The Methods of Industrial Waste Water Treatment

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The review work entitled "**THE METHODS OF INDUSTRIAL WASTE WATER TREATMENT"** has been submitted to the Department of Chemistry, St. Paul's Cathedral Mission College, Kolkata in partial fulfilment for the award of the degree of SEM-VI, DSE-B4 (Under CBCS) in the B.Sc. SEM-VI CEMA Examination, 2025, CU is a record Bonafide work carried out by **Bidisha Pal**.

The references which helps to carry out this review work have been cited with due importance.

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CONTENTS

The Methods of Industrial Waste Water Treatment

Abstract:

Nowadays, environmental pollution is a serious problem, and water pollution is one of the biggest concerns. Most water pollution comes from industrial waste. Other sources include waste from homes, sewage, medical and manufacturing waste, and municipal garbage. People are now more worried about the harmful effects of wastewater. There are many ways to treat wastewater. Common methods include coagulation, adsorption, and the activated sludge process. Aerobic wastewater treatment (which uses oxygen) is becoming popular because it's cheap and easy to maintain. Using low-cost materials to absorb pollutants is also helpful. Aerobic treatment is good at breaking down harmful substances. There are also electrolytic methods that help clean wastewater. This paper looks at different ways to treat wastewater and remove harmful substances like heavy metals, dyes, pigments, and halogenated hydrocarbons.

Keywords:

Industrial waste water; Adsorption; Filtration; Treatment; Environmental pollution.

1.Introduction:

Clean water is essential for human life, agriculture, and aquatic ecosystems. However, waste from homes and industries pollutes most of the world's water sources. With rapid population growth, especially in cities, clean water is becoming increasingly scarce [1]. By 2015, over 5 billion people were expected to live in cities, including 23 megacities (over 10 million people), mostly in developing countries [2]. This urban growth makes it hard to provide clean water, sanitation, housing, and healthcare, especially for low-income areas. Water use is rising much faster than population growth, which leads to health issues, limits development, and harms the environment. Wastewater is often released into rivers without treatment, carrying harmful substances. Although people have managed wastewater for centuries, proper treatment began in the late 1800s [3]. A key moment was in 1855, when John Snow linked a cholera outbreak in London to sewage-contaminated water. Nowadays, developed countries use systems like centralized aerobic treatment plants and lagoons to treat wastewater, though the quality and access to these systems vary between urban and rural areas, and among income groups. In many developing countries, most domestic and industrial wastewater is released into rivers without proper treatment [3]. Even in industrial countries like China, about 55% of sewage is untreated. This causes serious environmental and health problems:

1. Oxygen Depletion: Organic waste uses up dissolved oxygen in water, harming aquatic life.

2. Health Risks: Untreated wastewater carries harmful bacteria and toxic chemicals, threatening human health.

3. Eutrophication: Nutrients in wastewater promote excessive plant and algae growth, damaging lakes and rivers.

4. Bad Odor: Decomposing waste produces foul-smelling gases.

Historically, wastewater was often dumped near living areas, causing diseases and epidemics. Wastewater management has always been a technical and political challenge.

Wastewater must be treated before entering nature. Various methods are used like:

Biological degradation, ion exchange, chemical precipitation, adsorption, reverse osmosis, coagulation and flocculation

This review focuses on modern methods like:

•Biofilm technology

•Bio granulation

•Microbial fuel cells (MFC)

These advanced techniques offer effective solutions for wastewater treatment [4].

1.1.Waste Water Global Trends:

In rich countries, about 70% of wastewater from homes and factories is cleaned before being released. In middle-income countries, only 28–38% is treated, and in poor countries, just 8% gets treated. This means that, globally, over 80% of wastewater is dumped without being cleaned. Rich countries often treat wastewater to protect the environment or save water. Still, releasing untreated water is common in many places. Following water pollution rules is hard, but it's important for clean water. Everyone involved must work together and follow the rules to protect water sources. Getting people involved in making decisions helps. It's important to include poor communities, ethnic minorities, people in rural or informal areas, and especially women, who are most affected by poor sanitation. Everyone's input helps make sure safe systems are built, funded, and maintained over time.

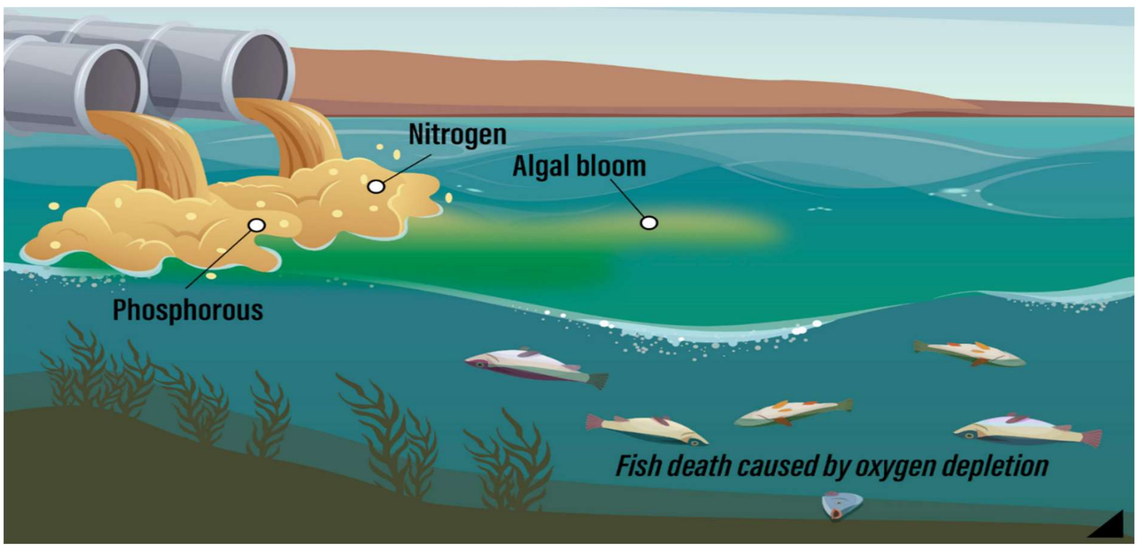

Figure 1: Waste water from industry and agal bloom

1.2. Waste Water Sustainable Development Agenda:

Better sanitation helps reduce health risks, and treating wastewater can improve health even more. Since 1990, 2.1 billion people have gained access to improved toilets, but 2.4 billion still lack them, and nearly 1 billion still defecate in the open. However, having better toilets doesn't always mean wastewater is managed safely. Only about 26% of urban and 34% of rural systems fully prevent contact with human waste, making them truly safe.

2. Wastewater Collection and Treatment:

Most people use sewer systems to get rid of wastewater, but only a small part of that water gets treated. In rural areas, on-site toilets work well, but they're hard to use in crowded cities. Big treatment plants are costly and may not suit modern cities. Smaller, local systems are growing in use—they cost less, save water, and can recycle energy and nutrients. Low-cost sewer systems that carry liquid waste without solids are popular in all types of communities. They are easy to manage locally and can connect to larger systems, but they can't handle stormwater. Nature can also help treat wastewater cheaply if the pollution is controlled and the ecosystem stays healthy.

3. Using Wastewater as an Alternative Source of Water:

Using untreated or diluted wastewater for farming has been common for centuries. Treated wastewater can also be a reliable water source for cities and industries, especially as water demand grows. Reusing water is cheaper when it's used near where it's treated. Treating wastewater to the needed quality makes it easier to cover costs. It becomes more cost-effective when freshwater is priced fairly and pollution is taxed properly. Using treated wastewater helps

save freshwater, recycles nutrients, and supports healthy ecosystems like fisheries by reducing pollution.

4. Pollutants of Industrial Waste Water:

Industrial waste water pollutants can be categorized on the basis of sector of the industries. Each industry has its own category of pollutant. Here is a table given bellow:

Table-1. Pollutants and its Sources

Sector	Pollutant
Iron and steel	BOD, COD, oil, metals, acids, phenols and cyanide
Textile and leathers	BOD, solids, Sulphate and chromium
Pulp and paper	BOD, COD, solids, Organic compounds
Petrochemicals and refineries	BOD, COD, solids, oils, phenols and chromium
Chemicals	COD, organic compounds, heavy metals, SS and cyanide
Non-ferrous	Fluorine and SS
Microelectronics	COD and organic chemicals
Mining	SS, metals, acids and solids

4.1. Reasons of Waste Water Treatment:

Waste water create different organic compounds and inorganic compounds whose adverse effects on environments is harmful for all kinds of living beings. Here are some of the reasons why waste water is essential for treatment [5].

1. Bad smell – Wastewater contains organic matter that breaks down and produces foul-smelling gases.

2. Oxygen loss in water – When released into rivers, untreated sewage uses up oxygen, harming fish and other aquatic life.

3. Algae growth – Nutrients in wastewater can cause too much plant and algae growth (eutrophication), damaging water bodies.

4. Health risks – Wastewater can carry harmful germs and toxic substances that pollute land and water, spreading diseases.

4.2. Factors Affecting the Waste Water Treatments:

There are several factors affecting the waste water treatment. These factors deal with the management of the waste water treatment by humans. Here are some of the factors are listed below

a) Community management

b) Level of service

d) Financial status

e) Materials and equipment

g) Monitoring and control of water treatment

4.3. Community Management :

The community manages water quality and treatment. Water treatment plants use machines and need regular monitoring. A maintenance schedule is followed to check performance. A full-time operator is needed to run and control the plant [5].

4.4. Level of Service :

Water quality depends on its physical, chemical, and biological properties. Treatment plants use several steps to clean water and make it safe to use. Such as

1. Reservoir – Stores up to 9 billion gallons of water.

2. Disinfection – Chlorine dioxide is added to kill bacteria.

3. Coagulation – Ferric chloride and polymers are mixed in to remove dirt.

4. Flocculation – Gentle mixing causes dirt to form clumps called "floc."

5. Sedimentation – Heavy floc settles and is removed.

6. Filtration – Water passes through layers of coal, sand, and gravel to remove leftover particles.

7. Final disinfection – Chlorine and ammonia are added before water is sent out.

These steps ensure clean and safe water [5].

4.5. Financial Status :

Running and maintaining a water treatment plant costs a lot of money. To support this, the government provides funding to keep the plant working properly. This ensures safe, clean water for users and good performance from the plant [5].

4.6. Materials and Equipment :

The machines used in water treatment are suitable for making water safe for drinking, farming, and industry. They are long-lasting and use modern technology to improve performance [5].

4.7. Monitoring and Control of Waste Water Treatment :

Water treatment needs proper monitoring, either manually or with automatic systems. There are two main types of systems: centralized (serving large areas) and decentralized (serving smaller or local areas).

Benefits of proper monitoring:

1. Reduces risk of using too little or too much chemicals

2. Ensures compliance with environmental rules

3. Improves plant performance

4. Saves water and energy

5. Increases overall plant productivity

4.8. Physical Method of Waste Water Treatment :

Industrial water treatment removes harmful pollutants from water. It uses different methods, including biological, chemical, and physical processes. Physical treatment mainly uses filters like screens, sand, or special membranes.

5. Greensand Filtration :

Glauconite, also known as green sand, is used in water filters to remove iron, manganese, and hydrogen sulfide. When coated with manganese oxide, it helps these substances react with oxygen, turning them into solid particles that the filter can trap [6].

6. Multi Media Filtration (MMF) :

Multimedia filtration is a water treatment method that uses layers like anthracite, sand, and garnet to remove particles from water. Larger particles are caught at the top, and smaller ones deeper down. It removes solids like clay, algae, and rust between 10–25 microns, but not viruses or bacteria [6].

7. Microfiltration :

Microfiltration uses a special membrane to remove tiny particles from water, ranging from 0.1 to 10 microns. It can remove solids, algae, and protozoa, but not bacteria, viruses, or dissolved substances [6].

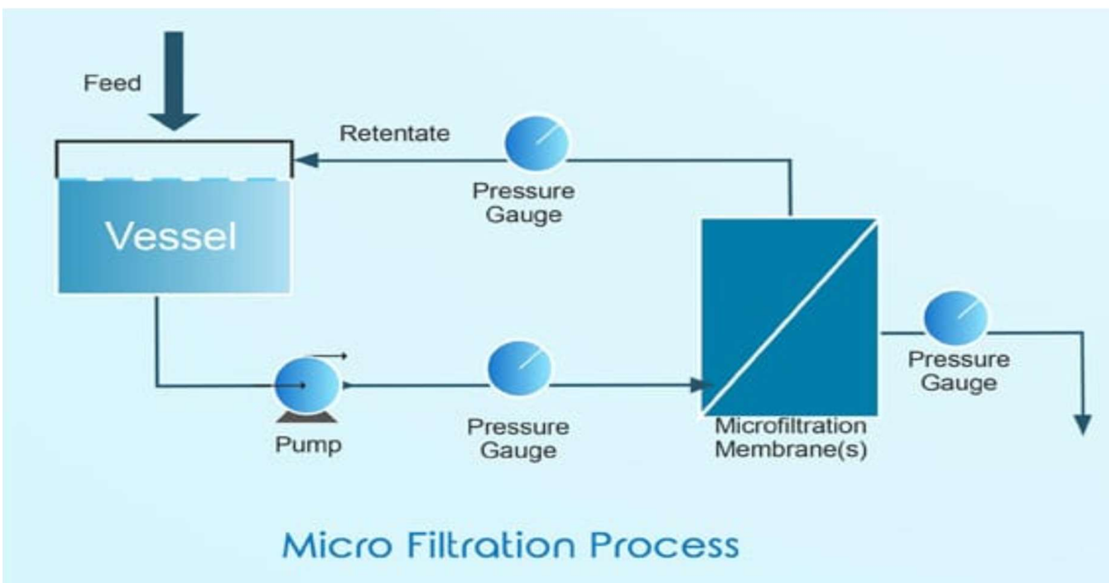

Figure2: Microfiltration

8. Ultrafiltration :

Ultrafiltration uses pressure and a membrane to remove tiny particles, bacteria, and some viruses from water (as small as 0.005 microns). It's often used before reverse osmosis but can't remove dissolved substances [7].

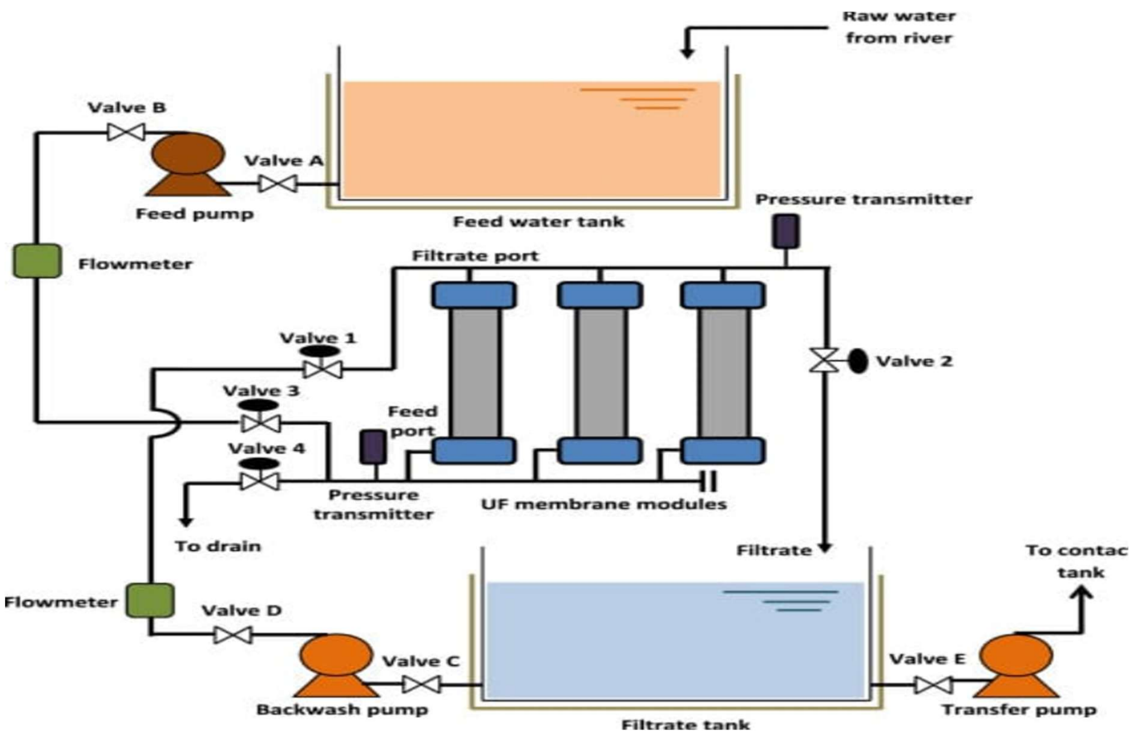

Figure 3: Ultrafiltration

9. Nanofiltration :

Nanofiltration is like ultrafiltration but uses a finer membrane. It removes bacteria, viruses, and larger ions like calcium and magnesium (0.001 to 0.005 microns). Because it removes hardness-causing ions, it's often called a "softening membrane" [7].

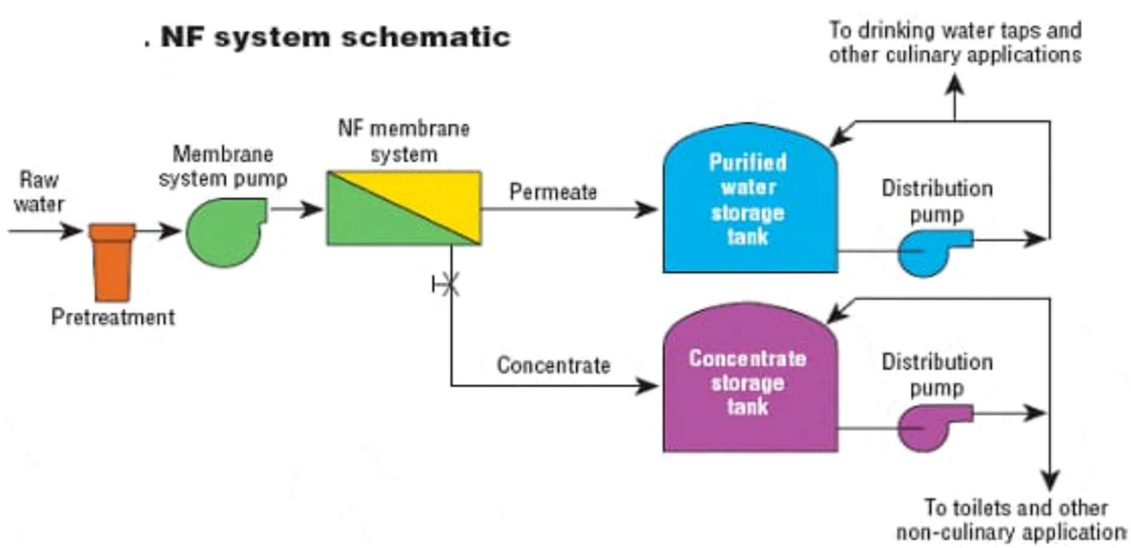

Figure 4: Nanofiltration

10. Reverse Osmosis :

Reverse osmosis (RO) is a common method used in industries to clean water. It works by using pressure to push water through a special membrane that removes impurities. This process can filter out things like salt, bacteria, viruses, and other tiny particles as small as 0.0001 microns [8].

11. Wastewater Treatment through Flotation :

Flotation is a method used to remove tiny particles or substances from liquids by using small gas bubbles. These bubbles carry the particles to the surface, where they are then removed. In wastewater treatment, flotation helps remove oils, fats, and fine solids. The smaller the bubbles, the better the removal works. A common and cost-effective method used is Dissolved Air Flotation (DAF). Chemicals like collectors and frothers are often added to help the process work better [8].

12. Coagulation – flocculation :

Sedimentation, also called clarification, is a common step in wastewater treatment where water flow slows down, allowing heavy particles to settle by gravity. Solids that sink are removed as sludge, while floating materials are taken out as scum. The process depends on factors like retention time, temperature, tank design, and equipment.

On its own, sedimentation removes only large particles. To improve it, chemicals called coagulants (like aluminium sulphate) are added in a process called coagulation-flocculation. These help smaller particles clump together and settle faster, removing up to 90% of suspended solids [9-10].

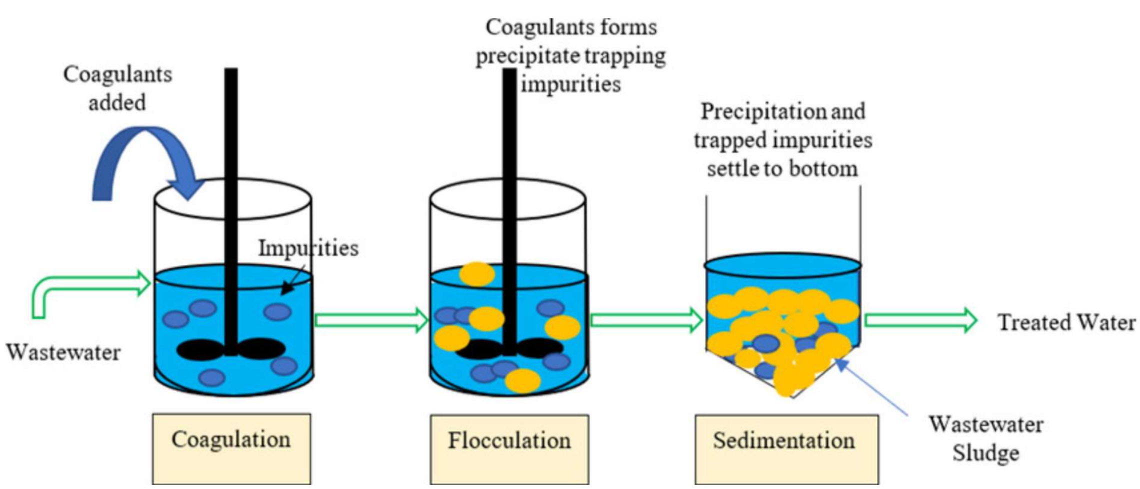

Figure 5: Coagulation, flocculaition,sedimentation

13. Chemical Method of Waste Water Treatment :

Wastewater contains particles of different sizes, and the treatment method depends on the particle size. These particles are grouped as:

Dissolved (< 0.08 µm)

Colloidal (0.08 – 1 µm)

Supra-colloidal (> 1 – 100 µm)

Settleable (> 100 µm)

Physical methods like settling, screening, and Dissolved Air Flotation (DAF) can remove larger, visible particles. However, very fine colloidal particles (less than 1 µm), which have a negative charge and stay suspended, can't be removed by regular physical methods or filters. These particles often cause high BOD (biological oxygen demand) in wastewater.

To remove them, chemical treatments using coagulants and flocculants are needed. These chemicals help the fine particles clump together into larger flocs that can settle and be removed.

13.1. Advanced Oxidation Process :

Advanced Oxidation Processes (AOP) are used to remove harmful organic pollutants that can't be broken down by normal biological methods [11]. They work by producing highly reactive oxygen compounds that can destroy a wide range of pollutants. AOPs use energy sources like electricity, UV light, or sunlight, making them more expensive than traditional treatments [12,13].

AOPs can also be used to disinfect water, air, and clean up polluted soil. Since no single method works for all cases, combining different techniques is often necessary for better and more cost-effective results [14].

13.2. Combination of Electrochemical and Photochemical Process :

Electrochemical treatment uses electric current and electrodes to clean wastewater through oxidation. This includes methods like electrocoagulation, electrodialysis, and ion exchange. Some advanced versions combine electrochemical treatment with photocatalysis, which improves color removal and reduces harmful chemicals.

One example is the Electro-Fenton process, which needs only a small amount of iron and produces hydrogen peroxide in the system, avoiding the need for dangerous chemicals. High-voltage methods can also generate powerful oxidants that help break down pollutants more effectively [15].

14. Hybrid Biological Process :

14.1. Biodegradation :

Traditional wastewater treatments use separate steps that work independently. In contrast, modern "integrated processes" combine biological and chemical treatments to improve results.

One example is combining activated sludge with chemical oxidation to break down tough pollutants into simpler, biodegradable ones. Recent studies have tested various partial oxidation methods (like ozonation, photocatalysis, and Electro-Fenton) on dye wastewater. These methods improved biodegradability and reduced toxicity without needing a biological reactor—but full treatment wasn't always achieved. Combining oxidation with biological treatment shows better overall effectiveness [14].

14.2. Membrane Bioreactors :

Membrane bioreactors (MBRs) combine activated sludge treatment with membrane filtration. They come in two main types: submerged and external membrane systems [14].

MBRs are used in treating many types of industrial and municipal wastewater, including from the pharmaceutical, textile, and petroleum industries.

Study showed that MBRs effectively removed over 99% of certain pollutants like 3-chloronitrobenzene, producing CO_2 as a byproduct. However, gas release and membrane fouling must be considered in reactor design.

To reduce fouling, the concept of critical flux (the flow rate below which no fouling happens) is used. MBRs with sulfate-reducing bacteria also offer an eco-friendly alternative for removing heavy metals from low pH wastewater, avoiding harmful byproducts of traditional methods like lime precipitation.

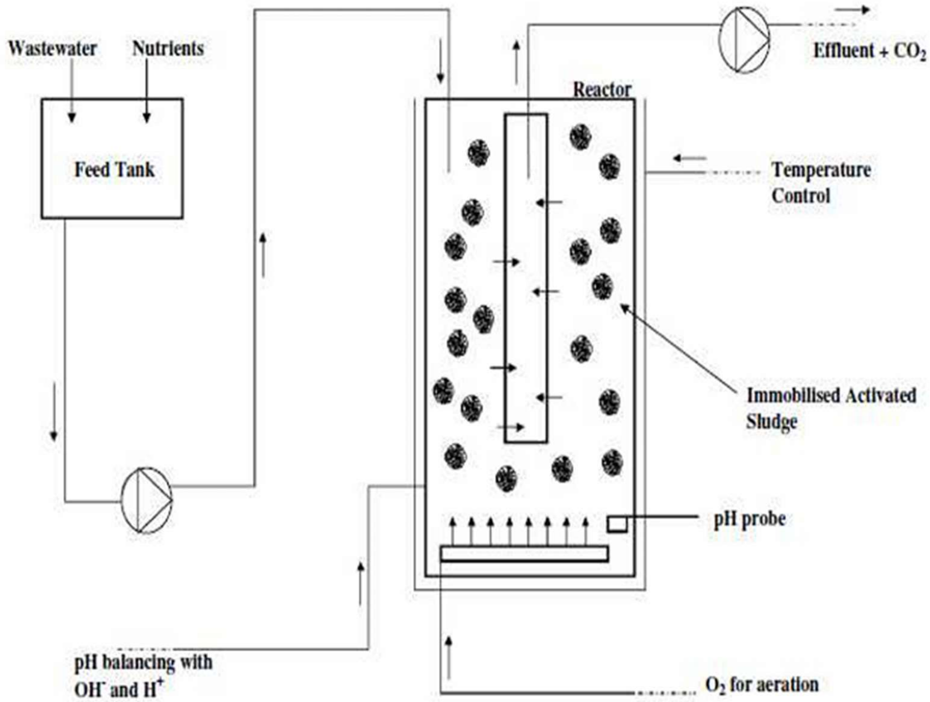

Figure 6: Membrane Bioreactors

Advantages of MBRs:

Smaller space required

Less sludge production

High-quality treated water

Can handle varying pollution levels

Disadvantages:

High cost

Regular maintenance

Sensitive to pressure, temperature, and pH changes

Prone to membrane fouling.

14.3. Physio-Chemical Treatment :

Coagulation is often used to remove colour from wastewater and can be applied before or after biological treatment, depending on factors like pH, sludge production, and pollutant type.

Treating alkaline wastewater works better with coagulation before biological steps. Pre-treatment usually creates less sludge and improves results for toxic, non-biodegradable dye waste. Combining physical, chemical, or advanced oxidation methods before biological treatment is often the most effective approach, chosen based on the specific wastewater type [14].

14.4. Adsorption :

Adsorption is commonly used to remove dyes from industrial wastewater, especially using activated carbon due to its high surface area and strong adsorption ability. It's most effective for certain dyes like cationic and acid dyes but less so for others.

However, using activated carbon on untreated wastewater isn't practical because of competition from other substances. It’s better used as a final or emergency treatment step. Since carbon is expensive and hard to regenerate, cheaper alternative materials are being explored.

Adsorption doesn’t destroy pollutants—it only transfers them, leading to sludge. To solve this, it's often combined with methods like oxidation to break down the adsorbed dyes. This allows reuse of the adsorbent and reduces waste. Combining adsorption with processes like ozonation or UV-H_2O_2 improves efficiency and helps regenerate the adsorbent.

More complex methods like solvent extraction followed by chemical stripping are also studied but are less common.

14.5. Adsorption with Biodegradation :

Biological treatments alone are not effective for textile wastewater due to tough chemicals. Adding activated carbon helps by absorbing toxins, protecting microbes, and boosting biodegradation. Most dye removal happens through microbial action, not just adsorption. This combined method improves treatment but has some limits.

14.6. Novel Biofiltration Method for the Treatment of Industrial Waste Water:

Heavy metals in industrial wastewater are toxic and harmful to life. Biofiltration is a low-cost method that can remove these metals even at very low levels (ppb). It’s effective for treating wastewater from industries like chemicals, textiles, dyes, and pharmaceuticals, helping meet regulations and reduce treatment costs. Biofilters are increasingly used for heavy metal removal [30].

15. Removal of Heavy Metals Using Ion Exchange Method :

Ion exchange removes harmful ions by replacing them with harmless ones. It's a simple and effective method for removing even tiny amounts of heavy metals like lead, mercury, cadmium, nickel, chromium, copper, and zinc from water and industrial wastewater using modern ion exchangers [31].

16. Removal of Mercury :

Mercury is a toxic pollutant that accumulates in living organisms and exists in various forms in wastewater. Ion exchange is a simple and effective method to remove even trace amounts of mercury. The ion exchanger Imac TMR, used in European industries, has thiol (-SH) groups that strongly bind Hg(II) ions. It can reduce mercury levels in wastewater to as low as 0.5–5 ppb, much better than other methods like precipitation, which only reach 1–3 ppm [31].

Table-2. Advantages and disadvantages of various waste water treatments

Process	Advantages	Disadvantages	References
Biological	A low-cost option, as direct, disperse, and basic dyes stick well to activated sludge.	Dyes are toxic and hard to break down. Acid and reactive dyes dissolve easily in water and don't stick well to sludge.	[16]
Coagulation	Cost-effective with good removal of disperse, sulfur, and vat dyes.	Works depends on pH, creates a lot of sludge, and poorly removes soluble dyes like azo, reactive, acid, and basic dyes.	[17-20]
Activated carbon adsorption	Effectively removes many dyes like azo, reactive, acid, and is especially good for basic dyes.	pH affects removal; not effective for disperse, sulfur, and vat dyes. Regeneration is costly with adsorbent loss and expensive disposal.	[21]
Ion exchange	Adsorbent can be reused, and dye recovery is possible in theory.	Dye recovery is possible, but ion exchange resins are dye-specific and costly to regenerate, making large-scale use expensive.	[22]
Advanced Oxidation Process	Creates many powerful radicals that remove color better than regular oxidants.	AOPs can form toxic byproducts, may not fully treat waste, are pH-sensitive, and currently too costly.	[23]
UV/O3	Used as a gas with no volume change, removes most dyes well—especially	Works best at neutral pH; poor for disperse dyes. Ozone is hard to handle,	[24-26]

	reactive dyes. Fast process with no sludge	costly, and has limited COD removal.	
UV/H2O2	No sludge, works quickly, and may reduce COD to some extent.	Not suitable for all dyes; needs solid removal and UV light has limits. Works better at low pH.	[27]
Photo-catalysis	No sludge, reduces COD well, and can use solar energy.	Limited light reach, catalyst clogs, and hard to separate fine catalyst from liquid.	[28]
Electro chemical	Effectively removes all dye types, can reduce COD, and works even with salty wastewater.	Produces sludge and possible pollution; costly power use; not fully industrial-ready; effectiveness varies by dye.	[29]

17. Conclusion:

This paper reviews different methods used for treating wastewater. It shows that there are many options available, especially for developing countries. Simple, low-cost technologies can be combined to create effective treatment systems.

Natural treatment methods—like wetlands or ponds—are becoming more popular among environmental experts. These methods are affordable, easy to maintain, last longer, and can help recover useful resources like clean water or nutrients.

The paper also discusses new challenges and treatment options, focusing on how these systems can be adjusted depending on the size and type of wastewater being treated.

References:

1. Almeida, M. C., Butler, D., and Friedler, E., 1999. "At-source domestic wastewater quality." Urban Water, vol. 1, pp. 49-55.

2. Touloumi, G., Pocock, S. J., Katsouyanni, K., and Trichopoulos, D., 1994. "Short-term effects of air pollution on daily mortality in Athens: a time-series analysis." International Journal of Epidemiology, vol. 23, pp. 957-967.

3. Okoh, A. I., Odjadjare, E. E., Igbinosa, E. O., and Osode, A. N., 2007. "Wastewater treatment plants as a source of microbial pathogens in receiving watersheds." African Journal of Biotechnology, vol. 6, pp. 2932 2944.

4. Gleick, P. H., 1998. "The human right to water." Water Policy, vol. 1, pp. 487-503.

5. Omran, A., 2011. "Factors influencing water treatment management performance in Malaysia: a case study in Pulau Pinang." Annals of the Faculty of Engineering Hunedoara, vol. 9, p. 53.

6. Brinck, W. L., Schliekelman, R. J., Bennett, D. L., Bell, C. R., and Markwood, I. M., 1978. "Radium removal efficiencies in water-treatment processes." Journal-American Water Works Association, vol. 70, pp. 31-35.

7. Li, Y. S., Yan, L., Xiang, C. B., and Hong, L. J., 2006. "Treatment of oily wastewater by organic–inorganic composite tubular ultrafiltration (UF) membranes." Desalination, vol. 196, pp. 76-83.

8. Sonune, A. and Ghate, R., 2004. "Developments in wastewater treatment methods." Desalination, vol. 167, pp. 55-63.

9. Sahu, O. P. and Chaudhari, P. K., 2013. "Review on chemical treatment of industrial waste water." Journal of Applied Sciences and Environmental Management, vol. 17, pp. 241-257.

10. coagulation: structures, mechanisms and practice." Journal of Water Supply: Research and Technology Aqua, vol. 48, pp. 201-210.

11. Arslan, I., Balcioğlu, I. A., and Bahnemann, D. W., 2000. "Advanced chemical oxidation of reactive dyes in simulated dyehouse effluents by ferrioxalate-Fenton/UV-A and TiO2/UV-A processes." Dyes and pigments, vol. 47, pp. 207-218.

12. Babel, S. and Kurniawan, T. A., 2003. "Low-cost adsorbents for heavy metals uptake from contaminated water: a review." Journal of Hazardous Materials, vol. 97, pp. 219-243.

13. Asgher, M., Azim, N., and Bhatti, H. N., 2009. "Decolorization of practical textile industry effluents by white rot fungus Coriolus versicolor IBL-04." Biochemical Engineering Journal, vol. 47, pp. 61-65.

14. Shah, M. P., 2016. "Industrial wastewater treatment: A challenging task in the industrial waste management." Advances in Recycling and Waste Management, vol. 2, p. 115.

15. Zhang, S., Wang, D., Quan, X., Zhou, L., and Zhang, X., 2013. "Multi-walled carbon nanotubes immobilized on zero-valent iron plates (Fe0-CNTs) for catalytic ozonation of

methylene blue as model compound in a bubbling reactor." Separation and Purification Technology, vol. 116, pp. 351-359.

16. Bandara, J., Morrison, C., Kiwi, J., Pulgarin, C., and Peringer, P., 1996. "Degradation/decoloration of concentrated solutions of Orange II. Kinetics and quantum yield for sunlight induced reactions via Fenton type reagents." Journal of Photochemistry and Photobiology A: Chemistry, vol. 99, pp. 57-66.

17. Borchate, S. S., Kullkarni, G. S., Kore, V. S., and Kore, S. V., 2014. "A review on applications of coagulation-flocculation and ballast flocculation for water and wastewater." International Journal of Innovations in Engineering and Technology, vol. 4, pp. 216-222.

18. Baughman, G. L. and Weber, E. J., 1994. "Transformation of dyes and related compounds in anoxic sediment: kinetics and products." Environmental Science and Technology, vol. 28, pp. 267-276.

19. Beydilli, M. I., Pavlostathis, S. G., and Tincher, W. C., 1998. "Decolorization and toxicity screening of selected reactive azo dyes under methanogenic conditions." Water Science and Technology, vol. 38, pp. 225-232.

20. Blümel, S. and Stolz, A., 2003. "Cloning and characterization of the gene coding for the aerobic azoreductase from Pigmentiphaga kullae K24." Applied Microbiology and Biotechnology, vol. 62, pp. 186 190.

21. Böhmer, U., Kirsten, C., Bley, T., and Noack, M., 2010. "White-rot fungi combined with lignite granules and lignitic xylite to decolorize textile industry wastewater." Engineering in Life Sciences, vol. 10, pp. 26 34.

22. Bragger, J. L., Lloyd, A. W., Soozandehfar, S. H., Bloomfield, S. F., Marriott, C., and Martin, G. P., 1997. "Investigations into the azo reducing activity of a common colonic microorganism." International Journal of Pharmaceutics, vol. 157, pp. 61-71.

23. Brown, J. P., 1981. "Reduction of polymeric azo and nitro dyes by intestinal bacteria." Appl. Environ. Microbiol., vol. 41, pp. 1283-1286.

24. Casieri, L., Varese, G. C., Anastasi, A., Prigione, V., Svobodova, K., Marchisio, V. F., and Novotný, Č., 2008. "Decolorization and detoxication of reactive industrial dyes by immobilized fungi Trametes pubescens and Pleurotus ostreatus." Folia Microbiologica, vol. 53, p. 44.

25. Singh, P. K. and Singh, R. L., 2017. "Bio-removal of azo dyes: A review." International Journal of Applied Sciences and Biotechnology, vol. 5, pp. 108-126.

26. Chen, H., Wang, R. F., and Cerniglia, C. E., 2004. "Molecular cloning, overexpression, purification, and characterization of an aerobic FMN-dependent azoreductase from Enterococcus faecalis." Protein Expression and Purification, vol. 34, pp. 302-310.

27. Chivukula, M. and Renganathan, V., 1995. "Phenolic azo dye oxidation by laccase from Pyricularia oryzae." Appl. Environ. Microbiol., vol. 61, pp. 4374-4377.

28. Chung, K. T., Stevens, S. E., and Cerniglia, C. E., 1992. "The reduction of azo dyes by the intestinal microflora." Critical Reviews in Microbiology, vol. 18, pp. 175-190.

29. Claus, H., Faber, G., and König, H., 2002. "Redox-mediated decolorization of synthetic dyes by fungal laccases." Applied Microbiology and Biotechnology, vol. 59, pp. 672-678.

30. Srivastava, N. K. and Majumder, C. B., 2008. "Novel biofiltration methods for the treatment of heavy metals from industrial wastewater." Journal of Hazardous Materials, vol. 151, pp. 1-8.

31. Dabrowski, A., Hubicki, ., Podko cielny, P., and obens, E., 200 . "Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method." Chemosphere, vol. 56, pp. 91-106.

TITLE OF THE DISSERTATION

NANOMATERIALS AND ITS APPLICATION IN ENERGY

UNIVERSITY OF CALCUTTA

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Signature of the Student

NANOMATERIALS
AND
ITS APPLICATION IN ENERGY

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ABSTRACT

Nanomaterials are materials with dimensions at nanoscale,giving them many unique properties. These features makethem highly useful in the energy sector.they enhance the performance of solar cells, batteries, fuel cells and Supercapacitors by improving efficiency,storage capacity and durability. As the world moves toward cleaner energy, nanomaterials play a vital role in developing advanced and sustainable energy solutions.

In this review work I discussed about introduction to nanomaterials, carbon nanotubes, solar cells, fuel cells, hydrogen storage, ultracapacitors and lithium ion batteries

Introduction

Nanomaterials are materials that have at least one dimension in the nanometer range, typically between 1 and 100 nanometers. This size range is crucial because it imparts unique physical, chemical, and biological properties to the materials that are not observed in their bulk counterparts. **At the nanoscale, materials exhibit increased surface area to volume ratios, quantum effects, and other phenomena that can significantly alter their behavior and interactions**.

Nanomaterials can be classified into various types based on their dimensions: zero-dimensional (0D) nanoparticles, one-dimensional (1D) nanowires and nanotubes, two-dimensional (2D) nanofilms and nanocoatings, and three-dimensional (3D) nanocomposites. Each type exhibits distinct characteristics and offers specific advantages for different technological applications.

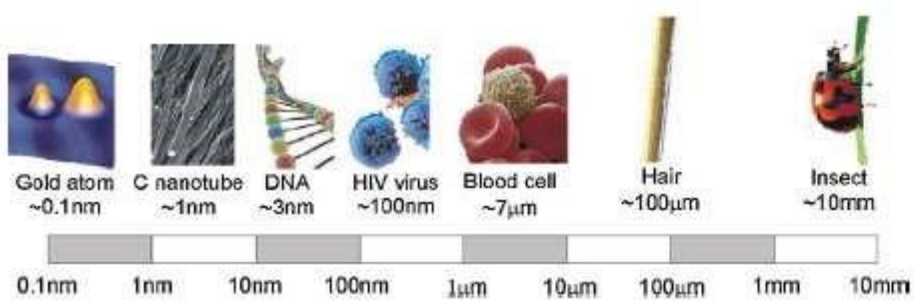


Figure 1: Length scale and sone examples

Types of Nanomaterials:

1. Nanoparticles: Nanoparticles are one of the most common forms of nanomaterials. Nanoparticles are particles with dimensions typically between 1 and 100 nanometers. They can be made from metals, metal oxides, polymers, and other materials.

2. Nanotubes and Nanowires: Carbon nanotubes (CNTs) and various nanowires (such as silicon nanowires) are prominent examples of one-dimensional nanomaterials. CNTs are renowned for their exceptional strength, electrical conductivity, and thermal conductivity, making them valuable in composite materials, electronics, and energy storage.

3. Nanofilms and Nanocoatings: These are thin layers of material applied at the nanoscale.

4. Nanocomposites: Nanocomposites combine nanoscale materials with other materials to enhance their properties.

❖ Unique Properties of Nanomaterials:

- Nanomaterials exhibit several unique properties that make them highly desirable for various applications:
- **Increased Surface Area**: Nanomaterials have a much higher surface area to volume ratio compared to bulk materials. This increased surface area enhances their reactivity, making them effective catalysts in chemical reactions.

- **Quantum Effects:** At the nanoscale, quantum effects become significant, altering the electrical, optical, and magnetic properties of materials. These effects can be harnessed in applications such as quantum computing, imaging, and photovoltaics.

- **Mechanical Strength:** Many nanomaterials exhibit superior mechanical properties. For example, carbon nanotubes and graphene have tensile strengths much higher than that of steel, making them ideal for use in lightweight, high-strength materials.

- **Optical Properties:** Nanomaterials can interact with light in unique ways. For example, gold nanoparticles exhibit different colors based on their size and shape, which can be utilized in sensors and imaging applications.
- **Electrical Conductivity:** Nanomaterials such as graphene and carbon nanotubes have excellent electrical conductivity, making them suitable for use in electronic devices, conductive films, and energy storage systems.

❖ Scope of Nanomaterials :

1. Scientific Research and Development
2. Electronics and computing
3. Medicine and healthcare
4. Energy and environment
5. Materials and manufacturing
6. Cosmetics and personal care
7. Agicalture and food and many more.

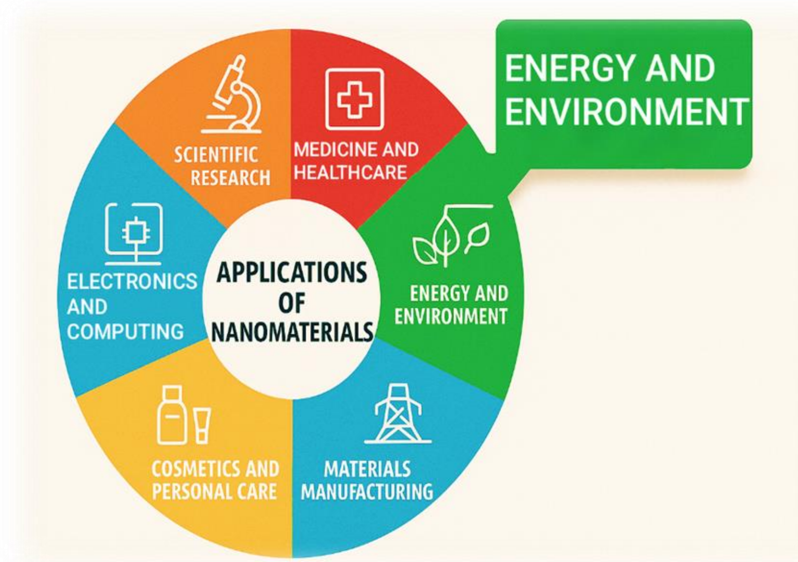


Figure 2: scope of nanomaterials

But before we further proceed about its application, let's first briefly discuss about one of the basis of nanotechnology, **Carbon nanotubes(**CNT**).**

❖ Carbon nanotubes: A brief introduction

- A carbon nanotube (CNT) is a hexagonal array of carbon atoms rolled up into a long, thin, hollow cylinder and are known for their size, shape, and remarkable physical properties. They can be manipulated chemically and physically for their application in material science, electronics, energy management, biomedical application and many more.

- **Types of Carbon Nanotubes**

Carbon nanotubes can be classified into two main types based on their structure:

1. Single-Walled Carbon Nanotubes (SWCNTs): These consist of a single layer of graphene rolled into a cylindrical shape with diameters typically ranging from 0.7 to 2 nanometers. The properties of SWCNTs depend on their chirality, which is defined by the angle at which the graphene sheet is rolled. Chirality affects the electronic properties, determining whether the SWCNT behaves as a metal or a semiconductor.

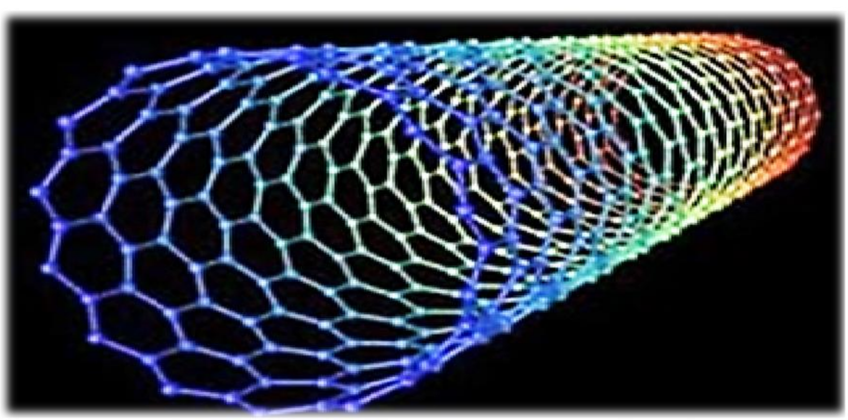


Figure 3: single walled carbon nanotubes

2. Multi-Walled Carbon Nanotubes (MWCNTs): These consist of multiple concentric layers of graphene rolled into cylinders, with diameters ranging from 2 to 100 nanometers. The interlayer spacing in MWCNTs is similar to the spacing between graphene layers in graphite. MWCNTs have more complex structures and typically exhibit higher mechanical strength and stability compared to SWCNTs.

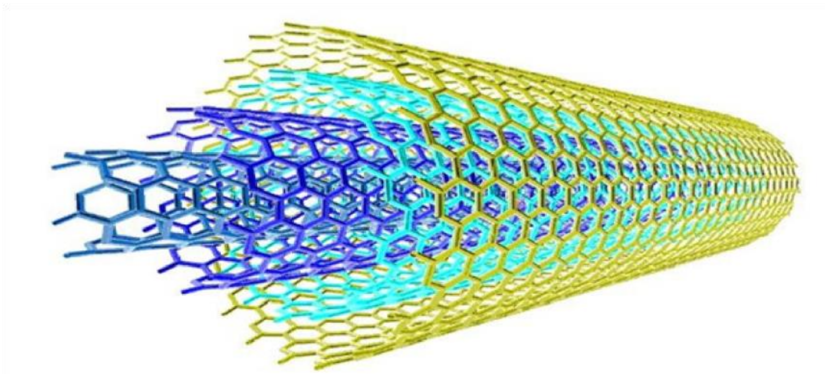


Figure 4: multi-walled carbon nanotubes

❖ Properties of Carbon Nanotubes:

- **1. Strength:** CNTs are among the strongest materials known, with a tensile strength about 100 times greater than steel at a fraction of the weight. This exceptional strength arises from the **strong sp2 carbon-carbon bonds** in the graphene structure. CNTs also **exhibit high flexibility** and can be bent without breaking.

- **2. Electrical Properties**: The sp^2 bonds between carbon atoms results in conducting nature of carbon nanotubes. Depending on their chirality, SWCNTs can be either metallic or semiconducting. Metallic SWCNTs have excellent electrical conductivity, making them potential candidates for nanoscale electronic devices. Semiconducting SWCNTs can be used in transistors, sensors, and other electronic components. MWCNTs generally exhibit metallic behavior due to the overlap of electronic states from multiple layers.

- **3. Thermal Properties:** CNTs have **high thermal conductivity,** surpassing that of diamond. This property makes them ideal for applications in thermal management, such as heat sinks and thermal interface materials. The thermal conductivity of CNTs arises from the **efficient phonon transport** along the length of the nanotube.

- **4. Chemical Properties:** The surface of CNTs can be chemically modified to enhance their solubility, dispersibility, and compatibility with other materials. Functionalization of CNTs involves attaching various chemical groups to the nanotube surface, enabling their use in composites, sensors, and biomedical applications.

Applications of Carbon Nanotubes:

1. Electronics: CNTs are used in the development of nanoscale electronic devices, including **transistors, interconnects, and sensors**. Their high electrical conductivity and small size make them suitable for future generations of **electronic circuits**.

2. Composite Materials: The exceptional mechanical properties of CNTs make them ideal for **reinforcing composite materials**. CNT-reinforced polymers, metals, and ceramics exhibit improved strength and durability.

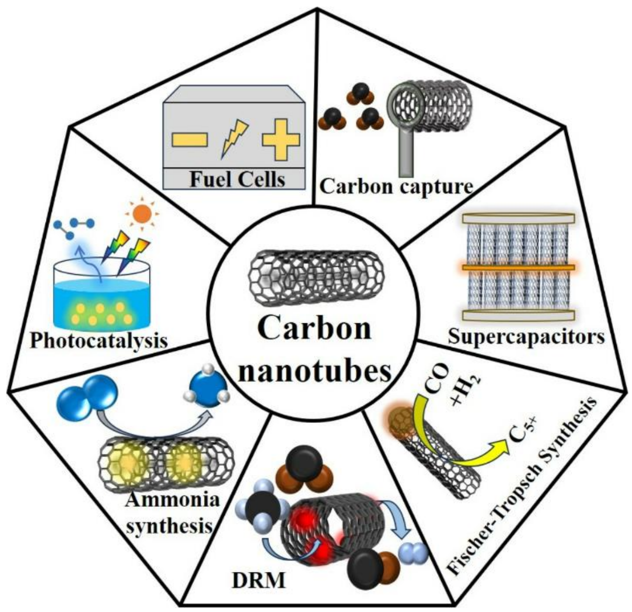


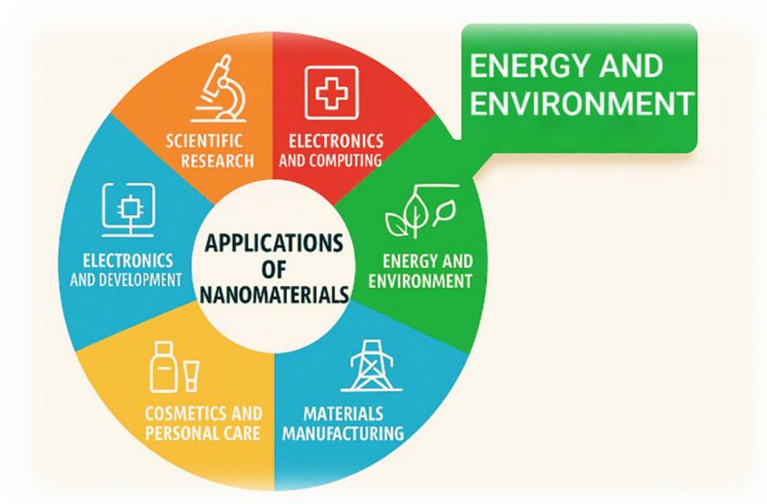
Figure 5: Recent advances in carbon nanotube technology

3. Energy Storage: CNTs are employed in energy storage devices, such as **batteries and supercapacitors,** due to their high surface area and excellent electrical conductivity.

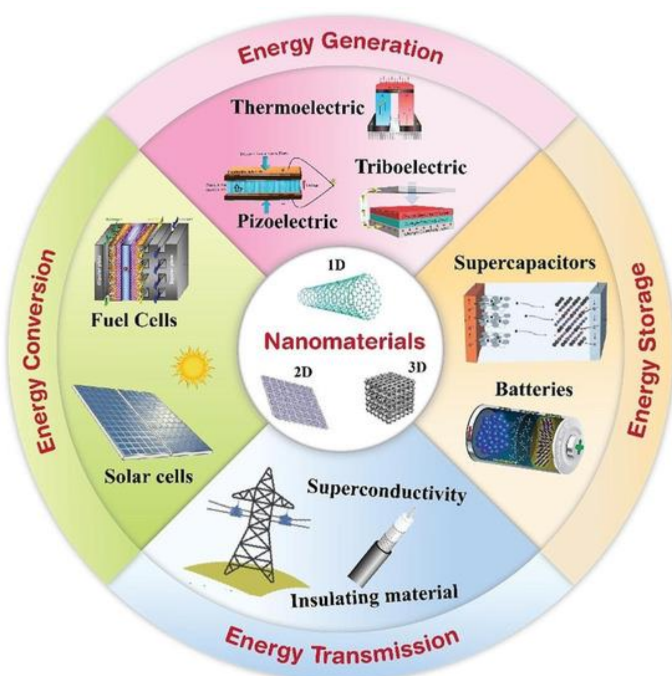
4. Biomedical Applications: CNTs are used in various biomedical applications, including **drug delivery, biosensing, and tissue engineering.**

5. Environmental Applications: CNTs are used in **water purification** and environmental remediation due to their high adsorption capacity and chemical stability.

Applications of Nanomaterials in Energy



The energy sector is undergoing a transformative shift towards more sustainable, efficient, and clean energy solutions. Nanomaterials play a critical role in this transformation due to their exceptional properties. These properties include increased surface area, quantum effects, and enhanced reactivity, which make nanomaterials highly suitable for a wide range of applications, including the energy sector.



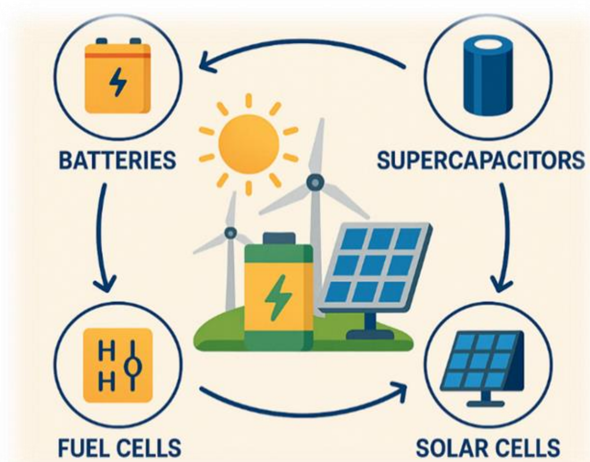
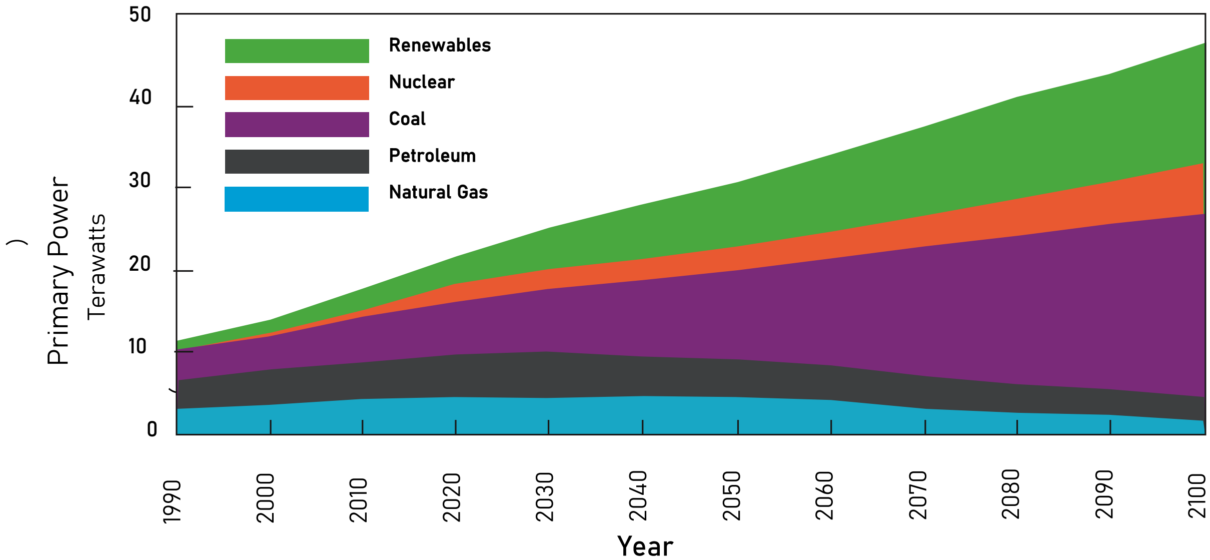


Figure 6: nanotech in energy



Projected Global Energy Demand

A rapidly increasing amount of renewable energy will be needed to meet global demand while lowering carbon emissions. And the role of nanotechnology in renewable energy production and storage is very significant.

A. Nanotechnology: Generating Energy

1. SOLAR CELLS

- The technology of solar cells, as a source of renewable energy, is still relatively expensive when compared with fossil fuels used to generate electricity. The **efficiency of solar cells is quite low**, i.e., a maximum of 30%, but its commonly used type has approximately 15%–20% efficiency. **However, it is hoped that by using nanotechnology, efficiencies of solar cells will be higher by enhancing light absorption, charge separation, and**

conversion processes. Solar cells can be used as a power source for electrical household or electronic items, such as calculators and computers.

- Solar cells generally consist of a surface oxide layer and the catalytic platinum layer that are able to convert sunlight into electrical energy. Basically, the working principle of a solar cell (photovoltaic cell) is that photons coming from the sun or light hit the solar cell and release electrons that produce electric current. When electrons are liberated, electrons will collide with the closest atoms. **Although the energy required to release electrons are sufficient, these electrons can no longer be released as a limited one electron per solar photon applied. Limitation of these released electrons causes low solar cell efficiency, which is 15%–20%.**

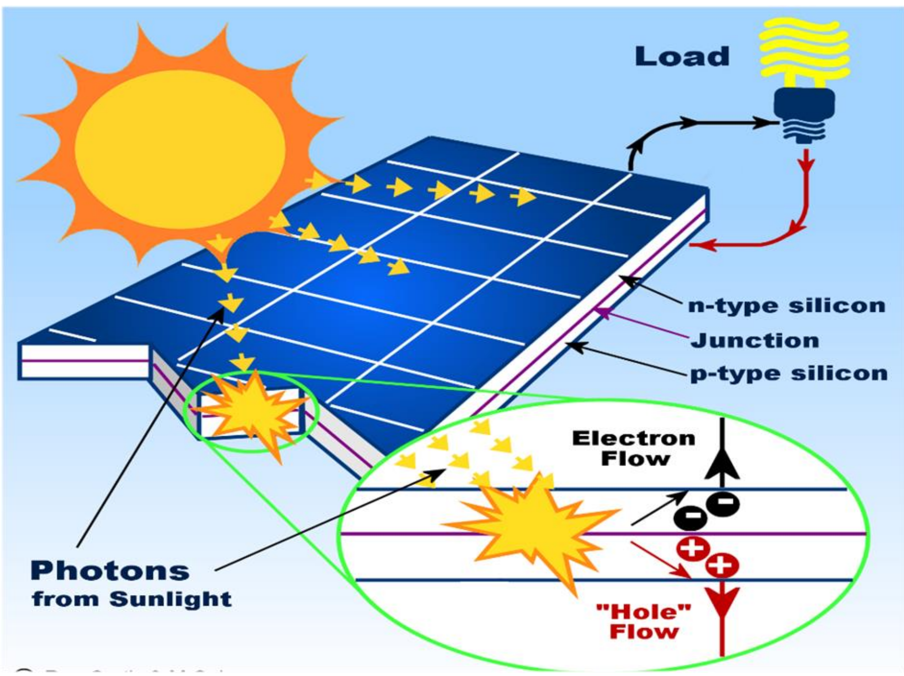


Figure 7: working principle of a solar cell

- **Use of nanometrials:**

Therefore, many are using nanotechnology to develop the tools for solar cell technology such **as carbon nanotubes (CNTs), fullerenes, and quantum dots** recently.

- **Quantum dots(QDs)** are nanoscale semiconductor crystals with **size-tunable** optical properties, making them ideal candidates for next-generation photovoltaic devices. By adjusting the size and composition of QDs, researchers can optimize their absorption spectra to match the solar spectrum more closely. This capability

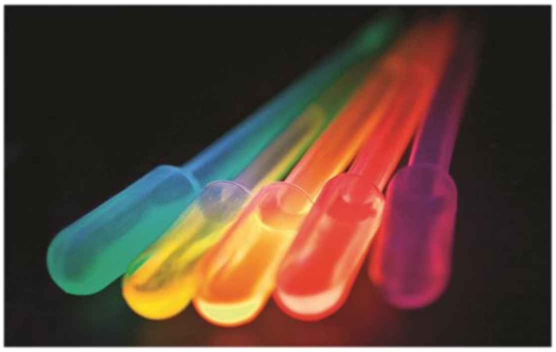


Figure 8: Quantum dots

enhances light harvesting and reduces energy losses due to mismatched bandgaps, thereby improving overall solar cell efficiency(**by about 42%**). Additionally, QDs can be integrated into thin-film solar cells and multi-junction solar cells to achieve higher efficiencies and lower production costs.

❖ **Gratzel cells**, one variant of solar cells, consist of a layer of nano particles (usually TiO2) that are immersed in a photosensitizer. These cells are often referred to as **Dye-Sensitized Solar Cells (DSSC)**. Gratzel cells have a function to convert the energy of sunlight into electrical current in which active chemicals continue to be regenerated in the cells. The idea was first introduced by Professor Gratzel.

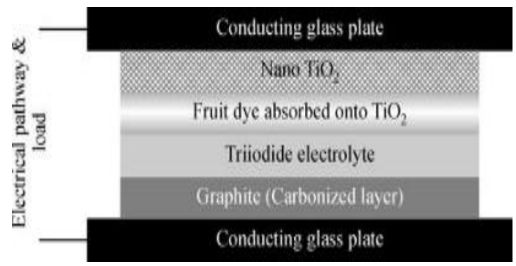


Figure 9: schematic figure of Gratzel cell layer

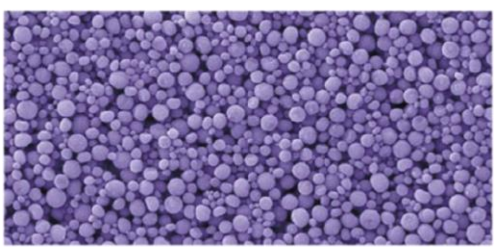


Figure 10: Scanning electron microscopy of nano-sized TiO_2 having particle size of 10–300 nm

2. FUEL CELL

Fuel cell is an electrochemical device that converts the chemical energy of a fuel(like hydrogen) and an oxidant (like oxygen) directly into electrical energy through chemical reaction. Unlike batteries fuel cells don't store energy; they produce it continuously as long as fuel source is applied.

❖ Fuel cell consists of **three main parts: anode, cathode, and electrolyte** in which charge transfer occurs from the anode to the cathode. As byproducts, fuel cells also produce water, heat, and nitrogen oxides in very small amounts (depending on the fuel used). . Energy efficiency of fuel cells in general is approximately 40%–60% or 85% when the waste heat is also converted back into electrical energy.

❖ Working principle for the fuel cell which uses hydrogen fuel and oxidizing agent in the form of oxygen, the hydrogen would releases electrons to form positively charged hydrogen ions at the anode. The electrons will pass through the wires and produce electric current. Meanwhile, the hydrogen ions will pass through the electrolyte to the cathode. Electrons will also return to the cathode, converting oxygen into negatively charged ion. The negatively charged oxygen then reacts with hydrogen ions to form water.

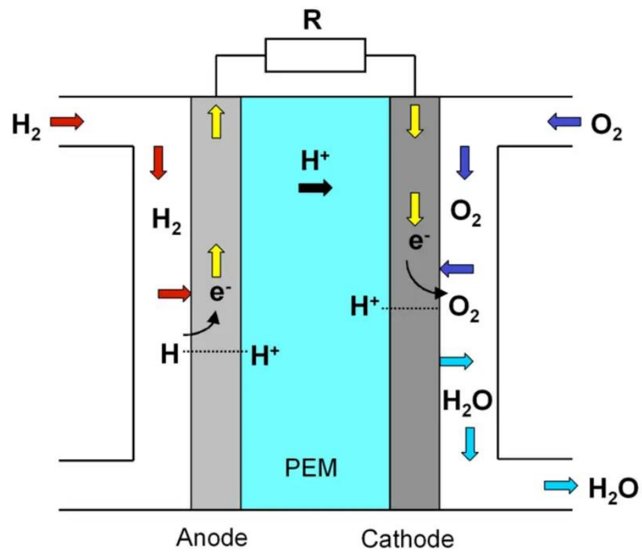


Figure 11: a hydrogen fuel cell and its working principle

❖ The most important parts of the fuel cell are:

1) Electrolytes (the type of electrolyte determines the type of fuel cell);

2) Fuels which are used for the operation;

3) The catalyst at the anode; the commonly used catalysts are **platinum;**

4) The catalyst at the cathode which is typically made of nickel.

❖ **The use of fuel cells is still very limited due to three main issues:**

1) The price is expensive because of the fabrication and the limited life time.
2) The platinum metal catalyst is too expensive to use in industrial application.
3) Hydrogen storage is difficult and expensive.

❖ **Use of nanomaterials:**

➢ One way to minimize the use of catalysts is the use of nano material, e.g., **forming a nano-sized platinum metal**. **Platinum nano-catalyst is much more active and requires smaller amounts** to produce the same conversion compared to the conventional catalyst. In addition, The use of pure platinum can be replaced with other metals or a mixture of platinum with other metals.

- In addition, researchers have shown that **carbon nanotubes with vertical arrangement can be used as catalysts for fuel cells**. Carbon nanotubes added to the nitrogen atom would be cheaper and more durable than currently used platinum catalysts. **Carbon nanotubes have a longer operational stability and less deactivated by carbon monoxide.**

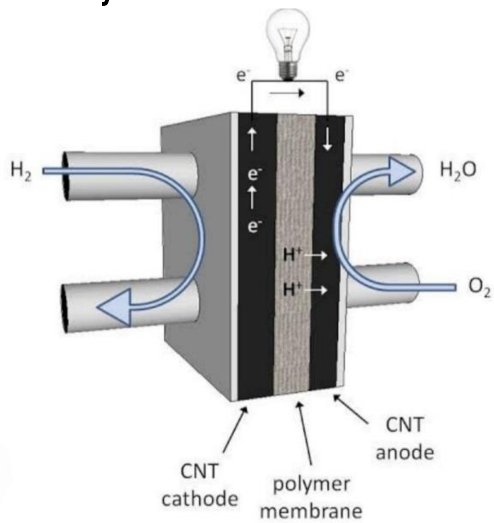


Figure 12: use of nanotube in fuel cell

- For **proton exchange membrane fuel cells (PEMFC)**, researchers have developed a proton exchange membrane using a silicon layer with a pore diameter of approximately 5 nm which is coated with a layer of **porous silica**. Water molecules attached to the **nanopore** wall will dilute acid compounds to form an acid solution, providing an **easy way for hydrogen to pass through the membrane**.

❖ HYDROGEN STORAGE

Fuel cell is being developed to replace the oil-based combustion engine. However, there are several obstacles to fuel cell develop ment. The greatest obstacle is the storage of hydrogen fuel cell. The current hydrogen storage system is not yet able to meet the needs of users of fuel cell vehicles. **Nanocatalysts**, such as metal nanoparticles and metal-organic frameworks (MOFs), enhance the efficiency of water electrolysis and hydrogen evolution reactions.

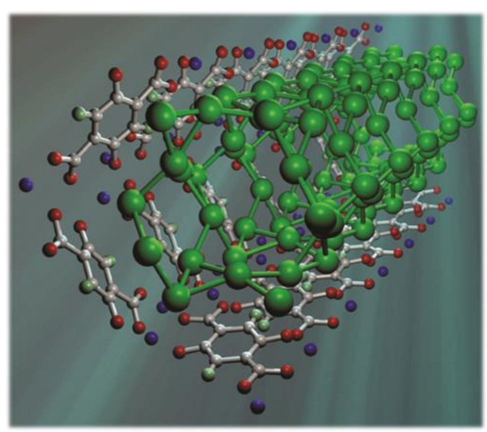


Figure 13: metal-organic framework

- **a reversible hydrogen absorption by metal-based compounds such as hydrides and nitrides:**

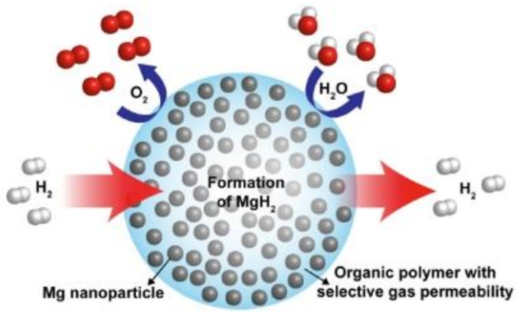


Figure 14: Formation of magnesium hydride

Researchers have used magnesium hydride (MgH2) to store hydrogen. However the release of hydrogen occurs at high temperatures only. **But Intensive milling has been able to produce nanocrystal line magnesium materials that have a larger surface area so that they can release and absorb hydrogen faster.**

- **storage in carbon nanostructures such as carbon nanotubes, alkali-doped carbon nanotubes:**

In addition to the hydride method, the current method under development is the use of **carbon nano structure**. **Large surface area** and **abundant pore volume** of this material makes the nanostructured material a potential hydrogen storage medium. It have been found that **single-walled carbon nanotube** has a high reversible hydrogen storage capacity.

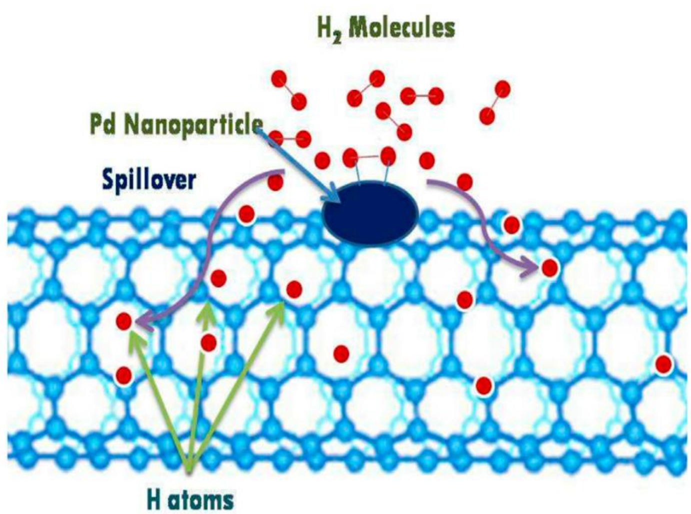


Figure 15: Hydrogen storage in carbon nanotube

Li-doped and K-doped multi-walled carbon nanotube has a high H_2 uptake capacity.

B. Nanotechnology: Storing Energy

1. ULTRACAPACITORS OR SUPERCAPACITORS

Figure 16: supercapacitors

- **Capacitors** have the ability to store energy in the form of an electric field. Capacitors physically store and release charge as electrons rather than as ions. They are held there by relatively **weak electrical forces** rather than by the stronger chemical bonds that hold ions in a battery. Thus, **a capacitor can charge and discharge very quickly**.

- A new type of capacitor, called **Ultra-capacitors** are capacitor-based energy storage cells that can **store and provide energy in large quantities** through a **double-layer nanostructure.** However, ultra-capacitors require a larger size than conventional batteries to charge the same amount of electricity. Ultracapacitors may be very useful for storing power generated **by solar panels or wind farms,** often used in **fuel cell vehicles** to provide extra power to the vehicle.

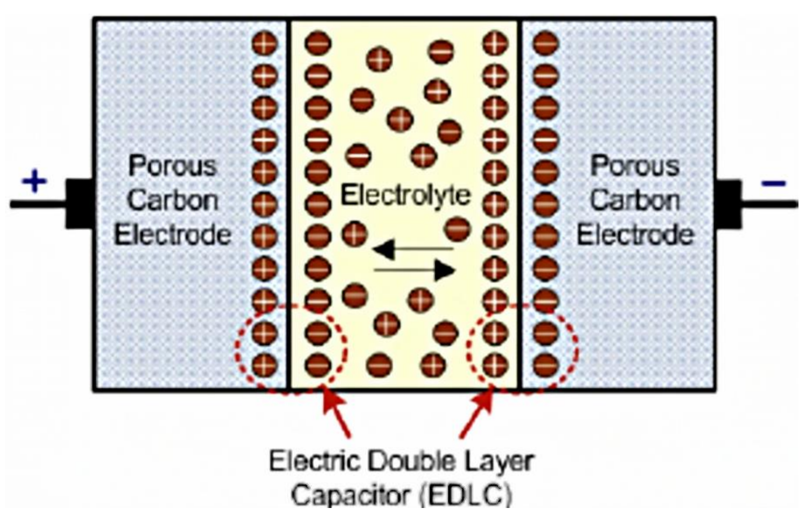


Figure 17: a working diagram of ultracapacitor

❖ **Limitations of energy storage** was overcome by using **carbon nanotubes** which have a layer in a vertical position. The current ultra-capacitors having electrodes made of activated carbon are so porous that the surface area of ultra-capacitors is very large. However, **carbon pores do not have a regular shape and size which result in low efficiency. Incorporating CNT results in the increase of the effective surface area** which further **increase the storage capacity** significantly similar to the Li-ion battery in the same size.

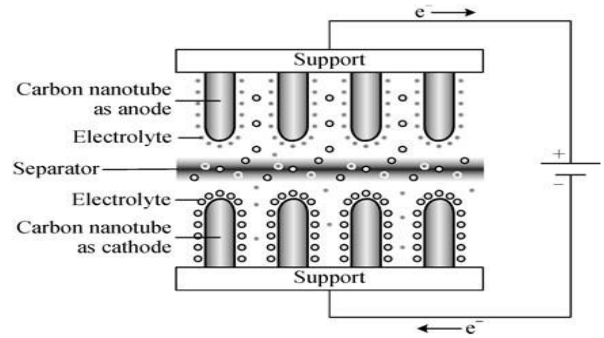


Figure 18: Diagram of CNT-based ultra-capacitors

2. LITHIUM-ION BATTERIES

Lithium-ion or Li-ion battery is one of the batteries that can be recharged and has a higher energy density than Ni-H and Ni-Cd batteries [8]. When the battery is used, the ion of lithium moves from anode (positive electrode) to cathode (negative electrode) and vise-versa when it is recharged.

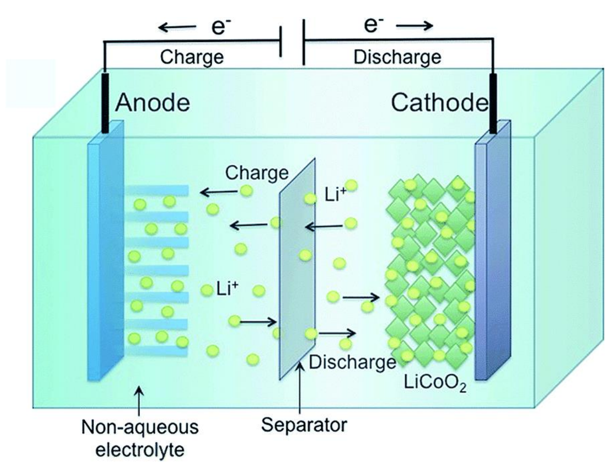


Figure 20: Li-ion battery

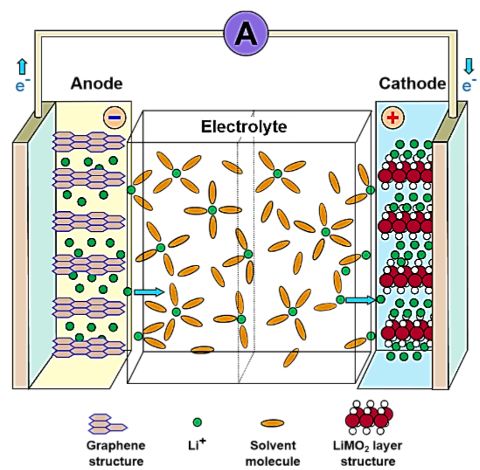


Figure 19: Li-ion battery in discharge mode

❖ Nanomaterials are known to have interesting and tunable optical, electrical and mechanical properties that can be used **for electrochemical energy storage.** The high surface area and unique electronic properties of nanomaterials enable **faster ion transport and greater storage capacity.**

❖ They can be used in nanoelectrodes as well as in solid polymer electrolytes. For example, nanostructured electrodes, such as those made from graphene or **silicon** nanowires, allow for more efficient charge and discharge cycles. This results in batteries with higher energy densities, faster charging times, and longer lifespans. Particularly the Si-C nanocomposites are worthy of interest as their specific capacity can reach 1000mA·h·g−1 for more than 100 cycles, while the theoretical capacity of graphene is only 372mA·h·g.

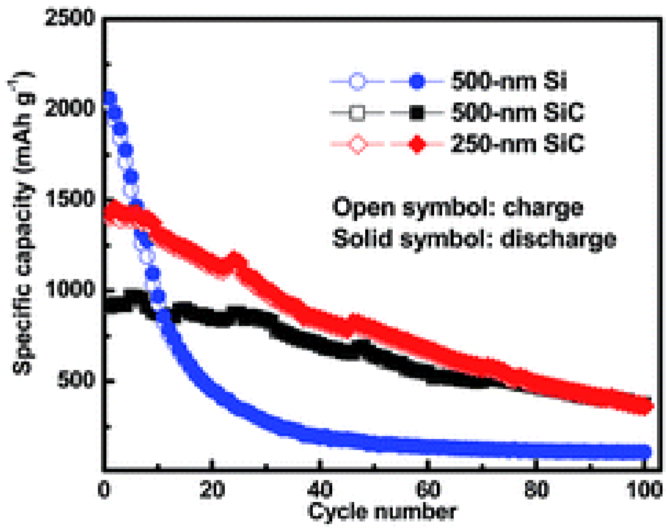


Figure 21: specific capacity vs cycle for Si-C

❖ Beyond lithium-ion batteries, nanomaterials are driving advancements in next-generation battery technologies, such as lithium-sulfur (Li-S) and lithium-air (Li-O2) batteries. Li-S batteries have the potential to offer higher energy densities compared to traditional lithium-ion batteries. However, challenges such as the dissolution of sulfur species and limited cycle life need to be addressed.

LIMITATIONS

Nonotechnology holds great promise for revolutionizing the energy sector,but there are still some challenges that needs to be addressed.

1. **High Production Cost** - Synthesis and processing of nanomaterials often require expensive equipment and complex techniques.
2. **Scalability Issues** - Difficult to scale up lab-based nanotech solutions to industrial levels while maintaining efficiency and cost-effectiveness.
3. **Integration with Existing Systems** - Difficulties in integrating nanotech components into current infrastructure (e.g., solar panels, batteries).

4. **Stability and Durability -** Nanomaterials may degrade faster under real-world conditions like heat, moisture, or UV exposure.
5. **Toxicity and Environmental Concerns -** Potential health and ecological risks due to unknown long-term effects of nanomaterial exposure.
6. **Recycling and Waste Management -** Limited knowledge on how to safely dispose of or recycle nanomaterials used in energy systems.
7. **Complex Fabrication Processes -** Many nanotech devices require precise and intricate fabrication steps, increasing time and cost.
8. **Energy Consumption in Production -** Some nanomaterial synthesis methods consume more energy than conventional alternatives.

CONCLUSION

In conclusion, nanomaterials represent a pivotal advancement in the field of energy technology, offering transformative solutions across various sectors including energy storage, renewable energy, and emerging technologies. The applications of nanomaterials in energy have demonstrated remarkable potential to address critical challenges such as energy sustainability, efficiency, and environmental impact. Looking forward, addressing challenges related to scalability, stability, safety, and integration will be critical to realizing the full potential of nanomaterials in commercial energy applications. By leveraging the unique properties of nanomaterials, we can pave the way towards a greener future while meeting the growing global demand for reliable and environmentally responsible energy solutions.

REFERENCES

1. Ferric Christian , Edith ,Selli,Dendy Adityawarman, Antonious Indarto,Application of nanotechnologies inn the energy sector: a brief and short review,Frontiers in energy,2003,7(1),7-16
2. R. Chaudhary, V.K. Jain, N. Ansar, Nanomaterials introduction and applications,9788197585937,1-11,119-127

3. Sonia Khanna and Nazmul Islam, Carbon Nanotubes-Properties and Applications, organic and medicinal chemistry international journal,2018,7(1), 1-5
4. Coline Boulanger, Nanomaterials for batteries, Journal de physique et de chimie des étudiants,2022,5,31-35
5. Umesh Kumar Singh, Application of Nanotechnology for Sustainable Energy: A Review Paper, JETIR,2018, Volume 5, Issue 9
6. nano_energy_brochure_upload_feb_12_2014 (1).pdf
7. Royal society and royal academy of engineering.(2004).nanoscience and nano technologies: opportunities and uncertainities
8. Luther W. Application of Nano-Technologies in the Energy Sector. Germany: Hessian Ministry of Economy, Transport, Urban and Regional Development, 2008
9. Bullis K. Higher-capacity lithium-ion batteries technology review. 2010-06-11, http://www.technologyreview.com/energy/ 17553/?a =f
10. Dai L, Chang D W, Baek J B, Lu W. Carbon nanomaterials for advanced energy conversion and storage. Small, 2012, 8(8): 1130 1166
11. Bewag A. Energy moving into the future. The fuel cell: A technical report. 2012-10, http://www.fuelcellpark.com/projekt/down/ Br_BZ_en.pdf
12. Sun S, Jaouen F, Dodelet J P. Controlled growth of Pt nanowires on Ferric CHRISTIAN et al. Application of nanotechnologies in the energy sector 17 carbon nanospheres and their enhanced performance as electro catalysts in PEM fuel cells. Advanced Materials (Deerfield Beach, Fla.), 2008, 20(20): 3900–3904
13. Wu X B, Chen P, Lin J, Tan K L. Hydrogen uptake by carbon nanotubes. International Journal of Hydrogen Energy, 2000, 25(3): 261–265
14. Sahoo,S.,Parija,B.,& Mohapatra,S.,limitations of nanomaterials in clean energy applications:an overview. journal of cleaner production,333,130171

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TOPIC : ***METALLODRUGS IN MEDICINAL INORGANIC CHEMISTRY.***

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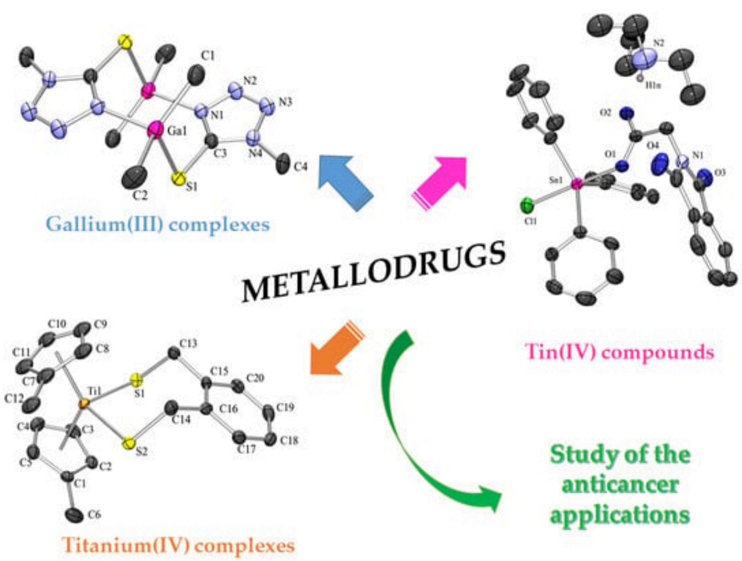
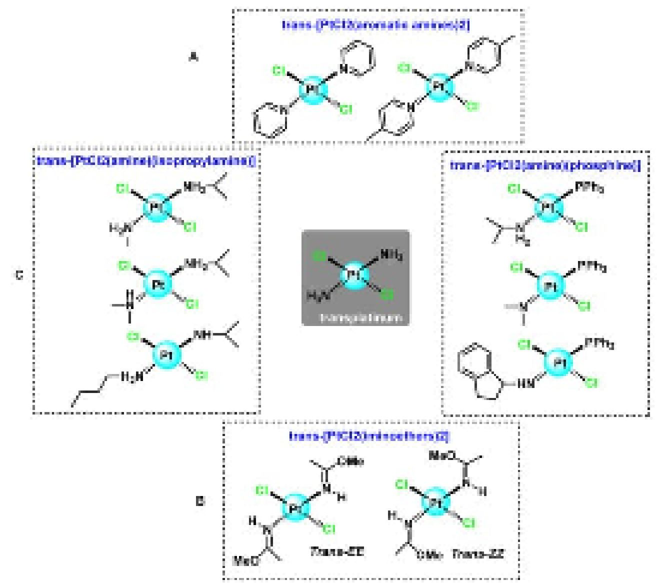
- I would like to express my gratitude to my respected professor Dr. Jaydip Gangopadhyay sir for guiding and helping me to execute my dissertation project which was about metallodrugs in medicinal inorganic chemistry .This research like project work turned beneficial for me as I get know about several drugs used world wide and also some about those drugs which are on the verge of emerging. I ,whole heartedly greatful to my mentor for his support throughout.

1.INTRODUCTION

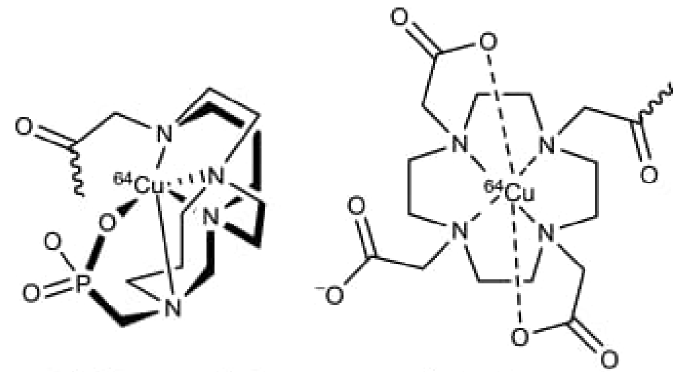
Metallodrugs are therapeutic agents that incorporate metal ions or metal-containing complexes, representing a vital area in medicinal inorganic chemistry. These drugs leverage the unique chemical properties of metals—such as variable oxidation states, coordination geometry, and redox activity—to interact with biological targets in ways that organic drugs cannot. Commonly used in cancer treatment, antimicrobial therapy, and diagnostics, metallodrugs expand the range of pharmaceutical mechanisms and offer novel approaches for disease management and targeted therapy.





2.DIAGNOSTIC METALLODRUGS

- Diagnostic metallodrugs are metal-containing compounds used in medical imaging to detect, monitor, or diagnose diseases. They often serve as contrast agents in techniques like MRI, PET, or SPECT, enhancing image clarity and targeting specific biological structures or functions.



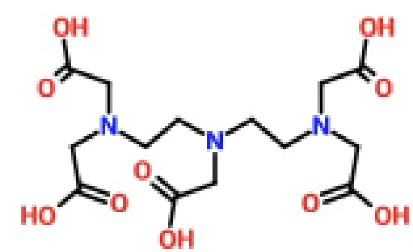
^{64}Cu CB-TE1A1P

^{64}Cu-TETA

Key Characteristics of Diagnostic Metallodrugs:

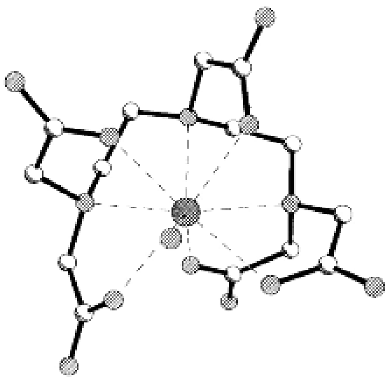
- **Metal Core** Usually transition metals or lanthanides (e.g., Gd^{3+}, Tc^{99m}, Ga^{68}, Cu^{64}). Metals adopt distinct three dimensional shapes (e.g., square planar, octahedral), influencing how the drug interacts with biological targets like DNA, proteins, or enzymes. Transition elements and lanthanides are vital in diagnostic metallodrugs due to their distinct chemical and physical properties.

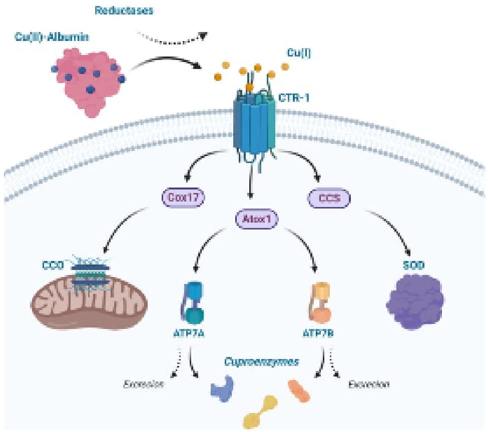
- **Chelator/Carrier Ligand** Stabilizes the metal and enhances target specificity. They enhance solubility, control biodistribution, and maintain the metal's diagnostic properties, such as radiolabeling or magnetic activity. Metal chelating agents are diethylenetriaminepentaacetic acid [H5DTPA] and 1,4,7,10-tetraaza-cyclododecane-1,4,7,10-tetracetic acid [H4DOTA].



- **Administration** Typically intravenous injection to ensure rapid and controlled delivery, especially for diagnostic or anticancer purposes. In some cases, oral or intramuscular

MAJOR CLASSES BY IMAGING MODALITY

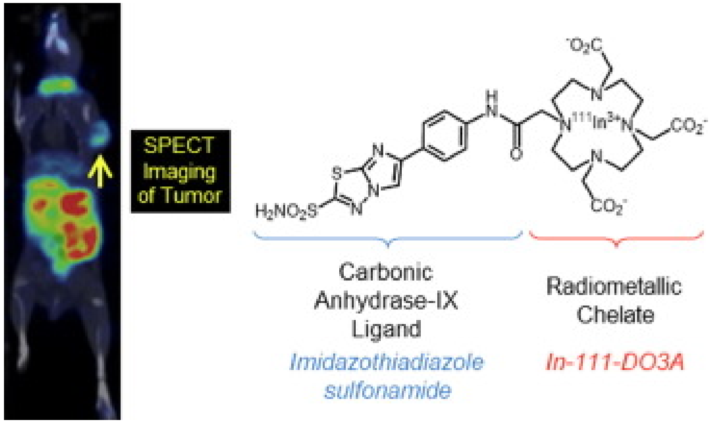




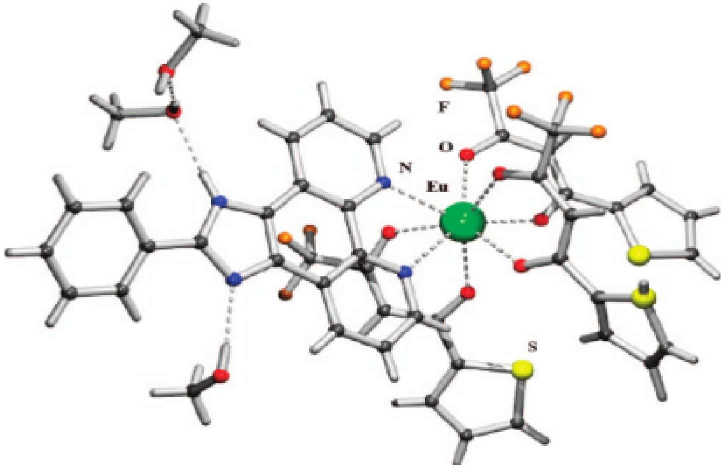
- **1. MRI (Magnetic Resonance Imaging) Contrast Agents**
- **Primary Metal:** **Gadolinium (Gd^{3+})**
- **Mechanism:** Shortens T1 (or T2) relaxation times of nearby water protons to improve image contrast.
- **Examples:**
  - **Gd-DTPA (Magnevist®)**: Most widely used T1 contrast agent.
  - **Gd-DOTA (Dotarem®)**: Macrocyclic, more stable than linear agents.
- **Risks:** Nephrogenic systemic fibrosis (NSF) in renal-impaired patients due to Gd release.
- **2. PET (Positron Emission Tomography) Imaging Agents**
- **Primary Metals:** **Gallium-68, Copper-64, Zirconium-89**
- **Mechanism:** Emit positrons (β^+) that annihilate with electrons to produce γ-rays detected by PET scanner.
- **Examples:**
  - **[^{68}Ga]Ga-DOTATATE**: Targets somatostatin receptors (used in neuroendocrine tumor imaging).
  - **[^{64}Cu]Cu-ATSM**: Used in hypoxia imaging.
- **Advantages:** High sensitivity, quantitative data, early detection.

MAJOR CLASSES BY IMAGING MODALITY

- **3. SPECT (Single Photon Emission Computed Tomography) Agents**
  Primary Metals: Technetium-99m (^{99m}Tc), Indium-111
  Mechanism: The mechanism of SPECT (Single Photon Emission Computed Tomography) with metallodrugs involves administering a radiolabeled metal complex that emits gamma rays, allowing real-time imaging of its biodistribution and accumulation in specific tissues or organs.
  Examples:
  - **^{99m}Tc-MDP**: Used for bone scans.
  - **^{99m}Tc-HMPAO**: Brain perfusion imaging.
  - **^{111}In-Octreotide**: Neuroendocrine tumor imaging.



- **4. Optical Imaging Agents**
  Primary Metals: Rare earth metals (e.g., Eu^{3+}, Tb^{3+}), or transition metals in luminescent complexes.
  Mechanism: Optical imaging agents work by absorbing and emitting light at specific wavelengths, enabling visualization of biological structures and processes in real time through fluorescence or bioluminescence.
  Example: Eu(III): Emits red fluorescence.
  Tb(III): Emits green fluorescence.
  Gd(III): Used primarily for MRI, but can be modified for dual imaging.



TARGETING STRATEGIES IN DIAGNOSTIC METALLODRUGS

- **Passive Targeting**: Passive targeting of metallodrugs exploits the enhanced permeability and retention (EPR) effect, allowing drug accumulation in tumor tissues due to leaky vasculature and poor lymphatic drainage (e.g., EPR effect in tumors).
- **Active Targeting:** Active targeting of metallodrugs involves attaching ligands, such as antibodies or peptides, to the drug complex to specifically bind receptors on target cells, enhancing selective uptake and therapeutic efficacy. (e.g., antibodies, peptides) (e.g., HER2, integrins).
- **Stimuli-Responsive Systems**: Release or activation of agent in response to pH, redox conditions, or enzymes.
- There are certain limitations and challenges:
- **Non-specific binding** – Off-target interactions can reduce imaging accuracy.

  Poor stability – Metal complexes may degrade or dissociate in vivo.

  Limited tissue penetration – Large or hydrophilic agents may not reach deep targets.

  Immunogenicity – Targeting ligands can trigger immune responses, affecting safety and distribution.

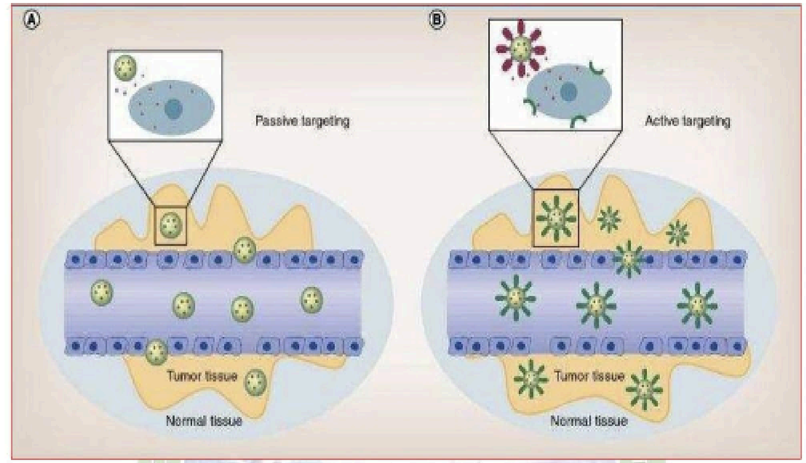
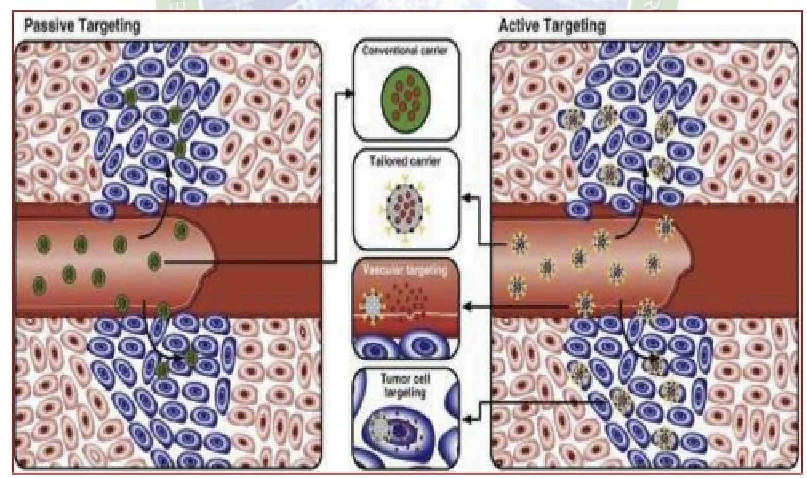


Fig.1: Types of Targeted Drug Delivery System



3. THERAPEUTIC METALLODRUGS

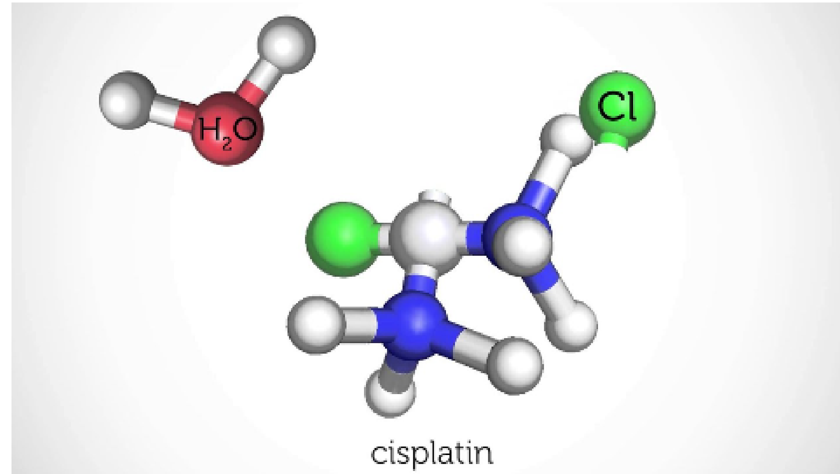
- **3.1 ANTICANCER METALLODRUGS**

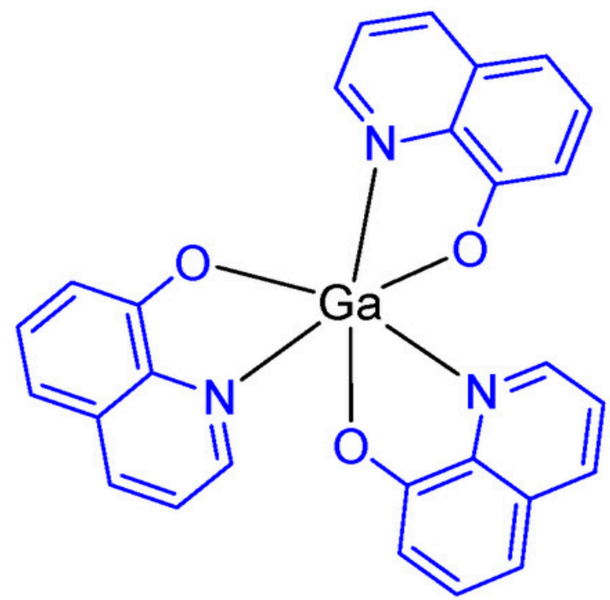
  Anticancer metallodrugs are therapeutic agents containing metal ions or complexes that target and destroy cancer cells. They act through mechanisms like DNA binding, redox reactions, and enzyme inhibition, offering unique advantages over traditional organic drugs in cancer treatment.

- **3.1.1 ANTICANCER THERAPEUTICS**

  Cisplatin is a platinum-based chemotherapy drug that forms DNA crosslinks, inhibiting replication and inducing apoptosis. It's effective against various solid tumors, including testicular, ovarian, and lung cancers, despite dose-limiting nephrotoxicity and resistance concerns.

- **Carboplatin**, a platinum-based anticancer drug, forms DNA crosslinks to inhibit cell division. It offers similar efficacy to cisplatin but with reduced nephrotoxicity and gastrointestinal side effects. Commonly used for ovarian, lung, and head-neck cancers, it has better tolerability.
- **Oxaliplatin** is a third-generation platinum-based anticancer agent. It forms DNA crosslinks, disrupting replication and transcription. Effective in colorectal cancer, it has lower nephrotoxicity than cisplatin but causes dose-limiting peripheral neuropathy. It is often used in combination chemotherapy regimens.
- **KP46** is a gallium-based anticancer agent targeting iron metabolism in tumor cells. It disrupts DNA synthesis and induces apoptosis, showing promise against melanoma and other solid tumors. KP46 offers oral bioavailability and reduced toxicity compared to traditional chemotherapies.





KP46

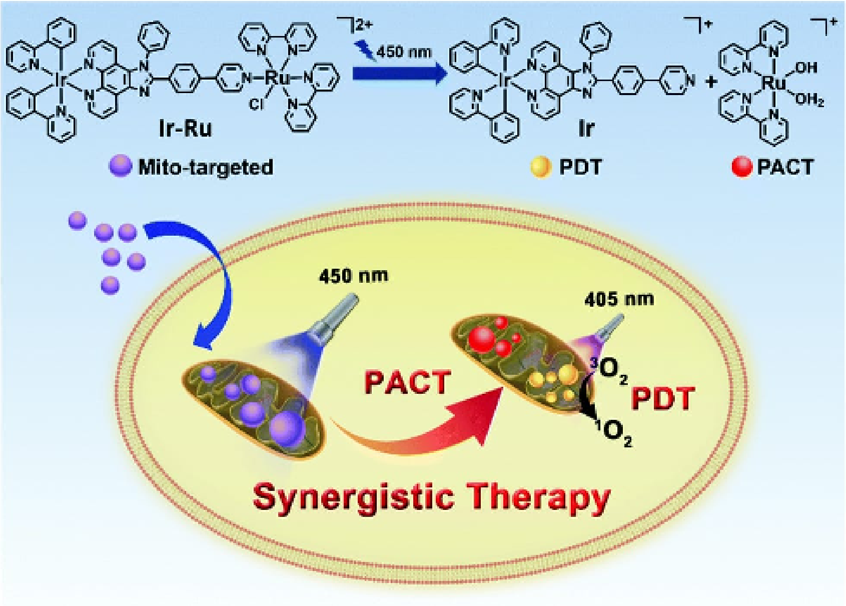
3.1.2 THERAPEUTIC RADIOPHARMACEUTICALS

- **Definition:** Therapeutic radiopharmaceuticals are radioactive drugs used to treat diseases, primarily cancer. They deliver targeted radiation to specific tissues, destroying or damaging diseased cells while minimizing exposure to healthy tissues.
- **Key Components:**
- **Radionuclide** –**1. Delivering Targeted Radiation**(e.g., **alpha**, **beta**, or **Auger electrons**)
  2. Enabling Internal Radiotherapy
  3. Facilitating Molecular Targeting(e.g., antibodies, peptides, or small molecules)
  4. Supporting TheranosticsLutetium-177 (Lu-177) emits both **beta radiation** (therapy) and **gamma rays** (imaging)

  Carrier Molecule – Carrier molecules in therapeutic radiopharmaceuticals transport radionuclides specifically to target cells or tissues, enhancing selective delivery. They improve treatment efficacy by binding to receptors or antigens on cancer cells, minimizing radiation exposure to healthy tissues and reducing side effects.(**e.g., tumor-targeting antibodies or peptides**).
- **Common Radiopharmaceuticals Used:**
- **^{131}I Sodium Iodide-** Primary use :Thyroid cancer, hyperthyroidism Function: Accumulates in thyroid tissue to destroy overactive or cancerous cells
- **^{177}Lu-DOTATATE- Primary use :**Neuroendocrine tumors **Function**: Targets somatostatin receptors, delivering beta radiation to tumor cells
- **^{177}Lu-PSMA- Primary use:** Prostate cancer **Function**:Binds to PSMA receptors on prostate cancer cells.
- **^{90}Y-Ibritumomab Tiuxetan- Primary use:** Non-Hodgkin's lymphoma **Function** :Targets CD20 receptors on B-cells
- **^{223}Ra-Dichloride (Xofigo)- Primary use-**Metastatic prostate cancer (bone involvement). **Function**: Mimics calcium to localize in bone metastases and emit alpha particles

3.1.3 PHOTOCHEMOTHERAPEUTIC METALLODRUGS

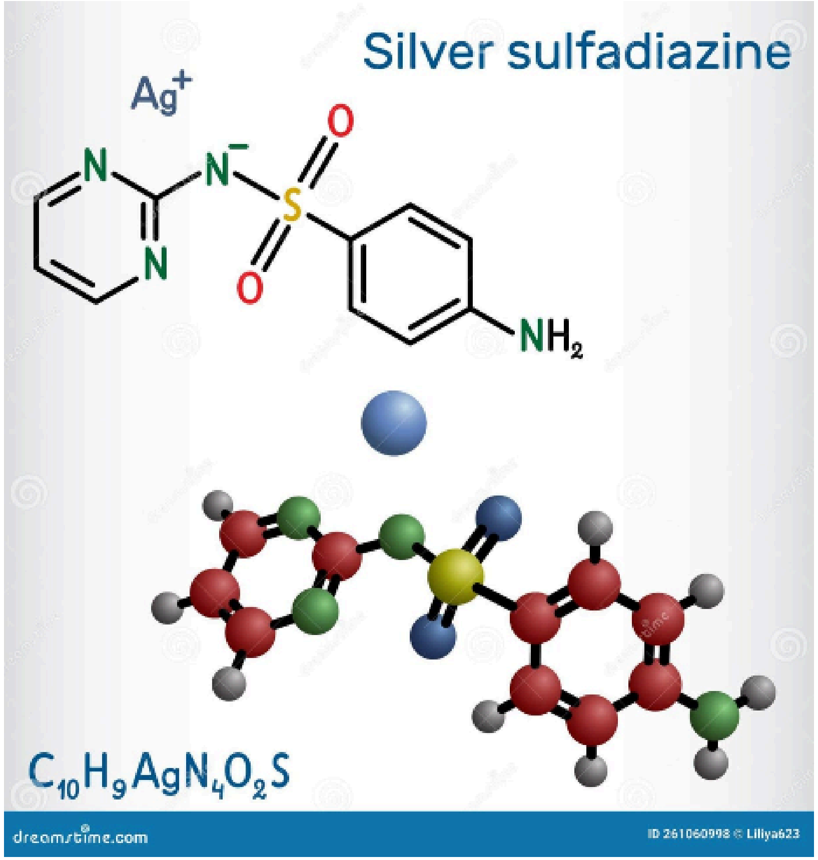
- **Photochemotherapeutic metallodrugs** are metal-based compounds designed to treat diseases, especially cancer, through a combination of **metal coordination chemistry** and **light activation**. These drugs are typically inactive or less toxic in the dark but become highly active upon exposure to specific wavelengths of light.
- **Key Features:**
- **Metal Core**: Usually involves transition metals like ruthenium, platinum, or titanium. The ability of metals to form complexes with different ligands allows for the creation of diverse structures with varying properties.
- **Photoreactivity:** Light exposure triggers a change—such as ligand release or generation of reactive oxygen species (ROS)—which leads to localized therapeutic effects.
- **Targeted Therapy:** Light can be focused on specific areas, minimizing damage to healthy tissues.
- **Applications:** Mainly in **photodynamic therapy (PDT)** or **photoactivated chemotherapy (PACT)** for treating cancer and microbial infections.
- These metallodrugs offer a promising route for more selective and less toxic treatments compared to traditional chemotherapy.



3.2 ANTIMICROBIAL AND ANTIPARASITIC METALLODRUGS

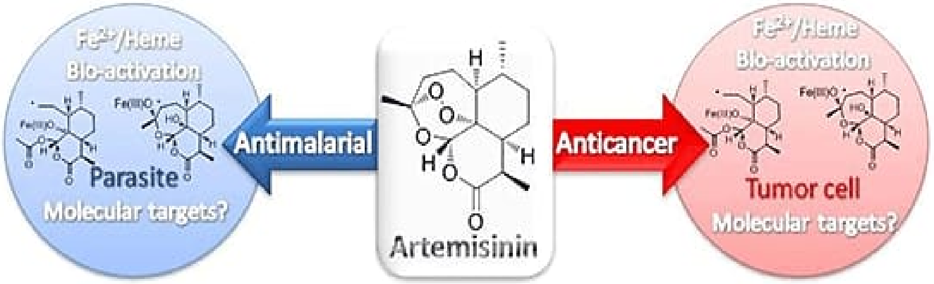
1. Antimicrobial Metallodrugs:

- These are metal-based compounds designed to combat bacterial, viral, and fungal infections. They often work by:
- **Disrupting microbial cell membranes.**
- **Interfering with Essential Processes.**
- **Targeting specific Enzymes.**
- **Examples:**
- **Silver compounds (e.g., silver sulfadiazine):** Used in wound care for their broad-spectrum antibacterial properties , **silver (Ag^+)** bind to microbial membranes increasing permeability and causing **cell lysis.**
- **Bismuth compounds** are Effective against *Helicobacter pylori* infections .
- **Gold (Au^{3+})** or **platinum (Pt^{2+})** can bind directly to DNA, leading to **replication inhibition** or **strand breaks**.
- **Gallium salts** are Mimic iron and disrupt bacterial iron metabolism.



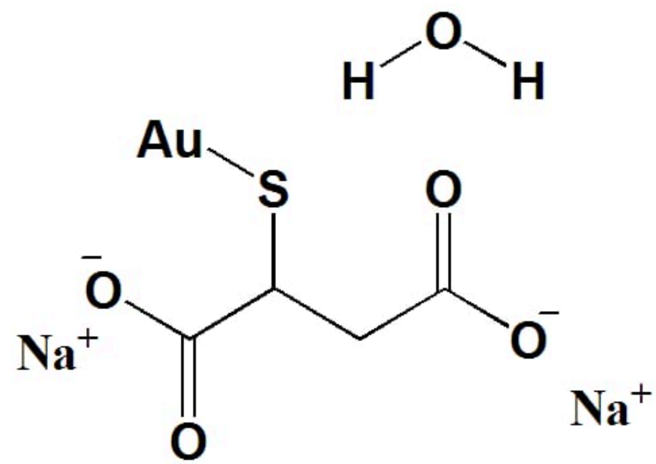
2. Antiparasitic Metallodrugs:

- These target parasitic infections (e.g., malaria, leishmaniasis, trypanosomiasis) by exploiting the parasite's metal-dependent pathways or generating oxidative stress.
- **Examples:**
- **Antimony-based drugs (e.g., meglumine antimoniate):** Used against *Leishmania* parasites.
- **Artemisinin-iron complexes:** Enhance antimalarial activity via radical formation.
- **Ferrocene derivatives**: Show promise in treating malaria and other parasitic diseases.

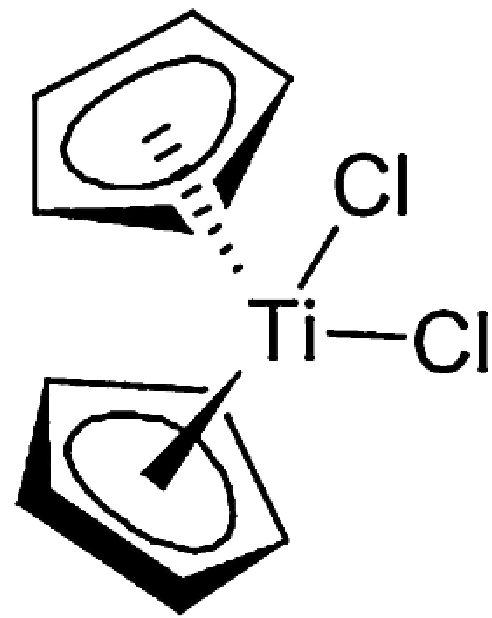


3.3 ANTIARTHRITIC METALLODRUGS

- Antiarthritic metallodrugs are metal-based compounds used to treat arthritis by reducing inflammation, modulating immune responses, and inhibiting joint degradation. Common examples include gold and titanium complexes, offering therapeutic effects in conditions like rheumatoid arthritis with targeted action and reduced toxicity.
- **Four examples of antiarthritic metallodrugs** and their **specific functions**:
- **Auranofin (Gold-based)**
  Function: Inhibits immune cell activity and reduces inflammation; used in rheumatoid arthritis to slow joint damage.
- **Sodium aurothiomalate (Gold-based)**
  Function: Modulates immune response by inhibiting cytokine production; used for long-term management of rheumatoid arthritis.
- **Titanocene dichloride (Titanium-based)**
  Function: Investigated for anti-inflammatory properties; may inhibit pro-inflammatory pathways in arthritis models.
- **Copper complexes (e.g., copper salicylate)**
  Function: Act as anti-inflammatory agents by mimicking superoxide dismutase (SOD) activity, reducing oxidative stress in joints.

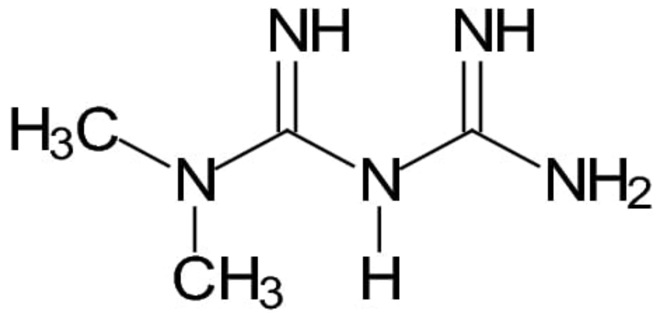


Gold sodium thiomalate

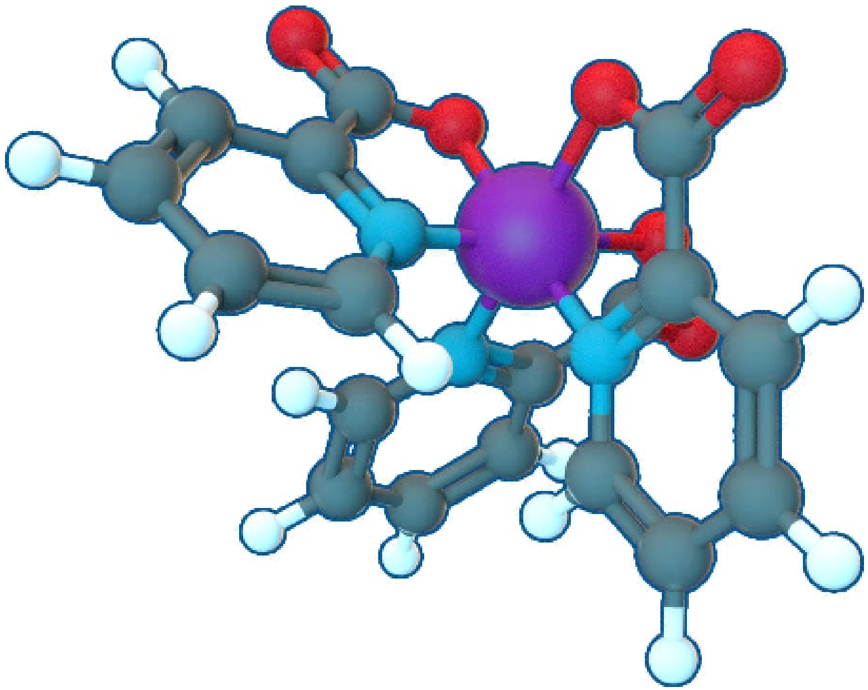


3.4 ANTIDIABETES METALLODRUGS

- Antidiabetes metallodrugs are a class of metal-based compounds investigated or used for the treatment of diabetes, particularly type 2 diabetes mellitus (T2DM).
- **Mechanism of Action:** Many act by mimicking insulin activity, enhancing glucose uptake in cells, or modulating key enzymes in carbohydrate metabolism (e.g., glycogen synthase, PTP-1B).
- **Common Metals Studied:**
  - **Vanadium**: Known for its insulin-mimetic properties; vanadyl sulfate has shown potential in clinical and animal studies.
  - **Zinc**: Enhances insulin action and has antioxidant effects.
  - **Chromium**: Improves insulin sensitivity; chromium picolinate is a widely studied supplement.
  - **Copper, Molybdenum, Titanium**: Explored for various mechanisms, including oxidative stress reduction and enzyme regulation.
- **Benefits:**
- Potential to lower blood glucose levels
- May reduce insulin resistance
- Some possess antioxidant or anti-inflammatory properties

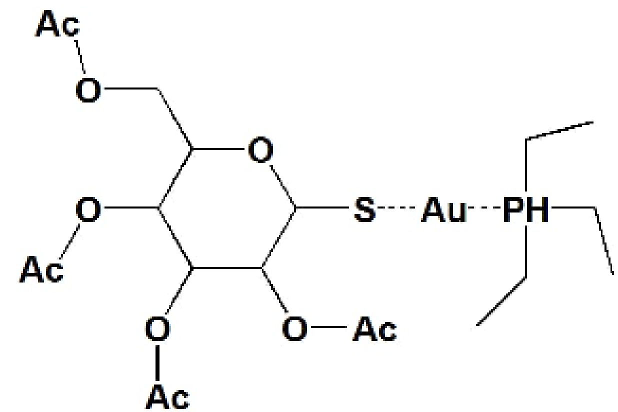


Metformin

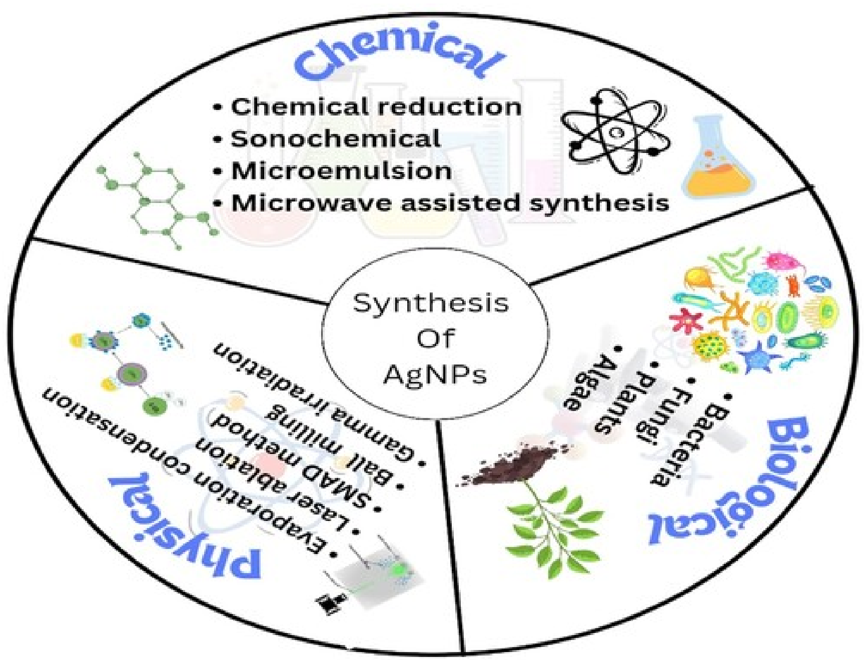


3.5 ANTIVIRAL METALLODRUG

- Antiviral metallodrugs are metal-based compounds that inhibit viral replication or entry by interacting with viral enzymes or genetic material, offering potential treatment for various viral infections with unique mechanisms.
- Common metals used include **platinum, gold, silver, ruthenium, and zinc**. Antiviral activity may arise from:
- **Disruption of viral enzymes** (e.g., proteases, polymerases)
- **Inhibition of viral genome replication**
- **Oxidative damage to viral components**
- **Blocking virus-host interactions**
- **Example: Gold (Au)** –Auranofin **, it target viruses like** HIV, Hepatitis B, SARS-CoV-2. **Silver (Ag) - Silver nanoparticles (AgNPs) , it target viruses like** HIV, Influenza, Herpes simplex virus (HSV), SARS-CoV-2. Ruthenium (Ru) , it **target viruses like** HIV, Influenza A, Hepatitis viruses.

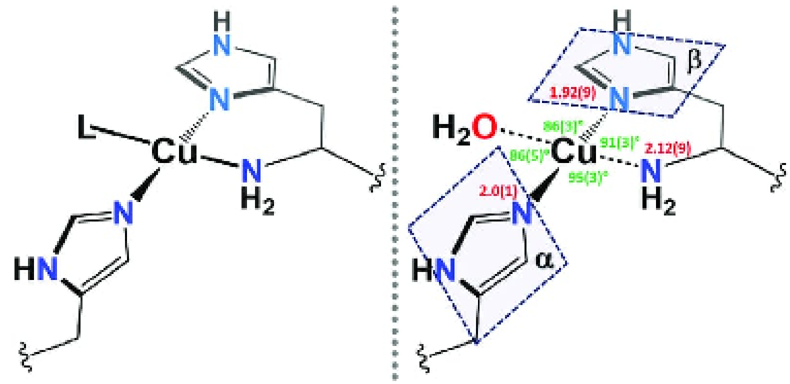


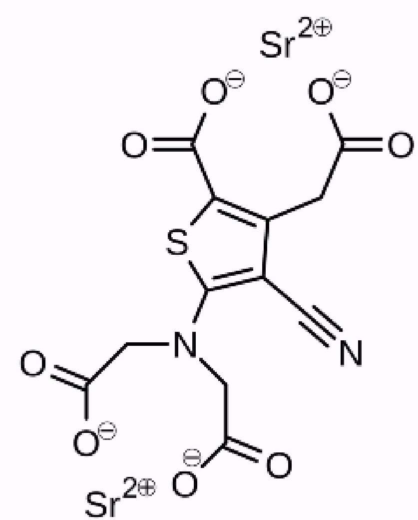
Auranofin



3.6 METALLODRUGS ADDRESSING DEFICIENCIES

- **1. Iron (Fe) and Vitamin B12**
- **Deficiency Disease** : **Biermer–Addison's anemia, older name: pernicious anemia.**
- **Treatment :** Iron dextran (Proferdex, Dexferrum, InFeD) or iron sucrose (Venofer) are required to treat iron deficiency. Co(III)-containing cyanocobalamin (CN-Cbl) and hydroxycobalamin (OH-Cbl) are available in form of a nasal spray (Nascobal) or parenteral injection (Vibisone) for the therapy of vitamin B12-deficiency.
- **2. Zinc (Zn)**
- **Deficiency Diseases**: **Acrodermatitis enteropathica is an autosomal recessive metabolic disorder affecting the uptake of zinc.**
- **Treatment :** There is no cure, and patients depend lifelong on zinc supplements to survive.
- **3. Copper (Cu)**
- **Deficiency Diseases**: **Menkes Disease (MD)**
- **Treatment :** . Copper histidine is currently in phase II clinical trials for therapy in Menkes Disease.
- **4. Calcium and Strontium (Sr)**
- **Deficiency Disease** : **Osteoporosis**
- **Treatment :** calcium supplements (e.g., Calcitrate) and strontium ranelate (Osseor, Protelos) are metal-based drugs employed in the management of osteoporosis.



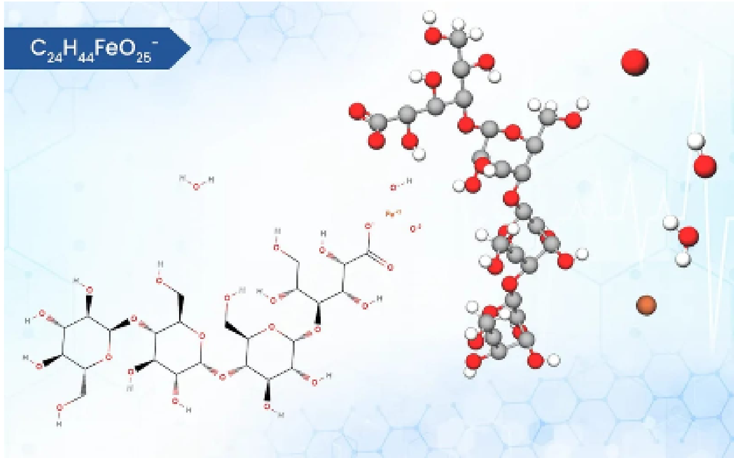


3.7 METALLODRUGS FOR THE TREATMENT OF CARDIOVASCULAR DISORDER

- **1. Metallodrugs in Cardiovascular Disorders**
- **A. Platinum-Based Drugs**

  Example: Low-molecular-weight **platinum(II) coordination complexes** formed with **amiodarone**, e.g. [Pt^{2+}–amiodarone] compounds.
- **Use:** Intended to treat arrhythmias and protect myocardium by enhancing mitochondrial resilience
- **B. Iron-Based Compounds**

  Example: Ferric Carboxymaltose (FCM)

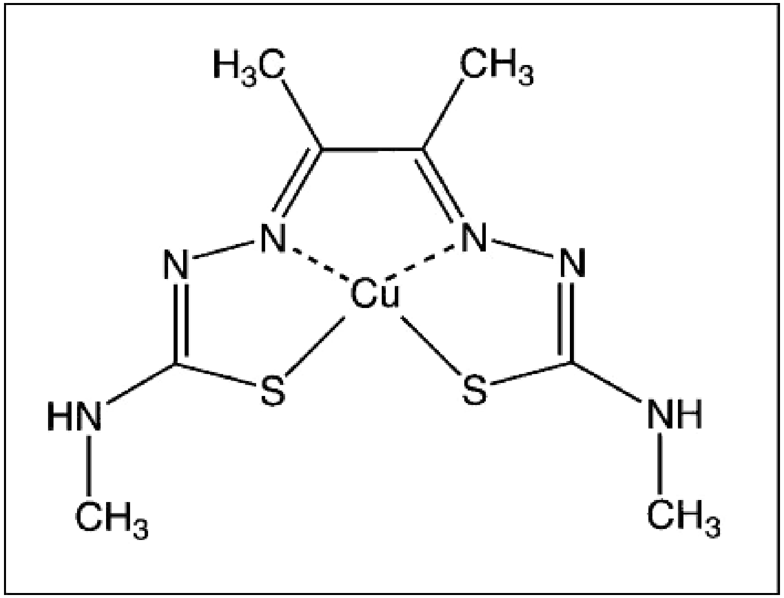


- **Use: Heart Failure with reduced ejection fraction (HFrEF)**
- **Chronic Kidney Disease (CKD)** with coexisting cardiovascular issues

  C. Copper Complexes

  Example: Copper(II)-Diacetyl-bis(N4-methylthiosemicarbazone)

  Use: Cu(ATSM) is an **antioxidant and cytoprotective copper complex** that has been investigated for its **cardioprotective effects**, especially in conditions involving **oxidative stress and ischemia-reperfusion injury**, which are central to many cardiovascular diseases.



- **D. Nitric Oxide-Releasing Metal Complexes**

  Example: Sodium Nitroprusside $Na_2[Fe(CN)_5NO]\cdot 2H_2O$
- **Use: Sodium Nitroprusside (SNP)** is a **nitric oxide donor** used clinically to manage **acute hypertensive crises** and **heart failure** due to its **potent vasodilatory effects**.
- **Acute decompensated heart failure**
- **Controlled hypotension during surgery**
- **Caution :** SNP can release **cyanide ions** during metabolism; hence, **short-term use** and **careful monitoring** are essential to avoid toxicity.

3.8 METALLODRUGS FOR THE TREATMENT OF GASTROINTESTINAL DISORDER

- **A. Bismuth-Based Drugs**
- **Example**: ***Bismuth subsalicylate***, ***Bismuth subcitrate***
- **Use**: Treat **Helicobacter pylori** infections, **peptic ulcers**, **diarrhea .**
- Antibacterial and protective coating for stomach lining.
- The **salicylate** part reduces inflammation in the stomach and intestines.
- **B. Zinc Compounds**

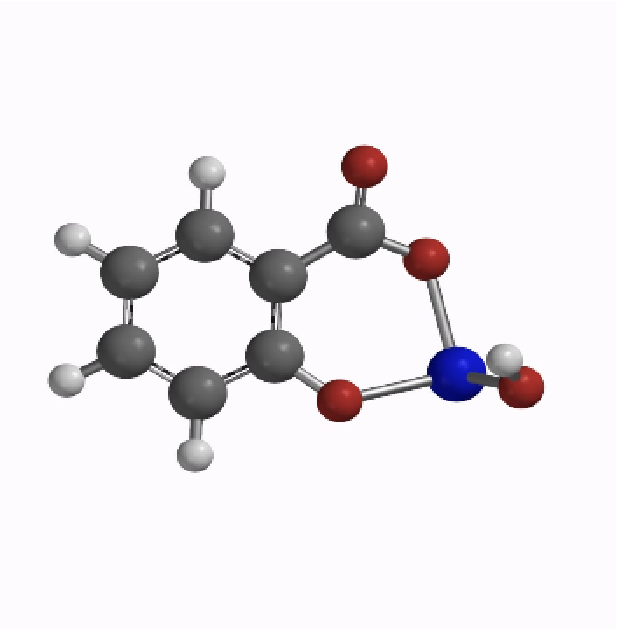
Example: Zinc Sulfate / Zinc Acetate / Zinc Gluconate, Zinc Carnosine (Polaprezinc)

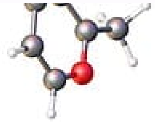
Use: **Diarrhea** treatment in children, improves intestinal barrier, **Mucosal protection and ulcer healing** in the **stomach and intestines.**

- **C. Iron-Based Drugs**

Example:Ferric Maltol, Ferric Carboxymaltose (FCM)

- **Use:** Used to **treat iron deficiency anemia in patients with Inflammatory Bowel Disease (IBD)** (e.g., **Crohn's disease**, **ulcerative colitis**) and other GI-related conditions without worsening mucosal inflammation.
- It is also used in post – bariatric surgery.





3.9 METALLODRUGS AS PSYCHOTROPICS

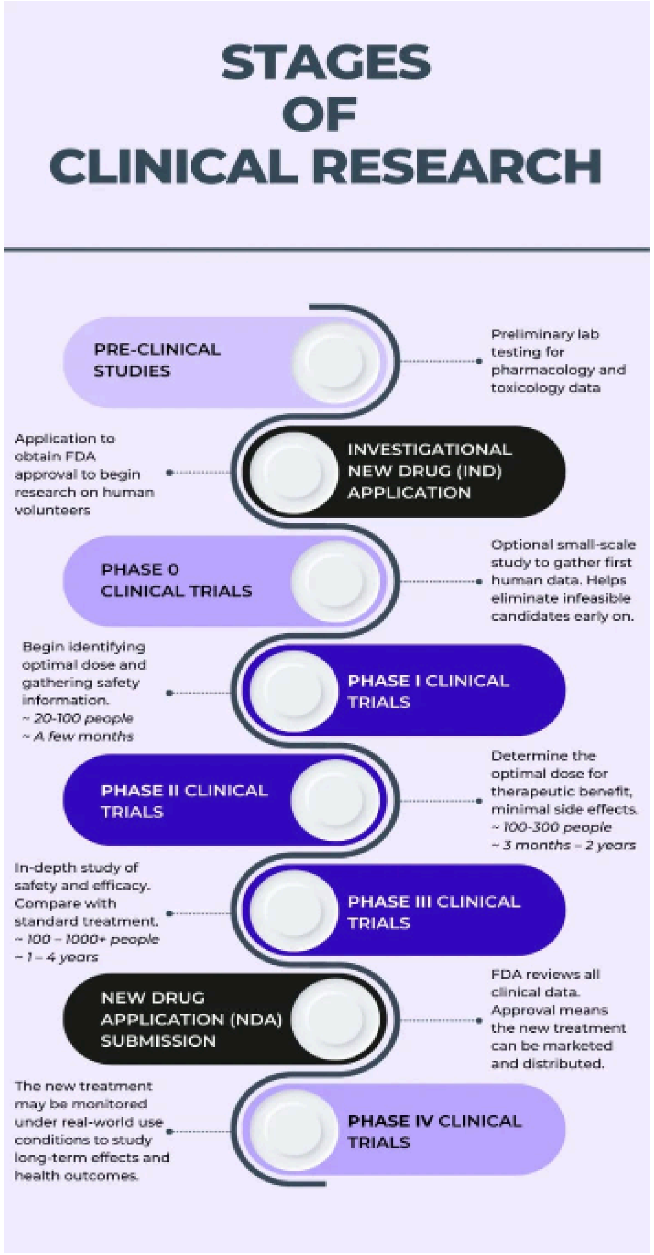
- **1. Mechanism of Action**
- Metallodrugs typically exert their effects through one or more of the following mechanisms:
- **Modulation of neurotransmission:** Certain metals can influence neurotransmitters like dopamine, serotonin, or GABA.
- **Enzyme inhibition or activation:** Metal complexes can inhibit enzymes like monoamine oxidase (MAO), which is involved in the breakdown of neurotransmitters.
- **Redox activity and oxidative stress control:** Some metallodrugs act as antioxidants or influence oxidative pathways implicated in neurodegeneration and psychiatric symptoms.
- **Interaction with DNA/RNA:** Metal complexes may modulate gene expression affecting neuronal function or plasticity.
- **Metals Investigated for Psychiatric Use**
- Here are some key metals and their potential psychiatric applications:
- **Lithium (Li)**
- **Approved for:** Bipolar disorder (mood stabilizer)
- **Mechanism:** Modulates second messenger systems, neuroprotective, reduces oxidative stress.
- **Status:** Widely used and FDA-approved.
- **Zinc (Zn)**
- **Potential for:** Depression, schizophrenia
- **Mechanism:** Influences NMDA receptors and GABAergic signaling; has antidepressant-like effects.
- **Status:** Used as a supplement in some treatment plans.
- **Copper (Cu) and Iron (Fe)**
- **Imbalance linked to:** Depression, schizophrenia, neurodegeneration
- **Note:** Not used as direct treatments but studied for their role in pathophysiology.

4. STRATEGIES FOR THE DESIGN OF METALLODRUGS

- **Brief strategies for the design of metallodrugs:**
- **Target-Specific Metal Binding**: Designing metal complexes that bind selectively to biological targets (e.g., DNA, enzymes, proteins) for therapeutic effect.
- **Ligand Design**: Tailoring ligands to control the metal's reactivity, stability, solubility, and selectivity in biological environments.
- **Redox Control**: Utilizing the redox properties of metals to activate drugs in specific cellular conditions (e.g., hypoxic tumors).
- **Prodrug Strategy**: Designing metal-based prodrugs that become active only inside the target site to reduce side effects.
- **Photoactivation**: Creating metal complexes that are activated by light, allowing localized treatment (e.g., photodynamic therapy).
- **Biomimetic Approach**: Mimicking natural metalloenzymes or metal-binding sites to interfere with biological processes.
- **Nanocarrier Integration**: Incorporating metallodrugs into nanoparticles for targeted delivery and controlled release.
- These strategies aim to enhance efficacy, reduce toxicity, and improve selectivity of metal-based therapeutics.

5.CLINICAL STUDIES OF METALLODRUG

- **1. Purpose of Clinical Studies**
- Testing new therapies
- Evaluate the **safety**, **efficacy**, and **pharmacokinetics** of metallodrugs in humans.
- Determine the **optimal dose**, **route of administration**, and **toxicity profile**.
- Focusing on comfort and well-being .
- **Phases of Clinical Trials**
- **Phase I**: Tests safety and dosage in a small group of healthy volunteers or patients.
- **Phase II**: Assesses efficacy and side effects in a larger patient group.
- **Phase III**: Confirms effectiveness, monitors side effects, and compares with standard treatments.
- **Phase IV**: Post-marketing studies to gather additional information on risks, benefits, and long-term effects.
- **Challenges in Metallodrug Development**
- **Toxicity** and **non-specific interactions** with biological molecules.
- **Stability** in the body and targeted delivery to diseased cells.
- Complex **regulatory approval** due to their unique properties.
- **Current Research Trends**
- Designing **targeted metallodrugs** to reduce side effects.
- Using **nanotechnology** for better delivery.
- Exploring **non-traditional metals** like ruthenium, gold, and titanium.



CONCLUSION

- Metallodrugs play a vital role in medicinal chemistry, offering unique therapeutic benefits through their diverse redox properties, coordination geometries, and reactivities. These metal-based compounds can target DNA, proteins, and enzymes, often in ways organic drugs cannot. Notable examples include cisplatin for cancer and gold compounds for rheumatoid arthritis. Ongoing research aims to enhance selectivity, reduce toxicity, and expand applications to areas like antimicrobial and antiviral therapies. As our understanding of bioinorganic chemistry deepens, metallodrugs continue to hold significant promise for the development of innovative, effective treatments across various diseases.

REFERENCES

- **CHEMICAL REVIEWS: Article published under an ACS author choice license.**
- **National Institutes of Health(NIH).**
- **.Wang D; Lippard SJ (2005). Cellular processing of platinum anticancer drugs. Nat. Rev. Drug. Discov 4, 307–320. [DOI] [PubMed] [Google Scholar]**
- **Gunatilleke SS; Barrios AM (2008). Tuning the Au(I)-mediated inhibition of cathepsin B through ligand substitutions. J. Inorg. Biochem 102, 555–563. [DOI] [PubMed] [Google Scholar]**
- **Clinical Neurotoxicology, Puneet Narang,Steven B. Lippmann.**
- **Waters J. E., Stevens-Cullinane L., Siebenmann L., Hess J. (2023). Recent advances in the development of metal complexes as antibacterial agents with metal-specific modes of action. Curr. Opin. Microbiol. 75, 102347. doi:**

THANK YOU

NUMEROV-COOLEY METHOD

B.Sc. Chemistry (Honours) Semester - VI (Under CBCS) Examination, 2025

Course: CEMA DSE-B4 (Dissertation)

CU ROLL NO. 223114-21-0045

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Signature of the Student

Introduction (One Dimension)

Quantum mechanics is a branch of physics that explains how very small particles—like electrons or atoms—behave. One of the most important tools in quantum mechanics is the Schrödinger equation. It allows us to find the allowed energy levels and wavefunctions of quantum systems.

To begin, we study the one-dimensional time-independent Schrödinger equation, which looks like this:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

Where:

- $\psi(x)$ is the wavefunction of the particle,

- $V(x)$ is the potential energy at position x,

- E is the energy,

- $\hbar$ is the reduced Planck's constant,

- m is the mass of the particle.

This equation is a boundary value problem—we try to find a function $\psi(x)$ that satisfies certain conditions at both ends of a region (for example, $\psi = 0$ at $x = 0$ and $x = L$).

Why Use One Dimension?

One-dimensional systems are easier to understand and solve. Even though they are simpler, they still teach us a lot about quantum behavior. Many textbook examples, like the infinite square well or harmonic oscillator, are one-dimensional.

Solving the Equation

Only a few potentials give exact (analytical) solutions to the Schrödinger equation. For most real-world problems, we need to solve it **numerically** using computers.

One method for doing this is the **shooting method**. It works like this:

1. Start from one side (say x=0) and guess the energy E.
2. Use the Schrödinger equation to calculate what the wavefunction would look like.
3. Check if it satisfies the boundary condition on the other side.
4. If not, change the energy and try again—like adjusting your aim in a game of darts.

This is why it's called "shooting"—we are trying to hit a target by guessing the right value.

Problems with Basic Shooting

Although the basic shooting method works, it can be:

- Unstable (especially for high energy guesses)
- Inaccurate if step sizes are too big
- Slower to converge if the guess is poor

To fix these problems, we use a better method that combines two powerful ideas:

- The Numerov method: a very accurate way to solve second-order equations like the Schrödinger equation.
- The **Cooley method**: instead of shooting from just one end, it shoots from both ends and matches the wavefunction in the middle.

Together, they form the Numerov–Cooley Shooting Method, which is more stable, more accurate, and works faster.

Numerov–Cooley Method

Numerov–Cooley shooting method, a high-accuracy numerical technique for solving second-order differential equations with two-point boundary conditions. Its application is particularly prominent in quantum mechanics, where it is used to solve the time-independent Schrödinger equation. The method combines the sixth-order accuracy of the classical Numerov method with the stability enhancements introduced by Cooley's bidirectional shooting technique. We provide an in-depth analysis of the algorithm, its theoretical underpinnings, and its computational performance, demonstrating results for several well-known quantum systems including the infinite square well and the harmonic oscillator. Comparisons with other methods such as Runge–Kutta and standard shooting techniques reveal the superiority of the Numerov–Cooley approach in terms of both efficiency and accuracy.

Introduction

Boundary value problems (BVPs) are a central class of problems in mathematical physics. In quantum mechanics, particularly in bound-state problems, one often encounters the time-independent Schrödinger equation. This equation is a second-order differential equation and typically requires numerical methods for non-trivial potentials.

While traditional shooting methods work by converting BVPs into initial value problems (IVPs), they often face challenges such as instability and divergence from the correct eigenvalue. The Numerov–Cooley method addresses these limitations by providing both higher-order accuracy and improved stability, making it suitable for problems involving oscillatory wavefunctions.

The Numerov Method

The Numerov method is a finite-difference method specialized for:

$$y''(x) = -g(x)y(x)$$

Its discretization yields a sixth-order accurate recurrence relation:

$$y_{n+1} = 2y_n - y_{n-1} + \frac{h^2}{12}(g_{n+1}y_{n+1} + 10g_n y_n + g_{n-1}y_{n-1})$$

After algebraic manipulation, this becomes:

$$y_{n+1} = \frac{2y_n(1 - \frac{5h^2}{12}g_n) - y_{n-1}(1 + \frac{h^2}{12}g_{n-1})}{1 + \frac{h^2}{12}g_{n+1}}$$

This method offers high accuracy and is particularly effective for wave-like or oscillatory solutions, which are common in quantum mechanics.

Cooley's Modification

Cooley proposed a modification to the basic shooting method:

1. Integrate the wavefunction from the left boundary up to a midpoint.
2. Integrate a second wavefunction from the right boundary down to the same midpoint.
3. At the match point, compare the **logarithmic derivatives**:

$$L(x) = \frac{\psi'(x)}{\psi(x)}$$

4. Adjust the energy E using a root-finding method (e.g., bisection) until both sides match.

This approach enhances numerical stability, particularly for higher energy levels or complex potentials.

The Numerov–Cooley Shooting Algorithm

Step-by-step Algorithm:

1. Define the spatial domain [a,b] and grid spacing h.
2. Choose an initial energy guess E.
3. Calculate $k^2(x) = \frac{2m}{\hbar^2}(E - V(x))$ at all grid points.
4. Initialize:
    - Left wavefunction: $\psi(a)=0, \psi(a+h)=\epsilon$
    - Right wavefunction: $\psi(b)=0, \psi(b-h)=\epsilon$
5. Use the Numerov method to integrate both wavefunctions up to a midpoint x_m.
6. Compute the logarithmic derivative on both sides at x_m.
7. Adjust E using a root-finding technique (bisection or secant).
8. Repeat until the derivative mismatch is within tolerance.

Boundary Value Nature of the Schrödinger Equation

Unlike classical initial value problems (IVPs), the Schrödinger equation is a **boundary value problem (BVP)**: one typically seeks solutions that satisfy specific values at both ends of a spatial domain. This introduces challenges:

- The solution may not be unique.
- Multiple solutions exist, each corresponding to different eigenvalues (energy levels).

This leads naturally to the concept of stationary states—eigenfunctions of the Hamiltonian operator that form a complete orthogonal basis in Hilbert space.

Numerical Methods and the Need for Shooting Techniques

Standard numerical techniques for BVPs include finite difference methods and matrix diagonalization. However, these can be inefficient or unstable when dealing with oscillatory solutions of the TISE.

One powerful approach is the shooting method. This involves:

1. Rewriting the BVP as an IVP.

2. Guessing the energy eigenvalue E.
3. Integrating from one boundary to another.
4. Adjusting E until the solution matches the second boundary condition.

This mimics the process of "shooting" at a target: if the wavefunction overshoots or undershoots the boundary, the energy guess is corrected and the process is repeated.

The Role of Symmetry and Node Counting

In symmetric potentials (e.g., harmonic oscillator), the wavefunctions exhibit even or odd symmetry, simplifying the domain and boundary conditions. Additionally, the number of nodes (zero crossings) in ψ(x) correlates with energy level:

- Ground state: 0 nodes
- 1st excited state: 1 node
- 2nd excited state: 2 nodes, and so on.

This node-counting property is crucial for identifying the correct eigenstate during numerical iteration.

Implementation and Results

Tools Used

- Python with NumPy and Matplotlib
- Discretized space of 1000–2000 points
- Step size h=0.01 or less
- Tolerance for derivative match: $<10^{-6}$

Infinite Square Well

$$V(x) = \frac{1}{2} m\omega^2 x^2$$

Energy levels:

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

With $m = \omega = \hbar = 1$, results were:

n	Analytical E_n	Numerical E_n
0	0.5	0.5000
1	1.5	1.5001
2	2.5	2.5001

Harmonic Oscillator

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$

Boundary conditions: $\psi(0) = \psi(L) = 0$

Analytical solution:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

Numerical results (L=1, m=1, ħ=1):

n	Analytical E_n	Numerical E_n
1	9.8696	9.8695
2	39.4784	39.4783
3	88.8264	88.8261

Excellent agreement was observed.

Discussion

Advantages:

- 6th-order accuracy with low computational cost
- Robust against oscillations and stiffness
- Ideal for bound-state problems

Limitations:

- Needs smooth potential functions
- Requires careful bracketing of E

- Matching point choice affects convergence

Conclusion

The Numerov–Cooley shooting method offers an elegant and accurate framework for solving quantum mechanical boundary value problems. By combining the high-order accuracy of Numerov's algorithm with the stability of Cooley's matching technique, it outperforms many traditional solvers, especially in eigenvalue problems like the Schrödinger equation. Its extension to higher-dimensional systems or relativistic equations opens pathways for further research.

Appendix – Python Code

```python
import numpy as np
import matplotlib.pyplot as plt

def V(x):
    return 0  # Example: infinite square well

def k2(x, E):
    return 2 * (E - V(x))

def numerov(psi0, psi1, k2_arr, h):
    N = len(k2_arr)
    psi = np.zeros(N)
    psi[0], psi[1] = psi0, psi1
    for n in range(1, N - 1):
        psi[n + 1] = (
            (2 * (1 - 5 * h**2 * k2_arr[n] / 12) * psi[n]
            - (1 + h**2 * k2_arr[n - 1] / 12) * psi[n - 1])
            / (1 + h**2 * k2_arr[n + 1] / 12)
        )
    return psi

# Example usage
x = np.linspace(0, 1, 1000)
h = x[1] - x[0]
E_guess = 10
k2_arr = k2(x, E_guess)
psi = numerov(0, 1e-5, k2_arr, h)
plt.plot(x, psi)
plt.title("Wavefunction for Infinite Square Well")
plt.xlabel("x")
plt.ylabel("ψ(x)")
plt.grid()
plt.show()
```

References

1. Numerov, B. V. (1924). Note on the numerical integration of $d^2x/dt^2 = f(x, t)$. Astronomische Nachrichten.

2. Cooley, J. W. (1961). An improved eigenvalue corrector formula for solving the Schrödinger equation for central fields. Mathematics of Computation, 15(74), 363–374.

3. Izaac, J., & Wang, J. B. (2018). Computational Quantum Mechanics. Springer Nature Switzerland AG. Chapter 9 – One Dimension. DOI: 10.1007/978-3-319-99930-2_9

4. Griffiths, D. J. (2005). Introduction to Quantum Mechanics (2nd ed.). Pearson Prentice Hall.

5. Press, W. H., Teukolsky, S. A., Vetterling, W. T., & Flannery, B. P. (2007). Numerical Recipes: The Art of Scientific Computing (3rd ed.). Cambridge University Press.

6. Smith, G. D. (1985). Numerical Solution of Partial Differential Equations: Finite Difference Methods. Oxford University Press.

7. Langtangen, H. P., & Linge, S. (2017). Finite Difference Computing with PDEs: A Modern Software Approach. Springer.

8. Thomas, J. W. (1995). Numerical Partial Differential Equations: Finite Difference Methods. Springer.

9. Landau, R. H., Páez, M. J., & Bordeianu, C. C. (2007). Computational Physics: Problem Solving with Computers. Wiley-VCH.

10. Trefethen, L. N. (2000). Spectral Methods in MATLAB. Society for Industrial and Applied Mathematics (SIAM).

11. Trefethen, L. N. (2000). *Spectral Methods in MATLAB*. Society for Industrial and Applied Mathematics (SIAM).

12. Boyd, J. P. (2000). *Chebyshev and Fourier Spectral Methods*. Dover Publications.

13. Canuto, C., Hussaini, M. Y., Quarteroni, A., & Zang, T. A. (2006). *Spectral Methods: Fundamentals in Single Domains*. Springer.

14. Baye, D., & Heenen, P. H. (1986). *Generalised meshes for quantum mechanical problems*. *Journal of Physics A: Mathematical and General*, 19(11), 2041.

15. Marston, C. C., & Balint-Kurti, G. G. (1989). *The Fourier grid Hamiltonian method for bound state eigenvalues and eigenfunctions*. *The Journal of Chemical Physics*, 91(6), 3571–3576.

16. Thijssen, J. M. (2007). *Computational Physics* (2nd ed.). Cambridge University Press.

DESIGN AND SYNTHESIS OF METAL-ORGANIC FRAMEWORKS (MOFS) FOR GAS STORAGE AND SEPARATION:
(AN OVERVIEW)

B.Sc. Chemistry (Hons) Semester VI (Under CBCS)
Examination, 2025
Paper: DSE-B4(Dissertation)

CU Roll no. : **223114-11-0046**
CU Reg no. : **114-1214-0220-22**

College: **St. Paul's Cathedral Mission College**

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AISHE ID C-11869
Estd. 1865

CERTIFICATE

This is to certify that the dissertation entitled "**Design and synthesis of Metal-Organic Frameworks(MOFs) for Gas storage and separation**", submitted to the Department of Chemistry, St. Paul's C. M. College, Kolkata in partial fulfilment for the award of the degree of SEM-VI, DSE-B4 (under CBCS) in the B.Sc. SEM-VI CEMA Examination, 2025, CU, is a record of bona fide work carried out Shreya Ghosh, CU Roll no. :223114-11-0046. (CU Reg no. :114-1214-0220-22), under my supervision and guidance. This is a review work and hasn't been submitted to receive any other degree. All help received by her from various sources have been duly acknowledged.

(Dr. Jishnunil Chakraborty)
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Student's Signature

Signature

Associate professor of St.Pauls' CM college
Department of chemistry

CONTENTS

Design and Synthesis of Metal-Organic Frameworks (MOFs) for Gas Storage and Separation

▪ What is MOF ?

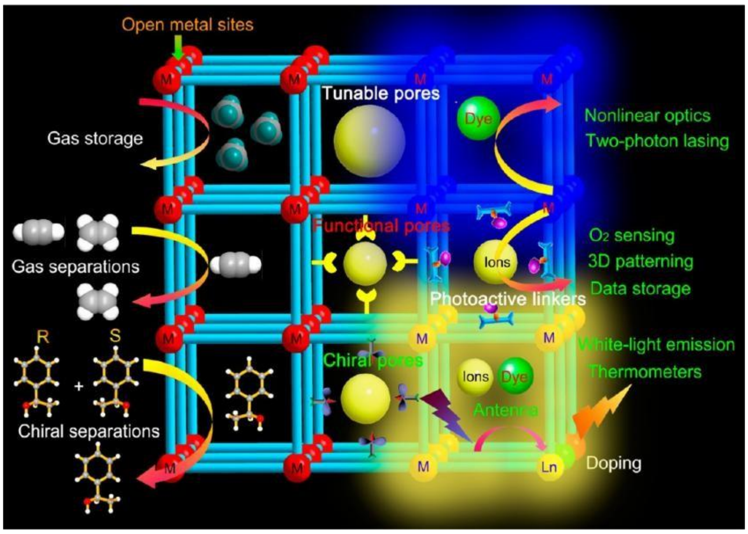
Metal-Organic Frameworks (MOFs) are a type of solid material made by combining metal ions with organic molecules in a highly organized way. These materials have a very large surface area and adjustable pore sizes. Their unique and attractive structures have made them a popular topic of research in recent years.

▪ Indroduction:

Research on Metal-Organic Frameworks (MOFs) and coordination polymers is one of the most active fields in chemistry and materials science. MOFs are built from metal ions or clusters and organic ligands via simple solvothermal synthesis, with structures characterized by X-ray, synchrotron, and neutron diffraction.

Compared to traditional porous materials, MOFs offer exceptionally high surface areas (up to 7000 m^2/g), adjustable pores, and diverse functional sites, making them ideal for gas storage, carbon capture, molecular separations, sensing, drug delivery, and catalysis. As organic-inorganic hybrid materials, MOFs combine the benefits of both components, with tunable pore sizes and functional sites.

Recent research has focused on designing MOFs for gas separation, enantioselective separations, and incorporating photoactive materials like lanthanide ions and organic dyes to develop MOFs for optical and photonic applications such as luminescent thermometers, oxygen sensors, white-light emitters, nonlinear optical devices, lasers, and 3D data storage. **[1-4]**



▪ Difference between co-ordination polymers (CP) and MOF:

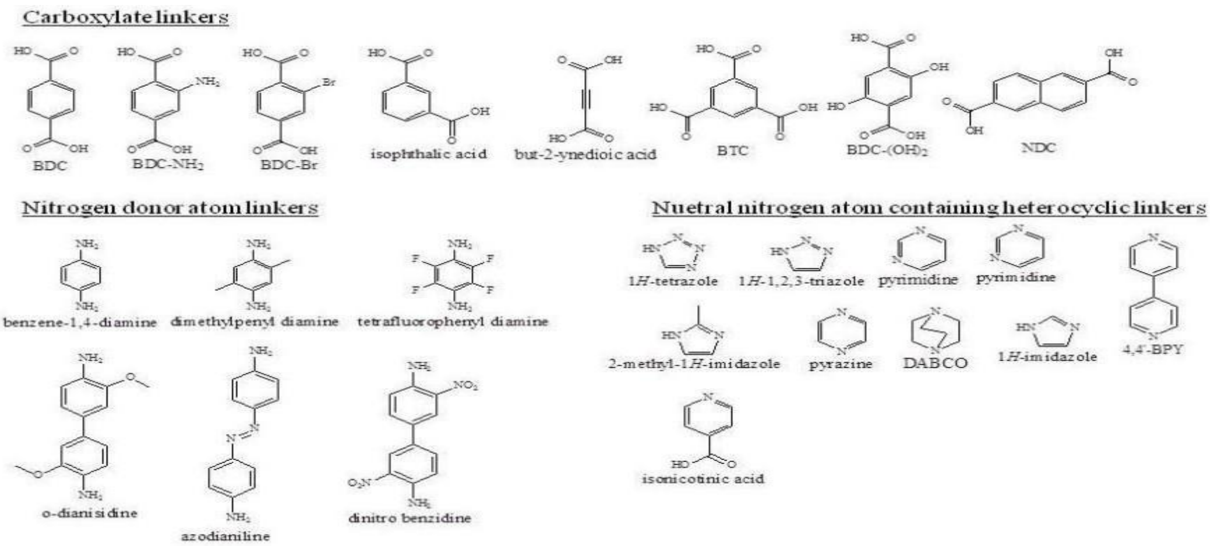
A classification system is proposed for coordination polymers, coordination networks, and metal-organic frameworks (MOFs). In this hierarchy, coordination polymers are the broadest category, with coordination networks as a subset, and MOFs as a further specialized subset. To be considered a MOF, a structure must have potential voids, though specific porosity measurements aren't required. additionally, the use of topology and topology descriptors is strongly recommended to better describe the crystal structures of MOFs and 3D coordination polymers.**[5]**

Objects	Coordination Polymers	MOFs
Structure	Can be 1D,2D or 3D structures	3D structures with voids or cages
Ligands	Can have a wide range of ligands	Organic ligands with potential voids
Properties	Can have various properties such as conductivity , magnetism and sensor capability	High surface area , porosity and tunable chemistry
Applications	Catalysis , sensing and optoelectronics	Gas storage , separation and drug delivery

▪ Structural aspects

➢ Primary building units (PBUs):

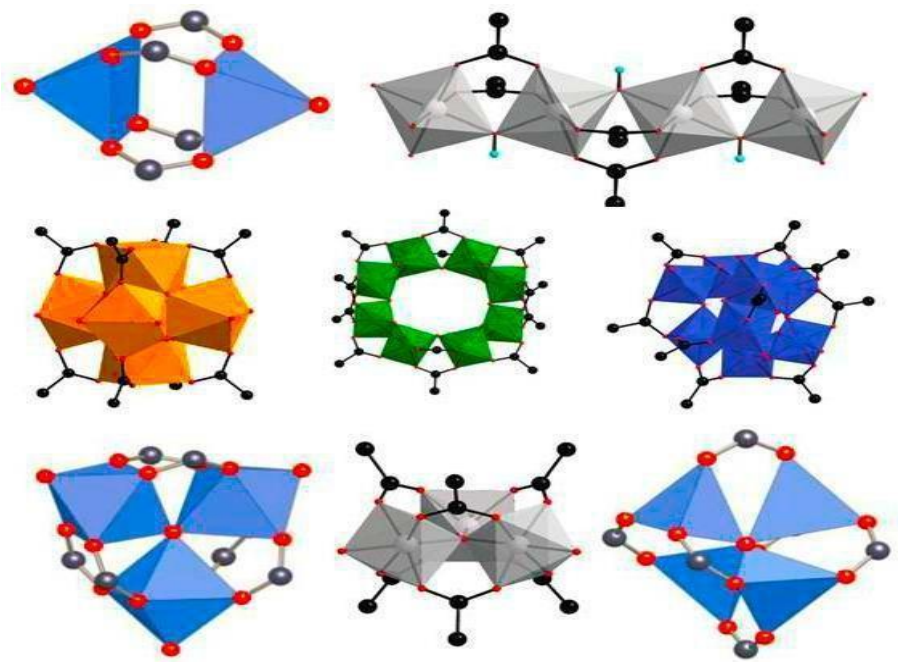
In Metal-Organic Frameworks (MOFs), metal ions (connectors) and organic linkers are the key components, known as Primary Building Units. These combine to form a porous, three-dimensional structure. Commonly, first-row transition metals like Cr^{3+}, Fe^{3+}, Co^{2+}, and Zn^{2+} are used as connectors, though alkali metals, alkaline-earth metals, and rare-earth metals can also be used.For synthesis, metal salts such as nitrates, acetates, sulfates, chlorides, and oxides serve as metal sources, while metal rods are used in electrochemical methods .The organic linkers connect metal ions through coordination bonds, typically involving functional groups like carboxylate, phosphate, sulfonate, amine, and nitrile.**[6-9]**



❖ **Some linkers used in synthesis of MOFs**

➢ <u>Secondary building units (SBUs)</u>:

In MOFs, organic linkers are connected through Metal-oxygencarbon clusters, instead of metal ions alone. These metal oxygen-carbon clusters are referred as "Secondary Building Units" (SBUs). SBUs have intrinsic geometric properties, which facilitate MOF's topology **[10-11]**. Some SBUs are shown below



❖ ***Some secondary building units***

Classification of Metal-organic frameworks:

On the basis of structural features, MOFs have been classified in following groups,

1. Rigid Frameworks:

• These MOFs are strong and don't change shape.
• They stay porous (full of tiny holes) and can hold or release other molecules.
• Useful for separating molecules (molecular sieving).**[12]**

2. Flexible/Dynamic Frameworks:

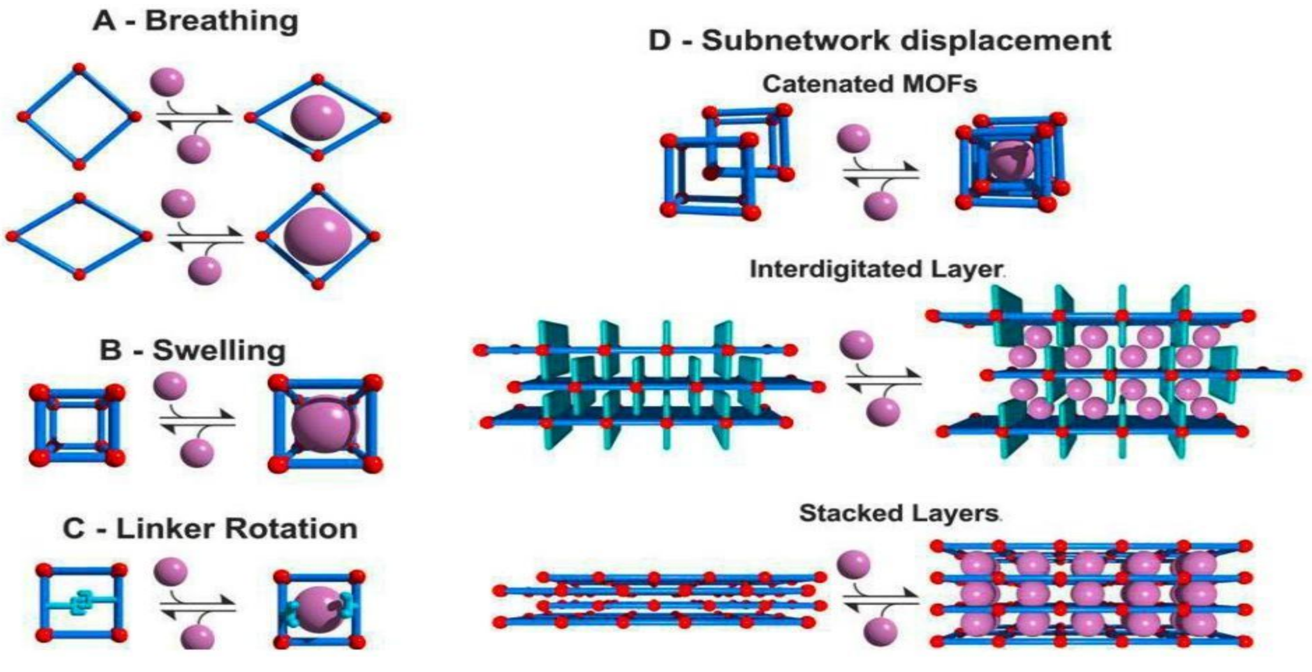
• These MOFs can change their shape when molecules enter or leave.
• Temperature or pressure can also affect them.
• Even when they lose solvent molecules, they stay porous and can take in gases under high pressure.

3. Open Metal Side:

• MOFs with open metal areas can hold more CO_2.
Example: HKUST-1 (with Cu metal parts) works better when it has 4% water.
• Water helps these sites capture more CO_2.**[13]**

3. Surface Functionalized Frameworks:

• These MOFs have special chemical groups added to their surface to improve their ability to capture CO_2 gas.
Example groups: arylamine, alkylamine, hydroxyl.
• These changes help MOFs capture and select CO_2 better by attaching these groups on the surface or to the metal inside.**[14-16]**



❖ Classification of different flexibility modes of MOFs

Synthesis of MOFs:

MOFs are prepared by combining metal ions and organic linkers under mild conditions in order to get a crystalline and porous network. This is termed as "Modular Synthesis". **[17]**

Metal ions + organic linkers →MOF

Conventional Methods:

1. ***Solvothermal & Hydrothermal Synthesis:***

• **Solvothermal:** Metal and organic parts are mixed in a solvent and heated above boiling point in a sealed container.
• **Hydrothermal:** Same as above, but uses water instead of other solvents.
Used often, but needs high heat and takes time.

2. **Non-Solvothermal:**
• Heated at lower temperatures (below boiling) in open air.
• Easier and faster than solvothermal.**[18]**

Unconventional Methods

1. **Mechanochemical Synthesis**

• Metal and organic parts are crushed together (like grinding in a machine) without any liquid.
• Then slightly heated to remove unwanted gases.
• Good for the environment and gives more product.**[19]**

2. Liquid-Assisted Grinding:
• A few drops of liquid are added while grinding.
• Helps the chemicals move and react faster.

Other (Alternative) Methods:

1. Microwave Method:
• Microwave quickly heats up the mixture.
• Makes crystals faster and smaller in size. **[20-23]**

2. Electrochemical Method:
• Metal slowly dissolves from an electrode and reacts with other parts in a liquid.
• Good for making special MOFs using ionic liquids. **[24]**

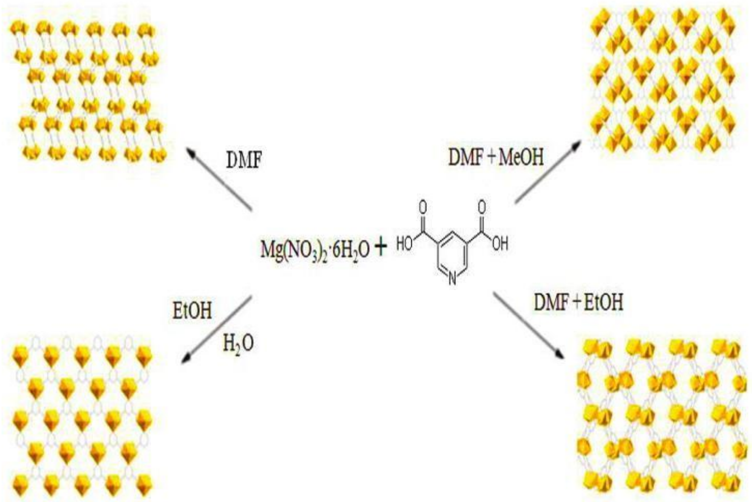
3. Sonochemical Method:
• Uses sound waves to make bubbles in the liquid, which then collapse and create heat.
• Speeds up the reaction and makes small-sized MOFs.**[25]**

4. Layer-by-Layer:
• A surface is dipped again and again into metal and organic solutions.
• Used to make thin layers of MOFs with control over thickness. **[26]**

▪ Factors Affecting MOF Synthesis:

1. Solvents:
• Solvents decide the shape and size (morphology) of MOFs.
• They act as coordinating agents or space fillers.
• Also guide the structure formation.
• Ideal solvents are polar and have high boiling points (e.g.,DMF, DEF, DMSO, DMA, alcohols, acetone).
• Solvent's polarity and deprotonation ability of linkers affect the final MOF. **[27]**

Example in diagram: Different solvent mixtures (like DMF+EtOH, EtOH+H_2O) lead to different MOF morphologies.



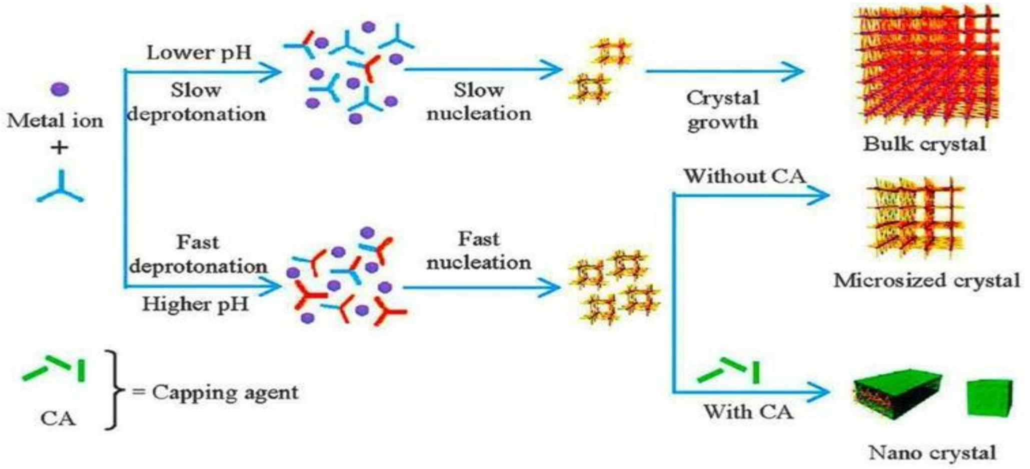
❖ Effect of solvent systems on morphology of MOF

2. pH:

- pH affects how metal ions and linkers bind.
- Higher pH = more deprotonation of linker = different MOF structures.
  Example MOFs: MIL-121 (pH 1.4),MIL-118 (pH 2),MIL-120 (pH 12.2).
- pH also affects color and whether the network is interpenetrated (layered). **[28]**

3. Temperature:

- Higher temperature = better solubility,faster reactions,bigger and better crystals.
- Promotes bulk, micro, or nano crystal formation.
- Especially in hydrothermal methods, higher temps give stable and complex MOFs. **[29-30]**



❖ Effect of pH control and crystal capping during coordination modulation

▪ **<u>Metal-organic frameworks for Gas storage and Gas separation:</u>**

The key to developing metal-organic frameworks (MOFs) for gas storage and the separation of small molecules lies in precisely controlling their pore size, shape, and surface functionalities. This allows MOFs to efficiently store gases and selectively recognize and capture specific molecules.

1. Methane storage:

- MOFs are special materials used to store gases like methane.

• To store more methane, the size and shape of the pores (tiny holes) in the MOF must be controlled very carefully.

• A MOF called UTSA-20 was made using a hexa-carboxylic acid and copper units. It has 1D pores and channels that help trap methane well.

• UTSA-20 has moderate porosity and can store 195 cm^3 of methane per cm^3 of material under room conditions (35 bar).

• Its micropores can hold methane very densely (0.22 g/cm^3), which is one of the best ever recorded.

• Adding pyrimidine groups (nitrogen-containing) improved storage further. The new MOF UTSA-76 (a modified version) stored 257 cm^3 of methane per cm^3 at higher pressure (65 bar).

• UTSA-76 showed the best methane working capacity of 197 cm^3 under tested conditions.

Conclusion:
Adding nitrogen-based groups to MOFs helps them store more methane. These findings can help develop better MOFs for future gas storage needs. **[31-34]**

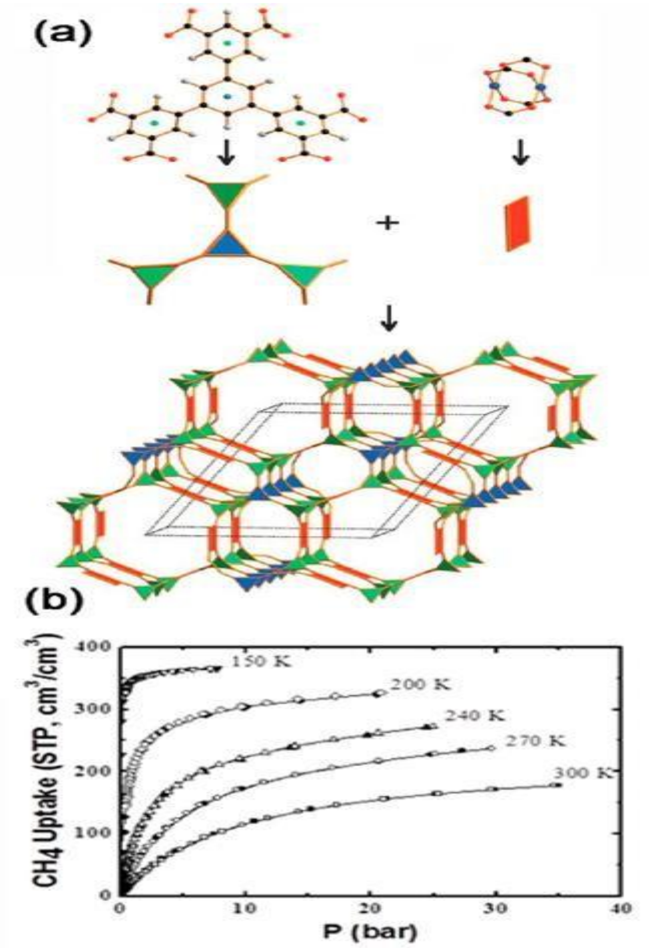


Figure 1. (a) Two types of 1D channels in UTSA-20, with open metal sites pointing to the pores.

(b) Temperature-dependent total high pressure methane sorption isotherms of UTSA-20.

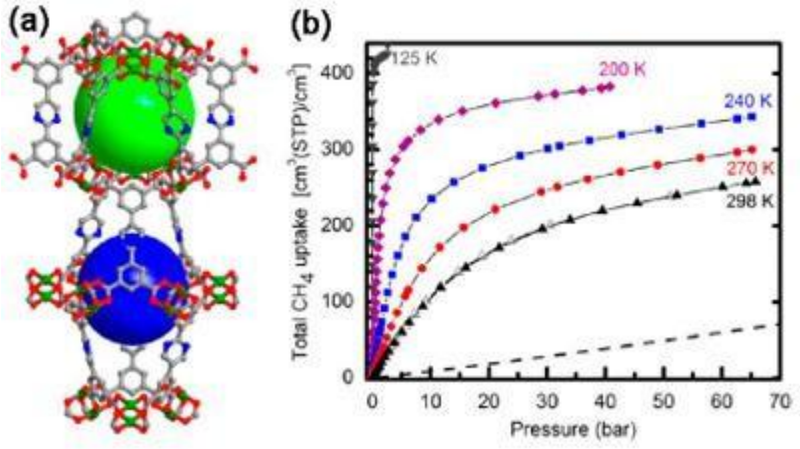


Figure 2. (a) Crystal structure of UTSA-76.
(b) Temperature dependent high-pressure methane sorption isotherms of UTSA-76a

2. Separations of C2H2/C2H4:

• Scientists created special porous materials called MOFs (Metal-Organic Frameworks) using mixed metals. These materials have tiny pores that can be finely adjusted.

• **Materials used:**
They used a compound called Cu(SalPycy) and added different ligands (like BDC=1,4-benzenedicarboxylate and CDC=1,4-cyclohexanedicarboxylate) to make MOFs called:
M'MOF-2 (M'MOF=mixed-metal-organic frameworks)
M'MOF-3

• M'MOF-3 has smaller pores than M'MOF-2, which helps separate C_2H_2 from C_2H_4 better because of stronger sieving effects.

• They improved how it works by adding different chemical groups—like diamines, carboxylates, and alkane chains—to adjust the pore sizes and how the molecules interact. The variant called M'MOF-3 showed the best performance, achieving a selectivity of 24.03, which means it separated things very effectively.

• MOF-4 worked best in real-world (industrial) conditions—giving >99.0% pure ethylene by removing acetylene effectively.

• Although MOF-74 can separate gases, it also binds both C_2H_2 and C_2H_4, making separation less efficient.

• A new MOF called UTSA-100 was developed.

• UTSA-100 is better because it has right-sized pores (3.3 Å openings and 4.0 Å cages) and $-NH_2$ groups that attract C_2H_2 better.It gives a good balance between gas separation and gas storage.

• UTSA-100 works better than many others (M'MOF-3, MgMOF-74, etc.) in removing acetylene from gas mixture. **[35-37]**

3. Carbon Dioxide Capture and Separation:

• Capturing CO_2 at room temperature and low pressure (1 bar) is hard because:
(a) CO_2 storage depends on pore size, volume, open metal sites, and functional groups.
(b) Most materials do not work well in these mild conditions.

• The solution – Special MOF (UTSA-16):
Scientists developed a new MOF called UTSA-16, made using:
A compound: $[K(H_2O)_2Co_3(cit)(Hcit)]$
"cit" stands for citric acid, a common and cheap chemical.

• UTSA-16 is good because,
It has a pore structure like a diamond.
It can hold a lot of CO_2 (160 cm^3 per gram) at room temperature.

How it captures CO_2:
Neutron diffraction studies show that CO_2 molecules fit perfectly into the pores.
CO_2 sticks better because of:
Hydrogen bonds that help hold it in place.
Water molecules inside the material that attract CO_2 and make it easier to capture.

Conclusion:

UTSA-16 is a powerful and efficient MOF for capturing CO_2 at ambient conditions, thanks to its special structure and bonding features. **[38]**

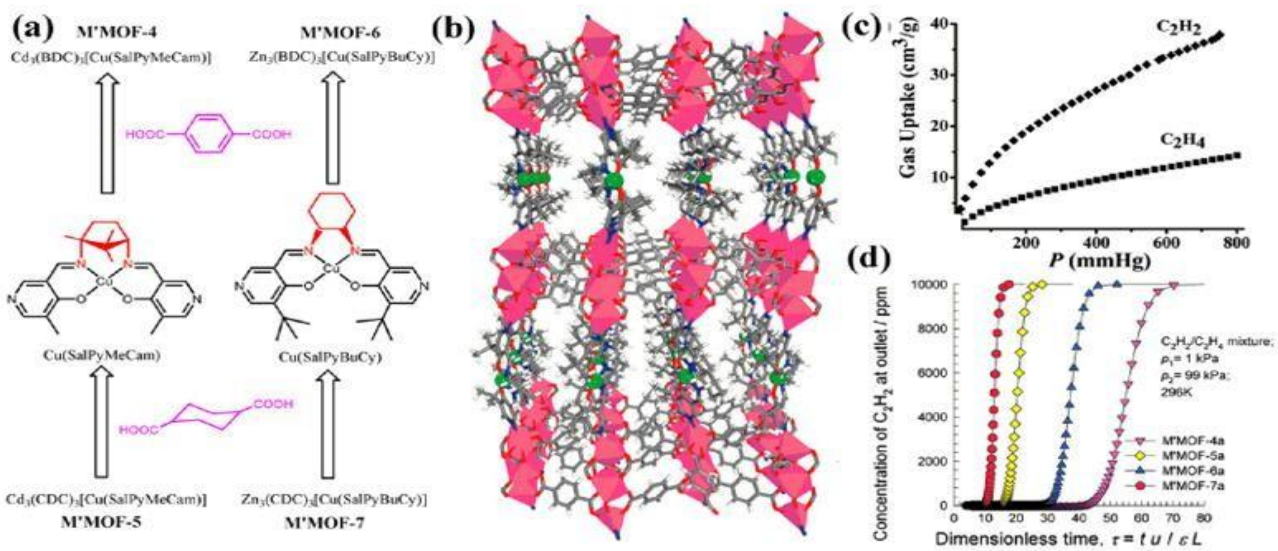


Figure 3. (a) Schematic diagram for the synthesis of four mixed-metal organic frameworks (M'MOFs)
(b) Single crystal structure of M'MOF-6 viewed along a axis.
(c)C_2H_2andC_2H_4 adsorption isotherms of M'MOF-6a at 295K.
(d Breakthrough plot showing C_2H_2 capture per liter vs. dimensionless time ($\tau_e$break).

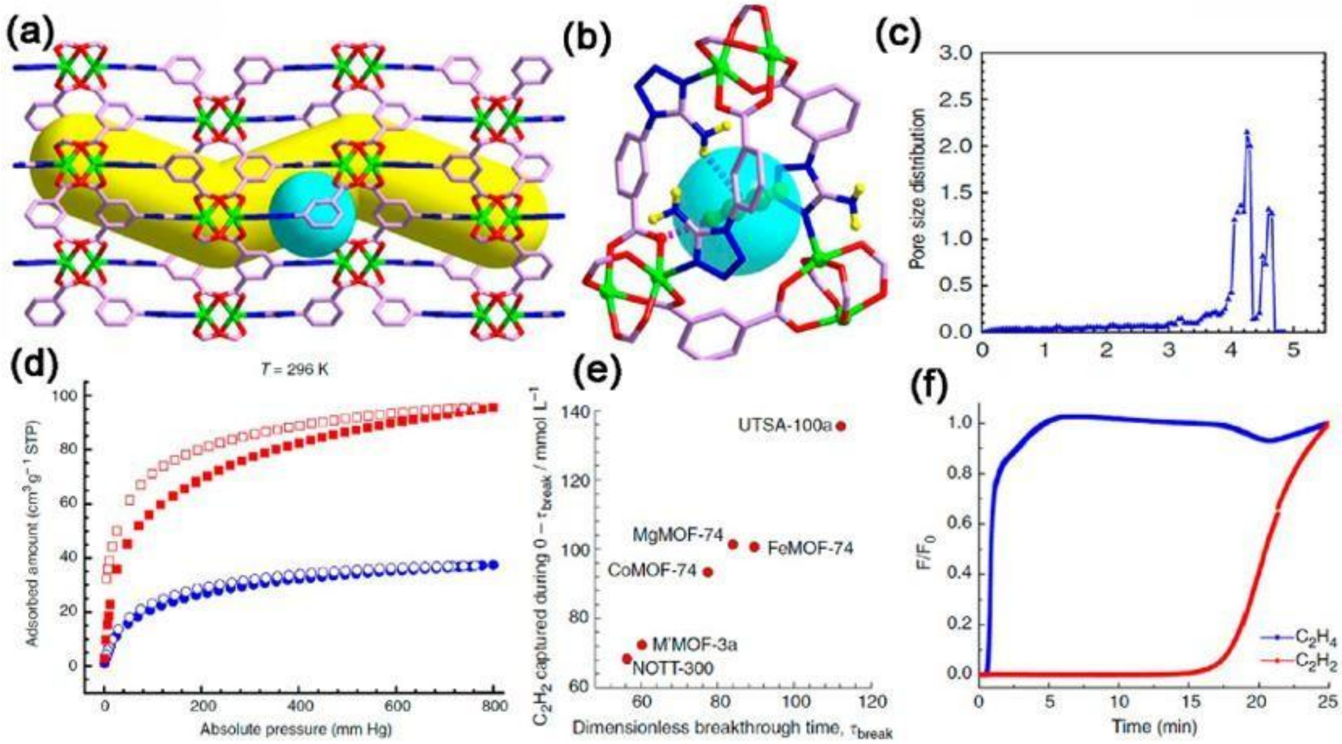


Figure 4. (a) Pore structure along c-axis and the cage with the diameter of about 4.0 Å in the pore wall with the window openings of 3.3 Å.

(b) Acetylene binding site showing interaction distances.

(c) Pore size distribution (PSD) of UTSA-100a.

(d) C_2H_2 vs. C_2H_4 adsorption isotherms at 296 K.

(e) Plot of C_2H_2 capture vs. $\tau_e$break for various MOFs.

(f) Breakthrough curve for 1% C_2H_2 / C_2H_4 mixture over UTSA-100a.

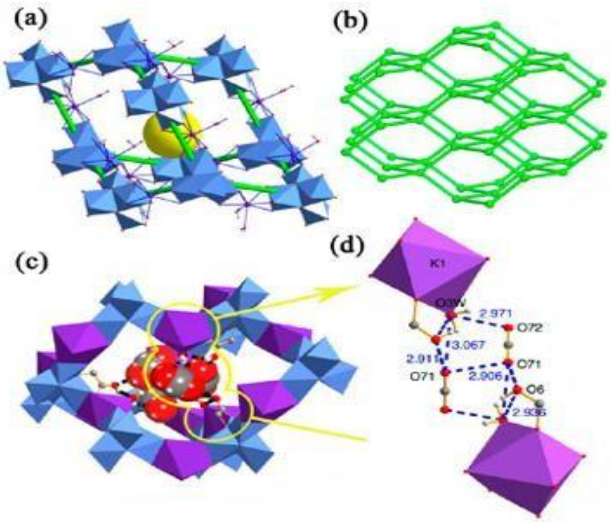


Figure 5. (a) Structure of UTSA-16

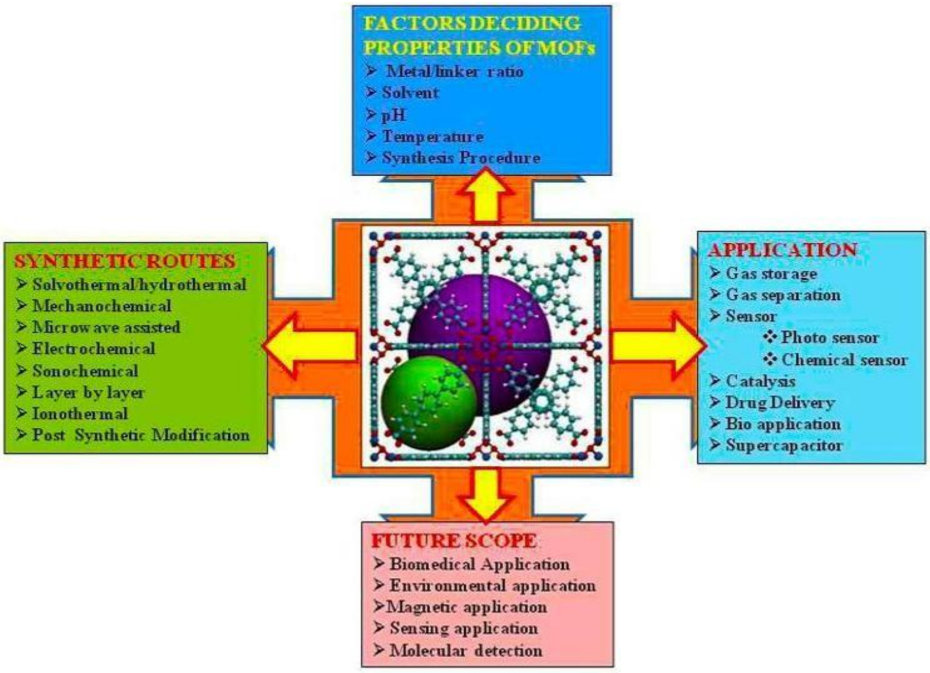
(b) Diamond framework topology.

(c) Structure of CO_2 loaded UTSA-16 indicating a couple of CO_2 molecules loaded within the cage.

(d) The cooperative interactions between CO_2 molecules and the framework.

▪ Future scope:

Research on metal-organic frameworks (MOFs) is growing rapidly, but there are still gaps in understanding their structure, stability, and properties. The reasons behind the breakdown of some MOFs over time are not yet fully studied. While MOFs have shown promise in delivering anticancer and antiviral drugs, they could be explored for other drugs as well. However, detailed toxicological studies are needed before such products can be safely commercialized.



❖ **Summarization: MOF at a glance**

▪ Conclusion and outlook:

This Account summarizes recent progress in designing functional metal–organic frameworks (MOFs) for diverse applications, including gas storage and separation, sensing, optics, and data storage. MOFs offer great versatility due to their tunable pore sizes, structures, and the ability to incorporate various metals, linkers, and guest species. Recent developments include protein-based MOFs and encapsulation of nanoparticles and biomolecules. These features make MOFs a highly promising platform for advanced materials. Ongoing commercialization and interdisciplinary collaboration are key to turning MOFs into practical technologies for everyday use.

■ REFERENCES:

(1) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal−Organic Frameworks. Science 2013, 341, 123044.

(2) Zhou, H.-C.; Kitagawa, S. Introduction. Metal−Organic Frame works (MOFs). Chem. Soc. Rev. 2014, 43, 5415−5418.

(3) Chen, B.; Xiang, S.; Qian, G. Metal−Organic Frameworks with Functional Pores for Recognition of Small Molecules. Acc. Chem. Res. 2010, 43, 1115−1124.

(4) Zhou, H.-L.; Zhang, Y.-B.; Zhang, J.-P.; Chen, X.-M. Supra molecular-jack-like Guest in Ultra microporous Crystal for Exceptional Thermal Expansion Behaviour. Nat. Commun. 2015, 6, 6917.

(5) Batten S R, Champness N R, Chen X M, GarciaMartinez J, Kitagawa S, Lars O ¨ hrstro¨m, O'Keeffe M,Suh M P and Reedijk J 2013 Terminology of metalorganic frameworks and coordination polymers (IUPAC Recommendations 2013) Pure Appl. Chem. 85 1715.

(6) Wu H, Zhou W, Yildirim T (2009) High-capacity methane storage in metal organic frameworks M2(dhtp): the important role of open metal site. J Am Chem Soc 131: 4995-5000.

(7) Zacher D, Shekhah O, Woll W, Fischer RA, (2009) Thin films of metal-organic fameworks. Chem Soc Rev 38: 1418-1429.

(8) Ma M (2011) Preparation, characterization of metal-organic frameworks for biological applications. Ph.D. thesis, Ruhr Universitty, Bochum.

(9) Maark TA, Pal S (2010) A model study of effect of M = Li, Na, Be, Mg and Al ion decoration on hydrogen adsorption of metal-organic framework-5. Int J Hydrogen Energy 35: 12846-12857.

(10) Yaghi OM, O'keeffee M, Ockwing NW, Chae HK, Eddaoudi M, Ki J (2003) Reticular synthesis and design of new materials Nature, 423: 705-714.

(11) Sabouni R (2013) Carbon dioxide adsorption by metal organic frameworks (Synthesis, testing and modeling) Ph.D. thesis, University of western Ontario, Electronic thesis and dissertation repository.

(12) Dincă M, Long JR (2005) Strong H2 binding and 15 selective gas adsorption within the microporous coordination solid Mg3(O2C-C10H6-CO2)3. J Am Chem Soc 127: 9376-9377.

(13) Liang Z, Marshall M, Chaffee AL (2009) CO2 adsorption-based separation by metal organic framework (Cu-BTC) versus zeolite (13X). Energy and Fuels 23: 2785-2789.

(14) Millward A, Yaghi OM (2005) Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature. J Am Chem Soc 127: 17998-17999.

(15) Demessence A, D'Alessandro D, Foo M, Long J (2009) Strong CO2 binding in a water stable, triazolate-bridged metal-organic framework functionalized with ethylenediamine. J Am Chem Soc 131: 8784-8786.

(16) Serre C, Bourrelly S, Vimont A, Ramsahye NA,Maurin G, Llewellyn P, Daturi M, Filinchunk Y,Leynaud O, Barnes P, Ferey G (2007) An explanation for the very large breathing effect of a metal-organic framework during CO2 adsorption. Advanced Materials 19: 2246-2251.

(17) Sumida K, Rogow DL, Mason JA, McDonald TM, Bloch ED, Herm ZR, Bae TH, Long JR (2012) Carbon Dioxide capture in Metal-organic frameworks. Chem Rev 112: 724-781.

(18)Wang C, Ying JY (1999) Sol-gel synthesis and hydrothermal processing of anatase and rutile titania nanocrystals. Chem Mater 11: 3113–3120. Doi: 10.1021/cm990180f.

(19) Nouar F, Eckert J, Eubank JF, Forster P, Eddaoudi M (2009) Zeolite like metal organic framework (ZMOFs) as hydrogen storage platform: Lithium and magnesium ion exchange and H2-(rho-ZMOF) interaction studies. J Am Chem Soc 131(8): 2864-2870.

(20) Jhung SH, Chang JS, Hwang JS, Park SE (2003) Selective formation of SAPO-5 and SAPO-34 molecular sieves with microwave irradiation and hydrothermal heating. Micropor Mesopor Mater 64: 33-39. Doi: 10.1016/S1387 1811(03)00501-8.

(21) ung SH, Lee JH, Yoon JW, Hwang JS, Park SE, and J. S. Chang JS (2005) Selective crystallization of CoAPO-34 and VAPO-5 molecular sieves under microwave irradiation in an alkaline or neutral condition. Micropor Mesopor Mater 80: 147-152. Doi: 10.1016/j.micromeso.2004.11.013.

(22) Jhung SH, Chang JS, Hwang YK, Park SE (2004) Crystal morphology control of AFI type molecular sieves with microwave irradiation. J Mater Chem 14: 280 285.
(23) Hwang YK, Chang JS, Park SE, Kim DS, Kwon YU, Jhung SH, Hwang JS, Park MS (2005) Microwave fabrication of MFI zeolite crystals with a fibrous morphology and their applications. Angew Chem Int Ed 44: 556-560.
(24) Richer I, Schubert M, Müller U Porous metal organic framework based on pyrroles and pyridinones. Patent WO2007/131955.
(25) Sono T, Mingos DMP, Baghurst DR, Lickiss PD (2004) Novel energy source for reactions. In the new chemistry: Hall N Ed, The press Syndicate of the university of Cambridge. Cambridge, Chapter 4.
(26) Zacher D, Yusenko K, Bétard A, Henke S, Molon M, Ladnorg T, Shekhah O, Schüpbach B, de los Arcos T, Krasnopolski M, Meilikhov M, Winter J, Terfort A, Wöll C, Fischer RA (2011) Liquid – phase epitaxy of multicomponent layer based porous coordination polymer of thin films of [M(L)(P)0.5] type: importance of deposition sequence on the oriented growth. Chem Eur J 17: 1448-1455.
(27) Yakovenko AA, Wei Z, Wriedt M, Li JR, Halder GJ, Zhou HC (2014) Study of guest molecules in metal- organic frameworks by powder X-ray diffraction: analysis of difference envelope density. Cryst Growth Des 14(11): 5397–5407.
(28) Seetharaj R, Vandana PV, Arya P, Mathew S (2016) Dependence of solvents, pH, molar ratio and temperature in tuning metal organic frameworks. Arabian journal of chemistry doi: 10.1016/j.arabjc.2016.01.003.
(29) Wang CC, Jing HP, Wang P, Gao SJ (2015) Series metal-organic frameworks constructed from 1,10- phenanthroline and 3,3’,4,4’-biphenyltetracarboxylic acid: Hydrothermal synthesis, luminescence and photocatalytic properties. J Mol Struct 1080: 44-51.
(30) Zang CY, Wang MY, Li QT, Qian BH, Yang XJ, Xu XY (2013) Hydrothermal synthesis, crystal structure and luminescent properties of two zinc(II) and cadmium(II) 3D metal-organic frameworks. Zeitschrift füranorganisch and allgemeine Chemie., 639(5): 826-831.
(31) Guo, Z.; Wu, H.; Srinivas, G.; Zhou, Y.; Xiang, S.; Chen, Z.; Yang, Y.; Zhou, W.; O’Keeffe, M.;Chen, B.A Metal−Organic Framework with Optimized Open Metal Sitesand Pore Spaces for High Methane Storage at Room Temperature. Angew. Chem., Int. Ed. 2011, 50, 3178−3181.
(32) He, Y.; Zhou, W.; Yildirim, T.; Chen, B. A Series of Metal− Organic Frameworks with High Methane Uptake and an Empirical Equation for Predicting Methane Storage Capacity. Energy Environ. Sci. 2013, 6, 2735−2744.
(33) Li, B.; Wen, H. M.; Wang, H.; Wu, H.; Tyagi, M.; Yildirim, T.; Zhou,W.;Chen, B.A Porous Metal−Organic Framework with Dynamic Pyrimidine Groups Exhibiting Record High Methane Storage Working Capacity.J. Am. Chem. Soc. 2014, 136, 6207−6210.
(34) Li, B.; Wen, H.-M.; Wang, H.; Wu, H.; Yildirim, T.; Zhou, W.; Chen, B. Porous Metal−Organic Frameworks with Lewis Basic Nitrogen Sites for High-Capacity Methane Storage. Energy Environ. Sci. 2015, 8, 2504−2511.
(35) Xiang, S. C.; Zhang, Z.; Zhao, C. G.; Hong, K.; Zhao, X.; Ding, D. R.; Xie, M. H.; Wu, C. D.; Das, M. C.; Gill, R.; Thomas, K. M.; Chen, B. Rationally Tuned Micropores within Enantiopure Metal−Organic Frameworks for Highly Selective Separation of Acetylene and Ethylene. Nat. Commun. 2011, 2, 204.
(36) Das, M.C.;Guo,Q.;He,Y.;Kim,J.;Zhao, C.G.;Hong,K.;Xiang, S.; Zhang, Z.; Thomas, K. M.; Krishna, R.; Chen, B. Interplay of Metallo ligand and Organic Ligand to Tune Micropores within Isostructural Mixed- Metal Organic Frameworks (M’MOFs) for Their Highly Selective Separation of Chiral and Achiral Small Molecules. J. Am. Chem. Soc. 2012, 134, 8703−8710.
(37) He, Y.; Krishna, R.; Chen, B. Metal−Organic Frameworks with Potential for Energy-Efficient Adsorptive Separation of Light Hydro carbons. Energy Environ. Sci. 2012, 5, 9107−9120.

(38) Guo, Z.; Wu, H.; Srinivas, G.; Zhou, Y.; Xiang, S.; Chen, Z.; Yang, Y.; Zhou, W.; O'Keeffe, M.;Chen, B.A Metal−Organic Framework with Optimized Open Metal Sitesand Pore Spaces for High Methane Storage at Room Temperature. Angew. Chem., Int. Ed. 2011, 50, 3178−3181.