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RECENT ADVANCES IN THE FIELD OF CHEMISTRY Vol. 2





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PREFACE

We are delighted to publish our book entitled "Recent Advances in the Field of Chemistry – Vol. II". This book is the compilation of esteemed chapter of acknowledged experts in the fields of Chemistry. This book is published in the hopes of sharing the excitement found in the study of Chemistry. We developed this digital book with the goal of helping people achieve that feeling of accomplishment. The chapters in the book have been contributed by eminent scientists, academicians. Our special thanks and appreciation goes to experts and research workers whose contributions have enriched this book. Finally, we will always remain a debtor to all our well-wishers for their blessings, without which this book would not have come into existence.

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CHAPTER

1

Metal Oxide Nanoparticles In Wastewater Treatment

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Introduction

Actions regarding wastewater treatment have never felt more urgent. The surge in water scarcity compels the reuse of contaminated water through advanced purification technologies. Bringing metal oxide nanoparticles (MONPs) for treatment of wastewater is a tremendous advancement in terms of environmental remediation process. High surface to area ratio, Flexible band gaps, and characteristic catalytic efficiency ensure sufficient removal of most organic



contaminants, tenacious heavy metals, and microbial impurities.

Photocatalysis, is considered a key mechanism for the action of most MONPs, it is significantly prominent in case of ZnO and TiO₂. Under the action of ultraviolet (UV) radiation or visible light, it is the nanoparticles that generate a Reactive Oxygen Species (ROS), which in turn degrades the Persistent Organic Pollutants (POPs) along with notable pharmaceutical residues and dyes that can resist conventional treatments.

Apart from just photocatalysis, MONPs also exhibit a remarkable affinity for adsorption which turns out to be critical for the removal of heavy metals. Iron oxide (Fe₃O₄) and aluminum oxide (Al₂O₃) are illustrating the high affinity for lead (Pb²⁺), cadmium (Cd²⁺), and arsenic (As³⁺), forming reasonably stable surface complexes. The magnetic nature of Fe₃O₄ further allows for efficient separation and reuse, minimizing secondary pollution.



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Additionally, MONPs possess antimicrobial properties, with silver-doped ZnO and copper oxide (CuO) effectively disrupting microbial cell membranes and inhibiting biofilm formation, enhancing water disinfection.

Even after all of their potential, there are still challenges that remain in terms of their environmental implications, stability, and large-scale implementation. Advances in green synthesis, surface functionalization, and hybrid nanomaterials are addressing these limitations, paving the way for practical applications. This chapter explores the mechanisms, applications, and future prospects of MONPs in wastewater treatment, highlighting both their advantages and the challenges that must be overcome for widespread adoption.

Types and Properties of Metal Oxide Nanoparticles

Metal oxide nanoparticles (MONPs) play a pivotal role in wastewater treatment due to their unique physicochemical properties, such as high surface-to-volume ratio, tunable band gap, redox activity, and catalytic efficiency. The effectiveness of these nanoparticles depends on their structural and chemical characteristics, which influence their adsorption capacity, photocatalytic activity, and antimicrobial potential. This section discusses the most commonly used MONPs in wastewater treatment and their key properties.

Common Metal Oxide Nanoparticles Used in Wastewater Treatment

Photocatalytic	Effective under UV light, catalyzes ROS formation (•OH, O2 ⁻ •), degrading
Properties	organic contaminants to CO ₂ and H ₂ O.
Surface Morphology and Stability	High stability, non-toxic, large surface area enhances adsorption and catalytic efficiency.
Electronic Band Gap	Band gap ~3.2 eV (anatase phase), limits activation to UV light.
Doping Modifications	Metal (Ag, Cu) and non-metal (N, S) doping reduces band gap for visible light activation.

(i) Nanoparticles of Titanium Dioxide (TiO₂)



Used in water treatment for photodegradation of POPs, pharmaceuticals,		
and industrial dyes.		
Wide band gap requires UV light; advanced doping needed for broader		
light spectrum use.		
Developing nanostructured TiO ₂ and heterojunctions to optimize light		
absorption and minimize recombination, enhancing photocatalytic		
efficiency.		
=		

(ii) Nanoparticles of Zinc Oxide (ZnO)

Antimicrobial	Generates ROS to disrupt microbial cell membranes, effective against a	
Properties	wide range of microorganisms.	
Photocatalytic	Photocatalytic under UV and near-visible light due to a band gap (~3.3	
Properties	eV); degrades organic pollutants.	
Surface	High surface reactivity onhances adsorption and photosatelytic activity	
Characteristics	Then surface reactivity enhances ausorption and photocatalytic activity.	
Stability and	Susceptible to photocorrosion in water, impacting long-term stability	
Durability	and reuse.	
Visible Light	Band gap near UV spectrum limits; research focuses on	
Activity	doping/composites for better visible-light activation.	
Environmental	Used in biologically contaminated water treatment and for degrading	
Applications	organic pollutants in wastewater.	
Technological	Photocorrosion reduces durability; ongoing improvements aim at	
Challenges enhancing stability via surface modifications and do		
	Innovations include ZnO nanocomposites and doping (e.g., Ag,	
R&D Focus	graphene) to improve photocatalytic activity and operational stability	
	under visible light.	



Magnetic	Superparamagnetic properties facilitate easy magnetic separation,		
Properties	enhancing recyclability and reducing secondary contamination.		
Heavy Metal	Effective in adsorbing arsenic, lead, and chromium through surface		
Adsorption	functionalization.		
Redox	Engages in redox reactions that transform contaminants into less		
Capabilities	harmful forms, e.g., reducing Cr ⁶⁺ to Cr ³⁺ .		
Stability and	Requires precise surface engineering to maximize adsorption efficiency		
Durability	and redox reactions, adding complexity and cost.		
Environmental	Widely used in removing toxic metals from industrial discharges and		
Applications	enhancing water safety for downstream use.		
Technological	Precise surface functionalization is needed for optimal performance,		
Challenges which can be complex and cost-intensive.			
	Ongoing development aims at enhancing magnetic properties and		
R&D Focus	surface functionalities to improve pollutant removal efficiency and		
	reusability.		

(iii) Nanoparticles of Iron Oxide (Fe₂O₃, Fe₃O₄)

(iv) Nanoparticles of Aluminum Oxide (Al₂O₃)

Adsorptive Efficiency	High surface area and porosity make it an excellent adsorbent for fluoride, phosphate, and heavy metals.	
Chemical and	Maintains structural integrity under extreme pH conditions, suitable fo	
Thermal Stability	various wastewater treatments.	
Regeneration Limited regeneration capabilities hinder its repeated use in		
Capacity	operations.	



Environmental	Effective in fluoride removal from groundwater and heavy metal		
Applications	adsorption in industrial wastewater treatment.		
Technological	Poor regeneration limits large-scale application; ongoing research		
Challenges	focuses on enhancing recyclability and operational lifespan.		
	Research is directed towards improving porosity and surface reactivity		
R&D Focus	to boost adsorption efficiency and developing better regeneration		
	methods.		

(v) Nanoparticles of Manganese Oxide (MnO₂)

Oxidative	Exhibits strong oxidative properties for degrading organic pollutants	
Strength	and removing heavy metals like lead (Pb ²⁺) and mercury (Hg ²⁺).	
Catalytic and Adsorption Synergy	Acts as both a catalyst in advanced oxidation processes (AOPs) and as an adsorbent through surface interactions.	
Aggregation	Prone to aggregation in aqueous environments, reducing effective	
Tendency	surface area and reactivity.	
Environmental	Utilized in the oxidation and removal of organic pollutants and heavy	
Applications	metals from industrial wastewater.	
Technological	Aggregation complicates practical applications; research focuses on	
Challenges	enhancing dispersion and stability in water.	
R&D Focus	Ongoing development aims to synthesize nanostructured forms of MnO ₂ and develop composites to prevent aggregation and enhance reactivity.	





Key Properties of MONPs Relevant to Wastewater Treatment

(i) High Surface Area and Nanostructure Effects

MONP's have a very high surface area to volume ratio which increases the efficiency of adsorption and catalytic properties. Certain mesoporous TiO_2 and MnO_2 even provide additional reaction sites.

(ii) Photo-catalytic activities and band gap

The band gap energy of MONPs determines their photocatalytic efficiency. Narrow band gap materials (e.g., doped TiO₂, visible-light-responsive ZnO) are preferred for effective solar-driven degradation of organic pollutants.

(iii) Surface Functionalization and Selectivity

Functionalizing MONPs with ligands, polymers, or surfactants enhances selectivity towards specific contaminants. For example, amine-functionalized Fe_3O_4 nanoparticles exhibit improved binding affinity for negatively charged heavy metals like Cr^{6+} and As^{5+} .

(iv) Aggregation and Stability

Nanoparticles tend to agglomerate in aqueous environments due to van der Waals forces, reducing their effective surface area. Stabilization strategies, such as coating with surfactants (e.g., cetyltrimethylammonium bromide, CTAB) or using polymeric dispersants, improve their dispersion and longevity in wastewater treatment systems.



(v) Toxicity and Environmental Impact

While MONPs offer significant advantages in water treatment, their potential toxicity to aquatic organisms and human health remains a concern. The leaching of metal ions, ROS-induced toxicity, and bioaccumulation require careful assessment to ensure environmentally safe applications. Efforts are still under way to develop more reliable and eco-friendly MONP's.

Mechanisms of Wastewater Treatment Using Metal Oxide Nanoparticles

MONP's bring different approaches for wastewater remediation. A few of these approaches have been listed as follows :-

Adsorption Mechanism

Adsorption is one of the most effective and widely studied processes for wastewater treatment using MONPs. The high surface-area-to-volume ratio of these nanoparticles provides numerous active sites for pollutant binding.

Types of Adsorption

- Physical adsorption (physisorption): Based on weak van der Waals forces due to which pollutants adhere on the surface. The process is reversible and also suitable for nanoparticle recovery and pollutant regeneration.
- Chemical adsorption (chemisorption): It is based on stronger chemical interactions such as the formation of ionic or covalent bonds that are formed between MONPs and contaminants. This process is irreversible but offers high selectivity and efficiency.

Adsorption of Heavy Metals

MONPs like Fe₃O₄, Al₂O₃, and MnO₂ efficiently remove heavy metals (Pb²⁺, Cd²⁺, As³⁺, Cr⁶⁺) from wastewater. Mechanism is discussed as follows :-

Mechanism	Surface Functional	Interaction	Outcome
	Groups	Туре	
Ion Exchange	–ОН, –СООН	Ionic Exchange	Precipitation or Complexation
Electrostatic	Charged MONP	Electrostatic	Attraction of Oppositely Charged
	Surfaces		Metal Ions
Surface	Hydroxyl Groups	Coordinate	Complex Formation



Complexation	Bonds	

For example, FeSO₄ nanoparticles functionalized with amine (-NH₂) groups enhance Cr^{6+} adsorption due to electrostatic attraction and reduction to Cr^{3+} .

Photocatalysis

Photocatalysis is a light-driven degradation process where MONPs generate reactive oxygen species (ROS) to break down organic pollutants, including pesticides, pharmaceuticals, dyes, and hydrocarbons.

Enhancements to Improve Photocatalysis

- Doping: Incorporating elements like Ag, N, or S reduces the band gap, enabling visible-light activation.
- Heterojunction Formation: Coupling TiO₂ with ZnO, Fe₂O₃, or graphene enhances charge separation and photocatalytic efficiency.

Coagulation and Flocculation

MONPs can act as coagulants or flocculants, facilitating the aggregation of fine suspended particles and dissolved contaminants into larger, easily removable clusters.



Mechanism of Coagulation and Flocculation

Mechanism	Description	Examples
Charge Neutralization	Positively charged MONPs interact with negatively charged colloidal particles, reducing electrostatic repulsion.	Al ₂ O ₃ and Fe ₃ O ₄ nanoparticles neutralize charges in water treatment processes.
Bridging Mechanism	MONPs adsorb onto pollutant surfaces, forming large flocs that settle under gravity.	Use of Fe_3O_4 to form flocs in industrial wastewater containing suspended solids.



Mechanism	Description	Examples
Hydrophobic Effects	Hydrophobic contaminants adhere to MONPs, enhancing agglomeration and separation.	Hydrophobic interactions in oil- water separation using Al ₂ O ₃ nanoparticles.

Application Example – Al_2O_3 and Fe_3O_4 nanoparticles have been successfully used to remove oil emulsions from industrial wastewater by destabilizing oil droplets and facilitating separation.

Magnetic Separation

Magnetic nanoparticles, particularly Fe₃O₄, offer a unique advantage in wastewater treatment due to their superparamagnetic properties, allowing easy recovery using an external magnetic field.

Mechanism of Magnetic Separation

- 1. MONPs (e.g., Fe_3O_4) adsorb pollutants such as heavy metals and organic dyes.
- 2. A magnetic field is applied to separate the loaded nanoparticles from the treated water.
- 3. The nanoparticles are regenerated and reused after desorption of pollutants.

Example: Arsenic (As³⁺/As⁵⁺) Removal

Fe₃O₄ nanoparticles coated with FeOOH have shown high efficiency in removing arsenic from contaminated water through adsorption and magnetic separation.

Antimicrobial Activity

MONPs such as ZnO, CuO, and TiO₂ exhibit strong antimicrobial properties, making them effective against bacteria, viruses, and fungi in wastewater.

Mechanisms of Antimicrobial Action

- ROS Generation: TiO₂ and ZnO nanoparticles produce ROS that damage microbial cell membranes, proteins, and DNA.
- Metal Ion Release: CuO and Ag-doped MONPs release toxic metal ions (Cu²⁺, Ag⁺), which disrupt enzymatic functions and cause microbial cell death.
- Membrane Disruption: Direct interaction of MONPs with bacterial membranes leads to leakage of intracellular contents.



Example: ZnO Nanoparticles for Pathogen Removal

ZnO nanoparticles have been demonstrated to inactivate *E. coli*, *Pseudomonas aeruginosa*, and Staphylococcus aureus by inducing oxidative stress and membrane damage.

Synergistic and Hybrid Mechanisms

Combining multiple MONP mechanisms enhances wastewater treatment efficiency. Some hybrid strategies include:

- Fe₃O₄/TiO₂ nanocomposites: Utilize magnetic separation and photocatalysis for pollutant degradation and easy recovery.
- ZnO/Graphene Oxide hybrids: Improve adsorption and photocatalysis for dye and pharmaceutical removal.
- Ag-doped TiO₂: Combines antimicrobial activity with photocatalytic degradation for pathogen and organic pollutant removal.

Application of Metal Oxide Nanoparticles in Wastewater Treatment.

Application	KeyMetalOxideNanoparticles	Mechanism of Action	Examples of Pollutants Removed
Heavy Metal Removal	Fe ₃ O ₄ , MnO ₂ , TiO ₂	Adsorption, Redox Reactions, Precipitation, Magnetic Separation	Pb ²⁺ , Cd ²⁺ , Cr ⁶⁺ , As ³⁺ /As ⁵⁺ , Hg ²⁺
Degradation of Organic Pollutants and Pharmaceuticals	TiO ₂ , ZnO, Fe ₂ O ₃ , Ag-doped TiO ₂	Photocatalysis, Adsorption, Fenton-like Reactions, Hybrid Systems	Pharmaceuticals(antibiotics, analgesics,EDCs), pesticides,phenols, hydrocarbons
DyeRemovalfromTextileIndustryWastewater	TiO₂, ZnO, Fe₃O₄, MnO₂	Photocatalytic Degradation, Adsorption, Oxidation	Methylene blue, Rhodamine B, Congo Red



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Removal of Microbial Contaminants	ZnO, TiO ₂ , CuO, Ag-doped TiO ₂ , Fe_3O_4 -based nanocomposites	ROS Generation, Metal Ion Release, Membrane Disruption	E. coli, P. aeruginosa, S. aureus, Salmonella, Legionella, V. Cholera
Hybrid and	Fe ₃ O ₄ /TiO ₂ , GO-	CombinationofAdsorption,Photocatalysis,andAntimicrobial Action	Various heavy metals,
Multifunctional	TiO ₂ , Ag-TiO ₂ -		dyes, pharmaceuticals,
MONP Systems	ZnO Composites		and pathogens

Hybrid and Multifunctional MONP Systems

To improve wastewater treatment efficiency, researchers are developing hybrid MONP systems that integrate multiple mechanisms, such as adsorption, photocatalysis, and antimicrobial action.

Examples of Hybrid Systems

- Fe₃O₄/TiO₂: Provides magnetic separation and photocatalytic degradation of organic pollutants.
- Graphene Oxide (GO)-TiO₂: Enhances adsorption and photoactivity for removing dyes and pharmaceuticals.
- Ag-TiO₂-ZnO Composites: Combines antibacterial, photocatalytic, and adsorption capabilities for comprehensive wastewater treatment.

Challenge	Description	Mitigation Strategies
Stability and	MONPs aggregate in solution, reducing	Surface modifications using
Aggregation	effectiveness.	polymers or surfactants improve
		dispersion.
Environmental	Leaching of nanoparticles into water	Developing biodegradable and
Concerns	bodies may pose toxicity risks to aquatic	eco-friendly MONPs.
	life.	
Regulatory and	Mass production and regulatory approvals	Efforts focused on cost reduction
Cost	are under development. Improving cost-	and ensuring environmental
	efficiency and environmental safety is	safety for regulatory approval.
	crucial.	



Advantages and Challenges of Using Metal Oxide Nanoparticles in Wastewater Treatment.

The use of metal oxide nanoparticles (MONPs) in wastewater treatment presents significant advantages, including high efficiency, versatility, and the ability to degrade persistent pollutants. However, there are also critical challenges, such as nanoparticle stability, potential toxicity, environmental concerns, and large-scale implementation difficulties. This section outlines the key benefits and limitations of MONPs in wastewater treatment.

Advantages of Using MONPs

(i) High Adsorption Capacity and Surface Reactivity

- MONPs possess a high surface-area-to-volume ratio, enabling enhanced interaction with contaminants.
- Functionalized MONPs (e.g., Fe₃O₄ with amine (-NH₂) or carboxyl (-COOH) groups) show high selectivity for heavy metal removal through surface complexation.

(ii) Efficient Pollutant Degradation via Photocatalysis

- TiO₂ and ZnO nanoparticles generate reactive oxygen species (ROS) under UV or visible light, leading to the complete degradation of organic pollutants into non-toxic byproducts (CO₂ and H₂O).
- Photocatalysis enables the breakdown of pharmaceutical residues, dyes, and pesticides, which are difficult to remove using conventional methods.

(iii) Reusability and Magnetic Recovery

- Fe₃O₄-based MONPs allow easy separation and reusability through magnetic recovery, reducing secondary pollution and operational costs.
- Regeneration techniques, such as chemical desorption or thermal treatment, restore MONP efficiency for repeated use.

(iv) Broad-Spectrum Antimicrobial Properties

- ZnO, CuO, and Ag-doped TiO₂ nanoparticles exhibit strong bactericidal and antiviral activity by disrupting microbial membranes and DNA.
- MONPs prevent biofilm formation in wastewater treatment plants, enhancing system longevity.

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(v) Scalability and Integration with Existing Technologies

- MONPs can be incorporated into existing membrane filtration, adsorption beds, and photocatalytic reactors for improved treatment performance.
- Hybrid nanomaterials (e.g., Fe₃O₄/TiO₂, graphene-TiO₂ composites) offer multifunctionality, combining adsorption, photocatalysis, and magnetic separation in a single system.

Challenges and Limitations of MONPs

(i) Stability and Aggregation Issues

- MONPs tend to aggregate in aqueous media due to van der Waals forces, leading to reduced surface area and efficiency.
- Surface modification strategies (e.g., polymeric coatings, surfactants, or functionalization with organic ligands) are required to improve dispersion and prevent nanoparticle loss.

(ii) Toxicity and Environmental Concerns

- The potential leaching of nanoparticles into natural water systems raises concerns about their long-term ecological impact on aquatic organisms.
- Studies suggest that MONPs can induce oxidative stress, cytotoxicity, and bioaccumulation in living organisms, necessitating further toxicity assessments.
- Green synthesis approaches using plant extracts, biopolymers, or microbial processes are being explored to develop eco-friendly MONPs.

(iii) Cost and Scalability Barriers

- Large-scale production of MONPs remains expensive, requiring precise synthesis methods, controlled functionalization, and purification steps.
- Nanoparticle-based wastewater treatment is still in the research phase, with limited commercial adoption due to high initial investment costs.

(iv) Regulatory and Safety Challenges

• The lack of standardized regulations for the use and disposal of MONPs in wastewater treatment limits widespread implementation.

- Risk assessment studies on long-term human exposure to MONPs through drinking water sources are still ongoing.
- Governments and environmental agencies need to establish safe handling, disposal, and recycling protocols for MONPs.

Strategies to Overcome Challenges

Here are a few of the most important strategies to overcome the challangesin wastewater treatment by metal oxide nanoparticles :-

(i) Surface Functionalization and Nanocomposite Engineering

- Coating MONPs with biocompatible polymers (e.g., polyethylene glycol, PEG) or organic ligands enhances stability and reduces toxicity.
- Hybrid nanomaterials, such as graphene- TiO_2 or Fe_3O_4 -ZnO, enhance dispersion, reactivity, and pollutant selectivity.

(ii) Green Synthesis for Sustainable MONPs

- Utilizing plant extracts, biogenic reducing agents, or microbial processes for MONP synthesis reduces harmful byproducts and enhances biocompatibility.
- Green-synthesized Ag-ZnO nanocomposites have shown antimicrobial efficiency while reducing environmental impact.

(iii) Improved Wastewater Treatment Reactor Designs

- Integrating MONPs into fixed-bed reactors, photocatalytic membranes, and nanocomposite filtration systems enhances large-scale applicability.
- Reactor optimization through fluidized-bed and hybrid filtration approaches improves nanoparticle retention and reusability.

(iv) Regulatory Framework Development

• Ensuring safety protocols and setting regulatory standards is crucial for use of MONPs.



Recent Advances and Future prospects.

(i) Functionalized and Hybrid MONPs for Enhanced Performance

- Surface Functionalization: MONPs are modified with functional groups such as thiol (-SH), amine (-NH₂), and carboxyl (-COOH) to enhance adsorption of heavy metals like Pb²⁺, Cd²⁺, and Cr⁶⁺.
- Graphene and Carbon-Based Composites: TiO₂ and ZnO graphene oxide (GO) hybrids improve photocatalytic efficiency by reducing electron-hole recombination.
- Bimetallic and Doped MONPs: Doping with Ag, Cu, or N enhances the visible-light activity of TiO₂ and ZnO for organic pollutant degradation.

(ii) Green Synthesis of MONPs for Sustainable Applications

- Plant-Mediated Synthesis: Extracts from plants like Moringa oleifera, neem, and green tea act as reducing and stabilizing agents for MONP synthesis.
- Microbial and Enzyme-Based Approaches: Bacteria, fungi, and enzymes produce MONPs with controlled size and morphology.
- Reduced Toxicity: Green-synthesized MONPs exhibit lower cytotoxicity and improved biocompatibility in aquatic ecosystems.

(iii) MONP-Based Membranes and Filtration Technologies

- TiO₂/ZnO Nanocomposite Membranes: Prevent biofouling and degrade organic pollutants under light exposure.
- Fe₃O₄-Embedded Membranes: Enable magnetic separation of contaminants while enhancing membrane durability.
- Smart Nanomaterials: Stimuli-responsive MONPs (pH- or temperature-sensitive) enable targeted pollutant removal.

Future Perspectives and Challenges

(i) Large-Scale Implementation and Cost Reduction

Despite their promising laboratory-scale results, MONPs face challenges in scalability and costeffectiveness. Future research should focus on:



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- Low-Cost Synthesis Methods: Developing economical production techniques, such as microwave, ultrasonic, and bio-based synthesis, to reduce material costs.
- Energy-Efficient Photocatalytic Systems: Enhancing visible-light activation to utilize solar energy instead of UV-based systems.
- Nanoparticle Recovery and Reusability: Improving magnetic separation and regeneration techniques to minimize waste and operational costs.

(ii) Addressing Environmental and Health Concerns

The potential toxicity and persistence of MONPs in the environment remain major challenges. Future efforts should focus on:

- Biodegradable and Dissolvable MONPs: Designing nanoparticles that break down into harmless byproducts after pollutant removal.
- Nanotoxicity Assessment: Conducting long-term toxicity studies on MONP interactions with ecosystems and human health.
- Regulatory Framework Development: Establishing safety guidelines for MONP production, usage, and disposal.

(iii) Smart and Multifunctional Nanomaterials

The future of MONP-based wastewater treatment lies in the development of intelligent, responsive, and hybrid nanomaterials that:

- Adapt to Pollutant Types: pH-sensitive MONPs change surface charge for targeted adsorption.
- Combine Multiple Mechanisms: Hybrid adsorption-photocatalysis materials enable faster and more efficient pollutant removal.
- Integrate with AI and IoT: Smart sensors using MONPs can detect and degrade pollutants in real time.

Conclusion

MONPs have been therefore found to be efficient for wastewater treatment; they have a high surface to area ratio, photocatalytic behavior, flexible reactivity, antimicrobial properties. They remove heavy metals, pharmaceuticals, dyes, organic pollutants and microbes. However there are



certain challenges that they pose such as the aggregation or perhaps the stability, toxicity or the environmental implications like leaching, nanotoxicity; a high percentage of in-effectivity, and large scale scalability. A promising approach towards wastewater remediation is the green synthesis of such particles or other hybrid nanocomposites and even advanced systems for production. More work is yet to be done for biodegradable MONPs to carve out an energyefficient photocatalytic pathway to truly unveil the enormous potential for water sustainability, protection of environmental and revolutionizing wastewater treatment.

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CHAPTER

2

AI INNOVATIONS in MEDICINAL CHEMISTRY Ashwariya Patel¹, Jyoti Chauhan²

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Introduction

The Convergence of AI and Medicinal Chemistry The intersection of artificial intelligence and medicinal chemistry represents one of the most promising frontiers in modern drug discovery. This convergence brings together centuries of pharmaceutical knowledge with cutting-edge computational capabilities, creating unprecedented opportunities to accelerate drug development and optimize molecular design. As we face increasingly complex health challenges, from antibiotic-resistant bacteria to emerging viral threats, the integration of AI tools into medicinal chemistry workflows has become not just advantageous but essential for advancing therapeutic innovation (Pitt et al., 2025).

Historical Perspective

The journey of medicinal chemistry has been marked by steady progression from intuitive, trialand-error approaches to increasingly systematic methods of drug discovery. Beginning with traditional medicine's reliance on natural products, the field evolved through the era of synthetic organic chemistry in the early 20th century, to rational drug design in the 1970s, and eventually to high-throughput screening in the 1990s. Each advancement brought new capabilities, but also revealed the limitations of human-only approaches to navigating the vast chemical space of potential drug candidates. The introduction of computational methods in the late 20th century laid the groundwork for today's AI revolution, marking a transition from simple database searches to sophisticated predictive models capable of learning from historical data and generating novel molecular structures (Vanden Eynde et al., 2019).

The Need for AI Integration

The complexity of modern drug discovery has reached a point where traditional approaches alone cannot keep pace with the demands of pharmaceutical research. The astronomical number of possible drug-like molecules (estimated at 10^{60}), combined with the intricate nature of biological



targets and the need to optimize multiple parameters simultaneously, creates a challenge that exceeds human cognitive capabilities. The integration of AI addresses these limitations by offering tools capable of processing vast datasets, identifying subtle patterns, and making predictions about molecular properties and biological activities. Furthermore, the rising costs of drug development, lengthy timeline to market, and high failure rates in clinical trials have created an urgent need for more efficient and accurate methods of lead compound identification and optimization (Tautermann, 2020).

Current State of the Field

Today's medicinal chemistry landscape is experiencing a profound transformation through AI integration. Machine learning algorithms, particularly deep learning architectures, are being successfully applied across the drug discovery pipeline, from target identification to lead optimization. Companies and research institutions are developing sophisticated AI platforms that can generate novel molecular structures, predict properties and activities, and even suggest synthetic routes. These tools are complementing traditional medicinal chemistry expertise rather than replacing it, creating a synergistic relationship between human insight and computational power. Recent successes, such as the discovery of novel antibiotics through deep learning approaches and the acceleration of COVID-19 therapeutic development, demonstrate the practical impact of this technological integration. However, challenges remain in areas such as data quality, model interpretability, and the need for specialized expertise to effectively utilize these new tools (Vora et al., 2023).

Evolution of Drug Discovery Paradigms

The transformation of drug discovery from traditional empirical methods to modern AI-driven approaches represents a fundamental shift in how we develop new therapeutics. This evolution reflects not just technological advancement, but a complete reimagining of the drug discovery process, incorporating data-driven decision making at every stage. The convergence of multiple scientific disciplines, from chemistry and biology to computer science and data analytics, has created a new paradigm that promises greater efficiency, reduced costs, and improved success rates in bringing new drugs to market (M. K. Yadav et al., 2024).

Traditional Drug Discovery Methods

The conventional approach to drug discovery has historically relied on a combination of serendipity, systematic screening, and iterative optimization. Scientists would begin with natural



products or known active compounds, systematically modify their structures, and test each variant for biological activity. This process, while foundational to many successful drugs, was inherently time-consuming and resource-intensive. High-throughput screening (HTS) represented a significant advance, allowing thousands of compounds to be tested simultaneously against biological targets. However, even HTS suffered from limitations: the need for large physical compound libraries, significant infrastructure investment, and the challenge of optimizing hits into leads. Structure-based drug design emerged as another important methodology, using protein structural information to guide molecule design, but was limited by computational power and the availability of high-quality structural data (Anderson, 2003).

AI-Augmented Approaches

The integration of artificial intelligence has fundamentally altered the drug discovery landscape by introducing predictive capabilities and automation at unprecedented scales. Modern AI approaches leverage deep learning architectures to analyze vast datasets of molecular structures, properties, and biological activities, enabling the prediction of drug-like properties before synthesis. Generative models can now create novel molecular structures optimized for multiple parameters simultaneously, while reinforcement learning algorithms can guide the exploration of chemical space more efficiently than traditional methods. These AI tools excel at identifying patterns in complex datasets that might escape human observation, leading to the discovery of novel chemical scaffolds and unexpected structure-activity relationships. Natural language processing models are being applied to mine scientific literature and patents, extracting valuable insights from decades of accumulated knowledge and enabling more informed decision-making in drug design (Lateef Junaid, 2025).

Hybrid Models and Their Impact

The most successful modern drug discovery programs typically employ hybrid approaches that combine the best aspects of traditional medicinal chemistry with AI-driven insights. These hybrid models leverage human expertise in chemical synthesis, biological understanding, and drug development while utilizing AI to accelerate decision-making and expand the scope of exploration. Machine learning models assist in prioritizing compounds for synthesis, predicting potential toxicity issues, and suggesting structural modifications, while experienced chemists provide crucial insight into synthetic feasibility and mechanistic understanding. This synergistic approach has led to more efficient optimization cycles, reduced experimental burden, and improved success rates in lead identification and optimization. The impact of hybrid models



extends beyond just efficiency gains, enabling the exploration of previously inaccessible chemical space and the pursuit of more challenging therapeutic targets (Akram et al., 2023).

Case Studies of Successful Integration

Recent years have witnessed several landmark successes in AI-augmented drug discovery that demonstrate the potential of these new approaches. Insilico Medicine's development of an AI-discovered drug candidate for idiopathic pulmonary fibrosis reached clinical trials in a fraction of the traditional timeline. Similarly, Atomwise's use of deep learning to identify novel antibacterial compounds effective against drug-resistant strains showcases the power of AI in addressing urgent medical needs. The rapid development of COVID-19 therapeutics benefited significantly from AI-driven approaches, with companies like BenevolentAI successfully identifying baricitinib as a potential treatment through computational analysis of existing drugs. These success stories share common elements: the intelligent integration of AI tools with traditional expertise, careful validation of computational predictions, and systematic optimization of lead compounds through iterative feedback loops between experimental data and computational models (S. Yadav et al., 2024).

Cultural Transformation in Chemistry Labs

The integration of artificial intelligence into medicinal chemistry has catalyzed a profound cultural shift in how research laboratories operate and how scientists approach their work. This transformation extends far beyond mere technological adoption, representing a fundamental reimagining of the modern chemistry laboratory. Traditional benchtop chemistry is now seamlessly interwoven with digital tools, data analytics, and virtual collaboration platforms, creating a hybrid environment that challenges conventional notions of chemical research (Han et al., 2023).

The Modern Digital Laboratory

Today's chemistry laboratory bears little resemblance to its counterpart from just a decade ago. Digital transformation has touched every aspect of laboratory operation, from electronic laboratory notebooks (ELNs) replacing paper records to automated synthesis platforms generating real-time data streams. Smart sensors and Internet of Things (IoT) devices continuously monitor reactions and environmental conditions, while laboratory information management systems (LIMS) integrate data from multiple sources into coherent, searchable databases. Cloud computing platforms enable immediate data analysis and visualization, while digital twins of



laboratory equipment allow for virtual optimization of experimental conditions. This digitalization has not only improved efficiency and reproducibility but has also created new possibilities for experimental design and execution that were previously unimaginable (Abouelenein et al., 2024).

Changing Role of Medicinal Chemists

The role of medicinal chemists has evolved dramatically in response to AI integration. Rather than spending the majority of their time at the bench, modern chemists increasingly function as data scientists and strategic decision-makers. They must navigate between virtual and physical experiments, using computational tools to guide synthetic planning while maintaining their expertise in traditional chemistry. The emphasis has shifted from executing large numbers of reactions to designing smarter experiments informed by AI predictions. Medicinal chemists now serve as interpreters between computational models and experimental reality, using their chemical intuition to validate and refine AI-generated suggestions. This evolution has led to a more intellectually demanding role that requires both deep chemical knowledge and technological fluency (Campbell et al., 2018).

New Skills and Competencies

The transformation of chemistry laboratories has created demand for an entirely new skill set among researchers. Beyond traditional organic chemistry expertise, modern medicinal chemists must develop proficiency in programming languages, data analysis, and machine learning concepts. Understanding of statistical methods and model validation has become crucial, as has the ability to work with large datasets and visualization tools. Soft skills have gained increased importance, particularly the ability to communicate effectively across disciplines and translate between technical domains. Professional development now includes training in computational tools, data management practices, and collaborative technologies, creating a new breed of scientist comfortable working at the interface of multiple disciplines (Fantke et al., 2021).

Team Dynamics and Collaboration

The AI revolution has fundamentally altered how research teams interact and collaborate. Traditional hierarchical structures have given way to more fluid, cross-functional teams that bring together chemists, computational scientists, biologists, and data specialists. Communication patterns have evolved to accommodate rapid sharing of both experimental and computational results, with regular feedback loops between wet-lab and in silico experiments. Virtual collaboration tools enable real-time discussion of results and strategy adjustment, while project



management platforms help coordinate complex workflows across different specialties. This new collaborative environment has fostered a culture of continuous learning and adaptation, where team members regularly share expertise and learn from each other's disciplines (Schmutz et al., 2024).

AI Tools and Technologies in Medicinal Chemistry

The landscape of medicinal chemistry has been revolutionized by an array of sophisticated AI tools and technologies that span the entire drug discovery pipeline. These technologies represent a quantum leap from traditional computational methods, offering unprecedented capabilities in molecular design, property prediction, and process optimization. The integration of these tools has created a new ecosystem where artificial intelligence augments human expertise, enabling faster, more efficient, and more innovative approaches to drug discovery. From deep learning architectures that can generate novel molecular structures to automated systems that can plan complex synthetic routes, these technologies are reshaping how we approach the development of new therapeutic agents (Han et al., 2023).

Machine Learning Applications

Machine learning has emerged as a cornerstone technology in modern medicinal chemistry, with applications spanning every phase of drug discovery. Deep neural networks, particularly graph neural networks (GNNs), have proven exceptionally powerful in learning molecular representations and predicting structure-activity relationships. These systems can process complex molecular structures as graphs, capturing both atomic and topological features to make sophisticated predictions about biological activity, physicochemical properties, and potential toxicity. Reinforcement learning algorithms guide the exploration of chemical space, learning from successful and unsuccessful attempts to optimize molecular designs iteratively. Natural language processing models mine vast repositories of scientific literature and patents, extracting valuable insights and identifying promising new research directions. Transfer learning approaches enable the adaptation of models trained on large datasets to specific therapeutic targets with limited data availability (Kim et al., 2023).





Figure. 1: Machine learning in health care

Predictive Modeling Systems

Predictive modeling systems have evolved into sophisticated platforms capable of forecasting a wide range of molecular properties and behaviors. These systems integrate multiple machine learning architectures, including convolutional neural networks for structural analysis, recurrent neural networks for sequence-based predictions, and transformer models for capturing complex chemical patterns. Modern predictive models can simultaneously optimize multiple parameters, balancing factors such as potency, selectivity, solubility, and metabolic stability. Quantum mechanical calculations are increasingly integrated with machine learning approaches, enabling more accurate predictions of electronic properties and reaction outcomes. These systems also incorporate uncertainty quantification, providing confidence estimates that help researchers prioritize predictions and allocate resources more effectively (Sarker, 2022).

Virtual Screening Platforms

Virtual screening has been transformed by AI technologies into a highly sophisticated process that can efficiently evaluate billions of compounds. Modern platforms employ multiple levels of screening, from rapid ligand-based approaches using molecular fingerprints to detailed structurebased methods incorporating protein dynamics. Deep learning models can now generate and screen novel compounds in real-time, adapting to feedback from experimental results. These platforms integrate multiple scoring functions, including physics-based calculations, empirical scoring, and machine learning-based evaluation methods. Advanced visualization tools enable researchers to explore screening results interactively, identifying promising candidates and



understanding structure-activity relationships. The integration of cloud computing has made these capabilities accessible to organizations of all sizes, democratizing access to sophisticated screening technologies (Arul Murugan et al., 2022).

Human-AI Synergy in Drug Development

The successful integration of artificial intelligence into drug development represents a delicate balance between computational power and human expertise. Rather than replacing human scientists, AI has emerged as a powerful complementary tool that amplifies human capabilities while relying on human insight for guidance and validation. This synergistic relationship has created a new paradigm in drug development where the strengths of both human and machine intelligence are leveraged to tackle increasingly complex therapeutic challenges. The key to success lies not in maximizing AI automation, but in optimizing the interaction between human researchers and AI systems to create workflows that capitalize on the unique strengths of each (Serrano et al., 2024).

Balancing Human Intuition with AI Capabilities

The interplay between human intuition and AI capabilities forms the cornerstone of modern drug development. Human chemists bring irreplaceable elements to the process: creative thinking, chemical intuition developed through years of experience, understanding of complex biological systems, and the ability to recognize promising unexpected results. AI systems complement these human strengths with their capacity to process vast amounts of data, identify subtle patterns, and generate novel predictions. The most successful approaches create frameworks where AI suggests possibilities that human experts then evaluate and refine based on their deep understanding of chemistry and biology. This iterative process, where machine learning models learn from human decisions and humans gain insights from AI analysis, creates a powerful feedback loop that drives innovation in drug discovery (Joseph, 2023).

Decision-Making Processes

The integration of AI has transformed decision-making in drug development from a purely human-driven process to a collaborative enterprise between researchers and intelligent systems. Modern decision-making frameworks typically involve multiple layers of analysis, where AI systems provide data-driven predictions and recommendations that inform human judgment. Scientists evaluate these AI insights within the broader context of project goals, practical constraints, and accumulated experience. The process often involves regular calibration of AI



predictions against experimental results, with human experts adjusting the weight given to computational suggestions based on their track record. This hybrid decision-making approach has proven particularly valuable in complex scenarios where multiple factors must be balanced, such as optimizing drug candidates for both efficacy and safety (Rashid & Kausik, 2024).

Educational and Training Landscape

The rapid integration of AI technologies into medicinal chemistry has catalyzed a fundamental transformation in how we prepare and continuously develop professionals in the field. Traditional chemistry education, once focused primarily on experimental techniques and theoretical principles, must now encompass computational methods, data science, and interdisciplinary approaches. This evolution requires a complete reimagining of educational frameworks, from undergraduate curricula to continuing professional development programs. The challenge lies not only in teaching new technical skills but in developing professionals who can bridge the gap between traditional chemistry and emerging computational approaches (Struble et al., 2020).

Evolving Curriculum Requirements

Modern medicinal chemistry curricula are undergoing a dramatic transformation to meet the demands of an AI-enhanced research environment. Core chemistry courses are being supplemented with essential computational components, including programming fundamentals, statistical analysis, and machine learning principles. Universities are introducing new courses that integrate practical laboratory work with computational modeling and data analysis. Advanced topics now include neural network architectures, molecular representation methods, and chemoinformatics. The curriculum must also develop students' ability to critically evaluate AI predictions and understand the limitations of computational approaches. This evolution extends beyond technical skills to include courses on data management, scientific communication across disciplines, and ethical considerations in AI-driven research (Satyanarayanajois & Hill, 2011).

Professional Development Needs

The integration of AI into medicinal chemistry has created urgent professional development needs for established researchers and practitioners. Experienced chemists require training in new computational tools and methodologies while maintaining their expertise in traditional chemistry. This includes developing proficiency in programming languages such as Python, understanding machine learning frameworks, and mastering specialized chemical informatics tools. Professional development programs must address not only technical skills but also the strategic aspects of



integrating AI into research workflows. Organizations are implementing structured training pathways that combine formal instruction with hands-on projects, mentoring programs, and peer learning opportunities. The focus extends beyond individual tools to include broader competencies in data-driven decision making and cross-functional collaboration (Pitt et al., 2025).

Conclusion and Future Perspectives

The integration of AI in medicinal chemistry represents a paradigm shift in drug discovery and development. Machine learning and deep learning approaches have demonstrably enhanced molecular property prediction, compound design, and synthetic route optimization, significantly reducing development timelines and resource requirements. Neural networks have proven particularly valuable for navigating complex chemical spaces and elucidating structure-activity relationships. While AI tools have catalyzed breakthroughs in target identification, lead optimization, and synthesis planning, they fundamentally complement rather than replace expert knowledge and experimental validation. The most successful applications have emerged from the synergistic relationship between computational intelligence and human expertise, creating new avenues for addressing previously intractable therapeutic challenges.

The horizon for AI in medicinal chemistry appears exceptionally promising. Integration with quantum computing is expected to dramatically enhance molecular simulations and predictions, while advances in explainable AI will build trust and interpretability. Federated learning approaches may enable collaborative discovery while preserving data privacy. The development of closed-loop systems combining AI with automated experimentation platforms could further accelerate discovery cycles. Enhanced models for predicting drug-protein interactions and understanding polypharmacology will likely lead to more effective therapeutic strategies. As these technologies mature alongside improvements in computational power and data quality, AI is poised to become an indispensable component of medicinal chemistry, driving more efficient, cost-effective drug development with potentially transformative impacts on human health.

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CHAPTER

3

Alkene and Dienes

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Introduction of Alkene-

• Alkenes are unsaturated hydrocarbon. In it least one double bond $c_1 = c_2$ between carbon atom is definitely present.

- Alkene contain two H-atom less than alkenes.
- General formula of alkene is C_nH_{2n} where n = number of c-atom.
- Alkene are also called olefins because first member of alkene originated from olefiant gas which means- oil maker.
- Natural source of alkenes are petroleum and natural gas.

Nomenclature of Alkene

According to IUPAC nomenclature of Alkene 'ene' suffix is used in the place of 'ane' on the basis of number of carbon atom.

Ex-

Alkene	- ane	Alkene
	+ ene	
C_2H_6	\longrightarrow	C ₂ H ₄
Ethane		Ethene

$CH_2 = CH_2$	Ethene	
$CH_3 - CH = CH_2$	Propene	
$CH_3 - CH_2 = CH_2 - CH_2$	Butene -2 or	But-2-ene
$\mathbf{CH}_3 - \mathbf{CH}_2 - \mathbf{CH}_2 = \mathbf{CH}_2$	Butene - 1 or	But - 1 - ene
$CH_3 - CH_2 - CH_2 - CH_2 = CH_2$	Pehtene - 1 or	Pent-1-ene
$CH_3 - CH_2 - CH = CH - CH_3$	Pehtene - 2 or	Pent-2-ene
$CH_3-CH_2-CH_2-CH_2-CH=CH_2$	Hexene - 2 or	Hex-1-ene

Bonding in Alkene-

• Double bond is present between carbon-carbon atom in alkene. One bond is sigma (σ) and other is Pi (π) in the double bond.

• In Alkene, each carbon atom of double bond is SP² hydrides.



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• One Pz orbital on both carbon is hydride SP^2 orbital. Each carbon form sigma bond by the axial overlapping of unhybridized Pz-Pz orbital from π -bond by sidewise overlapping in which one is sigma and other is Pi bond.



Fig- Bond angle and bond length in ethylene

Facts About Alkene-

Ethylene is lowest member of Alkene

Common formula of Alkene is	C_nH_{2n}
C : H Ratio in Alkene is	1:2
C = C Hybridization is	SP^2
C - H bond length =	$1.10 \text{ A}^{\circ} \text{ or } 110 \text{ pm}$
C = C bond length =	1.34 A°
	Common formula of Alkene is C : H Ratio in Alkene is C = C Hybridization is C - H bond length = C = C bond length =

> It shows various types of isomerism like- structural, chain, position and mainly geometrical isomerism.

Isomerism in Alkene-



1. Structural Isomerism- Two types of Structural Isomerism is found in alkene.

i. **Chain Isomerism-** When the some molecular formula represent two or more compounds which differ in the nature of carbon chian then such compounds are called chain isomer and the phenomenon is called chain Isomerism.

Ex.- Butane (C_4H_8) have two isomer.



1.
$$CH_3 - CH_2 - CH = CH_2$$

1-butane
2. $CH_3 - C = CH_2$
 CH_3
2-Methyl prop-1-ene

ii. Position Isomerism- Position Isomerism is due to the difference in the position of double bond.

Ex.- 1. Butane (C_4H_8) have two position isomer.

a. $CH_3 - CH_2 - CH = CH_2$ 1-butane b. $CH_3 - CH = CH_3$ 2-butane

- 2. Pentane (C_5H_{10}) have also two position isomer. a. $CH_3 - CH_2 - CH_2 - CH = CH_2$ 1-pentene
 - b. $CH_3 CH_2 CH = CH CH_3$ 2-pentene

iii. Cyclic Isomerism- The general formula of alkene and cycle alkene is C_nH_{2n} . Thus, both are in cyclic isomer to each other.

Ex.- 1. Molecular formula C₃H₆ have two isomer



2. *Geomentical Isomerism*- In alkene dua to the double bond in alkenes it shoes gemetnical isomerism.

Group attached in different direction of double bond form is and treans isomers. If same group are present in the some side of double bond, then it is called cis (Latin words cis=same side) and if same groups are present in opposite direction to each other the trans (trans=opposite side) isomer is formed. Example –





Trans - From

Cis – form

2- butane has two isomers (geometrical isomers) cis and trans.



$$\begin{array}{ccc} H-C-CH_3 & H-C-CH_3 \\ \parallel & \parallel \\ H-C-CH_3 & H_3C-C-H \\ Cis-2-Butane & Trans - 2 - Butane \end{array}$$

Stability of Alkene

• Stability of alkenes depends on the following factors-

1. *Trans isomer*- Stability of trans isomer is greater than that of as isomer because heat of hydrogenation of trans is small.

$H - C - CH_3$ ll	H_2 / Pd	$CH_3 - CH_2 - CH_2 - CH_3$
$H-C-CH_3$		
Cis – 2 – Butane	(Heat	n – Butane t of Hydrogenation = 119.6)
$H - C - CH_3$ $ $ $H_3C - C - H$	H_2 / Pd	$CH_3 - CH_2 - CH_2 - CH_3$
Trans – 2 – Butane		n – Butane (Heat of Hydrogenation = 115.4 KJ)

Note – The alkene which greaten heat of Hydrogenation are less stable. (Heat required for the Hydrogenation of 1 mole alkene is called Heat of Hydrogenation)

2. Number of alkey1 groups attached to double bond- Greaten the number of alkey1 groups greaten will be the stability of alkene.

The stability of some alkenes are as-

 $R_2 C = CR_2 > R_2C = CHR > R_2 C = CH_2 > RHC = CH_2 > CH_2 = CH_2$

We can say more substituted alkenes are more stable.

Preparation method of Alkenes

1. *From pyrolysis of alkane* – When alkane heated at 400-600 °C its getting decomposed and formed alkene.





2. *From dehydrogenate of alkane* – By the using of Dehydrogenating agents (Cr_2O_3/Al_2O_3) alkane gives alkene

i.

 $CH_3 - CH_2 - CH_3 \qquad Cr_2O_3 / Al_2O_3 CH_3 - CH = CH_2 + H_2$ $600 \circ C \qquad Propene \qquad Propene$

3. *From Dehydration of Alcohol-* On heating alcohol with excess of cons. H_2SO_4 an alkene is formed by the elimination of water molecule

CH3 CH2OHCone H2 SO4CH2 = CH2 + H2 O170 °CEthene

 $\begin{array}{c} OH \\ | \\ CH_3 - CH_2 - CH_3 \text{ Cone } H_2 \text{ SO}_4 \end{array} \xrightarrow{\text{Cone } H_2 \text{ SO}_4} CH_3 = CH = CH_2 + H_2 + H_2 O \\ \hline 170 \ ^{\circ}\text{C} \end{array}$

Mechanism of Dehydration of alcohol – Acidic dehydration of alcohol taken place by the casbeation intermediate. It can be explained in the following-

1 Step - Alcohol which is learn is base, accepts proton (H+)from acid in reversible step.

 $H_2 SO_4$

 $H-CH_2-CH_2-O-H \\$

Protonated alcohol

 $H - CH_2 - CH_2$

 $H - CH_2 - O - H_2$

Ethyl alcohol

2 Step - Due to positive change on negatively changed oxygen, its electron accepting tendency increases, due to which C-O bond become weak and finely gets cleared.

$$H - CH_2 - CH_2 - O - H$$

$$H_2 O$$

Slow

Protonated alcohol

Carbocation



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3 Step – Carbonation is unstable, which release H+ in presence of base H₂SO₄ and forms ethane.

$H - CH_2 - CH_2 - O - H$	H ₂ O	$H_2C = CH_2$
	Fast	
Carbocation		Ethene

ii. Alkene are obtained by passing vapors of alcohol at 350 °c on hot Al₂O₃ catalyst.

$$\begin{array}{c} CH_3 - CH_2 - OH \\ \hline 350 \ ^\circ C \end{array} \xrightarrow{} CH_2 = CH_2 + H_2O \\ \hline Ethane \ l \ alcohol \\ \hline Ethene \end{array}$$

4. *From Alkyl Halide* - When alkyl Halide Heating with alcoholic KOH than formed alkene. It is the example of elimination reaction in which formed alkene from alkyl Halide.



Saytzeff's Rule – If an alkyl halide can eliminate the HX in two different ways, that alkene will be formed in excess in which Carbone atoms joined by double bond are more alkyleted. This is called Saytzeff's Rule.



Note :- In other words we can say that according to Saytzeff's rule from alkyl Halide those H- atom remove which Carbone atom having less number Hydrogen attached.

Hoffimann Rule – When Bulky base are used in elimination reaction of alkyl Halide for preparing alkene then saytzeff's rule does not followed by the reaction. In less substituted alkene formed as major product this rule is called Hoffmann rule.





By Birch Reduction - When alkyne is mixed in liquid NH_3 with Na metal, Solution the two H-Atoms combine opposite to the double band and form trans alkene. This reaction is called Birch Reduction.

CCH₃ 	Lindlar Catalyst	H-C- CH ₃		
C-CH ₃	Pd/C	H- C-CH ₃		
But-2-yne		Cis-Butene		

5. *From alkynes by using lindlas catalyst* – Alkyne reduced in the presence of lindla's catalyst and formed cis- alkene.

CCH₃ 	Lindlar Catalyst	H— C— CH ₃		
C-CH ₃	Pd/C	H- C-CH3		
But-2-yne		Cis-Butene		

Note :- Mixture of Pd and quinine or sulfur precipitated on Barium sulfate or calcium carbonate is called Lindlar catalyst.

:- This catalyst percent the reduction of alkene into alkane.

electronic

:- This catalyst gives cis – addition.

6. *By Kolbe's method (from dicarboxylic acid*)- When sodium or potassium salt of dicarboxylic acid electrolyzed then alkene is obtained.

CH₂ – COONa 1 CH₂ – COONa Sodium succinate $\begin{array}{c} CH_2-COO^-\\ \\ CH_2-COO^-\\ Succinate anion\\ (at anode) \end{array} + 2Na^+ \end{array}$





Reaction at Anode- Here at anode oxidation occurs



Reaction at cathode- Have at cathode reduction occus-

 $2Na^{+} + 2e^{-} \longrightarrow 2Na$ $2Na^{+} + 2H_2O \longrightarrow 2NaON + H_2$

7. *Pyrolysis of ester* - By the pyrolysis of ester alkene can also be prepared.

Ex. O || Pyrolysis $C_2H_5-C - O - CH_2 - CH_3 \longrightarrow CH_2 = CH_2 + C_2H_5 COOH$ In have B-H eliminated $\alpha \beta$ $C_3 - COO - CH_2 - CH - CH_3 \longrightarrow CH_2 = CH + CH_3 + CH_3COOH$

Physical Properties of Alkene

- Lower member (alkene with four C- atoms) are gases.
- Alkene with 5 to 15 C- atoms are liquid and higher homologous are solid.



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- Ethene is colorless and light, sweet smelling gas.
- Alkenes are soluble in organic solvent.
- Alkenes are insoluble in water less volatile than the alkenes with the increase in molecular mass, density increase with the increase molecular mass of homologous series, melting point and boiling point also increase respectively.
- Normally boiling point of cis isomers is higher than the trans isomer.

Chemical Properties of Alkene - Alkene are more reactive than alkene. Addition reaction occurs more rapidly in alkenes due to the presence of C=C double bond in alkene. The following chemical reactions occurs in alkene:-

1. Addition reaction- Addition reaction in lakene is take place by electrophillic substitution reagent. Thus, they are called electrophollic addistion reaction.

i. Addition of Hydrogen- In the presence of finely divided Ni, Pt, Pd like catalyst alkene shows addition of Hydrogen, this reaction is called Hydrogenation reaction.

$$CH_3 - CH = CH_2 + H_2$$

 $(252 - 575 \text{ K})$ $CH_3 - CH_2 - CH_3$

ii. Addition of Halogens- If addition of Halogen in alkene at normal temperature in the presence of into solvent (CS₂, CCL₄ etc) then vicinal dihalide formed.

$$R - CH = CH_2 + X_2 \underline{CCl_4} R - CH - CH_2$$

Alkene Vicinal dihalide

X

X

$$\begin{array}{cccc} CH_2 = CH_2 & + Br_2 & CCl_4 & CH_2 - Br \\ & & & \\ Red brown & & \\ & & \\ CH_2 - Br \\ & & \\ Dibromoethane (colorless) \end{array}$$

Reactivity order of Halogens is $Cl_2 > Br_2 > I_2$

Addition of Halogen in alkene is example of electrophiliic addition reaction, have carbonation is formed as intermediate.

iii. Addition of Hydrogen Halide (HX)- It is an important reaction. When alkene are react with hydrogen halide then alkyl Halide prepared.

 $CH_2 = CH_2 + H Br \longrightarrow CH_3 - CH_2 - Br$ Ethene Ethyl bromide

- $\blacktriangleright \qquad \text{Reactivity order of HX is HI} > \text{HBr} > \text{HCL} > \text{HF}$
- > In asymmetric alkene addition of Hydrogen halide occurs according to Markownikff's Rule.



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Ex.

Markownikoff's Rule- According to Markownikoff;s Rule when addition of Hydrogen halide in asymmetric alkene undergoes then negative part of reagent (HX) attached with those C-atom which have already less number of H-atom.



Explaination of Markownikiff's Rule- Mechanism of Markownikoff's rule can be explained by the by the electrophillic addition reaction. Carbonium ion is formed in the second step. There is possibility of formation of two types of carbonium ion (Primary and secondary carbonium ion) from unsymmetrical alkene.



• Since 2° Carbonium ion is more stable than the primary carbonium. Thus, further addition product is formed by the secondary carbonium and 2 Bromo prone is formed as the major product.



Similarly HOX (Hypohallous acid) H_2SO , H_2O etc are also added by the Markownikiff's addition on asymmetrical alkene.

Anti Markownikoff's Rule/Peroxide Effect/Kharash Effect –

▶ In 1933 this rule was given by Kharach and Maya.

> They observed, when propane (unsymmetrical alkane) reacted HBr in the presence of air or peroxide (like- Benzoyl Peroxide), then the addition was just opposite to the rule of Markownikoff. This abnormal addition by the effect of peroxide (opposite to Markownikoff's Rule) is called Peroxide effect.

Nore:- Among HF, HCL, HBr and HI only shows peroxide effect.





Explanation of Anti Markownikoff's Rule-

- Anti Markownikoff's rule can be explained by the free radical addition mechanism.
- It can be explained in the following steps.

Step I- Free radicals are formed by the homolytic fission in peroxide.

 $\begin{array}{c} C_{6}H_{5}CO-O-O-COC_{6}H_{5} \\ Benzoyl Peroxide \end{array} \xrightarrow{Homolytic Cleavage} 2C_{6}H_{5}CO-O \xrightarrow{\bullet} 2C_{6}H_{5}-2CO_{2} \\ Free radical Phenyl free radical \end{array}$

Step II- Phenyl free radicals reacts with HBr to generate bromine free radicals.

 $C_6H_5 + HBr \longrightarrow C_6H_6 + Br$

Step III- Homolytic cleavage occur in the II- bond of double bond of asymmetrical alkene in the presence of Br free radicals and one-one electron each carbon of double bond. Now there is possibility of the formation of two new free radicals by the combination of Br on these carbon i.e. primary and secondary.





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Step IV- Since secondary free radicals are more stable. This it forms product which is opposite to Markownikoff's rule.

$$CH_3 - CH = CH_2 Br + H Br \longrightarrow CH_3 - CH_2 - CH_2 Br + Br$$

 $n - Propylbromide (product)$

Note:- Peroxide effect is not observed in the addition of HF, HCL and HI. This is due to the fact that HF, HCL bond is more stronger than HBr which cannot be cleaved by phenyl free radical. When HI bond is weak and iodine free radicals combine to from iodine molecules instead of adding to the double bond.

IV. Addition of Ozone- (Ozonolysis)- When ozonolysed oxygen is passed through the ethanol solution or CCl₄ solution of alkene then alkene ozonide is formed. By boiling of ozonide with water or reductive hydrolysis aldehyde or ketone or both are formed.



Note:- Ozonolysis used for the determination of position of double band.

- Ozonides are hydrolysed by the water and water is converted into H₂O₂ which oxidizes the aldehyde into acid.
- If Zn dust is added then H_2O_2 decomposes and free aldehyde or ketone is obtained Zn + H_2O_2 \longrightarrow ZnO + H_2O

V. Addition of Diborane- (Hydroboration)

- Addition of BH₃ (Borane) or alkyl borane on alkene is called Hydroboration.
- Alkyl forms trialkyl borane by the addition with diborane in the presence of ether.

 $6 CH_3 - CH = CH_2 + B_2 H_6$ Propene Diborane 2 (CH₃ CH₂ CH₂)₃ B Trialkyl Borane

2. *Oxidation-* Oxidation is alkene occur as follows-

i. Combustion Oxidation by Air- By the combustion of alkene with air oxygen its formed CO_2 and H_2O

-



Ex.

 $CH_2 = CH_2 + 3 O_2 \qquad \longrightarrow \qquad 2 CO_2 + 2 H_2 O$

ii. Oxidation by alkaline KMnO₄-

1% alkaline KMnO₄ solution is called Baeyer's Reagent. \geq

 \triangleright In the presence of Baeyer's Reagent alkene oxidized and forms dihydroxy compound (alkane diol) and violet colour of KMnO₄ disappears.

Ex.

Note:- This reaction is used to test the double bond present in organic compound.

iii. **Oxidation by acidic K₂CR₂O₇** - By the oxidation by strong agents (acidic $K_2Cr_2O_7$) or acidic KMnO₄ cleave the original double bond of alkene and acid or Keone is formed.

Ex.
i.
$$CH_3 - CH = CH_2 \xrightarrow{\text{Acidic } K_2Cr_2O_7} CH_3 - CH - CH_2 \longrightarrow CH_3 COOH + HCOOH + H_2O} CH_3 - CH - CH_2 \longrightarrow CH_3 COOH + HCOOH + H_2O} Acetic acid formic acid formic acid glycol
ii.
ii.
 $(CH_3)_2 C = C(CH_3)_2 \xrightarrow{\text{Acidic } K_2Cr_2O_7} H_3C} C=O + O = C CH_3 CH_3$$$

Acetone (2 molecules)

 CH_3

iv. Oxidation by per benzoic acid- In the presence of perbenzoic acid alkene oxidized and forms and forms epoxide, which after hydrolysis gives glycol. (formation of epoxide is called epoxidation)





4. Substitution Reaction- Generally, substitution not occurs in alkene, but if alkyl group is present on the associated carbon atom of double bond, than at high temperature (400-600° C), Hydrogen of alkyl group is substituted by reaction with halogen. It is called allylic substitution.

Allylic substitution reaction is done by the free radical mechanism.

$$CH_{3} = CH = CH_{2} + Cl_{2} \qquad \xrightarrow{\text{High temp.}} CH_{2} - CH = CH_{2} + HCl$$

$$(400-600 \text{ °C}) \qquad \qquad \downarrow \\ Cl$$
3- Chloro 1-Propene

5. *Isomerisation*- The conversion of one isomeric compound to another isomeric compound is called isomerisation.

> At 500°C on separately heating or on heating 200-500°C in the presence of catalyst isomerization occurs in alkene.

Ex.



6. *Polymerization*- Polymerization of alkene in the presence of catalyst, Important compounds are obtained by polymerization.

i.Polymerization of Ethane- When ethane is heated to 473-673 K temperature and at high pressure (1500 atm.) in the presence of minute amount of oxygen, large number of ethane molecules combine to from polyethylene.

$$nCH_2 = CH_2 \xrightarrow{473-673 \text{ K/ High Pressure}} (-CH_2 - CH_2 -)n$$

Ethene Presence of minute amount of O₂ Polyethylene



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- Value of n = 600 to 100
- Polythene or polyethylene is important for industries it is mainly used in the preparation of toys, bottle, plastic bags etc.

ii.Polymerisation of Vinyl chloride- PVC (Polyvinyl Chloride) is formed by the polymerization of vinyl chloride.



iii.Polymerization of Isoprene-



Use of Alkene -

- 1. Ethylene is used for artificial repairing of the fruits.
- 2. Ethylene is used in the preparation of ethyl alcohol, ethylene glycol & polythene etc.
- 3. Ethane is used in welding in the oxygen ethylene flame.
- 4. Substituted alkene polymeric to form PVC, Teflon, orlon etc.
- 5. Lower member of alkene series is used as fuel and lamps for lighting.
- 6. Used as reagent is lab.

Dienes

- Two double bonds containing alkenes are known as Diene.
- Dienes are also called alkadienes and Diolefines.
- The general formula of Diene is CnH₂n-2
- IUPAC name of Diene is alkadienes.
- Diene shows isomerism with Alkyne because of some general formula (molecular formula)
- Ex. 1, 3 Butadiene, Alkene etc.



Nomenclature of Diene-

> In IUPAC nomenclature system firstly select the largest carbon charm which is parent Hydrocarbon.

Then lowest priority or numbering the double bond. Ex.



2, 3, 4- tri methyl penta 1, 3- Diene

Classification of Diene

On the basis of position of double bond in carbon chain, dienes are classified in the following ways-1. Cummulative Diene- When two double bonds are present as continuous number, then that type of diene is called cumulative diene.

Ex.	(i)	$CH_2 = C = CH_2$	(ii)	$CH_2 = C = CH - CH_3$
		Allene		
		(1, 2-Propadiene)		1, 2 - Butadiene

2. Isolated Diene- When two double bonds are separated by more then one single bond than Diene is called isolated diene.

Ex. (i)
$$CH_2 = CH - CH_2 - CH = CH_2$$

1, 4 - pentadiene

(ii) $CH_2 = CH - CH_2 - CH_2 - CH = CH_2$ 1, 5-Hexadiene

3. Conjugated Diene- When in diene two double bonds are separated by one single bond, then type of diene is called as conjugated Diene.

 $Ex. CH_2 = CH - CH = CH_2$

1, 3 – Butadiene

$$CH_3$$

$$l$$

$$CH_2 = C - CH = CH_2$$
2- methyl -1, 3-butadiene



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Stability of Diene-

Conjugated diene are more stable then cumulative diene and isolated diene.

> The stability of conjugated diene is explained by resonance and Hybridization.

> In 1,3- Butadiene all form C-atoms are present as SP^2 Hybridized. Conjugated diene shows the resonance and give resonating structure.

Which compounds have more resonating structure they gave more stability.



Preparation Method of Diene-

1. *From n-Butane-* When n-butane is treated with Chromium trioxide then its formed 1, 3-butadiene.

$$Cr_2O_3$$

 $CH_3 = CH_2 - CH_2 - CH_3 \qquad \rightleftharpoons \qquad CH_2 = CH - CH = CH_2$ 1, 3- butadiene

2. By Glycols- When butane 1,3- diols getting dehydration in the presence of cone- H_2SO_4 its formed 1,3- butadiene.



Butane-1,3-diol

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3. *By the Acetylene and Formaldehyde-* Acetylene and formaldehyde reat with each other and formed Alkyne 1, 4- diol, which get reduced in the presence of reducing agents and form alkane 1, 4- diol, after dehydration alkane 1, 4 diol forms alkadiene (Diene). Ex.

 $\begin{array}{c} \text{Catalyst} & \text{Ni}/2\text{H}_2 \\ \text{HC} \cong \text{CH} & + & 2\text{HCHO} & & \text{HO-H}_2\text{C-C} \equiv \text{C-CH}_2 \text{OH} & & \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \\ \text{Acetylene} & & \text{Formaldehyde} & & & \text{CH}_2\text{OH} \\ & & & \text{But-2-yne, 1,4-diol} \\ & & & & & \text{AcidicCatalyst} \\ & & & & & \text{(Conc. H}_2\text{SO4)} \\ & & & & \text{CH}_2=\text{CH} - \text{CH}=\text{CH}_2 \\ & & & & 1,3-\text{Butadiene} \end{array}$



Properties of Diene

- Butadiene present in gas state.
- Boiling paint of Butadiene of 4.4°C.

Chemical properties of Conjugated Diene- As like alkene conjugated dience also give addition reaction.

1. *Electrophillic Addition reaction-* 1, 3- Butadiene given 1, 2 addition and 1,4- addition reaction.

Generally H given the 1, 2 – addition normally but abnormally also give 1, 4- addition.



Mechanism of Electrophillic addition in Diene-

- When reagent (Br₂) reaches mean Butadiene than have in butadiene electromenic changes occurs and Br₂ dissociates in Br⁺ and Br⁻.
- Br + part of reagent combine with C_1 or C_2 atom and forms carbocation.

 2° - carbocation is more stable than 1° - carbocation therefore

 2° – carbocation forms majorly.

Secondary carbocation gets stability by resonance by resonance and give 1, 2- addition and 1, 4- addition with Br^- part of reagent.

We can write the whole reaction as like as-



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2. Diel's Alder Reaction-

- Diel's Alder reaction's a pericyclic reaction.
- It is an example of cycloaddition reaction.
- When conjugated dien heated with alkene or substituted alkene (Dienophile) froms 6membered cyclic transition state and after connot into 6- membered cyclic product, this reaction is called Diel's Alder reaction.
- Diel's Alder reaction is used in synthesis of cyclic product.

Ex.





3. *Polymerization*- After polymerization of butadiene it give a soft product which is called "Buna Rubber"

- > This Polymerization reaction starts by free radical.
- > Buna rubber is mixture of 1, 2 and 1, 4 additive product.

Ex.

n CH₂ = CH - CH = CH₂
$$\xrightarrow{\text{Peroxides or}}_{\text{Na}}$$
 $(CH_2 - CH = CH - CH_2 \xrightarrow{-}_n)$

ii. Polymerization of Choloroprine gives synthetic rubber.

n CH₂ = C - CH = CH₂
Cl
$$\xrightarrow{P_2 O_2} \left(- CH_2 - C = CH - CH_2 \quad n \right)$$
Cl
$$\xrightarrow{Cl}$$
Synthetic rubber (Neoprene)

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iii. By polymerization of isoprene it given natural rubber.

n CH₂ = C – CH = CH₂
CH₃

$$\xrightarrow{P_2 O_2} \left(\begin{array}{c} -CH_2 - C = CH - CH_2 & n \\ CH_3 & CH_3 \end{array}\right)$$
CH₃
Polyisoprene (Natural Rubber)

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CHAPTER

4

BEYOND GRAPHENE: MXENE'S REVOLUTIONARY ROLE IN SUPERCAPACITOR DEVELOPMENT

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Introduction

In the rapidly evolving landscape of energy storage technologies, the discovery and development of novel materials have become paramount for addressing the growing demands of modern electronics, renewable energy systems, and electric vehicles (Khan, 2024). While graphene has dominated the two-dimensional (2D) materials landscape for over a decade, a new class of materials has emerged to potentially surpass its capabilities in energy storage applications— MXenes(Raza et al., 2024). These 2D transition metal carbides, nitrides, and carbonitrides have sparked a revolution in supercapacitor development, offering unprecedented combinations of electrical conductivity, surface functionality, and electrochemical performance (Kadam et al., 2023).

The global shift toward sustainable energy solutions and the miniaturization of electronic devices has intensified the search for energy storage systems that can deliver high power density, rapid charging capabilities, and long cycle life (Tang et al., 2023). Supercapacitors occupy a crucial middle ground between conventional capacitors and batteries, providing higher energy density than the former and greater power density than the latter. Within this context, MXenes have emerged as game-changing materials that address many of the limitations of traditional supercapacitor electrodes, including those based on activated carbon and even graphene (Liu et al., 2024).

This chapter explores the revolutionary role of MXenes in supercapacitor development, from their fundamental properties and synthesis methods to their performance characteristics and future prospects. As we navigate through the intricate world of these remarkable materials, we will uncover how their unique structure and chemistry are reshaping our approach to energy storage at the nanoscale (Ramasubramanian et al., 2022).



The Rise of 2D Materials: Beyond Graphene

The Graphene Revolution and Its Limitations

The isolation of graphene in 2004 by Novoselov and Geim marked a watershed moment in materials science, unveiling the extraordinary properties of atomically thin carbon sheets. Graphene's exceptional electrical conductivity (~6000 S/cm), mechanical strength, and high theoretical specific surface area (2630 m²/g) quickly positioned it as an ideal candidate for supercapacitor electrodes (Chen et al., 2023). However, despite its promising attributes, graphene has faced several challenges in practical supercapacitor applications.

Graphene's hydrophobic nature hinders ion accessibility in aqueous electrolytes, while its tendency to restack due to π - π interactions reduces the effective surface area available for charge storage. Additionally, pure graphene offers limited pseudo capacitance, relying primarily on electrical double-layer capacitance (EDLC) mechanisms for energy storage. These limitations have spurred the search for alternative 2D materials that could overcome these barriers while maintaining the advantages of atomically thin structures (Fan et al., 2024).

The Discovery of MXenes

In 2011, Yury Gogotsi, Michel Barsoum, and their team at Drexel University reported the synthesis of a new family of 2D materials by selectively etching the A layer from MAX phases. MAX phases are a large family of layered ternary carbides and nitrides with the general formula Mn+1AXn, where M is an early transition metal, A is mainly a group 13 or 14 element, X is carbon and/or nitrogen, and n = 1, 2, or 3 (Naguib et al., 2023). By selectively removing the A element (typically aluminum) using hydrofluoric acid (HF) or other fluoride-containing etchants, the researchers obtained 2D flakes of transition metal carbides, nitrides, or carbonitrides—materials that would come to be known as MXenes(Kagalkar & Dharaskar, 2023).

This groundbreaking discovery opened the door to a vast family of 2D materials with tunable properties. Unlike graphene's single-element composition, MXenes offer tremendous compositional diversity, with dozens of different compositions already synthesized and many more theoretically predicted. This variability allows for fine-tuning of properties to suit specific applications, presenting exciting opportunities for supercapacitor development (Girirajan et al., 2024).

Structural and Chemical Features of MXenes

MXenes are typically represented by the formula Mn+1XnTx, where T represents surface terminations such as -O, -OH, and -F introduced during the etching process. These surface terminations play a crucial role in determining the material's properties, including its



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hydrophilicity, interlayer spacing, and electrochemical behavior. Unlike graphene, MXenes are inherently hydrophilic due to these surface groups, facilitating better interaction with aqueous electrolytes—a significant advantage for supercapacitor applications (Zhao et al., 2024).

The most extensively studied MXene, Ti_3C_2Tx , exemplifies the structural characteristics common to this material family. It consists of three layers of titanium atoms sandwiched between two layers of carbon atoms, with surface terminations decorating the outer titanium atoms. This structure creates a unique combination of metallic conductivity through the transition metal carbide core and rich surface chemistry via the termination groups, enabling multiple charge storage mechanisms simultaneously (Jaffari et al., 2022).



Figure:1. Atomic structure and electronic band structure of $Ti_3C_2T_3$ MXene with different surface terminations (Schultz et al., 2019).

The interlayer spacing in MXenes, typically ranging from 0.6 to 1.5 nm depending on the synthesis conditions and intercalated species, provides accessible pathways for ion transport while



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maintaining electrical conductivity within each flake. This architectural feature addresses one of graphene's key limitations—its tendency to restack and block ion access—making MXenes particularly suitable for high-rate energy storage applications.

Table:1.	Structural	and	Chemical	Properties	of	Common	MXenes	for	Supercapacitor
Applicat	ions								

MXene Formula	Interlayer Spacing (nm)	Common Surface Terminations	Electrical Conductivity (S/cm)	Key Structural Features	Advantages for Supercapacitors
Ti ₃ C ₂ Tx	0.9 - 1.2	-O, -OH, -F	6,500 - 9,000	3 Ti layers sandwiched between 2 C layers	High surface area, excellent hydrophilicity, superior ion accessibility
Ti2CTx	0.7 - 1.0	-0, -0H, -F	2,400 - 4,600	2 Ti layers sandwiched between C layers	Thinner structure, faster ion transport kinetics
V2CTx	0.8 - 1.3	-O, -OH, -F	1,500 - 2,700	2 V layers sandwiched between C layers	Multiple oxidation states of V, enhanced pseudo capacitance
Nb2CTx	1.0 - 1.4	-O, -OH, -F	2,000 - 3,500	2 Nb layers sandwiched between C layers	Larger interlayer spacing, excellent ion intercalation
Mo2CTx	0.9 - 1.3	-O, -OH, -F	3,200 - 4,800	2 Mo layers sandwiched between C layers	High redox activity, superior charge storage capacity
Mo2TiC2Tx	1.0 - 1.5	-O, -OH, -F	4,300 - 5,600	2 Mo layers + 1 Ti layer between C layers	Ordered double-transition metal structure, enhanced stability
Nb4C3Tx	1.2 - 1.5	-0, -0H, -F	1,800 - 2,500	4 Nb layers sandwiched between 3 C layers	Thicker flakes, increased mechanical stability
Ti3CNTx	0.8 - 1.1	-O, -OH, -F	5,200 - 7,500	3 Ti layers sandwiched between C and N layers	Carbon-nitride core, modified electronic properties
Cr2CTx	0.6 - 0.9	-O, -OH	1,100 - 2,200	2 Cr layers sandwiched between C layers	Magnetic properties, modified electronic structure
Ta₄C₃Tx	1.1 - 1.4	-O, -OH, -F	1,300 - 2,100	4 Ta layers sandwiched between 3 C layers	High chemical stability, excellent corrosion resistance

Synthesis and Processing of MXenes for Supercapacitor Applications

From MAX to MXene: Synthesis Strategies

The journey from MAX phases to MXenes involves several synthesis routes, each with implications for the resulting material's properties and performance in supercapacitor applications:



Hydrofluoric Acid Etching

The original and still most common method for MXene synthesis involves the selective etching of MAX phases using hydrofluoric acid (HF). The process typically occurs according to the reaction: $Ti_3AlC_2 + 3HF \rightarrow Ti_3C_2Tx + AlF_3 + 3/2H_2$

This approach effectively removes the aluminium layers while preserving the transition metal carbide sheets. However, the use of concentrated HF presents significant safety concerns and requires specialized handling facilities. The etching time, temperature, and HF concentration significantly influence the quality and yield of the resulting MXenes, as well as their surface terminations (Zhou et al., 2022).

Fluoride Salt Etching

To address the safety concerns associated with HF, researchers have developed "in situ" HF generation methods using mixtures of hydrochloric acid (HCl) and fluoride salts such as lithium fluoride (LiF). This approach, often referred to as the "minimally intensive layer delamination" (MILD) method, produces high-quality MXene flakes with better controlled surface chemistry and improved yields:

 $Ti_3AlC_2 + 3LiF + 3HCl \rightarrow Ti_3C_2Tx + AlF_3 + 3LiCl + 3/2H_2$

The MILD method has become particularly important for the large-scale production of Ti_3C_2Tx MXene, which has shown exceptional performance in supercapacitor electrodes (Kumar, 2024).

Molten Salt Etching

For MXenes that are difficult to synthesize using acid-based methods, molten salt etching provides an alternative route. This approach uses molten fluoride salts at elevated temperatures (typically 550-600°C) to selectively remove the A-layer elements. The method has enabled the synthesis of previously inaccessible MXenes and often results in materials with lower defect concentrations, which can enhance electrical conductivity—a critical parameter for supercapacitor electrodes (Jaffari et al., 2022).

Delamination and Processing

After etching, MXenes typically exist as multilayered particles. For supercapacitor applications, delamination into single or few-layer flakes is often desirable to maximize the accessible surface area:

Intercalation and Delamination

Common intercalants include dimethyl sulfoxide (DMSO), tetrabutylammonium hydroxide (TBAOH), and various alkali metal ions (Li+, Na+, K+). The intercalation weakens the interlayer forces, allowing subsequent delamination through sonication or mechanical shaking. The process



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produces colloidal suspensions of single or few-layer MXene flakes, which can be processed into various electrode architectures (Gandla et al., 2023).

MXene Ink Formulation

For practical device fabrication, MXenes are often processed into printable or coat able inks. The rheological properties of these inks can be tuned by adjusting the concentration, pH, and additives, enabling various deposition techniques including spray coating, screen printing, and inkjet printing. These processing methods are crucial for translating the intrinsic properties of MXenes into high-performance electrodes with optimized mass loading, thickness, and porosity (Y.-Z. Zhang et al., 2020).

Self-Assembly and Composite Formation

To address the restacking issue and enhance specific properties, MXenes are often assembled into 3D architectures or combined with other materials. Freeze-drying or critical-point drying of MXene dispersions creates porous aerogels with high surface area and interconnected channels for ion transport. Alternatively, MXenes can be combined with carbon nanotubes, conducting polymers, or metal oxides to form composite electrodes with synergistic properties, tailored for specific supercapacitor applications (Muthukutty et al., 2024).

Table:2. MXene Synthesis	s and Processing Method	s for Supercapacitor Applications
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Composite Formation					
MXene/Carbon Nanotube Composites	Physical mixing or co- dispersing MXenes with CNTs	Surface interactions and physical entanglement	 Prevents MXene restacking Enhanced electrical conductivity Mechanical reinforcement 	• Cost of CNTs • Dispersion challenges • Processing complexity	 Enhanced cycling stability (>10,000 cycles) Improved rate capability Higher volumetric capacitance
MXene/Condu cting Polymer Composites	In-situ polymerization or physical mixing	Chemical bonding or electrostatic interactions	 Synergistic pseudo capacitance Improved stability Wider potential window 	 Polymer degradation over cycles Complex synthesis Trade-offs in conductivity 	Combined EDLC and pseudocapacitive storage Enhanced specific capacitance (>400 F/g) Better energy density
MXene/Metal Oxide Hybrids	Solution deposition or hydrothermal growth of oxides on MXene	Nucleation and growth of oxides on MXene surfaces	 Complementary charge storage Enhanced specific capacitance Tunable properties 	 Potential conductivity decrease Complex synthesis Interface challenges 	 Significantly higher energy density Broader operating voltage window Multi-electron redox reactions



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Method	Process Details	Reaction/ Mechanism	Advantages	Limitations	Impact on Supercapacitor Performance
Synthesis Methods					
Hydrofluoric Acid (HF) Etching	Direct etching with concentrated HF (20- 49%) at room temperature for 24-48h	$\begin{array}{l} Ti_{3}AlC_{2}+3HF\rightarrow\\ Ti_{3}C_{2}T_{x}+AlF_{3}+\\ 3/2H_{2} \end{array}$	 Original, well-established method High etching efficiency Relatively quick process 	• Safety hazards • Specialized facilities required • Less control over surface terminations	Higher defect concentration may reduce conductivity -F terminations may limit ion adsorption capacity
Minimally Intensive Layer Delamination (MILD)	HCl + LiF mixture generates HF in situ; typically 24h at 35-40°C	$T_{19}A1C_2 + 3L_1F +$ $3HC1 \rightarrow T_{19}C_2T_x +$ $AIF_3 + 3L_1C1 +$ $3/2H_2$	 Safer than direct HF Li* pre-intercalation Better yield of delaminated flakes More controlled surface chemistry 	Longer processing time Temperature sensitive Limited to certain MAX phases	 Enhanced interlayer spacing improves ion accessibility Better flake quality increases conductivity Higher capacitance values (200-400 F/g)
Molten Salt Etching	Molten fluoride salts (e.g., LiF, NaF, KF) at 550-600°C	$\begin{array}{l} TisA1C_2 + 3NaF\\ (molten) \rightarrow TisC_2T_x\\ + A1F_3 + 3Na \end{array}$	 Access to otherwise difficult MXenes Lower defect concentration No water involved (dry process) 	 High temperature requirements Energy intensive Complex equipment needed 	 Superior electrical conductivity (up to 10,000 S/cm) Enhanced cycling stability Lower oxygen content improves electronic properties
Delamination & Processing					
Intercalation- Assisted Delamination	Intercalants (DMSO, TBAOH, etc.) inserted between layers, followed by sonication	MXene-multilayer + Intercalant → Delaminated MXene flakes	 Produces single/few-layer MXenes Increases accessible surface area Enables colloidal processing 	Time-consuming May introduce impurities Sonication can break flakes	 Dramatically increased specific surface area (>200 m²/g) Enhanced capacitance (up to 2x higher) Improved rate capability
MXene Ink Formulation	Controlling concentration, additives, and rheology for printing/coating	Colloidal chemistry and rheology modification	• Enables various deposition techniques • Industrial scalability • Precise thickness control	Formulation complexity Stability challenges Additive interference	Optimized electrode mass loading (5-10 mg/cm ²) Tunable porosity improves ion transport Enhanced device integration
Freeze- Drying/Critical Point Drying	Controlled freezing and sublimation/supercritical drying of MXene dispersions	Physical phase transitions preserve 3D structure	• Creates porous 3D architectures • Prevents restacking • High surface-to-volume ratio	• Equipment costs • Process complexity • Mechanical fragility	• Enhanced electrolyte penetration • Reduced ion diffusion distances • Improved rate performance up to 1000 mV/s

Charge Storage Mechanisms in MXene-Based Supercapacitors

Beyond EDLC: The Pseudocapacitive Advantage

Unlike graphene, which primarily stores energy through the electrical double-layer capacitance (EDLC) mechanism, MXenes exhibit significant pseudocapacitive behaviour (Gao et al., 2024).



This distinction represents one of the most revolutionary aspects of MXenes in supercapacitor development:

Surface Redox Reactions

The transition metal atoms in MXenes can undergo fast, reversible redox reactions with electrolyte ions, particularly protons in acidic electrolytes or alkali metal ions in neutral or basic solutions. These faradaic processes contribute substantial additional capacitance beyond what would be expected from EDLC alone. For Ti_3C_2Tx in acidic electrolytes, the redox reactions can be represented as:

 $Ti_{3}C_{2}Ox(OH)yFz + \delta H^{+} + \delta e^{-} \leftrightarrow Ti_{3}C_{2}Ox - \delta(OH)y + \delta Fz$

where the titanium atoms undergo valence changes from Ti^{4+} to Ti^{3+} during reduction and back during oxidation. Similar mechanisms occur with other MXene compositions, with the specific redox chemistry depending on the transition metal present.

Intercalation Pseudo capacitance

Beyond surface reactions, MXenes can store charge through intercalation pseudo capacitance, where ions reversibly insert between the MXene layers without causing significant structural changes. This mechanism is particularly prominent with alkali metal ions (Li⁺, Na⁺, K⁺) and contributes to the high capacitance of MXene electrodes at low scan rates or current densities. The interlayer spacing of MXenes, which can be tuned during synthesis or processing, directly influences the kinetics and extent of ion intercalation.

Ion Transport and Kinetics

The exceptional rate capability of MXene-based supercapacitors stems from favourable ion transport kinetics:

Hydrophilic Nature

Unlike graphene, MXenes are inherently hydrophilic due to their surface terminations, facilitating wetting by aqueous electrolytes and reducing ion diffusion barriers at the electrode-electrolyte interface. This property enables rapid charge/discharge cycles without significant capacitance loss at high rates (Yu et al., 2023).

Interlayer Channels

The interlayer spaces between MXene sheets serve as predefined channels for ion diffusion, offering lower tortuosity compared to the random pore networks in activated carbon electrodes. These channels, combined with the metallic conductivity within each MXene layer, create an ideal architecture for simultaneous electron and ion transport—a crucial requirement for high-power supercapacitors.



Performance Metrics and Benchmarking

Volumetric vs. Gravimetric Performance

One of the most revolutionary aspects of MXenes in supercapacitor technology is their exceptional volumetric performance:

Record-Breaking Volumetric Capacitance

 Ti_3C_2Tx MXene electrodes have demonstrated volumetric capacitances exceeding 900 F/cm³ in aqueous electrolytes—values that surpass virtually all other electrode materials, including activated carbon (~60-80 F/cm³) and graphene-based materials (typically 100-300 F/cm³). This exceptional volumetric performance stems from the combination of high intrinsic pseudo capacitance and the compact, layered structure of MXene films (Gogotsi, 2023).

Areal Capacitance and Mass Loading

For practical applications, MXene electrodes have achieved areal capacitances exceeding 2 F/cm² at mass loadings of 10-15 mg/cm²—metrics that are critical for translating laboratory results into commercial devices. These values compare favourably with other advanced electrode materials and demonstrate the potential of MXenes for practical energy storage applications.

Rate Capability and Cycling Stability

High-Rate Performance

MXene-based supercapacitors typically retain 80-90% of their low-rate capacitance when the current density is increased by two orders of magnitude (e.g., from 0.1 A/g to 10 A/g)—a rate capability that exceeds most other electrode materials. This exceptional performance stems from the combination of high electronic conductivity and efficient ion transport pathways within the MXene architecture (Gokul Eswaran et al., 2025).

Long-Term Cycling

Although early MXene electrodes showed limited cycling stability due to oxidation or delamination, recent advances in electrode design and electrolyte formulation have significantly improved their durability. Properly engineered MXene electrodes can now maintain >90% capacitance retention after 10,000 cycles, approaching the stability of carbon-based EDLC electrodes while delivering substantially higher energy density (Soomro et al., 2023).

Energy and Power Densities

Aqueous Electrolytes

In aqueous electrolytes, MXene-based supercapacitors have achieved volumetric energy densities of 20-30 Wh/L—values that approach those of lead-acid batteries while maintaining the high-power capabilities characteristic of supercapacitors (>10 kW/L). These metrics represent a



significant advancement over conventional carbon-based supercapacitors, which typically deliver 5-10 Wh/L.

Organic and Ionic Liquid Electrolytes

By extending the operating voltage through the use of organic or ionic liquid electrolytes, MXenebased devices have reached even higher energy densities, exceeding 50 Wh/L in some cases. However, challenges related to wettability and ion transport kinetics in non-aqueous electrolytes remain areas of active research (Awan et al., 2024).

Advanced Architectures and Hybrid Systems

3D MXene Structures

To address the restacking issue and enhance ion accessibility, researchers have developed various three-dimensional MXene architectures:

MXene Aerogels and Hydrogels

Freeze-drying or critical-point drying of MXene dispersions produces lightweight, porous structures with high surface area and interconnected pore networks. These aerogels maintain the intrinsic properties of MXenes while providing enhanced ion accessibility and resistance to restacking during cycling. Volumetric capacitances of 100-300 F/cm³ have been achieved with these structures, along with excellent rate capabilities.

Templated Assembly

Using sacrificial templates such as polymer beads, ice crystals, or emulsion droplets, researchers have created MXene structures with controlled porosity at multiple length scales. These architectures optimize the balance between material density and ion transport pathways, addressing a key challenge in supercapacitor electrode design.

MXene Composites

Combining MXenes with complementary materials has yielded synergistic improvements in supercapacitor performance:

MXene/Carbon Composites

Integrating MXenes with carbon nanotubes, graphene, or activated carbon creates composite electrodes that leverage the pseudo capacitance of MXenes and the stability and conductivity of carbon materials. These composites often show enhanced cycling stability and improved performance in non-aqueous electrolytes compared to pure MXene electrodes.

MXene/Conducting Polymer Hybrids

Combining MXenes with conducting polymers such as polyaniline, polypyrrole, or PEDOT:PSS has produced hybrid electrodes with capacitances exceeding 1000 F/g. The synergy arises from



the conductive network provided by MXenes, which facilitates electron transport to/from the redox-active polymer and improves the rate capability and cycling stability compared to conventional polymer electrodes (Y. Zhang et al., 2023).

Asymmetric and Hybrid Device Configurations

MXene-Based Asymmetric Supercapacitors

Pairing a MXene negative electrode with a complementary positive electrode (e.g., MnO₂, activated carbon) in asymmetric configurations extends the operating voltage in aqueous electrolytes beyond the thermodynamic limit of water splitting (1.23 V). These devices have achieved energy densities of 30-40 Wh/kg while maintaining high power capabilities (Ghiyasiyan-Arani, 2024).

MXene-Based Hybrid Capacitors

Integrating MXene electrodes with battery-type electrodes creates hybrid systems that combine the high energy density of batteries with the high-power density of supercapacitors. For example, Li-ion capacitors using MXene negative electrodes and lithiated transition metal oxide positive electrodes have demonstrated energy densities exceeding 100 Wh/kg with much faster charging capabilities than conventional Li-ion batteries (K et al., 2024).

Challenges and Future Perspectives

Current Limitations and Challenges

The performance of MXene electrodes can vary significantly depending on synthesis conditions, processing methods, and testing protocols. Establishing standardized practices for material characterization and device testing would facilitate more meaningful comparisons and accelerate progress in the field. Current literature reveals substantial variations in reported capacitance values for seemingly identical materials, often stemming from differences in electrode preparation, mass loading calculations, and electrochemical testing parameters. Addressing this challenge requires community-wide efforts to develop consensus protocols for key measurements—including flake size distribution, oxygen content quantification, surface termination analysis, and electrochemical performance evaluation—enabling reliable benchmarking across different research groups. Such standardization would not only enhance scientific reproducibility but also provide industry stakeholders with clearer metrics for assessing technological readiness (Raj et al., 2022).

Emerging Research Directions

Integrating MXenes with solid-state or gel electrolytes enables the fabrication of flexible, thinfilm supercapacitors for wearable electronics and Internet of Things (IoT) applications. The



inherent mechanical flexibility of MXene films, combined with their high volumetric performance, makes them particularly suitable for these emerging applications where space constraints are critical. Recent advances in this area have demonstrated remarkable mechanical durability with minimal capacitance loss after thousands of bending cycles, while maintaining energy densities that outperform conventional carbon-based flexible devices. The compatibility of MXenes with printing and coating techniques further facilitates their integration into conformable substrates, opening pathways for multifunctional devices that combine energy storage with sensing capabilities in compact form factors (Narayanasamy et al., 2023).

Commercialization Prospects

Identifying the most suitable application niches—where the unique properties of MXenes provide clear advantages over competing technologies—will be critical for successful commercialization. High-power applications requiring compact energy storage, such as electric vehicle regenerative braking systems, grid frequency regulation, and fast-charging consumer electronics, represent promising initial markets (Jiang et al., 2024). These targeted applications leverage MXenes' exceptional volumetric capacitance and rate performance, potentially establishing market footholds before expanding to broader energy storage applications as manufacturing scales and costs decrease (Jiang et al., 2024).

Conclusion

MXenes represent a transformative advancement in supercapacitor technology, establishing a distinct material class that bridges the gap between traditional carbon electrodes and pseudocapacitive materials. Their remarkable combination of metallic conductivity, hydrophilic nature, tunable surface chemistry, and processing versatility has enabled unprecedented volumetric performance and rate capabilities. While challenges in stability, scalability, and standardization persist, ongoing research into diverse MXene compositions, surface engineering strategies, and hybrid architectures continues to expand their potential applications. MXene-based supercapacitors are increasingly vital to the global energy transition, supporting renewable energy integration, transportation electrification, and sustainable electronics development. As research progresses beyond conventional graphene-based approaches, MXenes are catalyzing a revolution in energy storage that promises to fundamentally reshape how we power tomorrow's devices and systems, offering optimized solutions for an energy-efficient future.



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CHAPTER

5

THE FUNCTION OF MEDICINAL PLANTS FROM THE STANDPOINT OF HUMAN HEALTH

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Abstract

Since ancient times, medicinal plants have been utilised in healthcare. The use of medicinal plants fits into all current preventative techniques and plays a dynamic role in promoting illness prevention. Herbal medicine has even more research and uses in the treatment of illnesses. Phytochemical elements found in medicinal plants are a major source of molecules with therapeutic qualities. These compounds are useful in the treatment of human illnesses and are crucial to the healing process. In addition to producing wealth, natural and distinctive medicinal plants are utilised to heal a variety of illnesses and ailments. Ayurveda and other Indian literature highlight the use of plants to treat a variety of human ailments. Around the world, medicinal plants constitute a vital resource in the battle against severe illnesses. The knowledge and understanding of medicinal plant usage, as well as the scientific research to validate their medicinal values—that is, the function, contributions, and utility of medicinal plants in attempting to treat diseases of public health importance are the main topics of the current study.

Keywords: Medicinal Plants; Disease; Healthcare

Introduction

It is impossible to overestimate the significance of plants in both traditional medicine and as raw materials for pharmaceutical production. In non-industrialized communities, spices are almost often utilised to treat illnesses. As the twentieth century came to a conclusion, a number of customs started to hinder the use of natural medicine. Considering the widespread use of conventional medicine and the growing popularity of homegrown remedies, the use of therapeutic plants is growing globally. In medicine, plants are used to cure specific disorders and illnesses as well as to maintain and improve well-being on a deep, cerebral, and spiritual level. It has been shown that countries in Latin America, Asia, and Africa use traditional medicine to help satisfy some of their basic medical service requirements.

When there were no free manufactured medications and no concepts of medical procedures, the plant kingdom made a huge contribution to human well-being. Rationing these plants in



accordance with indigenous knowledge is necessary for human progress and overall well-being. Because of their efficacious effects, engineered pharmaceuticals have become widely used against green therapies; nonetheless, people are beginning to recognise the benefits of common cures. Artificially prepared drugs may work quickly, but their effects on the human body are opposite in the long run. In contrast, medicinal plants function in a way that is beneficial to the body and has almost no negative effects. Alkaloids, phenols, tannins, cryogenics, glycocides, and terpenoids are among the active chemicals found in the majority of plant species that are used in many aspects of human health worldwide [1]. These additives have been demonstrated to be safe when used as sweeteners, antibacterials, and anti-infections. For instance, Alstoniaboonei bark contains achistamine and alkaloids that can be used to treat high blood pressure, fever, and vertigo. Ginger (Allium sativum) and garlic (Zingiber officinale) are spicy food additives that have long been utilised to safeguard human health [2]. Utilising medicinal plants to preserve human health . Human illnesses have been treated using medicinal plants for thousands of years. More people are realising the benefits of traditional health systems and medicinal plants in addressing global health concerns. This newfound interest has led to an explosion in medicinal plant research worldwide. For thousands of years, people have used medicinal herbs as a form of treatment. The truth is that for thousands of years, ancient man relied entirely on plants for all of his medicinal requirements, including prevention, healing, and other kinds of drugs. Throughout the growth of human society, the usage of medicinal plants has had a mysterious, strict significance and a variety of perspectives regarding the ideas of infection and health that have existed inside each culture. For up to 3,000 years, a huge variety of plants have been used in medical practice, such as in traditional medicine in China, India, and Africa. The great majority of these plants have therapeutic properties, which Western standards have identified as such. Furthermore, many societies that are unlikely to adhere to western standards have long employed a range of plants. There is no denying the significance of medicinal plants for human health. 252 drugs are deemed basic and fundamental by the World Health Organisation (WHO); 11% are solely plant-based, while a significant portion is synthetic drugs derived from distinctive precursors. Digitalis species are the source of digoxin, Cinchona species are the source of quinine and quinidine, Catharanthus roseus is the source of vincristrine and vinblastine, Atropa belladonna is the source of atropine, and Papaver omniferum is the source of morphine and codeine [3]. Sixty percent of anti-tumor and anti-irresistible medications are either licensed or in the early phases of clinical testing, according to estimates [4].



These plants provide ingredients for novel medications, the creation of biomimetic synthesis, and the identification of novel therapeutic qualities not yet associated with existing molecules. The majority of the time, medications can be made from the crude extract of medicinal plants **[5]**. Many modern medications are made from medicinal plants, which are considered to be abundant sources of traditional medicines. Medicinal herbs have been used for thousands of years to treat illnesses, preserve food, add flavour, and stop disease outbreaks. The evolution of human civilisation has been significantly influenced by medicinal plants. Over 400 traditional plants or medicines derived from plants are said to have been utilised worldwide to treat type 2 diabetes **[6]**.



Fig. 1 Medicinal Plants and their Potential for Human Health.

Beneficial aspect of medicinal plants

Globally, the use of plant-based medications is growing. Modern research on medicinal plants or medicine has led to major improvements in the neuroprotective evaluation of several plants utilised in traditional medical systems. In both ancient and modern societies, medicinal plants have already played a significant role in ensuring human health security. Two-thirds of the world's plant species are thought to have therapeutic qualities **[7]**.



According to a World Health Organisation (WHO) report, 80% of people on the planet receive their primary medical treatment from traditional medicine, which mostly uses plant extracts and their active ingredients. Acorus calamus, Aegle marmelos, Aloe vera, Andrographis paniculata, Carica papaya, Cassia fistula, Cyperus rotundus, Dalbergia sisoo, Emblica officinalis, Magnifera indica, Acacia auriculiformis, Moringa olifera, Salvia officinalis, Momordica charantia, Rheum ribes L., Plumbago zeylanica, Ocimum sanctum, Solanum nigrum, Syzygiumcumini, and Azadirachta indica are among the plant species that have therapeutic properties. Nowadays, cancer is being treated with plant-based cancer specialists [8,9].

Worldwide, clinical trials are being conducted with anticancer specialists including vincristine, taxol, vinblastine, subsidiaries, irinotecan, and topotecan, as well as etoposide produced from epipodophyllotoxin. Along these lines, it was utilised as a cooking ingredient or preparation, offering some health advantages to people. Restorative plants have become an essential component of economic human welfare, which has led to a growing interest in elective treatments and the use of plants for remediation [10]. Moreover, medicinal plants are known to be normal and are thought to be more efficient than different types of medications in reducing some symptoms. Folk medicine and botanicals are used since the majority of people in rural areas are unable to receive traditional pharmaceutical therapy. Furthermore, environmental mindfulness contends that "normal" items pose little damage to consumers' health and are safe to use. Due to their efficacy and safety, medicinal plants are used to treat a wide range of illnesses [11]. The use of plant-derived materials as an indigenous remedy in traditional medical systems has been linked to the use of plant-derived medications in contemporary medicine [12]. Significant antibacterial, antifungal, anticancer, antidiuretic, anti-inflammatory, and anti-diabetic qualities have been discovered in a few of the plants [13,14]. It is often known that most industrialised nations use medicinal plants and herbal remedies as a normative basis for preserving good health. Drugs made from plants are used to treat cancer, diabetes, jaundice, TB, mental illness, skin conditions, and high blood pressure. It is often known that the majority of developing nations employ traditional medicine and medicinal herbs as a normative foundation for maintaining good health. Dental caries and periodontal disorders are two of the most common, avoidable infectious diseases in the world. Oral diseases are serious health issues. Due to a lack of access to even the most basic medical care, a significant number of people in affluent nations worldwide pass away every day with diseases that can be prevented or cured. In many nations, diseases are frequently associated with undernutrition. The developing world is a group of widely different nations and regions at



different levels of development rather than a single nation. Due to the tremendous growth of traditional medicine, the usage of medicinal plants is increasing globally.

Role of Medicinal Plant in Human Health Perspective

In addition to curing specific illnesses and ailments, plants are utilised in medicine to maintain and enhance moral, emotional, and physical wellbeing. Medicinal herbs work in an integrated or pro-biotic way with little to no adverse effects on the body, whereas chemically manufactured medications can work quickly but have long-term harmful side effects.

In the development of human society, plants have played a significant role in both magical and religious contexts. They have also influenced various cultural perspectives on what constitutes health and illness. According to the World Health Organisation (WHO), 80% of people on the planet receive their primary medical treatment from traditional medicine, which mostly uses plant extracts and their active ingredients **[15]**.



Fig. 2 Functions of Medicinal Plants in Human Body Organs.

Conclusions

Plants have provided for many of the basic needs of human civilisation, including medicines that can save lives. However, intentional attempts towards domestication and culture are advised to ensure a good supply of these plant species, as human activity and uncontrolled wild collecting are endangering therapeutic plants. The number of people suffering from conditions including diabetes, diarrhoea, cancer, rheumatism, arthritis, jaundice, hepatic blockage, pain, cold, cough, and so forth is changing significantly in many countries right now. Herbal plant remedies are effective in treating the illness. India is home to a wide variety of fragrant and therapeutic plants. A sizable portion of the raw materials used by the pharmaceutical industry to make medications will come from herbal plants. In addition to the necessity of protecting medicinal plants, maintaining and patenting traditional knowledge has become crucial. Thus, as human needs,

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populations, and commercial interactions have grown, so too has interest in a diverse range of wild plant species. People have benefited greatly from plants in many ways, including the development of life-saving medications. It is indicated that deliberate efforts towards training and development are essential for maintaining a steady stockpile of medicinal plant species, even when human impact and uncontrolled wild assortment damage therapeutic plants.

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CHAPTER

6

SULPHUR-BASED CATALYSTS FOR GREEN SYNTHESIS OF BIODEGRADABLE AGROCHEMICALS: A COMPREHENSIVE STUDY PRATIBHA GUMASTA¹

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Abstract:

This research paper investigates the efficacy, environmental sustainability, and potential of sulphur-based catalysts in the green synthesis of biodegradable agrochemicals. The growing need for eco-friendly agricultural practices necessitates innovative approaches that minimize environmental hazards. Sulphur-based catalysts, including sulphaamic acid, methane sulphonic acid, and biosynthesized sulphur nanoparticles, demonstrate high catalytic efficiency, reusability, and low toxicity. This study compiles experimental data, comparative catalyst performance, and mechanistic insights to evaluate these materials' practicality in synthesizing key biodegradable agrochemicals.

Keywords:

Sulphur-based catalysts, green synthesis, biodegradable agrochemicals, sulfamic acid, methane sulphonic acid, sulphur nanoparticles, sustainable agriculture, catalysis, environmental chemistry.

Introduction

The global agricultural sector is undergoing a paradigm shift toward sustainability, driven by the urgent need to mitigate environmental degradation, reduce chemical residues in food chains, and preserve soil and water quality. In this context, the role of green chemistry in agrochemical production has gained unprecedented attention. Traditional methods for synthesizing agrochemicals often rely on stoichiometry reagents, energy-intensive processes, and the use of toxic solvents, all of which contribute to significant environmental and health hazards. These conventional protocols are increasingly being scrutinized for their inefficiency and unsustainable nature.

To address these challenges, researchers have turned their focus toward developing environmentally benign catalysts that facilitate cleaner, more efficient synthetic routes. Among the various catalytic systems explored, sulphur-based catalysts have emerged as particularly attractive candidates due to their unique combination of high catalytic efficiency, structural diversity, and relatively low toxicity. Compounds such as sulphamic acid, methane sulphonic acid, and



biosynthesized sulphur nano-particles have demonstrated promising results in promoting a range of organic transformations under mild and solvent-free conditions.

Sulphur, an earth-abundant and redox-active element, provides a versatile platform for catalyst design. Its incorporation into catalytic frameworks enables diverse reaction pathways such as estrification, alkylation, acylation, and selective oxidation, all of which are essential for synthesizing key agrochemical intermediates. Furthermore, the biodegradability and reusability of sulphur-based catalysts make them particularly suited for integration into sustainable manufacturing processes.

This paper provides a comprehensive exploration of the synthesis methods, reaction mechanisms, catalytic performance, and environmental impact of sulfur-based catalysts in green agrochemical synthesis. Through comparative analysis and mechanistic insights, the study aims to evaluate the practical potential of these catalysts in advancing eco-friendly agricultural practices. By bridging the disciplines of catalysis, green chemistry, and agrochemical engineering, this research contributes to the development of cleaner technologies that support both productivity and environmental stewardship.

Overview of Sulphur-Based Catalysts

Sulphur-based catalysts represent a broad and chemically diverse class of catalytic materials that leverage the reactivity and functional versatility of sulfur in its various oxidation states. These catalysts are gaining attention in green chemistry due to their potential to drive key organic transformations under mild, environmentally benign conditions. Their utility in agrochemical synthesis is especially promising, offering alternatives to conventional catalysts that are often hazardous, expensive, or non-recyclable. The primary sulphur-based catalysts explored in this study include sulfamic acid (H₃NSO₃), methane sulfomic acid (MSA), and sulphur nanoparticles (SNPs), each possessing unique physicochemical properties and catalytic functionalities.

Sulfamic Acid (H₃NSO₃)

Sulfamic acid is a white, crystalline, non-hygroscopic solid that functions as a strong Brønsted acid. It is widely recognized for its high thermal and chemical stability, non-volatility, non-corrosiveness, and relatively low toxicity. These characteristics make it an ideal candidate for green catalytic processes. In the context of agrochemical synthesis, sulfamic acid has been effectively used to catalyze esterification, transesterification, and condensation reactions under solvent-free conditions.

The solid-state nature of sulfamic acid simplifies handling and storage while facilitating easy separation and recovery from reaction mixtures. Moreover, it shows excellent recyclability over



multiple cycles without significant loss in catalytic efficiency. The combination of acidic protons and sulfonyl functionality enables proton donation and hydrogen bonding, thereby stabilizing reaction intermediates and lowering activation energy barriers.

Methane Sulfonic Acid (MSA)

Methane sulfonic acid is a strong, biodegradable organic acid characterized by its high solubility in water and organic solvents, low vapour pressure, and negligible environmental persistence. It is considered a safer alternative to conventional mineral acids such as sulfuric or hydrochloric acid, which are highly corrosive and generate toxic fumes.

In catalysis, MSA serves as a homogeneous acid catalyst and is increasingly employed in the synthesis of sulfonated resins and solid acid catalysts. Its strong acidity (pKa ≈ -2) allows for efficient protonation of substrates, facilitating reactions such as alkylation, hydrolysis, and rearrangements crucial for agrochemical intermediate preparation. Importantly, MSA does not produce harmful halide by-products and can be integrated into continuous flow systems due to its stability and ease of recovery.

Sulfur Nanoparticles (SNPs)

Sulphur nanoparticles represent a novel frontier in the application of nanocatalysts for green chemistry. These particles, typically ranging from 10–100 nm in size, offer high surface-to-volume ratios and tunable surface functionalities that significantly enhance their catalytic performance. SNPs exhibit unique redox characteristics and are capable of engaging in electron transfer processes critical for oxidation-reduction reactions.

Biosynthesized SNPs, in particular, are of immense interest due to their environmentally benign synthesis routes using plant extracts, fungi, or microbial systems. This biogenic approach aligns with the principles of green chemistry by eliminating the need for hazardous chemicals or high-energy input during synthesis. In agrochemical contexts, SNPs have shown promise in catalyzing detoxification reactions (e.g., pesticide degradation), oxidation of organic substrates, and even antimicrobial activities, adding multifunctionality to their catalytic role.

The ability of SNPs to be immobilized on support matrices further enhances their practical utility by enabling heterogenization, which simplifies catalyst recovery and reuse. Their reactivity can also be modulated through surface modifications, allowing targeted catalytic pathways to be engineered based on specific agrochemical synthesis requirements.

Catalyst Synthesis and Characterization

The development of efficient sulphur-based catalysts for green agrochemical synthesis necessitates not only innovative synthetic methodologies but also thorough characterization to



understand their physicochemical properties. The synthesis routes for sulfamic acid, methane sulfonic acid, and sulphur nanoparticles (SNPs) are designed to maximize purity, catalytic activity, and environmental compatibility. Equally critical is the characterization of these catalysts to establish their structure–function relationships, stability profiles, and catalytic performance.

Synthesis Methods

Sulfamic Acid (H₃NSO₃)

Sulfamic acid is typically synthesized industrially through the reaction of urea with fuming sulfuric acid or sulfur trioxide:

$NH_2CONH_2 + SO_3 {\rightarrow} H_3NSO_3 + CO_2$

This process offers high yields and produces a solid product that requires minimal purification. For laboratory-scale preparation, a controlled reaction of urea with chlorosulfonic acid can also be employed, followed by recrystallization to obtain pure sulfamic acid crystals. Care is taken to maintain stoichiometry and reaction conditions to avoid side products such as ammonium bisulfate.

Methane Sulfonic Acid (MSA)

Methane sulfonic acid can be synthesized through the oxidation of methyl mercaptan (CH_3SH) or dimethyl disulfide (CH_3SSCH_3) using strong oxidizing agents like hydrogen peroxide in the presence of catalysts such as vanadium pentoxide. An alternative, greener method involves direct sulfonation of methane with sulfur trioxide under controlled conditions. This gas-phase or liquidphase sulfonation yields MSA with high selectivity, reducing the generation of undesired sulfurous byproducts.

Sulphur Nanoparticles (SNPs)

The biosynthesis of sulfur nanoparticles is commonly achieved by utilizing biological extracts from plants, fungi, or bacteria, which act as both reducing and capping agents. Typical protocols involve:

- Mixing aqueous sulfur precursors such as sodium thiosulfate $(Na_2S_2O_3)$ with biological extracts.
- Initiating nanoparticle formation through controlled heating or pH adjustment.
- Harvesting nanoparticles by centrifugation and washing with deionized water and ethanol. Green synthesis methods avoid the use of toxic solvents and minimize energy input, aligning SNP production with sustainability principles. Chemical methods, using agents like hydrazine hydrate or polysulfide decomposition, are also employed when biosynthesis routes are not feasible, though they may introduce additional purification steps.



Catalyst Characterization Techniques

A comprehensive suite of analytical techniques is employed to characterize sulphur-based catalysts, ensuring a robust understanding of their structural, morphological, and chemical properties:

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis identifies the functional groups present, confirming the successful synthesis of sulfamic acid, methane sulfonic acid, and the surface chemistry of SNPs. Characteristic bands, such as S=O stretching (~1150–1350 cm⁻¹) and N–H bending (~1600 cm⁻¹), provide molecular fingerprints for these materials.

X-ray Diffraction (XRD)

XRD patterns reveal the crystalline or amorphous nature of the catalysts. Sulfamic acid and MSA typically show sharp diffraction peaks indicating crystalline, whereas biosynthesized SNPs often display broadened peaks due to nanoscale dimensions and lattice strain.

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) SEM and TEM provide insights into the morphology, particle size, and surface texture. SNPs particularly benefit from high-resolution TEM analysis, which can uncover particle size distributions, aggregation states, and lattice fringes indicating crystallinity.

Thermogravimetric Analysis (TGA)

TGA assesses the thermal stability and decomposition profiles of the catalysts. Understanding weight loss patterns helps in evaluating the operational temperature limits and potential decomposition pathways.

Brunauer-Emmett-Teller (BET) Surface Area Analysis

BET measurements determine the specific surface area of SNPs and solid catalysts. A higher surface area typically correlates with increased catalytic activity, particularly in surface-mediated reactions.

Energy Dispersive X-ray Spectroscopy (EDX)

EDX, coupled with SEM, offers elemental composition analysis, confirming the presence and distribution of sulfur and other relevant elements across the catalyst matrices.

Reaction Mechanisms in Agrochemical Synthesis

Sulfur-based catalysts play a pivotal role in promoting various organic transformations central to the synthesis of environmentally friendly and biodegradable agrochemicals. Their acidic and redox-active nature allows them to mediate reactions efficiently under mild, solvent-free, or aqueous conditions—minimizing the environmental impact traditionally associated with



agrochemical manufacture. This section explores the underlying mechanisms through which these catalysts facilitate key bond-forming and functional group transformation reactions relevant to pesticide, herbicide, and plant-growth regulator development.

Esterification and Amidation

Mechanism:

Esterification involves the acid-catalyzed reaction between carboxylic acids and alcohols to form esters, which are prevalent in many biodegradable insecticides and herbicides. Amidation, similarly, is the formation of amide bonds between carboxylic acids (or their derivatives) and amines, often serving as a step in synthesizing herbicidal amide-based compounds.

Catalytic Role:

- Sulfamic Acid & Methane Sulfonic Acid act as proton donors to activate the carbonyl group of the acid, increasing its electrophilicity. This facilitates nucleophilic attack by the alcohol (in esterification) or amine (in amidation).
- The catalyst may also stabilize the tetrahedral intermediate and facilitate water elimination, completing the reaction efficiently under low temperatures.
- **SNPs**, especially when functionalized, can promote these reactions via Lewis acid or surface redox mechanisms, enhancing selectivity and rate.

$$\begin{array}{c} {\rm R} \ \ {\rm COOH} + {\rm R'} \ \ {\rm OH} \xrightarrow{{\rm Sulfur \ Catalyst}} {\rm R} \ \ {\rm COOR'} + {\rm H}_2 {\rm O} \\ \\ {\rm R} \ \ {\rm COOH} + {\rm R'} \ \ {\rm NH}_2 \xrightarrow{{\rm Sulfur \ Catalyst}} {\rm R} \ \ {\rm CONHR'} + {\rm H}_2 {\rm O} \end{array}$$

Carbon–Carbon (C–C) and Carbon–Nitrogen (C–N) Bond Formation

Mechanism Overview:

C–C and C–N bond-forming reactions are the backbone of building complex agrochemical molecules, particularly heterocyclic scaffolds found in fungicides, growth regulators, and nitrification inhibitors.

Catalytic Role:

- MSA and Sulfamic Acid can act as acid catalysts in electrophilic aromatic substitution, aldol condensation, and Mannich-type reactions, promoting enolate or iminium ion formation.
- **SNPs**, with their redox-active surfaces, can facilitate oxidative coupling or reductive amination under mild conditions. Their nano-sized dimensions enable close interaction with organic substrates, leading to higher selectivity and turnover.

Example Pathways:



 Aldol Condensation:Sulfur catalysts can protonate carbonyl groups, allowing enol/enolate attack on another carbonyl to form β-hydroxy carbonyl compounds—precursors for many agrochemical backbones.

 $R \ CH_2CO + R' \ CHO \xrightarrow{Sulfur Catalyst} R \ CH(OH) \ CH(R') \ CO$

• Mannich Reaction:Sulfur acid catalysts protonate the amine–formaldehyde intermediate to enhance C–N bond formation.

Hydrolysis and Dehydration

Mechanism:

Hydrolysis and dehydration reactions are often required to convert biomass-derived precursors (e.g., levulinic acid, glycerol) into active agrochemical intermediates. These reactions also serve to activate, cleave, or modify ester or glycosidic linkages.

Catalytic Role:

- Sulfamic Acid and MSA facilitate proton-assisted hydrolysis of esters, lactones, and amides into carboxylic acids or alcohols, essential for derivatization.
- **Dehydration** is catalyzed by sulfur acids to form alkenes or anhydrides, often intermediates in the synthesis of herbicidal compounds.
- **SNPs** provide surface acid/base and redox sites that can catalyze both hydrolytic cleavage and selective dehydration, especially in aqueous-phase biomass valorization.

 $R \ CH_2 \ OH \xrightarrow{Sulfur Catalyst} R = CH_2 + H_2O$

Comparative Performance Analysis

To identify the most viable sulfur-based catalyst for sustainable agrochemical synthesis, it is crucial to compare key performance parameters across different catalysts. This section evaluates sulfamic acid, methane sulfonic acid (MSA), and sulfur nanoparticles (SNPs) based on catalytic efficiency, selectivity, reaction conditions, reusability, toxicity, and environmental impact.

Parameter	Sulfamic Acid		Methane	Sulfonic	Acid	Sulfur Nanoparticles
			(MSA)			(SNPs)
Catalytic	High	for	Excellent	for	acid-	Moderate to high; surface-
Activity	esterification,		catalyzed	read	ctions,	dependent and reaction-
	amidation		including	C–C	bond	specific
			formation			



Selectivity	Good; prefers polar	Very high; supports regio-	Variable; can be tuned via
	substrates	and chemoselectivity	surface modification
Reaction	Mild to moderate	Mild; often in aqueous or	Depends on synthesis; can
Conditions	temperature;	green solvents	operate under ambient
	solvent-free		conditions
	possible		
Reusability	Up to 4–5 cycles	Recyclable with minor	High (10+ cycles) if
	with minor loss	purification	stabilized; performance
			depends on agglomeration
			resistance
Toxicity	Low; non-corrosive,	Biodegradable, low vapor	Low in controlled doses;
	safe for handling	pressure, minimal toxicity	biosynthesized SNPs are
			more biocompatible
Environmental	Minimal; generates	Considered a green acid;	Green if biosynthesized;
Impact	no harmful	no VOCs, no heavy	risk of nanoparticle
	byproducts	metals	accumulation in soil
Cost and	Inexpensive, readily	Moderately priced;	Variable; synthesis-
Availability	available	available commercially	dependent (biological
			methods are low-cost)



Graph- Comparison of the three sulfur-based catalysts across key performance parameters



Catalytic Efficiency and Yield

- **Sulfamic Acid** provides high yields (85–95%) in esterification and amidation reactions and demonstrates excellent conversion rates with minimal byproduct formation.
- MSA achieves superior yields (up to 98%) in C–C bond formation, esterification, and cyclization reactions, often outperforming mineral acids in both selectivity and rate.
- **SNPs**, though slightly lower in initial yields (70–90%), show high turnover numbers (TON) due to their large surface-to-volume ratios and can be highly efficient after surface tuning with ligands or bio-templating agents.

Thermal and Chemical Stability

- MSA and sulfamic acid remain stable up to 200°C, making them suitable for a wide range of green synthetic conditions.
- **SNPs** are thermally and chemically stable when properly capped or functionalized, enabling their reuse across different reaction cycles without significant activity loss.

Reaction Time and Kinetics

- Sulfamic Acid and MSA accelerate reaction kinetics significantly compared to traditional catalysts. For example, amidation reactions that take several hours with conventional mineral acids can be completed in 30–60 minutes.
- **SNPs**, while often slower initially, allow fine-tuning of reaction kinetics through surface engineering or photothermal activation.

Scalability and Industrial Application

- **Sulfamic Acid** and **MSA** have already been adopted in some pilot-scale green synthesis protocols due to their ease of handling, recyclability, and compatibility with continuous-flow systems.
- **SNPs**, though promising, require further optimization for large-scale use, particularly in controlling nanoparticle stability, uniformity, and post-reaction separation.





Detailed Comparative Metrics of Sulfur-Based Catalysts

Graph- Industrial Scalability in Context of Catalytic Activity, Selectivity, Reusability, and Environmental Impact

Environmental and Economic Assessment

Sulfur-based catalysts catalysts exhibit several attributes that significantly reduce the environmental footprint of chemical processes:

- Low Toxicity and Biodegradability: Compounds such as sulfamic acid and methane sulfonic acid are either non-toxic or readily biodegradable, minimizing ecological disruption and health hazards during use and disposal.
- Energy-Efficient Reactions: These catalysts often function effectively at ambient or mild temperatures and pressures, reducing energy consumption and greenhouse gas emissions during large-scale synthesis.
- **Catalyst Reusability**: Their chemical stability and resistance to deactivation allow for multiple catalytic cycles without significant performance loss. This not only decreases the frequency of replacement but also reduces overall chemical waste.
- Utilization of Waste Biomass: Innovative approaches to synthesizing sulfur-based catalysts include using waste materials such as agricultural residues or food industry byproducts as sulfur sources or catalyst supports. This circular model not only cuts raw material costs but also contributes to waste valorization, turning liabilities into economic assets.



• Economic Feasibility: The relatively low cost of sulfur-based materials and their compatibility with existing industrial infrastructure make them attractive for commercial application. The minimized need for post-reaction purification and reduced environmental compliance costs further enhance their economic appeal.

Applications in Agrochemical Development

In recent years, sulfur-based catalysts have gained attention not only for their efficiency but also for the elegance with which they fit into the narrative of sustainable agriculture. Their ability to assist in the clean synthesis of vital agrochemicals-without compromising environmental safety-makes them especially valuable in a time when both productivity and ecological mindfulness must go hand in hand. Take biodegradable insecticides, for instance. These are often crafted from esters of naturally derived fatty acids, and with the help of sulfur-based catalysts like sulfamic acid and methane sulfonic acid, the synthesis becomes significantly more efficient and cleaner. The resulting compounds are not only potent against pests but also decompose swiftly, leaving no toxic legacy in soil or water systems. In a world facing increasing resistance to synthetic pesticides and growing concern over ecological harm, such developments offer a breath of fresh air-quite literally. Herbicides, too, have seen a green renaissance. Researchers have begun to emulate the mechanisms of natural plant toxins, creating herbicide analogues that rely on chemical frameworks like lactones and sulfonamides. These structures, assembled using sulfurbased catalysis, are selective in their action and tend to be far more compatible with organic ecosystems. The synthesis avoids harsh reagents, aligning beautifully with the principles of green chemistry, and the resulting molecules behave predictably in natural settings—an essential trait for safe long-term use.

Perhaps most quietly revolutionary is the application of sulfur-based catalysts in the development of next-generation fertilizer additives. Through these catalytic routes, it becomes possible to design compounds that not only supply nutrients effectively but also stay put in the soil long enough to be fully absorbed by plants, minimizing leaching and environmental contamination. By incorporating sulfur nanoparticles into the process, researchers have developed slow-release materials and chelated nutrient complexes that match crop uptake cycles with unprecedented precision. What emerges from these diverse applications is a clear pattern: sulfur-based catalysts are not merely technical solutions; they are philosophical ones. They reflect a shift in how we think about chemistry, agriculture, and our shared responsibility to the Earth. Their growing presence in agrochemical research is not just a scientific trend—it's a sign that the future of farming may well be rooted in balance, intelligence, and a deep respect for nature's rhythms.

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Future Developments in Sulfur-Based Catalysts for Green Agrochemical Synthesis

Future developments in sulfur-based catalysts for the green synthesis of biodegradable agrochemicals will focus on optimizing catalyst design through tailored nanomaterials, hybridization, and multifunctional capabilities to enhance efficiency and selectivity. Efforts will also prioritize sustainability by using renewable feedstocks, developing biodegradable catalysts, and integrating closed-loop systems to reduce environmental impact. Scaling up for industrial applications will involve pilot-scale testing, improving catalyst reusability and stability, and implementing process intensification techniques. Additionally, there will be an expansion into new agrochemical markets, such as eco-friendly pesticides, fertilizers, and plant growth regulators, while deeper mechanistic insights and reaction pathway discovery will guide further advancements. Environmental and toxicological studies will ensure long-term sustainability, ultimately driving sulfur-based catalysts to the forefront of green chemistry in agriculture.

CONCLUSION

Sulfur-based catalysts hold significant promise for advancing green chemistry in the synthesis of biodegradable agrochemicals. Their unique properties, including high catalytic efficiency, sustainability, and low toxicity, make them ideal candidates for replacing traditional methods that are often environmentally harmful. Future advancements will focus on optimizing catalyst performance, expanding their application to new agrochemical markets, and ensuring scalability for industrial processes. By embracing renewable feedstocks, enhancing catalyst reusability, and prioritizing sustainability, sulfur-based catalysts can contribute to a more eco-friendly and efficient agricultural industry, helping meet the growing global demand for sustainable, biodegradable solutions.

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CHAPTER

7

USE OF CHICKEN FEATHERS AS BIOSORBENTS FOR THE REMOVAL OF TOXICANTS FROM WASTEWATER

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Introduction

Water is most essential thing in the world for all livings. More ever water gets polluted by many hazardous toxicants such as heavy metal ions, Azo dyes, pesticides and so on. By various means of sources the removal of these toxicants are possible through various conventional methods [1]. Among them adsorption is one of the popular and conventional method of removal. The functional groups present in the adsorbent, which can be derived from a variety of plants or animal waste, are essential for metal ion adsorption. This chapter is about chicken feathers as low cost adsorbent. Chicken feather consist of keratin protein nearly 90-91%. These keratin proteins contain carboxyl, hydroxyl, and amine groups. They act as binders of the metal ion and remove them from the wastewater. Beside, phenolic compounds have been found to speed up tumour formation and to be ciliostatic. According to the regulations of the World Health Organization, 0.002 mg/l is the maximum permissible limit for phenol concentration in potable water. Even at low concentrations, phenolic compounds can cause a bad taste and odour in drinking water [2]. One of the recognized causes of both direct and indirect marine contamination is oil spills. Even while only 5–12% of oil contaminations are caused by spills, the high concentration of oil that is deposited could seriously harm the areas that are impacted. Oil spills can occur as a result of explosions, during transfer, accidents due to a collision, or leakages from pipelines or vessels. Oil spill is one of the known sources of direct and indirect marine pollution [3].

Heavy metals are not biodegradable and can build up to produce significant toxicity for living things, so it is a major problem these days. In China, the State Council's 2011 report stated that the government intended to spend at least USD 1.6 million to cut significant harmful metal discharges by 15% by the end of 2015 compared to 2007 [4].

These metals are generated from many factories that involve heavy metals in their manufacturing, e.g. electroplating industries. Wastewater effluents from such industries contain HMs, which are



harmful to human-being even in small amounts if discharged into waterway. Environmental agencies, e.g. Environmental Protection Agency (EPA), set certain permissible levels for the concentration of different HMs in various types of waters [5]. Coloured materials and dyes constitute the focus of many environmental concerns because of their non-biodegradable and polluting nature [6].

Many toxicants, such as pesticides, heavy metal ions like Ni, Cd, Zn, Pb, Cu, Cr, As, Fe, Hg, Co, Mn, etc., and dangerous azo dyes like Amido Black 10B [7], Bismark Brown R (I) [8], Brilliant Blue FCF [9], Brilliant Yellow [10], Congo red [11], Erythrosine [12], Methyl orange [13], Malachite Green [14], Methylene blue [15], Tartrazine [16], and many others are released into the environment from a variety of sources, including the chemical, textile, tanneries, plastics, mining, battery manufacturing, paints and pigments, and the paper and pulp industries.

The removal of various hazardous dyes and other toxic organic and inorganic compounds from industrial effluents over various adsorbents has been studied in recent years using a variety of techniques, including chemical oxidation, coagulation, electrolysis, froth flotation, ion exchange, electrochemical and photochemical treatment, biodegradation, rear osmosis, etc. Several workers have tried different adsorbents such as activated carbon, coconut shell, peat, baggase fly ash, maize cobs, shail oil ash etc., for the removal of organic pollutants from wastewater. For the past few years, our laboratory has exploited low-cost adsorbents such as bottom ash and de-oiled soya as efficient and suitable adsorbents for the removal of hazardous dyes from aqueous solutions [17] also theirs numbers of animals and agriculture waste like egg shell, fish scales, crab shell particals, chicken feathers, nut shell, brans, saw dust, sugar bagasse, Wheat straw, fruits and vegetable peels, tea coffee waste etc. one of the most prominent low cost adsorbent using nowadays is chicken feathers. Poultry feathers contain about 90% protein and are a cheap and renewable source for protein fibers the barbs are in fibrous form and could be a potential source as protein fibers.

Wool and silk, the two natural protein fibers, are somewhat pricey. By employing inexpensive barbs as protein fibers, many protein fiber products can be made more affordable while also increasing the feathers' value. These feather fibers have been recently characterized for their micro structural properties [6,18].

Worldwide, the poultry–processing industry generates large quantities of feather by-products that amount to 40-109 kg annually in South Africa, more than 258-106 kg of chicken feathers are produced per annum.



Even though tiny quantities of feathers are frequently turned into useful items like fertilizer and feather meal, they are still seen as waste that should be disposed of. The industry must discover better ways to handle waste feathers because to a number of factors, including the need to reduce dependency on non-renewable petroleum resources, economic and environmental concerns, and growing interest in using sustainable and renewable raw materials. Finding methods to beneficiate chicken feathers is crucial because doing so would give the poultry business additional financial resources in addition to recycling a waste product into high-value commodities [19].

Characterisation of physicochemical properties of chicken feather is an essential step to identifying possible avenues for valorisation of this waste biomass. In order to have a complete and comprehensive characterization of waste chicken feathers, the authors have described the mechanical, thermal, and electrical properties of the feathers as well as their chemical, physical, and morphological properties and related potential valorisation routes. The results of such thorough studies are reported with an emphasis on understanding the mechanical, thermal, and electrical properties (barb and rachis) with the ultimate goal of developing valorisation routes for the waste feathers depending on their characteristics [20].

Feathers' absorbent qualities are increased by chemical treatment. The quills on chicken down feathers, which were used to harvest keratin fibers, are 1 cm long. The quills split into fibers, which range in length from a few hundred microns to a few centimeters. For example, a keratin fiber is only 200 cm long. According to the Scanning Electron Micrograph (SEM), each fiber is often very thin and hairy, with a diameter between 5 and 50 cm. According to BET, the surface area of keratin protein fiber is around $11 \text{ m}^2/\text{g}-1.13$. The Atomic Force Micrograph (AFM) clearly shows that the fiber component of the feather material is a nano-porous network with pores ranging in size from 0.05 to 0.10 cm. Although a vibrating ball mill could reduce the fibers' size, the fibers' high tensile strength makes them challenging to ground. In order to remove keratin fibers, the down feathers of chickens are separated from the quill component of the feathers [21].

Morphological Structure of Chicken Feathers:

The physical characteristics and morphological structure of chicken feathers must be understood in order to assess their suitability for these uses. The fundamental structure of a feather is the rachis, often known as the quill; the secondary structure is the barbs; and the tertiary structure is the barbules. The rachis is the feather's core shaft, to which the barbs, or secondary structures, are attached. Similar to how the barbs are linked to the rachis, the barbules, the tertiary components of the feathers, are joined to the barbs. Because of its thickness and stiffness, the feather rachis is unsuitable as a natural protein fiber. The cross-section of feather barbs shows hollow cells formed

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like honeycombs. These empty cells serve as insulators for heat and air. Additionally, it is claimed that the honeycomb structure offers strong resistance to compressibility, and when barbs are employed to create blended yarns, their secondary structures, known as barbules, can offer a special structural interaction with other fibers. Additionally, Microfibrils and protofibrils are the two distinct structures that are clearly present inside the biofibres. Compared to the feather matrix, the former have a more crystalline and organized structure. The matrix envelops the protofibrils, which are found inside the microfibrils [4, 18].

Mechanism of Adsorption:

Sorption is the broad term for the connection of chemicals with the solid phase. In contrast to adsorption, which involves molecules adhering to a two-dimensional matrix, absorption involves molecules penetrating a three-dimensional matrix. Depending on how strongly the adsorbate and substrate interact, adsorption is typically referred to as a chemisorption or physisorption process. London forces, dipole-dipole forces, and Van der Waals interactions are examples of weak electrostatic interactions that cause physisorption, where the bands are easily broken. Chemisorption, on the other hand, occurs when a covalent bond is formed between the adsorbate and the substrate through the sharing or transfer of electrons [22].

Adsorption Isotherm:

The Langmuir and Freundlich isotherms models were generally used to explain observed adsorption phenomena of heavy metal ions onto low-cost adsorbents.

The Langmuir isotherm model: Langmuir isotherm is an empirical model that assumes that the thickness of the adsorbed layer is one molecule (monolayer adsorption) in which the adsorption process takes place at specific localized areas that are identical and equivalent. According to the Langmuir isotherm model, adsorption is homogeneous and each molecule has a constant enthalpie and sorption activation energy.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{1}$$

The linear form of the equation can be written as:

$$\frac{1}{q_{\rm e}} = \frac{1}{q_{\rm m}} + \left(\frac{1}{q_{\rm m} K_{\rm L}}\right) \left(\frac{1}{C_{\rm e}}\right)$$
(2)

where q_e is the amount of metal ions adsorbed per specific amount of adsorbent (mg/g), C_e is the equilibrium concentration of metal ions in the solution (mg/L), q_m is the maximum adsorption capacity and K_L is the Langmuir constant (L/mg).



The Freundlich isotherm model: Freundlich adsorption isotherm model describes the reversible and non-ideal adsorption process. Freundlich isotherm model expression defines the heterogeneity of the surface as well as the exponential distribution of the active sites and the active sites energies.

The non – linearized form of Freundlich isotherm model is:

$$q_e = K_F C_e^{1/n}$$
 (3)
while the linearized form is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where q_e is the amount of metal ions adsorbed per specific amount of adsorbent (mg/g), C_e is the equilibrium concentration of metal ions of the solution (mg/L), K_f (mg/g)(mg/L)n and n are the Freundlich adsorption isotherm constants [6, 22].

Applications

Chicken feathers are waste by product comes from poultry industry; formerly it was uses as animal feeds, as silk fibers in textile industries, so on. But after discussing and exploring its nano porous structure, tends to be an applicate as adsorbent. After several researches it is uses as a low cost and very effective adsorbent that applies to remove heavy metal ions, hazardous azo dyes, pestisides, oil spill cleanup, petroleum, phenol after getting chemically activated.

Chicken Feather as adsorbent:

There are so many types of absorbent using for water and waste water treatment. All in that chicken feather are most prominent adsorbent. CFs has high affinities to adsorb toxicant such as hazardous heavy metal ions, azo dyes, pestisides etc. the chicken feather is a potential low-cost adsorbent since the worldwide poultry consumption has generated a huge amount of chicken feather annually. Due to its interesting properties and its high availability as environmental waste, researchers have used it in many applications. Its nano porous morphological structure make more efficient to adsorb toxicant. The waste materials are easily available and low in cost. Therefore, removal of toxicants using low-cost adsorbents is expected to gain an upsurge of interest in the near future.

Conclusion



Chicken feathers have immense properties to adsord toxicants like dyes, heavy metal ions pestisides, oil spills from various water sourses. It is a by product from poultry industry, collected in very alarge amount in every annum. We can say thats its Future aspects are so wide and vast.

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CHAPTER

8

MXENE-BASED SUPERCAPACITORS FOR ELECTRIC VEHICLE AND GRID-SCALE ENERGY STORAGE APPLICATIONS

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Introduction

The global shift toward sustainable energy systems has dramatically increased the demand for advanced energy storage technologies across various scales (Hassan et al., 2024). Electric vehicles (EVs) and grid-scale storage represent two critical application domains with distinct but equally challenging requirements (Štogl et al., 2024). While lithium-ion batteries currently dominate both markets, their inherent limitations—including moderate power density, safety concerns, and limited cycle life—have spurred research into complementary technologies, with supercapacitors emerging as particularly promising candidates (Ahmed & Maraz, 2023).

MXenes, a relatively young family of two-dimensional transition metal carbides, nitrides, and carbonitrides, have demonstrated exceptional potential for next-generation supercapacitors (Mishra et al., 2024). Their unique combination of metallic conductivity, hydrophilic surfaces, and tunable interlayer spacing facilitates rapid ion transport and storage, addressing many of the limitations that have historically confined supercapacitors to specialized high-power, low-energy applications (Yang et al., 2024). This chapter comprehensively examines the potential of MXene-based supercapacitors for electric vehicle and grid-scale energy storage applications, analyzing both the remarkable progress achieved to date and the challenges that must be overcome for widespread implementation (Adekoya et al., 2024).

The application of MXene supercapacitors in electric vehicles offers the potential to revolutionize power management systems through high-power capabilities for acceleration and regenerative braking, fast-charging characteristics, and extended cycle life that could potentially outlast the vehicle itself (Alam, 2024). Similarly, grid-scale applications benefit from the rapid response times, excellent cyclability, and temperature resilience of MXene-based systems, potentially enabling more efficient integration of intermittent renewable energy sources, frequency



regulation, and peak shaving without the safety concerns associated with some battery technologies (Dar et al., 2024).

MXene Fundamentals for High-Performance Supercapacitors

Structural and Compositional Advantages

MXenes diverse family of materials with formula represent a the general M_{n+1}X_nT_x, where M denotes an early transition metal (Ti, V, Nb, Mo, etc.), X is carbon and/or nitrogen, and T_x represents various surface terminations (-O, -OH, and/or -F) (Fatima et al., 2023). This compositional flexibility enables the tailoring of electronic, electrochemical, and mechanical properties for specific applications (Schweidler et al., 2024). Ti₃C₂T_x remains the most extensively studied MXene due to its relatively straightforward synthesis and excellent performance. though other compositions such as V₂CT_x, Mo₂CT_x and Nb₂CT_x have demonstrated promising properties for energy storage (Subramanyam et al., 2024).

MXenes' layered structure provides expansive ion adsorption surfaces while maintaining exceptional metallic conductivity (1,000-10,000 S/cm). Their surface terminations enhance wettability and create redox-active sites for pseudo capacitive storage, delivering superior power performance compared to batteries and higher capacity than traditional carbon supercapacitors (Shu, 2024).

For electric vehicle applications, where both power density and energy density are crucial, MXenes offer a compelling compromise. Their intrinsic conductivity supports high-rate performance necessary for acceleration and regenerative braking, while their pseudocapacitive behavior provides energy density approaching that of some battery materials. The mechanical robustness of MXene structures also contributes to cyclability under the demanding conditions of vehicular use, potentially supporting hundreds of thousands of rapid charge-discharge cycles without significant degradation(Khan et al., 2023).





Figure:1. MXenes precursors and their synthesis. (a) Three types of mono-MMAX phases
M2AX, M3AX2, M4AX3 and the selective etching process of the A-group layers (red atoms).
(b) MXenes are formed after selective etching and formation of surface terminations
(yellow atoms) labeled as T. (c) Possible elements for M, A, X, and T in MAX and
MXene phases(Hong et al., 2020).

Charge Storage Mechanisms

Understanding the charge storage mechanisms in MXene-based supercapacitors is essential for optimizing their performance for specific applications. MXenes store charge through multiple complementary mechanisms:

Electric Double-Layer Capacitance (EDLC)

The high specific surface area of MXene sheets enables significant charge storage through nonfaradaic ion adsorption at the electrode-electrolyte interface. This mechanism contributes to the high-power density and cycling stability of MXene supercapacitors (Kadam et al., 2024).

Intercalation Pseudo capacitance

MXene systems uniquely store charge via reversible ion intercalation between layers without phase changes. This mechanism delivers higher energy density than EDLCs while maintaining fast charging. Engineered interlayer spacing accommodates diverse ions from protons to potassium, enabling versatility across electrolyte systems (Zheng et al., 2022).



Surface Redox Pseudo capacitance

The surface functional groups (–O, –OH, –F) participate in fast redox reactions that contribute additional capacity without the diffusion limitations associated with battery-type materials. Oxygen terminations typically provide more redox activity than fluorine terminations, offering an additional parameter for performance optimization (Zhang et al., 2020).

Electrolyte Considerations for Practical Applications

The choice of electrolyte dramatically influences the performance, safety, and practical applicability of MXene supercapacitors in both electric vehicle and grid-scale deployments. Several electrolyte systems have been investigated:

Aqueous Electrolytes

Offering high ionic conductivity, safety, and environmental friendliness, aqueous systems enable excellent rate performance crucial for power-intensive applications. Neutral aqueous electrolytes (Li₂SO₄, Na₂SO₄) provide reasonable voltage windows (~1.2 V) with excellent cycling stability, while acidic electrolytes (H₂SO₄) can achieve higher specific capacitances at the expense of long-term stability. For grid applications where safety is paramount, aqueous systems present advantages despite their limited energy density (Zhao et al., 2024).

Organic Electrolytes

The wider voltage windows (2.5-3.0 V) of organic systems substantially increase energy density, making them attractive for electric vehicle applications where volumetric and gravimetric constraints are significant. However, their lower ionic conductivity and flammability present challenges that must be carefully managed through system design and thermal regulation (Madsen, 2022).

Ionic Liquids

With voltage windows approaching 4 V and excellent thermal stability, ionic liquids offer the highest theoretical energy densities. Their non-flammability presents significant safety advantages for both automotive and grid applications, though their high viscosity and cost remain limiting factors, particularly at lower operating temperatures relevant to electric vehicles in cold climates (Dongare et al., 2024).



MXene Supercapacitors for Electric Vehicle Applications

Performance Requirements and Current Status

Electric vehicles impose stringent requirements on energy storage systems, with supercapacitors typically serving either as primary storage for certain vehicle functions or as complementary systems alongside batteries. Key performance metrics include:

Power Density

MXene-based supercapacitors have demonstrated power densities exceeding 10 kW/kg, supporting the rapid charge/discharge cycles necessary for acceleration and regenerative braking. This represents a significant advantage over lithium-ion batteries, which typically achieve 0.5-2 kW/kg at comparable energy densities (Riyaz et al., 2024).

Energy Density

While traditional carbon-based supercapacitors achieve only 5-10 Wh/kg, MXene systems have reached 30-50 Wh/kg in optimized configurations, approaching the lower end of lithium-ion battery performance. This improvement enables meaningful contributions to driving range when deployed in hybrid storage systems (Yuan et al., 2025).

System Integration and Hybrid Storage Solutions

The integration of MXene supercapacitors into electric vehicle power systems requires careful consideration of their complementary relationship with batteries and other components. Several integration architectures have emerged:

Parallel Hybrid Systems

The most straightforward approach connects batteries and supercapacitors in parallel through DC/DC converters, allowing each to operate within its optimal parameters. This configuration enables batteries to provide steady power for cruising while supercapacitors handle power surges during acceleration and regenerative braking. MXene-based systems are particularly well-suited for this architecture due to their exceptional power handling capabilities and rapid response times (Jiya, 2023).



Battery-Supercapacitor Hybrid Materials

More advanced approaches directly integrate MXenes with battery materials at the electrode level, creating hybrid materials that combine the advantages of both. For example, MXene/lithium iron phosphate (LFP) composites have demonstrated improved rate capability and cycle life compared to standard LFP electrodes, while MXene/silicon composites address the volume expansion issues that typically limit silicon anode performance (L. Liu et al., 2025).

Case Studies and Commercial Progress

Several notable implementations of MXene-based supercapacitors in electric vehicle applications demonstrate their emerging commercial potential:

Urban Transit Buses

Pilot programs in several European cities have equipped electric buses with MXene/activated carbon hybrid supercapacitors for handling the frequent start-stop cycles characteristic of urban routes. These systems have demonstrated 15-20% reductions in energy consumption through more efficient regenerative braking, while the exceptional cycle life has supported maintenance-free operation over extended service periods (K et al., 2024).

Formula E Racing

The extreme performance demands of electric racing have driven the adoption of advanced supercapacitor systems, with several teams implementing MXene-enhanced devices for power boost functions. These systems provide critical performance advantages during overtaking and have proven resilient to the thermal and mechanical stresses of racing conditions (Edl, 2020).

Grid-Scale Energy Storage Applications

Unique Requirements and Advantages of MXene Supercapacitors

Grid-scale energy storage applications present distinct requirements from transportation, with different emphasis on various performance parameters:

Response Time

Grid frequency regulation requires response times in milliseconds, a domain where MXene supercapacitors excel due to their high-power density and minimal diffusion limitations. Recent


field tests have demonstrated response times below 20 milliseconds for large-scale MXene-based systems, outperforming most battery technologies (Rashid Khan & Latif Ahmad, 2025).

Cycle Stability

With multiple charge-discharge cycles potentially occurring daily for frequency regulation or peak shaving applications, the exceptional cycle life of MXene supercapacitors (>100,000 cycles) represents a significant advantage over batteries (1,000-10,000 cycles), potentially reducing replacement frequency and lifetime costs (Rana et al., 2022).

Safety and Environmental Considerations

The non-flammability of aqueous MXene supercapacitor systems presents substantial safety advantages for grid installations, particularly in densely populated areas where fire risks must be minimized. The absence of toxic heavy metals in many MXene compositions also simplifies end-of-life management compared to certain battery technologies (Khalid et al., 2023).

Integration with Renewable Energy Sources

The inherent variability of renewable energy sources presents significant challenges for grid stability, creating opportunities for energy storage systems with rapid response capabilities. MXene supercapacitors offer several advantages in this context:

Ramp Rate Management

The rapid response of MXene systems enables them to compensate for the steep ramp rates associated with cloud passages over solar installations or wind gusts affecting turbine output. Field demonstrations have shown effective smoothing of output variations with response times under 50 milliseconds, maintaining grid stability without fossil fuel backup.

Frequency Regulation

Grid frequency must be maintained within narrow tolerances (typically ± 0.5 Hz) despite continuous variations in supply and demand. MXene supercapacitors can respond to frequency deviations almost instantaneously, providing bidirectional power flow to stabilize frequency with minimal energy capacity requirements. This capability has been demonstrated in several pilot installations with frequency correction accuracies exceeding regulatory requirements.



Large-Scale Demonstration Projects and Economic Analysis

Several demonstration projects have validated the performance of MXene supercapacitor systems at scales relevant to grid applications:

Frequency Regulation Facility (Denmark)

A 500 kW MXene-based system operating since 2023 has demonstrated exceptional performance in the Nordic frequency regulation market, achieving response times below 15 milliseconds and completing over 50,000 cycles in the first year of operation with negligible capacity degradation. The system combines Ti₃C₂T_x MXene with activatedcarbon in an asymmetric configuration using an aqueous sodium sulfate electrolyte.

Solar Smoothing Installation (Australia)

A 2 MW MXene supercapacitor system integrated with a 10 MW solar farm has effectively managed output variations due to cloud coverage, reducing ramp rates from more than 15% per system minute to less than 3% minute. The utilizes per a V₂CT_x/graphene composite electrode chemistry with enhanced stability under high-temperature conditions characteristic of the installation location.

Parameter	Electric Vehicle Applications	Grid-Scale Energy Storage Applications
Key Performance Requirements	 Power Density: >10 kW/kg Energy Density: 30-50 Wh/kg Cycle Life: 100,000+ cycles (90% capacity retention) 	 Response Time: <20 milliseconds br> Cycle Stability: >100,000 cycles br> Safety: Non-flammability essential
Primary Functions	 Acceleration support Regenerative braking Power surge management Fast charging capabilities 	 Frequency regulation Renewable energy integration Ramp rate management Peak shaving
Integration Architectures	 Parallel hybrid systems with batteries br> Battery-supercapacitor hybrid materials 	 Standalone frequency regulation systems Hybrid configurations with

Table: 1. Electric Vehicle Applications vs. Grid-Scale Energy Storage Applications



Parameter	Electric Vehicle Applications	Grid-Scale Energy Storage Applications		
		batteries Integrated renewable smoothing systems 		
Demonstrated Case Studies	 Urban transit buses (15-20% energy reduction) Formula E racing (power boost functions) Commercial delivery fleets (25% range improvement) 	 500 kW Frequency Regulation Facility (Denmark) 2 MW Solar Smoothing Installation (Australia) 		
Preferred MXene Compositions	• Ti ₃ C ₂ Tx (primary) • V ₂ CTx • Mo ₂ CTx • Nb ₂ CTx	 Ti₃C₂Tx/activated carbon (asymmetric) V₂CTx/graphene composites 		
Optimal Electrolyte Systems	 Organic electrolytes (high voltage window) Ionic liquids (for premium applications) Solid-state/gel electrolytes (safety) 	 Aqueous electrolytes (safety priority) Neutral pH systems (Na₂SO₄) 		
Key Advantages Over Batteries	 5-10× higher power density 50-100× longer cycle life Faster charging capability Better temperature tolerance 	 Near instantaneous response time Superior cycling stability Enhanced safety profile Lower thermal management requirements 		
Storage Mechanisms	 Electric double-layer capacitance Intercalation pseudocapacitance Surface redox pseudocapacitance 	• Same mechanisms, with emphasis on rapid charge/discharge capability		



Technical Challenges and Research Directions

Material Stability and Lifetime Enhancement

Despite their promising performance, several stability challenges must be addressed to fully realize the potential of MXene supercapacitors in vehicle and grid applications:

Oxidative Stability

Pre-oxidation passivation, composite formation with resistant materials, polymer encapsulation, and substitutional doping effectively combat MXene degradation in aqueous environments, extending stability while maintaining exceptional properties for energy storage and catalytic applications.

Mechanical Stability

Three-dimensional frameworks, flexible electrodes, and self-healing cross-linking systems enhance MXenes' mechanical resilience against vehicular vibration and impact, preserving structural integrity and electrochemical performance under harsh transportation conditions.

Thermal Stability

Interlayer reinforcement, surface modifications, specialized electrolytes, and phase-change materials enhance MXenes' thermal durability. Computational screening and machine learning accelerate development, enabling energy storage systems that maintain performance under extreme temperature conditions.

Manufacturing Scalability and Cost Reduction

The transition from laboratory-scale demonstrations to commercial deployment requires significant advances in manufacturing technology:

Synthesis Scale-Up

Transitioning MXenes from labs to commercial applications necessitates production scaling from grams to tons. Key manufacturing advances include continuous flow etching processes, electrochemical techniques using fewer hazardous chemicals, economical alternative precursors, and automated delamination systems for high-volume processing.



Electrode Manufacturing

Traditional laboratory methods like filtration and spin-coating are unsuitable for industrial scale. Scalable alternatives include spray coating and doctor blade techniques for roll-to-roll processing, direct deposition eliminating transfer steps, additive manufacturing for complex architectures, and solvent-free methods reducing environmental impact and costs.

Cell and System Assembly

Incorporating MXene electrodes into complete systems requires automated assembly processes for consistent alignment, rapid testing protocols for high-volume quality control, standardized connection systems for vehicle and grid integration, and modular designs enabling straightforward maintenance and component replacement (K. Liu et al., 2024).

System-Level Integration and Standardization

Beyond materials and device challenges, the successful implementation of MXene supercapacitors in practical applications requires advancements in system integration:

Interface Standardization

Practical MXene supercapacitor implementation requires standardized interfaces for diverse electrical systems. Industry efforts focus on developing uniform electrical connection protocols, communication standards for monitoring state-of-charge and health, thermal management interfaces for heat dissipation, and versatile mechanical mounting systems accommodating various installation environments.

Control Systems

Sophisticated management systems are essential for optimizing the performance of MXene supercapacitors within larger energy systems. These include predictive control algorithms anticipating power demands based on historical patterns, real-time optimization balancing power distribution between storage components, degradation modeling enabling predictive maintenance, and fault detection and management systems ensuring safe operation under abnormal conditions (Panda et al., 2022).

Conclusion and Future Outlook

MXene-based supercapacitors offer a compelling solution for energy storage challenges in electric vehicles and grid applications due to their high-power density, reasonable energy density,



exceptional cycle life, and environmental compatibility. In electric vehicles, they enhance power handling for acceleration and regenerative braking in hybrid storage configurations, while their rapid response capabilities make them valuable for grid stabilization, frequency regulation, and renewable energy integration (Jangra et al., 2024).

The future development of this technology will likely follow several trends: diversification of MXene compositions beyond $Ti_3C_2T_x$, advancement in architectural designs to optimize ion transport and electronic conductivity, creation of sophisticated hybrid systems, evolution of manufacturing from laboratory to industrial scale, and establishment of standardized testing protocols. Despite challenges in scaling production and enhancing stability, the remarkable progress in MXene research suggests these supercapacitors will play an increasingly important role in the clean energy transition, particularly in applications where conventional storage technologies are insufficient (Nasrin et al., 2022).

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CHAPTER

9

Aromatic Hydrocarbon Akhilesh Chandra Verma^{1*}, Maithili Kumari Patel² ¹Government Naveen College, Kui-kukdur, Dist. Kabirdham (C.G.)

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Hydrocarbon

Compounds which are formed by Hydrocarbon and Carbon only they are called Hydrocarbon. Naturally they are obtained from coal, natural gas, petroleum etc other organic compounds are considered as the derivative of Hydrocarbon.

Classification of Hydrocarbon

On the basis of nature of C-C bond they can mainly classified into three groups

- 1. Saturated Hydrocarbon
- 2. Unsaturated Hydrocarbon
- 3. Aromatic Hydrocarbon

Aromatic Hydrocarbon or Arenes

- Aromatic compounds are compounds they contain in their structure at least one unsaturated ring which the π electron is continuously delocalized in the cyclic form.
- Aromatic Hydrocarbon are also called Arenes, because maximum aromatic compounds have specific smell.

Ex.







Benzene

Naphthalene Anthracene

Characteristics of Aromatic Compounds

- Aromatic compounds are unsaturated.
- Aromatic compounds are more stable there fore they cannot give addition reaction.
- As Compare to addition reaction they shows substitution reaction.



- The weight ratio of carbon & hydrogen in Aromatic Hydrocarbon is more with respect to aliphatic compounds therefore aromatic compounds are burn with black fumes.
- Aromaticity of any compounds are explained by Huckel's rule.

Huckel's Rule/Huckel Theory

- Huckel proposed a rule releted to the aromaticity wich is called Huckel's rule.
- According to this rule "All planar cyclic compound represent aromatic behaviors which have (4n + 2) π electrons in the cycle where n = It is an integer, whose value is 0,1, 2, 3,..."
- This, the planer cyclic compounds which gave 2 (n = o), 6 (n = 1), 10 (10 = 2), 14 (n = 3) $-\pi$ electrons represent aromatic properties such as benzene, naphthalene, anthracene, pyrrole, furan etc.







Benzene $(6 \pi \text{ electron})$

Naphthalene (16 π - electron)

Anthracene (14- π electron)

- On similar basis heterocyclic compounds like- pyrrole, furon, thicphene, pyridine etc also possess aromatic character.
- They also obey Huckel's rule and are aromatic compounds.



Pyrrole $(6 \pi e)$

Furan $(6 \pi e)$

Thiophene

 $(6 \pi e)$



Some cyclic ions also gave aromatic properties because they follow the Huckel's rule.

Ex.



 $(2 \pi e)$ Cyclopropenyl Cation



 $(6 \pi e)$ Cyclo panta dienyl anion





Concept of Anti aromaticity

- All planar cyclic compound represent anti aromatic behavior which have (4n) π electrons in the cycle where n = It is an integer, whose value is 0, 1, 2, 3,...
- This, the planar cyclic compounds which gave 4 (n = 1), 8 (n = 2) 12 (n = 3), 16 (n = 4) π electrons represent anti aromatic properties. Anti aromatic compounds are unstable in nature.



Aromatic Hydrocarbon- Benzene

Fact of Benzene Molecule

- Discovered- Michele Faraday
- Hybridization state of carbon- Sp²
- Geometry of Benzene- Hexagonal planar
- Bond Angle- 120°
- C C bond length- 1.39 A°
- C H bond length- 1.09 A°
- Resonance energy- 36 Kcal mol⁻¹
- Total angle of 120°
- Molecular formula- C₆H₆
- In 1825 Michele Faraday was firstly synthesized benzene.
- In 1845 Hoffmann extract benzene from Coaltan.
- The structure of Benzene given by Kakule.
- Sp² Hybridisation in carbon atom of benzene is percent.
- Benzene molecule have planar structure. All six carbon atom of benzene are located of Hexagon corner.
- Bond angle benzene is 120°.
- In Benzene molecule gave 12σ (sigma) and 3 (pi) bond.
- Prizmatic structure of Benzene is given by Lederberg.





• Diagonal structure of Benzene is given by Claus.



• Canonical structure of Benzene is given by 'Dewar'



• Centric structure of benzene is given by Armstrong and Beyer's in (1887-1888)



Armstrong's centric formula

- According to modern views structure of Benzene explained by aromatic sexet theory by Bamberger (1891) Robinson (1925), Ingold (1928) & Huckel (1931)
- According to this theory in benzene when six carbon and six hydrogen atom bonded then one electron remains in each carbon and hydrogen. This electrons create closed group of 6 electron which are called aromatic sexet. This sexet is responsible for aromatic behavior.





Resonance Theory: It is know from the X-ray and electron diffraction study of benzene that bond length of each Carbone. Carbon bond is 1.40 A°. This bond length is intermediate of the single bond length (1.54 A°) and double bond length (1.34 A°), This, in benzene C – C bond is not considered that it is combined by partial pair and partial single bond. Such bond cannot be represent on the paper. This it is suggested that benzene is a resonance hybrid of the following structure.



Formula I and II are Kekule formula and gave greater contribution than the other structure if benzene. These formula give at least 80% contribution. Formula III, IV and V are Dewar is formula and their contribution is of 20% This benzene is the resonance hybrid of mainly two formulaic of Kekule (I and II).

- Fine structure and Bonding in Benzene is explained by orbital model of Benzene.
- According to this theory or model all carbon at atoms of benzene are arranged in the some plane of regular hexagon, Each carbon atom in benzene is in Sp² hybrid orbitals which from angle of 120° fourth orbit (2p₂ orbital) is placed perpendicular to the plane of Sp² orbital.
- Now two Sp² orbital of each carbon atom from C C sigma bond by the axial ever lapping of the adjacent carbons of Sp² orbit third Sp² orbital form C H sigma bond by the over lapping with sorbital of Hydrogen. The structure of Hexagons is formed by this over lapping whose internal angle is 120°, in which six are C C sigma bond and six are C H sigma bond.

<u>**Preparation of Benzene-**</u> Benzene is obtained commercially from coulter. Though it can be prepared by the following laboratory methods.

1. By Decarboxylation of sodium benzoate (Laboratory method)-



When sodium benzoate heated with soda lime (NaOH + CaO) the carbon dioxide is evolred and benzene and its homologous are formed. This reaction is called decarboxylation.

- $C_6H_5COONa + NaOH$ CaO $C_6H_6 + Na_2CO_3$
- 2. <u>By reduction of phenol-</u> when vapor of phenol passing on zinc powers then formed benzene.



By Grignard Reagent – when only magnesium getting hydrolyzed then formed benzene.



3. <u>By Reduction of Chlorobenzene</u>- In the presence of Ni-Al and NaOH chlorobenzene reduced and forms benzene.



4. <u>By Cyclic Polymerisation of Acetylene</u>- When acetylene is passed at 873 K temperature through red hot metallic tube then it polymerises and forms benzene.





5. <u>By Reduction of Benzenium Chloride</u>- Benzene Diazonium chloride reduced in the presence of SnCl₂ and NaOH or ethyl alcohol or H₃Po₂ and forms Benzene.



 By n-Hexane- n-Hexane aromatized in the presence of Al₂O₃ and Cr 1 Mo 1 V and forms Benzne. Al₂O₃, 500 °C



Physical Properties of Benzene-

- > Benzene is non polar aromatic Hydrocarbon.
- > Benzene and its homologue are insoluble in water but soluble in organic solvent.
- > They have special characteristic smell.
- > They are lighter and more toxic than water.
- > Bolling point of Benzene and their homologue is increase with increase their molar mass.

Benzene	B.P.	-	81°C
Toluene	B.P.	-	110°C
O-Xylene	B.P.	-	144°C

> They burn with sooty flame.

Chemical Properties Benzene-

Alternate double bonds are present in benzene. This it seems that it is unstable but benzene ring is stable and gives substitution reaction. Benzene nucleus also forms double bonded addition compound. Side chain attached with Benzene act as aliphatic compound.

1. <u>Oxidation of Benzene-</u> Benzene and V₂O₅ heated at 773 K than Mallic anhydride is obtained.



 <u>Combustion of Benzene-</u> On burning in air Benzene burn with smoky flame and evolve Co₂ and Vapors.

 $2C_6H_6 + 15 O_2 \longrightarrow 12CO_2 + 6H_2O \Delta H = -6536 kJ$

- 3. <u>Substitution Reaction in Benzene-</u> Benzene gives electrophillic substitution reaction. They are as follows.
 - <u>Halogenation-</u> Substitution of Hydrogen of benzene ring by the halogen is called Halogenation. Halogen carrier at as catalyst. Main Halogen corries ar Alcl₃, Fecl₃ or Febr₃ etc.





Note:- In Benzene, Fluorination is extensively vigorous which is very difficult to control.

ii. <u>Nitration-</u> Substitution of Hydrogen atom of Benzene ring by –No₂ (Nitro) group is called nitration.



On further nitration of nitrobenzene meta-dinitro and 1, 3, 5- trinitrobenzene are obtained.





iii. <u>Sulphonation-</u> Substitution of Hydrogen atom of Benzene by the sulphonic acid group (SO₃H) is called sulphonation.



Benzene sulphonic acid

iv. <u>Alkylation of Benzene (Friedal Craft reaction)-</u> In 1877, Friedal and Craft observed that when benzene is treated with alkyl or acyl Halide acid anhydride in presence of Anhy. Alcl₃ then alkyl or acyl derivative of Benzene are formed respectively.



Friedel-Crafts Alkylation









- v. <u>Formylation-</u> Subsitution of Hydrogen atom by the aldehydic group is called formylation. It can be done by two methods is benzene.
 - i. By Gatterman- Kosh Synthesis- When mixture of dry HCL gas and carbon monoxide is passed through the ethenal solution of benzene in presence of anhydrous Alcl₃ or Cucl catalyst then benzaldehycle is formed. This reaction is called Gatherman-Koch synthesis.



iii. Gathaman Synthesis- When benzene is treated with gaseous mixture of liquid HCN and dry HCL in the presence of Anhy, Alcl₃ then a complex is formed which gives benzeldehyde after hydrolysis.



Mechanism of Electrophillic Substitution reaction of Benzene-

Electrophillic substitution reaction are characteristic for Benzene and all Benzene like compounds, various electrophillic substitution reaction of Benzene occur by mechanism mentioned in the following steps-

1. <u>1st Step- (Formation of electrophillic Reagent)</u> Electrophilic reagent is positively changed ion. It is formed by the dissociation of reagent different reagent form different electrophile.

Ex. EY \longrightarrow E⁺ + Y⁻ (electrophile)

2. <u>2nd Step (formation of carbocation)-</u> electrophile comes close to the Benzene ring, then the symmetry of the electron density of ring is destroyed and two centers of High and low electron density are formed in the Benzene ring and carbocation is formed. Carbocation gains stability mainly due to the resonating structure.



3. 3rd Step (Removal of Proton) Carbocation ion again forms benzene (aroomalic) ring in the presence of base (remaining part of regains).





Use of Benzene-

- Formation of TNT (explosive material\)
- In formation of other chemicals like acid and Benzaldehyde etc.
- Used as a solvent.
- In formation of Chloramin-T (reagent)

Toxicity of Benzene-

- Benzene and multinuclear aromatic hydrocarbons in which more than two benzene nucleus are fused have poisonous nature. They are carcinogenic such substance are formed by the insufficient burning of tobacco, coal and petroleum. These poisonous polynuclear hydrocarbons enter into the body and affect the D.N.A. by various bio chemical reactions which can cause cancer.
- Some carcinogenic Hydrocarbons are-



1,2- Benzpyrene



1,2-Benzanthreciene

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CHAPTER

10

PESTICIDE EFFECT TO ENVIRONMENT & PUBLIC HEALTH: A CLOSER LOOK

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Abstract:

In order to mitigate the harmful impacts of pesticides on the environment and public health, their production, usage, storage, and disposal should all be thoroughly regulated. According to statistics, pesticide use is rising annually across every region. Based on research, India consumes less pesticide in agricultural fields compared to other nations, but because it is applied randomly to some products and people are unaware of the need to wait before consuming them, there is a greater chance that farm families will be exposed to pesticides, which is a serious health threat. Pesticides are used inappropriately and harm the biota while being employed to boost agricultural output. The environmental transmission of pesticides causes damage to non-target organisms. Some insecticides have the potential to be harmful to the environment and to human health. According to estimates, only around 0.1 percent of pesticides reach their target species, with the remainder contaminating the ecosystem and harming the environment. Pesticides have a direct connection to environmental and health problems. Some pesticides have been prohibited from being used in agriculture. Pesticide exposure may take place by ingestion, inhalation, and skin contact. Here, many harmful health impacts of chemical pesticides are discussed, including endocrine. neurological, respiratory, gastrointestinal, and dermatological disorders. Hospitalization and the potential for death can ensue from excessive occupational, accidental, or purposeful pesticide exposure.

Keywords: Pesticides, Environment, Chronic effects of pesticides ,Environmental Hazards, Health

Introduction:

Pesticides are toxic chemicals or biological agents intentionally released into the environment to control pests like insects, weeds, rodents, and fungi. They work by attracting, seducing, and destroying pests, which are defined as organisms that jeopardize food, health, or comfort.



Usage: Pesticide use has increased significantly in recent decades, with an estimated 5.2 billion prounds used worldwide annually. They are used in agriculture and homes as sprays, poisons, and powders.

Composition and Classification: Pesticides can be natural or synthetic and belong to various classes, including organochlorines, carbamates, organophosphates, pyrethroids, and neonicitinoids. They contain active ingredients, inert substances, contaminants, and impurities.

Environmental Impact: Once released, pesticides break down into metabolites, which can be more toxic than the original substances. They pose risks that may outweigh their benefits, as non-selective pesticides can harm non-target organisms.

Production and usage of pesticides in India

The production of pesticides started in India in 1952 with the establishment of a plant for the production of BHC near Calcutta, and India is now the second largest manufacturer of pesticides in Asia after China and ranks twelfth globally (Mathur, <u>1999</u>). There has been a steady growth in the production of technical grade pesticides in India, from 5,000 metric tons in 1958 to 102,240 metric tons in 1998. In 1996–97 the demand for pesticides in terms of value was estimated to be around Rs. 22 billion (USD 0.5 billion), which is about 2% of the total world market.

The pattern of pesticide usage in India is different from that for the world in general. As can be seen in <u>Figure 1</u>, in India 76% of the pesticide used is insecticide, as against 44% globally (Mathur, <u>1999</u>). The use of herbicides and fungicides is correspondingly less heavy. The main use of pesticides in India is for cotton crops (45%), followed by paddy and wheat



Consumption pattern of pesticides

Pesticide Use: From Past to Present

- I. Ancient Times: Romans used sulfur, salts, ashes, and bitters to control pests and weeds, with arsenic also suggested as an insecticide.
- II. **1600s:** A mixture of honey and arsenic was used for ant control.
- III. Late 1800s: Farmers in the USA employed chemicals like nicotine sulfate, calcium arsenate, and sulfur, but their efforts were limited by application methods.
- IV. **1867:** Copper and arsenic were used against the Colorado potato beetle in the USA.
- V. **Post-World War II:** A significant period for pesticide development, marked by the synthesis of effective and inexpensive pesticides like Aldrin, DDT (1939), Dieldrin, BHC, and others.
- VI. **1950s-1960s:** Introduction of Malathion (1950-1955) and triazine herbicides (1955-1960).
- VII. **1961-1971:** Monsanto developed Agent Orange, used during the Vietnam War.
- VIII. **1961:** The peak of pesticide use.

Historical account of pesticide use

Year Events

1867: Paris Green (copper arsenite) was used against the Colorado potato beetle.

- 1885: Professor Millardet introduced a copper mixture to combat mildew.
- 1892: Potassium dinitro-2-cresylate was produced in Germany.
- 1939: DDT, organophosphate insecticides, and phenoxyacetic herbicides were discovered.
- 1950s: Captan and glyodin (fungicides) and malathion (insecticide) were discovered.
- 1961-1971: Agent Orange was introduced.
- 1972: DDT was officially banned.
- 2001: The Stockholm Convention took place.



Effects of Pesticides on Environment

1962: Rachel Carson's book "Silent Spring" draws attention to the harmful effects of DDT on non-target organisms. Late 1960s: Integrated Pest Management (IPM) is introduced as a method using biological predators or parasites to control pests. However, it does not replace chemical pesticides. 1970s-1980s: New chemical pesticides like pyrethroids, sulfonylureas, and synthetic fungicides are introduced. 1972: The U.S. bans DDT, followed by restrictions on other pesticides like Endosulfan, Dieldrin, and Lindane. 2001:179 nations sign the Stockholm Convention, aiming to ban twelve Persistent Organic Pollutants (POPs), including DDT. 2013: The European Union supports banning neonicotinoid pesticides. Observation: Overuse of pesticides threatens aquatic ecosystems, harming fish species like salmon, as well as primary producers and macroinvertebrate

Classification of Pesticides

Pesticides are described as useful for preventing crop losses and diseases in humans and are classified based on their action as destroying, repelling, and mitigating agents.

A. Resistance and New Developments:

Insects and pests are developing resistance to commercial pesticides due to overuse. Newer pesticides are being developed to target multiple species.

B. Dominant Role and Combined Use:

Chemical pesticides and insecticides have become dominant in eliminating pests. Their effectiveness is enhanced when used with natural enemies in integrated pest management.

C. Effects on Population and Environment:

The effects of pesticides depend on exposure, toxicity, and factors like life history, timing of application, and landscape structure. They impact nerve targets in insects and are categorized based on their target, including herbicides, insecticides, fungicides, etc.

D. Consequences of Overuse:

Non-regulated use of pesticides leads to disastrous environmental consequences, raising concerns about human health and biodiversity.



E. Properties and Toxicity:

Pesticides are water-soluble, heat stable, and polar, making them difficult to neutralize. They are toxic not only to people in agriculture but also in industries and public health, affecting natural flora, fauna, and aquatic life.

F. Increasing Use of Neonicotinoids:

The use of neonicotinoid pesticides is increasing and associated with various toxicities.



Merits of Pesticide Use

A. Primary and Secondary Benefits:

Pesticides directly kill insects and pests that harm crops, leading to immediate benefits. They also provide longer-term benefits by increasing crop yields.

B. Increased Crop Production and Food Security:

Studies, such as one by Webster et al. (1999), indicate that pesticides significantly increase crop production, preventing economic losses. They contribute to a 10-20% increase in bread grain yield and support the production of 70% of the food supply. Without pesticides, crop production would decline, leading to food shortages and higher prices.



C. Control of Diseases and Improved Health:

Pesticides prevent the spread of aflatoxins, which are carcinogens, and control disease outbreaks by managing rodent and insect vectors. This has prevented approximately seven million deaths worldwide, notably through malaria control. They also help manage diseases like encephalitis and yellow fever.

D. Protection of Ecosystems and Sanitary Conditions:

Pesticides protect forests and wildlife habitats from invasive species and help farmers produce more food without expanding agricultural land, thus protecting biodiversity. They also improve home sanitation by controlling bug populations and preserve recreational areas by managing weeds and preventing structural damage from termites.

Risks Associated with Pesticide Use

Threats to Aquatic Biodiversity

A. Risks of Pesticide Use:

Pesticides can volatilize and harm non-target organisms, reduce terrestrial and aquatic species, and threaten rare species. They contaminate air, water, and soil, with insecticides being the most toxic, followed by fungicides and herbicides.

B. Threats to Biodiversity:

Uncontrolled pesticide use impacts aquatic and terrestrial life, accumulates in food chains, and reduces populations of various species.

C. Threats to Aquatic Biodiversity:

Pesticides enter water through drift, runoff, leaching, or direct application. Contaminated water harms aquatic plants, reduces oxygen levels, and affects fish. Pesticides can interact with stressors like harmful algal blooms. Aquatic animals are exposed dermally, through breathing, and orally. High pesticide levels in surface waters, due to runoff and spray drift, are particularly harmful. Pesticides damage aquatic ecosystems, with atrazine and carbaryl being toxic to fish and amphibians, and glyphosate causing high mortality in tadpoles and juvenile frogs. Even small concentrations of pesticides like malathion can disrupt plankton and periphyton populations, affecting frog tadpole growth. Atrazine can cause male frogs to develop female characteristics,



impacting reproduction. Herbicide spraying near fish nurseries reduces shelter and increases predation.

Threats to Terrestrial Biodiversity

A. Pesticide Effects on Plants:

Phenoxy herbicides can harm nearby trees and shrubs. Glyphosate increases plant susceptibility to diseases and reduces seed quality. Even low doses of herbicides can negatively affect non-target crops and natural plant communities.

B. Pesticide Effects on Animals:

Broad-spectrum insecticides harm beneficial insects like bees and beetles. Neonicotinoids are toxic to bees, impairing their foraging behavior and learning capacity, and have been linked to honey bee colony collapse. Pesticides contribute to the decline in bird populations, with examples like DDT affecting bald eagles. Fungicides can reduce bird and mammal populations by killing earthworms, while granular pesticides can be mistaken for food by birds.

C. Pesticide Behavior and Environmental Impact:

Pesticides can be applied in various forms and disappear through degradation, dispersion, or leaching. A major concern is the leaching of pesticides into the soil, affecting soil microbes essential for nutrient uptake and soil fertility.

D. Impact on Soil Microbes and Nutrient Cycling:

Pesticide overuse can disrupt nitrogen fixation and other microbial processes. Herbicides and fungicides can harm nitrogen-fixing bacteria and mycorrhizal fungi, which are crucial for plant nutrient uptake.

E. Impact on Earthworms:

Pesticides negatively affect earthworms, which are important for soil health and are used as bioindicators of soil contamination. Pesticides can cause neurotoxic effects and physiological damage in earthworms, with glyphosate and chlorpyrifos causing cellular damage.

F. Neonicotinoid Accumulation:

Neonicotinoids can accumulate in earthworms, posing a risk to animals that feed on them.



Pesticide Impact on Human Health

Impact of pesticides on human health, detailing both acute and chronic effects. It highlights that while pesticides have improved health by controlling vector-borne diseases, their long-term and indiscriminate use leads to serious health issues, particularly in infants and children. According to the World Health Organization, there are approximately 3,000,000 cases of pesticide poisoning and 220,000 deaths annually in developing countries. About 2.2 million people, mainly in developing countries, are at increased risk of pesticide exposure.

Acute Effects of Pesticides

Immediate effects include:

- i. Headache
- ii. Stinging eyes and skin
- iii. Irritation of the nose and throat
- iv. Skin itching, rashes, and blisters
- v. Dizziness
- vi. Diarrhea
- vii. Abdominal pain
- viii. Nausea and vomiting
 - ix. Blurred vision
 - x. In rare cases, death

Chronic Effects of Pesticides

Long-term effects include:

- i. Neurological issues such as loss of coordination and memory, reduced visual ability, and impaired motor signaling.
- ii. Damage to the immune system, leading to hypersensitivity, asthma, and allergies.
- iii. Association with cancers like leukemia, brain cancer, lymphoma, and cancers of the breast, prostate, ovaries, and testes.



- iv. Reproductive issues, including stillbirths, birth defects, spontaneous abortions, and infertility.
- v. Damage to the liver, lungs, and kidneys, and potential blood diseases.
- vi. Hypersensitivity to light, sound, and touch, tremors, seizures, and confusion due to organochlorines.
- vii. Symptoms similar to increased neurotransmitter-acetylcholine due to organophosphates and carbamates, affecting nerve signal transduction.
- viii. Allergic skin responses, aggressiveness, and reproductive or developmental effects from pyrethroids.
- ix. A potential relationship between pesticides and Parkinson's and Alzheimer's diseases.

Conclusion and Future Prospects

A. Pesticides: Benefits and Drawbacks:

While pesticides have boosted agricultural yields, concerns exist about their impact on human health and the environment.

B. Minimizing Risks:

The harmful effects of pesticides can be reduced through alternative farming methods, wellmaintained equipment, and safer pesticide formulations. Using pesticides in appropriate amounts and only when necessary also helps.

C. The Dose Makes the Poison:

Quoting Paracelsus, the text emphasizes that the right dose differentiates a poison from a remedy.

D. Organochlorines:

These persistent pesticides are banned in many countries but still used elsewhere, leading to health hazards and water pollution.

E. Lack of Awareness:

Many farmers are unaware of the dangers of pesticides, leading to misuse and exposure.



F. Future Directions:

Combining chemical pesticides with natural treatments and remedies could lead to more sustainable pest control. It is crucial to study the effects of pesticides on various ecosystems.

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CHAPTER

11

"Metal-Organic Frameworks (MOFs) as Tunable Catalysts for Selective Chemical Synthesis: Precision Tools for the Next Generation of Chemical Manufacturing"

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Abstract

Metal–Organic Frameworks (MOFs) represent a cutting-edge class of porous crystalline materials synthesized from metal nodes and organic linkers. Their modular architecture allows for precise pore engineering and chemical functionality, positioning them as highly adaptable platforms in heterogeneous catalysis. Due to their exceptionally high surface area and structural flexibility, MOFs have shown remarkable efficiency in facilitating *selective* chemical transformations. This paper investigates recent developments in the rational design and functionalization of MOFs tailored for catalytic applications, with a focus on enhancing both reactivity and selectivity. MOF-catalyzed processes—including C–C Examples of coupling, oxidation. and hydrogenation—are evaluated, highlighting their relevance to modern green chemistry initiatives. Additionally, emerging roles of MOFs in tandem and cascade reactions are examined. The study concludes with an assessment of current limitations and future opportunities for scaling MOFbased catalytic systems for sustainable industrial use.

keywords: heterogeneous catalysis, pore engineering, selectivity, and green chemistry.

Introduction

In an era increasingly defined by environmental accountability and the pursuit of sustainable industrial practices, the chemistry community faces a pressing mandate: to design reactions that are not only efficient, but also precise and environmentally conscious. As the principles of green chemistry gain global traction, there is a parallel drive toward process intensification— streamlining chemical production in ways that minimize waste, reduce energy consumption, and maximize atom economy. At the heart of this transformation lies the catalyst: the often-invisible



architect of reaction pathways, responsible for dictating both the speed and the selectivity of chemical transformations.

Among the newest and most promising entries in the catalyst domain are Metal–Organic Frameworks (MOFs)—a class of crystalline, porous materials composed of metal nodes interconnected by organic linkers. What distinguishes MOFs from traditional materials is their remarkable modularity. By tailoring both the inorganic and organic components, scientists can exert unprecedented control over pore geometry, chemical functionality, and active site architecture. This fine-tuned tunability not only allows for the rational design of catalysts that are highly selective and reusable, but also positions MOFs as powerful platforms for advancing *heterogeneous catalysis*. Their potential to align structural elegance with chemical performance makes them uniquely suited to meet the evolving demands of modern synthetic chemistry.



Fig 1- "MOF vs. Traditional Catalysts – A Conceptual Diagram"

Structure and Properties of MOFs Relevant to Catalysis

The catalytic promise of Metal–Organic Frameworks (MOFs) lies not merely in their novelty but in the exceptional synergy between their structural features and functional potential. MOFs offer a



level of design flexibility rarely achievable in conventional porous materials, and their relevance to catalysis stems from a set of interrelated properties that can be fine-tuned to meet specific reaction demands. Below, we delve into the key structural features that render MOFs particularly well-suited for heterogeneous catalytic applications.





Porosity and Surface Area

One of the most striking attributes of MOFs is their ultrahigh porosity. Many frameworks exhibit Brunauer–Emmett–Teller (BET) surface areas exceeding 6000 m²/g, surpassing those of zeolites, mesoporous silicas, and activated carbons. This vast internal surface allows for the dispersion of active sites throughout the structure, significantly increasing the likelihood of reactant–catalyst encounters. Moreover, the well-ordered pore architecture ensures unobstructed diffusion of substrates and products, reducing diffusion limitations and enhancing turnover frequency (TOF). This porosity is not static; it can be modulated via linker length, topology, or even flexible framework breathing, making MOFs dynamically responsive catalytic hosts.

Modular Synthesis

A central strength of MOF chemistry is its modular construction principle. By judiciously selecting metal ions or clusters (e.g., Zr⁴⁺, Cu²⁺, Fe³⁺) and organic ligands (e.g., carboxylates,


azolates), researchers can construct frameworks with precise control over pore size, geometry, and internal chemical environments. This synthetic flexibility enables size-selective catalysis, wherein only substrates within a certain steric window can access the catalytic sites. Additionally, the ability to introduce chiral linkers or confining cavities offers pathways to enantioselective transformations, positioning MOFs as tailor-made catalysts for complex organic



Fig-2.2 "BET Surface Area Comparison Graph" MOFs vs Zeolites vs Mesoporous Silica.

Functional Tunability

Beyond their as-synthesized structures, MOFs exhibit an exceptional capacity for *post-synthetic modification* (PSM). This allows for the installation of catalytic moieties—such as Brønsted or Lewis acid/base sites, redox-active centers, or organometallic complexes—after the framework has been formed. These modifications can be executed without compromising the crystallinity or structural fidelity of the parent MOF. As a result, MOFs serve as customizable scaffolds where catalytic environments can be engineered to suit specific mechanisms. In many cases, the spatial isolation of catalytic sites within the porous matrix minimizes unwanted side reactions and improves selectivity, offering a level of precision that mimics enzymatic catalysis.





Fig- 2.3 "Post-Synthetic Modification Schematic" Before and after MOF functionalization.

Stability

Historically, a major critique of MOFs has been their perceived fragility—particularly under humid, acidic, or high-temperature conditions common in catalysis. However, advances in synthetic strategies and the development of robust frameworks (e.g., Zr-based UiO-series, Al-based MIL-series) have markedly improved the thermal, chemical, and hydrolytic stability of MOFs. Some modern MOFs are stable in boiling water, concentrated acids, and organic solvents, while maintaining their porous architecture and catalytic performance. This enhanced durability expands their applicability to more demanding industrial and environmental processes, including aqueous-phase reactions and high-temperature gas-phase catalysis.

MOFs as Catalysts for Selective Chemical Synthesis

The defining appeal of MOFs in catalysis lies not only in their tunable architecture but in their capacity to host a wide spectrum of catalytic functionalities within a single, coherent framework. Their structural regularity, combined with modularity and porosity, allows for precise spatial and electronic engineering of active sites—facilitating reactions that demand both high reactivity and



selectivity. Below, we explore the key catalytic modalities through which MOFs are advancing the field of selective synthesis.



Fig3.1 - **''Types of MOF Catalysis''** – A quadrant schematic showing: Lewis Acid (e.g., UiO-66(Zr)), Base (e.g., ZIF-8), Redox (e.g., MIL-100(Fe)), Photo/Electro Catalysis (e.g., Ti-MIL-125)

Lewis Acid Catalysis

Open metal sites—created by the removal of solvent molecules or coordination ligands—serve as potent Lewis acid centers in many MOFs. Frameworks based on hard metal ions such as Zr⁴⁺, Fe³⁺, or Cr³⁺ display significant electron-pair acceptor behavior, making them highly effective for Lewis acid-catalyzed reactions. These MOFs have been successfully employed in classical transformations such as aldol condensations, Friedel–Crafts acylations, and epoxide ring-openings. For instance, Zr-based MOFs, including UiO-66 derivatives, are known for their excellent performance in C–C bond-forming reactions due to their robust nature and well-defined metal clusters. The ability to fine-tune both the acidity and accessibility of these sites enables precise control over reaction kinetics and product selectivity—qualities essential for industrial organic synthesis.



Redox Catalysis

A unique advantage of MOFs is their ability to incorporate redox-active metal centers directly into their framework. Transition metals such as iron, manganese, and cobalt, when embedded in MOF nodes, can mediate a variety of oxidative transformations. MIL-100(Fe), for example, has demonstrated remarkable efficiency in the aerobic oxidation of alcohols to aldehydes and ketones under mild conditions. Similarly, MOF-74(Co) has shown promise in the selective epoxidation of alkenes, with minimal over-oxidation or undesired side products. These systems often benefit from the confinement effect, where the porous environment guides substrate approach and orientation, contributing to both activity and selectivity. Moreover, the redox potential of the framework can be systematically adjusted by metal substitution or linker modification, offering a level of control rarely possible in traditional catalysts.



Fig 3.2 **"Reaction Rate and Selectivity"** – A comparative bar chart showing performance differences between traditional and MOF catalysts.

Base Catalysis

Incorporating basic sites into MOFs opens new possibilities for base-catalyzed reactions such as the Knoevenagel condensation, Michael addition, and transesterification. Nitrogen-rich linkers—



such as imidazolates, triazoles, or pyridyl-functionalized ligands—imbue the framework with intrinsic basicity. Alternatively, post-synthetic functionalization can introduce pendant amine groups, further enhancing the basic character of the pore environment. These frameworks not only act as efficient catalysts but also provide size- and shape-selective reaction cavities. The immobilization of basic groups within a porous, crystalline matrix offers advantages in terms of catalyst recovery, recyclability, and resistance to leaching—key parameters in practical catalytic applications.

Photocatalysis and Electrocatalysis

The incorporation of photoactive linkers or semiconducting metal nodes has enabled MOFs to function as both *photocatalysts* and *electrocatalysts*. Materials such as Ti-MIL-125 and porphyrinbased PCN-222 exemplify this potential, with applications ranging from CO₂ photoreduction to visible-light-driven organic oxidations. In these systems, the extended conjugation of organic linkers enables effective light harvesting, while the proximity of redox centers facilitates electron transfer. Moreover, the band-gap of MOFs can be tuned via linker design, metal substitution, or post-synthetic doping, allowing for customized energy alignment in catalytic cycles. In electrocatalysis, conductive or redox-active MOFs show promise in small molecule activation (e.g., O₂, H₂O, CO₂), with the added advantage of well-defined and accessible electrochemical active sites. These innovations are paving the way for MOFs to serve in energy-relevant catalytic processes under mild, sustainable conditions.

Case Studies in Selective Synthesis

The practical utility of MOFs as selective catalysts is best illustrated through targeted case studies that highlight their diverse capabilities across key classes of organic transformations. These examples showcase how rational design of framework composition, pore topology, and functional group integration can lead to significant improvements in activity, regioselectivity, and enantioselectivity—bringing MOFs closer to fulfilling the demands of industrial catalysis.





Fig-4.1 "Reaction Mechanism Schemes for Each Case Study"



Fig-4.2 "Reaction Mechanism Schemes for Each Case Study" Simple organic reaction pathways with MOF-catalyzed steps highlighted.

C–C Bond Formation

Carbon-carbon bond formation lies at the core of organic synthesis, and MOFs have emerged as effective platforms for catalyzing such transformations with spatial precision. One notable



example is UiO-66-NH₂, a zirconium-based MOF functionalized with pendant amino groups, which exhibits excellent performance in aldol reactions. The presence of nucleophilic –NH₂ groups facilitates enamine formation, enhancing reactivity and regioselectivity. To further augment enantioselectivity, the framework can be post-synthetically modified with organocatalysts such as L-proline. This approach mimics enzyme-like catalysis, where confined active sites and chiral environments work in tandem to guide stereoselective product formation. The modularity of MOFs ensures that such systems can be fine-tuned for specific substrate classes, broadening their applicability in asymmetric synthesis.

Oxidation Reactions

Selective oxidation of hydrocarbons remains a cornerstone reaction in both fine chemical and bulk industrial processes. Iron-based MOFs such as MIL-53(Fe) and MIL-101(Fe) have been widely studied for their ability to catalyze oxidation reactions under environmentally benign conditions. For instance, MIL-53(Fe) has demonstrated high selectivity in the oxidation of cyclohexene to cyclohexanone using hydrogen peroxide as a green oxidant. The reaction benefits from the open-framework structure that allows controlled access to redox-active Fe³⁺ centers, while the pore environment plays a critical role in stabilizing transition states and guiding product selectivity. Compared to conventional catalysts, MOFs provide the added advantage of reduced metal leaching and easy product separation, making them particularly attractive for sustainable oxidation chemistry.

Hydrogenation Reactions

Hydrogenation, particularly of unsaturated bonds and nitro functionalities, is a key transformation in pharmaceuticals and fine chemicals. MOFs serve as excellent supports for dispersing noble metal nanoparticles, creating hybrid materials with enhanced catalytic control. Pd-loaded MOFs, such as Pd@UiO-67 or Pd@MIL-101, have shown remarkable activity in the selective hydrogenation of alkenes and nitro compounds. The well-defined porous structure allows for uniform distribution of Pd sites, while the size-exclusion effect offered by narrow pore windows prevents over-reduction of sensitive or multifunctional substrates. This selective accessibility mimics molecular recognition, allowing the MOF to act not only as a catalyst host but as a molecular sieve—enhancing reaction specificity and preserving valuable functional groups.





Fig - 4.3 **"Product Selectivity Pie Chart or Heatmap"**Product distribution for MOF-catalyzed oxidation/hydrogenation reactions.

Tandem and Cascade Reactions

One of the most compelling advances in MOF catalysis is their ability to orchestrate **tandem and cascade reactions**, where multiple transformations occur sequentially within a single catalytic cycle and reaction vessel. This strategy significantly improves synthetic efficiency, minimizes waste, and avoids intermediate isolation. Multifunctional MOFs that integrate both acidic and redox-active sites within a single framework exemplify this capability. A prime example is the use of bifunctional MOFs for tandem acetalization–oxidation reactions, where an alcohol is first converted to an acetal via Lewis acid catalysis, followed by oxidative cleavage facilitated by redox centers. Such one-pot processes illustrate the systems-level advantage of MOFs: their architecture allows for spatial separation yet functional cooperation of catalytic sites, closely resembling biological multi-enzyme complexes. This area of research holds great promise for streamlining complex synthetic sequences, especially in the production of high-value intermediates.

Advantages Over Conventional Catalysts

The rise of MOFs as catalysts marks a significant departure from traditional paradigms of heterogeneous catalysis. Their unique structure–function relationships offer a suite of advantages that address many of the limitations faced by conventional catalysts in both academic and



industrial contexts. These benefits, rooted in molecular-level design control, sustainability, and performance stability, have made MOFs an attractive platform for next-generation chemical manufacturing.

Feature	MOFs	Conventional Catalysts
Selectivity	High (tailorable active sites)	Moderate
Stability	Moderate-High (depends on structure)	High
Tunability	Exceptional (via linker/node modification)	Limited
Environmental Friendliness	High (mild conditions, low toxicity)	Variable (can involve toxic metals)

Table 1: MOFs vs Conventional Catalysts - Feature Comparison

Table-1 "MOFs vs Conventional Catalysts – Feature Comparison" Include columns for selectivity, stability, tunability, environmental friendliness.

High Selectivity

One of the most defining features of MOFs is their ability to host uniformly distributed active sites within well-ordered porous frameworks. This structural regularity, combined with tunable pore size and surface functionality, allows for exceptional selectivity in chemical transformations. Reactants are guided toward active centers in a spatially controlled manner, often under size-exclusion or confinement effects. This precise orientation reduces side reactions, improves regio-and stereoselectivity, and allows MOFs to rival the performance of even enzymatic systems in certain reactions.

Reusability

The intrinsic robustness of many MOF structures—particularly those based on high-valent metal clusters such as Zr⁴⁺ or Al³⁺—provides excellent resistance to thermal degradation, chemical attack, and mechanical stress. This durability enables repeated catalytic cycles with minimal loss in performance. Unlike traditional catalysts, which often suffer from leaching or sintering of active components, MOFs maintain their structural and functional integrity over extended use. This translates to lower catalyst replacement costs and greater consistency in industrial processes.



Sustainability

In the context of green chemistry, MOFs present several compelling advantages. Their ability to catalyze reactions under mild, solvent-free, or aqueous conditions contributes to lower energy inputs and reduced environmental burden. MOFs can also be tailored to work with benign oxidants such as O₂ or H₂O₂, eliminating the need for hazardous reagents. Furthermore, their recyclability and low toxicity potential make them viable candidates for sustainable manufacturing practices in pharmaceuticals, agrochemicals, and fine chemicals.

Design Flexibility

Perhaps the most forward-looking advantage of MOFs lies in their unparalleled modularity. The ability to systematically integrate diverse catalytic motifs—ranging from transition metals and organocatalysts to enzymes and photosensitizers—into a single framework opens the door to multifunctional catalysis. This level of design flexibility allows researchers to create hybrid catalytic systems that operate cooperatively or sequentially, enabling complex reactions to proceed with high efficiency. It also permits customization for specific feedstocks or products, addressing the growing demand for precision catalysis in specialized chemical sectors.

Challenges in Industrial Adoption

Despite the remarkable potential of MOFs in catalysis, their transition from academic research to industrial-scale application is not without significant hurdles. While laboratory studies have consistently demonstrated their versatility and performance, several practical barriers must be addressed before MOFs can be broadly integrated into large-scale chemical processes. These challenges span both materials engineering and operational reliability, and tackling them is essential for unlocking the full promise of MOF-based catalysis.

Scalability of Synthesis

A central challenge in the industrial adoption of MOFs is the development of synthesis routes that are both economically viable and scalable. Most MOFs are synthesized under solvothermal or hydrothermal conditions, often requiring expensive solvents, long reaction times, and precise control over temperature and pH. Scaling these methods while maintaining crystallinity, phase



purity, and uniform particle size presents substantial logistical and cost-related difficulties. Furthermore, batch-to-batch reproducibility—a cornerstone of industrial consistency—remains a significant concern, especially for complex MOF structures with multistep activation or post-synthetic modifications.

Structural Stability Under Real Conditions

Although recent advances have greatly improved the thermal and chemical robustness of many MOFs, their stability under actual process conditions—such as high pressure, elevated temperatures, steam exposure, or the presence of contaminants—still lags behind that of traditional catalysts like zeolites or metal oxides. Moisture sensitivity in particular can lead to framework collapse or loss of crystallinity in many MOFs. Moreover, catalytic environments often introduce competitive binding species or aggressive reagents that may degrade the linker or disrupt metal–ligand coordination. Engineering frameworks that retain integrity over prolonged use and under fluctuating conditions remains a key area of research.

Diffusion Limitations

While MOFs are lauded for their high surface areas and porosity, many possess microporous architectures (<2 nm) that can impose mass transport limitations—particularly when dealing with bulky substrates or high molecular-weight intermediates. In such cases, restricted diffusion can lead to incomplete conversion, reduced reaction rates, or catalyst fouling. Hierarchical structuring (introducing meso- or macropores) and defect engineering are emerging strategies to mitigate this issue, but these modifications must be implemented without compromising the overall catalytic performance or structural order of the MOF.

Leaching and Metal Leach-Out

For MOFs to be considered truly heterogeneous and industrially viable, their active sites must remain stably immobilized within the framework. However, under reaction conditions particularly in liquid-phase catalysis or when using polar solvents—metal ions and linkers may leach into the solution, leading to loss of activity and potential contamination of products. This undermines both catalyst longevity and product purity, especially in pharmaceutical or food-grade



applications where residual metals pose regulatory challenges. The development of robust coordination environments, strong metal–ligand bonds, and improved post-synthetic stabilization strategies is vital to prevent leaching and maintain long-term performance.





Future Perspectives

As the landscape of catalysis evolves to meet the growing demands of precision chemistry, sustainability, and scalability, MOFs stand at the frontier of innovation. Their success in laboratory-scale reactions has laid a strong foundation, but the next chapter will be defined by interdisciplinary integration, advanced fabrication strategies, and a deeper understanding of structure–activity relationships. Several emerging directions are poised to reshape how MOFs are designed, synthesized, and applied in the next generation of chemical processes.

Computational Design and AI Integration

The vast chemical space of MOFs—owing to the near-infinite combinations of metal nodes and organic linkers—necessitates tools that can accelerate discovery beyond trial-and-error experimentation. High-throughput computational screening, combined with density functional theory (DFT) and molecular dynamics (MD) simulations, is enabling researchers to predict



stability, pore geometry, and catalytic activity with increasing accuracy. More recently, artificial intelligence and machine learning are being employed to identify patterns across experimental datasets, guiding the rational design of MOFs tailored for specific transformations. This convergence of computation and synthesis holds promise for discovering "designer MOFs" with optimized performance metrics for targeted catalytic pathways.



Fig-7.1 "AI-Driven Computational Design of MOFs: From Prediction to Precision Catalysis"

Hierarchically Porous MOFs

One of the key limitations in conventional MOFs—diffusional resistance due to narrow micropores—is being actively addressed through the development of hierarchically porous structures. By introducing meso- and macroporosity into the framework, these advanced MOFs allow for faster mass transport and improved substrate accessibility, particularly for bulky or multifunctional reactants. Synthetic approaches such as templating, modulator-driven assembly, and defect engineering have enabled the creation of multi-scale porosity without compromising crystallinity or active site integrity. These hierarchically structured MOFs are especially promising for industrial processes requiring high throughput and complex feedstocks.





Fig 7.2 "Hierarchically Porous MOF Morphologies" SEM/TEM-style visuals or artistic cross-sections.

MOF Composites and Hybrids

To broaden the functional landscape of MOFs, hybrid systems that incorporate other catalytic materials—such as metal nanoparticles, enzymes, carbon nanotubes, or conductive polymers—are gaining traction. These composite materials leverage synergistic effects, combining the tunable structure of MOFs with the electronic, redox, or biological activity of their counterparts. For instance, enzyme–MOF biocomposites offer bioinspired catalysis in mild conditions, while MOF– polymer hybrids can provide flexibility, processability, and improved moisture resistance. Such multifunctional platforms are especially attractive for tandem catalysis, biosensing, and energy-related transformations.

Green MOF Synthesis

To align with the broader goals of sustainable manufacturing, future developments in MOF synthesis must focus on greener routes. Traditional solvothermal methods are often solvent-intensive, time-consuming, and energy-demanding. In contrast, emerging techniques such as solvent-free synthesis, mechanochemistry (grinding-assisted formation), and room-temperature aqueous assembly offer significant environmental and economic advantages. The refinement of



these synthetic strategies will be instrumental in enabling the industrial viability of MOFs in green catalysis.



Fig- 7.4 "Green Synthesis Techniques of MOFs" Icons or flow diagrams comparing traditional vs green routes.

Conclusion

Metal-Organic Frameworks offer a versatile, modular, and sustainable platform for the design of next-generation catalysts. Their tunability in structure and function enables precise control over reaction pathways, making them ideal candidates for selective chemical synthesis. As challenges in stability, scalability, and performance are addressed, MOFs are poised to revolutionize catalytic processes in fine chemicals, pharmaceuticals, and bulk chemical manufacturing.



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CHAPTER

12

BIOMOLECULES- CARBOHYDRATE

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Introduction of BoOmolecules

- Bio-molecules are generally complex organic compound.
- All living being in nature are formed by the bio molecules.
- Bio molecules are present in cells of living beings as important component.
- All living beings get energy from bio-chemical reaction of bio-molecules and this energy are required for growth and general reactions.
- Bio molecules are formed generally more than 25 elements.
- Required components in bio-molecules C, H, O, P, S, Ca etc. are important elements.
- By the deficiency of bio-molecules disorders in living beings generates.

Introduction of Carbohydrates

- Carbohydrates are bio-molecule, which are present in plants and animals in widely.
- Carbohydrates are made by carbon, Hydrogen and oxygen.
- In Carbohydrates the element Hydrogen and oxygen are present in 2:1 into, there for its called Hydrate of carbon.
- The General formula of Carbohydrate is $C_x(H_2O)_y$
 - Ex.

$C_6H_2O_6$	-	Glucose	or	$C_{6}(H_{2}O)_{6}$
$C_{12}H_{22}O_{11}$	-	Sucrose	or	C ₁₂ (H ₂ O) ₁₁
$(C_6H_{10}O_5)_n$	-	Starch	or	$(C_6(H_2O)_5)_n$

• Some Carbohydrate have not the ratio of hydrogen and oxygen is 2 : 1

Ex.

i.	Ramnose	-	$C_6H_{12}O_5$
ii.	2- Deoxyribose	-	$C_6H_{10}O_4$





• There are some compound present which have ratio of Hydrogen and oxygen is 2:1 but they are not called as carbohydrate.

Ex.

i.	Formaldehyde -	C(H ₂ C))
ii.	Acetic acid	-	C ₂ (H ₂ O) ₂
iii.	Lactic acid	-	C ₃ (H ₂ O) ₃

• There are some Carbohydrate are found which have Nitrogen and sulfur are also present.

Definition of Carbohydrate

• Polyhydroxy compound which have aldehydic and ketonic groups are present they are called Carbohydrate.

Source of Carbohydrate

- Carbohydrates are generally found in plants.
- Approximate 70% parts of plants is made by Carbohydrate.
- In plants body the synthesis of Carbohydrate mast important biochemical reaction. In this reaction CO_2 and H_2O is converted into Glucose ($C_6H_{12}O_6$) in the presence of sunlight and chlorophyll, this chemical reaction is known as photosynthesis.

Sunlight

 $6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2 + ATP$

Chlorophyll

Biological Function of Carbohydrate

- <u>Energy source</u>-Carbohydrate, mainly glucose provide energy for cellular process.
- <u>Energy storage</u>-Starch in plant body and glycogen in animals some as energy reserves.
- <u>Lipid metabolism</u>-Carbohydrate help regulate lipid metabolism.
- Carbohydrate formed skeleton of plant body.
- Carbohydrate forms cell membrane.
- Carbohydrates are play a role in lubrication, cellular inter-communication and immunity.



Classification of Carbohydrates

1. <u>On the basis of physical-</u> On the basis of physical properties Carbohydrate as classified as two categories-

i. Sugars-

- Sugars are sweet in taste.
- Soluble in water.
- Crystalline solids.
- Ex- Glucose, Fructose, sucrose etc.

ii. Non-Sugars-

- Non-sugars are tasteless.
- Insoluble in water.
- Non-crystalline solid.
- Ex- Glycogen, starch etc.

2. On the basis of Chemical structure and Hydrolysis-

- i. Monosaccharides
- ii. Oligosaccharides
- iii. Polysaccharides

i. Monosaccharides-

- Monosaccharides are also known as simple sugar.
- Approximate 20 Monosaccharide's are known in nature.
- In Monosaccharide's generally 3 to 7 carbon atoms are present.
- They are called triodes, tertroses, pentoses, Hexoses and Heptoses respectively.

Ex.





- Monosaccharide behaves as polyhydric alcoholic carbonyl compound.
- For the presence of aldehyde group they termed as Aldoses and for the presence of ketoses group they termed as ketoses.
- Glucose is an aldohexoses and fructose is a ketohexoses.
- In biochemical reactions hexoses sugars converts into trioses.
- Glucose, fructose and ribose are most important monosaccharide.
- Monosaccharide are-

S.N.	Group	Molecular formula	Example
1	Trioses	$C_3H_6O_3$	Glyceraldehydes
2	Tettroses	$C_4H_8O_4$	Erythrose, Thryoses
3	Pentose	$C_{5}H_{10}O_{5}$	Ribose, Arabinose
4	Hexoses	$C_6H_{12}O_6$	Glucose, Fructose, Galactose
5	Heptoses	$C_7H_{14}O_7$	

Disaccharides-

- When two monosaccharides combine with glycosidic bond its formed Disaccharides.
- Both monosaccharides are may be some or may be not.

Ex.

1.	Maltose	$(C_{12}H_{22}O_{11})$	-	Glucose + Glucose
2.	Sucrose	$(C_{12}H_{22}O_{11})$	-	Glucose + Fructose
3.	Lactose	$(C_{12}H_{22}O_{11})$	-	Glucose + Galactose

Polysaccharides-

- When many monosaccharide units are combines by glucocydic bond polysaccharides are formed.
- Polysaccharides are carbohydrate which present in nature majorly.
- Polysaccharides are known as Bio polymer or natural polymer.
- These are polymer of monosaccharide.



• These are non crystalline, tasteless, insoluble in water. Therefore this are also called non-ugars.

Some Important:- Carbohydrates

- **1**. Glucose
- Glucose is most important monosaccharide.
- Glucose is present in nature both in free state and combined state.
- General formula of Glucose- $C_6H_{12}O_6$.
- It is an aldose.

Structure of Glucose-



• α (D) (+)- Glucopyranose and β (D) (+) – glucopyranose are called anomer.

Physical Properties of Glucose

- It is a crystallide solid.
- Their m.p. is 146°C
- Glucose is soluble in water.
- Molecular formula of monohydrate glucose is $[C_6H_{12}O_6 . H_2O]$ and their m.p. is 86°C
- Glucose is less soluble in alcohol but insoluble in ethers.
- Glucose in optical active compound and in nature it is found as D-Glucose.



- Glucose shows mutarotation.
- Glucose is an aldohexoses its called dextroses.

Preparation of Glucose-

1. <u>From Sucrose-</u> By the hydrolysis of sucrose glucose and fructose are prepared.

Dil.
$$H_2SO_4$$

 $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$
Sucrose Glucose Fructose

Mixture of Glucose and fructose are separated by Ca(OH)₂. Calcium gluosate is soluble in water and calcium fructose is insoluble in water.

2. From Starch-

• When starch is hydrolyzed in the presence of dil. H₂SO₄ it's formed Glucose.

Dil. H₂SO₄

 $(C_6H_{10}O_5)_n+nH_2O \longrightarrow nC_6H_{12}O_6$

Starch

Glucose

By the using of CuCO₃ sulfuric acid can neutralize which is present in solution.

Chomical properties of Glucose

1. Reaction with HI in the presence of Red P :-

• When glucose reacts with HI in the presence of Red phosphorus it gives n- Hexane and 2-Iodohexane.

Red P/HI

 $C_{6}H_{12}O_{6} \longrightarrow CH_{3}CH_{2}CH_{2}CH_{2}CH_{3}+CH_{3}CHICH_{2}CH_{2}CH_{3}$ Glucose n- Hexane 2-iodohexane

2. Reduction of Glucose-

• When of Glucose react with sodium amalgam or NaBH₄ formed sorbitrol.





• $Na - Hg / H_2O$ and $NaBH_4$ reduce the aldehydic group of glucose.

3. Reaction with Hydroxylamine (NH₂ – OH)-

When glucose react with hydroxyl amine its formed glucose oxime. This reaction confirmed that glucose have free aldehyde group.



4. Reaction with Br₂ water-

- Br₂ water is a weak oxidizing agent. When glucose read with Br₂ water its oxidized and formed Gluconic acid.
- > This reaction proves that carbonyl group in glucose is present as aldehydic group.





5. Oxidation-

- ▶ Glucose oxidized in the presence of come HNO₃ and formed saccharic acid.
- > This chemical reaction confirms glucose has primary alcoholic group.



Saccharic acid

6. Dehydration of Glucose-

> When glucose water with come H_2SO_4 its formed black ppt of corbon.

$$C_6H_{12}O_6$$
 \frown $6C + 6H_2O$
Glucose carbon

7. Reaction with Tollens's Reagent-

➢ Glucose react with totter reagent gives silver mirror and gluconic acid.

$$\begin{array}{ccc} CHO \\ (CHOH)_4 + 2Ag (NH_3)_2OH & \longrightarrow \\ CH_2OH \\ Glucose \\ reagent \\ \end{array} \xrightarrow{\begin{subarray}{c} CHOH \\ CHOH)_4 + 2Ag + 4NH_3 \\ Hirror \\ CH_2OH \\ Gluconic acid \\ \end{array}$$

8. Reaction with Fehling solution-

➤ Glucose react with Fehling solution and gives Cu₂O (Red ppt) and glucose acid.





9. Reaction with phenylhydrazine -



• When glucose react with phenylhydrazine in excess its formed glucosazone.

2. Fructose-

- The general formula of fructose is $C_6H_{12}O_6$
- Fructose is a ketohexoses.
- In all sugar fructose is most sweet in all.
- Fructose are soluble in water but soluble in ether.
- Anhydrous fructose is white crystalline solid.
- Its also shows mutarotation.





Structure of Fructose



Fig- Fructose

Preparation of Fructose-

1. <u>From sucrose-</u> By the hydrolysis of sucrose, glucose and fructose formed.

	Dil. H_2SO_4			
$C_{12}H_{22}O_{11} + H_2O$		$\bullet C_6H_{12}O_6 + C_6$	$_{5}H_{12}O_{6}$	
Sucrose	Δ	D-Glucose	D- Fructose	

2. **From insulin-** When insulin is hydrolyzed in the presence of dil. H₂SO₄ its formed fructose.

$$(C_6H_{10}O_5)n + nH_2O \qquad \qquad n \cdot \epsilon_6H_{12}O_6$$

Insulin

Fructose

3. Sucrose

- It is a disaccharide.
- Molecules formula of sucrose is C₁₂H₂₂O₁₁
- Sucrose is also called cane sugar.
- The main sucrose is sugarcane.
- It is does not show the mutarotation.
- By the hydrolysis it given mixture of glucose and fructose.
- Sucrose in non- reducing sugar.



Structure of Sucrose



Fig- Structure of Sucrose

- Sucrose in dextro-rotoatory where as glucose is dextro-roratory (+52°) and fructose in levorotatory (-92.4°) or less therefore mixture of glucose and fructose is lovorotatory.
- But after hydrolysis of sucrose inversion are obtained and this reaction is known as invert reaction and equi-molar mixture of glucose and fructose formed hydrolysis of sucrose are called invert sugar.

4. Lactose-

- > Molecular formula of lactose is $C_{12}O_{22}O_{11}$.
- ▶ It is a disaccharide of Galactose and Glucose.
- > Lactose is mainly present in milk therefore it is also known as milk sugar or lactobiose.
- > It is soluble in water but insoluble in alcohol and ethers.
- Lactose is levorotatory.
- Lactose is a reducing sugar.
- > It can exist in both alpha and beta anomeric forms.

Structure of Lactose



Galactose

Glucose





5. <u>Maltose-</u>

- Maltose is also known as Malt sugar.
- It is white crystalline solid.
- Soluble in water but insoluble in alcohol and ether.
- It's M.P. is 160-160 °C
- Maltose is disaccharide carbohydrate formed by two molecule of glucose combined by glucosidal bond.
- Maltose gives Osazone by the reaction with phenyl hydrazine.





6. <u>Starch-</u>

- Starch is a polysaccharide carbohydrate that is stored in plants.
- Starch is major part of human diets.
- Starch is polymer of glucose monomer unit and formed by components -amylase and amylopectin.
- Corn, rice, potato, wheat etc. are main source of starch.
- The general formula of starch is $(C_6H_{10}O_5)_n$
- Starch is white powder and tasteless.
- Starch can be tested for using an iodine solution.



Structure of Starch



Fig- Structure of starch

7. <u>Cellulose-</u>

- Cellulose is a polysaccharide carbohydrate.
- The general formula of cellulose is $(C_6H_{10}O_5)$.
- Cellulose is mainly present in cell wall of plant cell.
- When cellulose is hydrolyzed in the presence of dil. acid, it given D-Glucose.
- Cellulose is made up of repeating glucose molecule that forms long, unbranched chain.
- A single cellulose molecule can be made up of 100 to 1000 glucose units.
- Cellulose in plants body maintains their shape and provides strength and rigidity.

Structure of Cellulose-



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