef Index	11.01297	11.30274	10.45873	8.21579
	Shannon Wiener Index	4.065523	4.069573	4.02587	4.01238
S3	Species Richness	49	49	49	49
	Margalef Index	11.06163	10.89804	11.87250	11.23490
	Shannon Wiener Index	4.010821	4.122512	3.928690	4.028791
S4	Species Richness	49	49	49	49
	Margalef Index	11.06163	10.89804	11.024578	11.002359
	Shannon Wiener Index	4.010821	4.122512	4.027396	4.28364
S5	Species Richness	49	49	49	49
	Margalef Index	11.06163	10.89804	10.702546	11.42568
	Shannon Wiener Index	4.010821	4.122512	4.026053	4.702863

According to the study, Order Kurtiformes represented one genus, one species; Perciformes with three genera, four species; Order Anabantiformes represented four genera, eight species; Order Beloniformes shows one genus, one species; Order Clupeiformes with three genera, three species; Order Cypriniformes carries nine genera, nineteen species; Order Siluriformes represented six genera, eight species; Order Mugiliformes included one genus, one species; Order Gobiiformes with one genus, one species; Order Synbranchiformes two genera, two species; and Order Osteoglossiformes showed one genus, one species. The study of hydrological parameters during the study showed there were not many variations in all five study sites and might not have affected the ichthyofaunal diversity. The main damage that is evident in the Mridangabhanga river valley is the soil erosion and riverbank collapse every year; high rainfall destroys manmade earthen embankments during the monsoon, which

affects the ecology of river water as well as the aquatic faunal composition. Dhara and Paul (2016) extensively studied the topography of Patharpratima block, the rivers embankments, as well as the livelihood of local people in this block. Their research outcome indicated that the area showed a meshwork of distributaries of the River Ganga, including Mridanga-Bhanga, Baratala, Hoogly, Saptamukhi, Thakuran, Matla, Gosaba, bidya, Hatania-Duania, and Herobhanga. The rivers were filled by sea tides diurnally at high tide. Chakraborty *et al.* (2021) and Chakraborty and Adhikary (2014) explained the increased salinity during hightide damages cultivation and compels the local people to shift their livelihood more towards fishing. This study referred to the high salinity (Table 3) during high tide in the river water as well as blind channels that corroborate the research data of Dhara and Paul (2016). Brooks *et al.* (2002) indicated that transparency of river water is one of the essential factors for ornamental fishes to survive; this study's results indicated a better value of transparency throughout the study period (Table 3). Allison and Kepple (2001) and Sarkar (2024) indicated the pollution effect caused by the toxic metals in the lower stretch of the Damodar River which might have influenced the ichthyofaunal diversity in the lower stretch of the river. But the recent study indicated that there are some undisturbed areas in the Mridangabhanga river that provided shelter to the fishes. The blind channels originating from mainstream shows a good number of oozing females of *Macrognathus pancalus*, *Mastacembelus armatus*, *Rasbora daniconius*; *Lepidocephalichthys guntea*; *Notopterus notopterus*; *Wallago attu* (VU); *Channa orientalis* (VU); *Laubuka fasciatus* (VU). Among these fishes, *Wallago attu* and *Channa orientalis*, *Laubuka fasciatus* were marked as vulnerable fish species in the IUCN Red List 2025-1 (International Union for Conservation of Nature, n.d.). The Mridangabhanga River houses these fish species; moreover, the oozing females of those were the good source that might enhance the species population in this river.

Table 3: Hydrology (Min and Max) of in Five Study Sites of Mridangabhanga River

Month	Temperature of Water		pH		Salinity(PSU)		DO(mg/l)		Transparency (cm)		Alkalinity(%)	
	Min	Max	Min	Max								
August	24.8	29.94	8.8	8.99	6.9	80.96	6.12	7.16	11	12.2	13.8	14.88
September	19.2	24.68	6.5	7.6	14.2	29.4	6.4	7.5	14	18.6	16	25.2
October	18.8	18.96	6.9	7	16.5	44.76	6.20	8.9	10	12.6	28.10	2.92
November	12.64	14	6.5	6.8	10	56.52	2.56	7.58	10	13.4	1.59	19
December	11	12.94	7.01	7.9	11.2	15.90	6.23	8	10.8	1.42	13.2	16.6
January	12.2	12.66	6.2	6.8	14.8	89.26	7.9	8.2	12.0	12.2	1.58	13.88
February	11.4	11.88	8.8	7	22.3	74.56	8.5	8.9	16.8	16.82	21	22.3
March	13.64	14.08	4.9	5.9	14.10	84.02	6	8.5	12	14.2	18.27	19.6
April	17.9	17.99	6.0	6.2	24.8	58.88	8.3	8.7	15	1.52	14	15.8
May	31.28	31.58	6.8	8	10.6	28.82	5.9	6	12.9	13.6	20	20.88
June	30.70	32.12	7	7.2	14.5	79.0	7	8.4	7	8.01	12	19
July	30.62	33.67	4.5	5.6	11.8	66.9	6.9	7.5	9.6	12.6	27	28.9

Conclusion

The study reveals that the Mridangabhanga river houses a good number of food fishes and keeps a remarkable influence on the daily earnings for the local people. During this study, all the fish landing stations based on the fishes of the Mridangabhanga river, were surveyed; recorded data reveals that a daily constant supply of seven to ten metric

tonnes of fishes to the Kolkata fish markets was done.

The blind channels originating from the mainstream of the Mridangabhanga river show diverse ichthyofaunal composition in the post- and pre-monsoon seasons. The notable fact is that these river channels are least affected by draught effects during midsummer, *Lepidocephalichthysguntea*, *Rasbora daniconius*, *Danio rerio*, *Danio aequipinnatus*, *Chanda nama*, these fishes were recorded during premonsoon from these channels. Conservation of this river biota is of utmost necessity to protect the river as well as its unique ornamental fish species population. The fish farms at the riverbank should take care during seed collection to prevent overexploitation. Sustainable use of natural resources will definitely enhance the resource; on the other hand, it will increase the scope of economic opportunities, ensuring long-term resource availability. The farms should take care of the captive breeding of indigenous fish fauna and the farming of ornamental fishes. Mridangabhanga river ornamental fishes are a good alternate livelihood, which is more promising for the local people.

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References

- Allison, M. A., Kuehl, S. A., Martin, T. C., & Hassan, A. (1998). Importance of flood-plain sedimentation for river sediment budgets and terrigenous input to the oceans: Insights from the Brahmaputra-Jamuna River. *Geology*, 26(2), 175-178. [https://doi.org/10.1130/0091-7613\(1998\)026%3C0175:IOFPSF%3E2.3.CO;2](https://doi.org/10.1130/0091-7613(1998)026%3C0175:IOFPSF%3E2.3.CO;2)
- Allison, M., & Kepple, E. (2001). Modern sediment supply to the lower delta plain of the Ganges-Brahmaputra River in Bangladesh. *Geo-Marine Letters*, 21, 66-74. <https://doi.org/10.1007/s003670100069>
- American Public Health Association. (1999). *Standard Methods for the Examination of Water and Wastewater* (20th ed). American public health association.
- Bhattacharjya, B. K., Sugunan, V. V., & Choudhury, M. (2000, September). Potential of ornamental fishes of Assam. *In First Indian Science Congress* (p. 65).
- Brooks, T. M., Mittermeier, R. A., Mittermeier, C. G., Da Fonseca, G. A., Rylands, A. B., Konstant, W. R., ... & Hilton-Taylor, C. (2002). Habitat loss and extinction in the hotspots of biodiversity. *Conservation Biology*, 16(4), 909-923. <https://doi.org/10.1046/j.1523-1739.2002.00530.x>
- Chakraborty, P., Mishra, S. S., Saren, S. C., Sengupta, A., & Yardi, K. (2021). Ichthyofaunal integrity, hydrological and environmental features trade-off in the Sunderbans, India. *Ecological Questions*, 32(2), 7-25. <https://doi.org/10.12775/EQ.2021.010>

- Chakraborty, S., & Adhikary, M. (2014). Vulnerability and Risk Assessment of Environmental Hazards—A Case Study Of Patharpratima Block,(Sundarban Delta Region) South 24 Parganas, West Bengal, India. *IOSR Journal of Environmental Science, Toxicology and Food Technology*, 8, 67-87. Retrieved from: <https://www.iosrjournals.org/iosr-jestft/papers/vol8-issue9/Version-3/K08936787.pdf>. Accessed on 13th October 2024.
- Day, F. (1888). *The Fishes of India: Being A Natural History of the Fishes Known to Inhabit the Seas and Fresh Waters of India, Burma, and Ceylon* (Vol. 1).
- Dhara, S., & Paul, A. K. (2016). Status of agriculture-a case study at Patharpratima Block of South 24 Parganas district. *International Journal of Innovative Science, Engineering & Technology*, 3(2), 239-246. Retrieved from: https://ijiset.com/vol3/v3s2/IJISSET_V3_12_34.pdf. Accessed on 12th January 2025.
- International Union for Conservation of Nature (IUCN). (n.d.). *The IUCN Red List of Threatened Species*. Retrieved from: <https://www.iucnredlist.org>. Accessed on 13th October 2024.
- Jayaram, K. C. (1999). *The Freshwater Fishes of the Indian Region*. Retrieved from: <https://www.nphindia.com/book/9788190795210/the-freshwater-fishes-of-the-indian-region-2ed>, Accessed on 13th October 2024.
- Sarkar, L. (2021). Ichthyofaunal diversity of Mridangabhanga River. Retrieved from: <https://environmentandecology.com/wp-content/uploads/2024/09/MS39-1.pdf>. Accessed on 13th October 2024.
- Sarkar, L. (2024). Fish Species Diversity of the Lower Stretch of River Damodar with References to Pollution Effect. <https://doi.org/10.31674/book.2024scibe.003>
- Sarkar, L., & Banerjee, S. (2010). Breeding ground profile of food fish species in Damodar River system. *International Journal of Biology*, 2(1), 51. <https://doi.org/10.5539/ijb.v2n1p51>
- Sheikh, S., & Goswami, M. M. (2012). Ornamental fishes of Chandakhola Wetlands, Dhubri, Assam, India. *International Journal of Scientific Research* 3(3), 387-389. <http://dx.doi.org/10.15373/22778179/MARCH2014/132>
- Siligato, S., & Böhmer, J. (2001). Using indicators of fish health at multiple levels of biological organization to assess effects of stream pollution in southwest Germany. *Journal of Aquatic Ecosystem Stress and Recovery*, 8, 371-386. Retrieved from: <https://page-one.springer.com/pdf/preview/10.1023/A:1012954726016>. Accessed on 13th October 2024.
- Talwar, P. K., & Jhingran, A. G. (1991). *Inland Fishes of India and Adjacent Countries*. Volume 2. CRC press. Retrieved from: <https://books.google.co.in/books?id=UG90mc4yD50C&printsec=frontcover#v=onepage&q&f=false>. Accessed on 13th October 2024.

Thermal Stability and Swelling Behaviour in Aqueous Medium of Acrylamide Based Hydrogels

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ABSTRACT

Swelling behaviour of acrylamide-N,N'-methylene-bis-acrylamide (copolymer) hydrogel was investigated at 281K, 293K, and 303K in aqueous solutions. Amount of swelling of hydrogels increases with time, and ultimately an equilibrium volume swelling is attained. The extent of swelling of the gels prepared in a homogenous medium depends on temperature, whereas those prepared in a heterogeneous medium are less temperature dependent, indicating the formation of a highly crosslinked, tighter network structure, as also supported by the Differential Scanning Calorimetry (DSC) study. Diffusions of water were studied, and the values of the diffusional exponent were found to fall in the range between 0.45 and 0.5, indicating a Fickian type of diffusion in nature. Thermogravimetric study indicates that most of the gel samples are thermally stable up to 473K and achieve more thermal stability with more crosslinking when prepared in heterogeneous medium polymerisation.

Keywords: *Acrylamide; Hydrogel; Crosslinker; N,N'-Methylene-Bis-Acrylamide; Polymer Swelling; Redox Initiator*

Introduction

Hydrogels are hydrophilic-natured three-dimensional networks and have been used in medicine, bioengineering, biotechnology, pharmacy, the food industry, agriculture, photographic technology and other fields. Swelling properties of acrylamide-based hydrogels are very much responsible for their various uses, such as controlled release applications for delivery of enzymes, hormones, contraceptives, anticoagulants, etc. (Caykara *et al.*, 2006; Elvira *et al.*, 2002). The gel swelling phenomenon has been the subject of numerous studies in polymer physics (Flory, 1953). It has been observed that the minute changes in the external conditions, such as temperature, solvent composition, ionic strength, and external electric field, can induce drastic changes in the gel swelling network (Tanaka, 1978; Tanaka *et al.*, 1980; Ricka & Tanaka, 1984; Tavakoli *et al.*, 2006; Hirotsu, Hirokawa & Tanaka, 1987). In particular, it is well established that under certain conditions, polyelectrolyte gels may undergo a discontinuous volume change during swelling (Hooper *et al.*, 1990; Joanny & Leibler, 1990). Therefore, investigations of the swelling behavior of acrylamide-based hydrogels are very much interesting and have been reported repeatedly during the last four decades. The swelling property, which depends on the network structure, is intimately related to the conditions

under which the polymer gels were formed (Dusek, 1982; Yürüksoy, 2000). In both academic studies and industrial applications, acrylamide hydrogels were obtained by the free radical copolymerisation of acrylamide (AM) and N,N/-methylene-bis-acrylamide (Bis) using various initiator systems. Recently, hydrogels of AM – Bis copolymer have been synthesised using Fe(III)/thiourea (TU) and Ce(IV)/TU redox initiator systems in a homogeneous aqueous medium and also in the interlayer spaces of the vermiculite heterogeneous microenvironment (Debnath, Bit & Saha 2009). It was noticed that the interlayer space of vermiculite offers a novel reactor resulting in a dramatic change of polymerisation kinetics in which the linear termination process is hindered apparently due to the failure of the growing polymer chain to transfer electrons to the metal ions and consequently a high molecular weight polymer with high reaction yield results (Debnath, Bit & Saha, 2010a; Debnath, Bit & Saha, 2009). In the case of vermiculite medium polymerisation, the Fe(III) ions are preloaded into the intercalated spaces of vermiculite, a smectite, to produce FeV composites prior to the polymerisation reactions (Debnath, Bit & Saha, 2010b). In this article, we have studied some physicochemical characteristics like swelling and thermal properties of synthesised hydrogels and observed that the hydrogels apparently behaved as superabsorbent gels.

Experimental

Materials

Hydrogels of AM and Bis are prepared using Fe(III)/TU and Ce(IV)/TU redox initiator systems in homogeneous and heterogeneous media (vermiculite), following the method described elsewhere (Debnath, Bit & Saha, 2009).

Experiments of Swelling

The swelling behaviour of AM-Bis hydrogels was studied using a glass (Pyrex) apparatus designed purposefully as shown below in Figure 1, in which a graduated horizontal tube of 2 mm diameter (CD) is attached with a 'U' tube by standard joint connector at 'C'. One arm of the 'U' tube contains a sintered glass (B) (Borosil(R), Porosity Grade 1, Pore Size 90-150 microns) of 20 mm diameter fitted horizontally in a vertical crucible (A) in the same level of the graduated tube. Other end of the graduated tube is made funnel-like (E) in order to help with pouring water for the swelling experiment. During the running of the experiment, distilled water was filled up in the 'U' tube and the graduated tube up to the zero mark (D). The graduated tube is always kept horizontal, and the water level in the U-tube just touches and wets the sintered glass at the beginning.

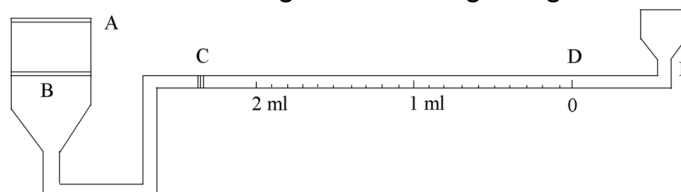


Figure 1: Swelling Apparatus

The system was maintained at a constant temperature using a water bath, keeping the two open ends of the apparatus in air above the water level of the bath. Accurately weighed (0.1 gm) gel sample in powder form is taken in the sintered glass crucible, and immediately the water content in the graduated tube starts decreasing due to the swelling of the hydrogel. Volume of water absorbed was measured directly after a definite time interval, and the percentage of water (S) absorbed by the hydrogel was calculated and plotted as a function of swelling time.

Experiments of Thermal Stability

The thermal stability of the hydrogels prepared under various conditions was analysed by thermogravimetry (TGA) performed from room temperature to 773K in air (rate of heating is 5K per minute).

Differential Scanning Calorimetry (DSC) was performed by a Perkin-Elmer (Pyris-6) system (rate of heating 5K per minute) to understand the behavior of polymers, like the softening temperature and glass transition temperature of dry and moist hydrogels.

Results and Discussion

The percentage of water (%S) absorbed by the hydrogels was calculated by using the following expression

$$\%S = \left[(V_0 - V_t) / M_p \right] \cdot 100 = (S_w / S_p) \cdot 100 \quad [1]$$

[Assuming $V_0 - V_t = S_w$ and $M_p = S_p$]

Where V_0 is the initial water volume in the zero position of the graduated tube. V_t is the final water volume in the graduated tube after time 't' in minutes. M_p is the weight of the gel particle in the dry condition.

Effect of Crosslinker Concentration on Swelling

Throughout the present study 'crosslinker (Bis) concentration' indicates the percent concentration of Bis in the AM and Bis monomer mixture in the reaction medium during polymerisation. The effect of Bis concentrations on the swelling behaviour of hydrogels is shown in Figure 2. In this experiment the crosslinker concentration was varied between 2 mol % and 14 mol %. Total monomer concentration (AM + Bis) was maintained at 0.4 M. Initially the rate of swelling is increased steadily but ultimately assumes a steady value.

However, with the rise of crosslinker concentration, decrease in swelling is noticed. It may be attributed to the fact that as the crosslinker concentration is increased, the molecules of the crosslinker occupy positions between the chains of monomers that lead to more rigid network structure. With increase in the crosslinker concentration, the composition of the hydrophilic group (i.e., amide group of polyacrylamide) in the resulting gels decreases, which leads to a lowering in the percent swelling, a fact which is also reported earlier (Buckley, Berger & Poller, 1962).

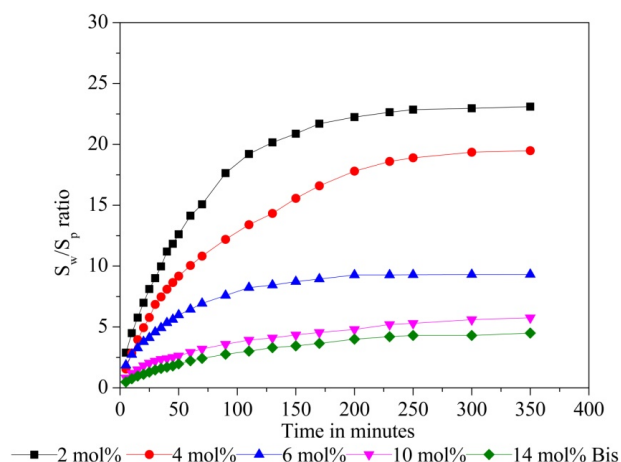


Figure 2: Variation of Swelling Ratio with Time of Hydrogels Prepared with Various Amount of Crosslinker by Fe(III)/TU Redox Initiator Systems at 303K

Table 1 depicts the equilibrium volume swelling [%S(V)] of the hydrogels prepared at different temperatures with different Bis percentage. It is obvious from the table 1 that %S(V) decreases with rise in Bis percentage in the AM-Bis monomer mixture at a particular temperature and also increases with a rise in temperature for particular hydrogels. With the increase in crosslinker, the network structure becomes more and more rigid, and water molecules can't diffuse easily into the network.

Table 1: Equilibrium Volume Swelling [%S(V)], Diffusion Constant (K), and Swelling Exponent (n) of Hydrogels Prepared Under Various Experimental Conditions

Sample no	Bis(mol%)	Temp (K)	%S(V)	Diffusion Constant (K)	Swelling Exponent(n)
1	2	303	2400	0.0311	0.501
2	4	303	2010	0.0321	0.573
3	6	303	930	0.0935	0.489
4	10	303	576	0.0757	0.458
5	14	303	457	0.0493	0.547
6	2	293	1982	0.0972	0.485
7	4	293	1485	0.1064	0.493
8	6	293	846	0.1108	0.523
9	10	293	448	0.1130	0.534
10	14	293	458	0.1097	0.499
11	2	281	1782	0.0837	0.499
12	4	281	814	0.0934	0.493
13	6	281	721	0.0982	0.485
14	10	281	325	0.0880	0.487
15	14	281	300	0.1033	0.476

Effect of Temperature

The swelling behaviour of the AM-Bis hydrogel samples was examined at three different temperatures (i.e., 281K, 293K, and 303K). Amount of swelling of hydrogels (I_{wpSS}),

prepared in homogeneous medium, increases with the rise in temperature. But, for the vermiculite medium hydrogels, the gel swelling varies little with temperature. The variation of gel swelling of 2 mol % Bis with temperature for homogeneous and heterogeneous media is shown in the Figure 3 (other compositions are not shown here). The gels prepared in vermiculite medium are less swellable, as shown in the figures, which indicate the formation of tighter network structure in the presence of more crosslinking in the sample.

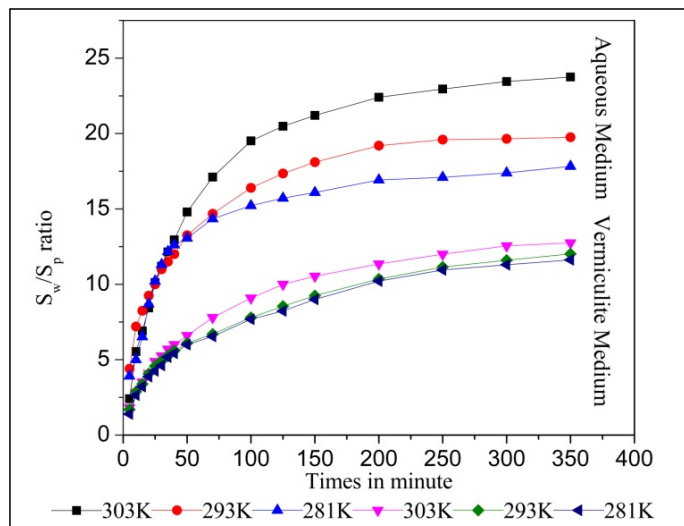


Figure 3: Variation of Swelling Ratio with Time of AM-Bis Hydrogels (2 mol % Bis) Obtained in Homogeneous Medium and in Vermiculite Medium at Various Temperatures

Diffusion of Water

Water molecules diffuse into the glassy hydrogels when brought in contact with water and swell. Diffusion induces water migration into pre-existing or dynamically formed spaces between hydrogel networks. Swelling of the hydrogel leads to larger-scale segmental motion, resulting in an increased distance of separation between hydrogel chains. The mechanism of water diffusion in swellable polymeric systems has received considerable attention recently because of the important applications of swellable polymers in the biomedical, pharmaceutical, environmental, and agricultural engineering fields, as has already been mentioned. In the case of drug delivery systems, Fick's law of diffusion provides the fundamental description of solute transport processes from polymeric matrices.

The following equation is used to determine the type of diffusion process of water into hydrogels (Peppas & Franson, 1983; Xue, Champ & Huglin, 2001).

$$F = (M_t / M_i) = Kt^n \quad [2]$$

$$\ln(M_t / M_i) = \ln K + n \ln(t) \quad [3]$$

Where M_t and M_∞ represent the amount of solvent diffused into the gel at time ' t ' and at infinite time, respectively. ' K ' is called Diffusion constant, related to the structure of the network, and the exponent ' n ' is Swelling Exponent or Diffusional Exponents which is a number to determine the type of diffusion.

The slope and intercept of the line obtained by plotting $\ln(M_t/M_\infty)$ versus $\ln(t)$ gives the values of n and K . There are three types of diffusion depending on the relative rates of diffusion and polymer relaxation. The first one is Fickian type diffusion ($n = 0.45$ to 0.5), in which the diffusion rate, R_{diff} is clearly slower than the relaxation rate of polymer chains, R_{relax} ($R_{diff} \ll R_{relax}$). Here the swelling is controlled by the diffusion of water into the polymer. Fickian diffusion refers to the solute transport process where the polymer relaxation time (t_r) is much greater than the characteristic solvent diffusion time (t_d). The second one is Case II diffusion ($n = 1.0$), where the diffusion of water is very rapid compared to relaxation of polymer network ($R_{diff} \gg R_{relax}$). The third class is non Fickian type or anomalous diffusion where ($R_{diff} \approx R_{relax}$). Here is the value of ' n ' in the range $0.5 < n < 1.0$, where both the diffusion of water and the relaxation of polymer network control the overall rate of water uptake. Equation 3 is applied to the initial stages of swelling (up to 60% swelling), the n and K values were calculated from the slopes and intercepts of the lines, respectively.

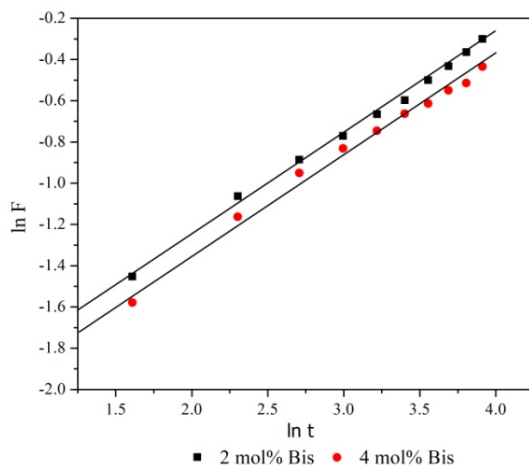


Figure 4: The Typical Curves of Swelling Kinetics of AM-Bis Hydrogels at 293K

The values of diffusion constants and diffusional exponents of all respective hydrogels are calculated and tabulated in Table 1, and a representative plot is shown in Figure 4. The values of diffusional exponent, n have been found to be in the range between 0.45 and 0.5, where a swelling constant, K varies between 0.0311 and 0.1130. Therefore, the diffusion of water into hydrogels may be considered as a Fickian type. This behavior is generally explained as a consequence of a slow diffusion rate, R_{diff} of the polymer matrix with respect to the relaxation rate of the polymer chains, R_{relax} (Peppas & Franson, 1983). Taking into account this diffusion type, the present hydrogels can further be studied for the controlled delivery of different drugs in future.

Thermogravimetric Analysis (TGA)

Thermograms of dry hydrogel samples, prepared under homogeneous solution conditions (in absence of vermiculite) by FeCl_3/TU initiators, are shown in Figure 5. In general, the thermograms display multistage weight loss features as a function of temperature. However, the samples are completely decomposed/charred at about 673K. For almost all the samples, weight loss started at around 473K. The maximum weight loss region lies between 523K to 673K, except for the sample with 4 mol % Bis, and it shows substantial weight loss at 473K. It was observed that the midpoints of this region (inflection point, T_{Gm}) vary substantially with crosslinker concentration. As the concentration of crosslinker is increased from 4 mol % (with respect to total monomer concentration) to 10 mol %, the thermal stability increases due to increase in the crosslinking network. However, it is interesting that 2 mol % of crosslinker gives the highest stability.

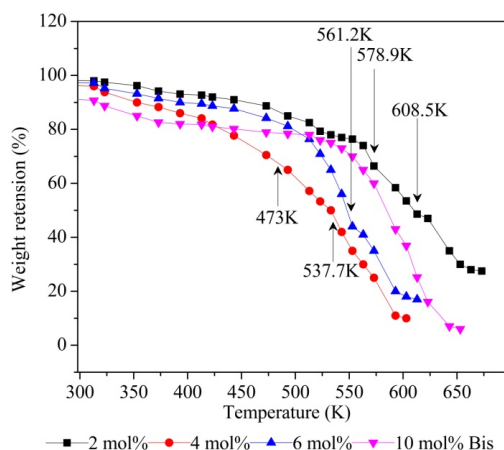


Figure 5: Thermal Behavior of Dry Hydrogels Prepared in Absence of Clay at 323K Using Fe(III) -TU Initiating System: $\text{FeCl}_3 = 1.5 \times 10^{-3} \text{ M}$, $\text{TU} = 0.04 \text{ M}$

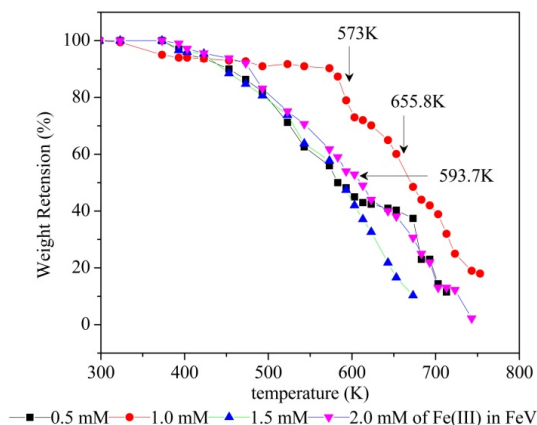


Figure 6: Thermal Behavior of Dry Hydrogels Prepared in Presence of Clay at 323K Using FeV -TU Initiating System: $\text{TU} = 0.04 \text{ M}$. Bis = 4 mol %

Figure 6 represents the thermograms of dry hydrogel samples prepared by FeV-TU redox initiator systems with variable FeV concentrations. It is also observed that although thermal stability of hydrogels, in general, increases with FeV concentration during polymerisation, maximum stability is displayed by an intermediate FeV concentration of 1.0 mM (FeV concentration indicates the concentration of Fe(III) in FeV). It is also interesting to note that only minor weight loss is observed up to 423K for all the samples except that prepared in presence of 1.0 mM FeV. This particular sample is thermally stable up to 573 K, and weight loss starts above this temperature. If attention is focused on the characteristic features of each thermogram of acrylamide hydrogel, it gives a clear impression that during decomposition of polyacrylamide in the course of heating, the non-stoichiometric loss of water takes place, followed by subsequent loss of ammonia and other gaseous products from the polyacrylonitrile structure formed, along with those from the remaining polyacrylamide (Iwahara *et al.*, 2000).

Differential Scanning Calorimetric (DSC) Study

The DSC profile (Figure 7) show endothermic peaks at 330K, 343K and 338K that indicates the presence of glass transition for the hydrogels having 2 mol %, 6 mol % and 10 mol % Bis concentrations respectively.

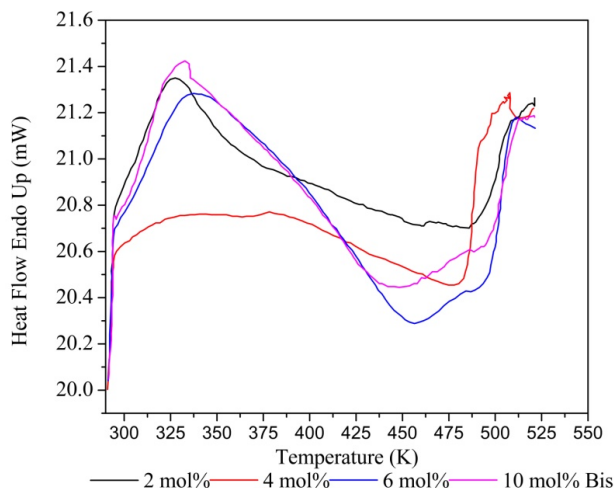


Figure 7: DSC Curve of Dry AM - Bis Hydrogel Prepared in Clay Medium: Fe(III) in FeV = 1.5 mM, TU = 0.04 M, Temp= 323K

The DSC profiles also display the characteristic temperature where softening of the copolymer starts. The onset of softening temperature occurred for the above three samples at 493K, 488K and 498K respectively. Previous workers have reported different values of glass transition temperature and softening temperature for polyacrylamide homopolymer and copolymer samples (Greenberg & Kusy, 1980). Unlike all other samples, the copolymer having 4 mol% Bis concentration, however, shows a DSC profile with a broad endothermic band (centred at 353K) instead of a well-defined peak. However, the softening temperature at 483K is fairly well defined.

Figure 8 shows DSC profiles of hydrogel samples under moist conditions (i.e., gel

phase), prepared in different experimental conditions with varying amounts of FeV concentrations. Two types of moist gels are collected for DSC study: one is low FeV content hydrogels (which are collected from the upper portion of the sample vessel after polymerisation with FeV), and another is high FeV content hydrogel (which is collected from the lower portion of an unstirred suspension after polymerisation with FeV). The techniques of the polymerisation process were discussed elsewhere (Debnath, Bit & Saha, 2010a; Debnath, Bit & Saha, 2010b). The endothermic peaks at different temperatures are displayed by samples and ranged between 383K to 433K for loss of water. However, interestingly, the endothermic peaks displayed by these samples are

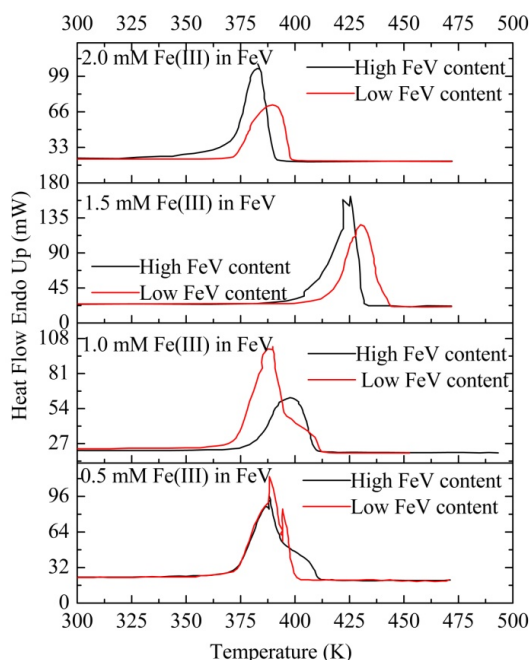


Figure 8: DSC Curve of Moist AM-Bis Hydrogel Prepared in Clay Vermiculite Medium: Bis = 4 mol%, Fe(III) in FeV = 0.5 mm to 2 mm, TU = 0.4M, Temp = 323K

actually overlaps of three closely separated peaks in each case, indicating three different potential sites for water retention in the acrylamide hydrogels. Water retention characteristics of the hydrogel may be discussed in terms of DSC endothermic peak positions as well. Endothermic peak temperatures on the DSC profiles clearly manifest the water binding power of the hydrogel samples. Hydrogels prepared in the presence of 1.5×10^{-3} M Fe(III) in FeV displayed the highest water removal temperature, indicating strongest bond with water molecules. The enthalpy change associated with the endothermic phase change of hydrogels under moist conditions varies from 2398 J/g to 4433 J/g. The enthalpy change for the samples is plotted as a function of concentration of Fe(III) ions in FeV in Figure 9, which shows that the profile passes through a maximum for the samples prepared at 1.5×10^{-3} M Fe(III) ions in FeV concentration.

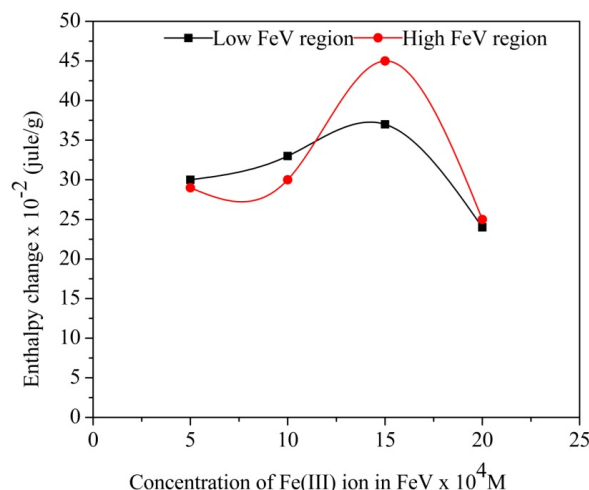


Figure 9: Enthalpy Change as a Function of Concentration of Fe(III) Ion in FeV

This indicates that the water molecules are strongly bonded with the network structure of the gels that are prepared in the presence of 1.5×10^{-3} M Fe(III) ions in the vermiculite mineral (TU = 0.04 M, Bis = 4 mol %).

Conclusion

The present method of measuring the swelling property of hydrogel samples is found to be simple, reproducible and accurate, whereas previous methods of measuring swelling were error-prone (e.g., blotting and weighing). The hydrogel prepared by Fe(III)/TU redox system can be termed a supergel because of its high water-absorbing capacity. High crosslinking may be achieved in vermiculite heterogeneous phase reaction, leading to more rigid network formation. The process of swelling in each case is found to be of the Fickian type.

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References

- Buckley, D. J., Berger, M., & Poller, D. (1962). The swelling of polymer systems in solvents. I. Method for obtaining complete swelling–time curves. *Journal of Polymer Science*, 56(163), 163–174. <https://doi.org/10.1002/pol.1962.1205616314>
- Caykara, T., Bulut, M., Dilsiz, N. & Akyüz, Y. (2006). Macroporous Poly(Acrylamide) hydrogels: swelling and shrinking behaviors. *Journal of Macromolecular Science Part A*, 43(6), 889–897. <https://doi.org/10.1080/10601320600653699>

- Debnath, B.D., Bit G. & Saha, S.K. (2010a) Water-soluble co-polymers of acrylamide with N-(1, 1-dimethyl-3-oxybutyl) acrylamide and N-tert-butylacrylamide on aqueous vermiculite microenvironment: Synthesis and Characterisation. *Journal of Surface Science and Technology*, 26(1), 23-38.
- Debnath, B.D., Bit, G. & Saha, S.K. (2009). Free radical cross-linking copolymerization of acrylamide and N,N/ methylene-bis-acrylamide by using Fe(III)/thiourea and Ce(IV)/thiourea redox initiator systems. *Indian Journal of Chemical Technology*. 16, 196-199. Retrieved from: <https://nopr.niscpr.res.in/bitstream/123456789/4222/1/IJCT%2016%282%29%20196-199.pdf>. Accessed on 15th January 2025.
- Debnath, B.D., Bit, G. & Saha, S.K. (2010b). Redox polymerization of acrylamide in aqueous vermiculite clay environment: Kinetics and mechanism. *Journal of Surface Science and Technology*. 26(1), 39-61.
- Dusek, K. (1982). Developments in polymerization-3. *Applied Science, London*, 143.
- Elvira, C., Mano, J., Román, J. S. & Reis, R. (2002). Starch-based biodegradable hydrogels with potential biomedical applications as drug delivery systems. *Biomaterials*, 23(9), 1955–1966. [https://doi.org/10.1016/s0142-9612\(01\)00322-2](https://doi.org/10.1016/s0142-9612(01)00322-2)
- Flory, P. J. (1953). *Principles of Polymer Chemistry*. Cornell University Press.
- Greenberg, A. R. & Kusy, R. P. (1980). Viscoelastic behavior of highly crosslinked poly (acrylic acid). *Journal of Applied Polymer Science*, 25(12), 2795-2805. <https://doi.org/10.1002/app.1980.070251212>
- Hirotsu, S., Hirokawa, Y., & Tanaka, T. (1987). Volume-phase transitions of ionized N-isopropylacrylamide gels. *The Journal of Chemical Physics*, 87(2), 1392–1395. <https://doi.org/10.1063/1.453267>
- Hooper, H. H., Baker, J. P., Blanch, H. W., & Prausnitz, J. M. (1990). Swelling equilibria for positively ionized polyacrylamide hydrogels. *Macromolecules*, 23(4), 1096–1104. <https://doi.org/10.1021/ma00206a031>
- Iwahara, K., Hirata, M., Honda, Y., Watanabe, T., & Kuwahara, M. (2000) Free-radical polymerization of acrylamide by manganese peroxidase produced by the white-rot basidiomycete *Bjerkandera adusta*. *Biotechnology Letters*, 22(17), 1355–1361. <https://doi.org/10.1023/A:1005698415575>
- Joanny, J., & Leibler, L. (1990). Weakly charged polyelectrolytes in a poor solvent. *Journal De Physique*, 51(6), 545–557. <https://doi.org/10.1051/jphys:01990005106054500>
- Peppas, N. A. & Franson, N. M. (1983). The swelling interface number as a criterion for prediction of diffusional solute release mechanisms in swellable polymers. *Journal of Polymer Science Polymer Physics Edition*, 21(6), 983–997. <https://doi.org/10.1002/pol.1983.180210614>
- Ricka, J., & Tanaka, T. (1984). Swelling of ionic gels: quantitative performance of the Donnan theory. *Macromolecules*, 17(12), 2916–2921. <https://doi.org/10.1021/ma00142a081>

- Tanaka, T. (1978). Collapse of gels and the critical endpoint. *Physical Review Letters*, 40(12), 820–823. <https://doi.org/10.1103/physrevlett.40.820>
- Tanaka, T., Fillmore, D., Sun, S., Nishio, I., Swislow, G., & Shah, A. (1980). Phase transitions in ionic gels. *Physical Review Letters*, 45(20), 1636–1639. <https://doi.org/10.1103/physrevlett.45.1636>
- Tavakoli, J., Jabari, E., Etrati, K. S. S., & Boroujerdi, M. (2006). Swelling characterization of anionic acrylic acid hydrogel in an external electric field. *Iranian Polymer Journal*, 15(11): 891–900.
- Xue, W., Champ, S., & Huglin, M. B. (2001). Thermoreversible swelling behaviour of hydrogels based on N-isopropylacrylamide with a zwitterionic comonomer. *European Polymer Journal*, 37(5), 869–875. [https://doi.org/10.1016/s0014-3057\(00\)00220-2](https://doi.org/10.1016/s0014-3057(00)00220-2)
- Yürüksoy, B. I. (2000). Swelling behavior of acrylamide-2-hydroxyethyl methacrylate hydrogels. *Turkish Journal of Chemistry*, 24(2), 147–156. Retrieved from: <https://journals.tubitak.gov.tr/chem/vol24/iss2/5>. Accessed on 16th January 2025.

Study of Heavy Metal Bioaccumulation in Commonly Consumed Prawns of Genus *Penaeus* and the Associated Human Health Risks

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ABSTRACT

Heavy metals are inherent in the aquatic environment, arising through natural processes as well as through human actions such as mining, industrial practices, unscientific use of fertilisers, discharge of municipal sewage sludge, etc. Aquatic organisms can be subjected to contamination with heavy metals occurring in both surface water and sediments of their respective ecosystems. Metals such as Copper, Zinc, Lead, Cadmium can affect human beings and aquatic organisms, as they can find their way through the food chain and are biomagnified from one trophic level to another. Shellfish have high commercial value as people cherish the shellfish almost throughout the world. The objective of this study is to monitor the metal concentrations present in the tissue of the muscle of the most preferred edible and commercially viable species of prawns namely, *Penaeus monodon* and *Penaeus indicus*, collected from the lower part of the Hooghly estuarine system. In the case of zinc, the concentration values found in the shellfish were mostly below the recommended level defined by WHO and FAO. The other heavy metals, i.e. Cu, Pb and Cd, showed mostly higher levels than that recommended. The value of Cu (up to 86.67 mg/kg) and Pb (up to 42.1 mg/kg) in the prawns exhibited higher concentrations. Heavy metals accumulated in the muscle tissue of prawns as Zinc > Copper > Lead > Cadmium in most of the cases. This study is crucial from the human wellbeing viewpoint and also represents how the aquatic bodies are contaminated by heavy metals which make their way to the most profitable and edible shellfish of the Hooghly estuarine system.

Keywords: Heavy Metals; Muscle Tissue; Prawns; Shellfish

Introduction

Heavy metals are inherent in the aquatic environment, arising through natural processes as well as through human actions such as mining, industrial practices, unscientific use of fertilisers, discharge of municipal sewage sludge, etc. Aquatic organisms can be subjected to contamination with heavy metals from their respective ecosystems (Hossain, Ahmed & Sarker, 2018).

India is a country of great rivers. The Ganga is one of the most significant rivers of India. In West Bengal, it is known as the Hooghly River, which after traversing a considerable distance finally reaches the Bay of Bengal. Many religious practices and anthropogenic activities take place at the banks of the river. Recently, there has been an increasing public health risk associated with the concentration of the heavy metals found in the

environment. The lower part of the Hooghly estuary receives effluents from miscellaneous industries such as paper, pharmaceuticals, textiles, leather, jute, chemicals, etc. These factories or industries serve as the sources of metal pollution in the aquatic ecosystem (Mondal *et al.*, 2021). As these metals are concentrated in the shellfish bodies, assessment of heavy metal concentration is required to determine the health of the water body. Essential heavy metals such as Zinc and Copper are less harmful at lower concentrations. Cadmium and Lead are the non-essential metals which can be extremely toxic even at smaller concentrations.

Shellfish have high commercial value as people cherish the shellfish almost throughout the world. They act as a source of minerals, as well as proteins. The shellfish do not migrate often. Therefore, they can be a key indicator for identifying pollution (van Oosterom *et al.*, 2010). However, the shellfish's accumulation of heavy metals depends upon the category of metal and the kind of tissue of the shellfish. The objective of this study is to monitor the metal concentrations present in the tissue of the muscle of the most preferred edible and commercially viable species of prawns namely, *Penaeus monodon* and *Penaeus indicus*. The accumulation of the heavy metals under the study in the shellfish muscle has been explored considering the literature available and the work done by the author.

Methodology

Collection of Primary Data

Study Area

Sampling site namely, Diamond Harbour in the lower Gangetic delta, was selected (Figure 1) to collect the shellfishes (in this case, two species of *Penaeus*) inhabiting the zone.



Figure 1: Study Site Selected for Collection of Primary Data

The sampling site was in the vicinity of Hooghly estuary at 22°11'4.2''N Latitude 88°11'22.2''E Longitude. Diamond Harbour is a busy area nearer to the Haldia Port cum Industrial complex.

Collection of Secondary Data

This was obtained through a literature survey of almost the same aquatic system.

Collection of specimens

Two species of prawns namely *Penaeus monodon* and *Penaeus indicus* were collected randomly from the markets and fishermen. The samples were preserved in crushed ice. For further analysis, the samples were brought to the laboratory. Sorting of similarly sized specimens of each species was done for analysing the heavy metal content in the muscle tissue of prawns.

Evaluation of Heavy Metal Content

At first, dry ashing of the muscle tissues of prawns under study was done. Using a microwave digester, the dried samples were digested in nitric acid. Then it was transferred to a volumetric flask of 50 ml. Using demineralised water, the solution was made up to the marking line of the volumetric flask. It was then filtered using Whatman filter paper. For heavy metal analysis this filtrate was used as the sample solution. Measurement of the absorbance of the samples (Zn, Cu, Pb and Cd) was done by an atomic absorption spectrophotometer (Model Perkin Elmer Type 2380) and expressed as ppm (mg/kg dry wt. basis).

Results and Discussion

Description of the species under study:

Penaeus monodon, commonly known as the giant tiger prawn/ Asian tiger shrimp/ black tiger shrimp, is a marine crustacean that is widely reared for food.

Description

Morphological characteristics

Penaeus monodon are usually dark coloured with a transversely banded abdomen with black and white marks. Females are generally 25–30 cm long, while males are slightly smaller, 20–25 cm long. Pleopods are biramous (Figure 2).

Distribution

It is found in the Indo-Pacific region, coastal areas of Africa, Arabian Peninsula, Southeast Asia, the western Pacific Ocean and northern Australia.

Ecology

P. monodon can inhabit a multitude of environments. *P. monodon* burrow into the substrate during daytime and feed at night on molluscs, polychaetes, smaller

crustaceans, and algae as well as detritus (Chimsung, 2014; Burford *et al.*, 2020). However, on farms, the shrimps are also given a compound diet. The optimal temperature required for their growth is between 28nd 33°C and the salinity around 15-25 g/L (Shekhar *et al.*, 2014).



Figure 2: Tiger Prawns -*Penaeus Monodon* Displayed in a Supermarket

Penaeus indicus

The Indian prawn (*Fenneropenaeus indicus*, formerly *Penaeus indicus*) is used for human consumption and is an important commercial species of marine fishery.

Description

Morphological characteristics

Body is yellowish white or greyish green with a body length of 23 cm (females) and 17 cm (males) with a smooth carapace. Rostrum is slender, long and slightly curved at the tip and bears teeth (Figure 3).

Distribution

Its natural distribution is in India, China, Malaysia, Indonesia, Thailand, Vietnam, Africa and northern Australia.

Ecology

They prefer sandy substrates at depths of 2–90 metres. They require high salinity,

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about 20–30 ppt. The lethal temperature is above 34°C (Pillay, 1990). They feed several times at night and search the bottom for food like algal mats, smaller crustaceans, slow-moving organisms, molluscs, etc.



Figure 3: *Penaeus Indicus*

The results of the heavy metal concentrations of the shellfish are shown in Table 1. The maximum recommended limits of heavy metals for human consumption as defined by WHO and FAO (World Health Organisation, 1976) for shellfish are 100, 30, 2, and 1 mg/kg for Zn, Cu, Pb and Cd, respectively. In the case of zinc, the concentration in all the samples analysed showed a lower value than the recommended level, as shown in table 1. The other heavy metals, i.e. Cu, Pb and Cd, showed mostly higher levels than that recommended. Cu (up to 86.67 mg/kg) and Pb (up to 42.1 mg/kg) in the prawns showed relatively higher concentrations, as summarised in table 1. Heavy metals cumulated in the muscle tissue of prawns as Zinc > Copper > Lead > Cadmium in most of the cases.

Table 1: Contamination Level of Heavy Metals in the Prawn Species-*penaeus Monodon* and *Penaeus Indicus* Collected From Different Localities of Lower Gangetic Delta (in mg/kg)

Species	Heavy metal concentration				Studied by	Locality
	Zn	Cu	Pb	Cd		
<i>Penaeus monodon</i>	99.8±2.30	71.18± 1.12	4.18± 0.38	2.3± 0.55	Present study	Diamond Harbour, lower Gangetic delta
<i>Penaeus indicus</i>	95.5±2.41	62.99±1.16	3.76±0.43	1.89± 0.62	Present study	Diamond Harbour, lower Gangetic delta
<i>Penaeus monodon</i>	7.3–4809.5	---	22.9–42.1	0.11– 3.2	Guhathakurta and Kaviraj, 2000	Sunderban mangrove system, India.
<i>Penaeus monodon</i>	78.88 ±1.22	59.18 ±1.13	9.18 ±0.68	--	Mitra and Zaman, 2012	Nayachar island, Hooghly estuary
<i>Penaeus indicus</i>	124.03±1.25	86.67±0.70	11.10±0.30		Bhattacharyya <i>et al.</i> , 2013	Sagar South, Western sector of Indian Sunderbans.

The concentrations of Zn and Cu usually remain higher than the other trace elements or heavy metals because they are essential elements that are needed by the organisms for various metabolic actions. A study conducted by Biswas, Bandyopadhyay and Chatterjee (2013) in oysters regarding the concentrations of heavy metals showed that in the bodies of the shellfish, Zn, Cu or Fe may build up preferentially in comparison to the other heavy metals.

The higher concentration of zinc in the shrimps is probably related to the increased bioavailability of this element in the aquatic environment. Also, Zinc plays an enzymatic role as a regulator of several enzymes. According to do Amaral *et al.* (2005), due to the high affinity of zinc for metallothionein, it has a low excretion rate and tends to accumulate inside the body. Thus, its congregation is higher in all the tissues compared to the other metals. In the present study in the Diamond Harbour region of the Gangetic plain, the sources of Zn are the industrial units such as galvanising, paint factories and pharmaceuticals, originating from the Haldia industrial sector.

Although the crustaceans can excrete toxic elements (Simkiss & Taylor, 1995), the concentrations of Cu were greater than the threshold value of Cu in most of the studies indicated in table 1. In the study site, the major sources of Cu are the bottom paints designed for underwater surfaces in the different fishing vessels and trawlers. However, industrial discharges are also there in addition.

Pb is one of the extremely toxic heavy metals that has deleterious effects on human health even at a very low concentration. Pb may accumulate throughout the body in brain, liver, bones, kidneys and in due course may accumulate in teeth and bones also (Jaishankar *et al.*, 2014). Pb navigates in the water body via the effluents of various factories of paints, oil distilleries, battery production units, etc. Lead-containing antifouling paints are used by the fishermen to prevent the growth of barnacles or other marine organisms at the bottom of the fishing boats and also trawlers. Leaching of toxic metals from these paints into the water is noxious to the aquatic organisms. Although Lead may also enter the water body from both land-based sources and the atmosphere.

Cadmium (Cd) is also very harmful if its level in man exceeds the permissible limit. Electroplating, Batteries, welding, etc., act as sources of cadmium (Roy *et al.*, 2022). As these kinds of heavy metals are not biodegradable, they accumulate in the water, mainly settling at the undermost water, and form different complex compounds reacting with different organic and inorganic materials. Heavy metals or trace elements are not biodegradable and are snowballed in the human bodies, leading to undesirable effects such as slow maturation, renal disease, and carcinogenesis, and may be lethal also (Paul, 2017). Heavy metals exceeding threshold limits in the aquatic ecosystem are threatening to mankind and other aquatic organisms also.

Shellfish are one of the most competent hydrographic animals to accumulate heavy metals. This is because they live in the sediment or bottom of the water, operate very

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slowly, take their food by filtering water, and their food is detritus at the undermost portion of the aquatic body. So the possibility of these metals entering their bodies is enormous.

As per the study conducted by Tahity *et al.* (2022), concentrations of metals also vary between organs, which may be due to the different physiological functions of the different organs.

This study is crucial from the human wellbeing viewpoint and also represents how the aquatic bodies are contaminated by heavy metals which make their way to the most profitable and edible shellfish of the Gangetic delta. It is a cause of concern that food ingredients that contain heavy metals, even if in a small amount, if consumed continuously, will accumulate in the human body and tend to be harmful (Biswas *et al.*, 2021; Siahaan, Silalahi & Lubis, 2022).

Conclusion

Biomonitoring of heavy metals in the muscle tissue of the shellfish can serve as an effective index of water body fouling. It may be noted that prawns or shrimps are commonly edible and very preferred seafood in India and also throughout the world. The prawns *P. monodon* and *P. indicus* are available almost everywhere in the markets. Most heavy metals were detected with a concentration tendency exceeding the recommended level. So proper planning to check these contaminations and monitoring of these edible species is highly needed. Such biomonitoring studies should be done regularly for the safe food supply to mankind.

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References

- Bhattacharyya, S. B., Roychowdhury, G., Zaman, S., Raha, A. K., Chakraborty, S., Bhattacharjee, A. K., & Mitra, A. (2013). Bioaccumulation of heavy metals in Indian white shrimp (*Fenneropenaeus indicus*: A time series analysis). *International Journal of Life Sciences, Biotechnology and Pharma Research*, 2(2), 97-113. <https://doi.org/10.13140/2.1.3785.5360>
- Biswas, C., Soma, S. S., Rohani, M. F., Rahman, M. H., Bashar, A., & Hossain, M. S. (2021). Assessment of heavy metals in farmed shrimp, *Penaeus monodon* sampled from Khulna, Bangladesh: An inimical to food safety aspects. *Heliyon*, 7(3). <https://doi.org/10.1016/j.heliyon.2021.e06587>
- Biswas, T., Bandyopadhyay, P. K., & Chatterjee, S. N. (2013). Accumulation of cadmium, copper, lead, zinc and iron in the edible oyster, *Saccostrea cucullata* in coastal areas of West Bengal. *African Journal of Biotechnology*, 12(24). Retrieved from: <https://www>

- cabidigitallibrary.org/doi/full/10.5555/20133263387. Accessed on 4th February 2025.
- Burford, M. A., Van Sang, N., Khoi, C. M., Thu, N. K., Faggotter, S. J., Stewart-Koster, B., ... & Sammut, J. (2020). Does natural feed supply the nutritional needs of shrimp in extensive rice-shrimp ponds?—A stable isotope tracer approach. *Aquaculture*, 529. <https://doi.org/10.1016/j.aquaculture.2020.735717>
- Chimsung, N. (2014). Maturation diets for black tiger shrimp (*Penaeus monodon*) broodstock: a review. *Songklanakarin Journal of Science & Technology*, 36(3), 265-273. Retrieved from: <https://www.thaiscience.info/journals/Article/SONG/1096830.pdf>. Accessed on 4th February 2025.
- Amaral, M. C. R., de Freitas Rebelo, M., Torres, J. P. M., & Pfeiffer, W. C. (2005). Bioaccumulation and depuration of Zn and Cd in mangrove oysters (*Crassostrea rhizophorae*, Guilding, 1828) transplanted to and from a contaminated tropical coastal lagoon. *Marine Environmental Research*, 59(4), 277-285. <https://doi.org/10.1016/j.marenvres.2004.05.004>
- Guhathakurta, H., & Kaviraj, A. (2000). Heavy metal concentration in water, sediment, shrimp (*Penaeus monodon*) and mullet (*Liza parsia*) in some brackish water ponds of Sunderban, India. *Marine Pollution Bulletin*, 40(11), 914-920. [https://doi.org/10.1016/S0025-326X\(00\)00028-X](https://doi.org/10.1016/S0025-326X(00)00028-X)
- Hossain, M. B., Ahmed, A. S. S., & Sarker, M. S. I. (2018). Human health risks of Hg, As, Mn, and Cr through consumption of fish, Ticto barb (*Puntius ticto*) from a tropical river, Bangladesh. *Environmental Science and Pollution Research*, 25(31), 31727-31736. <https://doi.org/10.1007/s11356-018-3158-9>
- Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., & Beeregowda, K. N. (2014). Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary Toxicology*, 7(2), 60–72. <https://doi.org/10.2478/intox-2014-0009>
- Mitra, A., & Zaman, S. (2012). Heavy Metals in Edible Crustaceans from Gangetic Delta. *Journal of Research in Environmental Science and Toxicology*, 1(11). <https://doi.org/10.13140/2.1.2434.9762>.
- Mondal, P., Lofrano, G., Carotenuto, M., Guida, M., Trifuoggi, M., Libralato, G., & Sarkar, S. K. (2021). Health risk and geochemical assessment of trace elements in surface sediment along the Hooghly (Ganges) River Estuary (India). *Water*, 13(2), 110. <https://doi.org/10.3390/w13020110>
- Paul, D. (2017). Research on heavy metal pollution of river Ganga: A review. *Annals of Agrarian Science*, 15(2), 278-286. <https://doi.org/10.1016/j.aasci.2017.04.001>
- Pillay, T.V.R. (1990). *Aquaculture- Principles and practices*. Blackwell Publications, 1-575.
- Roy, M., Majumder, R., Shamim, F., & Ghosh, C. (2022). Evaluation of the Water Quality Status of Hooghly River (Ganges) in West Bengal, India. *Bull. Env. Pharmacol. Life Sci.*, 3, 383-389. Retrieved from: <https://bepls.com/beplsspl32022/66.pdf>. Accessed on 4th February 2025.

Bioaccumulation of Heavy Metals in Prawns

- Shekhar, M. S., Kiruthika, J., Rajesh, S., & Ponniah, A. G. (2014). High salinity induced expression profiling of differentially expressed genes in shrimp (*Penaeus monodon*). *Molecular Biology Reports*, 41 (9), 6275–6289. <https://doi.org/10.1007/s11033-014-3510-1>
- Siahaan, R. Y., Silalahi, J., & Lubis, Z. (2022). Analysis of heavy metals in shellfish in Tanjung Balai waters. *Journal of Food and Pharmaceutical Sciences*, 10(1), 610-619. <https://doi.org/10.22146/jfps.3734>
- Simkiss, K., & Taylor, M. G. (1995). Transport of metals across membranes. *Metal Speciation and Bioavailability in Aquatic Systems*, 3, 1-44.
- Tahity, T., Islam, M. R. U., Bhuiyan, N. Z., Choudhury, T. R., Yu, J., Noman, M. A., ... & Hossain, M. B. (2022). Heavy metals accumulation in tissues of wild and farmed barramundi from the northern Bay of Bengal coast, and its estimated human health risks. *Toxics*, 10(8), 410. <https://doi.org/10.3390/toxics10080410>
- van Oosterom, J., King, S. C., Negri, A., Humphrey, C., & Mondon, J. (2010). Investigation of the mud crab (*Scylla serrata*) as a potential bio-monitoring species for tropical coastal marine environments of Australia. *Marine Pollution Bulletin*, 60(2), 283-290. <https://doi.org/10.1016/j.marpolbul.2009.09.007>
- World Health Organization. (1976). List of maximum levels recommended for contaminants by the Joint FAO/WHO Codex Alimentarius Commission-Second series. Retrieved from: <https://agris.fao.org/search/en/providers/122621/records/647762335eb437ddff786555>. Accessed on 6th February 2025.

Comparative Study on Morphological Changes of Copper Nanoparticles Synthesised in Different Non-Ionic Surfactant Series of Polysorbates

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ABSTRACT

Several techniques can be used to create metallic nanoparticles. The wet chemical technique is the most widely used of all. Coinage metal nanoparticles are highly appealing to novice researchers due to their versatility. Due to its low cost, copper has been utilized extensively as a precursor. A variety of surfactants are employed as capping agents to stop particle oxidation and agglomeration. Here, the nature and morphological alterations of Copper Nanoparticles (CuNPs) are examined using three distinct polysorbate surfactants at varied concentrations. Here concentrations are used on the basis of Critical Micellar Concentration (CMC) of each surfactant. The nature of the particles is compared using Transmission Electron Microscopy (TEM) examination, DLS research, and UV-visible spectroscopy. This research has successfully investigated the impact of various non-ionic polysorbate surfactant micelles on the morphological changes of CuNPs.

Keywords: *Copper Nanoparticles; Micelles; Non-Ionic Surfactants; Polysorbates*

Introduction

Research on metal nanoparticles with unique chemical, optical, and electrical properties has increased recently. The catalytic (Crooks *et al.*, 2001; Vitulli *et al.*, 2002; Dhas, Raj & Gedanken, 1998), optical, and electrical properties (Athanassiou, Grass & Stark, 2006 ; Chen & Sommers, 2001) of copper nanoparticles (CuNPs) make them appealing among metal nanoparticles. CuNPs are particularly significant because of their high catalytic activity and electrical conductivity, which make them a good substitute for more costly metals like silver and gold. There have been numerous attempts to precisely control the size and shape of CuNPs because their properties depend on their size and shape (Lisiecki, Billoudet & Pileni, 1996; Mott *et al.*, 2007; Zhu, Zhang & Yin, 2005). Controlling size, and especially shape, at the nanoscale level is still an unsolved issue, though. A layer of copper oxide invariably forms a surface covering over the CuNPs (Chen *et al.*, 2005; Gao *et al.*, 2001) due to their high reactivity towards air oxygen, which makes it difficult to synthesise pure CuNPs in their metallic state. Pure CuNPs are typically stabilised in their metallic state by applying a protective covering. Polymers and surfactants are the most often used stabilisers (Dang *et al.*, 2011; Salkar *et al.*, 2000; Pootawang, Saito & Lee, 2013; Nandi, Gupta, & Banthia, 2002; Pileni *et al.*,

1998). More recently, the surface of CuNPs has been shielded by a graphene multilayer (Wang *et al.*, 2012).

Chemical reduction, thermal decomposition, radiation techniques (Joshi *et al.*, 1998), laser ablation (Liu *et al.*, 2012), sonochemical reduction (Kumar *et al.*, 2001), and microwave heating (Tu & Liu, 2000) are common synthetic procedures for CuNPs. Because of its ease of use, affordability, and ease of reaction condition optimisation, wet chemical reduction is the most popular of these. This method's main flaw is that it frequently produces wide NP size distributions. However, with the right surfactants, NP growth can be controlled. Micelles, reverse micelles, microemulsions, and vesicles are examples of ordered assemblies (Barnickel & Wokaun, 1990; Schramm, Stasiuk & Marangoni, 2003; Zhang & Han, 2003; Evans & Needham, 1987) that surfactant molecules can produce. These assemblies can be used as templates or microreactors to control the formation of nanomaterials. Through steric factors, Van der Waals forces, electrostatic forces, and occasionally hydrophobic interactions, surfactant molecules can also increase the system's stability. Certain surfactants exhibit preferential adsorption along other lattice planes, which can result in unidirectional growth along those planes (Jana, Gearheart & Murphy, 2001).

Numerous successful attempts to synthesise stable CuNPs in surfactant media have been made in the past. Pileni *et al.* (1998) have synthesised stable CuNPs in AOT [sodium bis(2-ethylhexyl) sulfosuccinate] reverse micelles (Cason & Roberts, 2000) in supercritical solvents. Other workers have synthesised CuNPs in AOT reverse micelles in supercritical solvents (Qi, Ma & Shen, 1997). CuNPs have also been synthesised in micelles formed by cationic surfactants such as Cetyltrimethylammonium Bromide (CTAB) (Wu & Chen, 2004; De & Mandal, 2013). It has been discovered that Cu-nanorods can be produced by fine-tuning the surfactant concentration.

Since NaBH_4 is a potent reducing agent and is frequently used in CuNP synthesis, the CuNPs produced in aqueous solution contain adherent negative charges. Consequently, both cationic and non-ionic surfactants will function as efficient growth controllers and stabilisers. It could be beneficial to carry out the synthesis in a non-ionic surfactant medium given the well-known cytotoxicity of several cationic surfactants, such as CTAB (Alkilany *et al.*, 2009). Non-ionic polymeric surfactants known as polysorbates or Tweens are frequently utilised in food and cosmetic products as well as in pharmaceutical formulations. Nontoxic surfactants known as polysorbates are frequently authorised pharmaceutical excipients for use in pharmaceutical formulations (O'Sullivan, Wood & O'Brien, 2004). The polysorbates for CuNP synthesis are a homologous non-ionic surfactant series that I have used in this work. In the food sector, polysorbate 60 is frequently used as an emulsifier (Dalglish, Srinivasan & Sing, 1995). Noble metal nanoparticles have previously been synthesised using polysorbate 80 (Duy *et al.*, 2010; Premkumar *et al.*, 2007; Habibi, Kamrani & Mokhtari, 2010; Koroleva *et al.*, 2011; Li *et al.*, 2012; Hormozi-Nezhad, Karami & Roberjazi, 2013). Other

polysorbates are not used as frequently. The synthetic process described here is simple, affordable, environmentally friendly, and can be used in a range of biological and biomedical applications. This article has been written in a revised way on my published paper (Mandal & De, 2015).

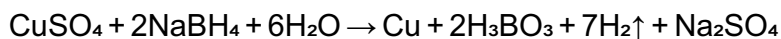
Experiment

Materials

Analytical grade (AR) compounds were all utilised without additional purification. Polyoxyethylene Sorbitan Monolaurate (Tween 20), Polyoxyethylene Sorbitan Monopalmitate (Tween 40) and Polyoxyethylene sorbitan monostearate (Tween 60) are non-ionic surfactants that were acquired from E-Merck and utilised accordingly. To create the appropriate solutions, measured volumes of Tween 20, Tween 40, and Tween 60 were dissolved in water. E. Merck, Germany, was also the source of sodium borohydride (NaBH₄). Copper sulphate was the precursor salt utilised to create copper nanoparticles. All of the water used in the synthesis process was double-distilled and deionised.

Methodology

Freshly aqueous polysorbate solutions (Tween 20/polysorbate 20, Tween 40/polysorbate 40 and Tween 60/polysorbate 60) of different concentrations (maintaining CMC of all the polysorbates) were made and mixed with aliquots of CuSO₄ stock solution to synthesise copper nanoparticles (Lisiecki, Billoudet & Pileni, 1996) in an aqueous surfactant media of different polysorbates. After that, the necessary volume of ice-cold NaBH₄ solution was added. Immediately a mild brownish colouration developed. After that, the mixture was sonicated for 30 minutes, which resulted in the formation of a clear, stable brown solution. All of the experiments were conducted using bubbling nitrogen gas in an inert atmosphere.



Characterisation

A Shimadzu spectrophotometer, Model No. UV2401PC, was used to capture the absorption spectra of the resultant nanoparticles. Dynamic light scattering (DLS), performed in a Nano-ZS (Malvern) apparatus equipped with a 4 mW He-Ne laser ($\lambda = 632 \text{ nm}$), was used to determine the size distribution and hydrodynamic radii. A 0.2 μm filter was used to filter the solutions to create the samples for this investigation. The nanoparticles were studied using Transmission Electron Microscopy (TEM) at a resolution of 1.9 using a Japanese JEOL, JEM-2100 electron microscope. Microdrops of solution were applied on a carbon sheet that was held up by a copper grid to create TEM specimens.

Results and Discussion

Copper nanoparticles in aqueous solutions of three different concentrations of all the

surfactants are made with the wet chemical reduction process. Different colorations of the sample indicates the distinct natures of the synthesised CuNPs. The different stability of the colorations tells the effect of the surfactants of varying concentration. To investigate the complete morphology of the CuNPs synthesised in the surfactants, UV-vis spectroscopy, DLS technique and transmission electron microscopy analysis are used here.

Metal nanoparticles with surface plasmon peaks in UV-vis spectroscopy are the common features. Copper nanoparticles show this peak in the visible region of 550 nm to 570 nm (Creighton & Eadon, 1991). Various research revealed that peak positions may change due to particle nature, which may depend on the surfactants. Here, a series of polysorbates (Tween 20, Tween 40, and Tween 60) are used as surfactants, and stable CuNPs were synthesised in different concentrations of aqueous solutions of the surfactants. Polysorbates with different hydrophobicity are used here, and Tween 60 is the most hydrophobic surfactant among all the polysorbates used. Hydrophobicity of the surfactant may affect the stability of the CuNPs and their sizes, which is reflected in the UV-vis spectra with different SPR peak positions of CuNPs.

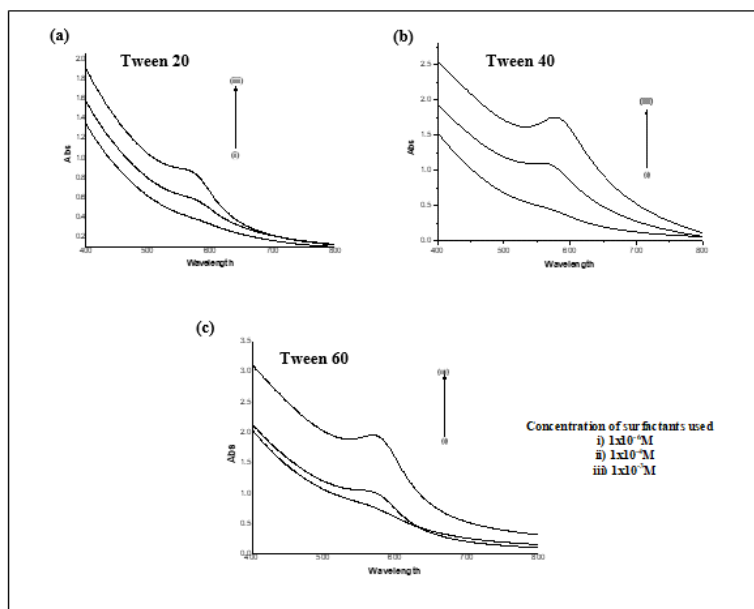


Figure 1: Absorption Spectra of CuNPs in Various Concentrations of Different Polysorbates (Mandal & De, 2015)

SPR peak position is related to the particle sizes. Particles with tiny diameters are produced in high concentrations of all the polysorbate surfactants (Creighton & Eadon, 1991). Figure 1 shows the temporal evolution of the SPR peak of CuNPs at various concentrations of polysorbates.

The dynamic light scattering (DLS) technique is the important technique for detecting the particle nature present in the aqueous medium. It helps to find out the hydrodynamic radius of the particles and their electronic charge. I.e., the technique can reveal the particle sizes and their environments in the aqueous medium. Capping agents like surfactants, polymers, proteins, and carbohydrates are used to restrict the particles' agglomeration and oxidation.

Here, different polysorbates (Scheme 1) of a homologous series are used to prevent the agglomeration of the synthesised CuNPs. High hydrodynamic sizes of the particles are due to agglomeration. Being less hydrophobic, the Tween 20 surfactants can form micelles in tiny sizes (Figure 2b) with respect to other polysorbates. Critical Micellar Concentration (CMC) is the important factor that measures the micelle formation in the aqueous medium. Below CMC, micelle formation is not possible, so it is expected there should be a lack of stability of the CuNPs; i.e., agglomeration (Figure 2a) may be the outcome of that. With two different concentrations of all the surfactants used to investigate the particle's nature in the DLS technique. The size distribution and number distribution curve show the different natures of the CuNPs in various concentrations of Tween 20, Tween 40, and Tween 60, respectively. From the DLS study, it has been observed that above the CMC of each surfactant helps to produce CuNPs of average size below 40 nm (except Tween 60) (Figures 2b, 2c, 2d), while in low concentrations of surfactant, approximately 100 nm (Figure 2a) of CuNPs are synthesised.

Table 1: Tabular form of HLB and CMC Values of Different Polysorbates

Name of the surfactants	CMC Value	HLB Value	Used Concentration (below CMC)	Used Concentration (above CMC)
Tween-20	$5.9 \times 10^5 \text{M}$	16.7	$1 \times 10^6 \text{M}$	$1 \times 10^{-3} \text{M}$
Tween-40	$2.7 \times 10^5 \text{M}$	15.6	$1 \times 10^6 \text{M}$	$1 \times 10^{-3} \text{M}$
Tween-60	$2.3 \times 10^6 \text{M}$	14.9	$1 \times 10^6 \text{M}$	$1 \times 10^{-3} \text{M}$

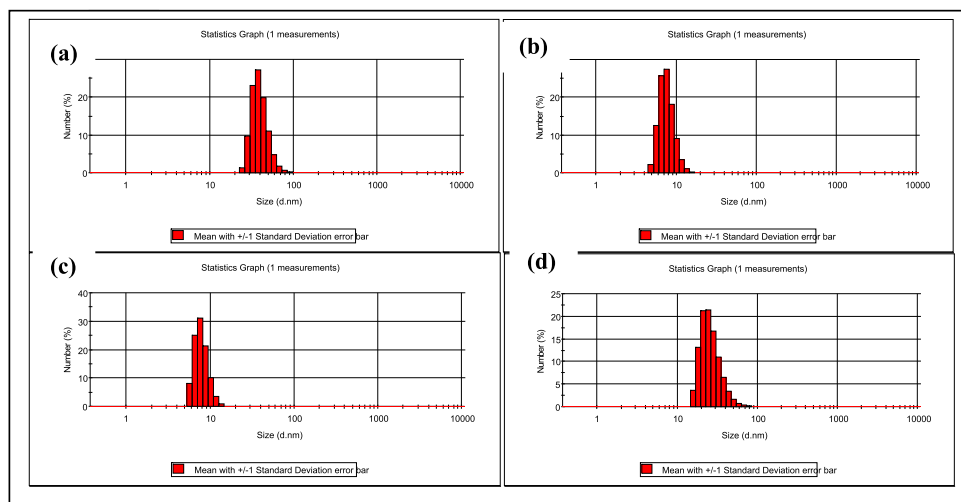
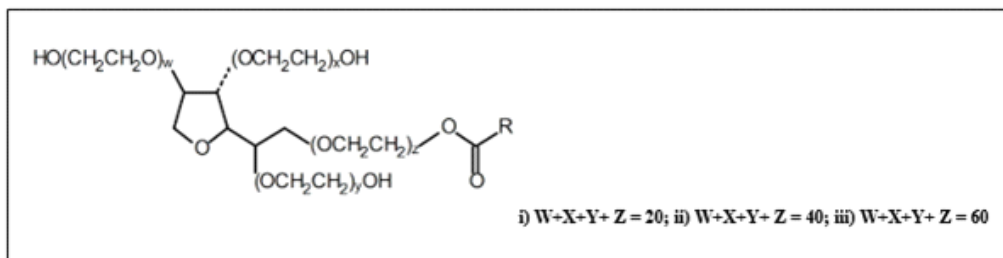


Figure 2: Size Distribution Plots of CuNPs Obtained from DLS Data at Surfactant Concentration $1 \times 10^{-6} \text{M}$ b) at $1 \times 10^{-3} \text{M}$ Tween 20; c) $1 \times 10^{-3} \text{M}$ Tween 40; c) $1 \times 10^{-3} \text{M}$ Tween 60 (Mandal & De, 2015)

In comparison to the surfactants of the polysorbate series, it has been found that Tween-60, being highly hydrophobic in nature and having a lower hydrophilic-lipophilic balance (HLB) value, can form micelles of greater size with respect to other surfactants



Scheme 1: Molecular structure of polysorbate) Tween 20 ii) Tween 40 iii) Tween 60

Transmission electron microscopy gives pictorial images of the CuNPs synthesised in various concentrations of aqueous solutions of polysorbates. The nature of the particles on the basis of crystallinity or amorphousness may be found out by this analysis. Crystal planes can be calculated from TEM. Two different concentrations of each polysorbate surfactant are used here. One is below CMC, and the other is above CMC for the corresponding surfactant. The concentration of Cu^{2+} ion used is $5 \times 10^{-3} \text{ M}$, and $1 \times 10^{-2} \text{ M}$ NaBH_4 solution is used as a reducing agent.

Polysorbate 20 at a lower concentration of $1 \times 10^{-6} \text{ M}$, i.e., below its CMC, is not so helpful to produce stable micelles and so allow CuNPs in aerial oxidation. Oxides of CuNPs are attached to each other due to static electric forces, and agglomeration (Figure 3a) occurred. At the high concentration of $1 \times 10^{-3} \text{ M}$ ($> \text{CMC}$), the polysorbate 20 forms stable micelles of small size that allow for the formation of 10 nm spherical CuNPs (Figure 3b) by a favourable reduction process with NaBH_4 in colloidal solution.

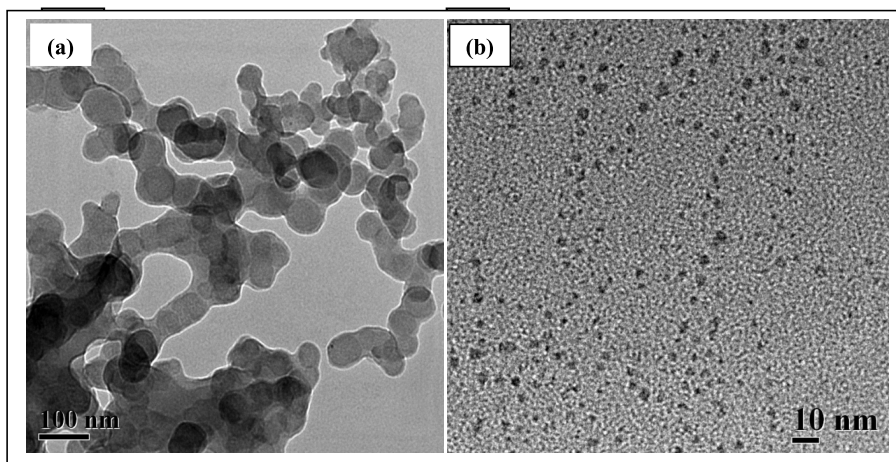


Figure 3: TEM Images of CuNPs in Different Concentrations of Polysorbate 20; a) $1 \times 10^{-6} \text{ M}$ b) $1 \times 10^{-3} \text{ M}$ (Mandal & De, 2015)

Like polysorbate 20, polysorbate 40 at its lower concentration of $1 \times 10^{-6} \text{M}$ shows the tendency of oxide formation, but from the TEM image, a honeycomb pattern (Figure 4a) of CuNPs is observed. Further increasing the concentration of the surfactant solution may form micelles of uniform spherical size that can help to build up the crystallinity of those synthesised spherical CuNPs (Figure 4b) in the micelles. The SAED pattern (Figure 4c) of the sample shows the metallic CuNPs feature a face-centred cubic lattice. The fringe patterns correspond to the (200), (222), (311) and (333) planes of metallic copper. i.e., polysorbate 40 is very helpful to produce well-shaped spherical CuNPs.

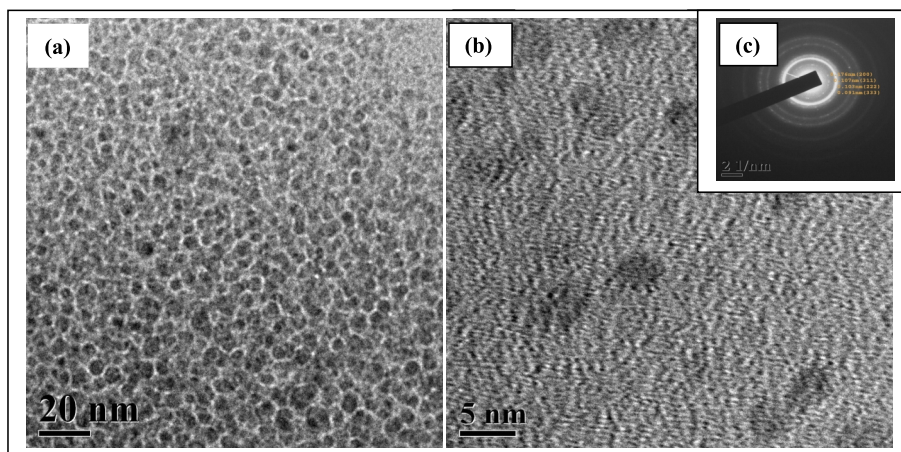


Figure 4: TEM Images of CuNPs in Different Concentrations of Polysorbate 40; a) $1 \times 10^{-6} \text{M}$ b) $1 \times 10^{-3} \text{M}$ (Mandal & De, 2015)

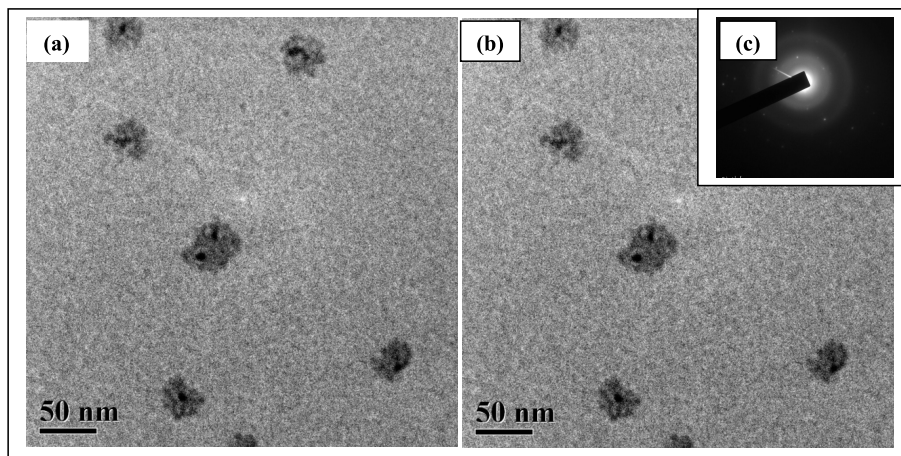
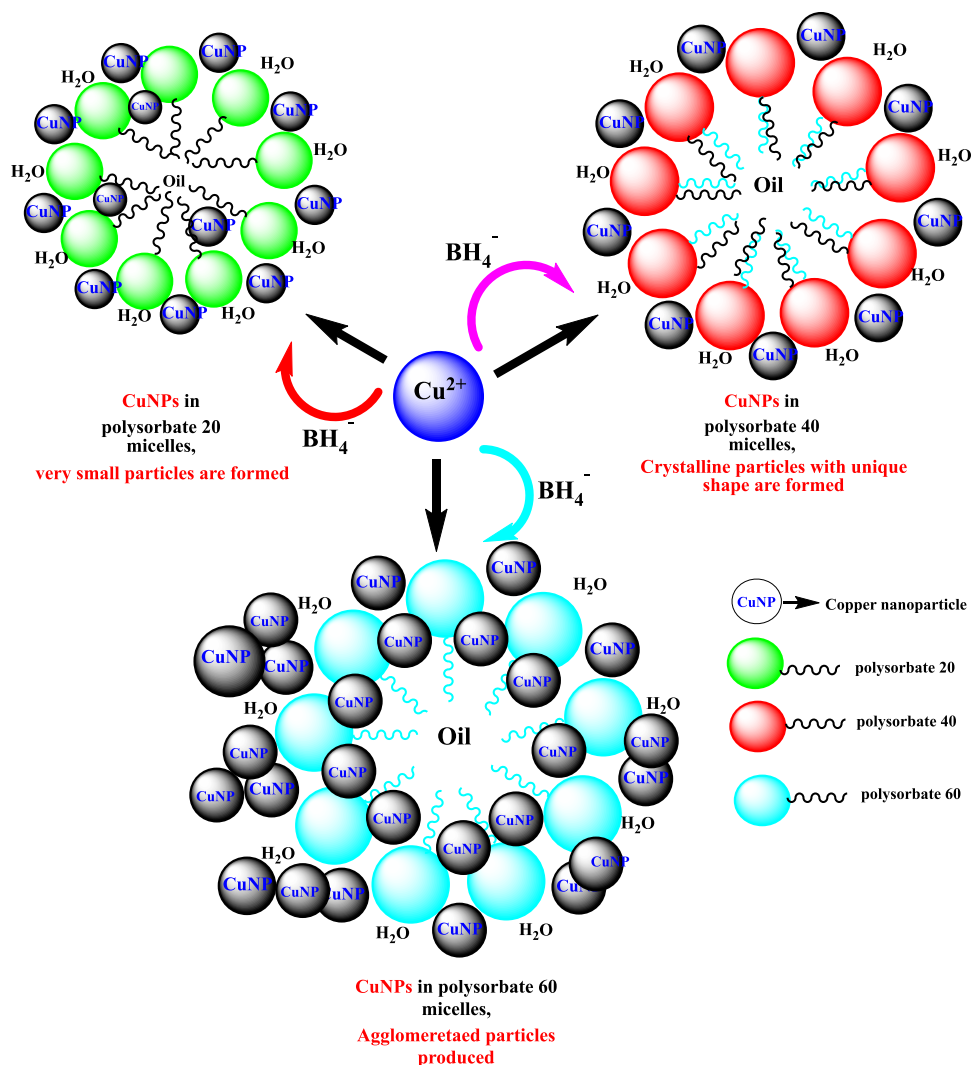


Figure 5: TEM Images of CuNPs in Different Concentrations of Polysorbate 60; a) $1 \times 10^{-6} \text{M}$ b) $1 \times 10^{-3} \text{M}$ (Mandal & De, 2015)

From the UV-visible spectra and DLS data, it was expected that particles synthesised in polysorbate 60 would not be so attractive. The nature of the particles in both

Morphological Changes in Copper Nanoparticles with Polysorbate Surfactants

concentrations is bigger and clumsier (Figures 5a & 5b). The SAED pattern (Figure 5c) also shows the amorphous nature of the particles. Here, the concentrations of $1 \times 10^{-6} \text{M}$ and $1 \times 10^{-3} \text{M}$ are used for TEM analysis. The agglomerated particles may be produced due to the labile and bigger micelle formation, which is not so useful for capping the CuNPs in the aqueous medium; i.e., in polysorbate 60, the CuNPs get oxidised, and so the particle size increases to 60 nm.



Scheme 2: Schematic Diagram of Synthetic Protocol of CuNPs

In this experiment, three different types of polysorbates are used on the basis of HLB value; polysorbate 60 is highly hydrophobic, and polysorbate 20 is the least hydrophobic in nature. Micelle formation is related to HLB values and CMC values.

Micelles allow the Cu^{2+} ions into their core and help to form CuNPs by BH_4^- ions. Below CMC, all surfactants are unable to form micelles, so CuNPs do not get any help from surfactants, i.e., at very low concentrations, synthesised CuNPs become agglomerated and oxidised to form copper oxides. Above CMC, polysorbate molecules can form micelles that can form a framework for producing stable nanoparticles (Scheme 2). Due to different HLB values, the types of the micelles will be different, and their intermolecular interactions will also be different. It may be expected that due to the greater hydrophobicity of polysorbate 60, it can form micelles with a lower density of surfactant molecules. So synthesised CuNPs are not so much capped by micelles; i.e., in this circumstance, agglomerated CuNPs are formed. On the other hand, polysorbate 20, being less hydrophobic (HLB value 16.7), can form close-packed, small-sized micelles in which CuNPs can form with uniform shapes and sizes. No agglomeration can be seen above the CMC concentration ($1 \times 10^{-3} \text{M}$) of the polysorbate 20. Absorption spectra (Figure 1) of CuNPs in various concentrations of different polysorbates gave the idea initially. With increasing the concentration of all the surfactants, the nature of the plot of CuNPs changes in a similar fashion. The tendency of agglomeration in low concentrations of polysorbate 20 (Figure 1(a)-i) is there. This is very much similar to Figure 1(b) & Figure 1(c). i.e., broad spectra. In the case of high concentration, the nature of the plasmon peaks is different; that may be due to the change of particle nature. It has been clearly seen with the resemblance of DLS data and TEM images of CuNPs. Below 10 nm of particles are formed in a $1 \times 10^{-3} \text{M}$ concentration of polysorbate 20 solution. The polysorbate 40 with an intermediate HLB value can form stable micelles with a uniform size that can allow for the formation of CuNPs with unique crystallinity (Figures 4b & 4c).

Conclusion

This work is a simple work in which a comparative study on different polysorbates of the same homologous series has been done successfully. The comparison is on the basis of copper nanoparticle synthesis in different concentrations of polysorbate surfactant micelles. The morphological changes of the CuNPs have been investigated successfully. It has been revealed that at very low concentrations of polysorbate surfactants, i.e., below CMC, CuNPs get agglomerated and oxidised. Among all the polysorbates (Tween 20, Tween 40 & Tween 60), Tween 40 is very helpful to produce stable micelles of unique shape that help to synthesise spherical and crystalline CuNPs.

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References

- Alkilany, A. M., Nagaria, P. K., Hexel, C. R., Shaw, T. J., Murphy, C. J., & Wyatt, M. D. (2009). Cellular uptake and cytotoxicity of gold nanorods: molecular origin of cytotoxicity and surface effects. *Small*, 5(6), 701-708. <https://doi.org/10.1002/smll.200801546>
- Athanassiou, E. K., Grass, R. N., & Stark, W. J. (2006). Large-scale production of carbon-coated copper nanoparticles for sensor applications. *Nanotechnology*, 17(6), 1668. <https://doi.org/10.1088/0957-4484/17/6/022>
- Barnickel, P., & Wokaun, A. (1990). Synthesis of metal colloids in inverse microemulsions. *Molecular Physics*, 69(1), 1-9. <https://doi.org/10.1080/00268979000100011>
- Cason, J. P., & Roberts, C. B. (2000). Metallic copper nanoparticle synthesis in AOT reverse micelles in compressed propane and supercritical ethane solutions. *The Journal of Physical Chemistry B*, 104(6), 1217-1221. <https://doi.org/10.1021/jp9931051>
- Chen, C. H., Yamaguchi, T., Sugawara, K. I., & Koga, K. (2005). Role of stress in the self-limiting oxidation of copper nanoparticles. *The Journal of Physical Chemistry B*, 109(44), 20669-20672. <https://doi.org/10.1021/jp0546498>
- Chen, S., & Sommers, J. M. (2001). Alkanethiolate-protected copper nanoparticles: spectroscopy, electrochemistry, and solid-state morphological evolution. *The Journal of Physical Chemistry B*, 105(37), 8816-8820. <https://doi.org/10.1021/jp011280n>
- Creighton, J. A., & Eadon, D. G. (1991). Ultraviolet-visible absorption spectra of the colloidal metallic elements. *Journal of the Chemical Society, Faraday Transactions*, 87(24), 3881-3891. <https://doi.org/10.1039/ft9918703881>
- Crooks, R. M., Zhao, M., Sun, L., Chechik, V., & Yeung, L. K. (2001). Dendrimer-encapsulated metal nanoparticles: synthesis, characterization, and applications to catalysis. *Accounts of Chemical Research*, 34(3), 181-190. <https://doi.org/10.1021/ar000110a>
- Dalgleish, D. G., Srinivasan, M., & Singh, H. (1995). Surface properties of oil-in-water emulsion droplets containing casein and Tween 60. *Journal of Agricultural and Food Chemistry*, 43(9), 2351-2355. <https://doi.org/10.1021/jf00057a007>
- Dang, T. M. D., Le, T. T. T., Fribourg-Blanc, E., & Dang, M. C. (2011). Synthesis and optical properties of copper nanoparticles prepared by a chemical reduction method. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 2(1), 015009. <https://doi.org/10.1088/2043-6262/2/1/015009>
- De, S., & Mandal, S. (2013). Surfactant-assisted shape control of copper nanostructures. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 421, 72-83. <https://doi.org/10.1016/j.colsurfa.2012.12.035>
- Dhas, N. A., Raj, C. P., & Gedanken, A. (1998). Synthesis, characterization, and properties of metallic copper nanoparticles. *Chemistry of Materials*, 10(5), 1446-1452. <https://doi.org/10.1021/cm9708269>
- Duy, J., Connell, L. B., Eck, W., Collins, S. D., & Smith, R. L. (2010). Preparation of surfactant-

- stabilized gold nanoparticle–peptide nucleic acid conjugates. *Journal of Nanoparticle Research*, 12, 2363–2369. <https://doi.org/10.1007/s11051-010-9996-0>
- Evans, E., & Needham, D. (1987). Physical properties of surfactant bilayer membranes: thermal transitions, elasticity, rigidity, cohesion and colloidal interactions. *Journal of Physical Chemistry*, 91(16), 4219–4228. <https://doi.org/10.1021/j100300a003>
- Gao, T., Meng, G., Wang, Y., Sun, S., & Zhang, L. (2001). Electrochemical synthesis of copper nanowires. *Journal of Physics: Condensed Matter*, 14(3), 355. <https://doi.org/10.1088/0953-8984/14/3/306>
- Habibi, M. H., Kamrani, R., & Mokhtari, R. (2010). Fabrication and characterization of copper nanoparticles using thermal reduction: The effect of nonionic surfactants on size and yield of nanoparticles. *Microchimica Acta*, 171, 91–95. <https://doi.org/10.1007/s00604-010-0413-2>
- Hormozi-Nezhad, M. R., Karami, P., & Robatjazi, H. (2013). A simple shape-controlled synthesis of gold nanoparticles using nonionic surfactants. *RSC Advances*, 3(21), 7726–7732. <https://doi.org/10.1039/c3ra40280k>
- Jana, N. R., Gearheart, L., & Murphy, C. J. (2001). Wet chemical synthesis of silver nanorods and nanowires of controllable aspect ratio Electronic supplementary information (ESI) available: UV–VIS spectra of silver nanorods. See <http://www.rsc.org/suppdata/cc/b1/b100521i>. *Chemical Communications*, (7), 617–618. <https://doi.org/10.1039/b100521i>
- Joshi, S. S., Patil, S. F., Iyer, V., & Mahumuni, S. (1998). Radiation induced synthesis and characterization of copper nanoparticles. *Nanostructured Materials*, 10(7), 1135–1144. [https://doi.org/10.1016/s0965-9773\(98\)00153-6](https://doi.org/10.1016/s0965-9773(98)00153-6)
- Koroleva, M. Y., Kovalenko, D. A., Shkinev, V. M., Katasonova, O. N., Spivakov, B. Y., & Yurtov, E. V. (2011). Synthesis of copper nanoparticles stabilized by Polyoxyethylene Sorbitan Monolaurate. *Russian Journal of Inorganic Chemistry*, 56, 6–10. <https://doi.org/10.1134/s0036023611010141>
- Kumar, R. V., Mastai, Y., Diamant, Y., & Gedanken, A. (2001). Sonochemical synthesis of amorphous Cu and nanocrystalline Cu₂O embedded in a polyaniline matrix. *Journal of Materials Chemistry*, 11(4), 1209–1213. <https://doi.org/10.1039/b005769j>
- Li, H. J., Zhang, A. Q., Hu, Y., Sui, L., Qian, D. J., & Chen, M. (2012). Large-scale synthesis and self-organization of silver nanoparticles with Tween 80 as a reductant and stabilizer. *Nanoscale Research Letters*, 7, 1–13. <https://doi.org/10.1186/1556-276X-7-612>
- Lisiecki, I., Billoudet, F., & Pileni, M. P. (1996). Control of the shape and the size of copper metallic particles. *The Journal of Physical Chemistry*, 100(10), 4160–4166. <https://doi.org/10.1021/jp9523837>
- Liu, Q. M., Zhou, D. B., Yamamoto, Y., Ichino, R., & Okido, M. (2012). Preparation of Cu nanoparticles with NaBH₄ by aqueous reduction method. *Transactions of Nonferrous Metals Society of China*, 22(1), 117–123. [https://doi.org/10.1016/s1003-6326\(11\)61149-7](https://doi.org/10.1016/s1003-6326(11)61149-7)

- Mandal, S., & De, S. (2015). Catalytic and fluorescence studies with copper nanoparticles synthesized in polysorbates of varying hydrophobicity. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 467, 233-250. <https://doi.org/10.1002/andp.19083300302>
- Mott, D., Galkowski, J., Wang, L., Luo, J., & Zhong, C. J. (2007). Synthesis of size-controlled and shaped copper nanoparticles. *Langmuir*, 23(10), 5740-5745. <https://doi.org/10.1021/la0635092>
- Nandi, A., Gupta, M. D., & Banthia, A. K. (2002). Sulfonated polybutadiene random ionomer as stabiliser for colloidal copper nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 197(1-3), 119-124. [https://doi.org/10.1016/s0927-7757\(01\)00853-6](https://doi.org/10.1016/s0927-7757(01)00853-6)
- O'Sullivan, S. M., Woods, J. A., & O'Brien, N. M. (2004). Use of Tween 40 and Tween 80 to deliver a mixture of phytochemicals to human colonic adenocarcinoma cell (CaCo-2) monolayers. *British Journal of Nutrition*, 91(5), 757-764. <https://doi.org/10.1079/BJN20041094>
- Pileni, M. P., Gulik-Krzywicki, T., Tanori, J., Filankembo, A., & Dedieu, J. C. (1998). Template design of microreactors with colloidal assemblies: Control the growth of copper metal rods. *Langmuir*, 14(26), 7359-7363. <https://doi.org/10.1021/la980461m>
- Pootawang, P., Saito, N., & Lee, S. Y. (2013). Discharge time dependence of a solution plasma process for colloidal copper nanoparticle synthesis and particle characteristics. *Nanotechnology*, 24(5), 055604. <https://doi.org/10.1088/0957-4484/24/5/055604>
- Premkumar, T., Kim, D., Lee, K., & Geckeler, K. E. (2007). Polysorbate 80 as a tool: synthesis of gold nanoparticles. *Macromolecular Rapid Communications*, 28(7), 888-893. <https://doi.org/10.1002/marc.200600858>
- Qi, L., Ma, J., & Shen, J. (1997). Synthesis of copper nanoparticles in nonionic water-in-oil microemulsions. *Journal of Colloid and Interface Science*, 186(2), 498-500. <https://doi.org/10.1006/jcis.1996.4647>
- Salkar, R. A., Jeevanandam, P., Kataby, G., Aruna, S. T., Koltypin, Y., Palchik, O., & Gedanken, A. (2000). Elongated copper nanoparticles coated with a zwitterionic surfactant. *The Journal of Physical Chemistry B*, 104(5), 893-897. <https://doi.org/10.1021/jp9908045>
- Schramm, L. L., Stasiuk, E. N., & Marangoni, D. G. (2003). 2 Surfactants and their applications. *Annual Reports Section "C" (Physical Chemistry)*, 99, 3-48. <https://doi.org/10.1039/b208499f>
- Tu, W., & Liu, H. (2000). Continuous synthesis of colloidal metal nanoclusters by microwave irradiation. *Chemistry of Materials*, 12(2), 564-567. <https://doi.org/10.1021/cm9906371>
- Vitulli, G., Bernini, M., Bertozzi, S., Pitzalis, E., Salvadori, P., Coluccia, S., & Martra, G. (2002). Nanoscale copper particles derived from solvated Cu atoms in the activation of molecular oxygen. *Chemistry of Materials*, 14(3), 1183-1186. <https://doi.org/10.1021/cm011199x>

- Wang, S., Huang, X., He, Y., Huang, H., Wu, Y., Hou, L., ... & Huang, B. (2012). Synthesis, growth mechanism and thermal stability of copper nanoparticles encapsulated by multi-layer graphene. *Carbon*, 50(6), 2119-2125. <https://doi.org/10.1016/j.carbon.2011.12.063>
- Wu, S. H., & Chen, D. H. (2004). Synthesis of high-concentration Cu nanoparticles in aqueous CTAB solutions. *Journal of Colloid and Interface Science*, 273(1), 165-169. <https://doi.org/10.1016/j.jcis.2004.01.071>
- Zhang, Z., & Han, M. (2003). Template-directed growth from small clusters into uniform silver nanoparticles. *Chemical Physics Letters*, 374(1-2), 91-94. [https://doi.org/10.1016/s0009-2614\(03\)00705-x](https://doi.org/10.1016/s0009-2614(03)00705-x)
- Zhu, H., Zhang, C., & Yin, Y. (2005). Novel synthesis of copper nanoparticles: influence of the synthesis conditions on the particle size. *Nanotechnology*, 16(12), 3079. <https://doi.org/10.1088/0957-4484/16/12/059>

The Future of Zinc Implant: Its Revolutionary Effects in Modern Advancements – A Short Overview

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ABSTRACT

Conventional non-biodegradable medical implants made of stainless steel, cobalt and titanium alloys used as fixation devices in various orthopaedic applications in human body need to go for secondary surgical removal, as it leaves the effect of patient trauma and medical device-associated infections, creating a challenging complication. Current research has shown an optimistic pathway by developing next-generation temporary orthopaedic implants holding the hand of Zn-based biodegradable alloys and its composites as an alternative to customary implants that could eliminate the scope of revision surgeries and ease the biocompatibility issues. The fundamental benefit of using Zn-alloys, including Zn-Mg, Zn-Mn, Zn-Ca and Zn-Al, instead of pure zinc metal as biomedical implants in terms of its mechanical properties, considering its strength, hardness, tensile and corrosion properties along with its composition and microstructure, has been discussed here. Usage of zinc as a metal in the implant has an additional utility to overcome its deficiency in human body. Surface coating with bioactive material, hydroxyapatite on the zinc medical implant becomes fruitful, enabling better interaction with biological tissues and enhancing its osteogenic potential, making it suitable for placing in the body. This article methodically discusses the overview about the utility of biodegradable bone implants in fracture healing and its effects on the reduction of implant-associated infections. The future direction regarding the problems of using zinc implants and further betterment in its orthopaedic application reducing the risk of side effects has also been reviewed here. Overall, the purpose of using zinc biomedical implants is considered to offer greater cost-effectiveness compared to traditional metallic implants such as titanium or stainless steel.

Keywords: Alloying; Biocompatibility; Corrosion Resistance; Orthopaedic Surgeries; Zinc Implant

Introduction

Bone fractures present a significant global health challenge, with an increasing prevalence due to factors like an ageing population, trauma from traffic accidents, sports injuries and metabolic diseases. The most commonly fractured bones are those of the lower leg, including the patella, tibia, fibula and ankle, which can lead to momentous long-

term burdens for patients due to their frequent occurrence (Shuai *et al.*, 2019; Wu *et al.*, 2021). The process of fracture healing is intricate and involves the restoration of both the biological and biomechanical integrity of the bone, including the repair and regeneration of bone tissue. Successful healing is heavily dependent on the mechanical stability provided during the recovery phase, which is typically achieved through internal fixation surgical methodology by the use of screws, plates and pins, placing them strategically to hold the fractured bone fragments in place, providing the necessary support for the bone to heal by minimising movement that could disrupt the healing process (Foster *et al.*, 2021).

In recent years, the field of biomedical engineering has witnessed significant advancements aimed at enhancing the efficacy, high strength and safety of medical implants. Metallic materials and their alloys are widely favoured as implant materials due to their considerable strength, adequate ductility, formability, reasonable corrosion, wear resistance and hardness, which becomes extremely difficult to achieve with other conventional materials. Millions of patients worldwide rely on these implants to restore physiological functions and enhance their quality of life significantly. Fracture fixation implants are commonly used in orthopaedic surgery to stabilise bone fractures and facilitate proper healing. These implants are designed to provide mechanical support to the bone during the healing process, allowing patients to recover by minimising the risk of malunion or nonunion of fractured bones. These implants predominantly consist of non-biodegradable metals like stainless steel, cobalt (Co) and titanium (Ti) alloys, serving both permanent and temporary implant needs (Al-Shalawi *et al.*, 2023). However, employing non-biodegradable materials in medical applications can lead to future complications and the risk of chronic inflammation or infection, often necessitating revision surgery to remove or replace the implants once they have fulfilled their purpose.

In response to these confinements, the exploration of biodegradable metals, particularly zinc, is revolutionising the way medical implants are conceived and used. Recent research on biodegradable metals offers the potential to eliminate the need for secondary surgeries, significantly enhancing patient compliance and reducing medical expenses (Paiva *et al.*, 2022). Unlike traditional permanent implants, the medical field has shown significant interest in biodegradable metals such as magnesium, iron and zinc alloys because of their exceptional mechanical properties that are comparable to traditional permanent implants made of stainless steel or titanium in addition to their ability to degrade naturally. These metals are strong enough to support bone healing or provide structural stability in cardiovascular devices during the necessary healing period.

Among the materials explored for implant applications, zinc, a material long known for its essential biological functions in the human body, has garnered significant attention in the medical field as a promising candidate for its use as biodegradable implants due to its unique combination of bio-compatibility and corrosion resistance (Paiva *et al.*, 2022). This material, when used in the body, does not provoke an adverse immune response or

cause toxicity and also integrates well with biological tissues. Zinc exhibits a favourable combination of corrosion resistance and biodegradability, making it an ideal candidate for temporary implants.

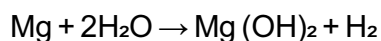
In orthopaedic surgeries, zinc-based implants have materialised as a propitious alternative, particularly for the repair and reconstruction of injured or damaged bones. Owing to their eccentric combination of mechanical properties, biocompatibility and biodegradability, zinc materials are establishing to be highly promising for a wide range of biomedical applications. By harnessing zinc's natural properties, involving its ability to promote tissue integration and minimise inflammatory responses, this mini-review article drives towards substantial advancements in the field of implantology, with the ultimate goal of developing safer, more efficient medical devices. Furthermore, this review article seeks to address key challenges in implant technology, such as ensuring long-term stability and improving material properties, through the exploration of innovative approaches. By expanding the understanding of the potential of zinc implants, the advancement of medical technology is promoted, leading to improved patient outcomes across a variety of surgical treatments.

Literature Review

Zn Vs Other Biodegradable Metals for Implant Technology

When comparing Zn to other biodegradable metals like Mg, Fe for implant technology, it's crucial to consider several critical factors, such as biocompatibility, degradation rate, mechanical properties and biological response of the body. Zinc is considered biocompatible, elucidating that upon its implantation into the body, it does not trigger any significant immune response or cause detrimental reactions (Li *et al.*, 2024). Principally, it refers to the ability of a material to interact with the body without causing adverse effects, such as inflammation, toxicity or rejection, making it a scatheless preference for medical implants. Zinc's biocompatibility can be attributed to its natural presence in the body, reduced toxicity, healing-promoting effects, gradual degradation and minimal inflammatory response, converting it to an exemplary material for curative implants that communicate safely with living tissue (Roesner *et al.*, 2023).

Magnesium is also a lightweight metal with marvellous biocompatibility, shaping it a challenging material for biodegradable implants. Magnesium alloys are especially favoured in bone implants because of their close resemblance of mechanical properties to those of natural bone (Tsakiris, Tardei & Clicinschi, 2021). In spite of having some explicit qualities, magnesium metal has a comparatively faster corrosion rate in the human body. Upon degradation, it reacts with water and body fluids, producing hydrogen gas. The general reaction is:



During accumulation of hydrogen gas in the surrounding tissue, gas pockets formation

appear, giving rise to swelling and discomfort at the implant site potentially leading to gas embolism (Tsakiris, Tardei & Clicinschi, 2021). It disrupts the normal flow of blood, resulting in ischaemia or tissue death. The production of hydrogen gas can persuade an inflammatory reaction, as the body tries to remove or encapsulate the gas bubbles, delaying the healing process or even causing potentially local tissue damage, swelling and pain. In addition to this, the expeditious corrosion of magnesium could lead to the implant losing its structural integrity before the bone or tissue gets enough time to get fully healed, as the implant degrades at a much faster rate, leading to premature degradation (Chakraborty Banerjee *et al.*, 2019).

Iron is another option as a biocompatible material, investigated for its utilisation as a biomedical implant, distinctly in the form of iron-based alloys. Familiarity with iron due to its strong mechanical properties is beneficial for load-bearing applications. The rate of corrosion of iron is typically slower than magnesium, resulting the formation of iron oxide and other by-products which can be accumulated around the implant. Slow corrosion, although it creates a lesser problem in terms of gas formation, can lead to long-term complications. The reasonably slow release of corrosion products like iron oxide into the surrounding tissue can cause an inflammatory response. In the long run, these corrosion products might lead to the formation of fibrous tissue around the implant, interfering with the healing process, or cause a foreign body reaction. This lowers the efficiency of the implant appreciably, which may require removal or replacement. Due to slower rate of corrosion of iron, the implant may persist in the body for an extended period. While this could be beneficial in some cases, it may also prevent the body from naturally replacing the implant with native tissue. This could lead to long-term issues like chronic inflammation, infection or even the implant's failure to integrate properly with surrounding tissue. Additionally, the implant may not degrade in particular time for complete healing of the body which may not allow the bone or tissue around it to bear the normal stresses, resulting in stress shielding (Liverani *et al.*, 2021). The surrounding tissue becomes weaker with time as the implant takes on too much of the mechanical load.

Zinc exhibits a moderate corrosion rate that is generally slower and more controlled than Mg but faster than iron. This intermediate rate can be advantageous in implant applications, as it allows for gradual degradation, avoiding rapid gas formation like magnesium or long-term persistence in the body like iron. A moderate corrosion rate ensures more predictable degradation timeline of zinc-based implants, which aligns better with the body's natural healing processes (Liu *et al.*, 2025). Moreover, zinc exhibits more favourable corrosion behaviour in a physiological environment. Unlike Fe, upon corrosion zinc forms zinc oxide, which is biocompatible and non-toxic to the body. Zinc degrades into products that can be easily handled and metabolised by the body (Kabir *et al.*, 2021). Zn offers a favourable balance of mechanical properties, including sufficient strength and ductility, which can be customised through alloying. In contrast, Mg is less mechanically stable due to its rapid corrosion, which may be a limitation in load-bearing implants. Its low modulus of elasticity fails to match the mechanical properties of bone

well, leading to stress shielding (Liverani *et al.*, 2021). Iron, while stronger than magnesium, is prone to forming rust when exposed to moisture, leading to the weakening of its structure over time, diminishing necessary stimulation for bone growth. Iron has a high modulus of elasticity, meaning it is rigid and resists deformation under stress. Although this stiffness can be advantageous in some situations for structural integrity, it can be problematic when used in the human body. Especially biomedical implants, while inserted into bone or soft tissue, they are usually at risk of bacterial colonisation, which can lead to infections. Natural antibacterial properties of zinc metal diminish this risk, making it an appropriate option for orthopaedic purposes. Zinc ions possess intrinsic antibacterial properties, offering a significant advantage in reducing the risk of infection at the implant site (Sirelkhatim *et al.*, 2015). Zinc ions inhibit the growth of a wide range of bacteria by disrupting bacterial cell walls, interfering with the enzymatic activity and promoting oxidative stress within the bacteria. This distinction in the properties of Zn from Mg and Fe, those lacking such antibacterial properties, makes it an optimistic member because it presents a well-rounded profile, striking a balance between all of these factors. Its antibacterial properties, along with its biocompatibility, moderate mechanical strength and predictable degradation rate, make it an ideal choice for biodegradable implant applications.

Importance of Zinc in the Human Body

Zinc is an indispensable trace mineral that plays a vital role in many of the human body's biological processes. It is found to be present in all organs, tissues, fluids and body secretions (Weyh *et al.*, 2022). However, its concentration varies remarkably across different parts of the body. Zinc is particularly present in significant abundance in skeletal muscles and bones, as it plays a crucial role in protein synthesis, enzyme activation and bone mineralisation. It helps in bone growth, tissue repair and largely in maintaining muscle integrity, promoting recovery after exercise or injury. A small amount of the body's total zinc is present in the skin as well. Zinc is involved in wound healing and immune function of the skin, protecting against infections and supporting tissue regeneration (Mutlu *et al.*, 2022). The liver stores a small percentage of the body's total zinc and is involved in digestion and zinc metabolism. It plays a key role in detoxification, hormone synthesis, and storage of essential nutrients and produces proteins such as albumin. In the brain also, zinc is involved in several important functions, such as neurotransmitter regulation, neuroplasticity and synaptic transmission. It has significant role in memory formation, learning and cognitive function. It is also crucial for the enzymes in the brain that manage oxidative stress and safeguard neurones from damage (Li *et al.*, 2022). The remaining percentage of zinc in the body is distributed across various other tissues and fluids, including blood plasma, cerebrospinal fluid, saliva, etc., and in semen, breast milk, urine and sweat as a part of body secretions. Zinc plays a crucial role in various physiological processes.

Functions

1 Impact of Zinc in Immune Function

Zinc is an essential mineral for the actual functioning of the immune system, playing a role of the utmost importance in both innate and adaptive immunity (Weyh *et al.*, 2022). Innate immunity provides a rapid, non-specific response to a broad spectrum of pathogens, including bacteria, viruses, fungi and parasites, while adaptive immunity is highly specific to the pathogen as it encounters by recognising unique molecules known as antigens on the surface of pathogens. It assists in the development, differentiation and activation of key immune cells, most impressively T-cells and B-cells, which are central to the body's ability to defend against pathogens such as viruses, bacteria and other harmful invaders (Maywald & Rink, 2022).

Zinc plays a pivotal role in the development and differentiation of T-cells, which are typically a subset of white blood cells that is essential in the immune system. T-cells are responsible for directly attacking infected cells, simultaneously coordinating the overall immune response. Zinc is necessary for the activation of T-cells upon encountering pathogens. When the immune system detects an infection, T-cells are activated to either attack infected cells directly via cytotoxic T-cells or regulate other immune cells to orchestrate an effective immune response through helper T-cells. A zinc deficiency results in lowering number of T-cells and hinders T-cell response, which becomes difficult for the body to effectively mount an immune response. Individuals with zinc deficiency are more susceptible to infections due to a compromised T-cell-mediated immunity. Zinc is equivalently important for the development and function of B-cells, which are necessary for adaptive immunity. B-cells are fundamentally responsible for producing antibodies, also known as immunoglobulin, which are proteins that recognise and bind to specific pathogens, neutralising them and signalling for their destruction by other immune cells. Inadequate zinc levels in the body can result in a reduced ability to produce antibodies, leaving the body more susceptible to infections and disturbing the formation of immune memory (Haase & Rink, 2009).

2. Zinc as a Co-Factor in Enzyme

Zinc serves as a predominant cofactor for many enzymes may be more than 300 (Sangeetha *et al.*, 2022), which is a non-protein substance required for the proper functioning of these enzymes. Zinc is essential for enabling critical biochemical reactions in the body. Insufficient amount of zinc results in making the enzymes incapable of functioning efficiently, leading to disruptions in various biological processes. Zinc dependent enzymes, DNA Polymerases are responsible for DNA replication, a crucial process where a cell duplicates its DNA before division. Zinc acts as a cofactor in DNA polymerase to facilitate the addition of nucleotides and ensure the smooth progression of DNA replication (Costa, Sarmento-Ribeiro & Gonçalves, 2023). Zinc is also involved in the activity of DNA ligases, enzymes that are essential for DNA repair. Another enzyme where zinc plays an essential role is RNA polymerase, which is responsible for

transcribing DNA into RNA. This is a crucial step in the process of protein synthesis. Zinc ensures the correct function of RNA polymerase, facilitating the process of transcription.

3. Bone Health: The Importance of Zinc in Mineralization

Zinc contributes an essential character for the bone formation, remodelling, and mineralisation and in the activity of osteoblasts (O'Connor *et al.*, 2020). It also influences calcium metabolism by maintaining bone density and strength by supporting collagen synthesis, which is a primary component of bone matrix. It also escalates mineral deposition, mainly calcium and phosphorus into the bone matrix, which are crucial for the hardening and strengthening of bones. Zinc helps in maintaining balanced bone turnover that involves both bone resorption by breaking down old bone and bone formation through the building of new bones. Requisite zinc levels are essential for preventing conditions like osteoporosis and promoting overall skeletal health, preventing fractures.

4. Wound Healing and Tissue Repair

Zinc accelerates wound healing by promoting collagen synthesis at the proliferative phase of wound healing, when new tissue is formed. It is responsible for modulating inflammation, preventing excessive or chronic inflammation, which could impair healing. An imbalance in the inflammatory response can lead to prolonged healing times or poor wound closure. Zinc has a direct impact on cell proliferation and differentiation, which makes the formation of new tissue and the closure of the wound difficult. Zinc provides significant antioxidant protection involving prominent cellular activity, including cell turnover, immune cell function, and collagen synthesis, all of which generate reactive oxygen species (ROS) or free radicals. Excessive ROS can cause oxidative stress, which can damage cells and impair the healing process (Mutlu *et al.*, 2022). It is mention-worthy that, in spite of frequent recommendations of zinc supplements for individuals with chronic wounds or impaired healing processes, one should be careful in terms of avoiding excess zinc intake. Overall, zinc plays a major role in all stages of the wound healing process, ensuring efficient tissue repair and regeneration.

5 Sources of Zinc for Optimal Health

Zinc is a vitally important trace mineral that takes part in an extensive role in several key biological processes, such as supporting the immune system, facilitating protein synthesis, promoting wound healing and availing DNA synthesis. As zinc cannot be stored in the body system, its intake must be in a regular fashion from various dietary sources. These sources can be classified into two main groups: animal-based foods and plant-based foods.

1. Animal-Based Sources of Zinc

Animal-based foods are considered the most bioavailable sources of zinc. Compared to plant-based sources, animal-based ones are more easily absorbed by the body. In animal-based products, zinc is bound to proteins and is generally better absorbed due to

reduced levels of compounds like phytates that inhibit absorption. The richest sources of zinc are available in shellfish, chiefly oysters and other seafood like crab and lobster are also considered to be wonderful sources. Among red meats, beef and lamb, particularly from their lean cuts, are excellent sources of zinc along with pork, chicken, and most importantly, organ meats like liver, which also provide substantial amounts of zinc. Dairy products like cheese, especially cheddar, are a perfect source of zinc. Milk, yoghurt and eggs are also considered to be the animal-based sources of zinc in moderate amounts (Sangeetha *et al.*, 2022).

2. Plant-Based Sources of Zinc

Most legumes, involving chickpeas, lentils, kidney-beans and soy products, are excellent sources of zinc. Different kinds of nuts and seeds particularly pumpkin seeds, sesame seeds, cashews, almonds, peanuts, and hemp seeds have very good contribution to the daily intake of zinc as plant-based sources (Ayaz *et al.*, 2024). Certain vegetables like spinach, mushrooms, asparagus and broccoli provide some zinc, making it a good addition to a balanced diet. Quinoa, brown rice, whole wheat, oats and fortified cereals contain good amounts of zinc. But it is mention-worthy that, like legumes, phytate in grains can reduce adsorption of zinc in human body (Sangeetha *et al.*, 2022). Maintaining a varied diet and employing strategies to improve zinc absorption can help ensure optimal zinc levels in the body.

3. Systematic Symptoms of Zinc Deficiency and Excess in Human Body

Zinc has appeared as a dominant trace element owing to its remarkable characteristics in carrying out an assorted set of physiological processes in human body. Problems arising out of deficiency and excess amounts of zinc intake can give rise to various significant symptomatic impacts in bodily systems.

Inadequate dietary intake, poor absorption arising from illness or mal-absorption disorders can show broad effects causing zinc deficiency. Deficiency of zinc results in immune system dysfunction, leading to increased susceptibility to infections and delayed wound healing. It affects growth and development issues, causing stunted growth in infants and children along with their delayed sexual maturation. It causes skin problems involving dermatitis, particularly acrodermatitis enteropathica, acne and hair loss complications. The effects of cognitive dysfunction and delayed mental development are also the outcomes of zinc deficiency. Anorexia-like symptoms showing impairment in the senses of taste and smell together with the problem of infertility also materialise due to a lack of zinc intake (Prasad, 1985).

Consumption of higher concentration of zinc supplements or prolonged exposure to its high level, i.e., more than 40 mg/day for adults, can cause severe toxicity showing a wide range of symptoms in the body (Hussain *et al.*, 2022). It results in gastrointestinal distress, including nausea, vomiting, abdominal cramps and diarrhoea along with loss of appetite. Excessive zinc intake can cause immune system dysfunction, disrupting the

balance of copper in the body, leaving one more disposed to infections. Chronic zinc toxicity can interfere with the absorption of copper, leading to copper deficiency, resulting in symptoms such as anaemia. Zinc excess in the body can show neurological disorders, with cognitive impairments having issues such as difficulty in concentrating and memory problems. Kidney and liver damage and elevated cholesterol levels are also the effects arising out of excessive zinc consumption. There also develops a metallic taste in the mouth diminishing the sense of taste and smell (Prasad, 1985). It is of the foremost importance to balance zinc intake to avoid toxicity while it ensures vital benefit for optimal health.

Potentiality of Zinc in Bio-Application

For human health, zinc, as an essential trace element, plays a decisive role in numerous biological processes. Its key role in the involvement of crucial enzymatic reactions, cellular signalling, and gene expression makes it indispensable for maintaining cellular function and overall health (Stiles, Ferrao & Mehta, 2024). Beyond these fundamental physiological functions, the distinctive properties of zinc have led to its growing importance in biomedical applications. In the biomedical industry, zinc holds considerable promise, with a broad range of potential applications. Its use in drug delivery system has been increasingly explored, where it enhances its efficacy in the targeted release of medications to specific areas of the body, developing therapeutic effectiveness and diminishing side effects. Besides its role in drug delivery, zinc is also being investigated for its utilisation in medical imaging, where its unique properties can aid in the detection and monitoring of diseases through advanced imaging techniques (Firth *et al.*, 2022). Moreover, zinc's bactericidal properties make it an ideal candidate for developing antimicrobial coatings. These coatings can be applied to medical devices, such as catheters or surgical instruments, to reduce the risk of infections and enhance patients' safety. Zinc's ability to combat bacterial growth is also being harnessed by the development of coatings on implants, which are used in orthopaedic and dental procedures. Zinc-based materials are particularly attractive in implant technology because they can promote cell growth, reduce inflammation, support the healing process and, most importantly, provide an antimicrobial effect. Zinc oxide coatings are well known for their antifungal and antibacterial properties, making them useful for coating biomedical devices and reducing the risk of becoming infected. All in all, zinc's versatility and distinct biological properties make it a highly valuable element in advancing multiple aspects of biomedical technology, boosting treatment effectiveness, and enhancing the safety and performance of medical devices and implants.

Zinc in Medicine: Applications and Therapeutic Roles

Zinc has numerous applications in medicine due to its essential role in various physiological processes.

1. Treatment of Diarrhoea

Zinc is comprehensively recognised for its effectiveness in the treatment of diarrhoea, particularly in children. Diarrhoea is one of the dominant causes of mortality in children under five years of age, especially in developing countries. The World Health Organisation (WHO) and UNICEF recommend zinc supplementation, typically 10-20 mg per day for 10-14 days at a particular dosage, as part of the treatment for acute diarrhoea in children (Ali *et al.*, 2024).

2. Treatment of Wilson's Disease

Zinc is used in the treatment of Wilson's disease, a rare genetic disorder characterised by excessive copper accumulation in the liver and other tissues, including the brain and kidneys in the body (Avan *et al.*, 2022). Zinc helps in lowering the copper level in the body by blocking copper absorption in the intestines and promoting its excretion through the gastrointestinal tract. It is considered a safe and effective long-term treatment, especially for maintenance therapy after initial treatment with chelating agents.

3. Dental Application

Zinc oxide-eugenol is widely used in dentistry for temporary fillings and as a base for dental cements (Peutzfeldt & Asmussen, 1999). Its soothing properties and ability to form a tight seal in cavities make it effective in protecting the underlying dental pulp and also reduce sensitivity, preventing further decay. In addition to this, zinc in dental alloys enhances their resistance to corrosion and wear, ensuring longer-lasting dental restoration that is less likely to degrade or cause adverse reactions in the mouth.

4. Topical Treatment

Zinc in topical treatments is significantly used for its anti-inflammatory, antimicrobial and wound-healing properties. Zinc oxide is one of the most common forms of zinc used in topical applications. It is a common ingredient in creams and ointments which treat skin conditions like diaper rash, minor burns and irritations. It also forms a protective barrier on the skin that helps soothe irritation, prevent infections, and promote wound healing (Lin *et al.*, 2018). It also helps to reduce the risk of infection by preventing microbial growth. Zinc also has antibacterial and anti-inflammatory properties that help minimise the growth of acne-causing bacteria on the skin.

Understanding the Antimicrobial Properties of Zinc

For simultaneous immune function and infection control, zinc has a wide range of antimicrobial properties, making it an essential element for human body. In combating bacterial, viral and fungal pathogens its function has been well achieved and it is increasingly utilized in various medical and industrial applications due to its effectiveness in treating infections.

1. Antiviral Treatment

Zinc contributes to antiviral treatment by inhibiting viral replication through preventing viruses from multiplying and spreading within the body. Zinc boosts the immune response by helping the body, strengthening its defence against viral invaders. Zinc interferes in the viral entry into host cells by disrupting the receptors that viruses use to bind to the cell surface. It has also an impact on protein synthesis by inhibiting the viral machinery that produces proteins essential for viral replication (Read *et al.*, 2019). It can also obstruct genome replication by disrupting the enzymes that viruses use to replicate their genetic material. Zinc supplements and formulations are explored for their therapeutic potential to combat viral infections, mainly respiratory viruses like influenza and coronaviruses, by reducing the severity and duration of viral infections.

2. Antibacterial Agent

Zinc nanoparticles and complexes are explored as unique alternatives in the fight against bacterial infections. These zinc-based materials exhibit significant antibacterial properties, showing diverse applications involving surface disinfection, water treatment and food preservation. Due to very small size i.e., on a nanoscale, zinc nanoparticles show its high potential, allowing for a higher surface area for interaction with bacterial cells, enhancing their antimicrobial effect, which can penetrate bacterial cell membranes and disrupt their cellular structures, leading to cell death or inhibition of bacterial growth. They also help in the release of zinc ions, which are toxic to bacteria, further boosting their antibacterial action. These show their positive effectivity for fighting against a wide range of bacterial strains, including those that have developed antibiotic resistance. Potentiality of zinc to act as a replacement for traditional antibiotics contributes a new pathway for treating infections, specifically where antibiotics no longer work (Haider *et al.*, 2011).

3. Anti-inflammatory Effects

Zinc is popularly known for its anti-inflammatory properties, which regulate the immune system and reduce oxidative stress by supporting antioxidant shielding systems in the body, preventing damage to cells and tissues. Zinc also regulates the production of pro-inflammatory cytokines, which are signalling molecules that balance the immune response (Maywald, Wessels & Rink, 2017). It also stabilises cell membranes and protects against chronic inflammation-related damages, such as acne, dermatitis and other inflammatory skin risks.

These three aspects of antiviral activity, antibacterial properties and anti-inflammatory effects highlight zinc's potential as a multifaceted and valuable element in both medical and environmental fields. Whether through supplementation or as a part of nanoparticles, zinc continues to show challenges in fighting infections and alleviating inflammation-related diseases.

Role of Zinc in Advancing Implant Technology

In the evolution and progress of implant technology, zinc has emerged as a multifaceted and indispensable trace element, which has gained reminiscent attention in the field of biomaterials. Its eccentric combination of biocompatibility, bioactivity and corrosion resistance makes it an attractive option for strengthening the performance of medical implants. As an orthopaedic implantable device, the role of zinc in improving their functionality is becoming increasingly critical. The performance of zinc to assist tissue regeneration, support bone healing and reduce the risk of infections plays a pivotal role in its integration into modern implant materials.

1. Biocompatibility of Zinc

Zinc and its alloys are highly regarded for their fabulous biocompatibility, where it can coexist with biological tissues of the human body without causing adverse reactions or harmful effects when used as implants. In its proper utility as a biomedical material, zinc does not trigger significant immune responses, making it safe for long-term implantation in the human body. It helps in promoting bone regeneration, stimulating osteoblast activity and escalating the bone healing process (O'Connor *et al.*, 2020). Its contribution to the prevention of bone loss cannot be ignored. Unlike other non-biodegradable metals, such as titanium or stainless steel, zinc as an implant material eliminates the requirement of secondary surgery for its removal. It reinforces cellular functions, such as enzyme activity and protein synthesis, which are very much crucial for tissue growth and repair. Furthermore, zinc is involved in collagen formation and bone mineralisation, speeding up the healing process. By incorporating zinc into implant materials or coatings, the risk of bacterial colonisation and infection is minimised, leading to faster recovery and enhanced patient safety. Its antimicrobial properties inhibit growth of harmful bacteria by disrupting their cell membranes, which is particularly beneficial in preventing infections associated with implants.

2. Mechanical Strength

Zinc has gathered significant attention in its usage as biodegradable implant due to its significant amalgamation between mechanical and biological properties. In comparison to some other metals, such as titanium or stainless steel, several limitations are there regarding the mechanical properties of zinc which can be mitigated by alloying zinc with other metals. Alloy formation results in enhancing the strength and mechanical compatibility of zinc with biological tissues as a medical implant.

The tensile strength of zinc is relatively low compared to metals like titanium or stainless steel. It can withstand much lower forces before it begins to stretch under tension. Pure zinc's low tensile strength limits its application in high-stress environments, where higher-strength metals are necessary to resist breaking or permanent deformation. When pure zinc has a tensile strength of approximately 110 to 120 MPa, titanium has a tensile strength around 900 MPa, and stainless steel can range from 500 MPa to 1500

MPa depending on the alloy (Yuan *et al.*, 2024). The tensile strength of zinc is sufficient for some applications but limits its use in high-stress environments, such as load-bearing joints or structures.

Zinc's yield strength is appreciably low, which makes pure zinc less suitable for application as an implant, enduring high mechanical stress unless its alloy formation with stronger metals (Hagelstein *et al.*, 2022). Alloying with other metals improves zinc's yield strength, making it suitable for application as an implant in a broader aspect.

Zinc's elastic modulus is around 83 GPa, indicating its stiffness, which is somewhat lower than the elastic modulus of metals like titanium, about 110 GPa. The elastic modulus of zinc very closely matches the elastic modulus of human bone. Stress shielding gets reduced due to having such similarity. It is due to the closeness in elastic modulus value to human bone; zinc helps distribute stress more evenly, which promotes better integration and less bone resorption around the implant. Additionally, due to the high ductility of zinc, it undergoes significant plastic deformation without fracturing (Aghajani & Alizadeh, 2024). This well-versed characteristic makes zinc ideal for orthopaedic temporary or paediatric implants, where flexibility and malleability are highly required. Zinc's flexibility enables it to withstand stresses without breaking, which is beneficial in implants to adapt to the body's dynamic conditions.

In order to overcome its inherent mechanical constraints, zinc is alloyed with other metals like magnesium, calcium and aluminium to improve mechanical properties, making them stronger, more durable and better suited for specific applications, particularly in biomedical contexts. Upon alloy formation zinc can greatly enhance its tensile and yield strengths. These alloys not only improve zinc's sturdiness but also enhance its mechanical compatibility with surrounding biological tissues.

3. Corrosion Resistance

Zinc demonstrates a significant role in advancing implant technology, particularly in terms of improving corrosion resistance. Zinc is often used as a coating or alloying element for metallic implants, such as titanium, steel and aluminium, to provide a protective layer that resists corrosion. Corrosion in a physiological environment is driven by certain factors like pH, temperature and the presence of bodily fluids, which results in degradation of metals. Zinc helps to form a thin protective oxide layer on the implant surface, which helps in protecting the direct exposure of the metal to corrosive environments (Jain *et al.*, 2021). Another important characteristic of zinc is the usage of it in implants as a part of a galvanic protection system, functioning as a sacrificial anode (So, Park & Kim, 2023). This signifies that zinc corrodes preferentially, safeguarding the underlying metal like titanium or steel from corrosion. Zinc's gradual corrosion is beneficial for biodegradable implants, offering strength and stability as tissue heals. Its corrosion rate is optimal, preventing premature failure. The corrosion products, which typically consist of zinc salts, are non-toxic, biocompatible and easily processed by the

body.

Zinc and Titanium Implants: A Comparative Study for Medical Practice

The perfect placement of metallic implants in the human body is a challenge in the field of modern medicine, especially orthopaedics. Traditional biomedical materials, like titanium, have long been found to be favourable as a consequence of their strength, durability and biocompatibility. Ongoing research reveals that zinc-based implants have the potential to replace titanium, primarily due to their biodegradable nature and other unique contributions. It is needed to explore the advantages and challenges of using zinc implants over titanium implants in the human body, focusing on factors like biocompatibility, mechanical properties, degradation behaviour and clinical applications.

Titanium is a strong, lightweight and highly corrosion-resistant metal that has been used in various biological implant applications for decades. Its excellent nature of biocompatibility facilitates osseointegration, when often the implant integrates well with the surrounding bone. As it forms a stable passive oxide layer of titanium dioxide on the surface of its medical implant, it prevents corrosion when exposed to the air, making it suitable for long-term implants in various body systems. Titanium implants can cause a stress shielding effect due to their stiffness, and it can bear a significant portion of the mechanical load, leading to bone resorption and potential failure of the implant (Niinomi & Nakai, 2011). This effect helps in reducing the amount of stress placed on the surrounding bone. It also can produce particles that induce an inflammatory response, potentially leading to osteolysis, resulting in bone degradation over time. But its permanence can be disadvantageous in certain situations. Although titanium is usually counted as biocompatible, its lengthy usage leads to adverse biological responses. Wear particles from titanium implants may induce local inflammation and bone loss and, in some cases, result in implant failure.

Zinc, as a biodegradable metal, has recently emerged as an encouraging alternative to titanium due to its bioabsorbability and potential for bone regeneration. Zinc degrades gradually over time, which means it naturally disappears from the body after fulfilling its purpose, reducing the need for a secondary surgery for implant removal. This becomes advantageous for temporary implants or devices that support healing and then dissolve, such as those used for bone fractures. Zinc degrades more rapidly than titanium, which can release zinc ions that may be less likely to cause chronic inflammation compared to titanium. Again, if the degradation rate becomes too fast, it may cause local toxicity or inflammation. Zinc is mechanically weaker than titanium, which could limit its use in high-load-bearing applications (Wang *et al.*, 2021). The main challenge of using zinc implants lies in controlling the corrosion rate. The uncontrolled corrosion rate fails to match the healing process and prevent premature failure. Excessive corrosion could lead to virulence, as elevated concentrations of zinc ions in the body may disrupt cell function in the body. However, the corrosion of zinc implants can be harnessed to support bone

healing by motivating the body's natural regenerative processes. During the use of zinc implants in the human body, the fear of zinc deficiency occurring due to zinc implants gets much lower. At the same time, in some infrequent instances of excessive degradation, an unrestricted release of zinc ions may lead to zinc toxicity. This may create several health issues. Therefore, it is very much crucial to carefully manage the degradation rate of zinc implants to avoid such complications.

In comparison to titanium, zinc and its alloys typically have lower mechanical strength. However, zinc can be superior in some applications, as the mechanical properties of zinc match more closely to those of natural bone, reducing stress shielding and promoting finer bone healing. Titanium is widely considered the gold standard for many permanent implant applications due to its strength, biocompatibility, and resistance to corrosion. However, zinc implants offer a promising option for temporary applications due to their close resemblance of biodegradability and mechanical properties to natural bone. The choice between zinc and titanium implants ultimately depends on certain factors, such as the clinical needs, the intended duration of the implant and the biological environment at the implant site. Researchers are developing zinc-based alloys with improved strength and corrosion resistance

Exploring the Development of Zinc-Based Medical Implant

Alloying of Zinc

Relatively soft nature and due to the lack of required mechanical strength for several medical applications, particularly for load-bearing implants such as bone fixation devices, alloy formation of zinc with elements like magnesium (Mg), calcium (Ca), manganese (Mn) or aluminium (Al) is very much needed, which results in appreciable improvement in its tensile strength, hardness and overall mechanical stability in order to make it an acceptable medical implant giving support and remaining unaffected by any physical forces in the human body. In addition to mechanical properties, alloying of zinc enhances the corrosion resistance, making the implant more durable, and by controlling the degradation rate, it aligns with the healing process of the tissue.

Addition of magnesium to zinc alloys enhances the tensile strength, hardness and ductility of zinc. Zn-Mg alloys can achieve tensile strengths exceeding 250 MPa, converting them to be more appropriate for high-stress applications like orthopaedic implants (Zhou *et al.*, 2025). Additionally, magnesium accelerates the degradation rate of the alloy, which is important for temporary implants to dissolve with time as tissue heals. Upon such alloy formation, zinc forms solid solutions and precipitates that strengthen the alloy's microstructure, making it an ideal candidate for structural applications like medical implants. A minimum percentage of Mg ranging from 0.1% to 5% by weight is usually found to be contained in Zn-Mg alloys to strategically balance the alloy's mechanical properties, corrosion rate, and biocompatibility (Zhou *et al.*, 2025).

The presence of calcium in alloy formation with zinc enhances the potentiality of the zinc

implant, improving its bioactivity through interaction between the implant and the surrounding tissue. Calcium is also biocompatible, which plays an important role in bone health, stimulating osteogenesis (Su *et al.*, 2019). It is an important element in bone mineralisation that promotes bone regeneration, making it suitable for structural applications. For several orthopaedic requirements, like joint repairs or spinal fixation devices, where temporary support is needed, Zn-Ca alloys can be extensively used. In a Zn-Ca alloy, zinc (Zn) is present in major form over 90% of the composition, while the presence of calcium is generally ranging from 0.1% to 5% by weight. This particular composition, balancing the presence of major and minor metals, maintains strength and support without compromising the alloy's biodegradability or its performance as a biomedical implant.

Manganese addition to zinc escalates the strength, hardness and tensile properties of the alloy, making it more useful for load-bearing applications, such as bone fixation devices. This alloy formation also improves both corrosion resistance and mechanical strength for maintaining implant integrity and longevity (Lu *et al.*, 2024). Incorporation of trace amounts of other elements, Mn converts zinc, making it ideal for a range of applications, from biodegradable implants to protective coatings in corrosive environments. Controlling the Zn-Mn alloy's composition precisely and its microstructure are highly essential to ensure the correct degradation rate.

Zn-Al alloys can be considered as a lightweight alternative to traditional implant materials like stainless Steel (Su *et al.*, 2019), releasing the burden on patients and potentially enhancing comfort for medical applications as an implant. Aluminium addition to zinc can improve the overall stability of the alloy, increasing its resistance to corrosion, which is required for ensuring the implant's longevity inside the body. Aluminium controls the degradation rate, allowing the implant to dissolve gradually. Zinc-aluminium alloys are suitable for biomedical applications where a complete fulfilment of strength, lightness and corrosion resistance is needed. It is critically required to optimise the Zn-to-Al ratio, which ensures the alloy's mechanical properties, degradation rate and biocompatibility that are appropriate for the intended applications.

Advancements in Surface Modification Techniques for Zinc-Based Implants

The process of surface modification of zinc-based biomedical implants is an important as well as censorious thing that strengthens their activity and longevity when used in orthopaedic applications. As a biomaterial for medical implants, the role of zinc cannot be ignored due to having several characteristics involving its biocompatibility, biodegradability and osteogenic potential. As a result of that, improvement of mechanical properties, corrosion resistance and overall performance in the biological environment of zinc implants is very much needed to make it more appropriate for placing it in the human body.

1. Coating with Bioactive Materials

Hydroxyapatite or HA coatings present several superiority on its application to medical implants, while interacting with bone tissue. HA is basically a mineral form of calcium phosphate, whose coating on zinc implant enhance biocompatibility stimulating osteointegration (Shoeib & Abdel-Gawad, 2023). This also assists the process of bone bonding, facilitating the growth of bone tissue at the implant surface. Out of several techniques, three of them have been mentioned for the application of HA coatings to zinc-based implants, which are chosen depending upon the implant's design and on the desired properties of the coating. They are Dip-coating, plasma-spraying method and sol-gel method.

Dip-coating is a simple and economical method where the surface of the zinc implant is cleaned thoroughly to immerse it into a liquid solution, typically containing a coating solution material and HA particles, and then withdrawn from the solution at a controlled speed to allow the uniform coating to get solidified as it dries or cures across the surface, often involving heat or UV light (Nikolova & Apostolova, 2023). This method of dip coating results in thin and uniform coatings over complex geometries, which is especially effective for implants with intricate shapes or surfaces that need to be covered uniformly. Such coatings by bioactive materials promote better tissue integration, reducing the risk of complications and improving osseointegration. It also enhances the corrosion resistance power of zinc implants.

For coatings by using bioactive material, the sol-gel method is also broadly utilised to create thin films over zinc implants. Here transformation takes place from a liquid precursor, sol, into a three-dimensional gel-like solid network resulting in gelation, which is heat-treated and then dried to form a solid coating. The zinc implant is submerged in the sol or sprayed with the sol to form a thin layer of the material. Sol-gel coatings intensify substrate properties like corrosion resistance, wear resistance, and biocompatibility along with optical transparency, thereby improving the all-inclusive performance and expanding the lifespan of coated materials. For large-scale production, compared to other methods like physical or chemical vapour deposition, sol-gel coating is considered frequently for its cost-effectiveness, particularly for biomedical applications in bone regeneration (Nikolova & Apostolova, 2023).

Another method, plasma spraying, involves a thermal spray coating process, which is commonly used to deposit protective coatings in a molten or semi-molten state on various materials, including metallic implants (Nikolova & Apostolova, 2023). This method is effective in improving several properties like wear resistance, corrosion resistance and thermal insulation in various biomedical applications. In addition to this, such a coating of hydroxyapatite (HA) or some other bio-ceramic materials on zinc-based implants mimics the properties of bone, enhancing its biocompatibility. Certain challenges such as coating, adhesion, porosity and uniformity must be consciously

handled to optimise the activity of the coated implants. The process is carried out in a controlled environment, typically utilising an inert gas atmosphere like argon or nitrogen.

Conclusion

The whirlwind magnification in the development of zinc-based biomedical implants has been found to have emerged as a global challenge in the field of orthopaedic surgical applications because of its good alignment of biodegradability and biocompatibility with the human body system. Zinc alloys have been considered as densely potent orthopaedic internal fixation implants because of having notable characteristics like controllable corrosion rate, adaptable mechanical strength, osteo-inductivity and inherent anti-microbial properties. In order to overcome certain limitations of using pure zinc metal as a medical implant related to its strength, plasticity and hardness which hinder its effectiveness in medical applications, alloying of zinc with several other metals like Mg, Fe, Al have been developed which enhances mechanical properties of zinc such as strength and ductility. A comprehensive and systematic comparison for the superiority of zinc and its alloys as an orthopaedic implant with other metals remains still lacking.

Further intensive research is needed with a strong focus on long-term evaluations to identify critically the advantages and limitations of zinc material for medical purposes. Prioritisation on research should be given to understand molecular mechanisms of zinc and its alloys in promoting advantageous cellular remodelling and managing corrosion rates to reduce toxicity and inflammation. It also ensures the degradation rate of zinc material to fasten biological healing processes.

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References

- Aghajani, S., & Alizadeh, R. (2024). Severe plastic deformation of Zn and Zn-based alloys. *Journal of Materials Research and Technology*, 33, 6508-6533. <https://doi.org/10.1016/j.jmrt.2024.10.240>
- Ali, A. A., Naqvi, S. K., Hasnain, Z., Zubairi, M. B. A., Sharif, A., Salam, R. A., ... & Das, J. K. (2024). Zinc supplementation for acute and persistent watery diarrhoea in children: A systematic review and meta-analysis. *Journal of Global Health*, 14, 1-16. <https://doi.org/10.7189/jogh.14.04212>
- Al-Shalawi, F. D., Mohamed Ariff, A. H., Jung, D. W., Mohd Ariffin, M. K. A., Seng Kim, C. L., Brabazon, D., & Al-Osaimi, M. O. (2023). Biomaterials as implants in the orthopedic field for regenerative medicine: metal versus synthetic polymers. *Polymers*, 15(12),

- 2601–2632. <https://doi.org/10.3390/polym15122601>
- Avan, A., Członkowska, A., Gaskin, S., Granzotto, A., Sensi, S. L., & Hoogenraad, T. U. (2022). The role of zinc in the treatment of Wilson's disease. *International Journal of Molecular Sciences*, 23(16), 9316–9332. <https://doi.org/10.3390/ijms23169316>
- Ayaz, A., Zaman, W., Radák, Z., & Gu, Y. (2024). Green strength: The role of micronutrients in plant-based diets for athletic performance enhancement. *Heliyon*, 10(12). <https://doi.org/10.1016/j.heliyon.2024.e32803>
- Chakraborty Banerjee, P., Al-Saadi, S., Choudhary, L., Harandi, S. E., & Singh, R. (2019). Magnesium implants: prospects and challenges. *Materials*, 12(1), 136–157. <https://doi.org/10.3390/ma12010136>
- Costa, M. I., Sarmento-Ribeiro, A. B., & Gonçalves, A. C. (2023). Zinc: from biological functions to therapeutic potential. *International Journal of Molecular Sciences*, 24(5), 4822–4848. <https://doi.org/10.3390/ijms24054822>
- Firth, G., Yu, Z., Bartnicka, J. J., Parker, D., Kim, J., Sunassee, K., ... & Blower, P. J. (2022). Imaging zinc trafficking in vivo by positron emission tomography with zinc-62. *Metallomics*, 14(10). <https://doi.org/10.1093/mtomcs/mfac076>
- Foster, A. L., Moriarty, T. F., Zalavras, C., Morgenstern, M., Jaiprakash, A., Crawford, R., ... & Metsemakers, W. J. (2021). The influence of biomechanical stability on bone healing and fracture-related infection: the legacy of Stephan Perren. *Injury*, 52(1), 43-52. <https://doi.org/10.1016/j.injury.2020.06.044>
- Haase, H., & Rink, L. (2009). The immune system and the impact of zinc during aging. *Immunity & Ageing*, 6, 1-17. <https://doi.org/10.1186/1742-4933-6-9>
- Hagelstein, S., Zankovic, S., Kovacs, A., Barkhoff, R., & Seidenstuecker, M. (2022). Mechanical analysis and corrosion analysis of zinc alloys for bioabsorbable implants for osteosynthesis. *Materials*, 15(2), 421–435. <https://doi.org/10.3390/ma15020421>
- Haider, B. A., Lassi, Z. S., Ahmed, A., & Bhutta, Z. A. (2011). Zinc supplementation as an adjunct to antibiotics in the treatment of pneumonia in children 2 to 59 months of age. *Cochrane Database of Systematic Reviews*, 10. <https://doi.org/10.1002/14651858.CD007368.pub2>
- Hussain, S., Khan, M., Sheikh, T. M. M., Mumtaz, M. Z., Chohan, T. A., Shamim, S., & Liu, Y. (2022). Zinc essentiality, toxicity, and its bacterial bioremediation: A comprehensive insight. *Frontiers in Microbiology*, 13. <https://doi.org/10.3389/fmicb.2022.900740>
- Jain, D., Pareek, S., Agarwala, A., Shrivastava, R., Sassi, W., Parida, S. K., & Behera, D. (2021). Effect of exposure time on corrosion behavior of zinc-alloy in simulated body fluid solution: Electrochemical and surface investigation. *Journal of Materials Research and Technology*, 10, 738-751. <https://doi.org/10.1016/j.jmrt.2020.12.050>
- Kabir, H., Munir, K., Wen, C., & Li, Y. (2021). Recent research and progress of biodegradable zinc alloys and composites for biomedical applications: Biomechanical and biocorrosion perspectives. *Bioactive Materials*, 6(3), 836-879. <https://doi.org/10.1016/j.bioactmat.>

2020.09.013

- Li, P., Dai, J., Li, Y., Alexander, D., Čapek, J., Geis-Gerstorfer, J., ... & Li, A. (2024). Zinc based biodegradable metals for bone repair and regeneration: Bioactivity and molecular mechanisms. *Materials Today Bio*, 25. <https://doi.org/10.1016/j.mtbio.2023.100932>
- Li, Z., Liu, Y., Wei, R., Yong, V. W., & Xue, M. (2022). The important role of zinc in neurological diseases. *Biomolecules*, 13(1), 28–43. <https://doi.org/10.3390/biom13010028>
- Lin, P. H., Sermersheim, M., Li, H., Lee, P. H., Steinberg, S. M., & Ma, J. (2018). Zinc in wound healing modulation. *Nutrients*, 10(1), 16–36. <https://doi.org/10.3390/nu10010016>
- Liu, S., Yuan, C., Gao, K., Shi, R., Zhu, B., & Pang, X. (2025). Degradation Characteristics and Biocompatibility of Zinc Alloy in Advanced Biomedical Bone Implants. *Langmuir*. <https://doi.org/10.1021/acs.langmuir.4c05260>
- Liverani, E., Rogati, G., Pagani, S., Brogini, S., Fortunato, A., & Caravaggi, P. (2021). Mechanical interaction between additive-manufactured metal lattice structures and bone in compression: implications for stress shielding of orthopaedic implants. *Journal of the Mechanical Behavior of Biomedical Materials*, 121. <https://doi.org/10.1016/j.jmbbm.2021.104608>
- Lu, G., Chen, C., Zhang, D., Guo, L., Lin, J., & Dai, Y. (2024). Optimization of mechanical, corrosion properties and cytotoxicity of biodegradable Zn-Mn alloys by synergy of high-pressure solidification and cold rolling process. *Journal of Alloys and Compounds* 1005(3). <https://doi.org/10.1016/j.jallcom.2024.175988>
- Maywald, M., & Rink, L. (2022). Zinc in human health and infectious diseases. *Biomolecules*, 12(12), 1748–1777. <https://doi.org/10.3390/biom12121748>
- Maywald, M., Wessels, I., & Rink, L. (2017). Zinc signals and immunity. *International Journal of Molecular Sciences*, 18(10), 2222–2256. <https://doi.org/10.3390/ijms18102222>
- Mutlu, N., Liverani, L., Kurtuldu, F., Galusek, D., & Boccaccini, A. R. (2022). Zinc improves antibacterial, anti-inflammatory and cell motility activity of chitosan for wound healing applications. *International Journal of Biological Macromolecules*, 213, 845-857. <https://doi.org/10.1016/j.ijbiomac.2022.05.199>
- Niinomi, M., & Nakai, M. (2011). Titanium-based biomaterials for preventing stress shielding between implant devices and bone. *International Journal of Biomaterials*, 2011(1). <https://doi.org/10.1155/2011/836587>
- Nikolova, M. P., & Apostolova, M. D. (2023). Advances in multifunctional bioactive coatings for metallic bone implants. *Materials*, 16(1), 183-236. <https://doi.org/10.3390/ma16010183>
- O'Connor, J. P., Kanjilal, D., Teitelbaum, M., Lin, S. S., & Cottrell, J. A. (2020). Zinc as a therapeutic agent in bone regeneration. *Materials*, 13(10), 2211–2233. <https://doi.org/10.3390/ma13102211>
- Paiva, J. C., Oliveira, L., Vaz, M. F., & Costa-de-Oliveira, S. (2022). Biodegradable bone implants as a new hope to reduce device-associated infections—a systematic review.

- Bioengineering*, 9(8), 409–444. <https://doi.org/10.3390/bioengineering9080409>
- Peutzfeldt, A., & Asmussen, E. (1999). Influence of eugenol-containing temporary cement on efficacy of dentin-bonding systems. *European Journal of Oral Sciences*, 107(1), 65-69. <https://doi.org/10.1046/j.0909-8836.1999.eos107110.x>
- Prasad, A. S. (1985). Clinical manifestations of zinc deficiency. *Annual Review of Nutrition*, 5, 341-363. <https://doi.org/10.1146/annurev.nu.05.070185.002013>
- Read, S. A., Obeid, S., Ahlenstiel, C., & Ahlenstiel, G. (2019). The role of zinc in antiviral immunity. *Advances in Nutrition*, 10(4), 696-710. <https://doi.org/10.1093/advances/nmz013>
- Roesner, M., Zankovic, S., Kovacs, A., Benner, M., Barkhoff, R., & Seidenstuecker, M. (2023). Biocompatibility assessment of zinc alloys as a new potential material for bioabsorbable implants for osteosynthesis. *Materials*, 16(15). <https://doi.org/10.3390/ma16155224>
- Sangeetha, V. J., Dutta, S., Moses, J. A., & Anandharamakrishnan, C. (2022). Zinc nutrition and human health: Overview and implications. *EFood*, 3(5), e17. <https://doi.org/10.1002/efd2.17>
- Shoeib, M. A., & Abdel-Gawad, S. A. (2023). High performance nano hydroxyapatite coating on zinc for biomedical applications. *Journal of Materials Science*, 58(2), 740-756. <https://doi.org/10.1007/s10853-022-08034-6>
- Shuai, C., Li, S., Peng, S., Feng, P., Lai, Y., & Gao, C. (2019). Biodegradable metallic bone implants. *Materials Chemistry Frontiers*, 3(4), 544-562. <https://doi.org/10.1039/C8QM00507A>
- Sirelkhatim, A., Mahmud, S., Seeni, A., Kaus, N. H. M., Ann, L. C., Bakhori, S. K. M., ... & Mohamad, D. (2015). Review on zinc oxide nanoparticles: antibacterial activity and toxicity mechanism. *Nano-Micro Letters*, 7, 219-242. <https://doi.org/10.1007/s40820-015-0040-x>
- So, Y. S., Park, E. H., & Kim, J. G. (2023). Effect of zinc addition in filler metal on sacrificial anode cathodic protection of fin-tube aluminum heat exchanger. *Journal of Electrochemical Science and Technology*, 14(4), 349-360. <https://doi.org/10.33961/jecst.2023.00374>
- Stiles, L. I., Ferrao, K., & Mehta, K. J. (2024). Role of zinc in health and disease. *Clinical and Experimental Medicine*, 24(1), 38–57. <https://doi.org/10.1007/s10238-024-01302-6>
- Su, Y., Cockerill, I., Wang, Y., Qin, Y. X., Chang, L., Zheng, Y., & Zhu, D. (2019). Zinc-based biomaterials for regeneration and therapy. *Trends in Biotechnology*, 37(4), 428-441. <https://doi.org/10.1016/j.tibtech.2018.10.009>
- Tsakiris, V., Tardei, C., & Clcinschi, F. M. (2021). Biodegradable Mg alloys for orthopedic implants—A review. *Journal of Magnesium and Alloys*, 9(6), 1884-1905. <https://doi.org/10.1016/j.jma.2021.06.024>
- Wang, K., Tong, X., Lin, J., Wei, A., Li, Y., Dargusch, M., & Wen, C. (2021). Binary Zn–Ti alloys

- for orthopedic applications: Corrosion and degradation behaviors, friction and wear performance, and cytotoxicity. *Journal of Materials Science & Technology*, 74, 216-229. <https://doi.org/10.1016/j.jmst.2020.10.031>
- Weyh, C., Krüger, K., Peeling, P., & Castell, L. (2022). The role of minerals in the optimal functioning of the immune system. *Nutrients*, 14(3), 644–661. <https://doi.org/10.3390/nu14030644>
- Wu, A. M., Bisignano, C., James, S. L., Abady, G. G., Abedi, A., Abu-Gharbieh, E., ... & Vos, T. (2021). Global, regional, and national burden of bone fractures in 204 countries and territories, 1990–2019: a systematic analysis from the Global Burden of Disease Study 2019. *The Lancet Healthy Longevity*, 2(9), e580-e592. [https://doi.org/10.1016/S2666-7568\(21\)00172-0](https://doi.org/10.1016/S2666-7568(21)00172-0)
- Yuan, K., Deng, C., Tan, L., Wang, X., Yan, W., Dai, X., ... & Wang, G. (2024). Structural and temporal dynamics analysis of zinc-based biomaterials: history, research hotspots and emerging trends. *Bioactive Materials*, 35, 306-329. <https://doi.org/10.1016/j.bioactmat.2024.01.017>
- Zhou, K., Lu, Q., Shi, Haichuan, Qin, J., Shi, H., Zhang, P., Yan, H., Shi, H., & Wang, X. (2025). A view of magnesium alloy modification and its application in orthopedic implants. *Journal of Materials Research and Technology*, 36, 1536–1561. <https://doi.org/10.1016/j.jmrt.2025.03.188>

Pharmacological Properties of Guava (*Psidium guajava* L.): An Overview

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ABSTRACT

Psidium guajava L. is an important crop plant belonging to the family Myrtaceae, commonly known as guava. *P. guajava* fruit is considered a poor man's apple due to its immense nutritious properties and wide distribution in tropical and sub-tropical countries around the world. Different parts of the plant have been used for the treatment of myriad ailments since ancient times in different parts of the world, including Latin America, Africa, China and India. Traditionally the plant is known for the treatment of diseases like diabetes, dysentery, diarrhoea, gastroenteritis, hypertension, wounds, reducing fever and pain, etc. Recent pharmacological studies support a wide variety of its pharmacological properties, including anti-diarrhoeal, anti-inflammatory, anti-microbial, hypoglycaemic, hepatoprotective, antioxidant, anti-cancerous, etc. While some pharmacological properties have been studied for decades leading to clinical trials, some studies are at a preliminary stage limited to *in vitro* and few *in vivo* studies. This review is aimed at recent developments on the pharmacological properties of *P. guajava* plant and its future prospects in the field of drug development. *P. guajava*.

Keywords: Anti-Diabetic; Anti-Diarrheal; Anti-Microbial; Anti-Oxidant; Pharmacological Property; *Psidium Guajava*

Introduction

Psidium guajava L. (Family: Myrtaceae), commonly known as guava for its nutritious fruits, is widely distributed and consumed throughout the world in tropical and sub-tropical areas. Botanically, the plant can be described as a dicotyledonous small tree with opposite and entire leaves. Flowers are white in colour, large, solitary, with 4 to 5 sepals, connate in bud stage in an urceolate or ovate calyx with valvate aestivation. Corolla is white in colour, consisting of 4 to 5 free petals. Stamens are many in number, inserted in several series on a wide disc, ovary is inferior with numerous ovules. Fruit is globose, ovoid or pyriform berry with persistent calyx (Fig. 1). Numerous seeds with hard testa are present in the fruit pulp (Prain, 1908).

Guava is considered a poor man's apple due to its immense nutritional value, delicious taste and traditional therapeutic use in tropical and sub-tropical nations (Anand *et al.*, 2016). The species *P. guajava* can grow in various soil types and adapt to dry as well as humid environmental conditions. The adaptability and resilience of the plant species have contributed to widespread cultivation around the world. Countries including China,

India, Mexico, Brazil, Thailand and Indonesia lead global production of guava. Apart from the utilisation of fruits of *P. guajava* as food, different countries, including Latin America, China, India, Africa and many more countries, have been utilising different parts of the plant species, including leaves, bark, seeds and roots, for treatment of numerous diseases, including diabetes, cough, dental problems, pain management, amenorrhoea, hepatic diseases, microbial infection, etc. (Barbalho *et al.*, 2012). Several parts of the plant *P. guajava* including leaves, stem bark, fruit pulp, seeds and fruit peels, are known to produce myriad phytochemicals. Pharmacological investigations have confirmed several biological activities in the plant extracts and its important secondary metabolites. This review is aimed at recent developments on the pharmacological properties of *P. guajava* plant and its future prospects in the field of drug development.

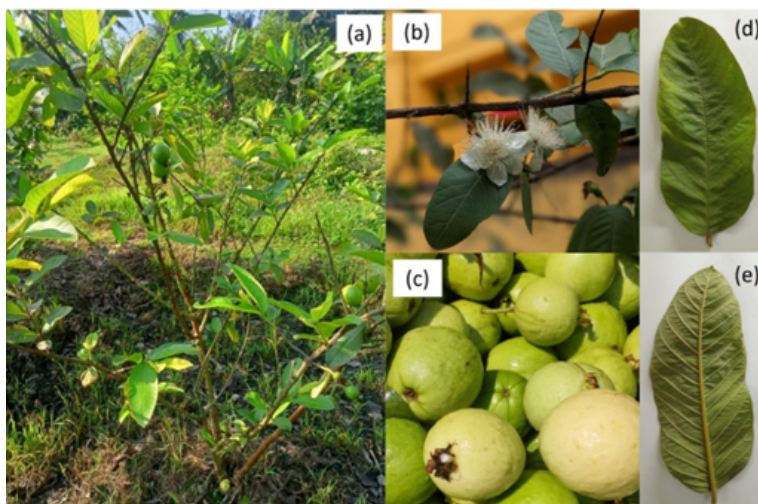


Figure 1. (a) Plant body, (b) Flower, (c) Fruits, (d,e) Single leaf (dorsal surface) and (ventral surface) respectively of *Psidium guajava* L. (Myrtaceae).

Phytochemical Profile

Qualitative phytochemical analyses have shown a wide array of secondary metabolites present in the different parts of *P. guajava*, mainly in the leaves and barks of the plant in addition to its fruit. Leaf extracts of guava plant are reported to show the presence of different alkaloids, anthraquinones, cardiac glycosides, flavonoids, glycosides, phytosteroids, polyphenols, saponins, steroids, tannins and terpenoids (Barbalho *et al.*, 2012; Porwal, Singh & Gurjar, 2012; Krishnarathi, Issac & Kannan, 2014; Thenmozhi & Rajan, 2015; Oncho, Ejigu & Urgessa, 2021; Adamu, 2021). The major bioactive compound identified in the leaves is the phenolic compound quercetin. Other bioactive compounds reported in leaf extracts of *P. guajava* include catechin, epicatechin, gallic acid, rutin, avicularin, isoquercitrin, apigenin, guajaverin, kaempferol, hyperin, and myricetin (Wang, Du & Song, 2010; Liu *et al.*, 2014; Wang *et al.*, 2017a,b). Several

essential oils are found in the leaves of guava, with 1,8-cineole and trans-caryophyllene as the major compounds identified, along with more than 50 other compounds, including limonene, eucalyptol, caryophyllene oxide, caryophyllene, and nerolidol (Lee *et al.*, 2012; Mandal *et al.*, 2022). Similarly, a plethora of phytochemicals are detected in the bark extracts as well, namely, alkaloids, anthraquinones, carboxylic acids, cardiac glycosides, coumarin, flavonoids, quinines, resins, saponins, steroids, tannins and terpenoids (Barbalho *et al.*, 2012; Velmurugan *et al.*, 2012; Abdulhamid *et al.*, 2014; Oncho, Ejigu & Urgessa, 2021). Atik *et al.* (2019) reported a range of secondary metabolites in the fruit extracts of *P. guajava*, including flavonoids, tannins, quinones, saponins, and triterpenoids/steroids. Recently, more than 550 secondary metabolites have been identified in the fruit's pulp by modern instrumentation techniques like MS/UPLC-ESI-MS. Metabolic profile of the fruit varies with different coloured pulps and revealed a type of anthocyanin (cyanidin-3-O-sophoroside) to act as the primary pigment responsible for variance in fruit pulp colour along with some co-pigments, namely, chlorogenic acid, myricetin, myricitrin, quercetin, and quercitrin (Zheng *et al.*, 2020).

Pharmacological Properties

Psidium guajava plants are not only known to the world for its palatable fruit, but it is also known all over the world for its wide range of medicinal uses. Different parts of the world, namely, Asia, Africa, Mexico and Central America, are known to employ plant parts of *P. guajava* for treatment of different ailments. Traditional use of the plant is known for the treatment of diseases like diabetes, dysentery, diarrhoea, gastroenteritis, hypertension, wounds, reducing fever and pain, etc. Recent pharmacological studies support a wide variety of its pharmacological properties, including anti-diarrhoeal (Birdi *et al.*, 2020), anti-inflammatory (Oktavia, 2021), anti-microbial (Rayjade Meghana, Bhambar & Attarde Daksha, 2021), anti-hyperglycaemic (Zhu *et al.*, 2020), hepatoprotective (Alves *et al.*, 2023), anti-oxidant (Gomes August *et al.*, 2025), anti-cancerous (Lok *et al.*, 2023), etc. The following section elaborates on the various pharmacological activities reported in different plant parts of *P. guajava*.

Anti-microbial Property

Different parts of the plant *Psidium guajava* have been reported to possess antimicrobial properties against a wide range of micro-organisms, including Gram-positive bacteria, Gram-negative bacteria fungi, etc. (Naseer *et al.*, 2018). Leaf, root and bark extracts of *P. guajava* are reported to be active against Gram-positive bacteria, including *Staphylococcus aureus* and *Bacillus subtilis* (Sanches *et al.*, 2005). The study showed ethanol:water (7:3) extracts of the leaf, root and bark to be more active than aqueous extracts of the same against the tested bacterial strains. Phytochemical analyses of the leaf extracts in the same study suggested flavonoids to be the active secondary metabolite to be involved in the antibacterial property of the plant (Sanches *et al.*, 2005). Later on, the effect of five different flavonoids extracted from the leaves of *P. guajava* for antimicrobial activity was studied by Metwally *et al.* (2010). In addition to

different leaf extracts and its fractions, quercetin and its glycosides were observed to exhibit strong antimicrobial activity against *S. aureus* (Gram-positive bacteria), *Escherichia coli* and *Pseudomonas aeruginosa* (Gram-negative bacteria) and the fungus *Candida albicans* (Metwally *et al.*, 2010). Crude extracts of *P. guajava* leaves are reported to be active against Gram-positive bacterial species like *Streptococcus pneumoniae* and *Staphylococcus aureus* (Gashe, Belete & Gebre-Mariam, 2010). Essential oils freshly extracted from leaves of *P. guajava* are reported to have antibacterial effects against Gram-positive bacteria, namely, *B. cereus* and *Lactobacillus lactis*, Gram-negative bacteria, viz., *Enterobacter aerogenes* and *Glucanobacter oxidans* (Joseph *et al.*, 2010). Huang *et al.* (2021) separated seven different compounds, including flavonoids, from ethanolic extract of guava leaves and reported Psidinone to exhibit strong antimicrobial activity against *S. aureus*, *S. epidermidis* (Gram-positive bacteria) and *Mycobacterium smegmatis* (Acid-fast bacterium). Rayjade Meghana, Bhambar and Attarde Daksha (2021) reviewed in detail the antimicrobial activity of guava leaf extracts and found the extracts to be active against a wide range of microbes, including *B. cereus*, *S. aureus*, (Gram-positive bacteria), *E. coli*, *Salmonella enteritidis*, *Vibrio* and *Aeromonas* species (Gram-negative bacteria), *Aspergillus niger*, *Saccharomyces cerevisiae* (fungi) as well as against periodontal pathogens. In addition to the above-mentioned microbial species, extracts from different parts of *P. guajava* (leaf, bark, fruits, peels, etc.) are reported to be active against a plethora of Gram-negative bacteria like *Klebsiella pneumoniae*, *Salmonella typhi*, *Shigella dysenteriae*, *Shigella flexneri*, *Vibrio cholerae*, *Salmonella enteritidis* and fungi including *Aspergillus niger* (Dona & Rajapakse, 2024). The findings support the traditional use of different parts of the guava plant in the treatment of microbial diseases like diarrhoea and periodontal diseases.

Anti-diarrheal Property

Diarrhoea is one of the world's major health concerns in developing as well as economically developed countries. It is the third leading cause of death among children less than 5 years old, with 4.44 lakh child deaths per year, and is estimated to remain a global health concern for the upcoming decades (Meyrowitsch & Bygbjerg, 2007; World Health Organisation, 2024). Diarrhoea may be the result of infection by a number of causal organisms, including viruses, bacteria or protozoa. Medicinal plants have been employed traditionally for the treatment of infectious diarrhoea around the world, including the use of different parts of *Psidium guajava*. The extracts of *P. guajava* plants have been found to have antidiarrheal activity in vitro (Vieira *et al.*, 2001) as well as in vivo (Lu *et al.*, 2020). Anti-diarrhoeal activity of the plant has been tested in animal models as well as preclinical and clinical trials are reported with positive results as reviewed in detail recently by Garrido *et al.* (2024) and Liu, Jullian and Chassagne (2024). The antidiarrheal property of this plant is mainly attributed to the anti-microbial property of its extracts, including some microbes responsible for diarrhoea (as discussed above). Furthermore, different extracts of guava leaf have been reported to

have positive effects on gastrointestinal propulsion in animal models by increasing absorption of water and lowering ingested food movement rate. The inhibitory rate of gastrointestinal function by these leaf extracts is reported to be comparable to loperamide, an FDA-approved anti-diarrhoeal medicine (Liu, Jullian & Chassagne, 2024). Multiple reports thus support and scientifically validate the traditional use of guava leaves in the treatment of diarrhoea and possible mechanisms of action. However, more investigations are required to standardise the dosage and extraction procedure for safe application of the plant in treatment of diarrhoea.

Anti-diabetic Property

Extracts of guava leaves have been employed in the treatment of diabetes since ancient times in east Asia and other countries. Pharmacological investigations have confirmed extracts of this plant to exhibit antidiabetic properties at various levels, including *in vitro* and *in vivo* studies (Oh *et al.*, 2005; Mukhtar *et al.*, 2006; Basha & Kumari, 2012; Zhu *et al.*, 2020; Tella, Masola & Mukaratirwa, 2022; Rahman *et al.*, 2023). Ethanolic extract of the plant bark showed significant anti-hyperglycaemic activity in alloxan-induced diabetic mice subjects (Mukhtar *et al.*, 2006). However, the maximum number of reports are available for leaf extracts to possess anti-diabetic properties. In *Leprdb/Leprdb* diabetic mice, methanolic leaf extract of *Psidium guajava* showed significant reduction in blood sugar level after intraperitoneal injection of the extract (Oh *et al.*, 2005). Guava leaf extracts have been reported to show significant antidiabetic properties in vitro analysis as well. Basha and Kumari (2012) observed that methanolic extracts of the plant leaf show significant inhibition of glucose diffusion in vitro. Anti-diabetic activity of *P. guajava* leaf extracts against Type 2 diabetes in a mouse model is suggested to be mediated by the inhibition of the enzyme tyrosine phosphatase1B which acts as a negative regulator in insulin signalling (Oh *et al.*, 2005). Zhu *et al.* (2020) reported leaf flavonoids (namely, Guaijaverin and avicularin) of *P. guajava* to have active antidiabetic effects on a streptozotocin-induced diabetic mice model by decreasing insulin resistance, fasting plasma glucose and glucose tolerance on flavonoid supplementation. Tella, Masola and Mukaratirwa (2022) observed after studying the effect of aqueous leaf extract on streptozotocin-induced diabetic rat models that the anti-diabetic property of the plant extract is mediated by modification of glycogen metabolism pathways enzymes. The group further attributed the anti-diabetic property of the plant to its phenolic compounds and triterpenes present in the leaf extract (Tella, Masola & Mukaratirwa, 2022). Oral treatment with aqueous leaf extracts has shown positive results for the anti-diabetic effect on neonatal streptozotocin-induced diabetic rat models as well (Rahman *et al.*, 2023). Rahman *et al.* (2023) demonstrated oral treatment with leaf extract to increase insulin secretion and promote glycogen synthesis in the diabetic rats, thus contributing to potential anti-diabetic natural drug development.

Anti-inflammatory Property

Inflammation plays an important role in a large number of diseases, including diabetes,

pulmonary diseases, cancer, arthritis, etc. Different plants are reported to possess anti-inflammatory properties, including *Psidium guajava*. Pharmacological investigations have revealed the presence of anti-inflammatory properties in different parts (fruit and leaf extracts) of *P. guajava* plant in both *in vitro* and *in vivo* studies (El-Ahmady, Ashour & Wink, 2013; Oktavia, 2021; Yu *et al.*, 2022; Singh *et al.*, 2023; Mohan *et al.*, 2024). Extracts of *P. guajava* are reported to demonstrate anti-inflammatory properties in different carrageenan-induced oedema in mice model studies as well as in lipopolysaccharide-activated macrophage cell lines of mice (Oktavia, 2021). Study conducted with dechlorophyllised ethanolic extract of *P. guajava* leaves showed anti-inflammatory effects against macrophage cells stimulated with lipopolysaccharides (Singh *et al.*, 2023). Oils isolated from both the leaf (β -caryophyllene and selin-7(11)-en-4 α -ol) and fruit (β -caryophyllene and limonene) of the guava plant are also reported to have anti-inflammatory properties by evaluation of inhibition of 5-lipoxygenase (El-Ahmady, Ashour & Wink, 2013). Psidial F, a monoterpenoid identified from leaf extracts of the guava plant, is observed to show anti-inflammatory activity (Yu *et al.*, 2022). Fermented *P. guajava* fruits with *Lactiplantibacillus* sp., FSA-4, showed enhanced activity by significantly alleviating inflammatory responses in *in vitro* conditions due to the presence of a distinct group of flavanols supporting the traditional use of fermented food for overall well-being (Mohan *et al.*, 2024). Oktavia (2021) suggested the anti-inflammatory property of the plant is mainly mediated by inhibition of PGE2, COX-2, NO, iNOS, ERK1/2, leukocyte cell migration, and suppression of oedema and paw withdrawal latency and by membrane stabilisation.

Hepatoprotective Property

Guava extracts are long known for their hepatoprotective nature. Oral administration of aqueous extract of *Psidium guajava* leaves (200 mg/kg bw) did not show significant improvement in histological and biochemical parameters for liver function in male and female rat models; however, an increase in RBC, haematocrit and haemoglobin was noted by Uboh, Okon and Ekong (2010). On the contrary, ethanolic extract of *P. guajava* leaves (200, 400 mg/kg) and its phospholipid complex (100 mg/kg) are reported to exhibit significant hepatoprotective activity against paracetamol overdose-induced hepatic damage in rats (D'mello & Rana, 2010). D'mello and Rana (2010) further deduced phospholipid complexes isolated from the leaves to show better activity compared to crude extracts, which was comparable to the standard drug silymarin. Ethanolic extract of guava leaves is also reported to restore liver functional markers to normal levels in CCl₄-induced rats (Vijayakumar *et al.*, 2020). The authors observed that quercetin, isolated from leaves of *P. guajava*, had better hepatoprotective activity compared to crude ethanolic extract. Fruits of *P. guajava* are also reported to possess hepatoprotective properties in pharmacological investigations. Aqueous extract of raw fruit peel of guava when administered orally to streptozotocin-treated rats at a dose of 400 mg/kg, showed a significant decrease in all parameters for liver function after 21 days (Rai, Mehta & Watal, 2010). Intra-peritoneal administration of guava fruit puree at

doses of 200 and 400 mg/kg for 21 days showed significant hepatoprotective activity in alloxan monohydrate-treated rats without any toxicity up to 5000 mg/kg in addition to anti-diabetic properties (Joshua *et al.*, 2022). Lycopene extract from *P. guajava* ameliorated liver degenerative changes in a hamster model on oral administration without any cytotoxic effects, although it did not improve blood markers for liver function (Alves *et al.*, 2023). Guavinoside B, a major benzophenone glycoside in the fruits of *P. guajava*, showed positive hepatoprotective properties both *in vitro* and *in vivo*, significantly reducing serum and hepatic biochemical markers (Li *et al.*, 2020).

Anti-oxidant Property

Metabolic processes result in the production of free radicals, which play a key role in different diseases. Plant secondary metabolites, particularly phenolic compounds like flavonoids, are capable of scavenging free radicals, contributing to natural anti-oxidants. Different plant parts of *P. guajava* are rich in varied types of phenolic compounds (as discussed above), contributing to its anti-oxidant property. Role of such compounds isolated from *P. guajava* plant parts demonstrating antioxidant properties has been reported in a number of studies (Zahin, Ahmad & Aqil, 2017; Ruksiriwanich *et al.*, 2022; Gomes August *et al.*, 2025). Methanolic fraction of guava leaf extract, with a high amount of phenolics, showed maximum anti-oxidant activity, comparable to that of ascorbic acid in four different biochemical assays (Zahin, Ahmad & Aqil, 2017). Ethanolic extract of guava leaves was reported to be rich in phenolic compounds namely, catechin, gallic acid and quercetin, which showed anti-oxidant activity in both DPPH and ABTS radical scavenging assays (Ruksiriwanich *et al.*, 2022). The vanillic acid, ascorbic acid, flavonoids and tannins present in the leaf extract of *P. guajava* were correlated with anti-oxidant activity of the plant (Gomes August *et al.*, 2025). In addition, the leaf extracts were observed to produce a constant amount of total phenolics and exhibited stability in maintaining its anti-oxidant and photo-protective activity across the seasons for years (Gomes August *et al.*, 2025). It is evident from the various scientific reports that *P. guajava*, especially its leaf extracts, is a potent anti-oxidant which can be utilised in the future with proper safety measures.

Anti-cancerous Property

The International Agency for Research on Cancer (IARC), a World Health Organisation (WHO) unit, has recently estimated an incidence of 19.97 million cancer cases worldwide, causing 9.74 million deaths in 2022. Among the different types of cancers, the maximum number of death cases is reported to be caused by lung cancer, followed by colorectal, liver, breast, stomach cancers, etc. (Ferlay *et al.*, 2024). In addition to traditional therapeutic strategies like chemotherapy, radiation therapy and surgery, recent focus has been included in the area of alternative potential anti-cancer agents derived from natural products. Systematic review focusing on scientific evidence of potentially anti-cancerous plants covered more than fifty plant species, with their secondary metabolites playing an important role against different types of cancer in

both *in vitro* and *in vivo* studies (Chandra *et al.*, 2023). In the last two decades, extensive reports have been available on anti-cancerous properties of different parts of *Psidium guajava* plant, including leaf, fruit, seed, bark and root extracts against different human cancer cell lines as well as some *in vivo* animal models, as reviewed extensively by Lok *et al.* (2023). Leaf extracts of the plant are extensively reported to have anti-proliferative activity against a number of different cancer cell lines, including lung cancer, breast cancer, colon cancer, prostate cancer, leukaemia cancer, kidney cancer, ovarian cancer, etc. Among the phytochemicals tested, Guajadial, a monoterpenoid isolated from guava leaves, shows anti-neoplastic properties against cell lines of lung cancer, breast cancer, and cervical cancer *in vitro* as well as against some cancers like lung cancer *in vivo*. Other compounds reported from *P. guajava* leaves to be active against cancer cells include guavinoside C, F, quercetin (a flavonoid), against gastric cancer cell lines. Quercetin is suggested to work via inhibiting cancer cell proliferation and inducing apoptosis in different cancer cell lines. Compounds having strong anti-oxidant activity are believed to be one of the most important contributing factors in the fight against cancer. Polyphenol-rich fractions of *P. guajava* leaf extracts are known to limit the growth of human colon cancer cell lines in addition to inhibiting prostaglandin H synthase, thus limiting cancer cell adhesion, migration and invasion. Aqueous and ethanolic extracts of guava leaves were also found to be inhibiting vascular angiogenesis in colon cancer cell lines. Fruit extracts and its important phytochemicals, including guajadial A, D, psiguadial D, lycopene, apigenin, and resveratrol, are also reported to show anti-cancerous properties against various cancer cell lines *in vitro* like, leukaemia, liver cancer, breast cancer, skin cancer and prostate cancer cell lines (Lok *et al.*, 2023; George, Thangasamy & Geetha, 2025). Limited number of reports are available for guava plant parts against cancer *in vivo* studies in mouse models, including skin melanoma, prostate cancer cell line grafted mouse tumours, breast cancer and adenocarcinoma. Hence, booming research to date suggests anti-cancerous potential of different parts of *P. guajava* plant in numerous *in vitro* studies against impressive cancer cell lines and a few *in vivo* studies in animal models. Further clinical trials are necessary to validate the potentially anti-cancerous phytochemicals to be used as drugs in cancer treatment in the future.

Conclusion

Psidium guajava, a nutritionally rich fruit plant, is traditionally used for the treatment of various diseases. The plant is known for the presence of myriad phytochemicals in different plant parts, which contribute to various pharmacological properties. Numerous scientific studies support the use of various plant parts of *P. guajava* for the treatment of microbial diseases, including diarrhoea and periodontal diseases, due to its diverse anti-microbial properties against bacteria (both Gram positive and Gram negative) as well as various strains of fungi. Maximum number of such studies are reported for leaf extracts of the plant and flavonoids extracted from it. Anti-diarrheal property of the plant is not only due to its anti-microbial property, but a recent study suggests its role in gastrointestinal

propulsion, thus contributing to the inhibitory rate of gastrointestinal function comparable to FDA-approved drugs like Loperamide. However, a very limited number of clinical trials are available to date. Thus, more investigations on safe dosage are required for future implementation of the plant extract in diarrhoeal control. Anti-diabetic properties of the plant parts and its compounds have been reported in various *in vivo* studies in animal models on both oral application and intraperitoneal injection by decreasing insulin resistance, increasing insulin secretion, promoting glycogen synthesis and decreasing plasma glucose, thus contributing to potential anti-diabetic drug development in the future. Different *in vivo* reports are available suggesting anti-inflammatory and antioxidant properties of *P. guajava* extracts and its bioactive compounds, specifically flavonoids. Different extracts of the plant, including fruit pulp and its major glycosides, are reported to improve liver function parameters without any cytotoxic effects contributing to hepatoprotective properties. Research in the last two decades has highlighted the anti-cancerous property of the plant against different types of cancer in numerous *in vitro* cancer cell line studies as well as some *in vivo* studies. *P. guajava* extracts and various secondary metabolites isolated from the plants are reported to exhibit anti-proliferative properties and promote apoptosis in cancerous cells, inhibit cell adhesion, migration, invasion and angiogenesis. Further clinical trials in the area will help in drug development against the different diseases for which pharmacological activities are established through numerous studies.

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References

- Abdulhamid, A., Fakai, I. M., Sani, I., Argungu, A. U., & Bello, F. (2014). Preliminary phytochemical and antibacterial activity of ethanolic and aqueous stem bark extracts of *Psidium guajava*. *American Journal of Drug Discovery and Development*, 4(1):85–9. <https://doi.org/10.3923/ajdd.2014.85.89>
- Adamu, A. (2021). Phytochemical screening of guava leave extract. *International Journal of Pure and Applied Science Research*, 12(2), 89-95. Retrieved from: <https://www.arcnjournals.org/images/NRDA-IJPASR-12-1-8.pdf>. Accessed on 2nd March 2025.
- Alves, M. B., Vasconcelos, A. G., Silva de Carvalho, A. É., Slompo, R. C., Sá, B. S., Gonçalves, M. J. L., ... & Leite, J. R. D. S. D. A. (2023). Lycopene from Red Guava (*Psidium guajava* L.): From Hepatoprotective Effect to Its Use as Promising Self-Emulsifying Drug Delivery System for Anti-Inflammatory and Antioxidant Applications. *Pharmaceuticals*, 16(6). <https://doi.org/10.3390/ph16060905>
- Anand, V., Kumar, V., Kumar, S., & Hedina, A. (2016). Phytopharmacological overview of *Psidium guajava* Linn. *Pharmacognosy Journal*, 8(4). <https://doi.org/10.5530/pj.2016.4.3>

- Atik, N., Muda, I., Rahmadi, A. R., Achadiyani, A., & Djunaedi, D. D. (2019). Phytochemical screening and histology appearance of acute oral toxicity study on ethanol extract of *Psidium guajava* Linn. fruit in mice. *Asian Journal of Pharmaceutical and Clinical Research*, 12(1), 351-355. <https://doi.org/10.22159/ajpcr.2018.v12i1.30118>
- Barbalho, S. M., Farinazzi-Machado, F. M., de Alvares Goulart, R., Brunnati, A. C. S., Otoboni, A. M., & Ottoboni, B. J. M. A. P. (2012). *Psidium guajava* (Guava): A plant of multipurpose medicinal applications. *Med Aromat Plants*, 1(4), 1-6. <https://doi.org/10.4172/2167-0412.1000104>
- Basha, S. K., & Kumari, V. S. (2012). In vitro antidiabetic activity of *Psidium guajava* leaves extracts. *Asian Pacific Journal of Tropical Disease*, 2, S98-S100. [https://doi.org/10.1016/s2222-1808\(12\)60131-5](https://doi.org/10.1016/s2222-1808(12)60131-5)
- Birdi, T., Krishnan, G. G., Kataria, S., Gholkar, M., & Daswani, P. (2020). A randomized open label efficacy clinical trial of oral guava leaf decoction in patients with acute infectious diarrhoea. *Journal of Ayurveda and Integrative Medicine*, 11(2), 163-172. <https://doi.org/10.1016/j.jaim.2020.04.001>
- Chandra, S., Gahlot, M., Choudhary, A. N., Palai, S., de Almeida, R. S., de Vasconcelos, J. E. L., ... & Coutinho, H. D. M. (2023). Scientific evidences of anticancer potential of medicinal plants. *Food Chemistry Advances*, 2. <https://doi.org/10.1016/j.focha.2023.100239>
- D'mello, P., & Rana, M. (2010). Hepatoprotective activity of *Psidium guajava* extract and its phospholipid complex in paracetamol induced hepatic damage in rats. *International Journal of Phytomedicine*, 2(1). Retrieved from: <https://www.ijp.arjournals.org/index.php/ijp/article/view/22>. Accessed on 2nd March 2025.
- Dona, D. H. D. D., & Rajapakse, C. S. K. (2024). A Mini Review of the Antioxidant and Antimicrobial Activities and photoprotective properties of *Psidium guajava* L. *Oriental Journal of Chemistry*, 40(5). <http://dx.doi.org/10.13005/ojc/400505>
- El-Ahmady, S. H., Ashour, M. L., & Wink, M. (2013). Chemical composition and anti-inflammatory activity of the essential oils of *Psidium guajava* fruits and leaves. *Journal of Essential Oil Research*, 25(6), 475-481. <https://doi.org/10.1080/10412905.2013.796498>
- Ferlay J, Ervik M, Lam F, Laversanne M, Colombet M, Mery L, Piñeros M, Znaor A, Soerjomataram I, Bray F (2024). Global Cancer Observatory: Cancer Today. Lyon, France: International Agency for Research on Cancer. Retrieved from: <https://gco.iarc.who.int/today>. Accessed on 13th March 2025.
- Garrido, G., Garrido-Suárez, B. B., Martínez-Tapia, N., Valdés-González, M., & Ortega-Mardones, A. (2024). Antidiarrheal effect of *Psidium guajava* L. extract in acute diarrhea: a systematic review. *Journal of the Science of Food and Agriculture*, 104(13), 7731-7753. <https://doi.org/10.1002/jsfa.13515>
- Gashe, F., Belete, A., & Gebre-Mariam, T. (2010). Evaluation of antimicrobial and anti-inflammatory activities and formulation studies on the leaf extracts of *Psidium guajava* L. *Ethiop Pharm J*, 28, 131-42. <https://doi.org/10.4314/epj.v28i2.7>
- George, A. R., Thangasamy, K., & Geetha, N. (2025) *Psidium guajava* L. (Poor Man's Fruit)

- with Anticancer Potential: A Comprehensive Review. *Pomotherapeutic Insights on Wild Edible Fruits*, Editors: Parimelazhagan Thangaraj, Springer Singapore. Pg. 191-214. <https://doi.org/10.1007/978-981-96-0543-9>
- Gomes August, E. M., Horn, P. A., Cavichioli, N., Rebelo, A. M., Reinke, C. K., & Zeni, A. L. B. (2025). Seasonal Phenolic Profile, Antioxidant, and Photoprotective Activities of *Psidium guajava* L. Leaves. *Chemistry & Biodiversity*. <https://doi.org/10.1002/cbdv.202402852>
- Huang, J., Li, C., Ma, J., Xu, K., Chen, X., Jiang, J., & Zhang, D. (2021). Chemical constituents of *Psidium guajava* leaves and their antibacterial activity. *Phytochemistry*, 186. <https://doi.org/10.1016/j.phytochem.2021.112746>
- Joseph, B., Priya, R. M., Helen, P. M., & Sujatha, S. (2010). Bio-active compounds in essential oil and its effects of antimicrobial, cytotoxic activity from the *Psidium guajava* (L.) leaf. *J Adv Biotechnol*, 9, 10-4.
- Joshua, P. E., Iloka, O. C., Okeke, E. S., Aham, E. C., Oka, S. A., Onyemuche, T. N., & Nwodo, O. F. (2022). Antidiabetic and Hepatoprotective Effects of *Psidium guajava* L Fruit Puree on Alloxan-induced Diabetes in Wistar Rats. *Tropical Journal of Natural Product Research*, 6(5). <https://doi.org/10.26538/tjnpr/v6i5.22>
- Krishnarathi, A., Issac, S. S., & Kannan, M. (2014). Phytochemical analysis of selected plant leaves consumed by the folivory bats in Tirunelveli. *J. Environ. Appl. Biores*, 31, 14-18. Retrieved from: <https://api.semanticscholar.org/CorpusID:189857967>. Accessed on 12th March 2025.
- Lee, W. C., Mahmud, R., Pillai, S., Perumal, S., & Ismail, S. (2012). Antioxidant activities of essential oil of *Psidium guajava* L. leaves. *APCBEE Procedia*, 2, 86-91. <https://doi.org/10.1016/j.apcbee.2012.06.016>
- Li, Y., Xu, J., Li, D., Ma, H., Mu, Y., Huang, X., & Li, L. (2020). Guavinoside B from *Psidium guajava* alleviates acetaminophen-induced liver injury via regulating the Nrf2 and JNK signaling pathways. *Food & Function*, 11(9), 8297-8308. <https://doi.org/10.1039/d0fo01338b>
- Liu, C. W., Wang, Y. C., Lu, H. C., & Chiang, W. D. (2014). Optimization of ultrasound-assisted extraction conditions for total phenols with anti-hyperglycemic activity from *Psidium guajava* leaves. *Process Biochemistry*, 49(10), 1601-1605. <https://doi.org/10.1016/j.procbio.2014.06.009>
- Liu, C., Jullian, V., & Chassagne, F. (2024). Ethnobotany, phytochemistry, and biological activities of *Psidium guajava* in the treatment of diarrhea: a review. *Frontiers in Pharmacology*, 15. <https://doi.org/10.3389/fphar.2024.1459066>
- Lok, B., Babu, D., Tabana, Y., Dahham, S. S., Adam, M. A. A., Barakat, K., & Sandai, D. (2023). The Anticancer Potential of *Psidium guajava* (Guava) Extracts. *Life*, 13(2). <https://doi.org/10.3390/life13020346>
- Lu, J., Mao, D., Li, X., Ma, Y., Luan, Y., Cao, Y., & Luan, Y. (2020). Changes of intestinal microflora diversity in diarrhea model of KM mice and effects of *Psidium guajava* L. as the treatment agent for diarrhea. *Journal of Infection and Public Health*, 13(1), 16-26.

<https://doi.org/10.1016/j.jiph.2019.04.015>

- Mandal, A. K., Paudel, S., Pandey, A., Yadav, P., Pathak, P., Grishina, M., ... & Verma, A. (2022). Guava Leaf Essential Oil as a Potent Antioxidant and Anticancer Agent: Validated through Experimental and Computational Study. *Antioxidants*, 11(11). <https://doi.org/10.3390/antiox11112204>
- Metwally, A. M., Omar, A. A., Harraz, F. M., & El Sohafy, S. M. (2010). Phytochemical investigation and antimicrobial activity of *Psidium guajava* L. leaves. *Pharmacognosy Magazine*, 6(23). <https://doi.org/10.4103/0973-1296.66939>
- Meyrowitsch, D. W., & Bygbjerg, I. C. (2007). Global burden of disease-a race against time. *Dan Med Bull*, 54(1), 32-34. Retrieved from: <https://pubmed.ncbi.nlm.nih.gov/17349218/>, Accessed on 12th March 2025.
- Mohan, H., Sathya, P. M., Lee, S. W., Jeong, H. J., Ryu, S., Lee, A. H., & Oh, B. T. (2024). Enhanced health benefits of *Psidium guajava* peel fermented with *Lactiplantibacillus* from Myeolchi-jeot: Antioxidant, anti-inflammatory, and anti-cancer properties. *Food Bioscience*, 59. <https://doi.org/10.1016/j.fbio.2024.104211>
- Mukhtar, H. M., Ansari, S. H., Bhat, Z. A., Naved, T., & Singh, P. (2006). Antidiabetic activity of an ethanol extract obtained from the stem bark of *Psidium guajava* (Myrtaceae). *Die Pharmazie-An International Journal of Pharmaceutical Sciences*, 61(8), 725-727. Retrieved from: <https://pubmed.ncbi.nlm.nih.gov/16964719/>. Accessed on 12th March 2025.
- Naseer, S., Hussain, S., Naeem, N., Pervaiz, M., & Rahman, M. (2018). The phytochemistry and medicinal value of *Psidium guajava* (guava). *Clinical Phytoscience*, 4(1), 1-8. <https://doi.org/10.1186/s40816-018-0093-8>
- Oh, W. K., Lee, C. H., Lee, M. S., Bae, E. Y., Sohn, C. B., Oh, H., ... & Ahn, J. S. (2005). Antidiabetic effects of extracts from *Psidium Guajava*. *Journal of Ethnopharmacology*, 96(3), 411-415. <https://doi.org/10.1016/j.jep.2004.09.041>
- Oktavia, S. (2021). Potential anti-inflammatory effects of *Psidium guajava* L.: A review. *Asian Journal of Pharmaceutical Research and Development*, 9(2), 47-52. <https://doi.org/10.22270/ajprd.v9i2.941>
- Oncho, D. A., Ejigu, M. C., & Urgessa, O. E. (2021). Phytochemical constituent and antimicrobial properties of guava extracts of east Hararghe of Oromia, Ethiopia. *Clinical Phytoscience*, 7, 1-10. <https://doi.org/10.1186/s40816-021-00268-2>
- Porwal, V., Singh, P., & Gurjar, D. (2012). A comprehensive study on different methods of extraction from guajava leaves for curing various health problem. *International Journal of Engineering Research and Applications*, 2(6), 490-6. Retrieved from: https://www.ijera.com/papers/Vol2_issue6/BV26490496.pdf, Accessed on 12th March 2025.
- Prain, D. (1908). *Bengal Plants: A List of the Phanerogams, Ferns and Fern-Allies Indigenous to, or Commonly Cultivated in, the Lower Provinces and Chittagong, With Definitions of the Natural Orders and Genera, and Keys to the Genera and Species*, (Vol. 1). West, Newman and Company.

- Rahman, M. H., Asrafuzzaman, M., Tusher, M. M. H., Mosihuzzaman, M., Khan, M. S. H., Shoeb, M., & Rokeya, B. (2023). Elucidation of anti-hyperglycemic activity of *Psidium guajava* L. leaves extract on streptozotocin induced neonatal diabetic Long-Evans rats. *Journal of Ayurveda and Integrative Medicine*, 14(5), 100776. <https://doi.org/10.1016/j.jaim.2023.100776>
- Rai, P. K., Mehta, S., & Watal, G. (2010). Hypolipidaemic & hepatoprotective effects of *Psidium guajava* raw fruit peel in experimental diabetes. *Indian Journal of Medical Research*, 131(6), 820-824. Retrieved from: <https://pubmed.ncbi.nlm.nih.gov/20571173/>, Accessed on 12th March 2025.
- Rayjade Meghana, S., Bhambar R.S., & Attarde Daksha, L. (2021). A Review on Antimicrobial Activity of *Psidium guajava* L. leaves on different microbial species, antioxidant activity profile and herbal formulations. *Journal of Pharmaceutical Sciences and Research*, 13(7), 406-411. Retrieved from: <https://www.jpsr.pharmainfo.in/~ijcsitco/pharmainfo/jpsr/Documents/Volumes/vol13issue07/jpsr13072107.pdf>. Accessed on 13th March 2025.
- Ruksiriwanich, W., Khantham, C., Muangsanguan, A., Phimolsiripol, Y., Barba, F. J., Sringarm, K., ... & Sommano, S. R. (2022). Guava (*Psidium guajava* L.) leaf extract as bioactive substances for anti-androgen and antioxidant activities. *Plants*, 11(24), 3514. <https://doi.org/10.3390/plants11243514>
- Sanches, N. R., Garcia Cortez, D. A., Schiavini, M. S., Nakamura, C. V., & Dias Filho, B. P. (2005). An evaluation of antibacterial activities of *Psidium guajava* (L.). *Brazilian Archives of Biology and Technology*, 48, 429-436. <https://doi.org/10.1590/S1516-89132005000300014>
- Singh, S., Chidrawar, V. R., Hermawan, D., Nwabor, O. F., Olatunde, O. O., Jayeoye, T. J., ... & Chittasupho, C. (2023). Solvent-assisted dechlorophyllization of *Psidium guajava* leaf extract: Effects on the polyphenol content, cytocompatibility, antibacterial, anti-inflammatory, and anticancer activities. *South African Journal of Botany*, 158, 166-179. <https://doi.org/10.1016/j.sajb.2023.04.029>
- Tella, T., Masola, B., & Mukaratirwa, S. (2022). Anti-diabetic potential of *Psidium guajava* leaf in streptozotocin induced diabetic rats. *Phytomedicine Plus*, 2(2), 100254. <https://doi.org/10.1016/j.phyplu.2022.100254>
- Thenmozhi, S., & Rajan, S. (2015). GC-MS analysis of bioactive compounds in *Psidium guajava* leaves. *J Pharmacogn Phytochem*, 3(5), 162-6. Retrieved from: <https://www.phytojournal.com/archives/2015/vol3issue5/PartD/3-5-29.1.pdf>. Accessed on 12th March 2025.
- Uboh, F. E., Okon, I. E., & Ekong, M. B. (2010). Effect of aqueous extract of *Psidium guajava* leaves on liver enzymes, histological integrity and hematological indices in rats. *Gastroenterology Research*, 3(1), 32. <https://doi.org/10.4021/gr2010.02.174w>
- Velmurugan, S., Babu, M. M., Punitha, S. M. J., Viji, V. T., & Citarasu, T. (2012). Screening and characterization of antiviral compounds from *Psidium guajava* Linn. Root bark against white spot syndrome virus. *Indian Journal of Natural Products and Resources*, 3(2), 208-214. Retrieved from: <http://www.niscair.res.in>. Accessed on 12th March 2025.

- Vieira, R. H. S. D. F., Rodrigues, D. D. P., Goncalves, F. A., Menezes, F. G. R. D., Aragão, J. S., & Sousa, O. V. (2001). Microbicidal effect of medicinal plant extracts (*Psidium guajava* Linn. and *Carica papaya* Linn.) upon bacteria isolated from fish muscle and known to induce diarrhea in children. *Revista do Instituto de Medicina Tropical de Sao Paulo*, 43, 145-148. <https://doi.org/10.1590/s0036-46652001000300005>
- Vijayakumar, K., Arumugam, V. A., Ramasamy, M., Natesan, M., Palanisamy, S., Thajuddin, N. B., ... & Meyyazhagan, A. (2020). Hepatoprotective effects of *Psidium guajava* on mitochondrial enzymes and inflammatory markers in carbon tetrachloride-induced hepatotoxicity. *Drug Development and Industrial Pharmacy*, 46(12), 2041-2050. <https://doi.org/10.1080/03639045.2020.1843474>
- Wang, H., Du, Y. J., & Song, H. C. (2010). α -Glucosidase and α -amylase inhibitory activities of guava leaves. *Food Chemistry*, 123(1), 6-13. <https://doi.org/10.1016/j.foodchem.2010.03.088>
- Wang, L., Bei, Q., Wu, Y., Liao, W., & Wu, Z. (2017b). Characterization of soluble and insoluble-bound polyphenols from *Psidium guajava* L. leaves co-fermented with *Monascus anka* and *Bacillus* sp. and their bio-activities. *Journal of Functional Foods*, 32, 149-159. <https://doi.org/10.1016/j.jff.2017.02.029>
- Wang, L., Wu, Y., Bei, Q., Shi, K., & Wu, Z. (2017a). Fingerprint profiles of flavonoid compounds from different *Psidium guajava* leaves and their antioxidant activities. *Journal of Separation Science*, 40(19), 3817-3829. <https://doi.org/10.1002/jssc.201700477>
- World Health Organization. (2024). Diarrhoeal disease. Retrieved from: <https://www.who.int/news-room/fact-sheets/detail/diarrhoeal-disease>. Accessed on 12th March 2025.
- Yu, Y., Sun, X. Y., Xu, K. L., Ma, J., Zang, Y. D., Hou, Q., ... & Zhang, D. M. (2022). Meroterpenoids with unknown skeletons from the leaves of *Psidium guajava* including one anti-inflammatory and anticoagulant compound: psidial F. *Fitoterapia*, 159, 105198. <https://doi.org/10.1016/j.fitote.2022.105198>
- Zahin, M., Ahmad, I., & Aqil, F. (2017). Antioxidant and antimutagenic potential of *Psidium guajava* leaf extracts. *Drug and Chemical Toxicology*, 40(2), 146-153. <https://doi.org/10.1080/01480545.2016.1188397>
- Zheng, B., Zhao, Q., Wu, H., Wang, S., & Zou, M. (2020). A comparative metabolomics analysis of guava (*Psidium guajava* L.) fruit with different colors. *ACS Food Science & Technology*, 1(1), 96-106. Retrieved from: <https://pubs.acs.org/doi/10.1021/acsfoodscitech.0c00036>. Accessed on 12th March 2025.
- Zhu, X., Ouyang, W., Lan, Y., Xiao, H., Tang, L., Liu, G., ... & Cao, Y. (2020). Anti-hyperglycemic and liver protective effects of flavonoids from *Psidium guajava* L. (guava) leaf in diabetic mice. *Food Bioscience*, 35, 100574. <https://doi.org/10.1016/j.fbio.2020.100574>

Physico-Chemical Parameters for Checking Drinking Water Quality: A Review

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ABSTRACT

Water plays a crucial role in sustaining human life, as it is required for a variety of essential daily activities. However, water sources are increasingly polluted due to factors such as population growth, industrial expansion, modern agricultural techniques, and various human activities. Contaminated water becomes unsafe for consumption and other uses, making access to clean water critical for both public health and environmental preservation. The quality of water is typically evaluated through several physico-chemical parameters, including characteristics such as colour, temperature, pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), water hardness, acidity, alkalinity, and concentrations of substances like sulphate, chloride, Dissolved Oxygen (DO), Chemical Oxygen Demand (COD), and Biological Oxygen Demand (BOD). This study aims to provide an overview of the assessment of drinking water quality across various regions of India, employing a combination of these physico-chemical factors as well as the Water Quality Index (WQI) for a comprehensive evaluation.

Keywords: *Drinking Water; pH; Total Dissolved Solids; Water Hardness; Water Quality Index; Water Quality Parameters*

Introduction

Water is the most important natural resource for human survival. Not all water sources are suitable for drinking purposes. Water sources, particularly unimproved sources, are unhygienic not only due to contamination of heavy metals and other pollutants but also due to anthropogenic factors and natural factors such as climate, topography, flooding, weathering of parent material, and others that are also responsible for water pollution (Addisie, 2022). Water pollutants such as fertilisers and pesticides that are drained into rivers as agricultural run-off harm water resources. The water quality has affected tap water as well as groundwater due to inappropriate waste discarding and overutilization of resources (Nigam, Behl & Kanchan, 2013). The demand for fresh water remarkably increases due to population growth as well as the accelerated pace of industrialization. The availability of clean drinking water has become one of the most important necessities for human health. A little portion of water in the earth can be used for drinking purposes. Drinking water is now a global issue, as most of the fresh water bodies all over the world are getting contaminated, declining the portability of water.

Surface water, which is supplied in most of the cities in India by municipalities is unfit for direct consumption; more treatments are necessary for making surface water potable. According to the World Health Organisation, approximately 80% of human diseases are linked to contaminated or unsafe water (Dohare, Deshpande & Kotiya, 2014). Poor drinking water is responsible for some of the diseases, such as diarrhea, dysentery, polio typhoid, and cholera. In India, the presence of high fluoride concentrations in drinking water is a significant health concern, as prolonged consumption can lead to fluorosis, affecting both dental and skeletal systems. In India, different research teams are actively investigating water quality across different regions, using a range of instruments to analyse parameters like colour, temperature, pH, water hardness, alkalinity, acidity, chloride, sulphate, dissolved oxygen (DO), biological oxygen demand (BOD), and chemical oxygen demand (COD) (Jangamwar & Gahalod, 2025). This study provides a comprehensive review of physico-chemical parameters such as colour, temperature, pH, electrical conductivity, total dissolved solids (TDS), hardness, turbidity, total alkalinity, DO, BOD, and COD examined across different regions in India, along with an in-depth look into their testing methods, relevance, measurement techniques, and practical applications.

Literature Review

The Water Quality Index (WQI) is an effective tool used to evaluate the overall water quality in a specific region. It plays a crucial role in identifying potential pollution risks and provides a simplified representation of complex water quality data in the form of a single, easily understandable value. By integrating multiple water quality parameters into one comprehensive index, WQI offers insight into the suitability of water for various purposes such as drinking, agriculture, recreation, and industrial use. It serves as a clear indicator of the overall condition of water in a given area. In a study conducted by Kothari *et al.* (2021) the WQI was utilised to assess water quality across five districts in the Garhwal and Kumaon regions of Uttarakhand, India and they observed that the water quality was suitable for drinking purposes as the physico-chemical parameters were as per BIS standards. Dutta *et al.* (2022) reported WQI to evaluate water quality parameters in the South Sikkim district of India, located in the Eastern Himalayan region. Water scarcity has emerged as a significant concern in certain areas of South Sikkim, primarily due to the rapid development of the tourism industry. As a result, local residents are struggling to access sufficient spring water and are increasingly relying on alternative sources such as surface water and rainwater. The study analysed various physico-chemical parameters, including pH, hardness, turbidity, alkalinity, iron, fluoride, chloride, and nitrate using standard methods. The results indicated that the water is generally safe for drinking. Surface water in the study area was classified into two categories based on WQI values: "excellent" and "good" quality (Dutta *et al.*, 2022). Similarly, Gaur *et al.* (2022) collected water samples from 31 sites in Tawang, Arunachal Pradesh, India, to evaluate the suitability of water for

drinking during the winter season. Their study employed WQI estimation, considering key parameters such as pH, conductivity, TDS, salinity and hardness, as well as major cations and anions. The findings revealed that geogenic factors significantly influence water quality in the Tawang region. Based on WQI values, 61% of the water samples were deemed suitable for drinking, while the remaining 39% were classified as unfit for consumption. (Gaur *et al.*, 2022). Prasad *et al.* (2019) conducted an assessment of drinking water quality in Obulavaripalli Mandal, located in YSR District, Andhra Pradesh, using the Water Quality Index (WQI) approach. The evaluation of groundwater samples revealed that the overall quality of the groundwater in the area falls below the acceptable standards for safe drinking purposes, with only 30% of the samples classified as "excellent", 40% as "good", and the remaining 30% falling into the "poor" category (Prasad *et al.*, 2019). Tetali, Salomi and Gope, (2024) carried out an in-depth evaluation of key water quality parameters, including pH, total dissolved solids (TDS), turbidity, acidity, and hardness, across a range of water sources such as ponds, canals, borewells, lakes, rivers, seawater, and tap water. The study identified considerable variations among the samples, with several values diverging from the recommended standards. For example, pH levels were found to range between 6.81 and 8.33, TDS values spanned from 93 ppm in rainwater to 815 ppm in borewell water, and water hardness levels ranged from soft to extreme. Additionally, turbidity in all samples surpassed the acceptable limit of 0.3 NTU. These results demonstrate the value of implementing tailored water treatment solutions for different sources to safeguard drinking water quality and mitigate potential health hazards (Tetali, Salomi & Gope, 2024). Singh and Yadav reviewed the key physico-chemical parameters used in water quality assessments, discussing their definitions and explaining their effects on human and plant life. They also described the methodologies used to measure each parameter, emphasizing their importance in determining water quality (Singh & Yadav, 2022). Jangamwar and Gahalod provided a detailed review of various parameters for assessment of drinking water by the key tests of physical characteristics such as colour, temperature, pH, TDS, electrical conductivity, COD, and BOD, with providing a comprehensive understanding of their significance, test procedures, measurement techniques, and applications (Jangamwar & Gahalod, 2025).

Physico-Chemical Parameters

The presence of clean and high-quality water plays a crucial role in reducing the risk of disease and improving overall health and living standards. To effectively evaluate water quality, it is important to analyse key physico-chemical parameters such as colour, temperature, pH, hardness, alkalinity, acidity, chloride, sulphate, dissolved oxygen (DO), biological oxygen demand (BOD), and chemical oxygen demand (COD). Preliminary information, including temperature, colour, odour, pH, and turbidity, can be obtained through physical testing, while chemical analyses are required to determine parameters such as dissolved oxygen, alkalinity, hardness, BOD, COD, and other

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characteristics. This review provides a detailed description of these parameters, and the methods used to determine them are summarised in Table 1.

Parameters	Methods Employed	Bureau of Indian Standard (BIS)	World Health Organization (WHO)
p ^H	p ^H metery	6.5-8.5	6.5-9.5
Electrical Conductivity	Conductometry	300	-
Total Dissolved Solid	Conductometry	500	-
Total Hardness	Complexometry	300 ppm	200 ppm
Turbidity	Turbiditimetry	5 NTU	-
Total Alkalinity	Titrimetry	200 ppm	-
Chloride	Argentometry	250	250
DissolvedOxygen	Winkler method	4 mg/l	-
Biochemical Oxygen Demand	Incubation followed by titration	30	6
Chemical Oxygen Demand	COD digester	-	10

Discussion

Temperature

Water temperature is a key physical parameter that influences chemical reaction rates and biological processes such as growth, reproduction, decay, mineralisation, and production (Nigam, Behl & Kanchan, 2013). It also affects the health of aquatic ecosystems and drives seasonal and diurnal variations. The BOD, sedimentation and chlorination processes are temperature dependent. Typically, normal water source temperature is influenced by geographic position and water depth whereas temperature may be affected by chemical discharges in industrial or urban water sources. The temperature is measured using a thermometer (Jangamwar & Gahalod, 2025).

Colour

The color of the water is primarily caused by the presence of inorganic substances such as soil, stones, and rocks, organic matter, namely, vegetation as well as industrial waste also contributes to colour of water. This colour is classified into two categories, viz., true colour and apparent colour. True colour is measured after filtering all the suspended components in water whereas apparent colour is colour due to reflection of sky or trees. Colours are graded from 0 (pure water) to 70 colour units. Pure water is colourless.

pH

pH is a key parameter in evaluating water quality, as it reflects the concentration of hydrogen ions in the water, which determines its acidity or alkalinity. The pH scale spans from 0 to 14: values under 7 indicate acidic conditions, values above 7 suggest alkalinity, and a pH of 7 signifies neutral water. As the pH increases, conditions become more basic; as it decreases, the water becomes more acidic. The acceptable pH range for drinking water is between 6.5 and 8.5, as recommended by BIS. The higher pH value can cause scale build up on pipes while lower pH can release metals like lead or copper into the water due to corrosion of pipes. Both acidic and alkaline water conditions can influence the taste and appearance of water and may have significant health

implications. The pH is measured using a pH meter (Jangamwar & Gahalod, 2025).

Electrical Conductivity (EC)

Electrical Conductivity (EC) is an important indicator of water quality, as it measures an aqueous solution's ability to conduct electrical current. This conductivity is directly influenced by the presence and concentration of dissolved ions, which act as carriers of electric charge in the solution. The recommended maximum limit for EC in drinking water is 300 $\mu\text{S}/\text{cm}$. It is measured using a conductivity meter calibrated with a standard KCl solution, providing insight into the concentration of soluble salts in the water. The conductivity of distilled water is typically less than 1 $\mu\text{S}/\text{cm}$, due to the very low concentration of dissolved ions (Nigam, Behl & Kanchan, 2013).

Total Dissolved Solid (TDS)

Total Dissolved Solids (TDS) are closely linked to both the purity and overall quality of water. TDS gives information about minerals, salts, and organic compounds that are dissolved in water and it reflects the sum of all ions present, giving a sense of the mineral and chemical composition of the water. Salty or metallic taste refers to high TDS levels in drinking water. Very high TDS levels can be undesirable or even unsafe, as they affect water's suitability for industrial, agricultural, and personal uses. TDS is commonly measured in mg/L or parts per million (ppm) with the help of a TDS meter, which indirectly measures the electrical conductivity of the water and then calculates an approximate TDS value. TDS can also be measured using gravimetric methods, which involve evaporating the water sample and weighing the residual solids left behind in the laboratory. According to IS: 10500-2012 standards, the acceptable limit for TDS in drinking water is 500 mg/l, while the maximum permissible limit is 2000 mg/l (BIS, 2012).

Total Hardness

Hardness is commonly used as an indicator of water quality. In groundwater, hardness is primarily caused by the presence of calcium and magnesium salts in the form of carbonates, bicarbonates, sulphates, and chlorides. It is typically measured using the complexometric titration method with EDTA, which binds to calcium and magnesium ions responsible for hardness. According to drinking water standards, the total hardness should not exceed 300 mg/l expressed as CaCO_3 . Based on the classification by Durfor and Becker (1964), water hardness levels are categorised as follows: soft (0–60 mg/l), moderately hard (60–120 mg/l), hard (120–180 mg/l), and very hard (above 180 mg/l).

Turbidity

Turbidity is the cloudiness of water in which suspended particles interfere with the route of light. Turbidity refers to the clarity of water and is influenced by the presence of

suspended particles like clay, silt, organic substances, plankton, and other materials that scatter or absorb light, reducing its ability to pass through the water. The greater the concentration of these particles, the higher the turbidity, as light transmission becomes more difficult. Turbidity is measured using Turbidimetry (based on light transmission) or Nephelometry (based on light scattering). According to IS: 10500-2012 standards, the recommended turbidity level for drinking water is 1 NTU, while the maximum allowable limit is 5 NTU (Dohare, Deshpande & Kotiya, 2014).

Total Alkalinity

Alkalinity refers to the overall concentration of compounds in water that raise its pH and indicate its ability to neutralise acids. It mainly reflects the presence of carbonate, bicarbonate, and hydroxide ions, which serve as natural buffers by reducing excess hydrogen (H^+) ions, thereby making the water more alkaline. Alkalinity is commonly determined through titration using a standard acid until the pH reaches 4.5, and the results are typically reported in milligrams per litre as calcium carbonate (mg/L as $CaCO_3$). For drinking water, the acceptable alkalinity limit is 120 mg/L.

Chloride

Chloride is a key parameter in evaluating drinking water quality, as elevated levels can indicate a higher degree of organic pollution. While chloride naturally occurs in groundwater, streams, and lakes, concentrations above 250 mg/L in freshwater may signal contamination from industrial or domestic sources. Chloride levels in water are usually determined using a precipitation titration method, where standard silver nitrate is used along with potassium chromate as an indicator. The highest allowable concentration of chloride in drinking water is 250 mg/L, as levels above this threshold may lead to a laxative effect (Nigam, Behl & Kanchan, 2013).

Dissolved Oxygen (DO)

Dissolved oxygen (DO) is a crucial parameter for assessing water quality, as it is necessary for the respiration and survival of fish and other aquatic life. DO levels are influenced by both natural factors (such as water temperature, stream flow, and photosynthesis) and human activities within the catchment area. Warmer water holds less oxygen than cooler water, making temperature a key factor in DO availability. DO concentration indicates the quantity of oxygen gas present in water, usually measured in milligrams per litre (mg/L) or parts per million (ppm).

Biochemical Oxygen Demand (BOD)

Biochemical Oxygen Demand (BOD) quantifies the amount of oxygen utilised by microorganisms to decompose organic materials in water. Elevated BOD levels are a sign of degraded water quality, indicating substantial organic contamination that can reduce oxygen availability and negatively impact aquatic organisms (Singh & Yadav,

2022). The greater the BOD, the more organic material is present for microbes to decompose. For drinking water, a low BOD is desirable, as it reflects minimal organic contamination. BOD is determined by measuring the dissolved oxygen in a freshwater sample and comparing it to that in a duplicate sample, which is incubated under controlled conditions for several days. The difference in oxygen levels is expressed in milligrams per litre (mg/L).

Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) quantifies the amount of oxygen required to chemically oxidise both organic and inorganic substances in a water sample. It serves as an important indicator of water pollution. High COD values suggest a high concentration of oxidisable pollutants such as organic matter and certain inorganic compounds, indicating significant contamination. COD measures the total oxygen needed to break down all organic matter into carbon dioxide and water. While COD values are generally higher than BOD values, the COD test is much quicker, taking only a few hours, compared to the five days needed for BOD measurement.

Conclusion

Physico-chemical parameters such as colour, temperature, pH, hardness, alkalinity, acidity, chloride, sulphate, dissolved oxygen (DO), biochemical oxygen demand (BOD), and chemical oxygen demand (COD) play a crucial role in assessing drinking water quality, as they are vital for ensuring its safety and suitability for consumption. This study provides a comprehensive review of the evaluation of these parameters in drinking water across India. Most of the results were found to be within the recommended limits set by the Bureau of Indian Standards (BIS), particularly in the Eastern Himalayan region and Uttarakhand, where the water was deemed suitable for drinking.

However, 39% of the samples collected from Arunachal Pradesh were found to be unfit for consumption. In some instances, electrical conductivity, turbidity, and total dissolved solids either exceeded or were close to exceeding the BIS recommended limits, suggesting the presence of suspended particles and elevated ion concentrations. The Water Quality Index (WQI) has been used to classify the overall water quality in most cases. This review also demonstrates the importance, measurement techniques, procedures and applications of the above-mentioned physico-chemical parameters as due to increasing urbanisation and population growth, surface water as well as groundwater is getting over contaminated and more stringent treatments would be required to get drinking water.

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References

- Addisie, M. B. (2022). Evaluating drinking water quality using water quality parameters and esthetic attributes. *Air, Soil and Water Research*, 15. <https://doi.org/10.1177/11786221221075005>
- BIS. (2012). 10500 Indian standard drinking water–specification, second revision. *Bureau of Indian Standards, New Delhi*. Retrieved from: <https://law.resource.org/pub/in/bis/S06/is.10500.2012.pdf>. Accessed on 5th January 2025.
- Dohare, D., Deshpande, S., & Kotiya, A. (2014). Analysis of ground water quality parameters: A review. *Research Journal of Engineering Sciences ISSN*, 2278, 9472.
- Durfor, C. N., & Becker, E. (1964). *Public water supplies of the 100 largest cities in the United States, 1962 (No. 1812)*. US Government Printing Office.
- Dutta, N., Thakur, B. K., Nurujjaman, M., Debnath, K., & Bal, D. P. (2022). An assessment of the water quality index (WQI) of drinking water in the Eastern Himalayas of South Sikkim, India. *Groundwater for Sustainable Development*, 17. <https://doi.org/10.1016/j.gsd.2022.100735>
- Gaur, N., Sarkar, A., Dutta, D., Gogoi, B. J., Dubey, R., & Dwivedi, S. K. (2022). Evaluation of water quality index and geochemical characteristics of surfacewater from Tawang India. *Scientific Reports*, 12(1). <https://doi.org/10.1038/s41598-022-14760-3>
- Jangamwar, R. R., & Gahalod, A. (2025). A review on Various parameters for assessment of drinking water quality. *International Research Journal of Engineering and Technology*, 12(1), 629-634. Retrieved from: <https://www.irjet.net/archives/V12/i1/IRJET-V121195.pdf>, Accessed on 5th January 2025.
- Kothari, V., Vij, S., Sharma, S., & Gupta, N. (2021). Correlation of various water quality parameters and water quality index of districts of Uttarakhand. *Environmental and Sustainability Indicators*, 9. <https://doi.org/10.1016/j.indic.2020.100093>
- Nigam, V., Behl, N., & Kanchan, M. C. (2013). Physicochemical parameters for testing of water-a review. *Int J Pharmacy Biological Sci*, 3(3), 523-527.
- Prasad, M., Sunitha, V., Reddy, Y. S., Suvarna, B., Reddy, B. M., & Reddy, M. R. (2019). Data on water quality index development for groundwater quality assessment from Obulavaripalli Mandal, YSR district, AP India. *Data in Brief*, 24. <https://doi.org/10.1016/j.dib.2019.103846>
- Tetali, R. R., Salomi, K., & Gope, E. R. (2024). Analysis of Water Quality Parameters Across Diverse Sources. *Journal of Pharma Insights and Research*, 2(3), 210-216. <https://doi.org/10.69613/3jxm7e23>
- World Health Organization. (2002). Guidelines for Drinking-Water Quality. 2nd Edition. World Health Organization.
- Yadav, R., & Singh, M. (2022). Physico-Chemical Parameters for Water Quality Check: A Comprehensive Review. *International Journal of Research and Analytical Reviews*, 9(4), 287-293. Retrieved from: https://www.academia.edu/97844297/Physico_Chemical_Parameters_for_Water_Quality_Check_A_Comprehensive_Review. Accessed on 5th January 2025.

Influence of Magnetic Field on Electron Transfer Reaction in Homogeneous Medium

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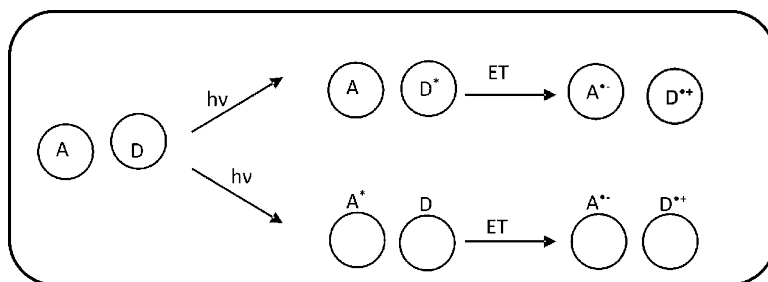
ABSTRACT

The influence of an external magnetic field has energetically very little effect on any reaction. However, during electron transfer reactions, unpaired electrons are generated in the reaction pathway that are susceptible to external magnetic fields. So to understand the mechanism of a reaction, an external magnetic field can be used. To retain the spin correlation between the radicals, either a confined medium like a micelle is required, or the radicals must be covalently attached to each other. However, in the current systems, the radicals are not found in a confined system or covalently bonded; instead, they are attached to each other through non-covalent weak interactions, such as excited-state hydrogen bonding, electrostatic forces of interaction, and hydrophobic interactions. Hence, in such systems, the influence of the magnetic field is watched in a homogeneous medium; that is a rare observation in literature.

Keywords: *Electron Transfer Reactions; Homogeneous; Magnetic Field*

Introduction

The primary reaction on earth, i.e., photosynthesis, which converts solar energy to a utilisable form, involves an electron transfer (ET) process (Stryer, 1999). For many years, scientists were haunted by the challenge of discovering the mechanisms behind the efficiency and control of photosynthesis pathways and various biological processes to replicate those reactions artificially. Photoinduced electron transfer (PET) is one of the fundamental processes in chemistry and biology (Marcus & Sutin, 1985). The most unique aspect of PET is the conversion of light energy into chemical potential. Due to the ubiquitous nature and wide applications of PET reactions,



Scheme 1: A Simplified Outline of the PET Reaction

understanding and controlling them comprise one of the broadest and most flourishing areas of research today.

The PET phenomenon involves photoexcitation of either an electron-rich species (donor, D) or an electron-deficient species (acceptor, A) prior to ET. The following scheme 1, elucidates the process:

The ET between the donor and the acceptor may occur in the singlet state (just immediately after excitation) or may occur in the triplet state (after intersystem crossing from the singlet state). The spin multiplicity of the electron in the excited state is generally conserved during electron transfer, and the memory of this initial spin multiplicity is preserved in the resulting RIP. The nature of the product will depend on its initial spin state; e.g., a singlet-born RIP favours recombination, while a triplet-born RIP prefers escape. However, the spin multiplicity of RIP is not stationary and can coherently evolve between S and T configurations. After the generation of a PET radical ion pair (RIP) or radical pair (RP) that contains unpaired electrons, these pairs become susceptible to an external magnetic field (Gould, Turro & Zimmt, 1984). An applied magnetic field thus alters the fate of the PET reaction by influencing this spin evolution, though it contributes negligibly to the chemical energy.

Photoinduced Electron Transfer Reaction in the Presence of an External Magnetic Field

Immediately after the electron transfer, the new RIP/RPs are sufficiently close so that the singlet-triplet energy difference is significant, making singlet-triplet interconversion impossible. After several diffusive motions, RIP/RPs move apart so that the exchange interaction becomes negligible and singlet-triplet interconversion occurs. On application of an external magnetic field, the degeneracy of the triplet state breaks down, and only the T_0 state remains degenerate with the singlet state, and so intersystem crossing between the $S \rightarrow T_{\pm}$ states no longer remain feasible. Thus, in the presence of a magnetic field, the population of the RIP/RPs increases whether electron transfer occurs in the singlet or triplet state, as spin flipping is required for the $S \rightarrow T_{\pm}$ state, which needs much time and energy. Hence, this study is very crucial in the identification of the RIP/RPs as well as determining the actual mechanistic pathway of an electron transfer reaction, i.e., whether the electron transfer occurs in a singlet or triplet state. Moreover, this method needs optimal closeness between the RIP/RPs, where the exchange integral becomes zero. Excessive closeness between RIP/RPs prevents $S \leftrightarrow T$ inter-conversion due to a significant energy difference from exchange interaction, whereas increased separation between RIP/RPs disrupts the spin correlation. If the donor and acceptor molecules are not covalently linked, then observation of such an effect needs a confined medium like micelles, reverse micelles or vesicles, or a highly viscous solvent at low temperature. In a homogeneous medium, the RIP/RPs disperse more quickly, leading to the rapid disappearance of the spin

correlation between them. In confined systems, after electron transfer occurs, the non-covalently bound RIP/RP can separate slightly due to solvation, resulting in a solvent-separated ion pair where exchange interaction is negligible and intersystem crossing can occur. Hence, due to confinement, the RIP/RPs cannot move far apart where spin correlation is lost. However, non-covalent weak interactions like hydrogen bonding in ground or excited states, electrostatic forces of interaction, stacking, etc., often play a vital role in keeping spin correlation between RIP/RPs. In this review, a few such examples are highlighted, where non-covalent interactions are responsible for maintaining spin correlation in a homogeneous medium.

Radical Ions Associated Through Excited-State Hydrogen Bonding

In its first excited state, Dibenzo[a,c]phenazine (DBPZ) (figure 1) forms hydrogen bonds with various hydrogen bond donating solvents (Dey *et al.*, 2007a), a phenomenon that does not occur in its ground state. Upon photoexcitation, the dipole moment of Dibenzo[a,c]phenazine (DBPZ) increases abruptly, resulting in strong hydrogen bonding through its nitrogen atoms. However, the two nitrogen atoms are not very approachable by other molecules due to the presence of hydrogen atoms at 1 and 8 positions. Alcohols with bulkier alkyl groups make less successful hydrogen bonding with DBPZ. Thus, the most efficient excited-state hydrogen bonding is formed with water molecules. This phenomenon is reflected by the enhancement of its fluorescence intensity, with a concomitant red shift from 420 nm to 500 nm compared to non-hydrogen-bonded species in acetonitrile (Figure 2). In the presence of organic amines, photo-induced electron transfer occurs from the amines to DBPZ, resulting in the formation of a radical cation.

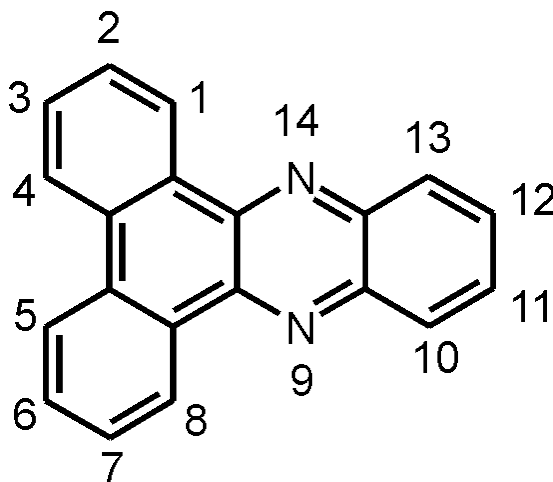


Figure 1: Molecular Structure of DBPZ

The amine and the radical anion of DBPZ are clearly identified in polar solvents, such as acetonitrile (Dey *et al.*, 2007b). However, in an acetonitrile-water mixture, those

radical ions remain attached to each other via excited-state hydrogen bonding and show greater intensity in transient absorption spectra in the presence of an external magnetic field. This finding suggests that in the excited state $\text{DBPZ}^{\bullet+}\text{-H}_2\text{O-Amine}^{\bullet-}$ remains similar to a linked system via intervening water molecules and shows spin correlation among radical ions even in a homogeneous medium.

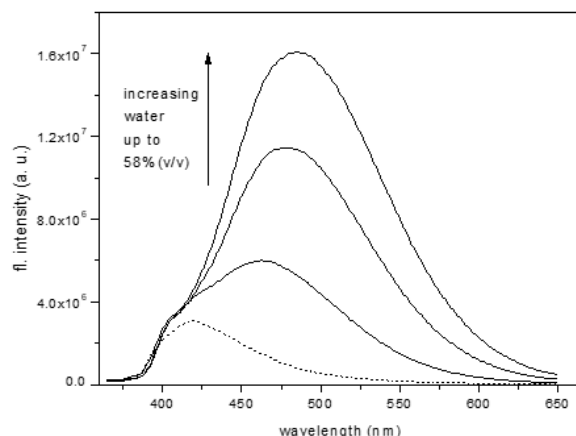


Figure 2: Steady-State Fluorescence Spectra of DBPZ (1×10^{-5} M) ($\lambda_{\text{ex}} = 350$ nm) in Acetonitrile With Increasing Amounts of Water: 0% (---), 23%, 48%, and 58% (Dey et al., 2007a)

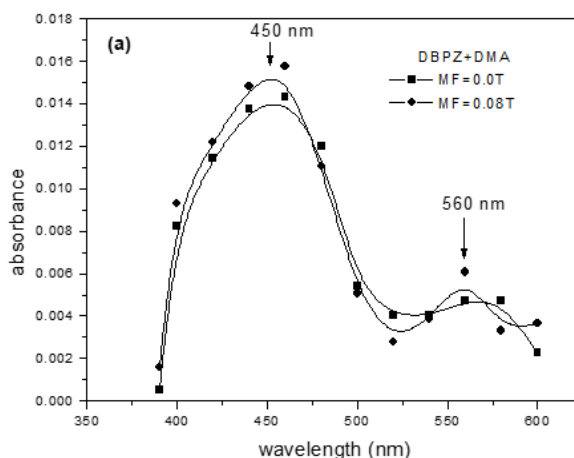


Figure 3: Triplet Transient Absorption Spectra of DBPZ (5×10^{-5} M) - DMA (2.5×10^{-3} M), in Acetonitrile/H₂O Mixture in Absence (■) and Presence (●) of 0.08 T MF at a delay of 0.6 ms After the Laser Flash (Dey et al., 2007b)

Radical Ions Associated through Non-covalent Weak Interaction

Photoinduced electron transfer reactions are of immense importance in nature, especially during photosynthesis. In living systems, there are innumerable enzymatic reactions that involve electron transfers. Scientists have tried to imitate those in

various environments. The evidence reveals that during the electron transfer reactions, the non-covalent weak interactions, e.g., hydrogen bonding in the ground state, electrostatic attractions, and aromatic ring stacking, etc., play a significant role in maintaining the required distance of separation between the donor and acceptor. They are often present in various drug and DNA interactions and secondarily undergo electron transfer among them. Interaction of transition metal complexes with DNA has attracted scientists since the discovery of cis-platin as an anti-cancer drug. Transition metal complexes primarily interact with double-stranded DNA through electrostatic forces and also undergo electron transfer. Electron transfer among metal complexes and nucleic acids is often initiated by photoinduction. Transition metal complexes with a planar ligand(s) often interact with the base pairs of calf thymus DNA (CT DNA), possibly through partial intercalation. Initially the positively charged complex and the poly-negatively charged DNA come closer due to the electrostatic force of interaction. Then, the insertion of the planar hydrophobic ligand into the DNA base pairs results in partial intercalation, which refers to the attachment of the DNA and the metal complex through non-covalent weak interactions.

In living systems, many proteins undergo electron transfer reactions. The constituent amino acids of the peptides, viz. cysteine, phenylalanine, tyrosine, tryptophan, etc., can act as intermediate charge carriers. These amino acids especially facilitate long-range electron transfer. Amino acids with aromatic side chains are particularly suitable for these phenomena. During long-range electron transfers, the radical ions of tryptophan, phenylalanine, and tyrosine are recognised. Moreover, they have a planar side chain for which they can also participate in non-covalent weak interactions like stacking.

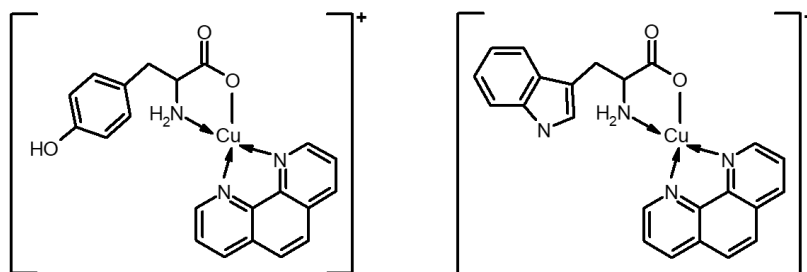


Figure 4: Schematic Diagram of Complex (1) and Complex (2)

It has been observed that tyrosine involves proton-coupled electron transfer in ribonucleotide reductase and oxidises cysteine residues almost 35 Å away via multiple aromatic residues (McCaslin *et al.*, 2019). Very recently it has been found that when Cu^{2+} is exchanged with redox inactive Zn^{2+} in blue copper protein azurin, a neutral tryptophyl radical is formed with a longer lifetime (Rivera, Trinh & Kim, 2022). Hence, the study of ternary metal complexes comprising aromatic amino acids, e.g., tyrosine and tryptophan, and a second ligand which contains a planar moiety such as '2,2'-bipyridyl or 1,10-

phenanthroline, is important to understand the electron transfer reactions between the amino acid and heterocyclic molecules in aqueous solution.

$[\text{Cu}(\text{phen})(\text{Htrp})]^+$ (1), $[\text{Cu}(\text{phen})(\text{Htyr})]^+$ (2) (phen: 1,10 phenanthroline; Htrp: tryptophan; Htyr: tyrosine) Both complexes contain a planar phen ligand that interacts with DNA through partial intercalation (Dey, Pramanik & Basu, 2009; Dey & Basu, 2011). This partial intercalation can be proved by a quenching study with ethidium bromide (EtBr), a known intercalator of the DNA double helix. The fluorescence intensity of EtBr increases many times when it intercalates between the DNA base pairs compared to the free molecule in aqueous medium. On addition of both the complexes, the fluorescence intensity of DNA intercalated EtBr decreases, suggesting that both complexes can displace EtBr from DNA base pairs and itself interact with the nucleic acid (figure 4).

On photoexcitation, the amino acid complexes (1) and (2) undergo intra-molecular electron transfer from amino acid to phen ligand, resulting in $\text{phen}^{\bullet+}$, $\text{trp}^{\bullet+}$, and $\text{tyr}^{\bullet+}$ radical ions. As phen and amino acids are both covalently attached to copper, the radical ions remain spin correlated for a longer time and show greater transient absorption in the presence of an external magnetic field (Scheme 1).

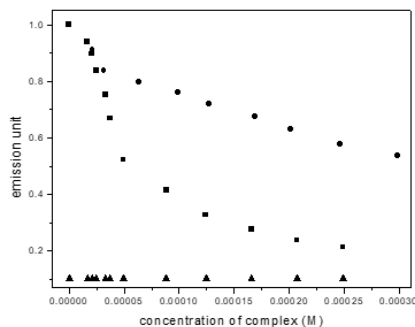
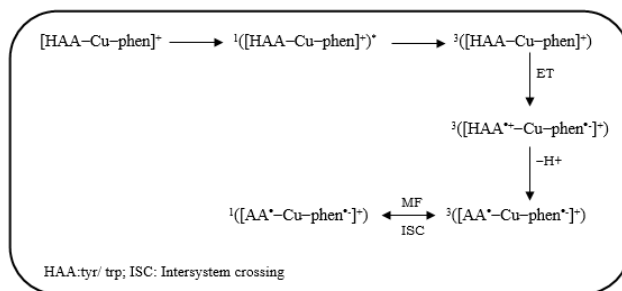
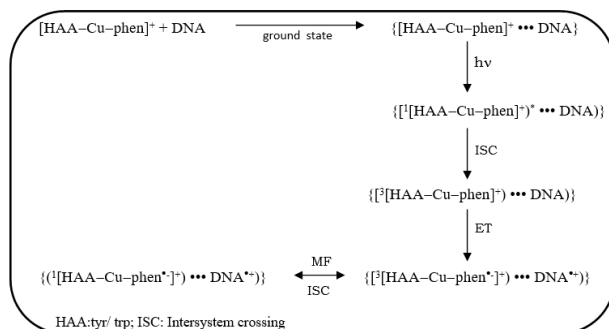


Figure 5: Fluorescence Quenching of EtBr (4.5 μM) Bound to CT DNA (100 μM) at Different Complex (1) (●) and (2) (■) Concentrations (λ_{ex} = 512 nm)

The intrinsic fluorescence of EtBr is not quenched with the concentration of both complex (1) and (2) (▲)



Scheme 1: Mechanism for Photoinduced Intramolecular ET within the Complexes (Dey, Pramanik & Basu, 2009; Dey & Basu, 2011)



Scheme 2: Illustrates the Mechanism for Photoinduced Intermolecular Electron Transfer (ET) Between DNA and the Specified Complexes (Dey, Pramanik & Basu, 2009; Dey & Basu, 2011)

In the CT DNA-bound copper complexes, the electron transfer occurs from the guanine base (G) instead of the amino acids to phen^{•+} at first, giving rise to G^{•+} and phen^{•+} for both the complexes. Thus, primarily the electron donor is guanine instead of amino acids. The reduction potential of guanosine radical is 1.29 v, considerably higher than both tryptophan (1.01 v) and tyrosine (0.9 v). It has been well investigated that DNA damage can be repaired by proteins. More specifically, amino acids that are susceptible to redox reactions, like cysteine and tyrosine, play an important role in this aspect. Theoretical studies using density functional theory also revealed that radiation- induced DNA damage can be recovered by amino acids of proteins (Jena, Mishra & Suhai, 2009). Milligan *et al.* (2003) reported that in oxidative damage guanyl radicals are produced in plasmid DNA. Derivatives of cysteine, methionine, tyrosine and tryptophan react and repair the guanyl radical in plasmid with a time scale ranging from 10⁵ to 10⁷ dm³ mol⁻¹ s⁻¹. For the copper complexes also, there is a possibility of repairing the guanyl radical by the amino acid. The repair of the radicals will take a longer time, within which the radicals will separate out, forming individual solvent- separated ion pairs. In other words, the geminate characteristics of the primarily produced radicals will be lost. For such an e, an external magnetic field cannot have any influence on the RIP/RPs. Actually, a prominent increase in transient absorption spectra was observed for primarily generated G^{•+} and phen^{•+} radical ions only (scheme 2). No influence of an external magnetic field was observed for the time-delayed repaired radicals.

Conclusion

The RIP/RP produced during electron transfer bears free electrons and is susceptible to external magnetic fields. After generation, the RIP/RP undergo diffusive movement, and when they are separated by a certain distance, the exchange interaction between them becomes negligible, allowing for S $\leftrightarrow$ T intersystem crossing to occur. If an external magnetic field is applied under such conditions, the T state splits into T₊, T₀, and T₋, making intersystem crossing possible only between S and T₀. Thus, whether the electron transfer occurs in a singlet or triplet state, the forbidden intersystem between S

and $T_{\pm}$ increases the population of the RIP/RP in their initial spin state. This increment in RIP/RP population is reflected as greater transient absorption of the RIP/RPs. In a homogeneous medium, if the donor and acceptor are not covalently bound, the RIP/RPs move apart and become separately solvated, which causes them to lose their geminate characteristics; consequently, no change occurs in the presence of a magnetic field. In this review excited- state hydrogen bonding and non-covalent weak interactions (electrostatic force of interaction and intercalation) are responsible for keeping the geminate characteristics of the RIP/RPs even in a homogeneous medium, which is a rare observation in literature.

Acknowledgement

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References

- Dey, D., & Basu, S. (2011). Direct observation of radical intermediates during electron transfer between DNA and a ternary copper complex. *Journal of luminescence*, 131(4), 732-738. <https://doi.org/10.1016/j.jlumin.2010.11.027>
- Dey, D., Bose, A., Bhattacharyya, D., Basu, S., Maity, S. S., & Ghosh, S. (2007a). Dibenzo [a, c] phenazine: a polarity-insensitive hydrogen-bonding probe. *The Journal of Physical Chemistry A*, 111(42), 10500-10506. <https://doi.org/10.1021/jp0731811>
- Dey, D., Bose, A., Chakraborty, M., & Basu, S. (2007b). Magnetic field effect on photoinduced electron transfer between dibenzo [a, c] phenazine and different amines in acetonitrile– water mixture. *The Journal of Physical Chemistry A*, 111(5), 878-884. <https://doi.org/10.1021/jp0661802>.
- Dey, D., Pramanik, N. R., & Basu, S. (2009). Exploring the mechanism of electron transfer between DNA and a ternary copper complex. *The Journal of Physical Chemistry B*, 113(25), 8689-8694. <https://doi.org/10.1021/jp810778b>
- Gould, I. R., Turro, N. J., & Zimmt, M. B. (1984). Magnetic field and magnetic isotope effects on the products of organic reactions. *Advances in Physical Organic Chemistry*, 20, 1-53. [https://doi.org/10.1016/S0065-3160\(08\)60147-1](https://doi.org/10.1016/S0065-3160(08)60147-1)
- Jena, N. R., Mishra, P. C., & Suhai, S. (2009). Protection against radiation-induced DNA damage by amino acids: a DFT study. *The Journal of Physical Chemistry B*, 113(16), 5633-5644. <https://doi.org/10.1021/jp810468m>
- Marcus, R. A., & Sutin, N. (1985). Electron transfers in chemistry and biology. *Biochimica et Biophysica Acta (BBA)-Reviews on Bioenergetics*, 811(3), 265-322. [https://doi.org/10.1016/0304-4173\(85\)90014-X](https://doi.org/10.1016/0304-4173(85)90014-X)
- McCaslin, T. G., Pagba, C. V., Hwang, H., Gumbart, J. C., Chi, S. H., Perry, J. W., & Barry, B. A. (2019). Tyrosine, cysteine, and proton coupled electron transfer in a ribonucleotide reductase-inspired beta hairpin maquette. *Chemical Communications*, 55(63), 9399-9402. <https://doi.org/10.1039/C9CC04067F>.

Magnetic Field Influence on Electron Transfer in Homogeneous Medium

- Milligan, J. R., Aguilera, J. A., Ly, A., Tran, N. Q., Hoang, O., & Ward, J. F. (2003). Repair of oxidative DNA damage by amino acids. *Nucleic Acids Research*, 31(21), 6258-6263. <https://doi.org/10.1093/nar/gkg816>
- Rivera, J. J., Trinh, C., & Kim, J. E. (2022). Photoinduced Electron Transfer from the Tryptophan Triplet State in Zn-Azurin. *ACS Physical Chemistry Au*, 3(1), 63-73. <https://doi.org/10.1021/acspyschemau.2c00042>
- Stryer, L. (1999). *Biochemistry*. (4th ed.). Freeman, United States.

Functional Molecules for Organic Light-Emitting Diodes (OLEDs)

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ABSTRACT

Organic optoelectronics is an exciting field that combines chemistry, physics, materials science, and biology to create modern electronic devices that are lightweight, flexible, and cost-effective. One of the most popular applications of this technology is in organic light-emitting diodes (OLEDs), which are widely used in display screens and lighting. This chapter explores the roles of various functional organic molecules in OLEDs, with emphasis on amorphous molecular materials that support uniform thin-film formation. It provides insights into the design and properties of essential components, such as hole- and electron-transporting materials, charge-blocking layers, and emissive materials. Special focus is given to thermally activated delayed fluorescence (TADF) materials, recognised as next-generation emitters due to their high efficiency and metal-free nature. Although remarkable progress has been made, further research is required to enhance OLED device longevity and sustainability. Improvements in organic material design are likely to contribute meaningfully to technological progress and eco-friendly solutions.

Keywords: *Emission Material; Hole and Electron Transporting Material; Optoelectronic Devices; Organic Light-Emitting Diodes*

Introduction

Recently, organic optoelectronics has emerged as a transformative domain at the intersection of materials science, chemistry, and applied physics. This interdisciplinary field focuses on the development of electronic and photonic devices based on organic semiconductors, offering several advantages over traditional inorganic systems. Organic light-emitting diodes (OLEDs), one of the most prominent applications in this field, have revolutionised display and lighting technologies with their thin, lightweight, and flexible structures (Forrest, 2004; Tang & VanSlyke, 1987). Unlike conventional inorganic semiconductors, organic materials can be synthetically tuned at the molecular level to tailor their electronic and optical properties. The structural flexibility of organic molecules enables solution processing, reduced fabrication costs, and

mechanical adaptability—critical attributes for next-generation devices such as foldable displays and wearable electronics (Reineke *et al.*, 2013). OLEDs are notable for their self-emissive nature, high contrast ratios, and capacity to achieve full-colour emissions with low power consumption.

A typical OLED device consists of multiple organic layers, each performing specific functions such as hole and electron transport, charge blocking, and light emission. The selection and design of functional molecular materials for each layer are central to optimising device efficiency and longevity. Amorphous molecular materials are often preferred over crystalline counterparts due to their superior film-forming capabilities and morphological stability (Shirota, 2000).

Recent developments in emitter technology have introduced thermally activated delayed fluorescence (TADF) materials as efficient alternatives to phosphorescent emitters. These third-generation emitters exploit reverse intersystem crossing to harvest both singlet and triplet excitons without requiring heavy metal complexes, thereby enhancing device efficiency while maintaining environmental sustainability (Uoyama *et al.*, 2012).

Despite significant advances, challenges such as operational stability, material degradation, and end-of-life recyclability remain. Addressing these issues through molecular engineering and device architecture innovation is essential to fully realise the potential of OLEDs in commercial and sustainable technologies.

This chapter aims to explore the design and application of functional organic molecules in OLEDs, with a special focus on amorphous materials, offering insights into their roles in enhancing device performance and enabling future optoelectronic applications.

Literature Review

Organic light-emitting diodes (OLEDs) have gained significant traction in the realm of display and lighting technologies due to their remarkable attributes, such as thin-film form factors, wide viewing angles, high contrast ratios, and the ability to emit across the visible spectrum (Reineke *et al.*, 2013; Tang & VanSlyke, 1987). These devices are now extensively used in smartphones, televisions, smartwatches, and even automotive displays. Their intrinsic flexibility and compatibility with solution processing make them highly suitable for next-generation, flexible, and wearable electronics (Forrest, 2004). A key distinction in the performance of OLED devices lies in the choice of organic materials. Crystalline materials, though known for their superior charge-carrier mobility, often struggle with poor film-forming ability, resulting in grain boundaries that disrupt device uniformity and performance. In contrast, amorphous molecular materials offer better morphological stability, uniform film formation, and compatibility with both vacuum and solution-processing techniques (Shirota, 2000; Friend *et al.*, 1999). This has led to their widespread adoption in OLEDs over their crystalline counterparts.

OLED structures generally consist of multiple organic layers performing specialised roles such as hole transport, electron transport, charge blocking, and emission. Materials with appropriate energy levels for hole and electron injection and transport are selected to ensure balanced charge recombination within the emissive layer (Kido, Kimura & Nagai, 1995). Amorphous hole-transport materials such as TCTA and α -NPD (Shirota, Kobata & Noma, 1989) have shown promise due to their stable thin-film characteristics and reversible redox behaviour.

In recent years, research focus has shifted towards third-generation emitters, particularly thermally activated delayed fluorescence (TADF) materials, which enable efficient upconversion of triplet excitons to singlets without relying on expensive noble metals (Uoyama *et al.*, 2012). This innovation not only improves internal quantum efficiency but also aligns with sustainability goals.

Furthermore, host materials for emissive dopants must possess high triplet energy levels and balanced bipolar charge-transport properties to ensure effective energy transfer and exciton confinement (Ikai *et al.*, 2001). Such careful molecular engineering has been crucial in improving both the efficiency and operational stability of OLED devices.

In summary, the literature reflects a consistent evolution in the molecular design and functional tuning of materials for OLEDs, with amorphous small molecules and TADF compounds at the forefront of current research.

Discussion

Fluorescence or phosphorescence emission is the basis of organic electroluminescence (EL) which originates from the excited singlet or triplet electronic states. These excitons within the device are produced by hole-electron recombination, injected from the anode and cathode, respectively, in presence of an external electrical stimulation.

In case of single-layer devices, the materials should be capable of not only accepting both holes and electrons from the electrodes but also transporting them. In addition, they should have emissive properties, too. It is very difficult to find a single material capable of functioning in various roles. Multiple materials are employed together in the device, where each material is chosen to function as electrode charge injection, transport of charges, preventing charge leakage, and emission of light. Accordingly, they are termed as i) hole-conducting, ii) electron-conducting, iii) charge-blocking, and iv) emissive materials, respectively. Therefore, organic light-emitting diodes are multilayered devices that are normally assembled by vacuum deposition of the individual functional materials.

In general, materials used in OLEDs are expected to have the following characteristics:

1. Formation of uniform thin films with less pinholes is an essential parameter which can be achieved either by thermal deposition under vacuum conditions or by solution-

based processing of the amorphous materials.

2. Material should have a high glass-transition temperature (T_g).
3. High morphological stability.

Amorphous molecular materials are mostly found to be used in OLEDs, as they form smooth, uniform layers compared to crystalline material. The following section of this chapter includes a brief account of amorphous organic compounds used for hole and electron transport, hole and electron blocking, and light emission.

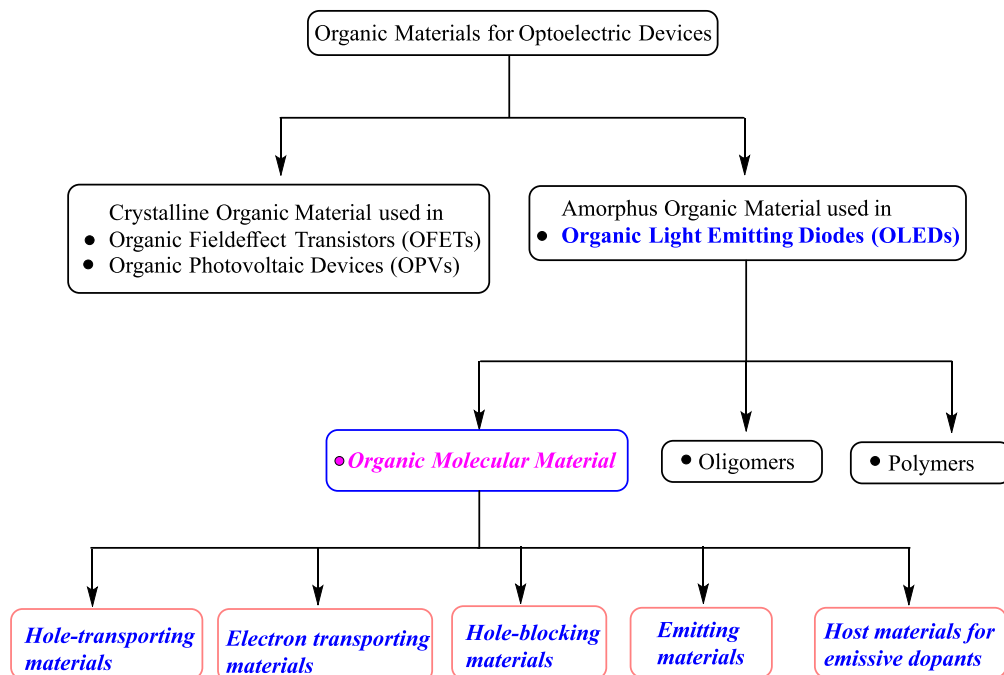


Figure 1: Classification of Organic Compounds Utilised in Optoelectronic Devices

Hole Transporting Materials

Materials used for hole transport should possess appropriate HOMO energy levels to accept the cation-radical species (hole carriers) from the anode through the hole-injection layer, indicating the reversibility of their anodic oxidation process. Organic molecules with low ionisation potential are mainly selected as hole-transporting components in the hole-injection layer. A variety of under this category have been reported to date and few representative examples include 4,4',4''-tris(3-methylphenyl(phenyl)amino)triphenylamine(m-MTDATA) 1 (Shirota, Kobata & Noma, 1989), 4,4',4''-tri-N-carbazolyltriphenylamine (TCTA) 2 (Kuwabara *et al.*, 1994) and α -NPD3 (Van Slyke, Chen & Tang, 1996), as illustrated in figure 2. Interestingly, m-MTDATA 1 is primarily employed as a hole injection materials whereas TCTA 2 and α -NPD 3 are the widely utilised amorphous molecular materials for hole transport in OLEDs.

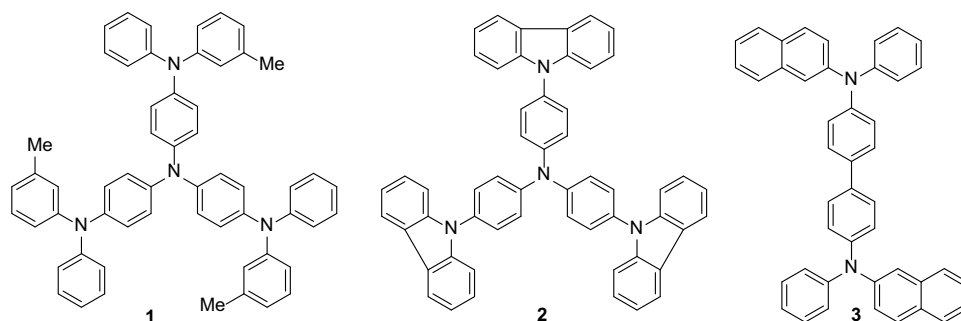


Figure 2: Amorphous Organic Compounds Utilised in Hole Transport

Electron-transporting Materials

In a similar way, materials used for electron transport should possess suitable LUMO energy levels to receive the anion-radical species (electron carriers) from the cathode via the electron-injection layer, reflecting the reversible nature of their cathodic reduction processes. Organic molecules in this category consist of central aromatic cores like benzene, 1,3,5-triazine, 1,3,5-triphenylbenzene and tetraphenylmethane, to which electron-accepting groups like pyridine, oxadiazole, triazine, triarylborane and dimesitylboryl are connected. In this direction, few examples of electron transporting materials are presented in figure 3 (Gao *et al.*, 1999; Noda & Shirota, 1998; Sasabe & Kido, 2011).

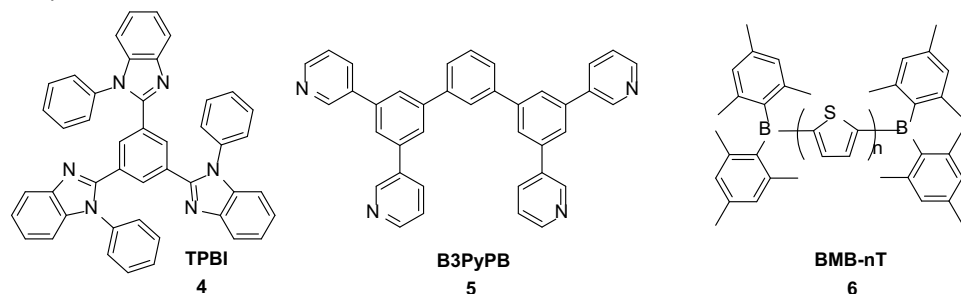


Figure 3: Amorphous Organic Compounds for Electron Transport

Hole-blocking Materials

These materials are used to develop charge blocking layers that trap both types of charge carriers within the emitting layer by effectively preventing leakage of charge from the emitting layer. Interestingly, hole-transporting materials are used to block electron charge carriers, whereas electron-transporting materials are naturally used in hole-blocking. Materials in this category should have high ionisation potential, which is essential to resist the uptake of hole carriers releasing from the emitting layer.

Emitting Materials

Molecule used as emitting materials should exhibit a bipolar characteristic in which

HOMO and LUMO energy levels are aligned in such a way that they can allow the acceptance of holes from the anode and electrons from the cathode. Emitting layer behaves like a recombination centre for holes and electrons. In this direction, it is important to mention that the stability of the charge carriers (both cation-radical and anion-radical) in emitting molecules is another critical parameter for the functioning of the emitting layer as a recombination centre.

Fluorescence-emitting Materials

Compounds BMA-nT **7** and FIAMB-nT **8** are used in OLED applications as bipolar amorphous molecular emitters (Figure 4). The emission colour depends on the extent of conjugation associated with the oligothiophene segment in BMA-nT (Noda *et al.*, 1997) and FIAMB-nT (Shirota *et al.*, 2000).

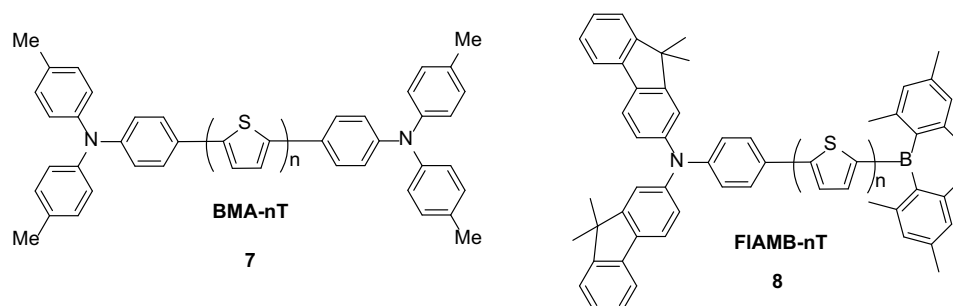


Figure 4: Bipolar-emitting Amorphous Molecular Materials

Thermally Assisted Delayed Fluorescence-Emitting Materials

TADF, or thermally activated delayed fluorescence, is produced by thermal up conversion of triplet to singlet exciton and is used in fluorescence-based OLEDs having high performance. TADF-emitting materials are superior compared to the phosphorescent dopant materials, as the former material does not contain any expensive transition metals. For this reason, TADF materials are referred to as third-generation emitters in OLED technology. In general, TADF emitting materials have a large extent of spin-orbit coupling and a slight energy gap between singlet-triplet states to promote intersystem crossing in the reverse direction.

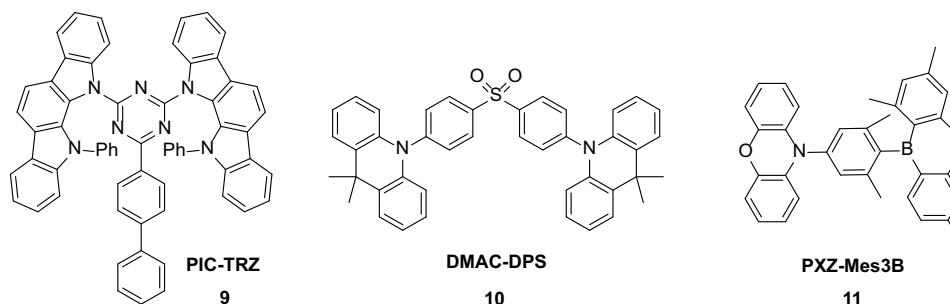


Figure 5: TADF-emitting Molecular Materials

It has been found that the reported TADF molecules possess carbazole, acridan or phenoxazine segments as electron donors and triazine (Endo *et al.*, 2011), triaryl boron (Suzuki *et al.*, 2015), diphenyl sulfone (Zhang *et al.*, 2014), or diphenylketone segments as electron acceptors. Amalgamation of electron donating and accepting moieties in TADF molecules is very important, as it facilitates intramolecular charge transfer. Few examples of synthesised TADF materials are given in figure 5.

Phosphorescence-emitting Materials

Transition metal complexes of platinum, iridium and osmium are usually used in OLEDs as room-temperature phosphorescent materials (figure 6) (Baldo *et al.*, 1999). These complexes are used as emissive dopants with a good film-forming host material, as metal complexes lack the ability to form films. However, the colour of the emissions depends on the structure of the ligands.

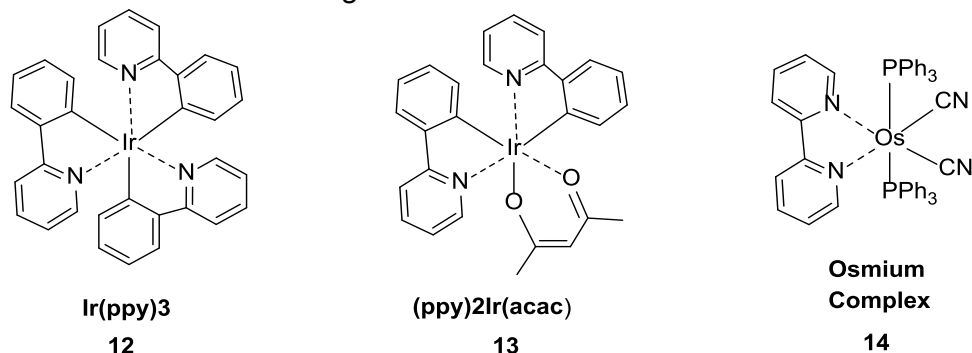


Figure 6: Phosphorescent Dopants for OLEDs

Host Material for Emissive Dopant

Emissive dopant materials used in OLEDs usually need host materials having good film-forming ability. The role of the host material is to generate excitons and then transfer the excitation energy to emissive dopant materials via the singlet-singlet or triplet-triplet process. The host materials possess a bipolar character to accept both types of charge carriers, and energy levels of singlet and triplet excited states should exceed that of emissive dopants to transfer exothermic energy efficiently. Transfer of energy in reverse direction, i.e., from dopant to the host, is energetically unfavourable. Some examples of such material are given in Figure 7 (Ikai *et al.*, 2001).

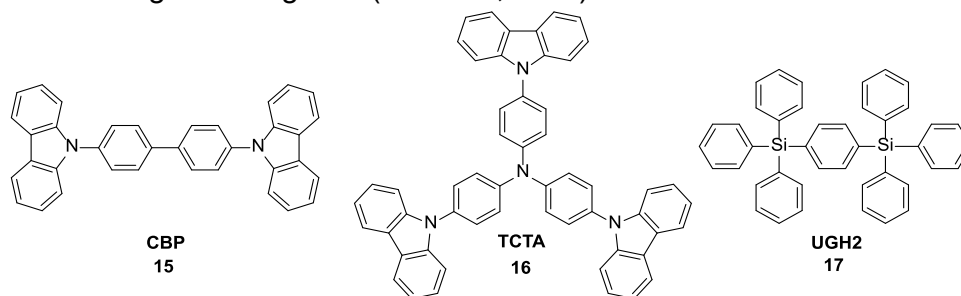


Figure 7: Examples of Materials for Emissive Dopants

Conclusion

This chapter has provided a brief account of the recent advancement in the field of organic optoelectronics, with a focus on the use of molecular organic amorphous materials in OLEDs. Several classes of organic molecular materials used in OLEDs to facilitate acceptance of charge from electrodes, charge blocking, charge transport, and emission were discussed along with the examples of each type. Discussion on the TADF materials as the third-generation OLED emitters has also been included in this chapter. Oligomers and polymer-based organic materials are not considered here despite having their roles in OLEDs.

Even though several types of organic molecular materials have been made targeting to improve external quantum efficiency for OLEDs, further improvements are still required for getting a better lifespan of OLED displays and lighting panels and to develop recycling and disposal methods for OLED devices. Research and development in functional organic material synthesis may reduce the production costs for OLEDs, which can make OLED technology more accessible to a broader range of consumers. OLEDs could have been integrated with other emerging technologies to solve the environmental and energy challenges of the 21st century.

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References

- Baldo, M. A., Lamansky, S., Burrows, P. E., Thompson, M. E., & Forrest, S. R. (1999). Very high-efficiency green organic light-emitting devices based on electrophosphorescence. *Applied Physics Letters*, 75(1), 4–6. <https://doi.org/10.1063/1.124258>
- Endo, A., Sato, K., Yoshimura, K., Kai, T., Kawada, A., Miyazaki, H., & Adachi, C. (2011). Efficient up-conversion of triplet excitons into a singlet state and its application for organic light emitting diodes. *Applied Physics Letters*, 98(8). <https://doi.org/10.1063/1.3558906>
- Forrest, S. R. (2004). The path to ubiquitous and low-cost organic electronic appliances on plastic. *Nature*, 428(6986), 911-918. <https://doi.org/10.1038/nature02498>
- Friend, R. H., Gymer, R. W., Holmes, A. B., Burroughes, J. H., Marks, R. N., Taliani, C. D. D. C., ... & Salaneck, W. R. (1999). Electroluminescence in conjugated polymers. *Nature*, 397(6715), 121-128. <https://doi.org/10.1038/16393>
- Gao, Z., Lee, C. S., Bello, I., Lee, S. T., Chen, R. M., Luh, T. Y., ... & Tang, C. W. (1999). Bright-blue electroluminescence from a silyl-substituted ter-(phenylene-vinylene) derivative. *Applied Physics Letters*, 74(6), 865-867. <https://doi.org/10.1063/1.123392>

- Ikai, M., Tokito, S., Sakamoto, Y., Suzuki, T., & Taga, Y. (2001). Highly efficient phosphorescence from organic light-emitting devices with an exciton-block layer. *Applied Physics Letters*, 79(2), 156–158. <https://doi.org/10.1063/1.1385182>
- Kido, J., Kimura, M., & Nagai, K. (1995). Multilayer white light-emitting organic electroluminescent device. *Science*, 267(5202), 1332-1334. <https://doi.org/10.1126/science.267.5202.1332>
- Kuwabara, Y., Ogawa, H., Inada, H., Noma, N., & Shirota, Y. (1994). Thermally stable multilayered organic electroluminescent devices using novel starburst molecules, 4,4',4"-tri(N-carbazolyl)triphenylamine (TCTA) and 4,4',4"-tris(3-ethylphenylphenylamino)triphenylamine (m-MTDATA), as hole-transport materials. *Advanced Materials*, 6(9), 677–679. <https://doi.org/10.1002/adma.19940060913>
- Noda, T., & Shirota, Y. (1998). 5,5'-Bis(dimesitylboryl)-2,2'-bithiophene and 5,5"-bis(dimesitylboryl)-2,2':5',2"-terthiophene as a novel family of electron-transporting amorphous molecular materials. *Journal of the American Chemical Society*, 120(37), 9714–9715. <https://doi.org/10.1021/ja9817343>
- Noda, T., Imae, I., Noma, N., & Shirota, Y. (1997). 5,5"-Bis{4-[bis(4-ethylphenyl)amino]phenyl}-2,2':5',2"-terthiophene and 5,5'''-bis{4-[bis(4-methylphenyl)amino]phenyl}-2,2':5',2":5",2'''-quaterthiophene as a novel family of amorphous molecular materials. *Advanced Materials*, 9(3), 239–241. <https://doi.org/10.1002/adma.19970090311>
- Reineke, S., Thomschke, M., Lüssem, B., & Leo, K. (2013). White organic light-emitting diodes: Status and perspective. *Reviews of Modern Physics*, 85(3), 1245-1293. <https://doi.org/10.1103/RevModPhys.85.1245>
- Sasabe, H., & Kido, J. (2011). Multifunctional materials in high-performance OLEDs: Challenges for solid-state lighting. *Chemistry of Materials*, 23(3), 621–630. <https://doi.org/10.1021/cm1024052>
- Shirota, Y. (2000). Organic materials for electronic and optoelectronic devicesBasis of a presentation given at Materials Chemistry Discussion No. 2, 13–15 September 1999, University of Nottingham, UK. *Journal of Materials Chemistry*, 10(1), 1-25. <https://doi.org/10.1039/A908130E>
- Shirota, Y., Kinoshita, M., Noda, T., Okumoto, K., & Ohara, T. (2000). A novel class of emitting amorphous molecular materials as bipolar radical formants: 2-{4-[Bis (4-methylphenyl) amino] phenyl}-5-(dimesitylboryl) thiophene and 2-{4-[Bis (9, 9-dimethylfluorenyl) amino] phenyl}-5-(dimesitylboryl) thiophene. *Journal of the American Chemical Society*, 122(44), 11021-11022. <https://doi.org/10.1021/ja0023332>
- Shirota, Y., Kobata, T., & Noma, N. (1989). Starburst molecules for amorphous molecular materials. 4, 4', 4"-Tris (N, N-diphenylamino) triphenylamine and 4, 4', 4"-tris [N-(3-methylphenyl)-N-phenylamino] triphenylamine. *Chemistry Letters*, (7), 1145-1148. <https://doi.org/10.1246/cl.1989.1145>
- Suzuki, K., Kubo, S., Shizu, K., Fukushima, T., Wakamiya, A., Murata, Y., Adachi, C., & Kaji, H.

- (2015). Triarylboron-based fluorescent organic light-emitting diodes with external quantum efficiencies exceeding 20%. *Angewandte Chemie International Edition*, 54(50), 15231–15235. <https://doi.org/10.1002/anie.201508270>
- Tang, C. W., & VanSlyke, S. A. (1987). Organic electroluminescent diodes. *Applied Physics Letters*, 51(12), 913–915. <https://doi.org/10.1063/1.98799>
- Uoyama, H., Goushi, K., Shizu, K., Nomura, H., & Adachi, C. (2012). Highly efficient organic light-emitting diodes from delayed fluorescence. *Nature*, 492(7428), 234–238. <https://doi.org/10.1038/nature11687>
- Van Slyke, S. A., Chen, C. H., & Tang, C. W. (1996). Organic electroluminescent devices with improved stability. *Applied Physics Letters*, 69(15), 2160–2162. <https://doi.org/10.1063/1.117151>
- Zhang, Q., Li, B., Huang, S., Nomura, H., Tanaka, H., & Adachi, C. (2014). Efficient blue organic light-emitting diodes employing thermally activated delayed fluorescence. *Nature Photonics*, 8(4), 326–332. <https://doi.org/10.1038/nphoton.2014.12>

Assessment of Total Flavonoid Content and Antioxidant Activity of Mango Pulp Extracts

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ABSTRACT

Antioxidants can control the progression of many chronic diseases by shielding the body from the oxidation caused by free radicals. Antioxidant properties of flavonoids enable them to function as defences against free radicals. Two extraction procedures, such as maceration and Microwave-Assisted Extraction (MAE), are used to extract flavonoids from mango pulp. Total flavonoid content is estimated by total flavonoid content assay as milligrams of Quercetin Equivalent (QE). Antioxidant activity of extract of mango pulp in four different solvents using two extraction techniques can be estimated by the Ferric Reducing Antioxidant Power (FRAP) assay. Antioxidant activity of pulp extracts has been expressed as mg of Ascorbic Acid Equivalent (AAE). All four solvent extracts of mango pulp have shown high amounts of total flavonoid contents as well as high reducing power. Hence, it may be concluded that eating mango pulp can render its antioxidant activity against free radical-associated diseases due to the presence of flavonoids as bioactive compounds.

Keywords: *Extraction Methods; Ferric Reducing Anti-Oxidant Power (Frap) Assay; Flavonoids; Maceration; Microwave-Assisted Extraction (Mae); Total Flavonoid Content Assay*

Introduction

Plants contain secondary metabolites called flavonoids, which serve a variety of purposes in their organs. Vegetables, wine, fruits, and drinks (tea) have all been claimed to contain them. Flavonoids' chemical structures are made up of C₆-C₃-C₆ rings, which stand for two aromatic rings A and B, connected by three carbon atoms. A third ring (C) develops as a result (Jucá *et al.*, 2020). The several subclasses of flavonoid substances are derived from variations in this fundamental structure. These include chalcones, flavonols, anthocyanins, flavonones, isoflavones, and flavones (catechins). According to reports, the kingdom Plantae has about 10,000 distinct types of flavonoids (Ekalu & Habila, 2020).

Numerous biological investigations have demonstrated the health benefits of flavonoids, including the prevention of disease. They have demonstrated anti-inflammatory, antioxidant, antibacterial, antiviral, and antiallergic qualities as well as anticarcinogenic ones (Mir *et al.*, 2024). Flavonoids have been shown to have protective effects via

lowering oxidative stress in the body. The hydroxyl group in flavonoids is more important for these biological actions.

Compounds known as antioxidants delay or stop oxidation in living cells. They counteract free radicals' actions. The body is shielded from reactive oxygen species by flavonoids. Flavonoids are chemically capable of scavenging free radicals because of their highly conjugated π -electron system and hydroxyl groups. Flavonoids' antioxidant properties enable them to function as defences against free radicals. Antioxidants slow the progression of many chronic diseases (Basu, 2020; Tungmunthum *et al.*, 2018) by shielding the body from the oxidation caused by free radicals.

Reactive oxygen species (ROS) are created when electron acceptors, including molecular oxygen, react quickly with free radicals. These ROS comprise non-radical hydrogen peroxide (H_2O_2), hydroxyl radicals ($\cdot OH$), and free radicals with unpaired electrons, e.g. superoxide anions. Enzymatically produced in aerobic living organisms, ROS are vital cellular components that are crucial to a variety of physiological and pathological processes. Excess ROS can harm cellular macromolecules including DNA, proteins, as well as lipids. This is primarily caused by external factors like radiation, infections, UV light, medications, etc. Nearly 200 illnesses, including cancer, diabetes mellitus, atherosclerosis, hypertension, cardiovascular disease, ischemia, neurological diseases such as Parkinson's disease, Alzheimer's disease (Ji *et al.*, 2025), and rheumatoid arthritis, may be linked to oxidative stress.

Antioxidants are compounds that, when present in low quantities, considerably slow down or stop the oxidation of an oxidisable substrate. Numerous health issues, such as infectious, systemic, and neurological disorders, have been demonstrated to respond well to antioxidant treatment. Flavonoids' distinct antioxidant qualities make them the most studied class of phytochemicals.

One of the most widely consumed tropical fruits worldwide is the mango (*Mangifera indica* L.). It is valued for its nutritional content as well as its sensory qualities. In addition to being high in phytochemicals such as phenolic compounds, flavonoids, and carotenoids, mango pulps also supply energy, dietary fibre, carbs, protein, and lipids. The medicinal qualities and high antioxidant activity of these bioactive chemicals make them fascinating (Basu, 2024).

Identifying and characterising flavonoids is the most difficult part of the extraction process, which is dependent on the polarity of the solvents and involves solvent extraction using a variety of solvents and an appropriate isolation methodology. To the best of our knowledge, this is the very first study to extract and characterise flavonoids from the Himsagar variety, despite the fact that other research groups have examined antioxidant activity and the phenolic content's reducing effect on various mango components (Umamahesh, Sivudu & Reddy, 2016; Fonseca *et al.*, 2011; Ma *et al.*, 2011).

Methodology

Plant Material

Fresh pulp samples of *Mangifera indica* L. are collected and cut into pieces to perform extraction of bioactive compounds.

Extraction Procedure

The process used to extract flavonoids from plant material is important and is determined by the objectives of the study. Typically, methanol, ethanol, acetone, acetonitrile, or their combinations with water are used to extract flavonoids. The type of flavonoid determines the necessary solvent polarity. Acetone, methylene chloride, chloroform, and diethyl ether are suitable solvents for less polar flavonoid structures such as flavanones, isoflavones, and flavones; alcohol or an alcohol–water mixture is typically used for more polar flavonoid fractions (Rodríguez De Luna, Ramírez-Garza & Serna Saldívar, 2020).

Optimization of Extraction Condition

The extraction techniques are classified into two groups: modern techniques (extraction by pressurised liquid, ultrasound, microwaves, enzyme assistance, supercritical fluid, matrix solid-phase dispersion, etc.) and conventional techniques (reflux, maceration, and Soxhlet extraction).

The conventional methods are simple to use, don't require specialised tools, may be used to extract a lot of samples, and produce a high yield of extract. They aren't selective, though. Depending on the polarity property of the target flavonoid fraction, the appropriate solvent can provide a certain level of selectivity (Tzanova *et al.*, 2020).

Maceration

The process of maceration involves soaking the plant material in an appropriate solvent in a stoppered container. The sample is shaken regularly and incubated at room temperature for at least three days. The soluble phytochemicals are released as the solvent breaks down and softens the plant's cell wall. The mixture is then filtered after that.

Green Extraction Techniques

Long extraction times, expensive solvent requirements, massive solvent evaporation, poor extraction selectivity, and automation challenges are the main drawbacks of classical extraction methods. The limits of traditional extraction technologies are being overcome by the development of innovative and promising procedures (Chávez-González *et al.*, 2020; Chaves *et al.*, 2020). They fall within the category of unconventional, environmentally friendly extraction methods. They offer numerous benefits: a decrease in the amount of used organic solvents and sample deterioration,

avoidance of contamination, removal of superfluous sample concentration and cleanup procedures, enhancement of extraction efficiency and selectivity, and automation potential.

Enzyme-assisted extraction (EAE), pressurised liquid extraction (PLE), ultrasound-assisted extraction (UAE), supercritical fluid extraction (SFE), microwave-assisted extraction (MAE), and matrix solid-phase dispersion (MSPD) are a few of the most promising techniques.

Microwave-Assisted Extraction (MAE)

The extraction method known as MAE encourages the analytes to pour out of the sample into the solvent by using microwave power. Polar and polarisable materials' dipoles are affected by microwave radiation, which heats the materials close to their surface. Conduction is how the heat is transmitted. When dealing with polar compounds and liquids that have a high dielectric constant, MAE might be regarded as a selective technique. In contrast to traditional extraction techniques, MAE provides a number of benefits: enhanced recovery, decreased extraction time, solvent volume, energy and processing costs, and the potential to utilise fewer hazardous solvents. However, only tiny compounds that are stable under microwave heating conditions can be used using this approach.

Mango peels are removed by using a sharp knife, and the underlying mango pulp is recovered by scraping with the sharp edge of the knife, and the pulp is washed with distilled water and air-dried. 8.5 gm, 7.4 gm, 6.9 gm and 7.1 gm of mango pulp are successively extracted by maceration with water, methanol, acetone and ethanol, respectively, for 72 h stirring. A second extraction method, Microwave-Assisted Extraction (MAE), is carried out with 5.6 gm, 7.0 gm, 5.6 gm and 6.3 gm of mango pulp with the same four solvents, respectively. The obtained extracts are stored under dark conditions until biological assay.

Determination of Total Flavonoids Content

According to Pękal and Pyrzynska's description (Pękal & Pyrzynska, 2014), aluminium chloride is used to colorimetrically assess the total flavonoid concentration. Typically, quercetin is utilised as a standard. Methanol is used to dissolve 10 mg of quercetin, which is further diluted to 10, 20, 50, and 100 µg/ml. After vigorously shaking the diluted standard solution (1.0 ml) and sample solutions with 1.0 ml of water and 0.5 ml of 2% (w/v) aluminium chloride, they are incubated for 30 minutes at room temperature. For 300–600 nm, the absorbance is estimated using a blank. Except for test samples (extracts, standard), all reagents are added in blank. The milligrams of quercetin equivalent per gram of dry mass (mg of QE/g) are calculated to indicate the overall flavonoid content. In another procedure, 1 ml sample solutions are added with 0.3 ml NaNO₂ (5% w/v) and kept for 5 minutes. Then 0.5 ml of 2% (w/v) aluminium chloride is mixed with the mixtures, and after 6 minutes, 0.5 ml of 1M NaOH solution is added. The whole mixtures are incubated at room temperature for 10 minutes and finally scanned

for 300-600 nm.

Ferric-Reducing Antioxidant Power (FRAP) Assay

The change of iron (III) to iron (II) in the presence of plant extracts using two distinct extraction methods, water, methanol, acetone, and ethanol, is the basis for the reducing power. The development of Perl's blue at 700 nm can be used to measure iron (II). With a few minor adjustments (Oyaizu, 1986), the process approach outlined by Saeed, Khan and Shabbir (2012) is used to reduce ability. In short, 1 millilitre of the aforementioned extracts (100 µg/ml) is combined with 2.5 millilitres of phosphate buffer (0.2 M, pH 6.6) and 2.5 millilitres of potassium ferricyanide (10 mg/ml) using Vertex. After 20 minutes of incubation at 50°C, 2.5 millilitres of trichloroacetic acid (100 mg/l) are added to the solutions.

The mixtures are centrifuged for 10 minutes at 3000 rpm in order to obtain the supernatant layer. 2.5 ml of each of the aforementioned mixes is combined with 0.5 ml of 0.1% (w/v) fresh ferric chloride solution and 2.5 ml of distilled water. The absorbances are measured at 700 nm following a 10-minute incubation at room temperature. The calibration curve is made with standard ascorbic acid. In triplicate, the iron (III) reducing activity is measured and reported as µMol Ascorbic Acid Equivalent (AAE)/g of extract. A higher reducing power is demonstrated by an increase in absorbance.

Results and Discussion

Total Flavonoids Content

A quercetin standard solution is considered as a guide to correlate between quercetin concentration and its absorbance value on a calibration curve, as shown in Figure 1. In order to prove the existence of active compounds in mango pulp, the content analysis had been done targeting flavonoids using a colorimetric assay. A colorimetric assay using aluminium chloride is a method that can detect flavonoids in the flavone and flavanol groups of flavonoids. Aluminium chloride in the assay will react with flavonoid and create a stable, colour-signature complex. The reaction involved in the keto group at carbon number 4 and the hydroxyl group in either carbon number 3 or 5 forms an acid-stable complex; meanwhile, the reaction within the ortho-dihydroxyl group present in the A- and B-rings of a flavonoid could also be responsible for several acid-labile complexes. These resulting complexes formed by flavone have a maximum absorbance at around 400 nm. By applying an aluminium chloride colorimetric experiment to the extracts of mango pulps, the total flavonoid content can be detected. Using the calibration equation ($y = 0.0005x + 0.2762$) and a correlation coefficient of 0.9012, the quercetin concentration of the samples can be calculated.

The Total Flavonoid Content (TFC) for each sample for various extraction methods can be calculated using Equation 1 as milligrams of Quercetin Equivalent (QE) per gram of mango pulp by multiplying the quercetin concentration of the sample solution in µg/ml (C) by the volume of the sample solution in mL (V) and then dividing it by pulp mass expressed in grams (W).

$$\text{TFC} = \text{CXV}/\text{WX1000} \text{ (1)}$$

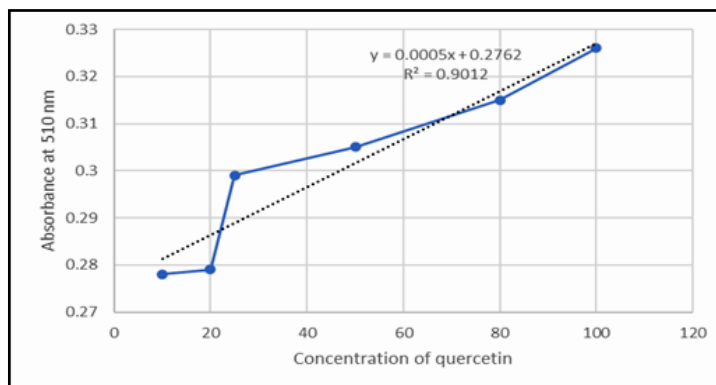


Figure 1: Standard Curve of the Quercetin Solutions

Ferric Reducing Antioxidant Power (FRAP) Assay

The reducing power method estimates the electron donation ability of the antioxidant agent present in the extracts for conversion of ferric ion Fe^{3+} into ferrous form Fe^{2+} . The amount of Fe^{2+} complex (formed as Pearl's Prussian blue colour complex) is calculated at 700 nm (Amarowicz *et al.*, 2010), and the increase in absorbance is proportional to the increase in the reducing power activity of the sample solution. The antioxidant activity of different extracts of mango pulp can be calculated with a standard curve of ascorbic acid, as shown in Figure 2. The results of the FRAP assay are often expressed as AAE, which represents the concentration of ascorbic acid (vitamin C) that would produce the same absorbance change as the sample being tested. The reducing power is shown to be in the following order: Ethanolic extract from MAE > Methanolic extract from MAE > Methanolic extract from maceration > Aqueous extract from MAE > Ethanolic extract from MAE > Acetone extract from maceration > Aqueous from maceration, respectively. Considering the reducing power of bioactive compounds using the FRAP assay, the MAE technique has higher extraction power compared to maceration.

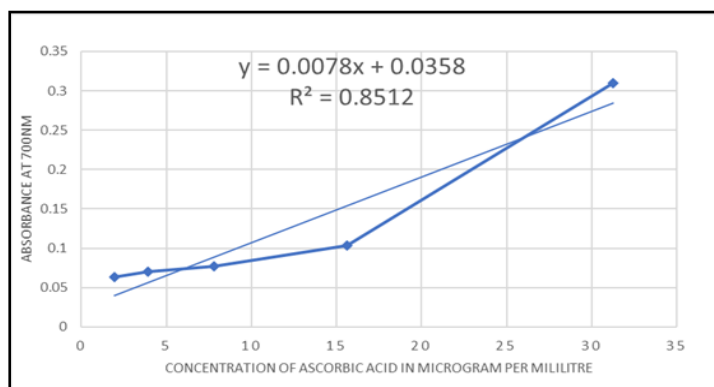


Figure 2: Standard Curve of Ascorbic Acid Solutions

Conclusion

The present study shows that all four solvent extracts of mango pulp for two different extraction methods have shown high amounts of total flavonoid contents, which can impart antioxidant activity. Hence, it may be concluded that eating mango pulp can render its antioxidant activity against free radical-associated diseases due to the presence of flavonoids.

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References

- Amarowicz, R., Estrella, I., Hernández, T., Robredo, S., Troszyńska, A., Kosińska, A., & Pegg, R. B. (2010). Free radical-scavenging capacity, antioxidant activity, and phenolic composition of green lentil (*Lens culinaris*). *Food Chemistry*, 121(3), 705-711. <http://dx.doi.org/10.1016/j.foodchem.2010.01.009>
- Basu, A. (2020). Study of Nutraceuticals in Cancer Treatment: An In Silico Approach. In *Nutraceuticals and Dietary Supplements* (pp. 121-156). Apple Academic Press. <http://dx.doi.org/10.1201/9780367821517-8>
- Basu, A. (2024). Extraction and Characterization of Flavonoid Kaempferol-3-Glucuronide from Mango for Treatment of Different Types of Cancers. *London Journal of Research In Science: Natural and Formal*, 24(1), 1-10. Retrieved from: <https://journalspress.uk/index.php/LJRS/article/view/467>, Accessed on 26th November 2024.
- Chaves, J. O., De Souza, M. C., Da Silva, L. C., Lachos-Perez, D., Torres-Mayanga, P. C., Machado, A. P. D. F., ... & Rostagno, M. A. (2020). Extraction of flavonoids from natural sources using modern techniques. *Frontiers in Chemistry*, 8. <http://dx.doi.org/10.3389/fchem.2020.507887>
- Chávez-González, M. L., Sepúlveda, L., Verma, D. K., Luna-García, H. A., Rodríguez-Durán, L. V., Iliina, A., & Aguilar, C. N. (2020). Conventional and emerging extraction processes of flavonoids. *Processes*, 8(4). <http://dx.doi.org/10.3390/pr8040434>
- Ekalu, A., & Habila, J. D. (2020). Flavonoids: isolation, characterization, and health benefits. *Beni-Suef University Journal of Basic and Applied Sciences*, 9, 1-14. <http://dx.doi.org/10.1186/s43088-020-00065-9>
- Fonseca Maciel, L., da Silva Oliveira, C., da Silva Bispo, E., & da P. Spínola Miranda, M. (2011). Antioxidant activity, total phenolic compounds and flavonoids of mangoes coming from biodynamic, organic and conventional cultivations in three maturation stages. *British Food Journal*, 113(9), 1103-1113. <http://dx.doi.org/10.1108/00070701111180319>
- Ji, D., Zhang, J., Liang, J., Huang, Z. S., Shu, B., & Li, D. (2025). Efficient strategy for

- alleviating neuronal apoptosis and oxidative stress damage of Alzheimer's disease through dual targeting BCL-2 gene promoter i-motif and β -amyloid. *Redox Biology*, 82. <http://dx.doi.org/10.1016/j.redox.2025.103600>
- Jucá, M. M., Cysne Filho, F. M. S., de Almeida, J. C., Mesquita, D. D. S., Barriga, J. R. D. M., Dias, K. C. F., ... & Vasconcelos, S. M. M. (2020). Flavonoids: biological activities and therapeutic potential. *Natural Product Research*, 34(5), 692-705. <http://dx.doi.org/10.1080/14786419.2018.1493588>
- Ma, X., Wu, H., Liu, L., Yao, Q., Wang, S., Zhan, R., ... & Zhou, Y. (2011). Polyphenolic compounds and antioxidant properties in mango fruits. *Scientia Horticulturae*, 129(1), 102-107. <http://dx.doi.org/10.1016/j.scienta.2011.03.015>
- Mir, S. A., Dar, A., Hamid, L., Nisar, N., Malik, J. A., Ali, T., & Bader, G. N. (2024). Flavonoids as promising molecules in the cancer therapy: An insight. *Current Research in Pharmacology and Drug Discovery*, 6. <https://doi.org/10.1016/j.crphar.2023.100167>
- Oyaizu, M. (1986). Studies on products of browning reaction antioxidative activities of products of browning reaction prepared from glucosamine. *The Japanese Journal of Nutrition and Dietetics*, 44(6), 307-315. <https://doi.org/10.5264/eiyogakuzashi.44.307>
- Pękal, A., & Pyrzyńska, K. (2014). Evaluation of aluminium complexation reaction for flavonoid content assay. *Food Analytical Methods*, 7, 1776-1782. <http://dx.doi.org/10.1007/s12161-014-9814-x>
- Rodríguez De Luna, S. L., Ramírez-Garza, R. E., & Serna Saldívar, S. O. (2020). Environmentally friendly methods for flavonoid extraction from plant material: Impact of their operating conditions on yield and antioxidant properties. *The Scientific World Journal*, 2020(1). <http://dx.doi.org/10.1155/2020/6792069>
- Saeed, N., Khan, M. R., & Shabbir, M. (2012). Antioxidant activity, total phenolic and total flavonoid contents of whole plant extracts *Torilis leptophylla* L. *BMC Complementary and Alternative Medicine*, 12, 1-12. <http://dx.doi.org/10.1186/1472-6882-12-221>
- Tungmunnithum, D., Thongboonyou, A., Pholboon, A., & Yangsabai, A. (2018). Flavonoids and other phenolic compounds from medicinal plants for pharmaceutical and medical aspects: An overview. *Medicines*, 5(3). <http://dx.doi.org/10.3390/medicines5030093>
- Tzanova, M., Atanasov, V., Yaneva, Z., Ivanova, D., & Dinev, T. (2020). Selectivity of current extraction techniques for flavonoids from plant materials. *Processes*, 8(10). <http://dx.doi.org/10.3390/pr8101222>
- Umamahesh, K., Sivudu, S. N., & Reddy, O. V. S. (2016). Evaluation of antioxidant activity, total phenolics and total flavonoids in peels of five cultivars of mango (*Mangifera indica*) fruit. *Journal of Medicinal Plants Studies*, 4(2), 200-203. Retrieved from: <https://www.plantsjournal.com/archives/2016/vol4issue2/PartC/4-1-41.pdf>. Accessed on 26th November 2024.

Ionic Liquids and its Application in Organic Synthesis

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ABSTRACT

Ionic liquids comprise ionic species but remain in a liquid state and have a melting point below 100°C. The significant characteristics of ionic liquid are its low vapour pressure and thermal stability. It can dissolve in both polar and non-polar substances, etc. The ionic liquids are salts in which one or both ions are large. The cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form, resulting in a low melting point. Ionic liquids are considered substitutes for volatile organic solvents due to its low vapour pressure; this characteristic appraise it as green solvents. Currently, the applications Ionic Liquids (ILs) are growing and are a highly vital topic in the fields of chemistry and organic synthesis.

Keywords: *Green Solvent; Ionic Liquid; Low Vapour Pressure; Organic Synthesis*

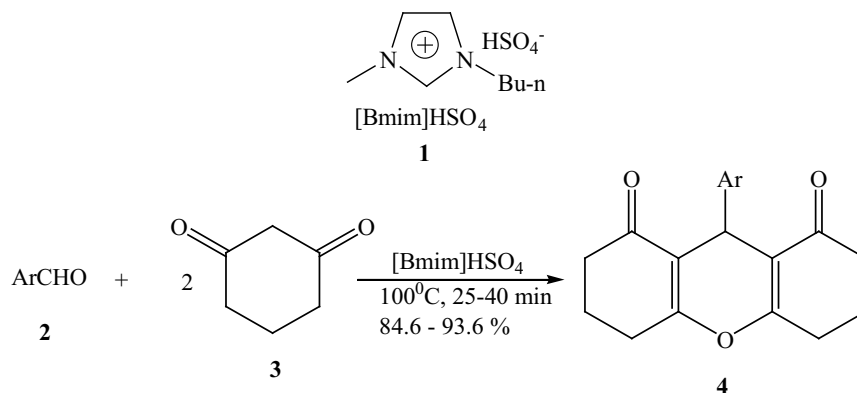
Introduction

Molecular solvents are generally used in most synthetic reactions. These organic solvents are inflammable, health hazards, expensive, high vapour pressure, extra care in handling and are difficult to recycle. Nowadays a novel class of solvent has been developed, which is ionic liquids characterised by low vapour pressure, liquid at room temperature and recyclable. In ionic liquids, the ionic species are composed of organic or inorganic cations and anions.

The thermodynamic and kinetic reactions carried out in ionic liquids are different from those carried out in conventional organic solvents. It is known as “green solvent” due to its eco-friendly nature and its unique characteristics. These many interesting properties make them of great interest to all chemists and scientists. In recent years, ionic liquid has been used by several chemists and scientists in chemical synthesis regarding environmental approaches. They have enormous and interesting attention in green synthesis, and in this short review, an attempt was made to capture a few of the works published. Several authors have reviewed ionic liquids including (Welton, 1999; Lei, 2017; Lei, 2024). The low melting point below 100°C of ionic liquids was first suggested in 1914 by Paul Walden. Ionic liquid from molecular level to industrial level has been demonstrated by Dong *et al.* (2017). Both or one ionic components of the ionic liquids are large, and the cations have a low degree of symmetry; this tends to minimise their lattice energy of the crystalline form, resulting in a low melting point

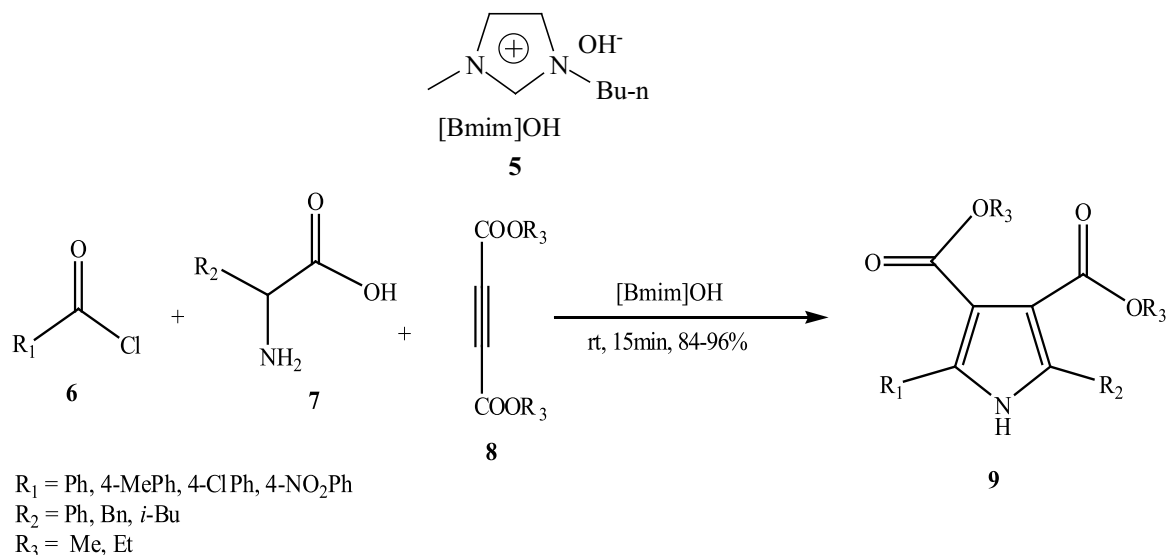
(Jaeger & Trucker, 1989). Ionic liquids, classified into simple salts and binary ionic liquids. The first one consists of a single anion and cation, while the second one is salts that involve equilibrium. $[\text{EtNH}_3][\text{NO}_3]$ is an example of simple salt, while mixtures of aluminum(III) chloride and 1,3-dialkylimidazolium chlorides are examples of binary ionic liquids. Sowbhagyam (2014) discussed the characteristics and applications of several ionic liquids, that served as a productive media for catalysis as well as synthesis reactions. Their tenable properties and design of ILs characterise their specific catalytic capabilities, enhancing reaction rates and selectivity. It is utilised in both homogeneous and heterogeneous catalysis reactions. The study concluded that ionic liquids are recognised as innovative chemical agents for synthesis and are increasingly acknowledged as a more environmentally friendly alternative to commonly used solvents due to their design flexibility, recyclability, and non-volatility. Previously, Chaturvedi *et al.*, (2014) had published a review explaining the recent developments in the area of task specific ionic liquids, particularly on their application in organic synthesis, nanoparticle synthesis and catalytic reactions. Here few of their applications are mentioned in organic synthesis.

Ma *et al.* (2007) have reported the green and productive synthesis of 9-aryl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione **4** by using different types of aromatic aldehydes **2** with cyclohexane-1,3-dione **3** (Scheme 1) by using $[\text{Bmim}]\text{HSO}_4$. $[\text{Bmim}]\text{HSO}_4$ is a task specific acidic ionic liquid.



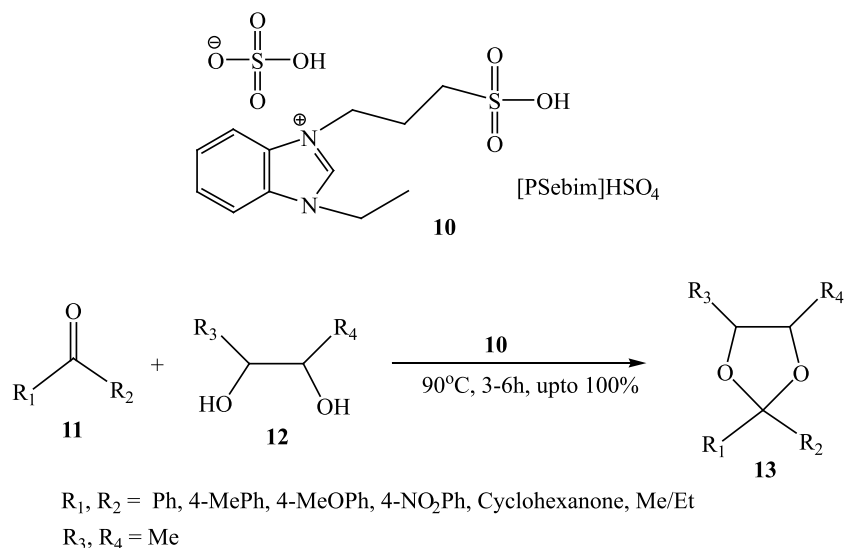
Scheme 1

The other ionic liquid, 1-butyl-3-methylimidazolium hydroxide, $[\text{Bmim}]\text{OH}$ **5**, catalysed the three-component reaction of acid chlorides **6**, dialkyl acetylenedicarboxylates **8** and amino acids **7** in water. This reaction produced a series of different pyrrole derivatives **9** with better yields (Yavari & Kowsari, 2008). They studied this reaction with other different kinds of ionic liquids, but it was found that $[\text{Bmim}]\text{OH}$ was the most effective catalyst at 80°C . This catalyst is basic functionalised. Benzoyl chloride, having an electron withdrawing group, gives a faster reaction (Scheme 2).



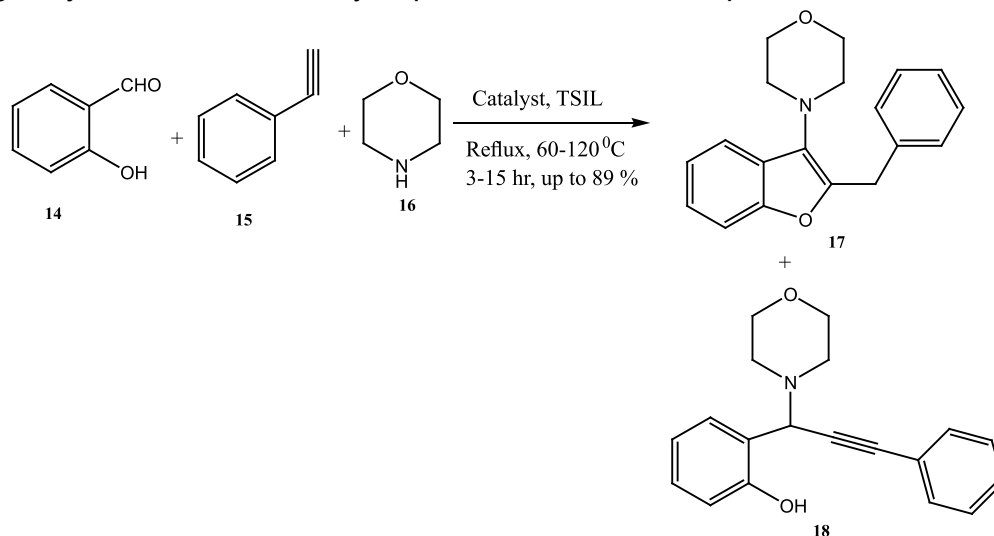
Scheme 2

Wang, Jiang and Dai (2008) proposed many ionic liquids, which were based on Brønsted acidic benzimidazolium, and used it for catalytic reactions in the acetalisation of many different ketones **11** with substituted 1,2-ethanediols **12**. This reaction produced acetals **13** in good yields (Scheme 3). However, they used different other types of catalysts, while it was found that the 1-ethyl-3-(3-sulfopropyl)benzimidazolium hydrogen sulfate, [PSebim]HSO₄ **10**, an ionic liquid, was most efficient and high yielding acetalisation reaction for this reaction.



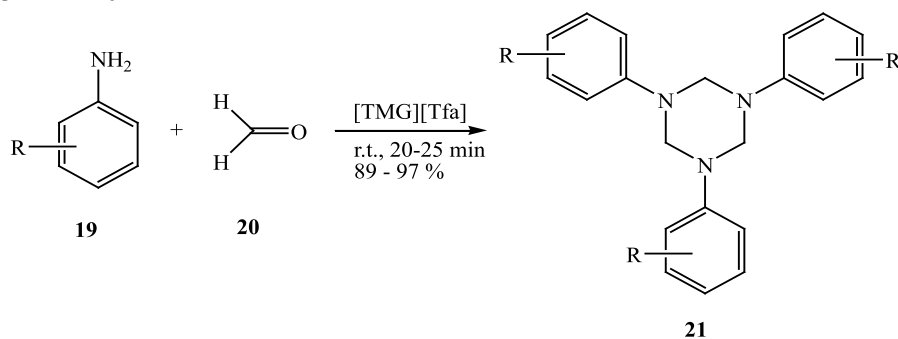
Scheme 3

Zhang *et al.* (2011) reported a most efficient and practical synthesis of benzo[b]furan 17 and propargylamine 18. The reaction of 2-hydroxybenzaldehyde 14, phenylacetylene 15 and morpholine 16 yield product 17 and 18. This reaction was carried out in the presence of different types of ionic liquids, such as [Bmim]OAc, [Bmim]BF₄ and [Bmim]PF₆ (Scheme 4). While it was found that the use of [Bmim]BF₄, the compound propargylamine 18 produced more affordably, with the use of other ionic liquids [Bmim]PF₆ and [Bmim]OAc, the compound of benzo[b]furan 17 produced affordably with good yield because of the hydrophobic nature of ionic liquid.



Scheme 4

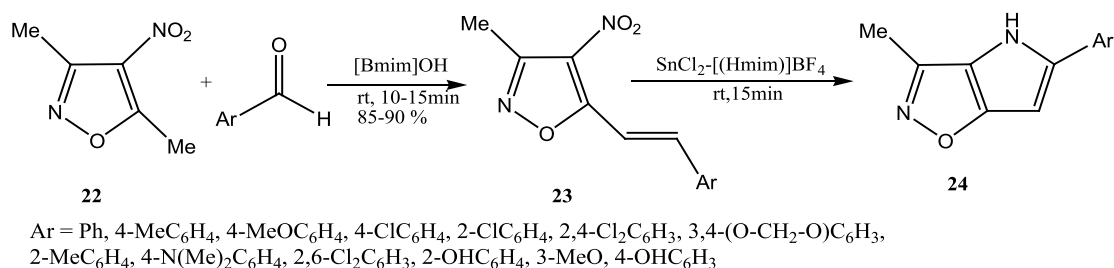
Dandia, Jain and Sharma (2014) reported the condensation reaction, in which the different substituted aniline 19 reacts with formaldehyde 20 to produce a derivative of 1,3,5-triazine 21 in the presence of ionic liquid 1,1,3,3-tetramethylguanidine trifluoroacetate [TMG][Tfa] (Scheme 5). This reaction was one of the green synthesis methods for the preparation of triazine derivatives. This compound showed great activity against *Mycobacterium tuberculosis*.



R= 2/3/4-F; 2/3/4-CF₃; 2-Cl,5-CF₃; 2-CF₃, 4-NO₂; 2-Br, 4-F; H; 4-Me;4-OMe; 4-Cl; 4-Br

Scheme 5

An effective method has been developed by Rajanarendar *et al.* (2010) for the synthesis of pyrrolo[2,3-d]isoxazoles 24 from the reaction between 3,5-dimethyl-4-nitroisoxazole 22 and several aldehydes. This reaction is carried out by using different types of ionic liquids: 1-Hexyl-3-methylimidazolium tetrafluoroborate [Hmim]BF₄ and 1-methyl-3-butylimidazolium hydroxide [Bmim]OH. The compound 22 undergoes Knoevenagel condensation with different types of aldehyde 1 to produce nitrostyrylisoxazoles 23 through condensation with ionic liquid [Bmim]OH, which is further converted into compound 24 with [Hmim]BF₄ and SnCl₂ (Scheme 6). The ionic liquid [Hmim]BF₄ gives excellent yield (85-92%) of compound 24 at room temperature.



Scheme 6

Conclusion

Ionic liquids are essentially molten salts, meaning they are composed entirely of ions, specifically organic or inorganic cations and anions. Ionic liquids are considered a green solvent due to their low vapour pressure and recycling nature. Ionic liquids give a wide range of organic synthetic reactions. Ionic liquid has been used by several chemists and scientists in chemical synthesis regarding environmental approaches. They have enormous and interesting attention in green synthesis. Regarding advantages of green chemistry, hopefully, the industry will alter conventional methods of synthesis of compounds with greener ones.

Acknowledgement

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References

- Chaturvedi, D., Kumar, C., Zaidi, S., & Chaturvedi, A. K. (2014). Task specific ionic liquids: Reaction selectivity in organic synthesis. *Journal of Organic & Biomolecular Chemistry*, 2, 51-79.
- Dandia, A., Jain, A. K. & Sharma, S. (2014). Task-specific Ionic Liquid-mediated Facile Synthesis of 1,3,5-Triaryltriazines by Cyclotrimerization of Imines and Their Biological

- Evaluation. *Chemistry Letters*, 43(4), 521–523. <https://doi.org/10.1246/cl.130839>
- Dong, K., Liu, X., Dong, H., Zhang, X. & Zhang, S. (2017). Multiscale Studies on Ionic Liquids. *Chemical Reviews*, 117(10), 6636–6695. <https://pubs.acs.org/doi/10.1021/acs.chemrev.6b00776>
- Jaeger, D. A. & Tucker, C. E. (1989). Diels-Alder reactions in ethylammonium nitrate, a low-melting fused salt. *Tetrahedron Letters*, 30(14), 1785-1788. [https://doi.org/10.1016/S0040-4039\(00\)99579-0](https://doi.org/10.1016/S0040-4039(00)99579-0)
- Lei, Z., Chen, B., Koo, Y-M. & MacFarlae, D. R. (2017). Introduction: Ionic Liquids. *Chem. Rev.*, 117, 6633–6635. <https://doi.org/10.1021/acs.chemrev.7b00246>
- Lei, Z., Dai, C., Hallett, J. & Shiflett, M. (2024). Introduction: Ionic Liquids for Diverse Applications. *Chemical Reviews*, 124(12), 7533-7535. <https://doi.org/10.1021/acs.chemrev.4c00291>
- Ma, J., Zhou, X., Zang, X., Wang, C., Wang, Z., Li, J., & Li, Q. (2007). A green and efficient synthesis of 9-aryl-3, 4, 5, 6, 7, 9-hexahydroxanthene-1, 8-dione using a task-specific ionic liquid as dual catalyst and solvent. *Australian Journal of Chemistry*, 60(2), 146-148. <https://doi.org/10.1071/CH06225>
- Rajanarendar, E., Raju, S., Reddy, A. S. R., Reddy, K. G. & Reddy, M. N. (2010). A Fast and Highly Efficient Protocol for Synthesis of Pyrrolo[2,3-d]isoxazoles and a New Series of Novel Benzyl Bis-pyrrolo[2,3-d]isoxazoles Using Task-Specific Ionic Liquids as Catalyst and Green Solvent. *Chemical and Pharmaceutical Bulletin*, 58(6), 833-839. <https://doi.org/10.1248/cpb.58.833>
- Sowbhagyam, D. V. (2014). Ionic Liquids as Green Solvents: A Comprehensive Review, *International Research Journal on Advanced Engineering Hub*, 2(2), 220-224. <https://doi.org/10.47392/IRJAEH.2024.0035>
- Wang, Y., Jiang, D. & Dai, L. (2008). Novel Brønsted acidic ionic liquids based on benzimidazolium cation: Synthesis and catalyzed acetalization of aromatic aldehydes with diols. *Catalysis Communications*, 9(15), 2475-2480. <https://doi.org/10.1016/j.catcom.2008.06.021>
- Welton, T. (1990). Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.*, 99(8), 2071-2084. <https://pubs.acs.org/doi/10.1021/cr980032t>
- Yavari, I. & Kowsari, E. (2008). Task-Specific Basic Ionic Liquid: A Reusable and Green Catalyst for One-Pot Synthesis of Highly Functionalized Pyrroles in Aqueous Media. *Synlett*, 6, 897-899. <https://doi.org/10.1055/s-2008-1042912>
- Zhang, X., Li, D., Jia, X., Wang, J. & Fan, X. (2011). CuI/[bmim]OAc in [bmim]PF₆: A highly efficient and readily recyclable catalytic system for the synthesis of 2,3-disubstituted benzo[b]furans. *Catalysis Communications*, 2011,12, 839–843. <https://doi.org/10.1016/j.catcom.2011.01.024>

Advancing Sustainable Chemical Processes through the Use of Green Solvents and Reaction Media

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Abstract

The push for sustainable chemical processes underscores the importance of green solvents and reaction media as eco-friendly alternatives to conventional, often harmful chemicals. Traditional solvents, widely used in industrial processes, pose risks to health, deplete resources, and cause pollution. Green solvents, derived from renewable sources and characterised by their low toxicity, biodegradability, and minimal environmental impact, offer a viable solution. This review examines green solvents' classifications, properties, and applications in solvent extraction, organic synthesis, polymerisation, and industrial cleaning. Key types, including bio-based solvents, supercritical CO₂, ionic liquids, deep eutectic solvents, and fluorinated solvents, present unique sustainability advantages. Green reaction media also enhance reaction efficiency, selectivity, and safety while reducing waste and energy use. Despite scalability and cost challenges, advancing green chemistry principles through interdisciplinary collaboration and research could drive the chemical industry towards sustainability and global environmental progress.

Keywords: *Bio-Based Solvents; Environmental Impact; Green Solvents; Reaction Media; Renewable Resources; Sustainable Chemistry*

Introduction

In modern chemical processes, the choice of solvents and reaction media plays a fundamental role in determining the efficiency and outcome of reactions (Sun *et al.*, 2024). However, the impact of these solvents extends far beyond the lab or industrial setting, as the widespread use of conventional solvents presents serious environmental and health concerns (Martínez-Pérez-Cejuela & Gionfriddo, 2024). Traditional solvents, such as chlorinated hydrocarbons, aromatic hydrocarbons, and volatile organic compounds (VOCs), are widely used for their ability to dissolve reactants and facilitate a range of chemical transformations (Huang *et al.*, 2024). These solvents, though effective, are often toxic, non-biodegradable, and derived from non-renewable sources, contributing to air, water, and soil pollution. They pose a multitude of risks, including occupational hazards, ecological damage, and contributions to climate change due to their persistence and volatility (Li *et al.*, 2024a).

The production, use, and disposal of conventional solvents result in significant emissions of hazardous air pollutants (HAPs), greenhouse gases (GHGs), and other toxic substances, exacerbating the environmental footprint of the chemical industry. The impact on human health is equally concerning (Khan *et al.*, 2023). Many traditional solvents are known carcinogens or neurotoxins, causing both acute and chronic health issues. Workers exposed to these chemicals in industrial or laboratory settings often experience skin irritation, respiratory distress, neurological effects, and, in severe cases, long-term illnesses such as cancer or liver damage (Otitolaiye, Al-Naaimi & Abdelrahim, 2024). The volatility of these compounds leads to their release into the atmosphere, contributing to poor air quality and increasing the risk of occupational exposure. In addition to the direct risks to workers, solvent emissions contribute to broader public health challenges, including respiratory diseases linked to air pollution (Zhou *et al.*, 2023). Furthermore, the environmental persistence of conventional solvents means that they often bioaccumulate, disrupting ecosystems and posing long-term ecological risks, including contamination of water sources and soil (Iyiola *et al.*, 2024). In light of these pervasive issues, it has become increasingly clear that the continued reliance on traditional solvents is unsustainable, both for human health and the environment. The need for safer, more environmentally benign alternatives is more urgent than ever.

This is where the principles of sustainable chemistry, specifically green chemistry, come into focus. Green chemistry emphasises the design of chemical products and processes that reduce or eliminate the generation of hazardous substances. These principles align with the growing recognition that the chemical industry must shift towards more sustainable practices to mitigate its environmental impact and safeguard human health. One of the foundational principles of green chemistry is the development and use of safer solvents and reaction media (Shaoo & Banik, 2024). Green chemistry encourages the replacement of toxic, non-renewable solvents with alternatives that are non-toxic, renewable, and biodegradable, thereby reducing the overall ecological footprint of chemical processes (Naeem *et al.*, 2024). By minimizing the production of hazardous waste and utilising renewable resources, green chemistry aims to create processes that are not only effective but also sustainable in the long term (Mohan *et al.*, 2024). This approach not only aligns with global environmental goals but also addresses growing regulatory pressures and societal demands for safer chemical practices. The adoption of green solvents and reaction media is crucial for advancing the goals of green chemistry (Sharma, Gallou & Handa, 2024). Green solvents are typically defined by their reduced toxicity, biodegradability, and minimal environmental impact. Many are derived from renewable resources, such as plants or biomass, and can be recycled or safely disposed of without causing harm to the environment (de Souza Mesquita *et al.*, 2024). These solvents present an opportunity to minimise the environmental and health risks associated with traditional solvents while maintaining the efficiency and functionality required for industrial and research applications. For example, water, supercritical carbon dioxide, ionic liquids, deep eutectic solvents, and bio-based solvents are among the most prominent alternatives being explored and implemented in various fields of chemistry (Dongare *et al.*, 2024). These solvents not only meet the criteria for environmental sustainability but also offer unique properties that can enhance the efficiency of chemical

reactions, such as improved selectivity, lower energy requirements, and reduced waste generation (González-Campos *et al.*, 2024). The incorporation of such solvents into mainstream chemical processes can significantly reduce the industry's dependence on harmful substances and help transition toward a more circular economy, where resources are reused and recycled.

The purpose of this review paper is to provide an in-depth analysis of green solvents and reaction media, emphasizing their potential to transform the chemical industry into a more sustainable enterprise. This review will explore the classification, properties, and applications of green solvents, illustrating how they can replace conventional solvents in a wide range of chemical processes, from solvent extraction and organic synthesis to polymerisation and industrial cleaning. By offering a comprehensive overview of the current landscape of green solvents, this paper aims to highlight both the progress that has been made and the challenges that remain in achieving widespread adoption of these environmentally friendly alternatives. Special attention will be given to the practical applications of green solvents in industrial and laboratory settings, as well as the economic and scalability considerations that influence their implementation. Furthermore, this review will address the future directions for research and innovation in this field, advocating for continued investment in the development of novel solvents and reaction media that are not only greener but also more efficient and cost-effective. By fostering collaboration between academia, industry, and regulatory bodies, the chemical industry can take significant steps toward realising a more sustainable future, wherein the principles of green chemistry become the norm rather than the exception. Green solvents and reaction media hold immense potential to reduce the ecological footprint of chemical processes while also improving safety and efficiency. This review aims to contribute to the ongoing discourse on sustainable chemistry by offering a thorough examination of the available green solvents (Figure 1) and their practical applications, as well as by identifying the barriers to their widespread adoption. The transition to green solvents is not without its challenges, but with continued research, innovation, and a commitment to sustainability, the chemical industry can pave the way for a greener, safer, and more responsible future.

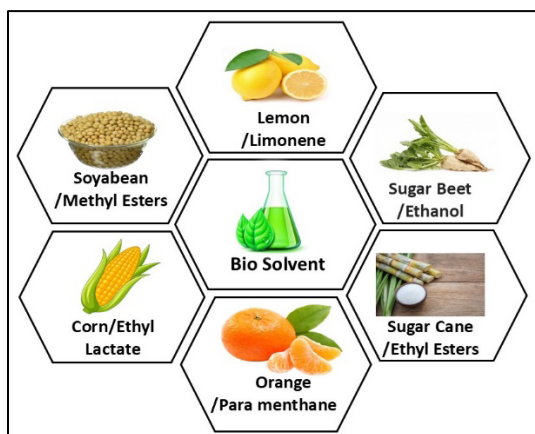


Figure 1: Schematic Representation of Different Sources of Green Solvents (Source: Author)

Traditional Solvents and Their Environmental Impact

In the realm of chemical processes, conventional solvents such as chlorinated hydrocarbons, aromatic hydrocarbons, and volatile organic compounds (VOCs) have long served as critical agents for dissolving reactants and facilitating various reactions (Ruan *et al.*, 2023). These solvents are prized for their solvating power, versatility, and capacity to dissolve a wide range of organic and inorganic compounds, making them indispensable in both laboratory research and large-scale industrial operations. Chlorinated hydrocarbons, such as chloroform, dichloromethane, and carbon tetrachloride, are often used in processes like extraction, degreasing, and dry cleaning due to their strong solvating capabilities (Mohr & Hatton, 2020). Aromatic hydrocarbons, such as benzene, toluene, and xylene, find extensive applications in the manufacture of plastics, pharmaceuticals, and paints (Saggu & Kumar, 2025), while volatile organic compounds (VOCs), which include a broad class of organic chemicals like acetone, hexane, and ethyl acetate, are frequently employed as solvents in adhesives, coatings, and cleaning products (Mangotra & Singh, 2024). Despite their widespread use and effectiveness, these traditional solvents present substantial risks due to their environmental persistence, toxicity, and tendency to volatilise into the atmosphere.

Chlorinated hydrocarbons, for example, are notorious for their environmental impact. These compounds are highly persistent in the environment, often bioaccumulating in ecosystems and causing long-term harm to wildlife. Their widespread use has led to significant contamination of air, water, and soil (Said & El Zokm, 2024). For instance, dichloromethane and chloroform are known to degrade slowly in the atmosphere, contributing to ozone depletion and global warming (Roozitalab *et al.*, 2024). When released into the environment, they can accumulate in water bodies, posing risks to aquatic life due to their toxicity and ability to disrupt biological processes. Similarly, aromatic hydrocarbons like benzene are highly toxic and carcinogenic, with prolonged exposure linked to severe health issues such as leukaemia (Saeedi, Malekmohammadi & Tajalli, 2024). Benzene is classified as a Group 1 carcinogen by the International Agency for Research on Cancer (IARC), and its presence in industrial effluents poses a significant public health risk (Zahed *et al.*, 2024). Benzene and other aromatic hydrocarbons are also volatile, readily vaporising into the atmosphere and contributing to the formation of ground-level ozone and smog, both of which are major components of air pollution (Isha *et al.*, 2024). VOCs are perhaps the most pervasive class of traditional solvents in terms of environmental impact. These compounds are highly volatile, and their emissions contribute to poor indoor and outdoor air quality. VOCs are responsible for the formation of photochemical smog, which not only degrades air quality but also exacerbates respiratory conditions such as asthma and bronchitis in humans (Edo *et al.*, 2024).

The health risks associated with traditional solvents are well-documented, affecting both workers in industrial settings and the general population through environmental exposure. Many of these solvents are classified as carcinogens, mutagens, or teratogens, meaning they can cause cancer, genetic mutations, or birth defects, respectively (Vulimiri *et al.*, 2022). Chlorinated hydrocarbons, for example, are known to cause liver and kidney damage with

prolonged exposure, and carbon tetrachloride is a potent hepatotoxin, causing liver failure in individuals exposed to high levels. Moreover, these solvents are highly volatile, meaning that even short-term exposure can lead to acute health effects such as dizziness, headaches, nausea, and respiratory irritation (Hahn, Botzenhart & Schweinsberg, 2024). Long-term exposure, particularly in occupational settings, can result in chronic conditions, including neurological damage, immune system suppression, and reproductive toxicity. Aromatic hydrocarbons like toluene and xylene have also been implicated in a range of health issues, from central nervous system depression to organ damage. Toluene exposure, even at relatively low levels, has been linked to cognitive impairments, while xylene can cause serious effects on the liver and kidneys (Rajput, Singh & Bhardwaj, 2025). Volatile organic compounds, due to their tendency to vaporise at room temperature, pose significant inhalation hazards. Workers in industries where VOCs are commonly used, such as painting, coating, and cleaning, are at particularly high risk of exposure. Short-term inhalation of VOCs can cause eye, nose, and throat irritation, headaches, and fatigue, while long-term exposure can result in more severe effects, such as liver and kidney damage or central nervous system disorders. Additionally, VOCs contribute to poor indoor air quality, a growing concern in both residential and industrial environments. For example, formaldehyde, a common VOC used in manufacturing, has been classified as a human carcinogen, and its presence in building materials, furnishings, and household products can lead to continuous low-level exposure, particularly in poorly ventilated spaces (Bhat *et al.*, 2024). Moreover, when released into the environment, VOCs react with nitrogen oxides in the presence of sunlight to form ozone and secondary organic aerosols, which are key components of smog. Smog is not only a significant environmental pollutant but also a major health hazard, as it has been linked to respiratory problems, cardiovascular diseases, and premature mortality (Yuan *et al.*, 2024).

Beyond the direct health risks, the environmental implications of traditional solvent use are profound, contributing to pollution, toxicity, and resource depletion. Chlorinated hydrocarbons, for example, persist in the environment, undergoing minimal biodegradation, which allows them to accumulate in ecosystems over time. This persistence leads to contamination of air, water, and soil, posing long-term risks to both human and ecological health. In aquatic environments, these solvents can be particularly harmful, as they tend to bioaccumulate in the tissues of aquatic organisms, leading to biomagnification in food chains and adverse effects on biodiversity (Adeola *et al.*, 2024). For instance, chlorinated solvents like trichloroethylene (TCE) are frequently detected in groundwater contamination sites, creating significant challenges for water treatment facilities and posing risks to communities reliant on these water sources. Moreover, the reliance on conventional solvents contributes to resource depletion, as many of these chemicals are derived from non-renewable fossil fuels (Gürses *et al.*, 2024). The extraction and processing of petroleum to produce solvents not only consumes finite natural resources but also results in significant carbon emissions, contributing to climate change. For example, the production of aromatic hydrocarbons such as benzene and toluene involves energy-intensive refining processes that release large quantities of CO₂ and other greenhouse gases into the atmosphere (Modirzadeh *et al.*, 2024). Furthermore, the disposal of traditional solvents often presents additional

environmental challenges. Improper disposal methods, such as incineration or landfilling, can result in the release of harmful by-products, including dioxins and furans, which are highly toxic and can persist in the environment for decades.

Green Chemistry: Principles and Guidelines

Green chemistry, also known as sustainable chemistry, represents a paradigm shift in chemical science and engineering. Its aim is to design chemical products and processes that reduce or eliminate the generation of hazardous substances (Verma *et al.*, 2024). Developed in response to the growing environmental concerns linked to conventional chemical practices, green chemistry seeks to create a more sustainable future by focusing on pollution prevention at the molecular level rather than relying on end-of-pipe treatment solutions. The 12 core principles of green chemistry, first articulated by Paul Anastas and John Warner in 1998, serve as a framework for guiding chemists toward more environmentally benign practices (Cannon *et al.*, 2024). These principles emphasise the importance of preventing waste, designing safer chemicals, using renewable feedstocks, and improving energy efficiency, among others. Within this context, solvent choice plays a critical role. Traditional solvents, as previously discussed, are among the most significant contributors to chemical waste and pollution. Consequently, the selection of greener solvents aligns with several key principles of green chemistry, particularly those aimed at reducing toxicity, enhancing safety, and improving the sustainability of chemical processes.

One of the central tenets of green chemistry is the careful selection and design of solvents that minimise environmental harm while maintaining efficacy in facilitating chemical reactions (Banjare *et al.*, 2024). Solvents are involved in nearly all stages of chemical production, from synthesis and purification to product formulation and application. Therefore, the choice of solvent directly impacts the overall sustainability of a process. For a solvent to be considered "green", it must meet several important criteria. First, it should exhibit low toxicity to both humans and the environment. This aligns with the principle of designing safer chemicals, which aims to minimise the adverse health effects associated with chemical exposure (Prabhune & Dey, 2023). Second, green solvents should be biodegradable or readily broken down by natural processes, thus preventing long-term persistence in the environment. Biodegradability ensures that solvents do not accumulate in ecosystems, reducing the risks of bioaccumulation and biomagnification in food chains (Qadeer *et al.*, 2024). Additionally, green solvents should be derived from renewable resources rather than non-renewable petrochemical feedstocks. This reflects the principle of using renewable materials, which is critical for reducing the dependence on fossil fuels and mitigating the environmental impacts of resource extraction and processing (Mohammad *et al.*, 2023).

Assessing the greenness of solvents requires the use of key metrics that help to quantify their environmental and health impacts. One of the most important metrics is toxicity, which refers to the potential of a solvent to cause harm to humans, animals, and ecosystems (Imam & Abdelrahman, 2023). Solvents with low toxicity profiles are preferred because they pose fewer risks to workers, consumers, and the environment. Another key metric is biodegradability, which measures the ability of a solvent to be broken down by microorganisms into harmless byproducts such as water and carbon dioxide. Solvents that

are biodegradable are less likely to persist in the environment and cause long-term contamination. In addition to toxicity and biodegradability, the environmental impact of a solvent is assessed through its potential to contribute to issues like global warming, ozone depletion, and smog formation (Usman *et al.*, 2023). For example, solvents that have high global warming potential (GWP) or contribute to the formation of tropospheric ozone are considered environmentally harmful and should be avoided (Ravanchi & Soleimani, 2023). The volatility of a solvent, measured by its vapour pressure, is another important factor to consider. Volatile solvents can easily evaporate into the atmosphere, contributing to air pollution and posing hazards for inhalation. As such, green solvents should ideally have low volatility to minimise these risks. Finally, energy efficiency is another metric to consider when evaluating solvents. Solvents that require lower energy inputs for synthesis, separation, and recycling are more sustainable, as they help to reduce the overall carbon footprint of chemical processes. This aligns with the green chemistry principle of increasing energy efficiency, which emphasises the importance of minimising energy consumption throughout the lifecycle of a chemical product.

In practice, green solvents encompass a variety of alternative solvent classes, including water, bio-based solvents, supercritical fluids, and ionic liquids (Dutta, 2024). Water, often referred to as the universal solvent, is a particularly attractive option in green chemistry due to its abundance, non-toxicity, and ability to dissolve a wide range of substances. Water-based reactions are already employed in industries such as pharmaceuticals and food processing, and advances in aqueous chemistry continue to expand its applications. However, the limitations of water—such as its high polarity and inability to dissolve certain organic compounds—necessitate the exploration of other green solvent alternatives (Ramos-Villaseñor, Sartillo-Piscil & Frontana-Urbe, 2024). Bio-based solvents, derived from renewable biological sources such as corn, soybeans, and citrus fruits, offer another promising category of green solvents. These solvents, which include bioethanol, limonene, and glycerol, are generally non-toxic, biodegradable, and renewable (Singh *et al.*, 2024). Supercritical fluids, such as supercritical carbon dioxide (scCO₂), are another green solvent option that has gained popularity due to their unique properties. scCO₂, in particular, is valued for its low toxicity, non-flammability, and ability to act as a solvent for a wide range of organic and inorganic compounds. Additionally, scCO₂ can be easily removed from reaction products, reducing the need for energy-intensive separation processes (Kessler *et al.*, 2024). Ionic liquids, which are salts in liquid form, are another class of green solvents known for their low volatility and tunable properties. While ionic liquids offer many advantages in terms of reduced environmental impact, their biodegradability and toxicity profiles remain areas of active research and development (Lei *et al.*, 2024). Each of these solvent classes offers distinct advantages and disadvantages, and their selection should be based on a holistic assessment of the specific needs of a given chemical process.

Classification and Properties of Green Solvents

Green solvents have become critical in modern chemical processes, providing environmentally friendly alternatives to traditional solvents, which often carry significant health and environmental risks. These solvents can be classified into several categories

based on their origin, chemical composition, and applications, each offering unique properties that cater to the growing demands of sustainable chemistry (Sharma, Gallou & Handa, 2024). This section provides an in-depth look at the most prominent classes of green solvents: bio-based solvents, water, supercritical CO₂, ionic liquids, deep eutectic solvents (DES), and fluorinated solvents. Each class of solvent possesses distinct characteristics and advantages that contribute to the overall greenness of chemical processes.

Bio-Based Solvents, Water, and Supercritical CO₂ Bio-based solvents are derived from renewable biological sources, such as plants, algae, or microorganisms, and are considered some of the most promising alternatives to traditional petrochemical solvents (Sheldon, 2024). Common examples of bio-based solvents include bioethanol (from the fermentation of corn or sugarcane), glycerol (a byproduct of biodiesel production), and limonene (extracted from citrus fruit peels). These solvents are typically non-toxic, biodegradable, and have a lower environmental footprint compared to their petroleum-derived counterparts (Vasileiadou, 2024). Their synthesis involves simple, energy-efficient processes, often relying on natural resources or waste materials, making them both sustainable and cost-effective. For example, limonene, widely used as a solvent in cleaning products, paints, and coatings, offers the dual benefit of being biodegradable and non-toxic while providing excellent solvency for a variety of applications (Mori, 2023). The environmental benefits of bio-based solvents are clear: by using renewable feedstocks, they help reduce dependency on fossil fuels and lower greenhouse gas emissions, thus aligning with the principles of green chemistry, particularly the use of renewable materials and the prevention of waste.

Water is another widely recognised green solvent due to its abundance, low cost, and non-toxic nature. It is often referred to as the "universal solvent" because of its ability to dissolve a wide variety of substances, making it indispensable in countless chemical processes (Queffelec *et al.*, 2024). However, water's unique properties extend far beyond its solubility power. Its high heat capacity and polarity make it suitable for facilitating a range of chemical reactions, including hydrolysis, oxidation, and acid-base catalysis. In recent years, significant advances have been made in the field of aqueous-phase catalysis, where water acts as the solvent for chemical transformations, such as the production of fine chemicals and pharmaceuticals (Kokkinos & Zachos, 2024). Additionally, water's ability to form hydrogen bonds with solutes enhances its effectiveness as a medium for certain organic reactions, such as cycloaddition and condensation reactions. The environmental benefits of using water as a solvent are numerous, including the elimination of hazardous waste and the reduction of solvent emissions. However, the primary limitation of water is its polarity, which can restrict its use in dissolving non-polar substances, necessitating the development of innovative water-based reaction systems that can expand its applicability (Gholami *et al.*, 2024).

Supercritical carbon dioxide (scCO₂) is another green solvent gaining popularity, particularly in the fields of extraction, catalysis, and material synthesis (Yıldırım *et al.*, 2024). scCO₂ is carbon dioxide that has been compressed and heated beyond its critical temperature and pressure, allowing it to exhibit the properties of both a liquid and a gas. This unique state enables scCO₂ to dissolve a wide range of solutes while maintaining the low viscosity and

high diffusivity of a gas. One of the most notable applications of scCO_2 is in supercritical fluid extraction (SFE), where it is used to extract bioactive compounds from natural products, such as caffeine from coffee beans or essential oils from plants (Herzyk, Piłakowska-Pietras & Korzeniowska, 2024). Unlike conventional organic solvents, scCO_2 is non-toxic, non-flammable, and can be easily separated from the extracted product by simply reducing pressure, eliminating the need for energy-intensive purification steps.

Moreover, since scCO_2 is obtained from naturally occurring carbon dioxide, it is considered a renewable solvent. Its use helps mitigate environmental concerns associated with organic solvent waste and reduces the overall carbon footprint of chemical processes (Hadi & Rahman, 2024). Despite its many advantages, the primary drawback of scCO_2 lies in its inability to dissolve highly polar substances, which limits its applicability to certain types of reactions (Kang *et al.*, 2024). Nonetheless, its use in green chemistry continues to expand, particularly in fields where clean, solvent-free processes are prioritised.

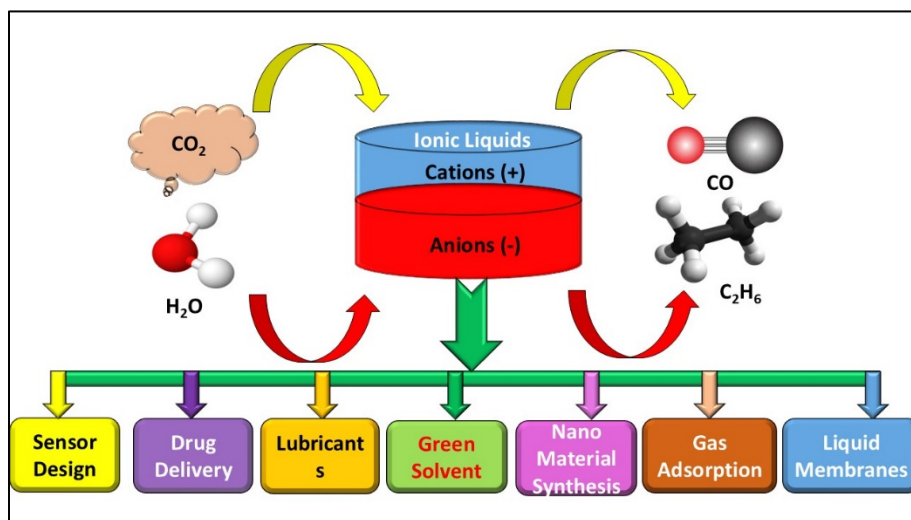


Figure 2: Schematic Drawing of Ionic Liquids and Their Applications (Source: Author)

Ionic Liquids, Deep Eutectic Solvents, and Fluorinated Solvents Ionic liquids (ILs) are salts in a liquid state, typically composed of large organic cations and smaller inorganic anions (Figure 2). Unlike traditional solvents, ionic liquids exhibit negligible vapour pressure, making them environmentally friendly due to the absence of volatile organic compounds (VOCs) (Gujjala *et al.*, 2024). Additionally, their tunable properties—such as polarity, hydrophobicity, and viscosity—make them highly versatile solvents for a wide range of applications, including catalysis, separation processes, and electrochemical reactions (Li *et al.*, 2024b). Ionic liquids have been particularly successful in facilitating reactions that involve difficult-to-handle reagents or products, such as in the synthesis of pharmaceuticals and the extraction of metals. Moreover, ionic liquids are often recyclable, allowing for their reuse in multiple cycles of a reaction without significant loss of performance (Shi *et al.*, 2024a).

However, despite their numerous advantages, the environmental profile of ionic liquids is still under investigation (Rothee *et al.*, 2024). While they are considered green solvents due to their non-volatility, concerns have been raised about their biodegradability and long-term ecological impact. As such, ongoing research is focused on developing more sustainable ionic liquids with improved biodegradability and reduced toxicity.

Deep eutectic solvents (DES) are another class of green solvents that have gained attention due to their simplicity and eco-friendliness (Elhamarnah, Qiblawey & Nasser, 2024). DES is formed by mixing two or more components, typically a hydrogen bond donor and a hydrogen bond acceptor, which interact to create a eutectic mixture with a melting point lower than that of the individual components. Common DES components include choline chloride and urea, both of which are inexpensive and readily available. DES offers several advantages, including low toxicity, biodegradability, and the ability to dissolve a wide range of substances. They have been used in various industrial applications, such as metal recovery, biomass processing, and organic synthesis (Najaf-Abadi, Ghobadian & Dehghani-Soufi, 2024). One of the key benefits of DES is its ability to replace traditional solvents in environmentally challenging processes, such as the extraction of bioactive compounds from plants or the recycling of waste materials.

Furthermore, DES is often synthesised from renewable materials, aligning with the principles of green chemistry that emphasise the use of renewable feedstocks (Weerasinghe *et al.*, 2024). However, DES still faces challenges related to their viscosity and thermal stability, which can limit their effectiveness in certain applications.

Fluorinated solvents, though not as widely recognised as other green solvents, play a significant role in specific applications, particularly in energy storage systems, such as lithium-ion batteries and supercapacitors (Molaiyan *et al.*, 2024). These solvents are designed to be chemically stable, non-flammable, and capable of dissolving electrolytes without decomposing under extreme conditions. Fluorinated solvents, such as fluorinated ethers and perfluorocarbons, offer the advantage of low toxicity and high chemical resistance, making them suitable for use in harsh environments, including high-temperature and high-voltage applications (Shi *et al.*, 2024b).

Additionally, their low global warming potential and low ozone-depleting potential contribute to their environmental credentials. In battery applications, fluorinated solvents help improve the stability and performance of the electrolyte, thereby enhancing the overall efficiency and lifespan of energy storage devices. However, the production and disposal of fluorinated solvents remain a concern, as they can be challenging to recycle and may pose environmental risks if not properly managed (Wang *et al.*, 2024). Despite these challenges, ongoing research is focused on improving the sustainability of fluorinated solvents to further reduce their environmental impact.

Applications for Green Solvents in Chemical Processes

The transition towards sustainable chemistry has prompted a reevaluation of traditional solvent use across various chemical processes, leading to the adoption of green solvents (Figure 3) as viable alternatives (Lin *et al.*, 2024). One of the primary applications of green

solvents is in solvent extraction and separation processes, where they have been shown to offer significant advantages over conventional solvents (Shrivastav *et al.*, 2024). Traditional solvents often pose health and environmental risks due to their volatility and toxicity, which can lead to hazardous waste and air pollution. Green solvents, on the other hand, provide a safer and more sustainable solution. For instance, bio-based solvents like ethyl lactate and glycerol have been successfully employed in the extraction of essential oils and natural products, offering lower toxicity and better biodegradability than their conventional counterparts. Additionally, the use of supercritical CO₂ in extraction processes eliminates the need for organic solvents entirely, minimising waste generation and facilitating easier product recovery. Studies have demonstrated that these green solvents can yield comparable or even superior extraction efficiencies, making them a preferred choice for industries aiming to reduce their environmental footprint.

In organic synthesis and catalysis, green solvents play a crucial role in enhancing reaction yields and selectivity. Traditional organic solvents often lead to undesirable side reactions and lower product purity, requiring extensive purification steps (Gao *et al.*, 2023). Green solvents can improve the efficiency of reactions by providing a more suitable medium for reactants. For instance, water as a solvent has been used in several catalytic reactions, significantly improving yields and simplifying product isolation.

The use of ionic liquids in organic synthesis also exemplifies the benefits of green solvents, as they can stabilise reactive intermediates, leading to increased selectivity and reduced by-product formation. Moreover, the ability to tune the properties of ionic liquids allows chemists to design solvents that are specifically tailored for particular reactions, further enhancing the efficiency of organic synthesis (Mohammed, Hadrawi & Kianfar, 2023). The incorporation of green solvents in these processes not only improves economic viability by reducing costs associated with purification and waste disposal but also aligns with the principles of green chemistry by minimising hazardous substances (de Souza Mesquita *et al.*, 2024).

Green solvents are also gaining traction in polymerisation and material synthesis, where they contribute to reducing volatile organic compound (VOC) emissions and producing more sustainable materials. Traditional solvents used in polymer production often emit VOCs, which pose significant health risks and contribute to environmental pollution. The adoption of bio-based solvents and supercritical fluids in polymerisation processes can significantly decrease or even eliminate VOC emissions. For example, bio-based solvents such as ethanol or bio-acetone have been employed in the synthesis of biodegradable polymers, enabling the production of eco-friendly materials with lower environmental impacts (Podapangi *et al.*, 2023).

Additionally, supercritical CO₂ has been utilised in the polymerisation of various monomers, resulting in high-purity polymers without the need for toxic solvents. This not only reduces the environmental burden of polymer production but also enhances the sustainability of materials used in various applications, including packaging and construction (Hayes *et al.*, 2022). The integration of green solvents into polymerisation processes thus represents a critical step toward more sustainable manufacturing practices.

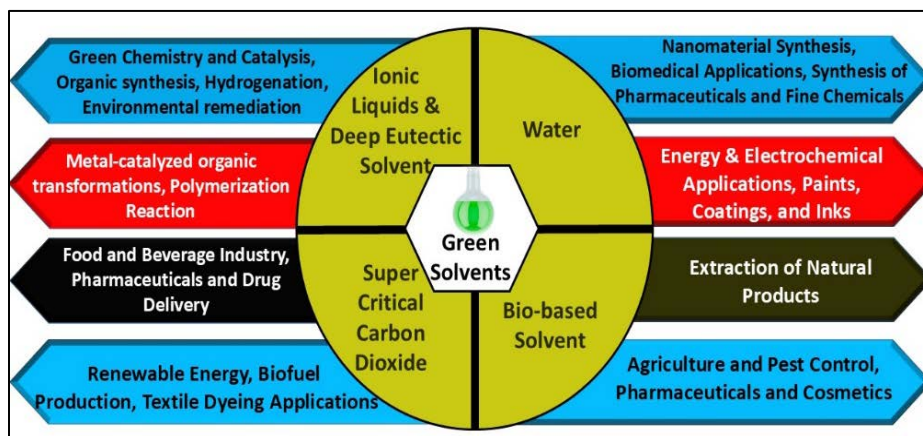


Figure 3: Schematic Representation of Different Green Solvents and Their Fields of Applications (Source: Author)

Cleaning and degreasing processes across various industries, including automotive and aerospace, are also increasingly adopting green solvents as effective alternatives to conventional solvents (Kanchana *et al.*, 2024). Traditional cleaning agents often contain hazardous chemicals that can be harmful to both human health and the environment. Green solvents, such as terpenes, bio-based solvents, and ionic liquids, offer safe and effective cleaning solutions without compromising performance (Usman *et al.*, 2023). For instance, citrus-based solvents have been employed in automotive cleaning applications, effectively removing grease and oil while biodegradable and non-toxic (Suri, Singh & Nema, 2021). In the aerospace industry, the use of supercritical CO₂ cleaning has gained traction as a method to clean complex components without the adverse effects associated with chlorinated solvents. These green cleaning agents not only meet regulatory requirements for reduced VOC emissions but also enhance workplace safety for employees. By replacing hazardous traditional solvents with green alternatives, industries can significantly improve their environmental profile while maintaining operational efficiency.

The pharmaceutical and agrochemical industries have also embraced the use of green solvents in their synthesis processes, leading to numerous advantages, including regulatory compliance and improved safety profiles (Dutta *et al.*, 2022). The increasing pressure from regulatory agencies to minimise the use of hazardous substances has propelled the adoption of green solvents in these sectors. Case studies demonstrate that the integration of bio-based solvents and other green alternatives has led to more efficient synthetic routes and reduced environmental impacts. For example, the synthesis of active pharmaceutical ingredients (APIs) using water or bio-based solvents has been shown to enhance product purity while reducing toxic waste generation (Schenck *et al.*, 2024). Additionally, the use of ionic liquids in agrochemical formulations has enabled the development of safer and more effective pesticides with lower environmental persistence. These advancements not only comply with regulatory standards but also align with the industry's commitment to sustainable practices. The incorporation of green solvents in pharmaceutical and

agrochemical synthesis exemplifies how the principles of green chemistry can be effectively applied to reduce the environmental footprint of chemical production while maintaining product quality and safety.

Designing Green Reaction Media

The design of sustainable reaction media is crucial in enhancing reaction rates, efficiency, and selectivity in chemical processes (Ahmed *et al.*, 2023). Traditional solvents often hinder reaction performance due to their toxicity, volatility, and environmental impact, necessitating the search for greener alternatives. Green reaction media not only reduce the environmental footprint but also improve the efficiency of chemical reactions by providing more favorable conditions for reactants. For example, water as a reaction medium has been widely recognized for its ability to facilitate numerous reactions due to its unique properties, such as high polarity and ability to solvate a wide range of organic and inorganic compounds. By utilising green solvents or solvent systems that are less toxic and more biodegradable, chemists can optimize reaction conditions while simultaneously addressing environmental and safety concerns. The shift toward green reaction media is aligned with the principles of green chemistry, which advocate for the design of processes that minimize waste and hazardous materials while enhancing the overall sustainability of chemical production (Martinengo *et al.*, 2024).

Solvent-free systems represent a promising approach to green chemistry, offering significant advantages but also posing certain challenges (Castiello *et al.*, 2023). In solvent-free reactions, the absence of traditional solvents can lead to higher reaction rates and improved selectivity due to increased concentrations of reactants. These systems often simplify the purification processes, as there is no solvent to remove, reducing waste and resource consumption. However, implementing solvent-free systems can also present challenges, such as difficulties in controlling reaction temperature and managing heat transfer, particularly in large-scale processes (Chen, Tariq & Gu, 2024). Some reactions may also require solvents to dissolve reactants or facilitate specific reaction mechanisms, making it essential to evaluate the compatibility of solvent-free systems with various types of reactions. Despite these challenges, the exploration of solvent-free systems is gaining traction, with many researchers demonstrating successful applications across a range of chemical transformations, further reinforcing the feasibility of this approach in sustainable chemistry.

Aqueous systems and other environmentally benign solvents have emerged as key components in the design of green reaction media, offering a variety of advantages in chemical processes. Water, as a universally accepted solvent, provides a safe and non-toxic alternative that enhances reaction kinetics and selectivity for many organic reactions, including substitutions, oxidations, and reductions. Other environmentally benign solvents, such as bio-based solvents and ionic liquids, have also been extensively researched and applied in various chemical transformations. For instance, ionic liquids have been recognized for their unique properties, such as low volatility and tunable polarity, making them effective for a wide range of applications, from catalysis to extraction processes. Several case studies highlight the successful use of these green reaction media in industries such as pharmaceuticals, where water and ionic liquids have been utilized to synthesize

complex compounds with improved yields and reduced environmental impacts (Costa, Forster-Carneiro & Hallett, 2024). These advancements underscore the importance of designing reaction media that not only meet the demands of modern chemistry but also align with the principles of sustainability, ultimately leading to safer and more efficient chemical processes that benefit both industry and the environment.

Challenges in Implementing Green Solvents

Despite the numerous advantages of green solvents in promoting sustainable chemical processes, several challenges hinder their widespread adoption in industry (Qiao *et al.*, 2024). One of the primary barriers is the scalability and cost-effectiveness of these alternatives. While many green solvents demonstrate favourable environmental profiles and safety benefits in laboratory settings, scaling up these processes for industrial applications often proves difficult (Amani *et al.*, 2024). The synthesis of green solvents can sometimes involve higher costs and complexities compared to conventional solvents, which are often derived from established processes and readily available fossil fuels. Additionally, industries frequently operate under tight profit margins, making the transition to greener alternatives financially challenging. Without significant economic incentives or regulatory pressures, companies may hesitate to invest in new technologies or change their established practices. Consequently, achieving large-scale implementation of green solvents necessitates not only further research into cost-effective production methods but also potential government support through subsidies, tax incentives, or stringent regulations on hazardous solvents (Lau *et al.*, 2024).

Another significant challenge in the transition to green solvents lies in the limited availability of alternatives for specific chemical reactions that still depend on hazardous solvents (Ramos-Villaseñor, Sartillo-Piscil & Frontana-Urbe, 2024). Many traditional solvents, such as chlorinated hydrocarbons or aromatic hydrocarbons, possess properties that are difficult to replicate with green alternatives, resulting in certain reactions remaining reliant on these toxic substances. Moreover, there are still many chemical processes for which suitable green solvent replacements have not yet been developed, creating a gap that hampers the complete adoption of sustainable practices (Mainkar, Ray & Chandrasekhar, 2024). This situation highlights the need for further research to identify and design novel green solvents with tailored properties that can meet the diverse requirements of various reactions. To bridge this gap, collaborative efforts among academia, industry, and regulatory bodies are essential to accelerating the discovery and optimisation of green solvents. By focusing on developing solvents that can perform similarly or even outperform traditional solvents while minimising environmental impacts, the chemical industry can move closer to achieving a more sustainable and responsible approach to chemical manufacturing.

Future Perspectives and Research Directions

The future of green solvents and sustainable practices in the chemical industry hinges on innovation, education, and collaboration. Advances in solvent synthesis are crucial, focusing on the development of novel green solvents from renewable sources, which can replace hazardous traditional solvents. Researchers are increasingly exploring bio-based materials,

waste feedstocks, and eco-friendly processes to create solvents with desirable properties that cater to various chemical reactions. Additionally, integrating green chemistry principles into educational curricula is paramount to fostering a generation of chemists equipped with the knowledge and skills to prioritise sustainability in their work. This educational shift will not only enhance awareness but also inspire innovative thinking among future scientists and engineers. Collaboration among academia, industry, and government entities is essential to drive the adoption of sustainable practices and ensure that research translates into practical applications. By working together, these stakeholders can facilitate the sharing of knowledge, resources, and best practices to overcome barriers to the widespread implementation of green solvents. Furthermore, technological advancements, including the development of smart reaction systems and process intensification techniques, hold the potential for breakthroughs in green chemistry. These innovations can streamline chemical processes, enhance efficiency, and reduce waste generation, making sustainable practices more attractive and feasible for industries. Ultimately, by focusing on these key areas, the chemical industry can move towards a more sustainable future, minimising environmental impact while ensuring safety and efficiency in chemical processes.

Conclusion

In conclusion, the transition to green solvents and reaction media represents a pivotal shift towards more sustainable chemical processes that can significantly mitigate environmental risks. The key benefits of adopting green solvents include reduced toxicity, a lower environmental impact, and the use of renewable resources, which collectively contribute to minimising pollution and promoting safer working conditions in the chemical industry. By replacing conventional solvents with environmentally friendly alternatives, companies can enhance the overall sustainability of their operations while adhering to increasing regulatory demands and consumer expectations for greener practices. However, the importance of continuous innovation and research cannot be overstated; ongoing efforts to develop novel green solvents with tailored properties are crucial for expanding the range of applications and addressing the specific needs of various chemical processes. Furthermore, as the chemical industry faces mounting challenges related to resource depletion and climate change, it is imperative to embrace a paradigm shift towards greener processes that prioritise environmental stewardship. This transition not only aligns with global sustainability goals but also positions the industry as a leader in responsible innovation. By investing in research, fostering collaboration among academia, industry, and regulatory bodies, and integrating green chemistry principles into education, the chemical sector can pave the way for a more sustainable future. The commitment to adopting greener solvents and reaction media will ultimately lead to enhanced efficiency, reduced waste generation, and a more harmonious relationship between chemical production and the environment, ensuring that future generations inherit a healthier planet.

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References

- Adeola, A. O., Paramo, L., Fuoco, G., & Naccache, R. (2024). Emerging hazardous chemicals and biological pollutants in Canadian aquatic systems and remediation approaches: A comprehensive status report. *Science of The Total Environment*, 176267. <https://doi.org/10.1016/j.scitotenv.2024.176267>
- Ahmed, M., Ahmad, K. A., Vo, D. V. N., Yusuf, M., Haq, A., Abdullah, A., ... & Athar, M. (2023). Recent trends in sustainable biodiesel production using heterogeneous nanocatalysts: function of supports, promoters, synthesis techniques, reaction mechanism, and kinetics and thermodynamic studies. *Energy Conversion and Management*, 280, 116821. <https://doi.org/10.1016/j.enconman.2023.116821>
- Amani, A. M., Tayebi, L., Vafa, E., Abbasi, M., Vaez, A., Kamyab, H., ... & Bazargan-Lari, R. (2024). On the horizon of greener pathways to travel into a greener future portal: Green MXenes, environment-friendly synthesis, and their innovative applications. *Journal of Cleaner Production*, 436, 140606. <https://doi.org/10.1016/j.jclepro.2024.140606>
- Banjare, M. K., Behera, K., Banjare, R. K., Tandon, M., Pandey, S., & Ghosh, K. K. (2024). Application of green chemistry for environmental remediation. In *Green Chemistry Approaches to Environmental Sustainability* (pp. 67-91). Elsevier. <https://doi.org/10.1016/B978-0-443-18959-3.00008-2>
- Bhat, A. A., Afzal, M., Goyal, A., Gupta, G., Thapa, R., Kazmi, I., ... & Dua, K. (2024). The impact of formaldehyde exposure on lung inflammatory disorders: insights into asthma, bronchitis, and pulmonary fibrosis. *Chemico-biological interactions*, 394, 111002. <https://doi.org/10.1016/j.cbi.2024.111002>
- Cannon, A. S., Warner, J. C., Vidal, J. L., O'Neil, N. J., Nyansa, M. M., Obhi, N. K., & Moir, J. W. (2024). A promise to a sustainable future: 10 years of the Green Chemistry Commitment at Beyond Benign. *Green Chemistry*, 26(12), 6983-6993. <https://doi.org/10.1039/D4GC00575A>
- Castiello, C., Junghanns, P., Mergel, A., Jacob, C., Ducho, C., Valente, S., ... & Mai, A. (2023). GreenMedChem: the challenge in the next decade toward eco-friendly compounds and processes in drug design. *Green Chemistry*, 25(6), 2109-2169. <https://doi.org/10.1039/D2GC03772F>
- Chen, S., Tariq, N. H., & Gu, Y. (2024). Recent Achievements in Organic Reactions in Bio-based Solvents. *Green Solvents in Organic Synthesis*, 107-135. <https://doi.org/10.1002/9783527841943.ch3>

- Costa, J. M., Forster-Carneiro, T., & Hallett, J. P. (2024). Progress in the applications of biocompatible ionic liquids: renewable commodity production, catalytic and pharmaceutical approaches—a review. *Green Chemistry*, 26(2), 705-719. <https://doi.org/10.1039/D3GC03693F>
- de Souza Mesquita, L. M., Contieri, L. S., e Silva, F. A., Bagini, R. H., Bragagnolo, F. S., Strieder, M. M., ... & Rostagno, M. A. (2024). Path2Green: introducing 12 green extraction principles and a novel metric for assessing sustainability in biomass valorization. *Green Chemistry*, 26(19), 10087-10106. <https://doi.org/10.1039/D4GC02512A>
- Dongare, S., Zeeshan, M., Aydogdu, A. S., Dikki, R., Kurtoğlu-Öztulum, S. F., Coskun, O. K., ... & Gurkan, B. (2024). Reactive capture and electrochemical conversion of CO₂ with ionic liquids and deep eutectic solvents. *Chemical Society Reviews*, 53(17), 8563-8631. <https://doi.org/10.1039/D4CS00390J>
- Dutta, P., McGranaghan, A., Keller, I., Patil, Y., Mulholland, N., Murudi, V., ... & Godineau, E. (2022). A case study in green chemistry: the reduction of hazardous solvents in an industrial R&D environment. *Green Chemistry*, 24(10), 3943-3956. <https://doi.org/10.1039/D2GC00698G>
- Dutta, S. (2024). Catalytic transformation of carbohydrates into renewable organic chemicals by revering the principles of green chemistry. *ACS omega*, 9(25), 26805-26825. <https://doi.org/10.1021/acsomega.4c01960>
- Edo, G. I., Itoje-akpokiniyovo, L. O., Obasohan, P., Ikpekor, V. O., Samuel, P. O., Jikah, A. N., ... & Agbo, J. J. (2024). Impact of environmental pollution from human activities on water, air quality and climate change. *Ecological Frontiers*. <https://doi.org/10.1016/j.ecofro.2024.02.014>
- Elhamarnah, Y., Qiblawey, H., & Nasser, M. (2024). A review on deep eutectic solvents as the emerging class of green solvents for membrane fabrication and separations. *Journal of Molecular Liquids*, 398, 124250. <https://doi.org/10.1016/j.molliq.2024.124250>
- Gao, F., Chang, H., Li, J., Wang, R., & Gu, Y. (2023). Replacing polar aprotic solvents with water in organic synthesis. *Current Opinion in Green and Sustainable Chemistry*, 40, 100774. <https://doi.org/10.1016/j.cogsc.2023.100774>
- Gholami, T., Seifi, H., Dawi, E. A., Pirsaeheb, M., Seifi, S., Aljeboree, A. M., ... & Salavati-Niasari, M. (2024). A review on investigating the effect of solvent on the synthesis, morphology, shape and size of nanostructures. *Materials Science and Engineering: B*, 304, 117370. <https://doi.org/10.1016/j.mseb.2024.117370>
- González-Campos, J. B., Pérez-Nava, A., Valle-Sánchez, M., & Delgado-Rangel, L. H. (2024). Deep eutectic solvents applications aligned to 2030 United Nations Agenda for Sustainable Development. *Chemical Engineering and Processing-Process Intensification*, 199, 109751. <https://doi.org/10.1016/j.cep.2024.109751>
- Gujjala, L. K. S., Kundu, D., Dutta, D., Kumar, A., Bal, M., Kumar, A., ... & Vo, D. V. N. (2024). Advances in ionic liquids: Synthesis, environmental remediation and reusability. *Journal of Molecular Liquids*, 396, 123896. <https://doi.org/10.1016/j.molliq.2023.123896>
- Gürses, A., Güneş, K., Şahin, E., & Açıkyıldız, M. (2023). Technological Applications for Green and Sustainable Production and Elimination of Environmental Pollution. In *Green Chemistry, its Role in Achieving Sustainable Development Goals, Volume1* (pp. 81-128). CRC Press. <https://doi.org/10.1201/9781003301769-4>

- Hadi, N. A., & Rahman, M. H. (2024). Green Solvent Modification of Starch: Ionic Liquids (ILs) and Supercritical Carbon Dioxide (ScCO₂). In *Advanced Research in Starch* (pp. 117-162). Singapore: Springer Nature Singapore. http://dx.doi.org/10.1007/978-981-99-9527-1_4
- HAHN, T., BOTZENHART, K., & SCHWEINSBERG, F. (2024). TOXIC EFFECTS OF SOLVENT. *Handbook of Solvents, Volume 2: Use, Health, and Environment*, 1433.
- Hayes, G., Laurel, M., MacKinnon, D., Zhao, T., Houck, H. A., & Becer, C. R. (2022). Polymers without petrochemicals: sustainable routes to conventional monomers. *Chemical Reviews*, 123(5), 2609-2734. <https://doi.org/10.1021/acs.chemrev.2c00354>
- Herzyk, F., Piłakowska-Pietras, D., & Korzeniowska, M. (2024). Supercritical extraction techniques for obtaining biologically active substances from a variety of plant byproducts. *Foods*, 13(11), 1713. <https://doi.org/10.3390/foods13111713>
- Huang, H., Xie, X., Xiao, F., Liu, B., Zhang, T., Feng, F., ... & Zhang, C. (2024). A Critical Review of Deep Oxidation of Gaseous Volatile Organic Compounds via Aqueous Advanced Oxidation Processes. *Environmental Science & Technology*, 58(42), 18456-18473. <https://doi.org/10.1021/acs.est.4c07202>
- Imam, M. S., & Abdelrahman, M. M. (2023). How environmentally friendly is the analytical process? A paradigm overview of ten greenness assessment metric approaches for analytical methods. *Trends in Environmental Analytical Chemistry*, 38, e00202. <https://doi.org/10.1016/j.teac.2023.e00202>
- Isha, Ali, S., Khalid, A., Naseer, I. A., Raza, H., & Chang, Y. C. (2024). Bioremediation of Smog: Current Trends and Future Perspectives. *Processes*, 12(10), 2266. <https://doi.org/10.3390/pr12102266>
- Iyiola, A. O., Ipinmoroti, M. O., Akingba, O. O., Ewutanure, J. S., Setufe, S. B., Bilikoni, J., ... & Wangboje, O. M. (2024). Organic chemical pollutants within water systems and sustainable management strategies. In *Water Crises and Sustainable Management in the Global South* (pp. 211-251). Singapore: Springer Nature Singapore. https://doi.org/10.1007/978-981-97-4966-9_7
- Kanchana, R., Ponnuchamy, M., Kapoor, A., & Sethupathi, P. B. (2024). Coatings in the Automobile Application. *Functional Coatings for Biomedical, Energy, and Environmental Applications*, 343-361. <https://doi.org/10.1002/9781394263172.ch15>
- Kang, X., Mao, L., Shi, J., Liu, Y., Zhai, B., Xu, J., ... & Guo, L. (2024). Supercritical carbon dioxide systems for sustainable and efficient dissolution of solutes: a review. *Environmental Chemistry Letters*, 22(2), 815-839. <https://doi.org/10.1007/s10311-023-01681-4>
- Kessler, J. C., Martins, I. M., Manrique, Y. A., Rodrigues, A. E., Barreiro, M. F., & Dias, M. M. (2024). Advancements in conventional and supercritical CO₂ extraction of *Moringa oleifera* bioactives for cosmetic applications: A review. *The Journal of Supercritical Fluids*, 106388. <https://doi.org/10.1016/j.supflu.2024.106388>
- Khan, N. A., López-Maldonado, E. A., Majumder, A., Singh, S., Varshney, R., López, J. R., ... & Aljundi, I. H. (2023). A state-of-art-review on emerging contaminants: Environmental chemistry, health effect, and modern treatment methods. *Chemosphere*, 344, 140264. <https://doi.org/10.1016/j.chemosphere.2023.140264>

- Kokkinos, N. C., & Zachos, D. K. (2024). Aqueous-phase hydroformylation processes with homogeneous catalysts. In *Homogeneous Carbonylation and Hydroformylation Reactions* (pp. 211-233). Elsevier. <https://doi.org/10.1016/B978-0-443-15560-4.00010-1>
- Lau, J. I. C., Wang, Y. S., Ang, T., Seo, J. C. F., Khadaroo, S. N., Chew, J. J., ... & Sunarso, J. (2024). Emerging technologies, policies and challenges toward implementing sustainable aviation fuel (SAF). *Biomass and Bioenergy*, 186, 107277. <https://doi.org/10.1016/j.biombioe.2024.107277>
- Lei, Z., Dai, C., Hallett, J., & Shiflett, M. (2024). Introduction: Ionic liquids for diverse applications. *Chemical Reviews*, 124(12), 7533-7535. <https://doi.org/10.1021/acs.chemrev.4c00291>
- Li, J., Qin, Y., Zhang, X., Shan, B., & Liu, C. (2024a). Emission characteristics, environmental impacts, and health risks of volatile organic compounds from asphalt materials: a state-of-the-art review. *Energy & Fuels*, 38(6), 4787-4802. <https://doi.org/10.1021/acs.energyfuels.3c04438>
- Li, Z., Han, Q., Wang, K., Song, S., Xue, Y., Ji, X., ... & Zhang, S. (2024b). Ionic liquids as a tunable solvent and modifier for biocatalysis. *Catalysis Reviews*, 66(2), 484-530. <https://doi.org/10.1080/01614940.2022.2074359>
- Lin, Q., Chee, P. L., Pang, J. J., Loh, X. J., Kai, D., & Lim, J. Y. (2024). Sustainable Polymeric Biomaterials from Alternative Feedstocks. *ACS Biomaterials Science & Engineering*, 10(11), 6751-6765. <https://doi.org/10.1021/acsbiomaterials.4c01154>
- Mainkar, P., Ray, A., & Chandrasekhar, S. (2024). SOLVENTS: From Past to Present. *ACS omega*, 9(7), 7271-7276. <https://doi.org/10.1021/acsomega.3c07508>
- Mangotra, A., & Singh, S. K. (2024). Volatile organic compounds: A threat to the environment and health hazards to living organisms—A review. *Journal of Biotechnology*, 382, 51-69. <https://doi.org/10.1016/j.jbiotec.2023.12.013>
- Martinengo, B., Diamanti, E., Uliassi, E., & Bolognesi, M. L. (2024). Harnessing the 12 Green Chemistry Principles for Sustainable Antiparasitic Drugs: Toward the One Health Approach. *ACS Infectious Diseases*, 10(6), 1856-1870. <https://doi.org/10.1021/acsinfecdis.4c00172>
- Martínez-Pérez-Cejuela, H., & Gionfriddo, E. (2024). Evolution of green sample preparation: fostering a sustainable tomorrow in analytical sciences. *Analytical chemistry*, 96(20), 7840-7863. <https://doi.org/10.1021/acs.analchem.4c01328>
- Modirzadeh, S. A., Khazaei, A., GhasemiKafrudi, E., Sobhani, Z., Kashefi, K., Moradi, M. A., & Moradzadeh, M. (2024). Potentials of greenhouse gas emission reduction through energy efficiency improvement in Iran's petrochemical sector. *Energy*, 311, 133297. <https://doi.org/10.1016/j.energy.2024.133297>
- Mohammad, R. E. A., Abdullahi, S. S. A., Muhammed, H. A., Musa, H., Habibu, S., Jagaba, A. H., & Birniwa, A. H. (2024). Recent technical and non-technical biorefinery development barriers and potential solutions for a sustainable environment: A mini review. *Case Studies in Chemical and Environmental Engineering*, 9, 100586. <https://doi.org/10.1016/j.cscee.2023.100586>
- Mohammed, K. J., Hadrawi, S. K., & Kianfar, E. (2023). Synthesis and modification of nanoparticles with ionic liquids: a review. *BioNanoScience*, 13(2), 760-783. <https://doi.org/10.1007/s12668-023-01075-4>

- Mohan, C., Robinson, J., Vodwal, L., & Kumari, N. (2024). Sustainable Development Goals for addressing environmental challenges. In *Green chemistry approaches to environmental sustainability* (pp. 357-374). Elsevier. <https://doi.org/10.1016/B978-0-443-18959-3.00007-0>
- Mohr, T. K., & Hatton, J. (2020). Environmental Fate and Transport of Solvent-Stabilizer Compounds. In *Environmental Investigation and Remediation* (pp. 125-214). CRC Press. <https://doi.org/10.1201/9780429401428>
- Molaiyan, P., Bhattacharyya, S., dos Reis, G. S., Sliz, R., Paoletta, A., & Lassi, U. (2024). Towards greener batteries: sustainable components and materials for next-generation batteries. *Green Chemistry*, 26(13), 7508-7531. <https://doi.org/10.1039/D3GC05027K>
- Mori, R. (2023). Replacing all petroleum-based chemical products with natural biomass-based chemical products: a tutorial review. *RSC Sustainability*, 1(2), 179-212. <https://doi.org/10.1039/D2SU00014H>
- Naeem, A., Saeed, B., AlMohamadi, H., Lee, M., Gilani, M. A., Nawaz, R., ... & Yasin, M. (2024). Sustainable and green membranes for chemical separations: A review. *Separation and Purification Technology*, 336, 126271. <https://doi.org/10.1016/j.seppur.2024.126271>
- Najaf-Abadi, M. K., Ghobadian, B., & Dehghani-Soufi, M. (2024). A review on application of deep eutectic solvents as green catalysts and co-solvents in biodiesel production and purification processes. *Biomass Conversion and Biorefinery*, 14(3), 3117-3134. <https://doi.org/10.1007/s13399-022-02644-5>
- Otitolaiye, V. O., Al-Naaimi, M., & Abdelrahim, R. (2024). Unlocking the impact of chemicals on the health and safety of pharmaceutical workers: A concise review. *International Journal of Occupational Safety and Health*, 14(3), 424-435. <https://doi.org/10.3126/ijosh.v14i3.64773>
- Podapangi, S. K., Jafarzadeh, F., Mattiello, S., Korukonda, T. B., Singh, A., Beverina, L., & Brown, T. M. (2023). Green solvents, materials, and lead-free semiconductors for sustainable fabrication of perovskite solar cells. *RSC advances*, 13(27), 18165-18206. <https://doi.org/10.1039/D3RA01692G>
- Prabhune, A., & Dey, R. (2023). Green and sustainable solvents of the future: Deep eutectic solvents. *Journal of Molecular Liquids*, 379, 121676. <https://doi.org/10.1016/j.molliq.2023.121676>
- Qadeer, A., Anis, M., Warner, G. R., Potts, C., Giovanoulis, G., Nasr, S., ... & Shuhang, W. (2024). Global environmental and toxicological data of emerging plasticizers: current knowledge, regrettable substitution dilemma, green solution and future perspectives. *Green Chemistry*. <https://doi.org/10.1039/D3GC03428C>
- Qiao, W., Zhang, R., Wen, Y., Wang, X., Wang, Z., Tang, G., ... & Liu, C. (2024). Green Solvents in Battery Recycle: Status and Challenges. *Journal of Materials Chemistry A*. <https://doi.org/10.1039/D3TA07905H>
- Queffelec, J., Beraud, W., Torres, M. D., & Domínguez, H. (2024). Advances in obtaining ready to use extracts with natural solvents. *Sustainable Chemistry and Pharmacy*, 38, 101478. <https://doi.org/10.1016/j.scp.2024.101478>
- Rajput, S. K., Singh, S., & Bhardwaj, R. (2025). Toluene toxicity: Outline, management, and prognosis. In *Hazardous Chemicals* (pp. 391-404). Academic Press. <https://doi.org/10.1016/B978-0-323-95235-4.00052-9>

- Ramos-Villaseñor, J. M., Sartillo-Piscil, F., & Frontana-Urbe, B. A. (2024). Opportunities and challenges for water/organic solvents mixtures and renewable green solvents in organic electrosynthesis. *Current Opinion in Electrochemistry*, 101467. <https://doi.org/10.1016/j.coelec.2024.101467>
- Ravanchi, M. T., & Soleimani, M. (2023). Global warming and greenhouse effect resulted from oil, gas, and petrochemical units. In *Crises in Oil, Gas and Petrochemical Industries* (pp. 257-282). Elsevier. <https://doi.org/10.1016/B978-0-323-95154-8.00002-5>
- Roozitalab, B., Emmons, L. K., Hornbrook, R. S., Kinnison, D. E., Fernandez, R. P., Li, Q., ... & Apel, E. C. (2024). Measurements and Modeling of the Interhemispheric Differences of Atmospheric Chlorinated Very Short-Lived Substances. *Journal of Geophysical Research: Atmospheres*, 129(2), e2023JD039518. <https://doi.org/10.1029/2023JD039518>
- Rothee, S. R., Heidari, H., Fortier, M. O., & Khan, E. (2024). Applications of ionic liquids in soil remediation: mechanisms, efficiency and life cycle assessment. *Soil & Environmental Health*, 100097. <https://doi.org/10.1016/j.seh.2024.100097>
- Ruan, T., Li, P., Wang, H., Li, T., & Jiang, G. (2023). Identification and prioritization of environmental organic pollutants: from an analytical and toxicological perspective. *Chemical Reviews*, 123(17), 10584-10640. <https://doi.org/10.1021/acs.chemrev.3c00056>
- Saeedi, M., Malekmohammadi, B., & Tajalli, S. (2024). Interaction of benzene, toluene, ethylbenzene, and xylene with human's body: Insights into characteristics, sources and health risks. *Journal of Hazardous Materials Advances*, 16, 100459. <https://doi.org/10.1016/j.hazadv.2024.100459>
- Saggu, G., & Kumar, A. (2025). Risk assessment of Xylene and its impact on environment and human health. In *Hazardous Chemicals* (pp. 375-389). Academic Press. <https://doi.org/10.1016/B978-0-323-95235-4.00019-0>
- Said, T. O., & El Zokm, G. M. (2024). Persistent Organic Pollutants in Aquatic Systems. *Classification, Toxicity, Remediation and Future Springer*, 1. <https://doi.org/10.1007/978-3-031-53341-9>
- Schenck, L., Risteen, B., Johnson, L. M., Koynov, A., Bonaga, L., Orr, R., & Hancock, B. (2024). A commentary on co-processed API as a promising approach to improve sustainability for the pharmaceutical industry. *Journal of Pharmaceutical Sciences*, 113(2), 306-313. <https://doi.org/10.1016/j.xphs.2023.11.034>
- Shaoo, B. M., & Banik, B. K. (2024). Solvent-less reactions: green and sustainable approaches in medicinal chemistry. In *Green approaches in medicinal chemistry for sustainable drug design* (pp. 387-408). Elsevier. <https://doi.org/10.1016/B978-0-443-16164-3.00017-0>
- Sharma, S., Gallou, F., & Handa, S. (2024). Towards a sustainable tomorrow: advancing green practices in organic chemistry. *Green Chemistry*, 26(11), 6289-6317. <https://doi.org/10.1039/D4GC01826E>
- Sheldon, R. A. (2024). Waste Valorization in a Sustainable Bio-Based Economy: The Road to Carbon Neutrality. *Chemistry—A European Journal*, 30(54), e202402207. <https://doi.org/10.1002/chem.202402207>
- Shi, H., Luo, Y., Yin, C., & Ou, L. (2024a). Review of the application of ionic liquid systems in achieving green and sustainable recycling of spent lithium-ion batteries. *Green Chemistry*, 26(14), 8100-8122. <https://doi.org/10.1039/D4GC01207K>

- Shi, J., Jiang, K., Fan, Y., Zhao, L., Cheng, Z., Yu, P., ... & Wan, M. (2024b). Advancing Metallic Lithium Anodes: A Review of Interface Design, Electrolyte Innovation, and Performance Enhancement Strategies. *Molecules*, 29(15), 3624. <https://doi.org/10.3390/molecules29153624>
- Shrivastav, G., Prava Jyoti, T., Chandel, S., & Singh, R. (2024). Eco-friendly extraction: innovations, principles, and comparison with traditional methods. *Separation & Purification Reviews*, 1-17. <https://doi.org/10.1080/15422119.2024.2381605>
- Singh, M. P., Kumar, P., Pal, P., Kumari, B., Prakash, O., Singh, A. K., ... & Prakash, A. (2024). Sustainable Solutions: Navigating Agrifood Waste with Eco-smart Approaches for a Greener Environment. In *Environmental Engineering and Waste Management: Recent Trends and Perspectives* (pp. 133-165). Cham: Springer Nature Switzerland. https://doi.org/10.1007/978-3-031-58441-1_5
- Sun, Y., Tong, Z., Yu, Y., Cheng, W., Li, Y., Zeng, S., ... & Yu, H. (2024). Solvent effects on carbohydrate transformation: insights into chemical pathway modulation. *Green Chemistry*, 26(12), 6900-6925. <https://doi.org/10.1039/D3GC04901A>
- Suri, S., Singh, A., & Nema, P. K. (2021). Recent advances in valorization of citrus fruits processing waste: A way forward towards environmental sustainability. *Food Science and Biotechnology*, 1-26. <https://doi.org/10.1007/s10068-021-00984-y>
- Usman, M., Cheng, S., Boonyubol, S., & Cross, J. S. (2023). Evaluating green solvents for bio-oil extraction: advancements, challenges, and future perspectives. *Energies*, 16(15), 5852. <https://doi.org/10.3390/en16155852>
- Vasileiadou, A. (2024). From Organic wastes to Bioenergy, Biofuels, and value-added products for urban sustainability and circular economy: a review. *Urban Science*, 8(3), 121. <https://doi.org/10.3390/urbansci8030121>
- Verma, C., Chauhan, D. S., Aslam, R., Banerjee, P., Aslam, J., Quadri, T. W., ... & Rasheed, T. (2024). Principles and theories of green chemistry for corrosion science and engineering: design and application. *Green Chemistry*, 26(8), 4270-4357. <https://doi.org/10.1039/D3GC05207A>
- Vulimiri, S. V., Pratt, M. M., Kulkarni, S., Beedanagari, S., & Mahadevan, B. (2017). Reproductive and developmental toxicity of solvents and gases. In *Reproductive and developmental toxicology* (pp. 379-396). Academic Press. <https://doi.org/10.1016/B978-0-12-804239-7.00021-4>
- Wang, Y., Wu, Z., Azad, F. M., Zhu, Y., Wang, L., Hawker, C. J., ... & Zhang, C. (2024). Fluorination in advanced battery design. *Nature Reviews Materials*, 9(2), 119-133. <https://doi.org/10.1038/s41578-023-00623-4>
- Weerasinghe, U. A., Wu, T., Chee, P. L., Yew, P. Y. M., Lee, H. K., Loh, X. J., & Kai, D. (2024). Deep eutectic solvents towards green polymeric materials. *Green Chemistry*. <https://doi.org/10.1039/D4GC00532E>
- Yıldırım, M., Erşatır, M., Poyraz, S., Amangeldinova, M., Kudrina, N. O., & Terletskaia, N. V. (2024). Green extraction of plant materials using supercritical CO₂: insights into methods, analysis, and bioactivity. *Plants*, 13(16), 2295. <https://doi.org/10.3390/plants13162295>

- Yuan, Q., Zhang, Z., Wang, M., Ho, K. F., Wang, T., & Lee, S. (2024). Characterization of a smog chamber for studying formation of gas-phase products and secondary organic aerosol. *Journal of Environmental Sciences*, 136, 570-582. <https://doi.org/10.1016/j.jes.2022.12.027>
- Zahed, M. A., Salehi, S., Khoei, M. A., Esmaeili, P., & Mohajeri, L. (2024). Risk assessment of Benzene, Toluene, Ethyl benzene, and Xylene (BTEX) in the atmospheric air around the world: A review. *Toxicology in Vitro*, 105825. <https://doi.org/10.1016/j.tiv.2024.105825>
- Zhou, X., Zhou, X., Wang, C., & Zhou, H. (2023). Environmental and human health impacts of volatile organic compounds: A perspective review. *Chemosphere*, 313, 137489. <https://doi.org/10.1016/j.chemosphere.2022.137489>

Advancements in Processing and Manufacturing of Nano-Engineered Materials: Exploring Nanotechnology Applications in Defence Materials

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Abstract

Nano-engineered content represents a land-breaking advancement in material science, offering unprecedented possibilities to the defence sector. Their extraordinary mechanical, electrical and thermal properties make them indispensable for applications such as light armour systems, stealth technologies, energy storage devices and advanced sensors. The review provides a comprehensive examination of the latest processing and manufacturing techniques for nanoengineered materials, including bottom-up and top-down approaches, as well as emerging technologies such as affordable manufacturing and laser-assisted fabrication. Along with possible solutions, challenges such as scalability, reproduction and integration are analysed with existing systems. The review also delays specific defence applications, highlighting the transformative ability of the nanometre in increasing operational efficiency and effectiveness. Closing with future prospects and moral ideas, this paper underlines the important role of interdisciplinary research in running innovations in nano-engineer materials for defence.

Keywords: Defence Material; Energy Storage; Fabrication; Nano-Engineered

Introduction

In the 21st century, pursuit of technical superiority has become integral for national security strategies worldwide. Among the innumerable factors running progress in defence systems, material has emerged as the cornerstone of science innovation (Patil, Vidhale & Titarmare, 2024). Increasing demands of modern war – ranging from increased mobility and survival to ranging logical burden – ensure the development of materials with extraordinary performance characteristics (Zabrodskiy *et al.*, 2022). Nano-engineer material, which takes advantage of the unique properties of the substance at the nanoscale, has attracted significant attention in this context. These materials provide unique opportunities to bring revolution in defence technologies, which provide lighter, strong, and multidisciplinary solutions to meet the complications of modern defence requirements (Simoes, 2024). The

unique properties of nanoengineered materials arise from their nanoscale dimensions, which increase the surface area, quantum effects and atomic precision. For example, nanosticated ceramics display exceptional hardness and wear resistance, making them ideal for protective coatings on aircraft and navy ships (Es-soufi *et al.*, 2024). Similarly, nanocomposites display exceptional mechanical conductivity and thermal stability, incorporating carbon nanotubes or graphene, which makes them invaluable in applications such as light body armour and advanced sensors (Fenta & Mebratie, 2024). The integration of nanotechnology in defence systems is no longer limited to experimental research but is moving rapidly towards the deployment in the real world, offering capabilities that were once considered science fiction.

The transformative ability of nanotechnology lies in the ability to engineer materials with those properties that can be accurately tuned for specific applications. This enables the development of accurate solutions that address important defence challenges, such as increasing stealth, improving energy efficiency, and protecting personnel in fighter environments (Guitton, 2021). Radar-absorbed material (RAMS) imitates this capacity by incorporating CNTs or graphene, roders of military assets significantly reduce cross-sections and improve survival in hostile areas. Similarly, nano-engineer coatings are designed to face extreme temperatures and oppose the corrosion, increasing the operational life of defence equipment deployed in a rigid environment (Hussain *et al.*, 2024). Adopting nano-engineer materials extends beyond traditional applications for the next generation technologies that redefine the boundaries of defence innovation. Autonomous systems, such as drones and unmanned ground vehicles, benefit from the integration of nanostructure materials in their light frames and energy-efficient power sources. In individual protective equipment, nanotechnology has led to the development of multicultural clothing that combines ballistic security with chemical and biological resistance (Selim *et al.*, 2024). In addition, progress in nanosensors and nanophotonics is paving the way for increased monitoring, communication and targeting systems, underlining the strategic value of nanotechnology in modern war (Turini, 2024).

Despite the huge promises of nanoengineered materials, their mass adoptions in defence systems face significant obstacles. Laboratory-scale research from industrial-scale production infections in the production scalability, cost-effectiveness and quality control (De Souza *et al.*, 2025) offers challenges. Unlike traditional materials, the synthesis of nanomaterials often involves complex techniques that require accurate control over parameters such as temperature, pressure, and reaction time. For example, the production of graphene through chemical vapour deposition (CVD) demands careful adaptation to ensure uniformity and defect-free structures (Kumar, Panda & Gangawane, 2024). Getting stability in properties in large batches of nanomaterials remains a major obstacle in their commercialisation. In addition, integration of nanoengineered materials in existing defence systems requires interdisciplinary cooperation in material science, engineering and defence technology. Current construction processes and infrastructure should be ensured to enable compatibility uninterrupted. The development of advanced manufacturing techniques, such as adorable manufacturing (3D printing) and atomic layer's statement, has shown promise in resolving these challenges (Hajare & Gajbhiye, 2022). However, high costs associated

with these methods and lack of standardised protocols obstruct widespread implementation. In addition, safety and environmental concerns related to nanomaterial production and disposal require stringent regulatory structures, giving another layer of complexity in the manufacturing process.

The purpose of these review papers is to provide intensive exploration of progressing and progress in the processing and construction of nano-engineered materials with special attention to their applications in defence. It begins by examining the basic properties of these materials that make them suitable for defence technologies, such as mechanical strength, thermal and electrical conductivity, and resistance to extreme conditions (Subham & Ray, 2024). The reviews, then the state-of-the-art techniques used in their construction include the down-up and top-down approaches, as well as innovative methods such as nanolithography and self-assembling. In addition to discussing current capabilities, the paper addresses the challenges associated with large-scale production and integration of nanoengineered content in defence systems. This examines moral ideas around their deployment, especially in terms of dual-use concerns and environmental impact (Singer *et al.*, 2025). The review ends by exposing future trends and possibilities in this rapidly developed area, including the convergence of nanotechnology with artificial intelligence, advanced manufacturing techniques and the development of smart and adaptive materials. By providing a comprehensive observation, this paper tries to contribute to the understanding of nano-engineered materials as a transformational force in defence, performing ground tasks for further research and innovation in this important field.

Fundamentals of Nano-Engineered Materials

Defining Nano-Engineered Materials

Nano-engineer content is a class of advanced materials defined by their structural dimensions within the nanoscale range (1–100 nanometres) (Gartia & Chakraverty, 2025). On this scale, the material displays an individual property that greatly deviates from their wholesale counterparts due to the emergence of quantum effects and an increase in surface-sector-to-volume ratio. These events lead to unique mechanical, thermal, electrical and optical characteristics that are unattainable in traditional materials. For example, nanoparticles have significantly greater reactivity and catalytic efficiency than their macroscopic forms, which is responsible for exponential growth in active surface area (Dutta *et al.*, 2024). This allows nanoscale manipulation engineers to tailor material for specific applications, making nano-engineered material indispensable in state-of-the-art technologies. In defence, the power of these materials, the ability to combine mild and multicultural, makes them a transformational force. From strong nanostructured coatings to radar-absorbed nanocomposites, their versatility operates innovation in various applications, including protective gear, stealth technologies and next-generation sensors (Shirke *et al.*, 2024).

Unique Properties of Nano-Engineered Materials

The extraordinary qualities of nano-engineer materials arise from their nanoscale accuracy and unique nuclear system. Materials such as mechanically, graphene and carbon

nanotubes increase many orders of magnitude more than traditional materials (Wang *et al.*, 2024). For example, graphene displays a tensile strength of about 130 GPA – 200 times stronger than steel – while being incredibly lighter. These properties make nano-engineer materials ideal for a strong armour system yet. Thermal properties also see remarkable enrichment; CNTs and graphene show more thermal conductivity than 3,000 W/m.K. Defence electronics and high-demonstration arms systems facilitate efficient heat wastage (Ren *et al.*, 2024). Similarly, electrical properties are enhanced, in which materials such as graphene enable the development of advanced energy storage systems and sensors. Optical properties, such as quantum dots and tuneable absorption spectra of quantum dots and gold nanoparticles, are exploited in applications ranging from stealth technology to advanced imaging systems (Zhou *et al.*, 2024). Finally, the chemical properties of nanomaterials, including high surface reactivity, enable their use in catalytic and environmental protection solutions, such as chemical war courses or pollution controls.

Comparison with Conventional Materials

When compared to traditional materials, nano-engineered content shows a different benefit in adaptability, efficiency and performance (Parvin *et al.*, 2025). Traditional materials such as steel or aluminium, while reliable and cost-effective, often lack essential multiplicity in modern defence applications. For example, steel is a go-to material for long-term armour systems, but its high density adds significant weight and limits mobility and energy efficiency in defence functions (Asgedom *et al.*, 2025). Nano-engineer options, such as graphene or CNT-reinforced nanocomposites, provide equivalent or better power with much lower weight, enabling increased dynamics and agility in military vehicles and personnel. In addition, traditional ceramics used in high-temperature applications can be replaced or enhanced with nanostructured ceramics such as zirconia, which provide better thermal stability and resistance to fracture (Lin *et al.*, 2025). The integration of nanomaterials not only addresses the boundaries of traditional materials but also introduces functionalities, such as self-treatment or adaptive behaviour, which were previously unattainable. This progress marks a paradigm change in how the material is designed and used in defence systems.

Types of Nano-Engineered Materials in Defence

Different types of nano-engineered materials complete a comprehensive spectrum of defence applications, taking advantage of their unique qualities to resolve each specific challenge. Carbon-based materials, including graphene, CNT and carbon nanofibers, have emerged at the forefront of defence innovation due to their unique mechanical, thermal and electrical properties (Fahri *et al.*, 2024). These materials are widely used in light body armour, energy storage devices and advanced electronics. Metal-based nanoparticles, such as gold, silver and iron oxide nanoparticles, have performed extraordinary optical and magnetic properties (Yameny, 2024). For example, gold nanoparticles – their surfaces are important in secret technology due to Plasmon resonance capabilities, which allow the manipulation of electromagnetic waves. Ceramic nanomaterials such as zirconia and alumina are used in high-temperature applications, such as thermal barrier coatings for jet engines and hypersonic vehicles. Overall nanomaterials, which combine polymers with

nanostructures, provide an optimal mixture of strength, flexibility and mild properties (Sabet, 2025). These composites are employed in protective gear and structural components for military equipment. Together, these materials represent a revolution in defence technology, providing innovative solutions for the versatile challenges of modern war.

Processing Techniques for Nano-Engineered Materials

Processing techniques for nano-engineered materials are important in shaping their properties and applications, especially in defence (Tian *et al.*, 2024). These techniques can be broadly classified into bottom-up and top-down approaches, with these paradigms to expand possibilities with emerging methods. While bottom-up methods focus on assembling by atom or molecule by molecule, top-down methods begin with bulk materials, breaking them into nanoscale dimensions. Both methods have their sets of advantages and boundaries with specific suitability depending on the desired properties and applications. In addition, recent innovations, such as adorable manufacturing and plasma-assisted fabrication, have greatly advanced the processing landscape, providing new avenues for scalable and cost-effective production of sequential nanomaterials for defence (Shah *et al.*, 2024).

Bottom-Up Approaches

Bottom-up approaches provide accurate control over physical properties by assembling structures at an atom or molecular level. These methods are important for creating high-quality nanomaterials with specific characteristics, making them indispensable in defence applications where accuracy and performance are paramount. Chemical vapour deposition (CVD) is one of the most widely planned bottom-up techniques, especially to synthesise graphene and carbon nanotube (CNTs) (Borane *et al.*, 2024). In this process, a precursor gas is decomposed at high temperatures, forcing nanomaterials on a substrate. The resulting structures are exceptionally similar, with applications ranging from advanced electronics to electromagnetic preservation in stealth technology. Similarly, the Sol-Gel process, a wet chemical technique, metal alkoxide (Zanurin *et al.*, 2022) enables the formation of ceramic nanoparticles and coatings by hydrolysing. This method is particularly valuable in creating heat-resistant coatings for defence applications, such as jet engine components and thermal security systems. Another important bottom-up approach is a self-regulatory assembly, where nanostructures spontaneously organise in high-order patterns. This technique is employed in the manufacture of nanosensors and photonic crystals, which are important for optical defence technologies and communication systems. Atomic layer deposition (ALD), a method associated with layer-by-layer deposits of the material, is another precise technique that is used to produce ultrathin films, which are accompanied by applications in electromagnetic preservation and secret technology (Kou *et al.*, 2024). These bottom-ups excel in producing materials with extraordinary uniformity and analogous properties. However, they often include boundaries in complex processes, high costs and scalability, which may be a hurdle for large-scale defence applications.

Top-Down Approaches

Top-down technology, by contrast, incorporates the breakdown of bulk material in nanoscale structures (Palagati & Reddy, 2024). While they have a lack of nuclear accuracy of down-up methods, their scalability and cost-effectiveness make them an attractive option for industrial-mammary applications in defence. For example, ball milling is a widely used top-down approach where high-energy confrontation between balls and a material leads to the formation of nanoparticles (Ogbezode *et al.*, 2024). This technique is particularly effective for the production of nanostructure powder used in light composites for body armour and structural components. Lithography, including electron-beam lithography and photolithography, allows for the manufacture of complex nanoscale patterns. These patterns are integral parts of microchips and other nanostructured devices that run modern defence technologies, such as precision-guided munitions and advanced sensors. Laser ablation, another notable technique, involves the use of high-energy lasers to evaporate wholesale materials in nanoparticles (Liang *et al.*, 2021). This method is especially useful for synthesising metal and ceramic nanoparticles, which are integral parts of energy-absorbing materials and protective coatings in defence systems. While top-down methods provide a practical approach to the production of nanomaterial, they often struggle with achieving a level of accuracy and uniformity as bottom-up techniques. In addition, it can introduce physical processes, such as mechanical pieces or laser evaporations, defects or irregularities that affect the performance of the material (Lu *et al.*, 2024). Despite these challenges, their scalability and relatively low cost make them an indispensable part of nanomaterials manufacturing.

Emerging Processing Methods

Beyond traditional bottom-up and top-down approaches, there are revolutions in the emerging methods such as adorable manufacturing, electrospinning and plasma-assisted fabrication. These techniques provide novel solutions for challenges for a long time, including scalability, complexity and cost-effectiveness, making them highly relevant to defence applications. Additive manufacturing (AM), commonly known as 3D printing, has obtained significant traction for the ability to directly create the complex nanostructure layer by layer (Onu & Lawal, 2024). This method is invaluable for rapid prototyping of components such as unmanned aerial vehicles (UAVs) and drones. By integrating nanomaterials in the process, AM allows for the manufacture of light, high-power components with complex designs; the material reduces waste and production time. Electrospinning, another innovative technique, polymer solution (Huang *et al.*, 2024) enables the production of nanofibers. These nanofibers are important for high-performance filtration systems used in the defence environment, such as protection against chemical and biological hazards.

Additionally, plasma-assisted fabrication employs plasma energy to modify or synthesise nanomaterials, such as hardness, wear resistance, and thermal stability, enhancing surface properties (Kumar *et al.*, 2024); this method is particularly useful for coverage systems, where enlarged surface properties can improve. These emerging methods bridge the gap between innovation on laboratory-mam and applications on industrial-fame. However, they also present new challenges, such as ensuring stability in physical properties and optimising production processes for cost efficiency (Zhao *et al.*, 2025).

Advantages and Limitations

Each processing technique comes with its set of advantages and boundaries to shape its suitability for specific defence applications. The exactness and tuneability offered by bottom-up approaches are unmatched, requiring highly specific physical properties, such as quantum sensors and stealth coatings (Mahajan *et al.*, 2024). However, their high cost and complexity often limit their use to niche applications. The top-down approach, while low in accuracy, excellence in scalability and cost-effectiveness, is suitable for mass production of nanomaterials used in light composites and structural components (Raghunathan *et al.*, 2024). Emerging methods such as additive manufacturing and plasma-assisted fabrication combine the strength of both approaches, which offer scalability without renouncing optimisation. Nevertheless, challenges such as maintaining environmental stability and management of production costs are important. Additionally, the environmental effects of some processing techniques, such as chemical vapour deposition or the generation of dangerous sub-products in Sol-Gel processes, require the development of greenery options (Sharma *et al.*, 2024).

Manufacturing Challenges and Solutions

Integration of nano-engineered materials in defence systems presents several manufacturing challenges that must be overcome for widespread use. While these materials provide significant benefits in terms of strength, weight loss and multifunctionality, such as scalability, cost, quality control, environmental impact, and issues such as integration in existing systems obstruct their adoption. A versatile approach is required to address these challenges, taking advantage of progress in manufacturing techniques, physics and cooperative efforts between industries, governments and defence sectors (Adeleke *et al.*, 2024). The section underscores the major challenges faced in the manufacture of nano-engineered materials for defence applications and examines potential solutions that can unlock their full capacity.

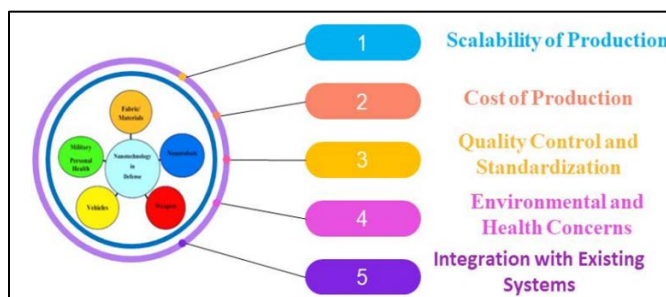


Figure 1 : Represents Several Manufacturing Challenges (Source: Author)

Scalability of Production

One of the most pressing challenges in adopting nano-engineered materials is scalability of production. Many of the promising nanomaterials, such as graphene, carbon nanotube

(CNT), and quantum dots, are commonly synthesised in low amounts under controlled laboratory conditions (Ayanda *et al.*, 2024). These synthesis methods often include complex processes that are difficult on a scale for mass production. As a result, laboratory-scale synthesis presents enough challenges in maintaining the uniformity and quality of infection materials in large-scale construction, especially when dealing with accurate properties such as size, size and surface characteristics (Mahmud *et al.*, 2024). The difficulty in increasing production limits the availability of these materials for large-scale defence applications, where there is a high demand for frequent quality and quantity.

Many solutions are being discovered to address these scalability issues. Advanced manufacturing technologies, such as roll-to-roll processing, have shown significant promise to increase the production of materials such as graphene (Marques *et al.*, 2024). This technique involves consistently feeding a substrate through a processing unit, which enables the production of large sheets of materials on high throughput, which is necessary for industrial applications. Additionally, the automation of the synthesis process can reduce the capacity for human error, improve reproducible qualifications and streamline production workflows. Automatic systems can also increase the accuracy of physical properties and ensure frequent output in large batches. In addition, hybrid technology, which combines top-down and bottom-up approaches, is being developed to gain high production efficiency by maintaining the desirable properties of nanomaterial (Agrawal, 2024). This integration can take advantage of the benefits of both methods – from top-down techniques like ball milling and accuracy in production capacity without increasing production capacity, to increasing the quality of accuracy from below-up techniques like chemical vapour deposition (CVD).

Cost of Production

The cost of production is another significant obstacle to widely adopting nanoengineered materials in defence applications. The refined tools required for the synthesis of high energy consumption and expensive raw materials contribute to the high cost of production (Sher *et al.*, 2024). For example, the cost of production of high-quality graphene or CNT can be prohibitive, especially when considering the quantity required for mass applications in defence areas such as aerospace, electronics and armour systems. These high costs limit the viability of nanoengineered materials for use in large-scale defence systems, where the cost is paramount.

To reduce production costs, several strategies are being followed. Cost-affected precursors can significantly reduce the overall cost of nanometre production (Brar *et al.*, 2022). For example, instead of using expensive petroleum-based sources for graphene production, researchers are discovering biomass-extracted forearmers, which are more inexpensive and environmentally durable. This can give rise to cheap ways to synthesise high-quality graphene on a scale. Energy optimisation for cost reduction is another avenue. Techniques such as microwave-assisted synthesis, which use low energy and low processing time, can help make nanomaterial production more energy-skilled (Dubey & Dube, 2024). In addition, the government and industry participation can help subsidise initial costs related to developing mass production facilities for nanoengineered materials. Cooperative efforts

between defence agencies and private industries can also promote innovation and reduce costs through shared investment in research, development and infrastructure.

Quality Control and Standardisation

It is important for their reliable performance in defence applications to ensure frequent quality of nanoengineered material. Conversion in properties such as particle size, purity and defect density can lead to unexpected behaviour under the transforcement operations (Zhao *et al.*, 2024). For example, the strength, conductivity, or thermal properties of inconsistent quality materials in graphene or CNT can affect performance, which reduces its performance in important defence applications such as sensors, electronics, and structural components (Mishra & Verma, 2024). Therefore, it is necessary to meet strong quality control and standardisation measures to ensure that nanomaterials meet the expected performance requirements in defence systems. Many solutions are being developed to solve the challenges of quality control and standardisation. A major solution is the installation of standardised protocols for the production and characterisation of the nanomaterials. International standards will ensure that all nanomaterials produced for defence applications follow a common set of performance benchmarks, which enable uniformity and prediction in their behaviour (Singh *et al.*, 2024). Additionally, real-time monitoring systems, such as in situ spectroscopy, can be applied to continuously track physical properties during production. This will enable immediate detection of any deviation from the desired specifications, allowing adjustments to the fly. In addition, from the source of raw materials to the final product test, quality assurance systems can be kept for monitoring the entire production process, ensuring that any batch variety is identified and the material is corrected before reaching the defence area.

Environmental and Health Concerns

The production and disposal of nanoengineered materials increase significant environmental and health concerns. Nanomaterials can cause risks due to their poisoning, potential bioaccumulation and environmental firmness (Edo *et al.*, 2024). For example, nanosilver, commonly used for its antimicrobial properties, has shown harmful effects on aquatic ecosystems, possibly disrupting the food chain. The small size and high reactivity of nanomaterials can also increase the possibility of toxicity, especially when they interact with biological systems (Khadanga & Mishra, 2024). As a result, addressing the environment and health implications of nanometre production and disposal is important to ensure permanent use of these materials in defence applications.

To reduce these risks, several solutions are being detected. Methods of green synthesis, which use environmentally benign techniques such as the mediation synthesis of the plant, can significantly reduce the ecological effects of nanomaterials production (Kirubakaran *et al.*, 2025). For example, using plant extracts to synthesise nanoparticles reduces the need for toxic chemicals and reduces waste production. Additionally, recycling of nanomaterials and recompulsion procedures are being developed, ensuring that nanomaterials can be recovered and represented, which can reduce the environmental burden. To ensure strict regulation and monitoring, it is also necessary that the environmental impact of nanomaterial

construction is closely monitored and managed (Tschiche *et al.*, 2022). Applying a regulatory structure that controls the disposal and recycling of nanomaterials will help reduce their ecological footprint and ensure safe practices in rescue-related industries.

Integration with Existing Systems

Integration of nanoengineered materials in existing defence systems presents important challenges due to comprehensive design modifications and the need for compatibility testing. Many defence systems have been developed with traditional materials, and to introduce new nanomaterials often require significant revival of these systems (Wang *et al.*, 2024). This can increase both the time and cost of deployment, delaying the benefits of nanoengineered materials in defence applications. Additionally, to ensure that these materials serve as an intention in complex defence systems, such as aerospace platforms or advanced communication networks, they require thorough testing to confirm their performance under various operating conditions. Many strategies can help remove the challenges of integration. A solution is the development of modular designs that allow nanomaterials to be used as interchangeable components within the existing systems. This approach will enable easy integration, which will reduce the requirement of extensive redesign of defence technologies. In addition, encouraging interdisciplinary cooperation among physicists, engineers and defence experts can promote better communication and ensure that nanomaterials are designed with compatibility kept in mind (Pandey *et al.*, 2024). Finally, simulation tools, such as computational modelling and virtual prototyping, can be used to estimate how nanomaterials will behave in defence systems. These devices can reduce expensive testing-and-trunk testing requirements, accelerate the integration process and reduce overall growth costs.

Applications in Defence Materials

The integration of nanoengineered materials in defence systems has revolutionised the region by offering adequate improvements in the performance of materials used for important defence applications. These materials are characterised by their nanoscale size, unique properties and tuneable characteristics, enhancing the abilities of various defence technologies, including light armour, silent systems, advanced sensors, energy storage, autonomous systems and chemical/biological defence. By taking advantage of the underlying benefits of the nanometre, better performance in the defence sector, increased efficiency, and a wide range of military applications can increase security for personnel and equipment. The following sections detect specific applications of nano-engineered content in defence systems.

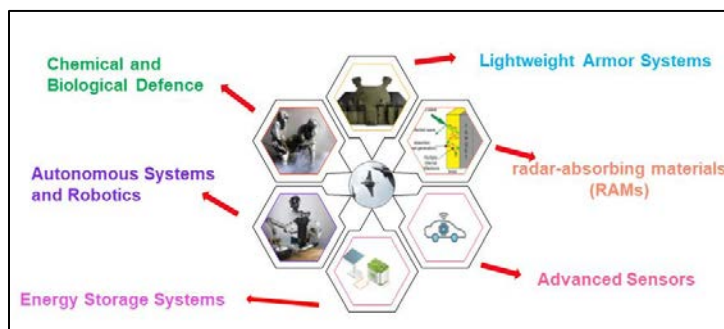


Figure 2 : Applications of Nano-engineer Content in Defence Systems (Source: Author)

Lightweight Armor Systems

Nano-engineer materials have described body armour and vehicle protection (Tawiah *et al.*, 2024) about significant progress in the development of light and highly effective armour systems for both. There is a requirement of materials that provide high strength, while the remaining is important for improving mobility without compromising on mild safety. Nanomaterials such as graphene, boron nitride, and nanocomposites exhibit extraordinary mechanical properties, including high tensile strength, cruelty and flexibility, which make them ideal candidates for advanced armour systems (Harish *et al.*, 2023). These materials can be integrated into various composites to create armour that is not only lighter than traditional materials but also provides better ballistic resistance.

The advantages of nanoengineered materials in the armour system are especially clear in their extraordinary power-to-wisdom ratio and flexibility, which makes them highly effective in preventing projectiles while reducing the overall weight of armour (Shukla *et al.*, 2024). For example, graphene-based composites have shown significant promise in increasing ballistic security, offering materials that are both strong and light. The internal properties of graphene, such as its high tensile strength and flexibility, allow for the development of armour systems that are much lighter than traditional materials such as steel or ceramics, while still providing excellent protection (Hafeezur *et al.*, 2024). Another promising material is carbon nanotube (CNT)-infused polymer, which improves energy absorption during high effects. CNTs increase the mechanical properties of the material, allowing the polymer to transmit energy more efficiently from the project, providing increased protection for soldiers and vehicles (Rani *et al.*, 2024).

Stealth Technologies

One of the most important applications of nanomaterials in defence is in secret technologies, where they are used in the development of radar-absorbing materials (RAMS) to reduce the visibility of military platforms such as aircraft, ships and drones (Peng & Li, 2024). Sneak technology depends on the ability to reduce the reflection of radar waves from one platform, making it more difficult to detect or track the object for the enemy radar system. Nanomaterials provide a significant advantage due to their tuneable electromagnetic properties in this domain, which allows accurate control over radar-absorbed characteristics

of the materials to be used (Ray & Panwar, 2024). By changing the size, shape and structure of nanomaterials, it is possible to design the content with increased radar absorption capabilities.

Graphene and Carbon Nanotube (CNTs) are two nanomaterials that have proved highly effective in radar wave absorption. These materials can be engineered to absorb radar waves in a wide range of frequencies, which can reduce the reflection of secret platforms. In some nanomaterials, metal nanostructures further enhanced the effectiveness of the RAMs, as they can be engineered to reduce reflections and maximise the absorption of electromagnetic waves (Kaushik *et al.*, 2024). The result is a mild, highly effective radar-absorbing material that can be used in the manufacture of secret aircraft, ships and drones, which reduces their signature and improves their survival in hostile environments.

Advanced Sensors

Nanotechnology plays an important role in increasing the capabilities of advanced sensors used in defence applications. Unique properties of nanomaterials, such as their high surface region, sensitivity and short capacity, make them ideal to make them sensors that are more efficient, strong and capable of detecting a wide range of dangers (Godja & Munteanu, 2024). In particular, the application of nanomaterials in chemical, organic and environmental sensors have greatly improved the sensitivity and accountability of these devices, making them invaluable tools for military operations that require rapid detection and reaction for potential hazards.

Quantum dots are an example of nanomaterials used in advanced sensing applications, especially in detecting chemical and biological hazards (Ahmed & Soylak, 2024). These nanoparticles made of semiconductor materials can be engineered to respond to specific chemical or biological agents, which provide highly sensitive identity capacity. Additionally, nanosensors are used to monitor the structural health of vehicles, buildings and infrastructure. Embedded in military equipment or structures, these nanosensors can detect changes in the environment, such as stress, and can send real-time data to operators, allowing initial warnings of potential failures or weaknesses. This application of nanotechnology enhances statutory awareness and security of military personnel and equipment.

Energy Storage Systems

The role of nano-engineered materials in energy storage systems is another area where they significantly increase the performance of defence technologies. Modern defence equipment, such as portable devices, communication systems and unmanned vehicles, often require high-capacity energy storage systems to ensure continuous operation (Lin *et al.*, 2024). Nanotechnology provides promising solutions to meet these demands by improving energy density, charge rates and batteries and supercapacitors. These progresses are important to ensure that the defence system can work for an extended period without the need for frequent recharging or battery replacement. For example, a graphene-enhanced lithium-ion battery is being developed to provide increased capacity and long-term lifetime compared to traditional batteries (Sama, 2024). The inclusion of graphene in the

anode material increases the surface area, allowing more efficient energy storage and rapid charging time. Similarly, nanostructure electrodes in supercapacitors improve the efficiency and energy storage capabilities of these devices, making them ideal for giving strength to high-demonstration systems that require rapid bursts of energy. Easy by nanotechnology, this progress in energy storage enables operation of defence systems more effectively, with prolonged operating time and rapid recovery between functions, which increases the endurance and effectiveness of military operations.

Autonomous Systems and Robotics

Nanotechnology has also enabled significant improvements in autonomous systems and robotics, where light, energy-skilled components are necessary to increase mobility, durability and functionality (Xu *et al.*, 2025; Velrani *et al.*, 2025). In terms of defence, autonomous systems such as drones and robots play an important role in reconnaissance, monitoring, and fighter operations. The integration of nanomaterials in these systems allows for increased dynamics, prolonged endurance, and an increase in functionality, which enables them to perform complex functions in a more versatile and challenging environment. Nanoactuators are an example of nanomaterials used to protect the robotic system and drones from harsh environmental conditions, including rust, wear and extreme temperatures (Sharma *et al.*, 2024). These coatings provide an additional layer of safety, expand the lifetime of defence equipment and ensure that they continue to perform better under the terms of the demand.

Additionally, nanoactuators are being developed for use in robotic organs and other accurate movement systems. These actuators, which are small and light, provide high precision and efficiency, which enable the robot to complete complex functions with minimal energy consumption. This combination of increased dynamics and precision makes nanotechnology a game-changer for autonomous systems in defence.

Chemical and Biological Defence

Nanotechnology plays an important role in chemical and biological defence, where nanomaterials are employed in protective gear and detection systems designed to combat dangerous agents (Ruiz-Gonzalez *et al.*, 2024). Nanomaterials offer high selectiveness and rapid response abilities, making them ideal for use in protective suits, filters and detection systems. In military operations, soldiers are often made aware of potential chemical and biological hazards, and rapid detection and effective security are paramount to ensure their safety. Nanofibrous membrane is used to filter toxic agents and dangerous particles in protective gear, providing extended protection against chemical and biological hazards (Le *et al.*, 2024). These membranes are designed to catch contaminants at the nanoscale, which offers a highly effective barrier without breathing or comfort compromise.

In addition, nanoparticle-based detectors are being developed in real time to detect dangerous substances, including chemical agents and biological pathogens. These detectors are highly sensitive and are capable of providing immediate alerts, which provide rapid reactions to potential hazards. The combination of selective filtration and rapid

detection ensures that nanomaterials provide a comprehensive solution for chemical and biological defence challenges in military settings (Darwish *et al.*, 2024).

Future Trends and Prospects

A transformative future is being shaped in the development of nanotechnology and its increasing integration in defence materials. Nanomaterials have already demonstrated their ability to bring revolution in various fields, especially defence (Francis *et al.*, 2024). Looking ahead to the coming decades, there is a clear tendency towards the development of advanced, adaptable, and energy-efficient materials. This section examines some emerging trends, successes and implications of nanotechnology in defence applications. These trends throw light on how nanotechnology can provide unprecedented benefits in terms of smart materials, manufacturing techniques, energy solutions, safety systems and space defence.

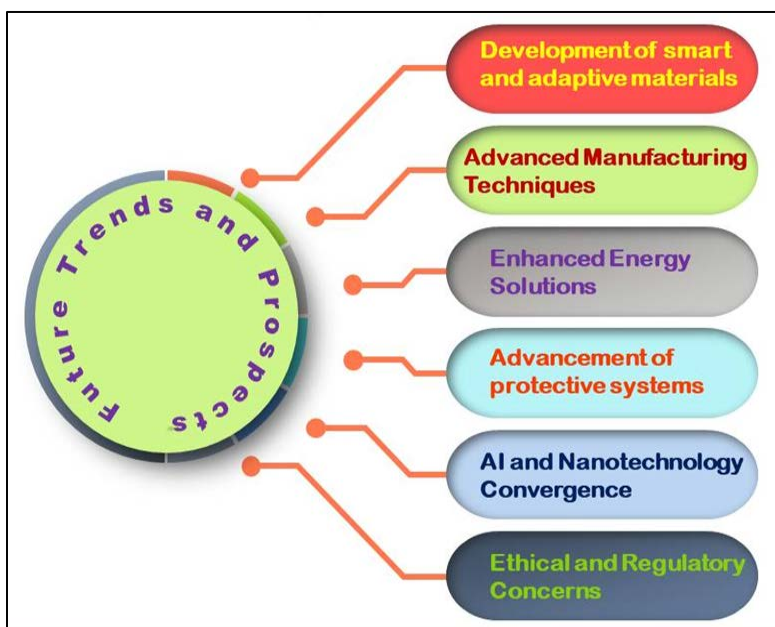


Figure 3: Shows the Schematic Representation of Future Trends and Prospects of Nanomaterials (Source: Author)

Smart and Adaptive Materials

One of the most exciting possibilities for nanotechnology in defence is the development of smart and adaptive materials. These materials are designed to dynamically respond to environmental changes, such as temperature, pressure, or electromagnetic fields, providing significant operational benefits in complex and developed defence scenarios (Wang *et al.*, 2023). Potential applications of these smart materials can lead to the next generation of protective equipment and adaptable systems and structures that respond to the demands of the battleground.

Self-healing material represents a major success in the region. By integrating nanotechnology, they can autonomously repair themselves when the materials are damaged, expanding the lifetime of significant defence tools and structures. For example, embedded polymer composites with nanocapsules can release the healing agents when the cracks are detected, thus preventing further damage and increasing the credibility of military gear (Ahmed *et al.*, 2024). This technique can prove invaluable in ensuring the longevity and stability of the armour and other high-demonstration devices.

Shape-Memory Alloys (SMA) is another exciting application. These alloys designed on the nanoscale can return to a predetermined shape in response to specific external stimuli, such as changes in temperature. In defence, these materials can be used to create deployable structures in aerospace, robotics and other applications where space deficiency and rapid adaptation are important (Rodino *et al.*, 2024). The capacity of materials that automatically return to their original shape after deformation can be highly beneficial for military applications where rapid deployment and adaptability are required.

In addition, metamaterials provide revolutionary ability due to their ability to display properties naturally found in nature. These materials can be engineered for unique characteristics in nanoscale, such as negative refractory index (Alkunte *et al.*, 2024). This capacity opens the door to stealth technologies for advanced applications such as cloaking devices, which can allow military property to be almost invisible to radar and other detection methods, providing a strategic advantage on the battlefield.

Advanced Manufacturing Techniques

Since nanotechnology is moving forward, manufacturing technology is developing to support the creation of highly sophisticated materials with unprecedented accuracy and scalability. One of the most promising techniques for the future is 4D printing, which is the expansion of 3D printing (Mahmood *et al.*, 2024). Unlike traditional 3D printing, which creates stable objects, 4D printing adds a cosmic dimension, which enables changing size or properties over time in response to external stimuli such as heat or humidity. It can give rise to the development of self-web structures, such as camouflage materials that adapt to their surroundings, or adaptable arming systems that are adjusted based on external environmental conditions.

The atomic priority manufacturing is another groundbreaking approach, which is expected to revolutionise the production of nanomaterials (Sharma *et al.*, 2024). With atomic precision, manufacturers can place individual atoms with great accuracy, allowing the formation of defect-free material with customised properties. This technique has the ability to produce advanced nanomaterials such as single-crystal graphene, known for its remarkable power and conductivity. Such progression will enable the creation of ultra-high-performance materials for defence applications and enhance the strength, durability and functionality of military assets (Tsirogiannis *et al.*, 2024).

In addition, the integration of digital twins and artificial intelligence (AI) is ready to change nanomaterial design and adaptation. By using digital simulation, it is possible to design, test and refine nanomaterials before physical manufacturing, dramatically reduce trial-and-error

in prototyping and speed up the growth cycle (Stier *et al.*, 2024). AI can be used to predict physical behaviour in various conditions, which enables the construction of highly customised and custom materials for specific defence requirements. The combination of AI and nanotechnology will be important in overcoming scalability and accuracy challenges associated with nanomaterial production.

Enhanced Energy Solutions

Energy solution is an essential aspect of modern defence systems. Nanotechnology has been designed to bring revolution in energy storage, generation and efficiency, making a significant impact on the operating capabilities of military systems (Mhetre *et al.*, 2025). Future progress in nanomaterials is expected to lead to more compact, durable and efficient energy systems, making soldiers and autonomous systems able to work for a longer period without the need for frequent recharging. One of the most promising developments in energy solutions is the use of a solid-state battery (He *et al.*, 2024). Unlike traditional lithium-ion batteries, which use liquid electrolytes, solid-state batteries appoint solid electrolytes and nanostructure electrodes to increase energy capacity. This technique has great capacity for military applications, offering high energy density and rapid charging time, which are important for portable power sources used by soldiers, drones and other defence technologies.

Another emerging technique is hydrogen storage. Nanomaterials such as Metal-Organic Frameworks (MOFs) are being detected for their ability to store hydrogen at high density, making them ideal for applications such as fuel cells, Unmanned Air Vehicles (UAVs), and other energy-intensive systems (Lavanya *et al.*, 2024). The ability to stimulate and use hydrogen can bring revolution in military energy solutions, providing a clean and abundant source of energy for defence applications. In addition, nanogenerators represent an exciting opportunity for energy harvesting. These devices use environmental energy, such as mechanical vibrations or temperature differences, use piezoelectric and thermoelectric nanomaterials, and convert it to electrical energy (Anbalagan *et al.*, 2024). Such techniques can be used for power sensors, wearable devices and other low-power systems used in defence, which help reduce dependence on traditional energy sources.

Advanced Protective Systems

The advancement of protective systems is another area where nanotechnology is expected to have a transformational effect. As such military dangers develop, defence systems should be more sophisticated and effective. Nanotechnology provides the ability to develop protective materials of the next generation that are stronger, lighter and more optimal than ever. The flexible body armour is an area where nanomaterials are expected to provide significant improvements. By combining nanocomposites, such as graphene-infected polymers, body armour can be made light without compromising their strength or protective abilities. For example, the reinforced Kevlar with graphene oxide can provide increased ballistic protection, allowing for more mobility, reducing the overall weight of the armour, and providing comfort for soldiers (Costa *et al.*, 2024).

Nanocoatings are also playing an important role in the development of advanced protective systems. These coatings can be applied to a variety of surfaces, including aircraft, naval ships and weapons, so that their resistance to corrosion, wear and extreme temperatures can be increased. Such protective layers help to expand the lifetime of defence equipment, ensuring their continuous performance in the harsh environment.

Additionally, radiation preservation is becoming increasingly important using nanostructure materials, especially with the expansion of space defence systems (Sales *et al.*, 2024). Nanomaterials designed to absorb or deform ionising radiation are important in protecting both military personnel and equipment from harmful radiation, whether in space exploration missions or during conditions of atomic results.

AI and Nanotechnology Convergence

The convergence of Artificial Intelligence (AI) and nanotechnology has immense ability to unlock new abilities in defence systems. AI can be used to adapt to the design of nanomaterials, predict their behaviour in different circumstances, and automate the manufacturing process, leading to more efficient and effective production of advanced defence technologies. AI-driven smart nanomaterial can be embedded with decision-making capabilities, which can suit the changing circumstances in real time (Han *et al.*, 2024). For example, a nanomaterial used in a defence application can understand its environment, detect a danger, and react autonomously by changing its properties or structure. This can provide significant benefits in situations with rapid decision-making, such as the atmosphere of the battlefield where conditions change quickly and unexpectedly. The use of AI to run nanostructures adapted to specific defence applications is another area where nanotechnology can offer a competitive edge (Grinin *et al.*, 2024).

By using the AI algorithm to tailor the properties of nanomaterial to suit special operational requirements, defence organisations can develop materials that are highly specialised and adapted to specific tasks, whether it is in terms of strength, flexibility, or energy efficiency.

Nanotechnology for Space Defence

As the defence landscape spreads into space, nanotechnology will play an important role in addressing the unique challenges generated by the space atmosphere (Singh & Kaur, 2023). Space-based defence systems require materials that can withstand the extreme temperatures, radiation, and vacuum of space while remaining light and efficient. Lightweight nanocomposites will be required to reduce the launch weight of the spacecraft by enabling more fuel-skilled missions. These materials can help improve the performance of satellites and other space-based assets by providing strong, light structures that can oppose the harsh situations of space travel. Radiation-resistant nanomaterial will be important to protect both spacecraft and astronauts from the harmful effects of cosmic radiation and solar particles (Zeng *et al.*, 2023).

While offering extended safety for space missions, nanostructured materials can be engineered to absorb or deform radiation. In addition, nanosensors will be used for several functions in satellites, including communication, navigation and monitoring. By shortening

the sensor for nanoscale, military organisations can create highly efficient and compact systems that perform important functions with minimal space requirements.

Ethical and Regulatory Considerations

With any emerging technology, the development and deployment of nanotechnology in defence applications increases significant moral and regulatory concerns (Subhan & Subhan, 2022). One of the most pressing issues is the dual-use nature of much nanotechnology, where the material developed for civil purposes can also be used for military applications. This creates strict regulation and inspection requirements, ensuring that nanotechnology is used responsibly and does not fall into the wrong hands. The installation of global standards is also important to ensure safe and responsible use of nanometres. International cooperation between governments, industries and research institutes would be necessary to create guidelines for the development, testing and use of nanotechnology in defence (Amutha *et al.*, 2024).

Conclusion

The consolidation of nano-engineered materials in defence applications identifies an important milestone in the evolution of modern warfare technology. These advanced materials, with their unique physicochemical properties, showed significant possibility in the traditional defence revolution from the adapted camouflage of systems weighing, high-power armour and stealth technology, which is the technology of enhanced energy storage and highly sensitive sensors. This review has explored the various processing and production techniques, including both top-down and bottom-up methods, as well as additive manufacturing and laser-assisted fabrication; each offers a distinct benefit of tailoring material performance. Progress: several critical challenges remain. Scalability, uniformity and consistency with existing defence infrastructure prevent extensive implementation. However, the procedure of synthesis and characterisation is progressing on tools slowly to address these limitations. Collective research and defence among the scientists of materials technologists and policymakers are the future potentials needed to overcome these obstacles. The development of smart nanomaterials capable of self-reliance, real-time threat identification and environmental adaptability presents the next border. Nevertheless, dual-use technology, environmental impact and moral concerns about the global impact of protection must be managed through the strong regulatory structure.

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References

- Adeleke, A. K., Montero, D. J. P., Lottu, O. A., Ninduwezuor-Ehiobu, N., & Ani, E. C. (2024). 3D printing in aerospace and defense: A review of technological breakthroughs and applications. *World Journal of Advanced Research and Reviews*, 21(2), 1149-1160. <https://doi.org/10.30574/wjarr.2024.21.2.0558>
- Agrawal, A. (2024). Top-down strategies for achieving high-quality graphene: recent advancements. *Journal of Industrial and Engineering Chemistry*. <https://doi.org/10.1016/j.jiec.2024.07.053>
- Ahmed, A., Ali, A., Alzahrani, B., & Sanada, K. (2024). Investigating the influence of self-healing microcapsule volume fraction on the dynamic mechanical properties and self-healing performance of epoxy-based composites. *Journal of Polymer Research*, 31(7), 201. <https://doi.org/10.1007/s10965-024-04037-w>
- Ahmed, H. E. H., & SOYLAK, M. (2024). Exploring the potential of carbon quantum dots (CQDs) as an advanced nanomaterial for effective sensing and extraction of toxic pollutants. *TrAC Trends in Analytical Chemistry*, 117939. <https://doi.org/10.1016/j.trac.2024.117939>
- Alkunte, S., Fidan, I., Naikwadi, V., Gudavasov, S., Ali, M. A., Mahmudov, M., ... & Cheepu, M. (2024). Advancements and challenges in additively manufactured functionally graded materials: a comprehensive review. *Journal of Manufacturing and Materials Processing*, 8(1), 23. <https://doi.org/10.3390/jmmp8010023>
- Amutha, C., Gopan, A., Pushbalatatha, I., Ragavi, M., & Reneese, J. A. (2024). Nanotechnology and Governance: Regulatory Framework for Responsible Innovation. In *Nanotechnology in Societal Development* (481-503). Singapore: Springer Nature Singapore. https://doi.org/10.1007/978-981-97-6184-5_14
- Anbalagan, S., Manojkumar, K., Muthuramalingam, M., Hajra, S., Panda, S., Sahu, R., ... & Vivekananthan, V. (2024). Progress and recent advances in self-powered gas sensing based on triboelectric and piezoelectric nanogenerators. *Chemical Engineering Journal*. <https://doi.org/10.1016/j.cej.2024.154740>
- Asgedom, G., Yeneneh, K., Tilahun, G., & Negash, B. (2025). Numerical and experimental analysis of body armor polymer penetration resistance against 7.62 mm bullet. *Heliyon*, 11(1). Retrieved from: <https://pubs.rsc.org/en/content/articlelanding/2024/nh/d4nh00056k> Accessed on 12th January 2025.
- Ayanda, O. S., Mmuoegbulam, A. O., Okezie, O., Durumin Iya, N. I., Mohammed, S. A. E., James, P. H., ... & Badamasi, H. (2024). Recent progress in carbon-based nanomaterials: critical review. *Journal of Nanoparticle Research*, 26(5), 106. <https://doi.org/10.1007/s11051-024-06006-2>
- Borane, N., Aralekallu, S., Boddula, R., Singh, J., & Kurkuri, M. D. (2024). Recent trends in the “bottom-up” and “top down” techniques in the synthesis and fabrication of myriad carbonaceous nanomaterials. In *Carbon-Based Nanomaterials in Biosystems* (91-120). Academic Press. <https://doi.org/10.1016/B978-0-443-15508-6.00002-6>
- Brar, K. K., Magdoul, S., Othmani, A., Ghanei, J., Narisetty, V., Sindhu, R., ... & Pandey, A. (2022). Green route for recycling of low-cost waste resources for the biosynthesis of nanoparticles (NPs) and nanomaterials (NMs)-A review. *Environmental Research*, 207. <https://doi.org/10.1016/j.envres.2021.112202>

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- Costa, U. O., da Costa Garcia Filho, F., Gómez-del Río, T., Júnior, É. P. L., Monteiro, S. N., & Nascimento, L. F. C. (2024). Characterization and ballistic performance of hybrid jute and aramid reinforcing graphite nanoplatelets in high-density polyethylene nanocomposites. *Journal of Materials Research and Technology*, 28, 1570-1583. <https://doi.org/10.1016/j.jmrt.2023.12.093>
- Darwish, M. A., Abd-Elaziem, W., Elsheikh, A., & Zayed, A. A. (2024). Advancements in nanomaterials for nanosensors: a comprehensive review. *Nanoscale Advances*. <https://doi.org/10.1039/D4NA00214H>
- De Souza Cardoso Delfino, C., de Paula Pereira, M. C., dos Santos Oliveira, M., de Carvalho Favareto, I., Valladão, V. S., de Oliveira Mota, M., ... & Balbino, T. A. (2025). Scaling nanopharmaceutical production for personalized medicine: challenges and strategies. *Journal of Nanoparticle Research*, 27(4), 1-19. <https://doi.org/10.1007/s11051-025-06293-3>
- Dubey, A., & Dube, C. L. (2024). Microwave processing of carbon-based materials: A review. *Nano-Structures & Nano-Objects*, 38. <https://doi.org/10.1016/j.nanoso.2024.101136>
- Dutta, S., Sinelshchikova, A., Andreo, J., & Wuttke, S. (2024). Nanoscience and nanotechnology for water remediation: an earnest hope toward sustainability. *Nanoscale Horizons*, 9(6), 885-899. <https://doi.org/10.1039/D4NH00056K>
- Edo, G. I., Samuel, P. O., Oloni, G. O., Ezekiel, G. O., Ikpekor, V. O., Obasohan, P., ... & Agbo, J. J. (2024). Environmental persistence, bioaccumulation, and ecotoxicology of heavy metals. *Chemistry and Ecology*, 40(3), 322-349. <https://doi.org/10.1080/02757540.2024.2306839>
- Es-Soufi, H., Berdimurodov, E., Sayyed, M. I., & Bih, L. (2024). Nanoceramic-based coatings for corrosion protection: A review on synthesis, mechanisms, and applications. *Environmental Science and Pollution Research*, 1-27. <https://doi.org/10.1007/s11356-023-31658-3>
- Fahri, M., Bolilanga, P. I. W., Gunaryo, G., Stiawan, E., & Kurniadi, T. (2024). Exploring the Potential of Carbon-based Radar Absorbing Material Innovations. *Indonesian Journal of Chemical Studies*, 3(2), 72-81. <https://doi.org/10.1002/adv.202412554>
- Fenta, E. W., & Mebratie, B. A. (2024). Advancements in carbon nanotube-polymer composites: Enhancing properties and applications through advanced manufacturing techniques. *Heliyon*, 10(16). Retrieved from: [https://www.cell.com/heliyon/fulltext/S2405-8440\(24\)12521-2](https://www.cell.com/heliyon/fulltext/S2405-8440(24)12521-2), Accessed on 16th January 2025.
- Francis, D. V., Asif, A., & Ahmed, Z. F. R. (2024). Nanoparticle-enhanced plant defense mechanisms harnessed by nanotechnology for sustainable crop protection. *Nanoparticles in Plant Biotic Stress Management*, 451-491. https://doi.org/10.1007/978-981-97-0851-2_19
- Gartia, A. K., & Chakraverty, S. (2025). Advanced Computational Modeling and Mechanical Behavior Analysis of Multi-Directional Functionally Graded Nanostructures: A Comprehensive Review. *Computer Modeling in Engineering & Sciences (CMES)*, 142(3). <https://doi.org/10.32604/cmcs.2025.061039>
- Godja, N. C., & Munteanu, F. D. (2024). Hybrid nanomaterials: a brief overview of versatile solutions for sensor technology in healthcare and environmental applications. *Biosensors*, 14(2), 67. <https://doi.org/10.3390/bios14020067>

- Grinin, L., Grinin, A., & Korotayev, A. (2024). Nanotechnologies, Robotics, Artificial Intelligence and Other MANBRIC Technologies in the Long-Term Development. In *Cybernetic Revolution and Global Aging: Humankind on the Way to Cybernetic Society, or the Next Hundred Years* (pp. 403-457). Cham: Springer International Publishing. https://doi.org/10.1007/978-3-031-56764-3_10
- Guitton, M. J. (2021). Fighting the locusts: Implementing military countermeasures against drones and drone swarms. *Scandinavian Journal of Military Studies*, 4(1). <https://doi.org/10.31374/sjms.53>
- Hafeezur, A. R., Sundeep, D., Sastry, C. C., Krishnaiah, J., & Varadharaj, E. K. (2024). Investigation of ballistic and mechanical properties of AINPB metal matrix composites reinforced with TiCN decorated graphene nano flakes for light armored vehicles. *Journal of Alloys and Compounds*, 992. <https://doi.org/10.1016/j.jallcom.2024.174482>
- Hajare, D. M., & Gajbhiye, T. S. (2022). Additive manufacturing (3D printing): Recent progress on advancement of materials and challenges. *Materials Today: Proceedings*, 58, 736-743. <https://doi.org/10.1016/j.matpr.2022.02.391>
- Han, C. E., Dong, X., Zhang, W., Huang, X., Gong, L., & Su, C. (2025). Intelligent Systems for Inorganic Nanomaterial Synthesis. *Nanomaterials*, 15(8), 631. <https://doi.org/10.3390/nano15080631>
- Harish, V., Ansari, M. M., Tewari, D., Yadav, A. B., Sharma, N., Bawarig, S., ... & Barhoum, A. (2023). Cutting-edge advances in tailoring size, shape, and functionality of nanoparticles and nanostructures: A review. *Journal of the Taiwan Institute of Chemical Engineers*, 149. <https://doi.org/10.1016/j.jtice.2023.105010>
- He, P., Tang, Y., Tan, Z., Lei, C., Qin, Z., Li, Y., ... & Zhao, J. (2024). Solid-state batteries encounter challenges regarding the interface involving lithium metal. *Nano Energy*. <https://doi.org/10.1016/j.nanoen.2024.109502>
- Huang, T., Zeng, Y., Li, C., Zhou, Z., Xu, J., Wang, L., ... & Wang, K. (2024). Application and development of electrospun nanofiber scaffolds for bone tissue engineering. *ACS Biomaterials Science & Engineering*, 10(7), 4114-4144. <https://doi.org/10.1021/acsbiomaterials.4c00028>
- Kaushik, N., Singh, P., Rana, S., Sahoo, N. G., Ahmad, F., & Jamil, M. (2024). Self-healable electromagnetic wave absorbing/shielding materials for stealth technology: current trends and New frontiers. *Materials Today Sustainability*, 27. <https://doi.org/10.1016/j.mtsust.2024.100828>
- Khadanga, V., & Mishra, P. C. (2024). A review on toxicity mechanism and risk factors of nanoparticles in respiratory tract. *Toxicology*. <https://doi.org/10.1016/j.tox.2024.153781>
- Kirubakaran, D., Wahid, J. B. A., Karmegam, N., Jeevika, R., Sellapillai, L., Rajkumar, M., & SenthilKumar, K. J. (2025). A comprehensive review on the green synthesis of nanoparticles: advancements in biomedical and environmental applications. *Biomedical Materials & Devices*, 1-26. <https://doi.org/10.1007/s44174-025-00295-4>
- Kou, X., Zhao, X., Xiong, X., Yuan, S., Huang, H., Li, X., & Zhao, Y. (2024). PMMA-assisted electrospinning uniformly incorporates magnetic particles into carbon nanomaterials for efficient microwave absorption. *Inorganic Chemistry Frontiers*, 11(21), 7633-7647. Retrieved

from: <https://pubs.rsc.org/en/content/articlelanding/2024/qi/d4qi02100b/unauth>, Accessed on 14th January 2025.

- Kumar, A., Panda, D., & Gangawane, K. M. (2024). Microfabrication: Techniques and technology. *Microfabr. Nanofabrication Precis. Manuf*, 11, 47. <https://doi.org/10.1515/9783111335537>
- Lavanya, M., Shrivastava, S., Lakshmi, T., Sandadi, E. R., Gour, S., Thomas, N. A., ... & Sudhakar, K. (2024). An overview of hydrogen storage technologies—Key challenges and opportunities. *Materials Chemistry and Physics*. <https://doi.org/10.1016/j.matchemphys.2024.129710>
- Le, B., Omran, N., Elnabawy, E., Hassanin, A. H., Mahmoud, K., Shehata, N., & Shyha, I. (2024). Exploring advances in nanofiber-based face masks: a comprehensive review of mechanical, electrostatic, and antimicrobial functionality filtration for the removal of airborne particulate matter and pathogens. *Emergent Materials*, 7(3), 765-800. <https://doi.org/10.1007/s42247-023-00622-9>
- Liang, S. X., Zhang, L. C., Reichenberger, S., & Barcikowski, S. (2021). Design and perspective of amorphous metal nanoparticles from laser synthesis and processing. *Physical Chemistry Chemical Physics*, 23(19), 11121-11154. <https://doi.org/10.1039/D1CP00701G>
- Lin, H., Shen, Q., Ma, M., Ji, R., Guo, H., Qi, H., ... & Tang, H. (2025). 3D printing of porous ceramics for enhanced thermal insulation properties. *Advanced Science*, 12(7). <https://doi.org/10.1002/advs.202412554>
- Lin, Z., Huang, Z., Yang, S., Wu, C., Fang, S., Liu, Z., ... & Zou, Y. (2024). Survey on task-centric robot battery management: A neural network framework. *Journal of Power Sources*, 610. <https://doi.org/10.1016/j.jpowsour.2024.234674>
- Lu, H., Wang, D., Wu, S., Pan, Z., Wang, G., Guo, G., ... & Xiang, D. (2024). A review of laser polishing on Ti6Al4V based on energy density. *Journal of Materials Processing Technology*, 331. <https://doi.org/10.1016/j.jmatprotec.2024.118520>
- Mahajan, U., Dhonde, M., Sahu, K., Ghosh, P., & Shirage, P. M. (2024). Titanium nitride (TiN) as a promising alternative to plasmonic metals: a comprehensive review of synthesis and applications. *Materials Advances*, 5(3), 846-895. <https://doi.org/10.1039/D3MA00965C>
- Mahmood, A., Perveen, F., Chen, S., Akram, T., & Irfan, A. (2024). Polymer composites in 3D/4D printing: materials, advances, and prospects. *Molecules*, 29(2), 319. <https://doi.org/10.3390/molecules29020319>
- Mahmud, M. M., Pandey, N., Winkles, J. A., Woodworth, G. F., & Kim, A. J. (2024). Toward the scale-up production of polymeric nanotherapeutics for cancer clinical trials. *Nano Today*, 56. <https://doi.org/10.1016/j.nantod.2024.102314>
- Marques, M. J. M., Lin, W., Taima, T., Umezu, S., & Shahiduzzaman, M. (2024). Unleashing the potential of industry viable roll-to-roll compatible technologies for perovskite solar cells: Challenges and prospects. *Materials Today*. <https://doi.org/10.1016/j.mattod.2024.06.013>
- Mhetre, H., Goyal, A., Kaduskar, V., Namekar, S., Chendake, Y., & Khomane, R. B. (2025). Integrating Nanoscience in the Realm of Renewable Energy. In *Nanotechnology* (pp. 209-243). Springer, Cham. https://doi.org/10.1007/978-3-031-86508-4_10

- Mishra, R. K., & Verma, K. (2024). Defect engineering in nanomaterials: Impact, challenges, and applications. *Smart Materials in Manufacturing*, 2. <https://doi.org/10.1016/j.smmf.2024.100052>
- Motalib Hossain, M. A., Ker, P. J., Tiong, S. K., Indra Mahlia, T. M., & Hannan, M. A. (2024). Recent progress in nanomaterials of battery energy storage: A patent landscape analysis, technology updates, and future prospects. *Nanotechnology Reviews*, 13(1). <https://doi.org/10.1515/ntrev-2023-0215/html>
- Ogbezode, J. E., Offia-Kalu, N. E., Bello, A., Anye, V. C., & Onwalu, P. A. (2024). Phase structure transformation and growth mechanism for iron oxide nanoparticles synthesized by mechanochemical method: A mini-review. *Journal of Alloys and Metallurgical Systems*. <https://doi.org/10.1016/j.jalms.2024.100103>
- Onu, P., & Lawal, S. L. (2024, April). Tribological Considerations in Additive Manufacturing: 3D Printing Materials and Techniques. In *2024 International Conference on Science, Engineering and Business for Driving Sustainable Development Goals (SEB4SDG) (1-8)*. IEEE. <https://doi.org/10.1109/SEB4SDG60871.2024.10629765>
- Palagati, S., & Reddy, J. (2024). Synthesis by Top-Down and Bottom-Up. In *Advanced Materials: Production, Characterization and Multidisciplinary Applications*, 201.
- Pandey, V., Sharma, A., Kumar, D., Samadhiya, N., & Tomar, S. S. (2024). Industrial Application of Bio-nanomaterials in Agriculture. *Bio-Nanomaterials in Environmental Remediation: Industrial Applications*, 225-254. <https://doi.org/10.1002/9783527848546.ch9>
- Parvin, N., Joo, S. W., Jung, J. H., & Mandal, T. K. (2025). Innovative Micro-and Nano-Architectures in Biomedical Engineering for Therapeutic and Diagnostic Applications. *Micromachines*, 16(4), 419. <https://doi.org/10.3390/mi16040419>
- Patil, A. T., Vidhale, B., & Titarmare, A. (2024, May). Strategic innovations in defense systems: a comprehensive analysis of emerging technologies and future trends. In *2024 International Conference on Intelligent Systems for Cybersecurity (ISCS) (1-7)*. IEEE. <https://doi.org/10.1109/ISCS61804.2024.10581013>
- Peng, S., & Li, P. (2024). Applications of Nanomaterials and Nanotechnology in Military and Aerospace Fields. In *Nanomaterials and Nanotechnology: Basic, Preparation and Applications* (pp. 265-308). Singapore: Springer Nature Singapore. https://doi.org/10.1007/978-981-97-8433-2_8
- Raghunathan, M., Kapoor, A., Mohammad, A., Kumar, P., Singh, R., Tripathi, S. C., ... & Pal, D. B. (2024). Advances in two-dimensional transition metal dichalcogenides-based sensors for environmental, food, and biomedical analysis: A review. *Luminescence*, 39(3), e4703. <https://doi.org/10.1002/bio.4703>
- Rani, M., Sehrawat, M., Sharma, S., Bharadwaj, S., Chauhan, G. S., Dhakate, S. R., & Singh, B. P. (2024). Carbon nanotube-based soft body armor: Advancements, integration strategies, and future prospects. *Diamond and Related Materials*. <https://doi.org/10.1016/j.diamond.2024.111446>
- Ray, S., & Panwar, R. (2024). Advances in Polymer Based Microwave Absorbers: From Design Principles to Technological Breakthroughs. *IEEE Journal on Flexible Electronics*. <https://doi.org/10.1109/JFLEX.2024.3432103>

- Ren, M., Guo, D., Wang, Q., Dong, S., Liu, X., Guo, J., ... & Li, Y. (2024). Recent Advances in Self-powered Sensors Based on Nanogenerators: From Material and Structural Design to Cutting-Edge Sensing Applications. *ACS Applied Electronic Materials*, 6(6), 3955-3997. <https://doi.org/10.1021/acsaelm.4c00157>
- Rodinò, S., & Maletta, C. (2024). Design considerations and applications of shape memory alloy-based actuation in morphing structures: A systematic review. *Progress in Engineering Science*. <https://doi.org/10.1016/j.pes.2024.100021>
- Ruiz-Gonzalez, A., Wang, M., Junior, P. T., Teixeira, D., Ekblom, P., Johnson, S., & Choy, K. L. (2024). Advances in nanomaterials applied to crime combat and prevention. *Materials Today Communications*, 39. <https://doi.org/10.1016/j.mtcomm.2024.109060>
- Sabet, M. (2025). Advanced functionalization strategies for carbon nanotube polymer composites: achieving superior dispersion and compatibility. *Polymer-Plastics Technology and Materials*, 64(4), 465-494. <https://doi.org/10.1080/25740881.2024.2409312>
- Sales, A. S. W., de Queiroz Pereira, V., & Dias, A. N. C. (2024). Advances in nanomaterials for radiation protection in the aerospace industry: a systematic review. *Nanotechnology*. <https://doi.org/10.1088/1361-6528/ada38f>
- Sama, A. (2024). Introducing graphene-enhanced technologies to the regulated market to mitigate carbon emissions. *Environmental Progress & Sustainable Energy*, 43(1), e14338. <https://doi.org/10.1002/ep.14338>
- Selim, M. S., El-Safty, S. A., Shenashen, M. A., & Elmarakbi, A. (2024). Advances in polymer/inorganic nanocomposite fabrics for lightweight and high-strength armor and ballistic-proof materials. *Chemical Engineering Journal*. <https://doi.org/10.1016/j.cej.2024.152422>
- Shah, K., Patel, J., Kumar, S., Pandey, R., Maity, G., & Dubey, S. (2024). Perspectives on sustainable and efficient routes of nanoparticle synthesis: an exhaustive review on conventional and microplasma-assisted techniques. *Nanoscale*. Retrieved from: <https://pubs.rsc.org/en/content/articlelanding/2024/nr/d4nr02478h/unauth>, Accessed on 12th January 2025.
- Sharma, D., Thakur, A., Sharma, A. K., Kherb, J., Kumar, A., & Om, H. (2024). Future Developments in Nano-Hybrid Smart Coatings. In *Nano-Hybrid Smart Coatings: Advancements in Industrial Efficiency and Corrosion Resistance* (385-415). American Chemical Society. <https://doi.org/10.1021/bk-2024-1469.ch016>
- Sharma, P., Singh, V., Thakur, A., & Malik, A. K. (2024). Nanotechnology, Artificial Intelligence, and the Future of Manufacturing. In *Nanotechnology in Societal Development* (307-332). Singapore: Springer Nature Singapore. https://doi.org/10.1007/978-981-97-6184-5_9
- Sharma, S., Kumar, R., & Kumar, K. (2024). Synthesis of biowaste derived carbon nanomaterials: efficiency, quality, and environmental impact. *Indian Chemical Engineer*, 1-20. <https://doi.org/10.1080/00194506.2024.2442719>
- Sher, F., Ziani, I., Hameed, M., Ali, S., & Sulejmanović, J. (2024). Advanced nanomaterials design and synthesis for accelerating sustainable biofuels production—A Review. *Current Opinion in Green and Sustainable Chemistry*. <https://doi.org/10.1016/j.cogsc.2024.100925>

- Shirke, N., Ghase, V., & Jamdar, V. (2024). Recent advances in stealth coating. *Polymer Bulletin*, 81(11), 9389-9418. <https://doi.org/10.1007/s00289-024-05166-4>
- Shubham, & Ray, B. C. (2024). Introduction to composite materials. In *Fiber reinforced polymer (FRP) composites in ballistic protection: microstructural and micromechanical perspectives* (1-20). Singapore: Springer Nature Singapore. https://doi.org/10.1007/978-981-99-9746-6_1
- Shukla, S., Sharma, J., Singh, O., & Behera, B. K. (2024). Auxetic textiles, composites and applications. *Textile Progress*, 56(3), 323-414. <https://doi.org/10.1080/00405167.2024.2328504>
- Simões, S. (2024). High-performance advanced composites in multifunctional material design: state of the art, challenges, and future directions. *Materials*, 17(23), 5997. <https://doi.org/10.3390/ma17235997>
- Singer, J. R., Mueller, E. F., & Kraus, R. (2025). Dual-Use or Omni-Use? Rethinking Technology in a Borderless World. *Rethinking Technology in a Borderless World*. <https://dx.doi.org/10.2139/ssrn.5185227>
- Singh, H., & Kaur, K. (2023). Role of nanotechnology in research fields: Medical sciences, military & tribology-A review on recent advancements, grand challenges and perspectives. *Materials Today: Proceedings*. <https://doi.org/10.1016/j.matpr.2023.02.061>
- Singh, N., Mehta, A., Vasudev, H., & Samra, P. S. (2024). A review on the design and analysis for the application of Wear and corrosion resistance coatings. *International Journal on Interactive Design and Manufacturing (IJIDeM)*, 18(8), 5381-5405. <https://doi.org/10.1007/s12008-023-01411-8>
- Stier, S. P., Kreisbeck, C., Ihssen, H., Popp, M. A., Hauch, J., Malek, K., ... & Kozdras, M. (2024). Materials acceleration platforms (MAPs): accelerating materials research and development to meet urgent societal challenges. *Advanced Materials*, 36(45). <https://doi.org/10.1002/adma.202407791>
- Subhan, M. A., & Subhan, T. (2022). Safety and global regulations for application of nanomaterials. In *Nanomaterials Recycling* (83-107). Elsevier. <https://doi.org/10.1016/B978-0-323-90982-2.00005-6>
- Tawiah, B., Ofori, E. A., & George, S. C. (2024). Nanotechnology in societal development. In *Nanotechnology in Societal Development* (1-64). Singapore: Springer Nature Singapore. https://doi.org/10.1007/978-981-97-6184-5_1
- Tian, Q., Zhou, J., Hou, J., Zhou, Z., Liang, Z., Sun, M., ... & Huang, J. (2024). Building the future: Smart concrete as a key element in next-generation construction. *Construction and Building Materials*, 429. <https://doi.org/10.1016/j.conbuildmat.2024.136364>
- Tschiche, H. R., Bierkandt, F. S., Creutzenberg, O., Fessard, V., Franz, R., Giese, B., ... & Laux, P. (2022). Environmental considerations and current status of grouping and regulation of engineered nanomaterials. *Environmental Nanotechnology, Monitoring & Management*, 18. <https://doi.org/10.1016/j.enmm.2022.100707>
- Tsirogiannis, E. C., Daskalakis, E., Vogiatzis, C., Psarommatis, F., & Bartolo, P. (2024). Advanced composite armor protection systems for military vehicles: Design methodology, ballistic testing, and comparison. *Composites Science and Technology*, 251. <https://doi.org/10.1016/j.compscitech.2024.110486>

- Turini, S. (2024). Nanomolecular electromagnetic interference agents in biological systems: Unraveling the mechanisms and implications for future Biowarfare strategies. *Middle East Journal of Applied Science & Technology*, 7(1). <http://dx.doi.org/10.46431/MEJAST.2024.7112>
- Velrani, K. S., Shanthi, T. S., Senthil, T. S., Kavitha, T., Deepa, P., & Muthuvel, S. (2025). A Study on IoT and AI-Integrated Advanced Lightweight Materials for Eco-Friendly Production. In *Innovations in Energy Efficient Construction Through Sustainable Materials* (1-32). IGI Global. <https://doi.org/10.4018/979-8-3693-3398-3.ch001>
- Wang, S., Liang, L., & Chen, S. (2024). Tensile strength and toughness of carbon nanotube-graphene foam composite materials and the corresponding microscopic influence mechanism. *Materials & Design*, 237. <https://doi.org/10.1016/j.matdes.2023.112529>
- Wang, W., Xiang, Y., Yu, J., & Yang, L. (2023). Development and prospect of smart materials and structures for aerospace sensing systems and applications. *Sensors*, 23(3), 1545. <https://doi.org/10.3390/s23031545>
- Wang, X. V., Xu, P., Cui, M., Yu, X., & Wang, L. (2024). A literature survey of smart manufacturing systems for medical applications. *Journal of Manufacturing Systems*, 76, 502-519. <https://doi.org/10.1016/j.jmsy.2024.08.017>
- Xu, S., Manshahi, F., Xiao, X., & Chen, J. (2025). Artificial intelligence assisted nanogenerator applications. *Journal of Materials Chemistry A*, 13(2), 832-854. <https://doi.org/10.1039/D4TA07127A>
- Yameny, A. A. (2024). A Comprehensive Review on Nanoparticles: Definition, Preparation, Characterization, Types, and Medical Applications. *Journal of Medical and Life Science*, 6(4), 663-672. <https://dx.doi.org/10.21608/jmals.2024.419629>
- Zabrodskiy, M., Watling, J., Danylyuk, O. V., & Reynolds, N. (2022). *Preliminary Lessons in Conventional Warfighting from Russia's Invasion of Ukraine, February-July 2022* (10-11). London: Royal United Services Institute for Defence and Security Studies. Retrieved from: <https://static.rusi.org/359-SR-Ukraine-Preliminary-Lessons-Feb-July-2022-web-final.pdf>, Accessed on 14th January 2025.
- Zanurin, A., Johari, N. A., Alias, J., Ayu, H. M., Redzuan, N., & Izman, S. (2022). Research progress of sol-gel ceramic coating: A review. *Materials today: proceedings*, 48, 1849-1854. <https://doi.org/10.1016/j.matpr.2021.09.203>
- Zeng, C., Kang, Q., Duan, Z., Qin, B., Feng, X., Lu, H., & Lin, Y. (2023). Development of polymer composites in radiation shielding applications: a review. *Journal of Inorganic and Organometallic Polymers and Materials*, 33(8), 2191-2239. <https://doi.org/10.1007/s10904-023-02725-6>
- Zhao, Q., Cui, B., Ji, A., Song, T., & Shen, Y. (2024). Experimental and numerical study of the effect of particle size distribution on hydrocyclone classification. *Advanced Powder Technology*, 35(4). <https://doi.org/10.1016/j.appt.2024.104398>
- Zhao, T., Wang, J., Wei, Y., Zhuang, Z., Dou, Y., Yang, J., ... & Wang, D. (2025). From lab-scale to industrialization: atomically M–N–C catalysts for the oxygen reduction reaction. *Energy & Environmental Science*. <https://doi.org/10.1039/D5EE00074B>

Zhou, Y., Rather, L. J., Yu, K., Yang, M., Lu, M., & Li, Q. (2024). Research Progress and Recent Advances in Development and Applications of Infrared Stealth Materials: A Comprehensive Review. *Laser & Photonics Reviews*, 18(12). <https://doi.org/10.1002/lpor.202400530>

Recent Developments in Cobalt-catalysed C-H Activation Reactions with Alkynes, Allenes and Arene Substrates

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ABSTRACT

Because of its simple availability, low cost, and low toxicity, cobalt (Co) has been the focus of research in the field of C-H functionalisation, replacing noble metals like Pd, Rh, and Ir. The range of transformations using alkynes, allenes, and arene substrates has greatly increased due to recent developments in cobalt-catalysed C-H activation processes. The technique has been used in a number of synthetic processes, including late-stage functionalisation, enantioselective C-H functionalisation, electrooxidative functionalisation, and annulation reactions with allenes. These advancements provide effective methods for building intricate molecular structures. This chapter's focus is on the latest developments in Co-catalysed C-H functionalisation procedures including alkynes, allenes, and arene substrates. A brief overview of various enantioselective transformations is also included.

Keywords: Alkynes; Allenes; Arene; C-H Activation; Cobalt-Catalysis

INTRODUCTION

One of the most fundamental areas of scientific study and industrial development, chemical science has many uses, from developing new and enhanced materials with unparalleled capabilities to comprehending the complex mechanistic paths of biological processes. This brief overview essay will look at the most recent advancements and innovative methods in organometallic chemistry, including the use of Co-catalysis to activate carbon chains in quinolone and pyridine-based nitrogen heterocycles using a variety of C-H activation mechanisms. Because it allows a C-H bond to be functionalised directly rather than through the traditional functional group modification method, Co-catalysed C-H activation has drawn a lot of attention in organic chemistry research in recent decades (Baccalini *et al.*, 2019). For many naturally occurring, bioactive, and significant compounds, it may be possible to create an atom- and step-efficient synthesis process if a particular carbon-hydrogen bond within the molecule can be targeted and functionalised. When C-H activation chemistry originally emerged, the region was dominated by 4d and 5d transition metals, particularly palladium, rhodium, ruthenium, and iridium. However, new techniques

based on easily accessible, low-cost 3D metals like cobalt have recently become more and more popular (Patel *et al.*, 2022). In addition to its special electrical properties, this idea is important from an economic and environmental perspective since it permits special patterns of reactivity and selectivity. Research on innovative C-H activation methods based on first-row transition metals is still in its early stages, despite these benefits.

Recent Developments:

i) Alkenylation of 8-Methyl Quinoline with Alkynes:

The authors used 5-decyne as a coupling partner and $\text{Cp}^*\text{Co}(\text{Co})\text{I}_2$ as a catalyst to activate the $\text{C}(\text{SP}^3)\text{-H}$ bond alkenylation of 8-methylquinoline (Figure 1) as a model substrate. To achieve a satisfactory yield, they added AdCO_2H and AgOTf along with $\text{CF}_3\text{CH}_2\text{OH}$ at 80°C and continued the reaction in argon for 24 hours (Sen *et al.*, 2016).

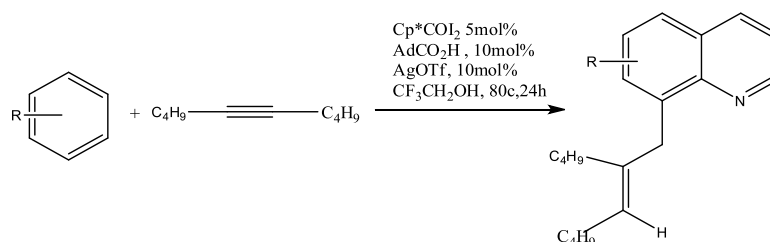


Figure 1: Alkenylation of 8-Methyl Quinoline

The authors' experiments using the aforementioned substrates (Figure 2) generated a range of products with decent yields.

Substrate Scopes:-

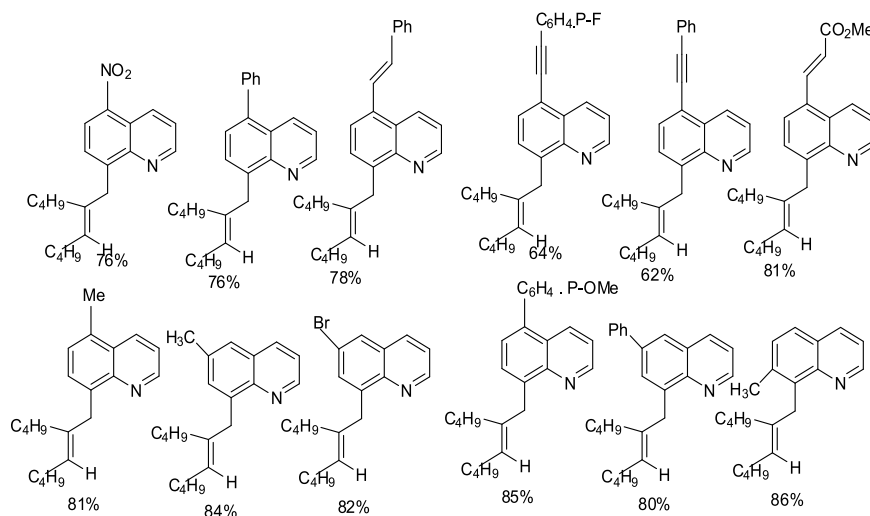
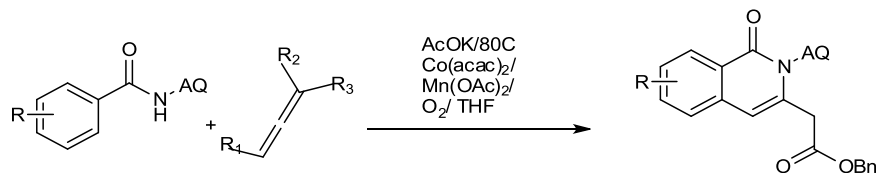


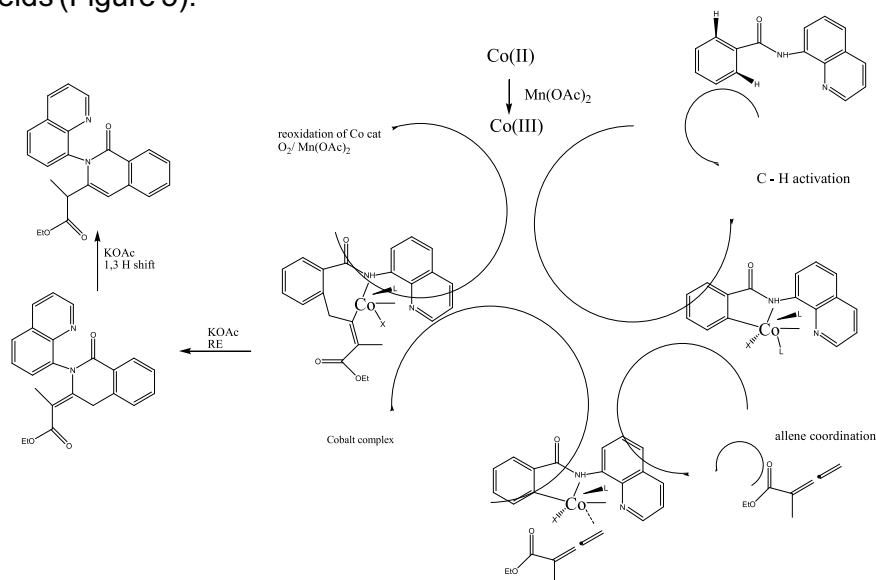
Figure 2 : Substrate scope

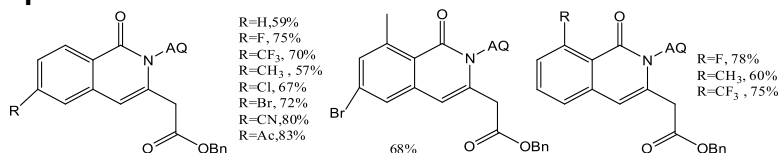
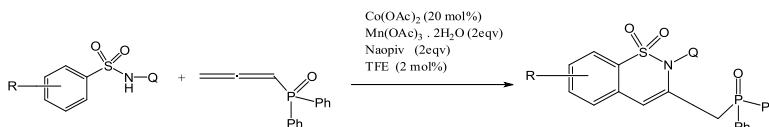
ii) Regioselective Intermolecular Annulations: -**Figure 3: Regioselective Intermolecular Annulations**

Under the reaction conditions shown above, the author obtained a good yield by initiating this reaction with the substrate shown in Figure 3. When TFE acts as a solvent, O_2 flows through the capillary after AcOK, $Co(acac)_3$, and $Mn(OAc)_2$ were added to the solution mixer at $80^\circ C$ (Li *et al.*, 2017).

Mechanism:-

The oxidation of Co(II) to Co(III), which is aided by $Mn(OAc)_2$, is the first step in the suggested reaction process (Figure 4). The allene can then co-ordinate with Co(III) after Co(III) activates a Sp^2 C-H bond to form an intermediate that undergoes ligand exchange. The allene is then inserted into the cobalt-link to create another intermediate, which, via reductive elimination, yields the cyclic ptd. The type of heterocycle created depends on the additive's base; KOAc produces a thermodynamic endocyclic isoquinone, whilst KOTf produces a kinetic exo-cyclic isoquinolinone. The Co-catalyst is renewed by $Mn(OAc)_2 / O_2$. In exo-cyclic isoquinolinone, the arylation of allenes occurs at the electron-rich carbon, with a less sterically hindered face. When compared to Pd/Rh run, the Co-catalyst shows distinct area selectivity, which is influenced by the nature of the allenes. The authors explored the substrate scopes too and obtained good product yields (Figure 5).

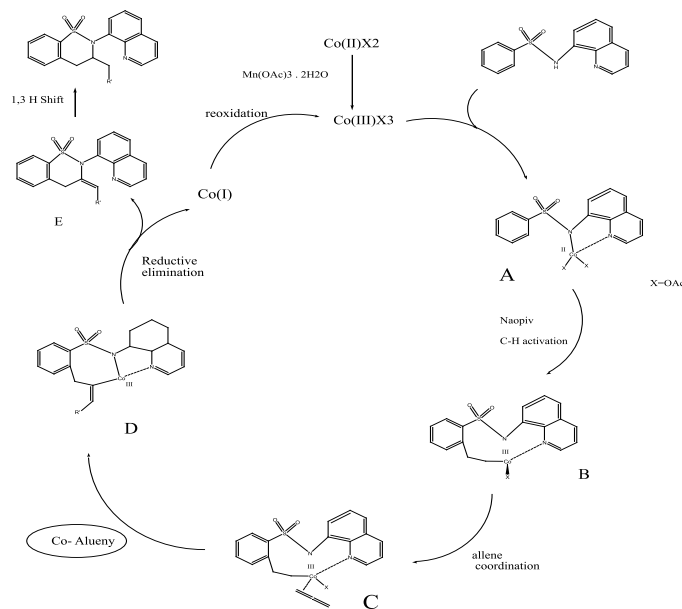
**Figure 4: Mechanism of the Reaction**

Substrate Scope:**Figure 5: Substrate scope****iii) Regio Selective Intermolecular Annulation of Sulfonamids with Allenes:-****Figure 6: Annulation of Sulfonamids**

In this article, the authors selected tosylsulfonamide and allenyl phosphonate as the coupling substrate to test under conditions for the C-H activation in the first inquiry (Figure 6). Using 20 mol% of Co(OAc)₂, Mn(OAc)₃, 2H₂O(eq), and NaOpiv in TFE at 100°C, a 32% yield was obtained (Thrimurtulu, Nallagonda & Volla, 2017).

Mechanism:-

A tenable explanation was put out in light of the aforementioned experiment (Figure 7) and earlier studies on Co-catalysed C-H bond activation. The in situ production of Co(III)- species via the catalytic cycle forms intermediate A by the oxidation of Co(II) precatalyst and the coordination of sulfonamide generated from 8-aminoquinine. When

**Figure 7: Mechanism of the Reaction**

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a base is present, C-H activation results in the formation of intermediate B. This intermediate was produced by using aryl sulfonamide to treat stoichiometric quantities of $\text{Co}(\text{OAc})_2$. The seven-membered cobalt cycle intermediate D is produced by the coordinate insertion of the C-Co bond of intermediate C with the less-substituted double bond of allene. After Co(I) is oxidised with an oxidant, reductive elimination from D yields the cyclic product E and regenerates the Co(III) species. The final product was yielded from Intermediate E via a 1,3-hydrogen shift.

The authors experimented with the substrate shown in Figure 8 and obtained a range of products with different yields.

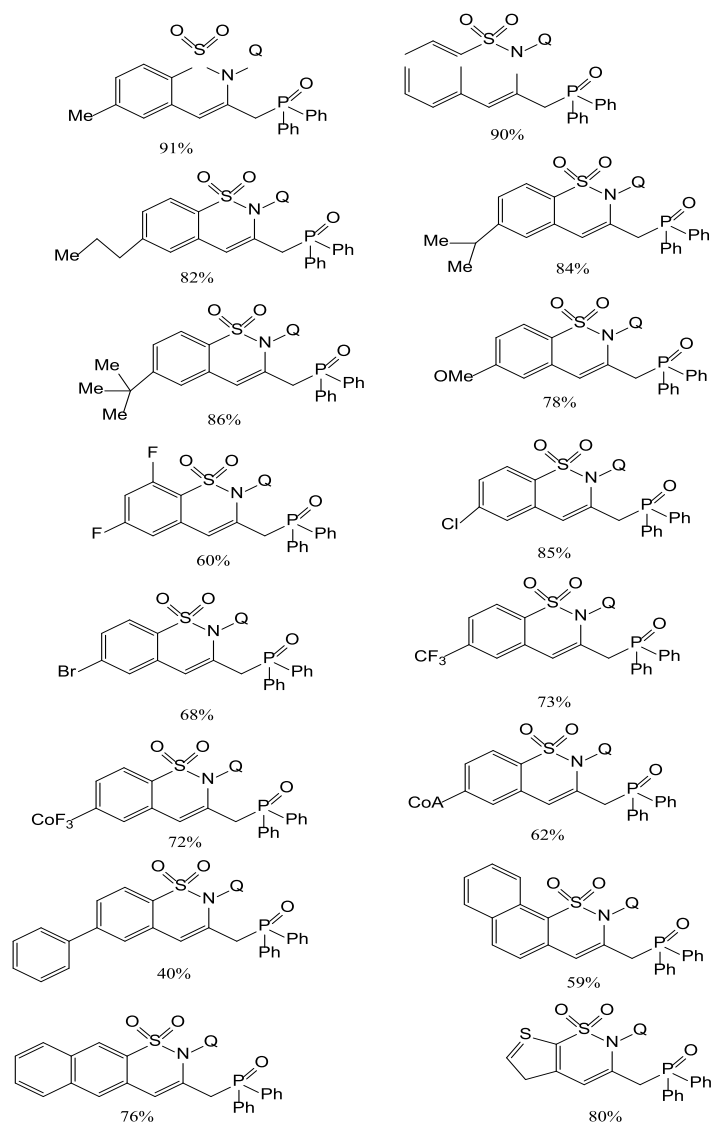
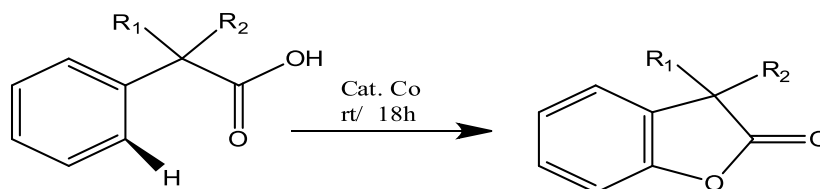
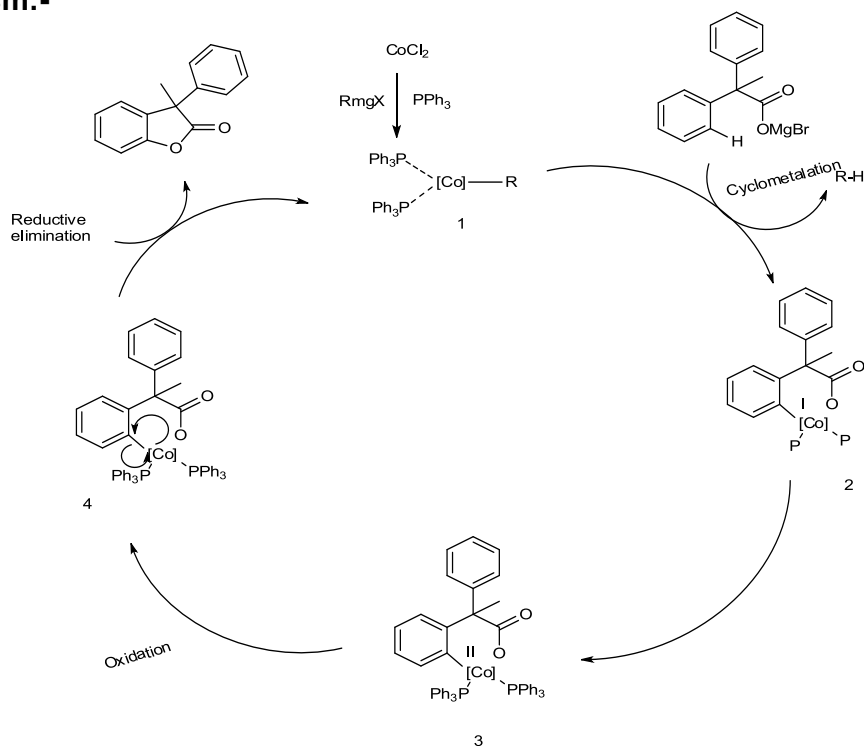


Figure 8: Substrate Scope

iv) Synthesis of Benzofuranones :-**Figure 9: Synthesis of Benzofuranones**

Without the use of an external oxidant, the authors of this study reported a Cp-free cobalt-catalysed C-H activation in mild reaction conditions (Figure 9) at room temperature (Hajipour & Khorsandi, 2020).

Mechanism:-**Figure -10: Mechanism of the Reaction**

For the synthesis of bezo-furarone at room temperature, the authors presented a simple, effective, environmentally friendly, and cost-effective technique (Figure 10). Using a ternary catalytic system made up of cobalt source, ligand, and grignard reagents, a palladium and external oxidant-free synthesis has been created. The carboxylic group serves as both a guiding and a reactive group in these processes, which included C-H activation and the creation of intermolecular C-O bonds.

Substrate Scopes:-

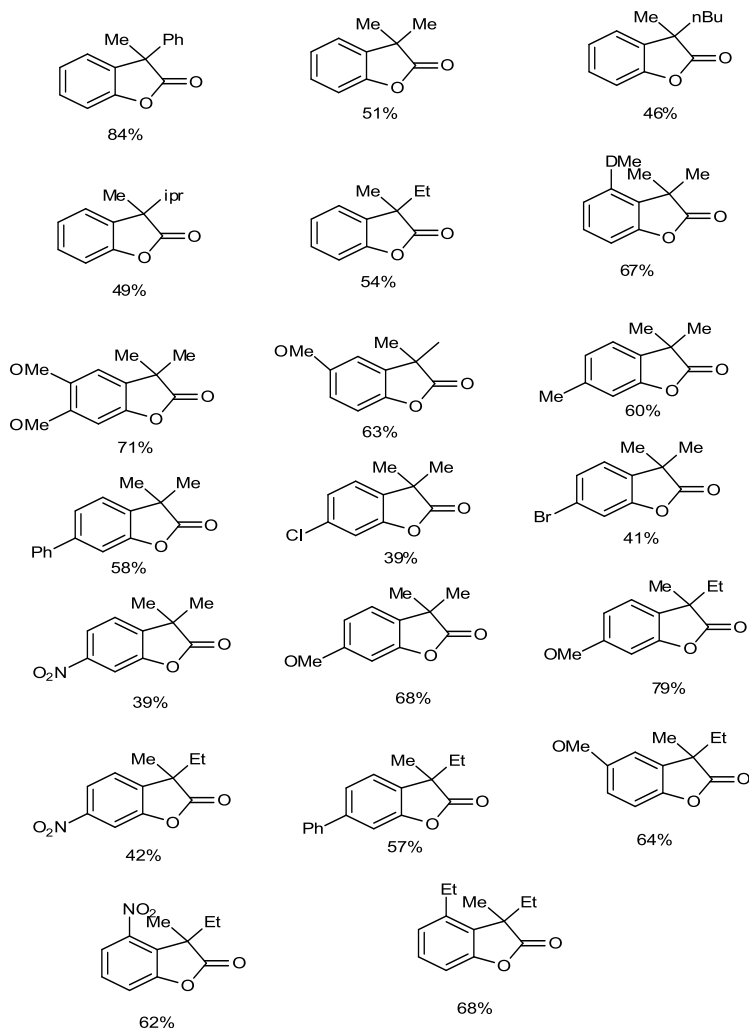


Figure 11: Substrate Scope

This protocol's substrate scope (Figure 11) has also been determined to be good, producing a range of compounds with acceptable yields.

v) Enantio Selective Intermolecular Carboaminations:-

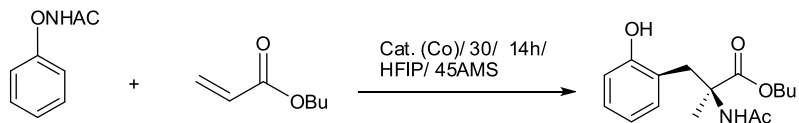


Figure 12: Enantioselective Intermolecular Carboaminations

In this study, phenoxyacetamide and butyl acrylate are used by the authors (Figure 12)

to initiate this reaction. Caesium acetate and silver trislate were used as catalyst ingredients in HFIP at 30°C. Co(I) first produced the product in a modest enantiomeric ratio with 41% yield. Co(II) and Co(III) significantly increased yield and achieved outstanding enantiomeric ratios of 99:1 (Ozols *et al.*, 2020).

vi) Lactonization of Benzamides under Acrobic Conditions: -

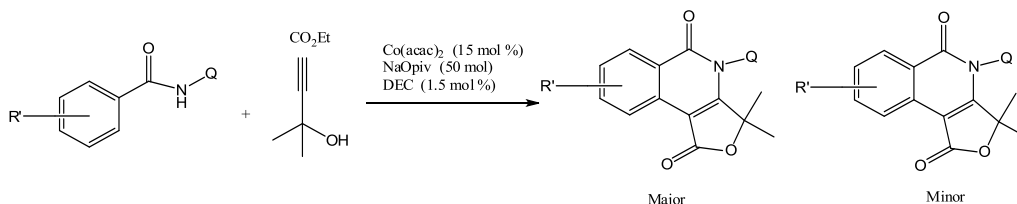


Figure 13: Lactonization of Benzamides

Using a cobalt (II) catalyst, this process explains a unique technique for regioselective alkenylation/annulations followed by lactonization (Figure 13). In contrast to many other methods now in use, this catalysed process reduces metal waste in large-scale synthesis by operating without the need for stoichiometric metal oxidants. The reaction is carried out in an open air setting with mild circumstances, exhibiting operational simplicity. Key variables affecting yield and region selectivity, including temperature, solvent selection, and catalyst type, are identified via optimisation studies. The adaptability of this technology for various applications in inorganic synthesis is highlighted by the fact that different directing groups on the amide moiety influence regioisomer formation (Muniraj, Kumar & Prabhu, 2019).

Plausible Mechanism :-

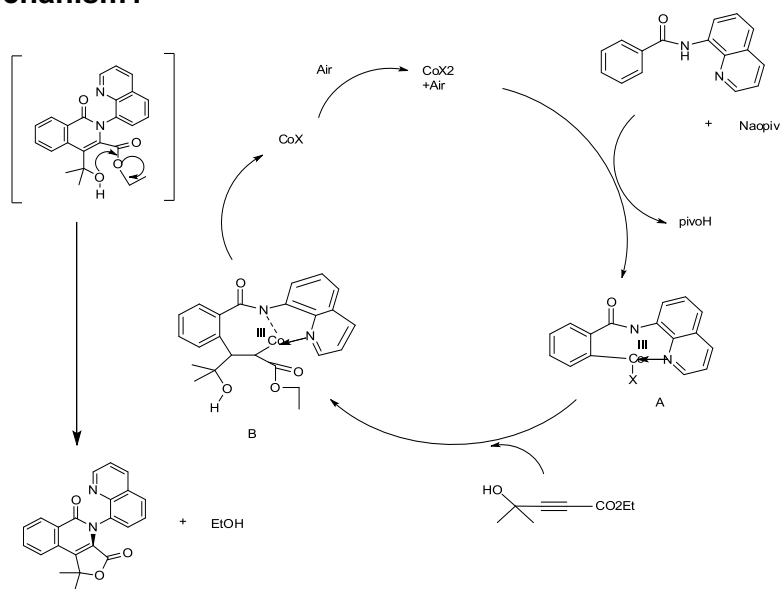
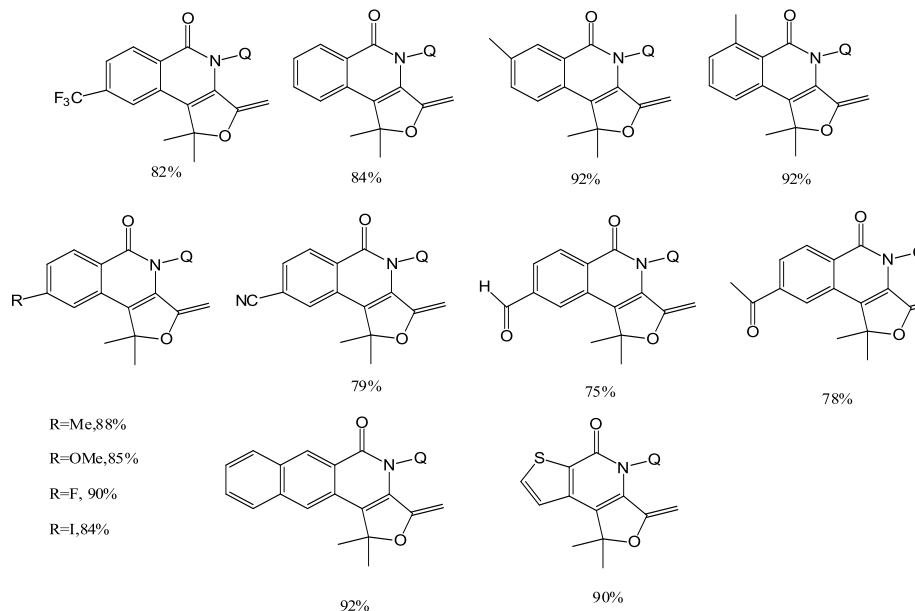
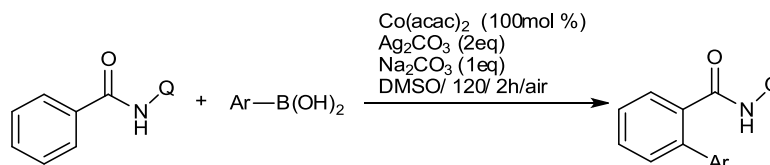


Figure 14: Mechanism of the Reaction

Substrate Scopes :-**Figure 15: Substrate Scope**

According to the suggested mechanism (Figure 14), a catalytic cycle is started by Co(II)–complex binding to the substrate, followed by aerial oxidation to Co(III), and finally, intermediate A is produced by C-H metalation aided by NaOPiv. After the hydroxylalkynoate is inserted, a seven-membered intermediate B is created, which is then subjected to reductive elimination. The cycle is finished when Co(I) is reoxidised to Co(II) via aerial oxidation. Under reaction circumstances, lactone is finally produced by intermediate C. It has also been found that the substrate scope of this technique (Figure 15) is good, yielding a variety of molecules with respectable yields.

vii) Cobalt (II) Catalysed C-H Functionalisation:-**Figure 16: Cobalt (II) Catalysed C-H Functionalisation**

The authors of this study used 8-aminoquinoline as the directing agent to investigate Co(II) catalysed arylation (Figure 16) of C-H bonds. The procedure used Na₂CO₃, Co(acac)₂, and Ag₂CO₃ as an oxidant in DMSO at 120°C for two hours. A variety of Co(III) salts, including Co(OAc)₂, CoBr₂ and CoSO₄, were tried, however the yields did not increase past high catalyst loading. Significantly, arylboronic acids with electron-donating

groups, such as OMe, and electron-neutral substituents produced good yields, but groups that withdrew electrons produced poorer yields (Kommagalla & Chatani, 2017).

Substrate Scopes:-

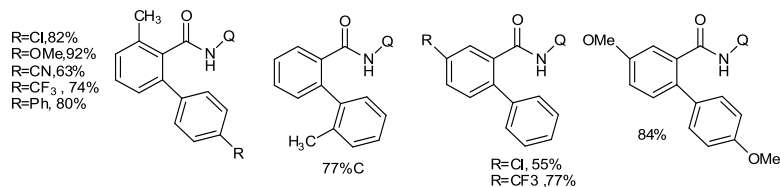


Figure 17: Substrate Scope

Additionally, it has been discovered that this technique's substrate scope (Figure 17) is good, producing a range of compounds with decent yields.

viii) C-H and C-O Coupling of Quinoline N-oxide :-

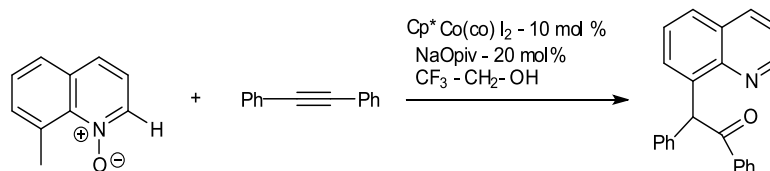


Figure 18: C-H and C-O Coupling of Quinoline N-oxide

The parameters for a reaction involving quinoline oxide and diphenylacetylene were investigated by the researchers (Figure 18). Initial attempts to produce the desired product using $\text{Cp}^*\text{Co}(\text{Co})\text{I}_2$ and NaOAc in dioxane at 80°C failed. They discovered that trifluoroethanol produced the pdt in an 80% yield under ideal circumstances. Yields were further enhanced by substituting Naopiv for other carboxylates. Control tests demonstrated that both the (Co) catalyst and NaOpiv were required for an effective reaction, which failed at lower temperatures. Diluting catalyst loading, temperature, or the use of silver salts did not improve product production. Other sources of Co did not work well for the transition (Barsu *et al.*, 2016).

Mechanism:-

The cyclometallation of a cationic complex is the first step in the suggested process for Co-catalysed functionalisation of quinoline. This is followed by alkyne coordination and migratory insertion to create an alkenyl cobalt acyclic intermediate (Figure 19). Following reductive elimination, a Co(I) intermediate is produced. This intermediate then goes through oxidative addition between nitrogen and oxygen atoms, which leads to a pro-dementalization step. This process produces the C-8 functionalised quinoline molecules and leads to catalyst renewal.

Furthermore, it has been found that the substrate scope of this approach is good, yielding a variety of compounds with respectable yields (Figure 20).

groups, such as OMe, and electron-neutral substituents produced good yields, but groups that withdrew electrons produced poorer yields (Kommagalla & Chatani, 2017).

Substrate Scopes:-

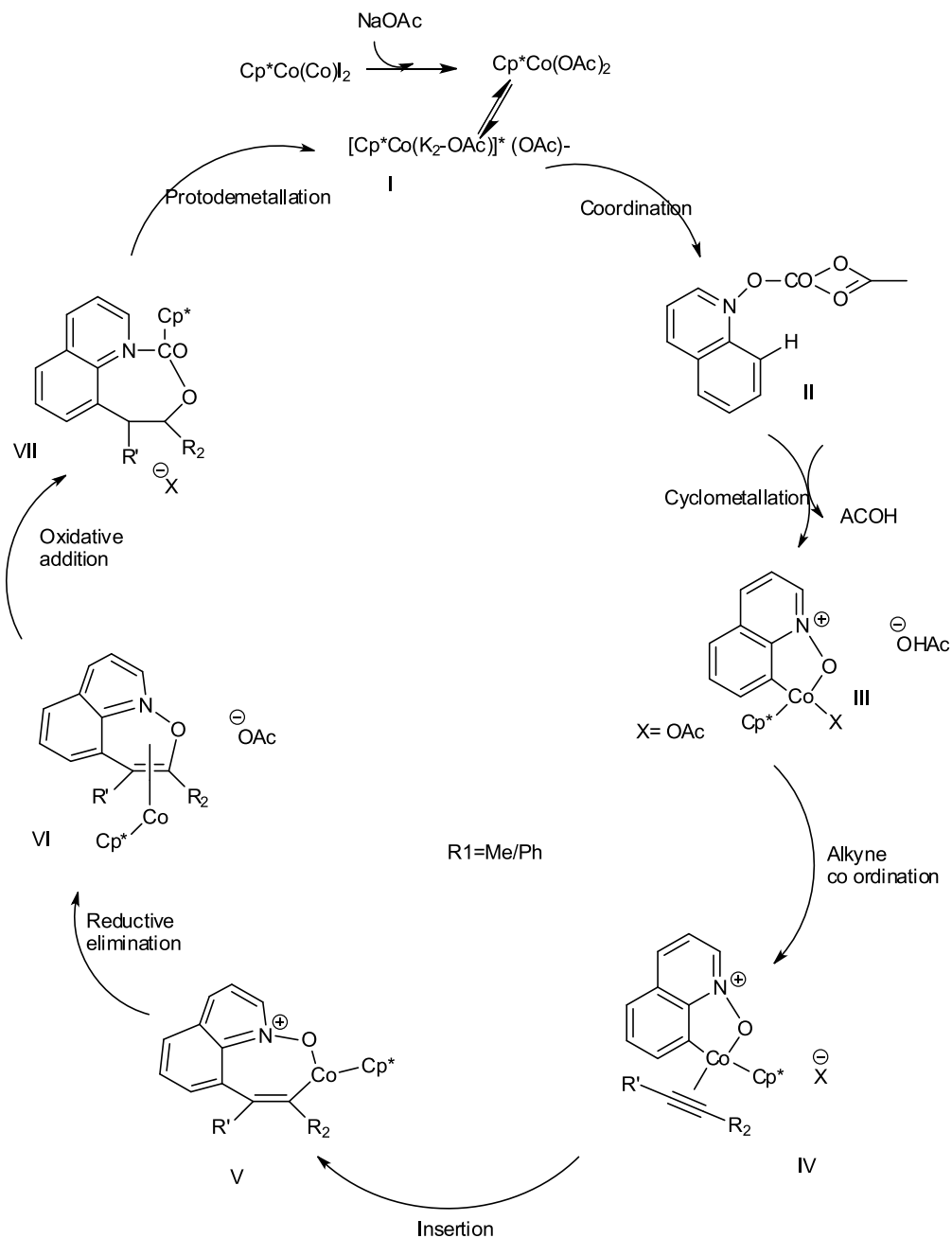
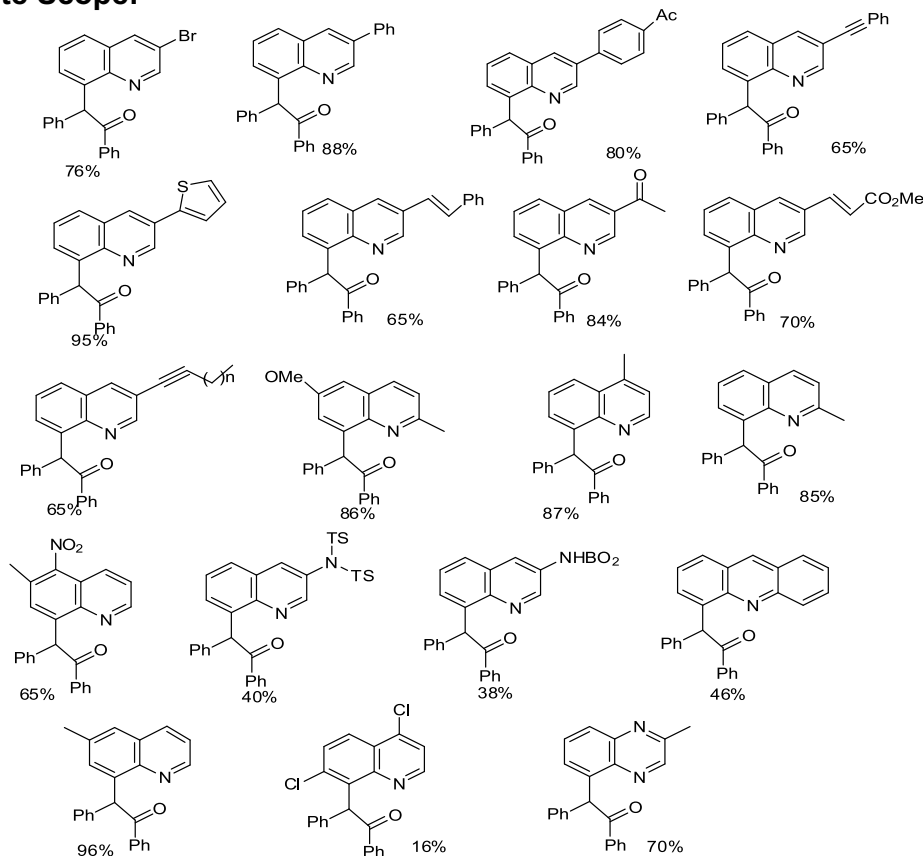
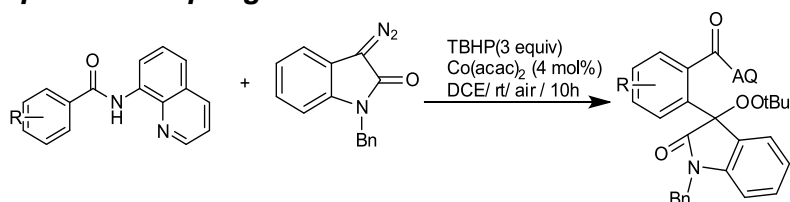


Figure 19: Mechanism of the Reaction

Substrate Scope:-**Figure 20: Substrate Scope****ix) Three Component Coupling :-****Figure 21: Three Component Coupling Reaction**

The coupling reaction (Figure 21) between N-(quinoline-8-yl) benzamide, 1-benzyle-3-diazoindolin-2-one and IBHP was investigated by the authors. They initially obtained a 62% yield for the intended product; however, the yield was lowered by solvent modifications, and various additions also showed decreased efficacy. Other cobalt salts also performed poorly; raising the temperature or altering the environment reduced the output. The yield was improved to 70% by further optimising TBHP to 30 eq. In the end, the optimal condition used 4 mol% Co(acac)₂ at rt, resulting in a 79% yield

control experiment that validated the crucial roles of TBHP and cobalt salt in this reaction (Li *et al.*, 2021).

Plausible Mechanism:-

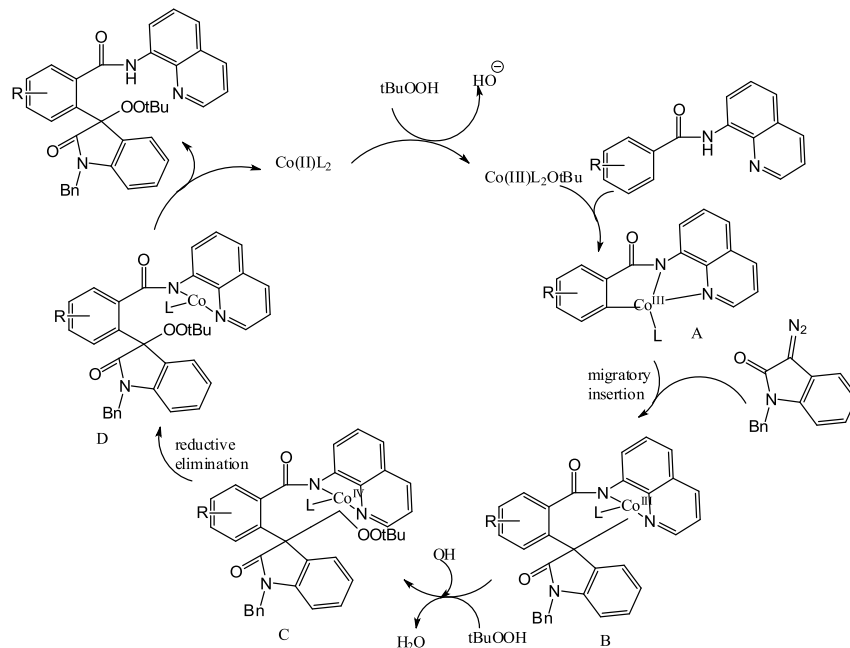


Figure 22: Mechanism of the Reaction

The oxidation of the Co(II) catalyst by TBHP, which yielded Co(III), is the first step in the suggested mechanism (Figure 22). This species forms a five-membered intermediate through a process called concerted metalation deprotonation (CMD). Through migratory insertion, this organometallic Co(II) species combines with a diazo compound to form a six-membered cyclometalated species. One electron is oxidised and Co(IV) is formed as a result of the interaction between hydroxyl radical and TBHP, which generates tBuoo-radical in situ. A Co(II) complex is the result of reductive elimination of this intermediate. Demetalation is the last stage, which regenerates the cobalt catalyst and yields the three-component coupling product.

Substrate Scopes :-

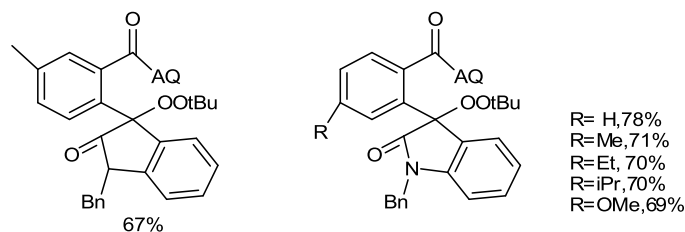


Figure 23: Substrate Scope

The authors discovered that this reaction was a generalised process with respectable product yields when they investigated it using a variety of substrates (Figure 23).

x) Azo-Directed Selective 1,4– Addition of Ortho C-H Bond to Maleimides:-

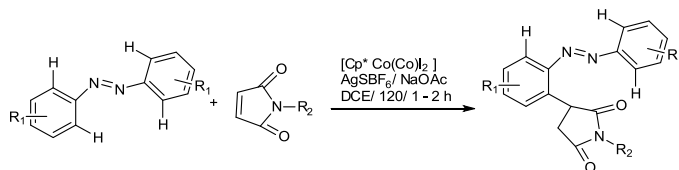


Figure 24: 1,4 – Addition of Ortho C-H Bond to Maleimides

The optimisation investigation of this study (Figure 24) started with the reaction of N-ethylmaleimide and several additives with (E)-1,2-di-p-tolyldiozene. Low yields of both mono- and di-activated PDTs were obtained at the initial circumstances. The yield of the product was greatly increased by reducing AgOAc to 20 mol%, which highlights the significance of a catalytic amount of acetate. Additional experiments with various additives, such as CsOAc, NaOAc and KOAc, significantly increased yields; Use of CsOAc and NaOAc pushed the product yield up to 68%. Acidic additions such as AcOH and PivOH also worked well. The yield was further enhanced by adjusting the reactant ratios and it reached a maximum of 75% with two equivalents of the azo-dye substrate (Muniraj & Prabhu, 2017).

Proposed Mechanism:-

In the procedure shown in Figure 25, $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ reacts with AgSbF_6 and NaOAc to produce a cationic $\text{Co}(\text{III})$ species (A) following co-dissociation. Following C-H activation, this active catalyst produces cobaltacycle B and releases AcOH . A seven-membered intermediate (C) is created when an alkene is inserted into the cobaltacycle; however, because it lacks a syn-peiplanar hydrogen atom, it is unable to remove the hydrogen atom. Ultimately, proto-demetalation produces the required product and regenerates the catalyst (A).

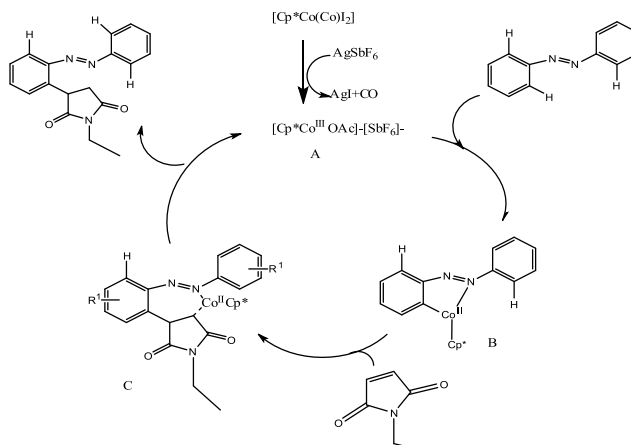


Figure 25: Mechanism of the Reaction

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Substrates Scope:-

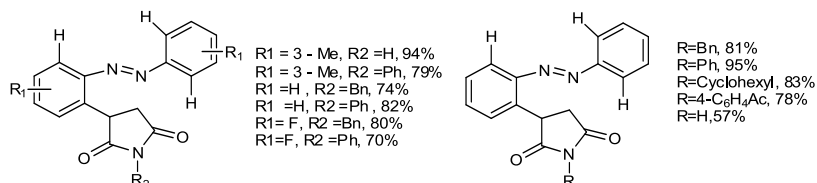


Figure 26: Substrate Scope

When the authors examined this reaction with a range of substrates, they found that it was a generalised process with decent product yields (Figure 26).

xi) Intermolecular Heterocyclization with Allenes at Room Temperature: -

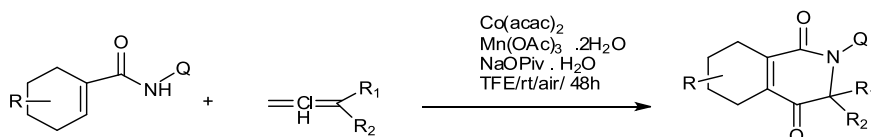


Figure 27: Intermolecular Heterocyclization with Allenes

The primary product in the reaction (Figure 27) between benzamide and phenyl allene with $\text{Co}(\text{acac})_2$ at room temperature was quinoline-1(2H)-one, showed a 5:1 ratio of regioisomers formation. $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ was found to be an essential oxidant, and $\text{NaOPiv} \cdot \text{H}_2\text{O}$ was found to be a crucial base in trifluoroethanol for efficient yielding. In contrast to the $\text{Rh}(\text{II})$ catalysed run, which favoured the less hindered side, this reaction exhibits great area selectivity, favouring the more substituted side.

Substrate Scopes:-

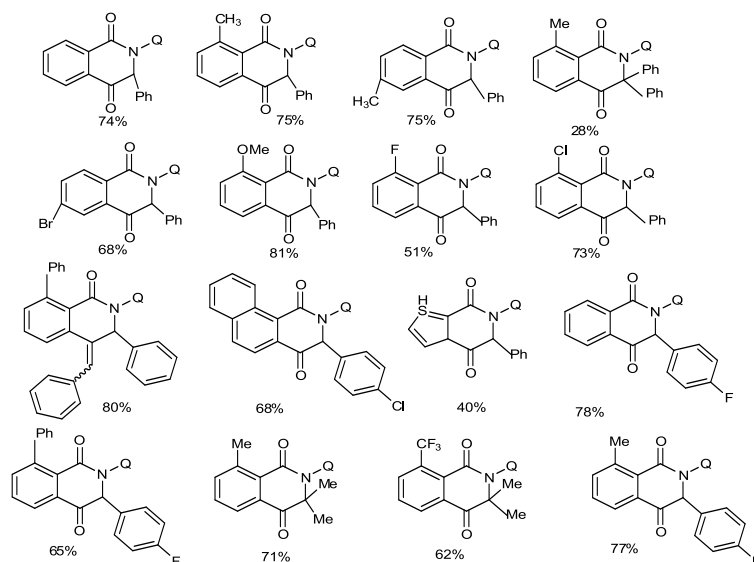


Figure 28: Substrate Scope

This selectivity was attributed to the use of cobalt, which has a smaller ionic radius than Rh. It was shown that a variety of aromatic substrates, both electron-rich and electron-poor, could tolerate functional groups such as methoxyfluoro, chloro, and bromo. Nevertheless, complicated regioisomer combinations with phenyl allene were generated by meta-substituted benzamides (Thrimurtulu *et al.*, 2016).

The authors discovered that this reaction was a generalised method with respectable product yields after analysing it with a variety of substrates (Figure 28).

Conclusion

This book chapter offers a glimpse into the latest developments in organometallic chemistry by highlighting some of the ground-breaking results of co-catalysis and its numerous uses in C-H bond activation methods. These results can undoubtedly be applied to different heterocycle derivatives to encourage more research and collaborative efforts, leading to a deeper understanding of the seemingly endless possibilities in cobalt chemistry. We think that academics from many sub-disciplines will use this article as a starting point to learn about more recent advancements in cobalt-catalysis.

Acknowledgement

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References

- Baccalini, A., Vergura, S., Dolui, P., Zanoni, G., & Maiti, D. (2019). Recent advances in cobalt-catalysed C–H functionalisations. *Organic & Biomolecular Chemistry*, 17(48), 10119–10141. <https://doi.org/10.1039/c9ob01994d>
- Barsu, N., Sen, M., Premkumar, J. R., & Sundararaju, B. (2016). Cobalt (III) catalysed C-8 selective C–H and C–O coupling of quinoline N-oxide with internal alkynes via C–H activation and oxygen atom transfer. *Chemical Communications*, 52(7), 1338–1341. <https://doi.org/10.1039/c5cc08736h>
- Hajipour, A. R., & Khorsandi, Z. (2020). Cobalt-catalysed CH activation/CO formation: Synthesis of benzofuranones. *Tetrahedron Letters*, 61(3), 151396. <https://doi.org/10.1016/j.tetlet.2019.151396>
- Kommagalla, Y., & Chatani, N. (2017). Cobalt (II)-catalysed CH functionalisation using an N, N'-bidentate directing group. *Coordination Chemistry Reviews*, 350, 117–135. <https://doi.org/10.1016/j.ccr.2017.06.018>
- Li, M. H., Si, X. J., Zhang, H., Yang, D., Niu, J. L., & Song, M. P. (2021). Directed Cobalt-Catalysed C–H Activation to Form C–C and C–O Bonds in One Pot via Three-Component Coupling. *Organic Letters*, 23(3), 914–919. <https://doi.org/10.1021/acs.orglett.1c00000>

1021/acs.orglett.0c04122

- Li, T., Zhang, C., Tan, Y., Pan, W., & Rao, Y. (2017). Cobalt-catalysed C–H activation and regioselective intermolecular annulation with allenes. *Organic Chemistry Frontiers*, 4(2), 204-209. <https://doi.org/10.1039/c6qo00567e>
- Muniraj, N., & Prabhu, K. R. (2017). Cobalt (III)-catalysed C–H activation: azo directed selective 1, 4-addition of ortho C–H bond to maleimides. *The Journal of Organic Chemistry*, 82(13), 6913-6921. <https://doi.org/10.1021/acs.joc.7b01094>
- Muniraj, N., Kumar, A., & Prabhu, K. R. (2019). Cobalt-Catalysed Regioselective [4+ 2] Annulation/Lactonization of Benzamides with 4-Hydroxy-2-Alkynoates under Aerobic Conditions. *Advanced Synthesis & Catalysis*, 362(1), 152-159. <https://doi.org/10.1002/adsc.201901119>
- Ozols, K., Onodera, S., Woźniak, Ł., & Cramer, N. (2020). Cobalt (III)-Catalysed Enantioselective Intermolecular Carboamination by C– H Functionalisation. *Angewandte Chemie International Edition*, 60(2), 655-659. <https://doi.org/10.1002/anie.202011140>
- Patel, M., Ajay, U., Padala, K., & Naveen, T. (2022). Recent Advances in Cobalt-catalysed Functionalisation of Unactivated Olefins. *Asian Journal of Organic Chemistry*, 11(8). <https://doi.org/10.1002/ajoc.202200201>
- Sen, M., Emayavaramban, B., Barsu, N., Premkumar, J. R., & Sundararaju, B. (2016). Cp* Co (III)-Catalysed C (sp³)–H Bond Activation: A Highly Stereoselective and Regioselective Alkenylation of 8-Methylquinoline with Alkynes. *ACS Catalysis*, 6(5), 2792-2796. <https://doi.org/10.1021/acscatal.6b00612>
- Thrimurtulu, N., Dey, A., Maiti, D., & Volla, C. M. R. (2016). Cobalt-Catalysed sp²-C–H Activation: Intermolecular Heterocyclization with Allenes at Room Temperature. *Angewandte Chemie*, 55(40), 12361–12365. <https://doi.org/10.1002/anie.201604956>
- Thrimurtulu, N., Nallagonda, R., & Volla, C. M. R. (2017). Cobalt-catalysed aryl C–H activation and highly regioselective intermolecular annulation of sulfonamides with allenes. *Chemical Communications*, 53(11), 1872–1875. <https://doi.org/10.1039/c6cc08622e>

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