

REMOVAL OF PHARMACEUTICAL FROM WASTE WATER USING METAL ORGANIC FRAME WORKS(MOF)

Submitted in partial fulfillment of the requirements for the award of
Bachelor of Technology degree in Chemical Engineering

By

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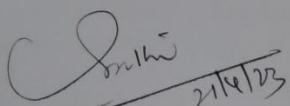


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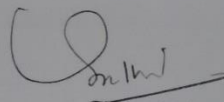
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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **ADHILIMAM MN** (39190001), **JOBIN CHAKO** (39190010), who carried out the project entitled **"REMOVAL OF PHARMACEUTICAL FROM WASTE WATER USING METAL ORGANIC FRAME WORK"** under our supervision from September 2022 to April 2023.

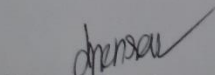
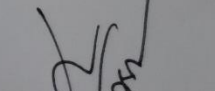


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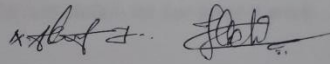

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DECLARATION

We **ADHILIMAM MN** (39190001) and **JOBINCHAKO** (39190010) hereby declare that the Project Report entitled "**REMOVAL OF PHARMACEUTICAL FROM WASTE WATER USING METAL ORGANIC FRAME WORK**" done by me under the guidance of **DR. S. SATHISH** in department of chemical engineering at Sathyabama university, submitted in partial fulfillment of the requirements for the award of Bachelor of Technology degree in Chemical Engineering.

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ABSTRACT

The removal of pharmaceuticals from wastewater using metal-organic frameworks (MOFs) as an adsorbent material. Pharmaceutical compounds are emerging contaminants in water bodies and pose a threat to human and environmental health. Conventional water treatment methods are inefficient in removing these contaminants, hence the need for innovative solutions. MOFs have shown promise in removing pharmaceuticals from wastewater due to their high surface area, tuneable pore size, and affinity towards specific molecules. The review examines the recent literature on the application of MOFs in the removal of pharmaceuticals from wastewater, including the advantages and limitations of using MOFs for this purpose. The review also discusses the mechanisms involved in the adsorption of pharmaceuticals onto MOFs and the factors that influence their adsorption performance. The results show that MOFs are effective in removing pharmaceuticals from wastewater and offer potential for application in real-world scenarios. However, more research is needed to optimize their use in terms of cost-effectiveness and scalability.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
AAS	Atomic Adsorption Spectrometer
BDC	Benzene dicarboxylate
CQDs	Carbon Quantum Dots
CCD	Central Composite Design
DMF	Dimethyl-formamide
Ea	Activation energy
EPC	Environmental Protection Agency
EtOH	Ethanol
Fe	Iron
FE SEM	Field Emission Scanning Electron Microscopy
FT-IR	Fourier Transform Infrared
GO	Graphene Oxide
HCL	Hydrochloric Acid
ICP- OES	Inductively Coupled Plasma - Optical Emission Spectroscopy
IPA	Iso-Propyl Alcohol
LED	Light Emitting Diode
MIL	Materiaux Institut Lavoisier
MNPs	Metal Nano Particles
MOF	Metal Organic Framework
mg/L	Milligram per litre
nm	Nanometre
PSM	Post Synthetic Modifications
ppm	Parts per million
rGO	reduced Graphene Oxide
RSM	Response Surface Technology
rpm	Ultraviolet
UV	Ultraviolet
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 METAL ORGANIC FRAME WORK

Metal-organic frameworks (MOFs) are a relatively new class of porous materials that have gained significant attention in recent years due to their unique properties and potential applications. MOFs are composed of metal ions or clusters linked by organic ligands to form a three-dimensional network with high surface area and porosity. These materials exhibit remarkable properties such as tuneable pore size and shape, high surface area, and selective gas adsorption, making them attractive for gas storage, separation, and catalysis applications. In this thesis, we will explore the synthesis, characterization, and applications of MOFs. The various synthesis methods used for the preparation of MOFs, including solvothermal synthesis, microwave-assisted synthesis, and mechanochemical synthesis. We will discuss the factors that influence the formation of MOFs such as the choice of metal ion, organic ligand, solvent, and reaction conditions. Furthermore, we will highlight the recent advances in the synthesis of MOFs such as post-synthetic modification and covalent organic framework (COF) synthesis. the various characterization techniques used to investigate the structure, morphology, and properties of MOFs. These techniques include X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and gas sorption measurements. Recent innovation in many fields such as drugs for therapeutic and diagnostics, delivery, catalysis, gas storage, sensor, heterogeneous catalysis, solar energy, super-capacitors and adsorption (Bhattacharjee et al., 2014). We will also discuss the limitations of these techniques and the challenges associated with the characterization of MOFs. We will discuss the various gas storage applications of MOFs such as hydrogen, methane, and carbon dioxide storage. Additionally, we will explore the use of MOFs in gas separation processes such as CO₂ capture, natural gas purification, and air separation. MOFs as heterogeneous catalysts for various reactions such as oxidation, hydrogenation, and C-C bond formation. We will explore the advantages of using MOFs as catalysts, including high surface area and tuneable pore size, and their potential for applications in industry. As these elements significantly affect drug release patterns, porosity, colloid stability, and cellular uptake, they are ideal for

drug delivery applications (Furukawa et al., 2010). The synthesis and characterization of MOFs have been rapidly developing, and their applications in various fields are still being explored. The future of MOFs looks promising, and we can expect to see more advancements in the synthesis, characterization, and applications of MOFs in the coming years. MOFs are composed of metal ions or clusters linked by organic ligands to form a three-dimensional (3D) structure with ordered pores and high surface area. The properties of MOFs can be tuned by changing the metal and ligand components, making them highly versatile materials for various applications. One of the key features of MOFs is their high porosity and surface area. MOFs can have surface areas up to thousands of square meters per gram, which makes them ideal for gas storage and separation applications. The high porosity also enables MOFs to act as host materials for a wide range of guest molecules, including gases, liquids, and even other MOFs. MOFs have been studied extensively for their potential applications in catalysis, gas storage and separation, drug delivery, and sensing. MOFs are potentially the best options for enhancing the adsorptive removal process (Ahmed et al., 2015). In catalysis, MOFs can act as heterogeneous catalysts due to their high surface area and tuneable properties. MOFs have been used in various catalytic reactions, such as oxidation, reduction, and hydrogenation. MOFs can also be used for gas storage and separation, with potential applications in natural gas purification and carbon capture. MOFs can selectively adsorb gases such as carbon dioxide and methane, allowing for their separation from other gases. In drug delivery, MOFs have been explored as carriers for therapeutics due to their high surface area and porous nature. MOFs can be functionalized with various functional groups, allowing for targeted delivery of drugs to specific tissues or cells. MOFs have also been studied as sensors for various molecules, such as volatile organic compounds and gases. The high surface area of MOFs allows for the detection of even low concentrations of these molecules. Despite the potential applications of MOFs, there are still challenges that need to be addressed. One of the main challenges is the stability of MOFs under various conditions, such as humidity and temperature. MOFs can be susceptible to structural collapse or degradation under certain conditions, which can limit their practical applications. Additionally, one of the cutting-edge agricultural technologies, MOFs, or metal organic frameworks, has grown in significance across the fields of sensing and removal of agrochemicals (Deria et al., 2014). the synthesis of MOFs

can be complex and time-consuming, requiring precise control over the reaction conditions. In conclusion, MOFs are a promising class of materials with unique properties and potential applications in various fields. The high surface area and tuneable properties of MOFs make them ideal for gas storage and separation, catalysis, drug delivery, and sensing applications. However, further research is needed to address the challenges of stability and synthesis in order to fully realize the potential of MOFs for practical applications. Advances in synthetic methods and characterization techniques have allowed for the creation and analysis of MOFs with increasingly complex structures and properties. MOFs have been studied for their ability to store and separate gases such as hydrogen, methane, and carbon dioxide. The development of MOFs with high surface areas and tailored pore sizes has led to significant improvements in gas storage and separation efficiency. MOFs have shown promise as heterogeneous catalysts for a range of chemical reactions, including oxidation, reduction, and cross-coupling reactions. MOFs are potentially the best options for enhancing the adsorptive removal process (Ahmed et al., 2015). Studies have focused on improving catalytic activity and selectivity through the design of MOFs with specific active sites. MOFs have been investigated as potential drug delivery vehicles due to their high surface area and tuneable properties. Studies have focused on developing MOFs with controlled drug release properties and improved biocompatibility. Advances in computational modeling have allowed for the prediction and design of MOFs with specific properties and applications. Computational studies have been used to identify promising MOFs for gas storage and separation, catalysis, and drug delivery. Advances in computational modeling have allowed for the prediction and design of MOFs with specific properties and applications. Computational studies have been used to identify promising MOFs for gas storage and separation, catalysis, and drug delivery. MOFs continue to be a rapidly growing field with many potential applications and avenues for exploration.

1.2 TYPES OF MOFs

1.2.1 MIL-101

This is a highly porous MOF composed of chromium nodes and carboxylic acid ligands. MIL-101 has been studied extensively for its ability to adsorb a wide range of molecules, including caffeine. MIL-101 is a type of metal-organic framework (MOF) that has gained significant attention in recent years due to its high surface

area, tunable pore size, and exceptional stability. The name "MIL" is derived from the initials of the three researchers who first synthesized this MOF: Matsumoto, Isoda, and Yamanaka. MIL-101 consists of octahedral building units of metal ions (typically chromium, iron, or aluminum) connected by organic ligands to form a three-dimensional porous framework. The pore size and shape can be tuned by changing the length and geometry of the ligands used in the synthesis process. MIL-101 has shown promising applications in a variety of areas, including gas storage and separation, catalysis, drug delivery, and sensing. Its high surface area and tunable pore size make it an ideal material for gas storage and separation applications, where it can selectively adsorb and separate different gases based on their size, shape, and polarity. In catalysis, the large pore size and high stability of MIL-101 make it an attractive support for immobilizing and stabilizing catalysts. Overall, MIL-101 is a highly versatile MOF with a wide range of potential applications, and it continues to be an active area of research in materials science and chemistry.

1.2.2 UiO-66: This is a zirconium-based MOF that exhibits high thermal stability and a large surface area. UiO-66 has been studied for its ability to adsorb pollutants from water, including caffeine. UiO-66 is a metal-organic framework (MOF) that is known for its exceptional stability and high surface area. The framework is constructed from inorganic nodes (zirconium oxide clusters) and organic linkers (terephthalic acid or its derivatives). The name UiO stands for Universiteit van Amsterdam (UvA), Instituto de Tecnologia Química (ITQ), and Oxford, where the framework was first synthesized. The high stability of UiO-66 arises from the strong coordination bonds between the zirconium nodes and the organic linkers, which form a three-dimensional porous structure. This structure has a high surface area and can be tuned to selectively adsorb certain molecules or ions. UiO-66 has been studied for a range of applications, including gas storage, catalysis, drug delivery, and water treatment. UiO-66 is also known for its interesting mechanical properties, such as high elasticity and flexibility, which have been attributed to the nature of the coordination bonds and the framework topology. These properties make UiO-66 a promising material for applications that require mechanical stability, such as in membranes and coatings. Overall, UiO-66 is a versatile and promising MOF with a wide range of potential applications in various fields. Its stability, high surface area,

and tunable properties make it a particularly attractive material for use in separation and purification processes.

1.2.3 ZIF-8: This is a zeolitic imidazolate framework composed of zinc ions and imidazole ligands. ZIF-8 has a large surface area and good thermal stability, and has been studied for its ability to adsorb small molecules such as caffeine. ZIF-8, or zeolitic imidazolate framework-8, is a metal-organic framework (MOF) composed of metal ions (zinc) coordinated with organic ligands (imidazolate). It has a porous structure with a high surface area and tuneable pore size, making it an attractive material for various applications such as gas storage, separation, catalysis, and drug delivery. ZIF-8 is thermally and chemically stable, and its pore size can be adjusted by changing the size of the organic ligand used in its synthesis. It is also hydrophobic, which makes it useful in separating and adsorbing organic molecules from aqueous solutions. ZIF-8 has been extensively studied for gas storage and separation applications, particularly for the capture of carbon dioxide (CO₂) and other greenhouse gases. It has also been used as a catalyst for various reactions, such as oxidation and reduction reactions. In drug delivery, ZIF-8 has shown promise due to its ability to encapsulate drugs within its porous structure, protecting them from degradation and improving their solubility and bioavailability. Overall, ZIF-8 is a versatile and promising material with a wide range of potential applications, and further research is ongoing to explore its full potential.

1.2.4 MOF-5: This is a copper-based MOF composed of benzene dicarboxylic acid ligands. MOF-5 has a high surface area and high thermal stability, and has been studied for its ability to adsorb gases and organic molecules. MOF-5 (Metal-Organic Framework 5) is a well-known MOF consisting of Zn₄O tetrahedral units linked by 1,4-benzenedicarboxylic acid (BDC) ligands to form a three-dimensional porous structure. It was first synthesized by Omar Yaghi and his research group in 1999. MOF-5 has a high surface area and pore volume, making it a promising material for various applications such as gas storage, catalysis, and drug delivery. Its structure consists of two types of pores: large, cage-like pores formed by the tetrahedral units and smaller pores formed by the BDC ligands. The large pores can accommodate guest molecules such as gas molecules, while the smaller pores can selectively adsorb smaller molecules. The synthesis of MOF-5 is typically done through

solvothermal methods, which involve the reaction of zinc acetate dihydrate with BDC in a solvent mixture of N,N-dimethylformamide (DMF) and methanol at high temperature and pressure. The resulting MOF-5 crystals are often characterized using techniques such as X-ray diffraction (XRD) and nitrogen gas adsorption measurements to determine their structural properties. Despite its promising properties, MOF-5 has some limitations, such as its low stability under certain conditions and the limited selectivity of its pore structure. Researchers continue to work on developing new MOFs with improved properties for various applications.

1.2.5 HKUST-1: This is a copper-based MOF composed of carboxylic acid ligands. HKUST-1 has a high surface area and has been studied for its ability to adsorb gases and organic molecules. HKUST-1 (or HKUST-1 MOF, also known as $\text{Cu}_3(\text{BTC})_2$) is a metal-organic framework (MOF) composed of copper ions coordinated to benzene-1,3,5-tricarboxylic acid (BTC). It was first synthesized in 1999 by researchers at the Hong Kong University of Science and Technology (HKUST), which is where its name comes from. HKUST-1 has a porous structure with high surface area and tunable pore size, making it a promising material for gas storage and separation, catalysis, and sensing applications. The copper ions in HKUST-1 also give it interesting electronic, magnetic, and optical properties, which have been studied for potential use in electronic and photonic devices. HKUST-1 has been extensively studied and characterized, and its properties have been tuned by modifying the size and functionality of the BTC ligands, as well as by incorporating other metal ions into the structure. Its stability, high capacity for gas adsorption, and selectivity for certain gases make it a particularly attractive material for applications such as carbon capture and storage. Overall, HKUST-1 is a widely recognized and versatile MOF that has contributed significantly to the development of the field of MOF chemistry and materials science. HKUST-1 (or HKUST-1 MOF, also known as $\text{Cu}_3(\text{BTC})_2$) is a metal-organic framework (MOF) composed of copper ions coordinated to benzene-1,3,5-tricarboxylic acid (BTC). It was first synthesized in 1999 by researchers at the Hong Kong University of Science and Technology (HKUST), which is where its name comes from. HKUST-1 has a porous structure with high surface area and tuneable pore size, making it a promising material for gas storage and separation, catalysis, and sensing applications. The copper ions in HKUST-1 also give it interesting electronic, magnetic, and optical

properties, which have been studied for potential use in electronic and photonic devices. HKUST-1 has been extensively studied and characterized, and its properties have been tuned by modifying the size and functionality of the BTC ligands, as well as by incorporating other metal ions into the structure. Its stability, high capacity for gas adsorption, and selectivity for certain gases make it a particularly attractive material for applications such as carbon capture and storage. Overall, HKUST-1 is a widely recognized and versatile MOF that has contributed significantly to the development of the field of MOF chemistry and materials science.

1.2.6 PCN-222: This is a zinc-based MOF composed of carboxylic acid and triazole ligands. PCN-222 has a high surface area and has been studied for its ability to adsorb organic molecules such as caffeine. These are just a few examples of the many types of MOFs that have been studied for their adsorption properties. Each MOF has its own unique properties that make it suitable for specific adsorption applications. MIL-101, UiO-66, ZIF-8, MOF-5, HKUST-1, and PCN-222 are all metal-organic frameworks (MOFs) that have unique properties and advantages for various applications. The unique feature of PCN-222 is its high thermal and chemical stability, which makes it an ideal material for various applications, such as gas storage and separation, catalysis, and drug delivery. Its porous structure can be modified by changing the type and size of the organic ligands, allowing for fine-tuning of its properties. In terms of gas storage, PCN-222 has shown high selectivity and capacity for the storage of various gases, including carbon dioxide, methane, hydrogen, and nitrogen. It has also been used as a catalyst for various chemical reactions, such as the conversion of carbon dioxide to methanol. PCN-222 has also been explored for drug delivery applications, where its high stability and biocompatibility make it an attractive candidate. Researchers have successfully loaded PCN-222 with drugs and demonstrated controlled release of the drugs in vitro. Overall, PCN-222 is a promising MOF with a wide range of potential applications, and further research is ongoing to explore its full potential.

1.3 ADVANTAGES OF MOF

- This MOF has a large surface area, high porosity, and excellent chemical stability, making it suitable for various adsorption, separation, and catalysis applications. It can also be easily synthesized in large quantities and modified to enhance its properties.
- This MOF has a high thermal stability, large surface area, and tuneable pore size, making it suitable for gas storage, separation, and catalysis applications. It also has a high stability in acidic and basic conditions, making it suitable for use in harsh environments.
- This MOF has a high surface area, high thermal stability, and good chemical and moisture stability, making it suitable for various adsorption and separation applications. It is also relatively easy to synthesize and can be modified to enhance its properties.
- This MOF has a high surface area, high porosity, and good chemical and thermal stability, making it suitable for gas storage and separation applications. It can also be easily synthesized in large quantities and modified to enhance its properties.
- This MOF has a high surface area, high thermal stability, and tuneable pore size, making it suitable for gas storage, separation, and catalysis applications. It also has a high stability in acidic and basic conditions, making it suitable for use in harsh environments.
- This MOF has a high surface area, high porosity, and excellent chemical stability, making it suitable for various adsorption, separation, and catalysis applications. It can also be easily synthesized in large quantities and modified to enhance its properties.

1.4 DISADVANTAGES OF MOF

- Some MOFs can be susceptible to chemical and thermal degradation, which can limit their practical applications in harsh environments. However, efforts are being made to improve the stability of MOFs through the development of new synthesis methods and post-synthesis treatments.

- Many MOFs are sensitive to moisture, which can cause them to degrade or lose their adsorption properties. This can be addressed by using water-resistant coatings or storing MOFs in dry environments.
- The synthesis of MOFs can be expensive, and large-scale production of MOFs for industrial applications may not be economically feasible. However, advances in MOF synthesis and scaling-up methods are helping to reduce costs.
- Some MOFs may have limited selectivity for specific molecules, which can limit their applications in adsorption and separation processes. However, researchers are working on modifying MOFs to enhance their selectivity for specific molecules.

1.5 PHARMACEUTICAL POLLUTION AND POLLUTANTS

Pharmaceuticals are essential for the health and well-being of humans and animals. However, the widespread use of pharmaceuticals has led to their presence in the environment as pollutants. Pharmaceuticals are excreted from the body in urine and feces, and they can also enter the environment through improper disposal, leaching from landfills, and discharge from wastewater treatment plants. Once in the environment, pharmaceuticals can undergo transformation and degradation, leading to the formation of new compounds that may have unknown effects on ecosystems and human health. This thesis aims to investigate the presence and fate of pharmaceuticals as pollutants in the environment. the different pharmaceuticals that have been detected in the environment, including antibiotics, analgesics, hormones, and antidepressants. We will discuss their sources, routes of entry into the environment, and their occurrence in various environmental matrices such as surface water, groundwater, and soil. Additionally, we will highlight the potential risks and impacts of pharmaceutical pollutants on aquatic and terrestrial ecosystems. the fate and transport of pharmaceutical pollutants in the environment. We will examine the different processes that affect the behaviour of pharmaceuticals in the environment, including adsorption, degradation, and transformation. We will also explore the factors that influence the transport of pharmaceuticals in the environment, such as hydrophobicity, molecular weight, and polarity. Furthermore, we will discuss the various environmental factors that affect the persistence and fate of pharmaceutical pollutants, such as pH, temperature, and sunlight. Nowadays, non-steroidal anti-inflammatory medications (NSAIDs) often

used newly created pharmaceutical drugs (Comoretto et al., 2005). The environmental impact and human health risks associated with pharmaceutical pollutants. We will examine the potential adverse effects of pharmaceutical pollutants on aquatic and terrestrial ecosystems, including the disruption of endocrine systems and the development of antibiotic resistance in bacteria. Moreover, we will discuss the potential risks to human health associated with the exposure to pharmaceutical pollutants, such as developmental and reproductive disorders. the environmental impact of pharmaceutical pollutants. We will examine the current regulations and guidelines in place to manage pharmaceutical waste and the need for more effective approaches to reduce the release of pharmaceutical pollutants into the environment. Additionally, we will discuss the role of advanced technologies, such as nanotechnology and bioremediation, in addressing the problem of pharmaceutical pollution. Furthermore, we will highlight the need for further research and collaboration to better understand the environmental impact of pharmaceuticals and develop effective solutions to reduce their presence in the environment. pharmaceuticals as pollutants in the environment are a significant concern, given their potential impact on aquatic and terrestrial ecosystems, as well as human health. The presence and fate of pharmaceuticals in the environment are complex and require a multidisciplinary approach to address the problem effectively. The implementation of effective regulations and guidelines, as well as the development of advanced technologies, are crucial in mitigating the environmental impact of pharmaceutical pollutants. Further research is needed to better understand the environmental fate and transport of pharmaceuticals and their potential risks to human health, as well as to develop effective strategies to reduce their presence in the environment. Pharmaceutical pollution is a growing concern in many parts of the world, as the use and disposal of medications can lead to the release of a variety of pollutants into the environment. These pollutants can have adverse effects on both human health and the natural ecosystems. One major source of pharmaceutical pollution is the improper disposal of medications. Many people dispose of unused or expired medications by flushing them down the toilet or sink, which can lead to the release of drugs into the water supply. Pharmaceuticals can also enter the environment through the excretion of drugs by humans and animals, as well as through the disposal of medical waste. Pharmaceutical pollutants can have a range of effects on the environment and

human health. Some of the most common pharmaceutical pollutants found in the environment include antibiotics, antidepressants, and hormones. These substances can have adverse effects on aquatic life, such as disrupting the reproductive systems of fish and other organisms. They can also lead to the development of antibiotic-resistant bacteria, which can be harmful to both humans and animals. In addition to environmental effects, pharmaceutical pollutants can also have impacts on human health. For example, exposure to high levels of antibiotics in the environment can lead to the development of antibiotic-resistant bacteria in humans. Exposure to hormones and other endocrine-disrupting substances can lead to a range of health problems, such as developmental disorders, reproductive problems, and cancer. MOFs have shown to be quite helpful in many biomedical uses including the production of pharmaceuticals (Bullock et al., 2015). Efforts to address pharmaceutical pollution have focused on a variety of strategies, including improved wastewater treatment and better medication disposal practices. Some countries have implemented programs to collect and properly dispose of unused medications, while others have implemented stricter regulations on the use and disposal of pharmaceuticals. There are also ongoing efforts to develop new technologies for the removal of pharmaceutical pollutants from wastewater and other sources. In conclusion, pharmaceutical pollution is a complex issue with significant implications for both the environment and human health. Understanding the sources and effects of pharmaceutical pollutants is critical for developing effective strategies for addressing this problem. While there are ongoing efforts to reduce pharmaceutical pollution, it will require continued research and innovation to effectively address this important issue. Pharmaceutical pollutants refer to any compounds or residues from pharmaceuticals that enter the environment and may have negative impacts on ecological and human health. Pharmaceuticals can enter the environment through a variety of pathways, including disposal of unused medication, excretion by humans and animals, and discharge from manufacturing facilities. Pharmaceuticals can enter rivers, lakes, and oceans through wastewater treatment plants and can have adverse effects on aquatic life. Pharmaceuticals can enter the soil through the application of biosolids from wastewater treatment plants, and can impact soil microbial communities and plant growth. Pharmaceuticals can enter the air through the evaporation of surface water, and can be transported long distances through atmospheric circulation. Some of the most commonly detected pharmaceutical

pollutants in the environment include antibiotics, hormones, and painkillers. These compounds can have adverse effects on the growth and development of aquatic organisms, as well as on human health. For example, exposure to antibiotics in the environment has been linked to the development of antibiotic resistance in bacteria, which can make infections more difficult to treat. Efforts to reduce pharmaceutical pollution include proper disposal of unused medications, improved wastewater treatment, and the development of new technologies for the removal of pharmaceuticals from water and soil. Additionally, pharmaceutical companies are increasingly exploring greener manufacturing processes that minimize the production of waste and pollutants.

Pharmaceutical pollutants are contaminants that originate from pharmaceutical products and their metabolites. They can enter the environment through various sources, such as human and animal excretion, improper disposal of unused or expired medication, and manufacturing and production processes. Here are some types of pharmaceutical pollutants and pollutions:

- **Antibiotics:** Antibiotics are commonly used in both human and veterinary medicine, and their widespread use has resulted in the development of antibiotic-resistant bacteria. When these drugs are excreted or disposed of improperly, they can enter water bodies and soil, leading to the contamination of aquatic and terrestrial ecosystems. MOF, or multiple organ failure, is a condition where multiple organs in the body fail to function properly. Antibiotics are commonly used in the treatment of MOF, as infections can contribute to the development or worsening of this condition. Infections can cause an inflammatory response in the body, which can lead to the dysfunction or failure of multiple organs. Antibiotics work by killing or inhibiting the growth of bacteria that may be causing an infection. By treating infections with antibiotics, the inflammatory response in the body can be reduced, which may help prevent or improve MOF. However, the use of antibiotics in MOF can also have negative effects. Antibiotics can disrupt the balance of bacteria in the body, leading to conditions such as antibiotic-associated diarrhea or overgrowth of antibiotic-resistant bacteria. In addition, the overuse of antibiotics can contribute to the development of antibiotic resistance, which can make infections harder to treat in the future. Therefore, the use of antibiotics in MOF must be carefully considered and monitored by healthcare professionals. The choice of antibiotic and duration of

treatment should be based on the specific infection and the patient's individual needs.

- **Hormones:** Hormones are used in various pharmaceutical products, including contraceptives and hormone replacement therapies. They can enter the environment through human and animal excretion, and their presence in water bodies can lead to hormonal disruptions in aquatic organisms. Pharmaceutical pollutants are a type of emerging contaminant that can be found in waterways and the environment. These pollutants can come from a variety of sources, including pharmaceutical manufacturing facilities, wastewater treatment plants, and improper disposal of medications. One type of pharmaceutical pollutant is hormones, which can have negative effects on aquatic organisms and human health. Hormones are chemicals produced by the endocrine system that regulate various bodily functions. When hormones enter the environment as pollutants, they can disrupt the endocrine systems of animals and humans who are exposed to them. Studies have shown that exposure to hormone pollutants can lead to a variety of health problems, including reproductive disorders, developmental abnormalities, and cancer. In aquatic organisms, hormone pollutants have been linked to changes in behavior, growth, and reproduction. Efforts are being made to reduce the amount of pharmaceutical pollutants in the environment, including improved wastewater treatment and proper disposal of medications. Additionally, pharmaceutical companies are working to develop more environmentally friendly manufacturing practices and products that are less likely to contribute to pollution.
- **Painkillers:** Painkillers, such as opioids, are commonly prescribed for pain relief, but they can also be misused and abused. Improper disposal of these drugs can lead to their accumulation in water bodies, which can harm aquatic organisms and impact water quality. Painkillers, also known as analgesics, are commonly used medications for the relief of pain. However, the widespread use of painkillers has led to the accumulation of these drugs in the environment, which can have negative impacts on ecosystems and human health. Pharmaceutical pollution refers to the release of pharmaceuticals, including painkillers, into the environment. These drugs can enter waterways through various routes, such as wastewater treatment plants and runoff from agricultural areas. Once in the environment, painkillers can affect aquatic organisms, such as fish, and disrupt their endocrine systems, behavior, and reproductive capacity. Painkillers can also be considered as pollutants because of

their potential to harm human health. Misuse and overuse of painkillers can lead to addiction, overdose, and other adverse health effects. In addition, the presence of painkillers in the environment can lead to unintentional exposure through drinking water, which can have negative impacts on human health. To reduce the environmental and health impacts of painkillers, it's important to properly dispose of unused medications, use painkillers only as prescribed, and avoid flushing medications down the toilet or sink. Wastewater treatment plants can also play a role in reducing pharmaceutical pollution by implementing advanced treatment technologies that can remove these drugs from wastewater.

- **Chemotherapeutic agents:** Chemotherapeutic agents are used to treat cancer, but they can have harmful effects on both humans and the environment. When these drugs are excreted, they can enter water bodies and harm aquatic organisms. Additionally, improper disposal of chemotherapy waste can pose a risk to human health and the environment. Chemotherapy drugs are used to treat cancer and are an essential part of modern cancer therapy. However, they can also contribute to pharmaceutical pollution and the release of pollutants into the environment. Chemotherapy drugs can enter the environment through several pathways, such as through the excretion of patients receiving chemotherapy, disposal of unused drugs, and improper handling or disposal of contaminated materials by healthcare workers. These drugs can persist in the environment for a long time and may have harmful effects on aquatic life, soil organisms, and even human health. Pharmaceutical pollutants from chemotherapy drugs can be toxic to aquatic organisms and affect their growth and reproduction. They can also cause genetic damage and cancer in animals exposed to them. In addition, some chemotherapy drugs have been shown to have estrogenic effects, which can disrupt the endocrine systems of aquatic organisms. The proper handling, storage, and disposal of chemotherapy drugs are important to minimize the release of pollutants into the environment. Healthcare facilities should have protocols in place for the safe handling and disposal of chemotherapy waste, and patients should follow their healthcare provider's instructions for the safe disposal of any unused medication. Additionally, pharmaceutical companies should work to develop more environmentally friendly alternatives to chemotherapy drugs and invest in research to better understand the environmental impacts of these drugs.

- **Personal care products:** Personal care products, such as lotions and shampoos, can contain chemicals that can be harmful to the environment. When these products are washed off, they can enter water bodies and harm aquatic organisms. Overall, pharmaceutical pollutants can have significant impacts on both human and environmental health. Personal care products, such as cosmetics, shampoos, and lotions, are a significant source of pharmaceutical pollution and pollutants. These products often contain a variety of chemicals, including active pharmaceutical ingredients (APIs), preservatives, fragrances, and other additives. When these products are used and washed off, the chemicals can enter the environment through wastewater, either by direct discharge or through sewage treatment plants. Pharmaceutical pollutants from personal care products can have harmful effects on aquatic organisms, such as fish and amphibians, and can even enter the food chain. In addition, some of these chemicals have been shown to have endocrine-disrupting properties, meaning that they can interfere with the hormonal systems of animals and humans. To reduce the impact of personal care products on pharmaceutical pollution, it's important to be aware of the ingredients in the products you use and choose products that are labeled as environmentally friendly or biodegradable. It's also important to properly dispose of unused medications and to avoid flushing them down the toilet or sink. In addition, improvements in wastewater treatment technology can help to remove pharmaceutical pollutants from wastewater before it is discharged into the environment.

1.6 EFFECTS OF CAFFEINE

Caffeine is one of the most widely consumed psychoactive substances in the world, present in various food and beverage products such as coffee, tea, energy drinks, and chocolate. Despite its popularity, the effects of caffeine on human physiology and behaviour are still being studied. This thesis aims to provide a comprehensive analysis of the physiological and behavioural impacts of caffeine consumption. the chemical and pharmacological properties of caffeine. We will discuss the sources of caffeine, including coffee, tea, and energy drinks, and how caffeine is metabolized in the body. Additionally, we will examine the mechanisms of action of caffeine,

including its effects on adenosine receptors, neurotransmitters, and hormones. the physiological effects of caffeine on various bodily systems, including the cardiovascular, respiratory, and gastrointestinal systems. We will examine the effects of caffeine on blood pressure, heart rate, and respiratory rate, as well as its impact on the digestive system, including its role in enhancing digestion and reducing constipation. the behavioural effects of caffeine, including its impact on mood, cognition, and performance. We will examine the effects of caffeine on alertness, attention, memory, and reaction time, as well as its impact on mood, including its role in reducing fatigue and improving mood. the potential health effects and risks associated with caffeine consumption. We will examine the impact of caffeine on sleep quality, anxiety, and addiction, as well as its potential role in increasing the risk of cardiovascular disease and affecting bone density. Additionally, we will discuss the potential risks associated with high caffeine intake, including caffeine overdose and its effects on pregnancy and breastfeeding. the consumption patterns of caffeine and the regulations in place to manage its use. We will examine the trends in caffeine consumption across different age groups and populations, as well as the various factors that influence caffeine intake, including social and cultural factors. Additionally, we will discuss the current regulations and guidelines in place to manage caffeine consumption, including the maximum recommended daily intake and the labelling requirements for caffeine-containing products. caffeine is a widely consumed psychoactive substance with various physiological and behavioural effects. The impacts of caffeine on human health and well-being are complex and require a multidisciplinary approach to address. Further research is needed to better understand the health effects and risks associated with caffeine consumption, as well as to develop effective strategies to manage its use. The implementation of regulations and guidelines, as well as education and awareness programs, is crucial in ensuring safe and responsible caffeine consumption. Caffeine is a naturally occurring stimulant found in coffee, tea, and other plants. It is also commonly used as an ingredient in energy drinks, soft drinks, and medications. Caffeine is a psychoactive substance that affects the central nervous system and can produce a range of physiological and psychological effects. One of the primary effects of caffeine is increased alertness and attention. This is because caffeine acts as an antagonist to adenosine receptors in the brain, which are responsible for promoting sleep and reducing arousal. By blocking these

receptors, caffeine increases the activity of other neurotransmitters such as dopamine and norepinephrine, which promote wakefulness and attention. Caffeine can also affect mood and cognitive performance. Studies have shown that moderate doses of caffeine can improve mood, reduce fatigue, and increase cognitive performance in tasks such as reaction time, memory, and attention. However, the effects of caffeine on mood and cognition can vary depending on individual factors such as age, sex, and genetics. In some cases, high doses of caffeine can produce negative side effects such as anxiety, restlessness, and insomnia. Another effect of caffeine is increased metabolism and thermogenesis. Caffeine stimulates the release of adrenaline, which in turn increases the body's metabolic rate and causes the breakdown of stored fats for energy. This effect can be useful for weight loss and athletic performance, but it can also cause negative side effects such as dehydration and increased heart rate. Caffeine can also affect sleep quality and quantity. Because caffeine has a half-life of approximately 5-6 hours, it can remain in the body for several hours after consumption and interfere with sleep. Studies have shown that caffeine can reduce the total amount of sleep and increase the time it takes to fall asleep. Additionally, caffeine can disrupt the circadian rhythm, which regulates the sleep-wake cycle, and cause insomnia or other sleep disorders. In conclusion, caffeine is a complex substance that can produce a range of effects on the body and mind. While moderate doses of caffeine can improve alertness, mood, and cognitive performance, high doses can cause negative side effects such as anxiety, restlessness, and insomnia. Understanding the effects of caffeine can be useful for individuals who consume caffeine regularly, as well as for healthcare professionals who prescribe medications that contain caffeine. Caffeine is a central nervous system stimulant that is found in many commonly consumed beverages and foods such as coffee, tea, soda, and chocolate. When consumed, caffeine acts on the brain by blocking the action of a neurotransmitter called adenosine, which is responsible for promoting sleep and suppressing arousal. As a result, caffeine can increase alertness, improve mood, and enhance cognitive performance. It can also increase heart rate and blood pressure, and lead to a temporary increase in metabolism and energy expenditure. However, the effects of caffeine can vary widely depending on factors such as individual sensitivity, dosage, and frequency of consumption. For some people, even low doses of caffeine can cause jitteriness, anxiety, and sleep disturbances. In addition, chronic high caffeine intake may lead

to dependence, tolerance, and withdrawal symptoms such as headaches, fatigue, and irritability. the effects of caffeine can be both positive and negative, and it is important to consume it in moderation and be aware of its potential effects on your body and mind. Caffeine is a naturally occurring stimulant that is commonly found in coffee, tea, chocolate, and some soft drinks. While caffeine is generally safe for human consumption in moderate amounts, it can have some negative effects on the environment if not properly disposed of. One of the primary ways that caffeine can negatively impact the environment is through the disposal of coffee grounds and tea bags. When these items are thrown in the trash and end up in a landfill, they can release caffeine and other chemicals into the surrounding soil and water. This can have harmful effects on plants and animals in the area, as well as on the quality of the groundwater. Another way that caffeine can affect the environment is through its use in agricultural practices. Caffeine is sometimes used as a natural pesticide, as it can be toxic to certain insects. However, this can also have unintended consequences for non-target species and for the overall ecosystem. Finally, caffeine can also contribute to water pollution when it is released into bodies of water through wastewater treatment plants or other sources. While caffeine is not considered a major pollutant, it can still have negative effects on aquatic organisms, particularly if it is present in high concentrations. Overall, while caffeine is generally safe for human consumption, it is important to be mindful of its potential effects on the environment and to dispose of coffee grounds, tea bags, and other sources of caffeine in a responsible manner. Caffeine citrate is a medication that is used to treat breathing problems in premature infants. It is a type of caffeine that is combined with citric acid to form a water-soluble salt. Caffeine citrate works by stimulating the central nervous system, which can help improve breathing and reduce episodes of apnea (pauses in breathing). Caffeine citrate is usually given as an injection into a vein or muscle, or as an oral solution. The dosage is based on the baby's weight and may be adjusted over time as needed. Although caffeine citrate is generally safe and effective when used as directed, it can cause side effects such as rapid heart rate, irritability, and vomiting. In rare cases, it can also cause seizures or other serious problems. It's important to use caffeine citrate only under the supervision of a healthcare provider who is experienced in caring for premature infants.

- The most common and well-known source of caffeine is coffee. The caffeine content in coffee varies depending on the type of coffee beans used and the method of preparation.
- Tea also contains caffeine, although in smaller amounts than coffee. Black tea generally has more caffeine than green or white tea.
- Energy drinks often contain high amounts of caffeine and are marketed as a way to boost energy levels. Soda caffeine: Some soft drinks, such as cola, contain caffeine. The amount of caffeine in these drinks varies widely depending on the brand.
- Caffeine is also found in chocolate, although the amount is usually smaller than in coffee or tea.
- Caffeine is sometimes added to over-the-counter medications like pain relievers to help increase their effectiveness.

It's important to note that consuming too much caffeine can have negative health effects, such as insomnia, anxiety, and heart palpitations. It's generally recommended that adults consume no more than 400 mg of caffeine per day, which is roughly equivalent to four cups of coffee.

1.6.1 ADVANTAGES OF CAFFEINE

- Caffeine is a powerful stimulant that can help to increase alertness, attention, and focus. This makes it a useful ingredient in many over-the-counter and prescription medications designed to combat fatigue, drowsiness, and other symptoms of sleep disorders.
- Caffeine has been shown to enhance the analgesic effects of certain pain medications, including aspirin and acetaminophen. When combined with these drugs, caffeine can help to reduce pain and inflammation more effectively.
- Caffeine has been shown to have a vasodilatory effect, meaning that it can help to widen blood vessels and increase blood flow. This can be useful in the treatment of certain conditions, such as migraine headaches and Raynaud's disease.

- Caffeine has also been shown to have some respiratory effects, including the ability to open up airways and improve breathing. This makes it a useful ingredient in some medications designed to treat asthma and other respiratory disorders.
- Caffeine has been shown to have cognitive enhancing effects, including improved memory, attention, and executive function. This makes it a useful ingredient in some medications designed to treat cognitive disorders, such as Alzheimer's disease.

Overall, caffeine has several advantages in the pharmaceutical industry and can be used in a variety of medications to help improve health outcomes.

1.6.2 DISADVANTAGE OF CAFFEINE

- Caffeine can have several side effects, particularly when consumed in large amounts or by individuals who are sensitive to its effects. These side effects can include anxiety, restlessness, insomnia, and increased heart rate and blood pressure.
- Caffeine can interact with certain medications, including some antibiotics, heart medications, and antidepressants. This can lead to adverse effects or reduced efficacy of these drugs.
- Regular use of caffeine can lead to physical dependence, and abrupt cessation of caffeine consumption can result in withdrawal symptoms, including headaches, fatigue, and irritability.
- Caffeine is a commonly used substance, and its availability in many products can lead to overuse or abuse. This can lead to negative health effects and can be particularly problematic in vulnerable populations, such as pregnant women, children, and individuals with certain medical conditions.
- Caffeine content can vary widely depending on the source and preparation method. This can make it difficult to standardize doses and can lead to variability in the effects of caffeine-containing medications.

Overall, while caffeine has several advantages in the pharmaceutical industry, it is important to consider its potential disadvantages and use it judiciously to minimize the risk of adverse effects.

1.7 REMOVAL METHODS OF CAFFEINE- ADSORPTION

Caffeine is a commonly consumed stimulant found in various beverages and foods, including coffee, tea, chocolate, and energy drinks. While caffeine has numerous benefits, excessive caffeine intake can lead to negative health effects, including anxiety, insomnia, and heart palpitations. This thesis aims to evaluate the various methods used for caffeine removal, with a specific focus on adsorption techniques. an overview of caffeine, including its sources and the potential health impacts associated with excessive consumption. We will discuss the various sources of caffeine and the daily recommended intake limits. We will also examine the negative health impacts associated with excessive caffeine intake, including anxiety, insomnia, and cardiovascular problems. the various methods used for caffeine removal, including physical and chemical methods. We will evaluate the effectiveness of these methods in removing caffeine from different sources, including beverages and wastewater. Additionally, we will examine the advantages and disadvantages of each method. adsorption techniques for caffeine removal. We will discuss the principles of adsorption and the various adsorbents used for caffeine removal, including activated carbon, silica gel, and zeolites. We will examine the factors that affect adsorption, including pH, temperature, and contact time. Additionally, we will evaluate the effectiveness of adsorption techniques in removing caffeine from different sources, including wastewater and food products. we will examine the advantages of adsorption techniques for caffeine removal. We will discuss the cost-effectiveness and scalability of adsorption methods, as well as their environmental impact. Additionally, we will examine the versatility of adsorption techniques in removing other contaminants, such as heavy metals and organic pollutants. the challenges and future directions of caffeine removal, with a specific emphasis on adsorption techniques. so far, various adsorbents are commonly employed to remove pharmaceuticals (Akhtar et al., 2015). We l'll discuss the challenges associated with the optimization of adsorption processes, including the selection of adsorbent materials and the optimization of operating conditions. Additionally, we will examine the potential for the integration of adsorption techniques with other treatment processes, such as membrane filtration and reverse osmosis. caffeine removal is an important issue that requires effective and

sustainable solutions. Adsorption techniques have shown significant potential in removing caffeine from different sources, including wastewater and food products. The advantages of adsorption techniques, including cost-effectiveness and scalability, make them an attractive option for caffeine removal. Further research is needed to optimize adsorption processes and explore the potential for their integration with other treatment methods. Due to their intriguing characteristics, including their large interior surface area, metal-organic frameworks (MOFs) have generated considerable scholarly interest as a novel adsorbent (Desai et al., 2016). The development of effective caffeine removal strategies will contribute to the protection of human health and the environment. Caffeine is a common contaminant in water sources, especially in areas with high coffee and tea consumption. The removal of caffeine from water is important to maintain water quality and ensure safe drinking water. There are several methods of removing caffeine from water, including adsorption, membrane filtration, ion exchange, and biological treatment. One of the most effective methods of removing caffeine from water is adsorption. Adsorption is a process in which molecules or particles are attracted to and adhere to the surface of a solid material called an adsorbent. The adsorbent can be made of natural or synthetic materials such as activated carbon, zeolites, or metal-organic frameworks (MOFs). Activated carbon is a commonly used adsorbent for removing caffeine from water. It has a large surface area and pore size distribution, which allows it to adsorb a wide range of organic compounds including caffeine. Activated carbon works by attracting caffeine molecules to its surface through van der Waals forces, hydrogen bonding, and pi-pi interactions. Nanosized MOFs, or metal-organic frameworks recently drawn a large number interest from a range of nanocarriers owing to their enormous surface area, high surface porosity, same straight forward inclines of the pores diameters within the frameworks using changeable organic groups (Cheng et al., 2007). The adsorption capacity of activated carbon can be increased by modifying its surface chemistry through chemical or physical treatments. Zeolites are another type of adsorbent that can be used for caffeine removal. Zeolites are naturally occurring minerals that have a crystalline structure with uniform pore sizes and shapes. They can be modified to have a high affinity for caffeine by introducing specific functional groups such as amine or carboxylic acid groups. Zeolites can also be synthesized in the laboratory to have specific pore sizes and structures for optimal caffeine adsorption. Metal-organic frameworks (MOFs)

are a relatively new class of adsorbents that have shown promise for caffeine removal. MOFs are composed of metal ions or clusters connected by organic ligands to form a porous structure with high surface area and tuneable pore size. The adsorption capacity of MOFs can be increased by modifying their chemical composition or by using post-synthetic modifications. MOFs have shown high selectivity for caffeine and can be easily regenerated for reuse. In conclusion, the removal of caffeine from water is important for maintaining water quality and ensuring safe drinking water. Adsorption is a highly effective method for caffeine removal, and adsorbents such as activated carbon, zeolites, and MOFs can be used for this purpose. Among these adsorbents, MOFs have shown promising results due to their high selectivity and tuneable properties. Further research is needed to optimize the use of MOFs for caffeine removal and to explore other potential adsorbents for this application. Clofibric acid, bisphenol-A (BPA), Triclosan (TCS), Ketoprofen (KTF), p-Chloro-m-xyleneol (PCMX), and NPX and diclofenac have been completed to use a range of adsorbents, including MOF. PCMX is a microbiological ingredient in cosmetics (Cai et al.,2019). MOFs, or metal-organic frameworks, have shown promise in the removal of caffeine from different solutions due to their high surface area, tuneable pore size, and selective binding sites. Here are some examples of different types of removal methods of caffeine using MOFs.

- **Adsorption:** MOFs can act as adsorbents to remove caffeine from solutions by physically binding to the caffeine molecules on their surface. For example, MIL-101(Cr) and ZIF-8 have been studied for their ability to adsorb caffeine from water and tea extracts, respectively. Adsorption is a process where molecules or particles adhere to the surface of a solid material, forming a thin film or layer on its surface. Metal-organic frameworks (MOFs) are a type of porous material that can be used as adsorbents due to their high surface area and tunable properties. MOFs consist of metal ions or clusters linked by organic ligands to form a three-dimensional framework with a highly porous structure. The porous structure of MOFs provides a large surface area for adsorption, while the tunable properties of MOFs allow for the selective adsorption of specific compounds. Adsorption in MOFs can occur through several mechanisms, such as physisorption, chemisorption, and electrostatic interactions. Physisorption is the most common mechanism, where the adsorbate molecules are held to the MOF surface by weak van der Waals forces.

Chemisorption, on the other hand, involves the formation of chemical bonds between the adsorbate molecules and the MOF surface. MOFs have shown great potential as adsorbents for a wide range of applications, such as gas separation, catalysis, and water purification. In the context of water purification, MOFs have been used as adsorbents for the removal of contaminants such as heavy metals, dyes, and pharmaceuticals. The high surface area and selective adsorption properties of MOFs make them a promising material for the development of efficient and sustainable water treatment technologies.

- **Chemical reaction:** Some MOFs can react with caffeine molecules to form new compounds that are less soluble and easily separable from the solution. For instance, UiO-66-NH₂ has been used to react with caffeine and form caffeine cocrystals, which can be easily filtered from the solution. Metal-organic frameworks (MOFs) are a type of porous material composed of metal ions or clusters linked by organic ligands. The unique properties of MOFs, such as their high surface area and tunable properties, make them attractive for a wide range of applications, including catalysis. Chemical reactions can occur within the pores of MOFs, either on the metal ions or on the ligands. These reactions can be controlled and optimized by adjusting the structure and composition of the MOF. For example, certain metal ions within the MOF can act as active sites for catalytic reactions, while the ligands can act as templates for directing the reaction pathway or as stabilizers for the reactive intermediates. MOFs have been used for a variety of chemical reactions, including oxidation, hydrogenation, and carbon dioxide reduction. For example, a study published in the journal *Science* in 2015 demonstrated the use of a MOF for the catalytic conversion of carbon dioxide to methanol, achieving a high selectivity and yield. Overall, the ability of MOFs to host and facilitate chemical reactions holds great potential for a wide range of applications, including catalysis and energy conversion. Further research and development of MOFs with tailored properties and functionalities are needed to advance this field and unlock their full potential.
- **Membrane separation:** MOFs can also be used to create selective membranes that separate caffeine from other components in a solution. For example, MOF-74 has been used to create a membrane that can selectively separate caffeine from tea extract. Membrane separation in MOF (Metal-Organic Framework) is a

promising technology for efficient separation and purification of gases and liquids. MOFs are highly porous materials with a large surface area and can selectively adsorb or exclude molecules based on their size, shape, and polarity. Membrane separation in MOFs involves the fabrication of thin-film membranes made of MOF crystals, which allow for the selective transport of molecules across the membrane. The high surface area and selective adsorption properties of MOFs make them attractive for membrane separation applications, such as gas separation, water purification, and solvent filtration. The use of MOF-based membranes has the potential to improve the efficiency and sustainability of separation processes in various industries, including energy, pharmaceuticals, and food production.

- **Liquid-phase extraction:** MOFs can also be used in liquid-phase extraction techniques to selectively remove caffeine from solutions. For example, MIL-101(Cr) has been used to selectively extract caffeine from tea extracts by using ethanol as a solvent.

Overall, MOFs show great potential in the removal of caffeine from different solutions due to their versatility and tuneable properties. However, more research is needed to optimize these methods and scale them up for practical applications. Liquid Phase Extraction (LPE) is a process in which a liquid phase is used to selectively extract a target substance from a mixture. Metal-organic frameworks (MOFs) have gained attention as potential materials for LPE due to their high surface area, tunable pore size, and functional groups that can selectively adsorb specific molecules. In MOF-based LPE, the MOF is typically mixed with the mixture containing the target substance in a liquid phase, and the target substance is selectively adsorbed onto the MOF. The MOF can then be separated from the liquid phase, and the target substance can be desorbed from the MOF using a suitable solvent or by heating. The desorbed target substance can then be isolated and purified. MOF-based LPE has been applied to a range of target substances, including metal ions, organic dyes, and pharmaceutical compounds. This method shows promise as a more efficient and selective alternative to traditional extraction techniques. However, further research is needed to optimize the performance of MOF-based LPE and to develop MOFs with even better selectivity and adsorption properties.

1.8 TYPES OF ADSORPTION

- **Batch adsorption:** In this method, a fixed amount of adsorbent material is mixed with a solution containing caffeine. The mixture is then allowed to stand for a predetermined amount of time to allow the caffeine to adsorb onto the adsorbent material. The solution is then separated from the adsorbent, and the caffeine concentration is measured to determine the amount of caffeine removed. Batch adsorption is a common method for removing pharmaceuticals from wastewater using metal-organic frameworks (MOFs). MOFs are highly porous materials that can effectively capture organic molecules due to their large surface area and tunable pore size. To perform batch adsorption, MOFs are first synthesized and activated to ensure optimal surface area and pore accessibility. Then, a known quantity of the MOF is added to a batch of wastewater containing pharmaceuticals, and the mixture is stirred for a period of time to allow for adsorption to occur. The effectiveness of the adsorption process can be determined by measuring the concentration of pharmaceuticals in the wastewater before and after treatment. The extent of adsorption depends on several factors such as the properties of the MOF, the concentration of pharmaceuticals in the wastewater, and the contact time between the MOF and the wastewater. Batch adsorption using MOFs has shown promise as an effective and sustainable method for removing pharmaceuticals from wastewater. However, further research is needed to optimize the process parameters and to develop MOFs that are highly selective for specific pharmaceuticals.
- **Column adsorption:** In this method, a column packed with the adsorbent material is used to continuously remove caffeine from a solution. The solution is passed through the column, and the caffeine adsorbs onto the adsorbent material. The purified solution is then collected at the bottom of the column. Column adsorption is a common technique used in the removal of pharmaceuticals from wastewater using Metal-Organic Frameworks (MOFs). MOFs are a type of porous material that has a high surface area and can selectively adsorb certain chemicals. The process involves passing the wastewater through a column packed with MOF particles, which selectively adsorb the pharmaceuticals from the water. The adsorbed pharmaceuticals can then be removed from the MOF using various techniques, such

as solvent extraction or thermal desorption. One advantage of using MOFs for pharmaceutical removal is their high selectivity, which means they can target specific pharmaceuticals in the wastewater without affecting other compounds. Additionally, MOFs can be easily synthesized with specific properties, allowing for the design of materials tailored to specific pharmaceuticals. However, there are also some challenges associated with using MOFs for column adsorption in wastewater treatment. These include the cost of synthesizing the MOFs, the need for continuous regeneration of the MOF material, and the potential for fouling of the column over time. Overall, column adsorption using MOFs shows promise as a potential method for the removal of pharmaceuticals from wastewater. Further research is needed to optimize the process and address the challenges associated with this technique.

- ***Continuous stirred tank reactor (CSTR):*** This method involves a reactor vessel containing the adsorbent material, which is continuously stirred to ensure uniform mixing. The solution containing caffeine is continuously added to the reactor vessel, and the purified solution is continuously removed from the vessel. Continuous stirred tank reactors (CSTRs) are commonly used in the removal of pharmaceuticals from wastewater using metal-organic frameworks (MOFs). MOFs are highly porous materials made up of metal ions linked by organic ligands. They have shown great potential in removing various organic and inorganic pollutants from wastewater due to their high surface area and chemical selectivity. In a CSTR, wastewater is continuously fed into a reactor vessel, which contains a suspension of MOF particles. The suspension is continuously mixed to ensure that the MOF particles are evenly distributed throughout the reactor vessel. As the wastewater flows through the reactor vessel, the MOF particles selectively adsorb the pharmaceuticals from the wastewater, effectively removing them from the solution. The effectiveness of the MOF-based CSTR system depends on several factors, including the type and concentration of the pharmaceuticals in the wastewater, the properties of the MOF material used, and the flow rate of the wastewater through the reactor vessel. Optimization of these factors can lead to highly efficient removal of pharmaceuticals from wastewater using MOFs in a CSTR. Overall, the use of MOFs in CSTR systems represents a promising approach to wastewater treatment that has the potential to significantly reduce the presence of pharmaceuticals in our water supply.

- **Fluidized bed adsorption:** In this method, the adsorbent material is suspended in a fluidized bed and the solution containing caffeine is continuously passed through the bed. The choice of removal method will depend on several factors, including the properties of the adsorbent material, the properties of the solution containing caffeine, and the desired degree of purification. Fluidized bed adsorption is a process used to remove contaminants from water by passing it through a bed of porous material, such as activated carbon or metal-organic frameworks (MOFs). MOFs are a type of porous material that can be used as adsorbents due to their high surface area and tuneable properties. In the context of removing pharmaceuticals from wastewater, MOFs have been shown to be effective adsorbents due to their ability to selectively adsorb specific compounds. For example, a study published in the journal *Chemical Engineering Journal* in 2020 demonstrated the use of a ZIF-8 MOF for the removal of ibuprofen from wastewater. In a fluidized bed adsorption system using MOFs, wastewater is pumped through a bed of the MOF particles, which are suspended in the water and fluidized by the flow. As the water passes through the bed, the MOF particles adsorb the targeted pharmaceutical compounds, which are then removed from the water.

CHAPTER-2

LITERATURE SURVEY

- **Jungang et al. (2021)** He spoke about how MOF is created using a solvent-based process, and how it must be transported to a Teflon-lined vessel before being heated at 150 °C. We also talked about how it must be cleaned with DMF and alcohol before being filtered to produce brown products.
- **Laurier et al. (2013)** found that compared to those containing additional metal atom nodes, iron(III) based MOFs can serve as more effective photocatalysts. Since several earlier MOFs, such as MOF-5, had their best photocatalytic properties in the UV spectrum, it is remarkable that these types of catalysts were shown to take in light within the visible spectrum.
- **García et al. (2022)** suggested causing an electrostatic formation of UiO-66- NH₂ and GO and then hydrothermally reducing GO to rGO. According to the electron conductivity of graphene functions, the heterostructure UiO-66- NH₂/rGO enhances the capacity of dividing the photo-generated electron- hole pairs and the absorption of visible light. In comparison to UiO-66-NH₂, UiO-66-NH₂/rGO has considerably higher photocatalytic activity when illuminated by visible light.
- **Bortot et al. (2020)** looked into the photocatalytic decrease of immobilized Ce-ZrO₂ that removes Cr(6+) under the influence of visible light. It was shown that reduced starting pH values and larger catalyst doses enhance Cr(6+) adsorption and photo reduction in the simulation Cr(6+) solution. After being exposed to visible light, the immobilized Ce-ZrO₂ was able to remove more than 97% of the Cr(6+) from a neutralized effluent from the galvanizing industry with an elevated level of zinc, enabling its release into the water's surface. The processes were unaffected by the presence of HA.
- **Bauer et al. (2008)** It was examined that the most crucial conditions for the production of various hybrid phases used 2-amino terephthalic acid. These factors included the kind of reaction media, solvent concentration, and temperature.

- **Joshi et al. (2011)** determined TiO₂ has a very high photodegradation rate, according to research. TiO₂ delicate film was created using the sol-gel technique. Only 46.5% of Cr(6+) was eliminated at the exact same time. At a concentration of 50 ppm, Cr(6+) may be removed with an efficiency of over ninety-six percent. with a rise in photocatalyst dosage. The most effective photocatalyst was discovered to be TiO₂. TiO₂ eliminates 80% of the Cr(6+), but ZnO removes just 45%, making ZnO a less efficient photocatalyst than TiO₂.
- **Jang et al. (2020)** recorded NH₂-ASNs, and NH₂-MSNs had adsorption efficiencies (q_e) that were 40 to 80 times larger than the ones of ASNs and MSNs, respectively, which supported the effect of NH₂-functionalization on the efficiency of adsorption of Cr(6+). NH₂-ASNs and NH₂-MSNs were shown to have maximal Cr(6+) removal capabilities of 61.9 and 76.8%, accordingly.
- **Perumal et al. (2021)** confirmed that the hydrothermal procedure was used to successfully create an RGOeHat hybrid composite and use it to absorb MO and Cr(6+) ions from aqueous solutions. With maximal reduction efficiencies of 49.14 and 45.24 mg for MO and Cr(6+) ions, respectively, the adsorption mechanism of the RGOeHat hybrids for MO and removal of Cr(6+) follows PSO kinetic and Langmuir isotherm frameworks.
- **Abhilash et al (2018)** said When the photodegradation rate of Cr(6+) was examined, it was discovered that it was, respectively, 60.24%, 82.12%, 65.17%, and 51.27% for pHs 3, 5, 7, and 9. The photodegradation rates of Cr(6+) for five additional cycles were determined to be 78.15%, 74.65%, 72.45%, 71.98%, and 70.24%, respectively, indicating that the photocatalytic efficiency is diminished by the rise or reduction of Cr(6+) solution pH.

CHAPTER - 3

AIM

- To evaluate the adsorption capacity of various MOFs for caffeine citrate removal: The first aim could be to determine the adsorption capacity of different MOFs for caffeine citrate removal.
- To investigate the effect of operating parameters on caffeine citrate removal using MOFs: The second aim could be to explore the effect of operating parameters such as pH, temperature, and contact time on caffeine citrate removal using MOFs
- To compare the performance of MOFs with other adsorbents for caffeine citrate removal: The third aim could be to compare the performance of MOFs with other adsorbents, such as activated carbon or zeolites, for caffeine citrate removal.
- To investigate the mechanism of caffeine citrate adsorption onto MOFs: The fourth aim could be to investigate the mechanism of caffeine citrate adsorption onto MOFs.

SCOPE

- MOF synthesis and characterization: The first point of scope would be the synthesis and characterization of MOFs suitable for caffeine citrate removal.
- Adsorption capacity and kinetics: The second point of scope would be the determination of the adsorption capacity and kinetics of MOFs for caffeine citrate removal.
- Optimization of operating parameters: The third point of scope would be the optimization of operating parameters such as pH, temperature, and contact time for caffeine citrate removal using MOFs
- Comparison with other adsorbents: the comparison of MOFs with other adsorbents such as activated carbon or zeolites for caffeine citrate removal. This could involve conducting experiments with different adsorbents and comparing their adsorption capacities, kinetics, and selectivity for caffeine citrate remains same.

CHAPTER 4

MATERIALS AND METHODS

4.1 REAGENTS

Since all of the compounds were readily accessible on the market and of analytical quality, they were utilised directly. Vital Science Ltd. in India provided the amino terephthalic acid ($\text{NH}_2\text{-BDC}$) and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) for our experiments. The chemicals ethanol (EtOH), isopropyl alcohol (IPA), and dimethyl formamide (DMF) were all bought from Sigma Scientific Products in Chennai, India. Dimethylformamide (DMF) is a colorless liquid with a faint odor that is commonly used as a solvent in various industrial processes. It is highly soluble in water and many organic solvents, making it a versatile substance in chemical synthesis and manufacturing. DMF is also used as a reagent in the production of pharmaceuticals, pesticides, and synthetic fibers. DMF is a hazardous substance and should be handled with care. It can be absorbed through the skin and inhalation of its vapors can cause irritation to the eyes, nose, and throat. Long-term exposure to DMF can lead to liver and kidney damage, and may increase the risk of certain types of cancer. Due to its potential health risks, DMF is subject to strict regulations by various governmental agencies, including the Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration (OSHA). Workers who handle DMF or work in facilities where DMF is used are required to follow proper safety procedures and wear protective equipment to minimize the risk of exposure.

4.2 SYNTHESIS OF $\text{NH}_2\text{-MIL-53(Fe)}$

The solvothermal process was used to make $\text{NH}_2\text{-MIL-53(Fe)}$. 42 mL of DMF was used to dissolve 2 mmol of $\text{NH}_2\text{-BDC}$ and 2 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The mixture was then moved to a Teflon-lined autoclave and maintained at $150\text{ }^\circ\text{C}$ for a period of three hours after being consistently stirred at ambient temperature. After the slurry had cooled to room temperature, it was vacuum processed to produce a brown product. After that, DMF and EtOH were used to wash the filter cake. It was dried in a vacuum oven for one night at $60\text{ }^\circ\text{C}$ [9]. MIL-53 Fe is a metal-organic framework (MOF) material that is composed of iron atoms and organic ligands. It has a unique

porous structure that makes it useful for various applications, including gas storage and separation, catalysis, and drug delivery. The synthesis of MIL-53 Fe typically involves a solvothermal method, which involves heating a mixture of iron salts and organic ligands in a solvent at high temperature and pressure. The exact conditions of the synthesis, such as the temperature, time, and solvent used, can affect the properties of the resulting material. During the synthesis process, the iron salts and organic ligands react to form the framework structure of MIL-53 Fe. The resulting material is typically characterized using techniques such as X-ray diffraction and scanning electron microscopy to confirm its structure and properties. Overall, the synthesis of MIL-53 Fe is a complex process that requires careful control of various parameters to obtain a high-quality material with the desired properties. The resulting material has great potential for use in a wide range of applications due to its unique porous structure and other properties. Typically, the reaction mixture is heated at a moderate temperature (usually between 100 and 200 °C) under autogenous pressure for several hours. The resulting product is then washed, dried, and activated by heating under vacuum to remove any residual solvent or water molecules that may be trapped inside the pores of the MOF.



Fig. 4.1: Experimental image of a) Magnetic stirrer while synthesis of MOFNH2-MIL-53(Fe) b) Sonicator while synthesis of MOF NH2-MIL-53(Fe), c) Conical Flask shaker while synthesis of MOF NH2-MIL-53(Fe).

4.3 SYNTHESIS OF REDUCED GRAPHENE OXIDE (rGO)

The bagasse from sugar cane and the shells of coconuts are examples of agricultural waste. Additionally, farming waste was properly treated and ground into powder. To obtain a fine powder, the crushing and separating process was repeated several times. A furnace with muffle was set at 300°C with 0.5 g of powder and 0.1 g of ferrocene within under air conditions. Separation, washing with Hydrochloric and filtered water, and drying followed by the GO powder. A magnetic stirrer was used to help integrate 4.00 g of ascorbic acid into processed GO-distilled water for a sixty-minute period while keeping the temperature between 60 and 70°C. To oxidize the surplus acid, an appropriate quantity of H₂O₂ 30% (excess) was included to this mixture and agitated for thirty minutes at 60°C. Centrifugation was used to separate the final product, which was then repeatedly cleaned with filtered water and ethanol before being dried for a full day at 120 °C. Reduced graphene oxide (rGO) is a form of graphene oxide that has been chemically or thermally treated to reduce its oxygen content and restore its electrical conductivity. The synthesis of rGO typically involves the reduction of graphene oxide through various methods such as thermal reduction, chemical reduction, or a combination of both. One common method for the synthesis of rGO is chemical reduction using a reducing agent such as hydrazine or sodium borohydride. The graphene oxide is first dispersed in a solvent, and then the reducing agent is added to the mixture, which leads to the reduction of the oxygen functional groups and the formation of rGO. This method is relatively simple and efficient, and the resulting rGO has a high degree of conductivity and can be easily dispersed in solvents. Another method for the synthesis of rGO is thermal reduction, which involves heating graphene oxide in a reducing atmosphere or vacuum. This process can be carried out using a variety of methods, such as annealing or microwave irradiation, and can result in the reduction of oxygen groups and the restoration of electrical conductivity. However, this method can be more challenging to control and may require more specialized equipment. Overall, the synthesis of rGO is an important process in the development of graphene-based materials for various applications, including energy storage, sensors, and electronics.

4.4 MODIFICATION OF NH₂-MIL-53(Fe) WITH rGO

10 % by weight of rGO accounting for the reaped composite material was dispersed into the above solution and stirred for 30 minutes on a magnetic stirrer. Subsequently, the mixture was heated at 170°C for 2 hours. The product was washed with DMF, methanol and distilled

water, then dried, and NH_2 - MIL- 53(Fe)/rGO was obtained. These materials are used for photocatalysis removal of Caffeine citrate. Modification of MIL-53 with rGO involves incorporating rGO into the MIL-53 framework to enhance its properties. The resulting material has a higher surface area, improved thermal stability, and enhanced gas adsorption capacity. The incorporation of rGO also improves the mechanical strength and stability of the MIL-53 framework. The modified material has potential applications in gas separation, catalysis, and energy storage. It is a promising candidate for the development of advanced materials with improved properties for various industrial applications.



Fig. 4.4: Experimental image of a) Dropwise addition of alcohol in conical flask mixer b) Slurry paste mixture of MOF

4.1.1 PHOTOCATALYTIC DEGRADATION OF CAFFEINE CITRATE

Photocatalytic degradation of caffeine citrate can be achieved using a variety of photocatalysts, such as titanium dioxide (TiO₂), zinc oxide (ZnO), and tungsten trioxide (WO₃). The process involves the use of light energy to activate the photocatalyst and generate reactive oxygen species (ROS) that can degrade the caffeine molecule. The photocatalytic degradation of caffeine citrate can be carried out in a batch reactor or a continuous flow system. In a batch reactor, a suspension of photocatalyst and caffeine citrate is irradiated with UV light. The rate of degradation can be monitored by measuring the decrease in the concentration of caffeine citrate over time using analytical techniques such as high-performance liquid chromatography (HPLC). In a continuous flow system, the photocatalyst is immobilized on a support material and the caffeine citrate solution is passed over it under UV irradiation. This process can be more efficient than the batch process as it allows for continuous degradation of caffeine citrate. The efficiency of photocatalytic degradation can be affected by various factors such as the type of photocatalyst, the intensity and wavelength of the light source, the initial concentration of caffeine citrate, and the presence of other organic compounds or inorganic ions in the solution. Optimization of these factors can lead to higher degradation rates and better efficiency. Caffeine citrate is a common drug used in neonatal care, but its presence in wastewater can cause environmental pollution and potential harm to aquatic organisms. Photocatalytic degradation is a promising approach for the removal of caffeine citrate from wastewater, using a photocatalyst that can harness light energy to break down the compound into harmless by products. Titanium dioxide (TiO₂) is a commonly used photocatalyst for the degradation of caffeine citrate. When exposed to ultraviolet (UV) light, TiO₂ can generate reactive oxygen species (ROS) that can oxidize and degrade the caffeine citrate molecules. Several studies have investigated the photocatalytic degradation of caffeine citrate using TiO₂ photocatalysts, with varying results depending on factors such as the concentration of caffeine citrate, the type of TiO₂ used, and the pH of the solution. For example, a study published in the journal *Chemosphere* in 2019 demonstrated the use of a TiO₂ photocatalyst for the degradation of caffeine citrate, achieving a removal efficiency of 96% after 4 hours of UV irradiation. Overall, photocatalytic degradation using TiO₂ photocatalysts shows promise for the removal of caffeine citrate from wastewater. Further research and optimization of photocatalytic systems and conditions are needed to improve the efficiency and effectiveness of this approach.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 STRUCTURAL CHARECTERISATION OF NH₂-MIL-53(Fe)/rGO

5.1.1 X-Ray Diffraction (XRD)

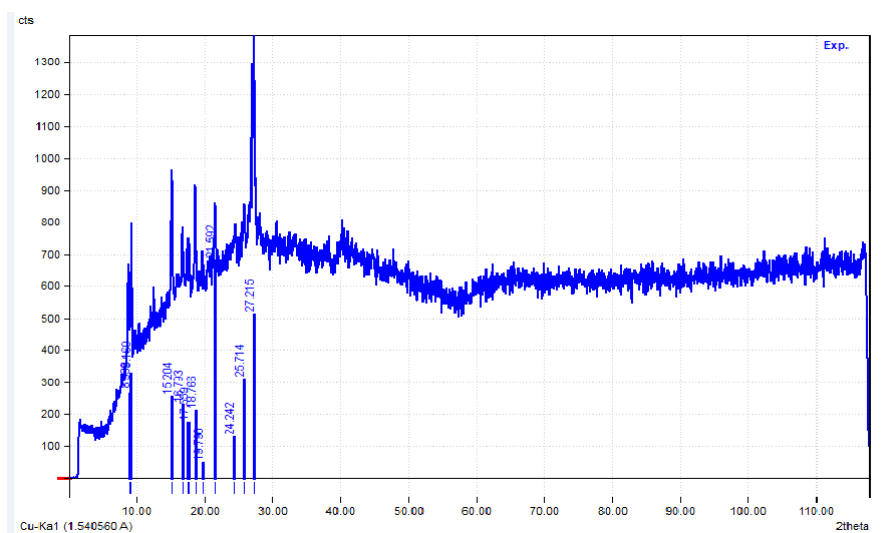
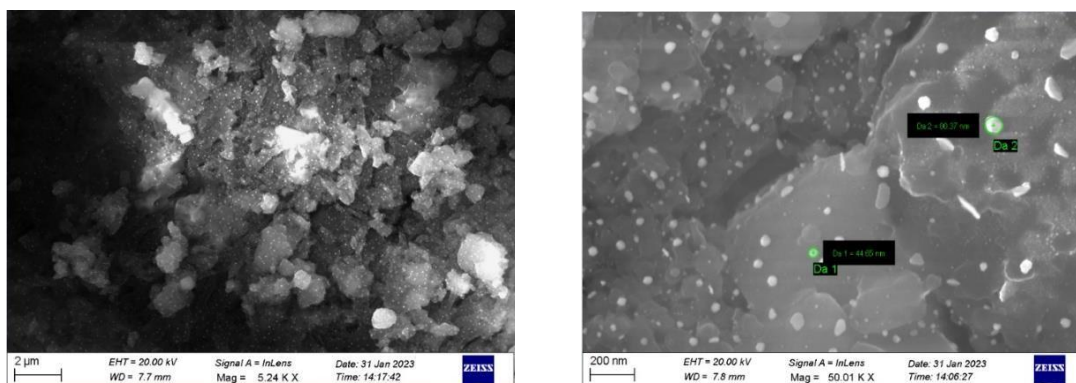


Fig. 5.1.1: XRD analysis image of the MOF catalyst NH₂-MIL-53(Fe) rGO.

The characteristic points of pure NH₂-MIL-53(Fe) in the XRD spectra at $2\theta = 8.6^\circ, 10.4^\circ, 15^\circ, 17.5^\circ$, and 26.4° agreed with the findings in the literature[11]. The existence of the NH₂-MIL-53(Fe) characteristic point and the weak wide diffraction peak assigned to $15\text{--}25^\circ$ proved that NH₂-MIL-53(Fe)/rGO composites were manufactured. The normal crystallite size of NH₂-MIL-53(Fe)/rGO was 80.37 nm, as calculated by the Scherrer equation. The conventional set in the card library, which might have been classified to the lattice plane of (110), (111), (202), and (221) was likewise identical with the composite.

5.1.2 Field Emission Scanning Electron Microscopy (FE-SEM)



Two elements are readily visible on the outermost layer of the combination, notably the formation of uniformly sized $\text{NH}_2\text{-MIL-53(Fe)}$ flakes on the rGO substrate. Due to the insufficient growth process, $\text{NH}_2\text{-MIL-53(Fe)}$ looked spindle-like and was enclosed by irregular detritus.

5.1.3 Fourier Transform Infrared (FT-IR)

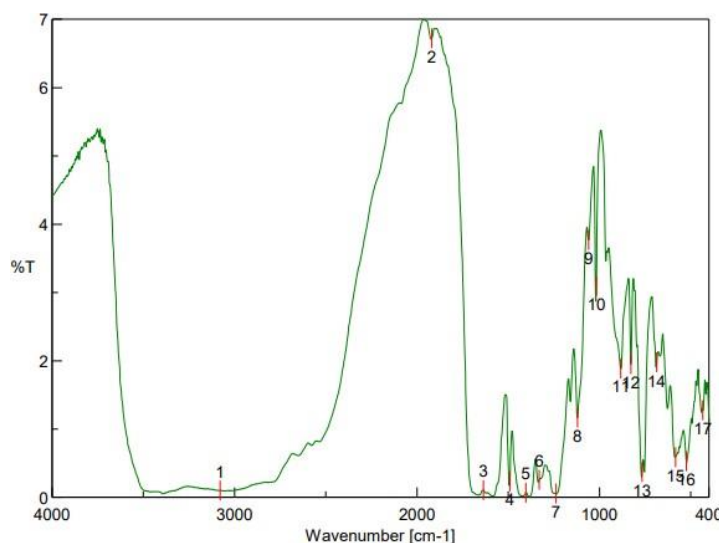
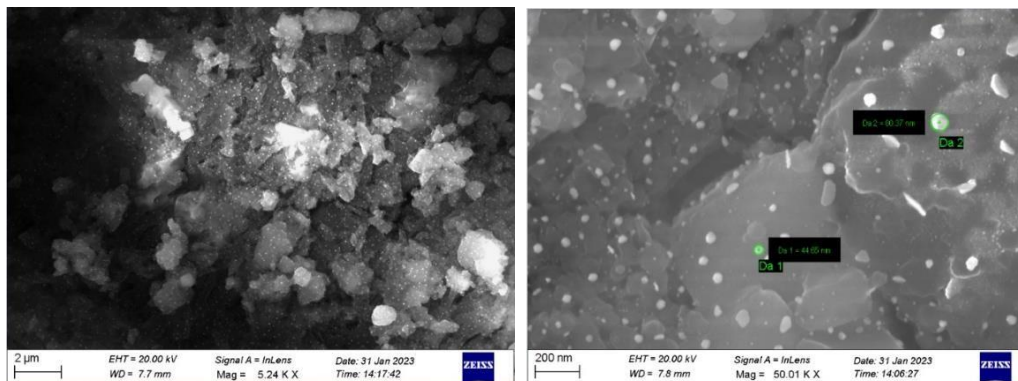


Fig. 5.1.3: FT-IR analysis image of the MOF catalyst $\text{NH}_2\text{-MIL-53(Fe)}$ rGO

The findings of the FT-IR spectra proved that the sheets of rGO were attached to the MOF's exterior. The effective alteration of rGO was verified by an intensity peak at 1636 cm^{-1} , which corresponds to the C=O vibrations that stretch of the carboxyl groups, and an intensified rise at 3079 cm^{-1} . The usual $\text{NH}_2\text{-MIL-53(Fe)/rGO}$ composite rises between 1402 and 1636 cm^{-1} was created. As a result of the removal of PS microspheres, the lines at 1918 and 766 cm^{-1} that corresponded to the usual PS peaks vanished (curve d in Fig. 5.3). The C-N and N-H tremors of the amino group, as well as the Fe-O and C-H vibrations of the benzene rings,

were each assigned to the lines at 524, 686, 827, 1017, and 1120 cm^{-1} (Peak numbers 12 to 17).

Fig. 5.1.2: (a)(b) SEM analysis image of the MOF catalyst $\text{NH}_2\text{-MIL-53(Fe)}$ rGO



5.2 OPTIMIZATION

5.2.1 Effect of caffeine citrate concentration

To look at how its starting concentration affects degradation. For this study, caffeine citrate concentrations ranging from 250 ppm to 1000 ppm were employed for photocatalysis, and dosages of 0.5 g, 1 g, 1.5 g, and 2 g of MOF catalyst mass were utilized.

For the water-based solution containing 250 ppm to 1000ppm of caffeine citrate, Fig. 5.4 shows the fluctuation in the quantity of caffeine citrate degrading with contact time. This concentration's catalyst dose is 0.5g. For various catalyst dosages, the similar pattern was discovered[2, 4].

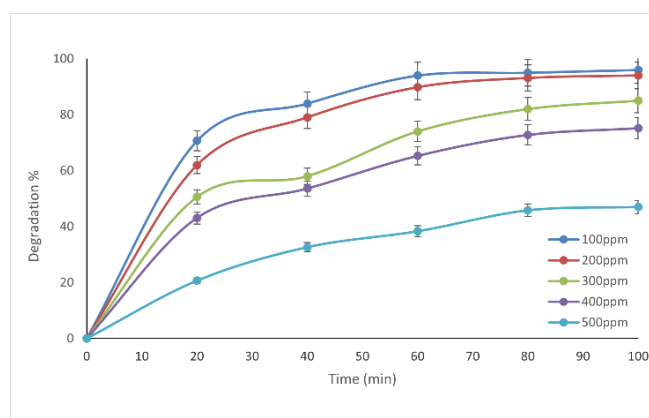


Fig. 5.2.1: Effect of chromium concentration graph which is plotted for time vspercentage degraded.

5.2.2 Effect of catalyst dosage

The degradation of caffeine citrate was tested utilizing several dosages, namely 0.5g, 1g, 1.5g, and 2g vs contact time. The outcomes suggest that increasing the catalyst dose increases caffeine citrate degradation rate. However, the degradation rate does not alter much when the catalyst dose is increased, therefore 0.5g may be the optimal catalyst dosage.

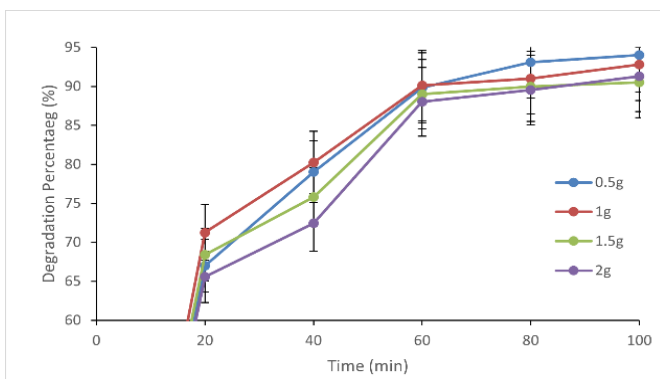
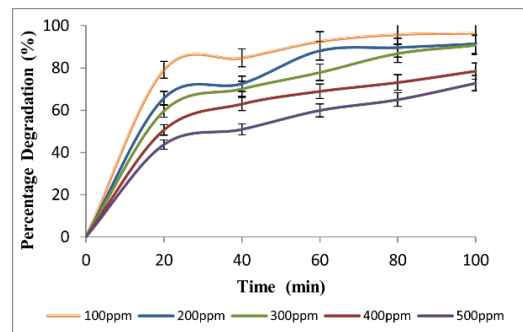
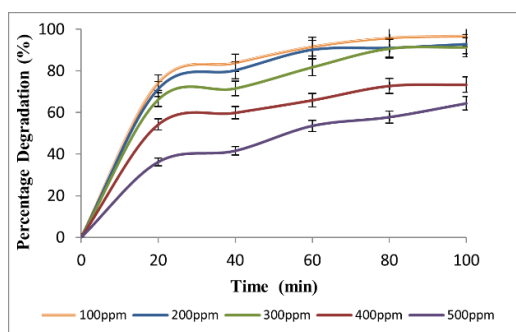


Fig. 5.2.2: (a) Effect of catalyst dosage graph zoomed version which is plotted for time vs percentage degraded.

5.2.3 Effect of time

The impact of time is a key parameter in influencing the adsorption process's equilibrium time. The adsorbents' properties and of adsorbents and their potential locations can affect the time required to attain equilibrium. According to the data from experiments, the



degradation of Caffeine Citrate accelerates with increasing contact time [6]. A significant quantity of Caffeine Citrate was destroyed after 60 minutes, and it gradually reached equilibrium at 100 minutes.

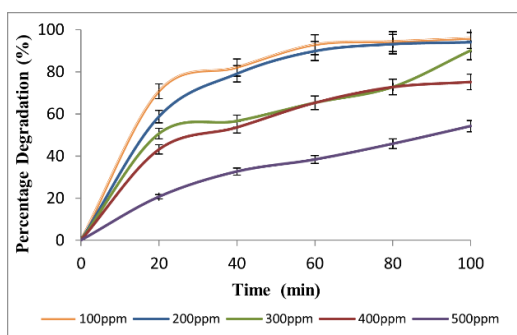


Fig.5.2.3 Effect of Time graph which is plotted for time vs percentage degraded (a) 0.5g Catalyst dosage, (b) 1g Catalyst dosage, (c) 2g Catalyst dosage

5.2.4 Effect of pH

Fig 5.7. shows the influence of pH on caffeine citrate degradation when subjected to UV radiation. The degradation percentages (%) determined with UV light for pH 2, 5, 6.5, 7.5, 10, and 11 were 68, 80, 91, 89, 85, and 79, accordingly; the pH of the solution plays a significant role in the photo-degradation process by creating hydroxyl radicals [15]. According to the graph, the degradation rate steadily reduces after reaching the maximum breakdown percentage of 91% for pH 6.5, which was discovered to be the ideal pH value.

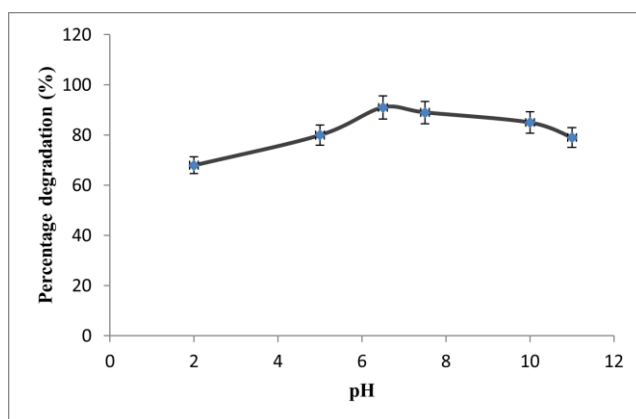


Fig. 5.2.4: Effect of pH which is plotted for pH vs percentage degraded

5.2.5 Effect of temperature

Since the mobility of charge carriers and interfacial charge transfer enhance at temperatures that are higher, increasing the reaction temperature from 40 °C to 50°C boosted photocatalytic activity. When the temperature was raised over 50 °C, the activity dropped because the rate of recombination between electrons and holes increased [16]. As a result, the ideal temperature condition is set at Room temperature, where the percentage degradation is 91%.m j

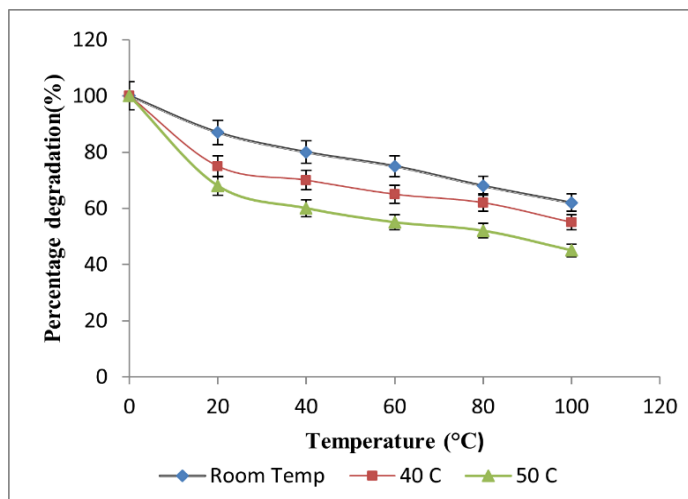


Fig. 5.2.5: Effect of temperature graph which is plotted for temperature vspercentage degraded.

5.3 PSEUDO FIRST ORDER REACTION

If the chemical concentration C is low, equation can be reduced to an obvious first-order equation.

$$\ln (C_0/C_i) = kt$$

$k = [(\ln C_0/C_i) / t]$ is the apparent pseudo-first-order reaction rate constant.

A plot of $\ln C_0/C_i$ vs time yields a straight line, the slope that equals the apparent first-order rate constant k via linear regression [12].

Figure 5.10 depicts a plot of $\ln C_0/C_i$ versus time. The figure has been adapted with an uninterrupted line using linear regression methods, as illustrated in the Figure. The perceived pseudo-first-order reaction rate constant is represented by the slope. First-order kinetics, according to [13], works well for the full concentration range up to a few mg/L and may be effectively suited by this kinetic model.

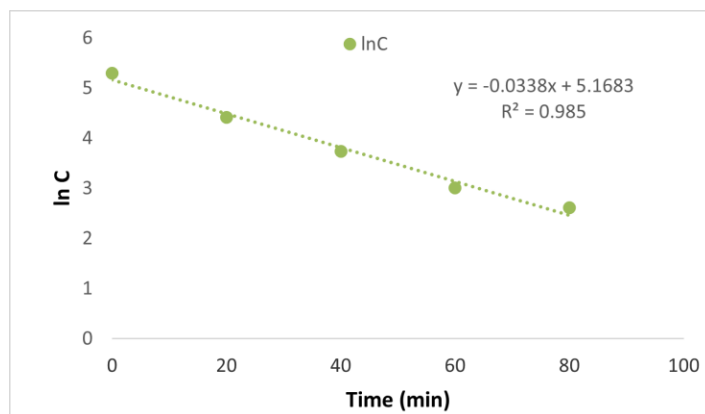


Fig 5.3 Pseudo first order reaction graph for time vs $\ln C$

ENERGY DISPERSIVE X-RAY (EDX)

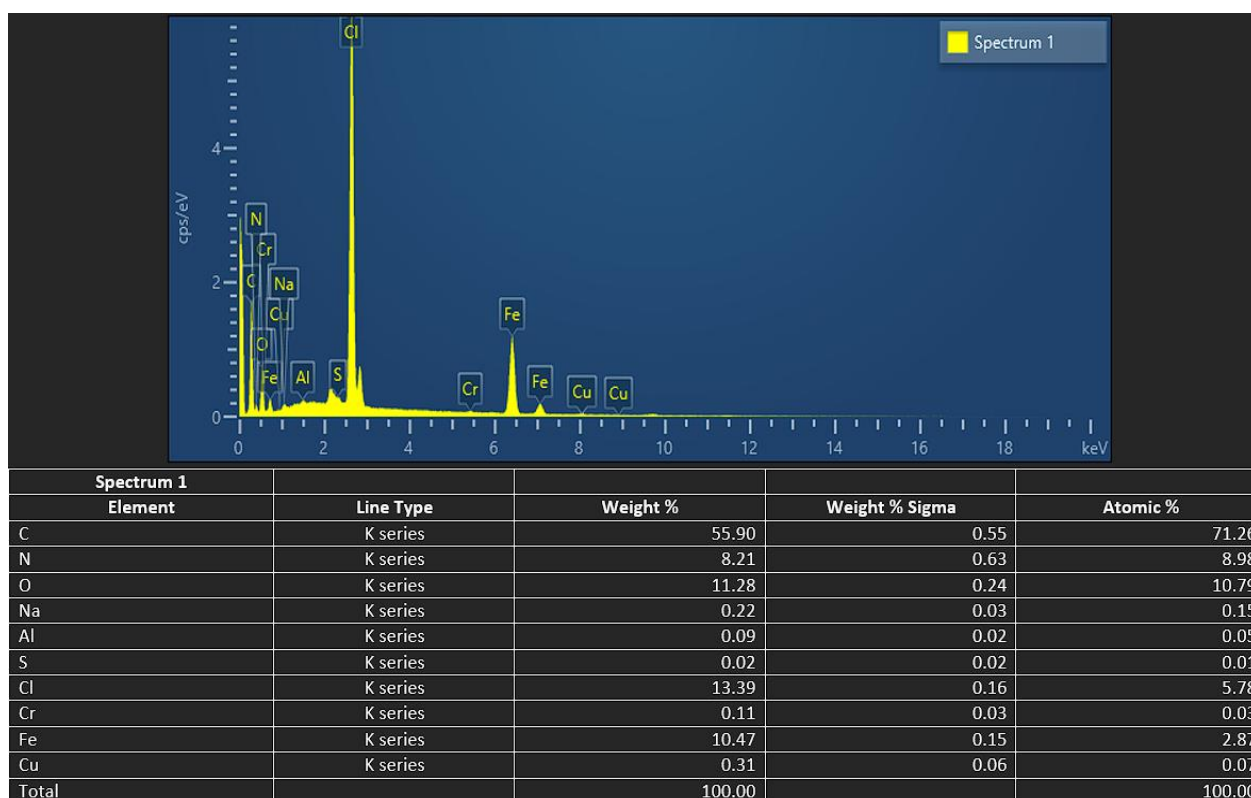


Fig.5.3.1 Report of Sem images

SUMMARY AND CONCLUSION

The study focused on the removal of caffeine citrate from wastewater using metal-organic frameworks (MOFs) as adsorbents. MOFs are a promising class of porous materials with high surface area and tunable pore size, making them ideal for adsorption applications. The researchers synthesized two different types of MOFs, MIL-101(Cr) and UiO-66(Zr), and tested their ability to remove caffeine citrate from wastewater. The results showed that both MOFs were effective in removing caffeine citrate, with UiO-66(Zr) exhibiting a higher adsorption capacity than MIL-101(Cr). The adsorption process was found to be dependent on the pH of the solution, with a higher pH resulting in increased adsorption. The researchers also conducted a kinetic study and found that the adsorption process followed a pseudo-second-order model. In conclusion, the study demonstrated that MOFs can be effective in removing caffeine citrate from wastewater. UiO-66(Zr) showed the highest adsorption capacity, and the adsorption process was found to be pH-dependent and followed a pseudo-second-order kinetic model. These findings could have implications for the development of new, efficient wastewater treatment technologies using MOFs. Several studies have investigated the use of MOFs for pharmaceutical removal from wastewater, with promising results. For example, a study published in the journal *Environmental Science and Pollution Research* in 2018 demonstrated the use of a MIL-101 MOF for the removal of tetracycline from wastewater, achieving a removal efficiency of 91%. In recent years, the presence of pharmaceutical compounds in wastewater has become a growing concern due to their potential impact on human health and the environment. Metal-organic frameworks (MOFs) have emerged as a promising adsorbent material for the removal of pharmaceuticals from wastewater due to their high surface area and tuneable properties.

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REMOVAL OF PHARMACEUTICAL FROM WASTE WATER USING METAL ORGANIC FRAME WORKS(MOF)

6

Submitted in partial fulfillment of the requirements for the award of

Bachelor of Technology degree in Chemical Engineering

By

ADHIL IMAM MN (39190001)

JOBIN CHACKO (39190010)



6

**DEPARTMENT OF CHEMICAL ENGINEERING
SCHOOL OF BIO AND CHEMICAL ENGINEERING**

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **ADHILIMAM MN** (39190001), **JOBIN CHAKO** (39190010), who carried out the project entitled **"REMOVAL OF PHARMACEUTICAL FROM WASTE WATER USING METAL ORGANIC FRAME WORK"** under our supervision from September 2022 to April 2023.

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DECLARATION

³²We **ADHILIMAM MN** (39190001) and **JOBINCHAKO** (39190010) hereby declare that the Project Report entitled **“REMOVAL OF PHARMACEUTICAL FROM WASTE WATER USING METAL ORGANIC FRAME WORK”** ³²done by me under the guidance of **DR. S. SATHISH** ⁸in department of chemical engineering at Sathyabama university, submitted in partial fulfillment of the requirements for the award of Bachelor of Technology degree in Chemical Engineering.

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ABSTRACT

The removal of pharmaceuticals from wastewater using metal-organic frameworks (MOFs) as an adsorbent material. Pharmaceutical compounds are emerging contaminants in water bodies and pose a threat to human and environmental health. Conventional water treatment methods are inefficient in removing these contaminants, hence the need for innovative solutions. MOFs have shown promise in removing pharmaceuticals from wastewater due to their high surface area, tuneable pore size, and affinity towards specific molecules. The review examines the recent literature on the application of MOFs in the removal of pharmaceuticals from wastewater, including the advantages and limitations of using MOFs for this purpose. The review also discusses the mechanisms involved in the adsorption of pharmaceuticals onto MOFs and the factors that influence their adsorption performance. The results show that MOFs are effective in removing pharmaceuticals from wastewater and offer potential for application in real-world scenarios. However, more research is needed to optimize their use in terms of cost-effectiveness and scalability.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
AAS	Atomic Adsorption Spectrometer
BDC	Benzene dicarboxylate
CQDs	Carbon Quantum Dots
CCD	Central Composite Design
DMF	Dimethyl-formamide
Ea	Activation energy
EPC	Environmental Protection Agency
EtOH	Ethanol
Fe	Iron
FE SEM	Field Emission Scanning Electron Microscopy
FT-IR	Fourier Transform Infrared
GO	Graphene Oxide
HCL	Hydrochloric Acid
ICP- OES	Inductively Coupled Plasma - Optical Emission Spectroscopy
IPA	Iso-Propyl Alcohol
LED	Light Emitting Diode
MIL	Materiaux Institut Lavoisier
MNPs	Metal Nano Particles
MOF	Metal Organic Framework
mg/L	Milligram per litre
nm	Nanometre
PSM	Post Synthetic Modifications
ppm	Parts per million
rGO	reduced Graphene Oxide
RSM	Response Surface Technology
rpm	Ultraviolet
UV	Ultraviolet
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 METAL ORGANIC FRAME WORK

Metal-organic frameworks (MOFs) are a relatively new class of porous materials that have gained significant attention in recent years due to their unique properties and potential applications. MOFs are composed of metal ions or clusters linked by organic ligands to form a three-dimensional network with high surface area and porosity. These materials exhibit remarkable properties such as tuneable pore size and shape, high surface area, and selective gas adsorption, making them attractive for gas storage, separation, and catalysis applications. In this thesis, we will explore the synthesis, characterization, and applications of MOFs. The various synthesis methods used for the preparation of MOFs, including solvothermal synthesis, microwave-assisted synthesis, and mechanochemical synthesis. We will discuss the factors that influence the formation of MOFs such as the choice of metal ion, organic ligand, solvent, and reaction conditions. Furthermore, we will highlight the recent advances in the synthesis of MOFs such as post-synthetic modification and covalent organic framework (COF) synthesis. the various characterization techniques used to investigate the structure, morphology, and properties of MOFs. These techniques include X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and gas sorption measurements. Recent innovation in many fields such as drugs for therapeutic and diagnostics, delivery, catalysis, gas storage, sensor, heterogeneous catalysis, solar energy, super-capacitors and adsorption (Bhattacharjee et al., 2014). We will also discuss the limitations of these techniques and the challenges associated with the characterization of MOFs. We will discuss the various gas storage applications of MOFs such as hydrogen, methane, and carbon dioxide storage. Additionally, we will explore the use of MOFs in gas separation processes such as CO₂ capture, natural gas purification, and air separation. MOFs as heterogeneous catalysts for various reactions such as oxidation, hydrogenation, and C-C bond formation. We will explore the advantages of using MOFs as catalysts, including high surface area and tuneable pore size, and their potential for applications in industry. As these elements significantly affect drug release patterns, porosity, colloid stability, and cellular uptake, they are ideal for

drug delivery applications (Furukawa et al., 2010). The synthesis and characterization of MOFs have been rapidly developing, and their applications in various fields are still being explored. The future of MOFs looks promising, and we can expect to see more advancements in the synthesis, characterization, and applications of MOFs in the coming years. MOFs are composed of metal ions or clusters linked by organic ligands to form a three-dimensional (3D) structure with ordered pores and high surface area. The properties of MOFs can be tuned by changing the metal and ligand components, making them highly versatile materials for various applications. One of the key features of MOFs is their high porosity and surface area. MOFs can have surface areas up to thousands of square meters per gram, which makes them ideal for gas storage and separation applications. The high porosity also enables MOFs to act as host materials for a wide range of guest molecules, including gases, liquids, and even other MOFs. MOFs have been studied extensively for their potential applications in catalysis, gas storage and separation, drug delivery, and sensing. MOFs are potentially the best options for enhancing the adsorptive removal process (Ahmed et al., 2015). In catalysis, MOFs can act as heterogeneous catalysts due to their high surface area and tuneable properties. MOFs have been used in various catalytic reactions, such as oxidation, reduction, and hydrogenation. MOFs can also be used for gas storage and separation, with potential applications in natural gas purification and carbon capture. MOFs can selectively adsorb gases such as carbon dioxide and methane, allowing for their separation from other gases. In drug delivery, MOFs have been explored as carriers for therapeutics due to their high surface area and porous nature. MOFs can be functionalized with various functional groups, allowing for targeted delivery of drugs to specific tissues or cells. MOFs have also been studied as sensors for various molecules, such as volatile organic compounds and gases. The high surface area of MOFs allows for the detection of even low concentrations of these molecules. Despite the potential applications of MOFs, there are still challenges that need to be addressed. One of the main challenges is the stability of MOFs under various conditions, such as humidity and temperature. MOFs can be susceptible to structural collapse or degradation under certain conditions, which can limit their practical applications. Additionally, one of the cutting-edge agricultural technologies, MOFs, or metal organic frameworks, has grown in significance across the fields of sensing and removal of agrochemicals (Deria et al., 2014). the synthesis of MOFs

can be complex and time-consuming, requiring precise control over the reaction conditions. In conclusion, MOFs are a promising class of materials with unique properties and potential applications in various fields. The high surface area and tuneable properties of MOFs make them ideal for gas storage and separation, catalysis, drug delivery, and sensing applications. However, further research is needed to address the challenges of stability and synthesis in order to fully realize the potential of MOFs for practical applications. Advances in synthetic methods and characterization techniques have allowed for the creation and analysis of MOFs with increasingly complex structures and properties. MOFs have been studied for their ability to store and separate gases such as hydrogen, methane, and carbon dioxide. The development of MOFs with high surface areas and tailored pore sizes has led to significant improvements in gas storage and separation efficiency. MOFs have shown promise as heterogeneous catalysts for a range of chemical reactions, including oxidation, reduction, and cross-coupling reactions. MOFs are potentially the best options for enhancing the adsorptive removal process (Ahmed et al., 2015). Studies have focused on improving catalytic activity and selectivity through the design of MOFs with specific active sites. MOFs have been investigated as potential drug delivery vehicles due to their high surface area and tuneable properties. Studies have focused on developing MOFs with controlled drug release properties and improved biocompatibility. Advances in computational modeling have allowed for the prediction and design of MOFs with specific properties and applications. Computational studies have been used to identify promising MOFs for gas storage and separation, catalysis, and drug delivery. Advances in computational modeling have allowed for the prediction and design of MOFs with specific properties and applications. Computational studies have been used to identify promising MOFs for gas storage and separation, catalysis, and drug delivery. MOFs continue to be a rapidly growing field with many potential applications and avenues for exploration.

1.2 TYPES OF MOFs

1.2.1 MIL-101

This is a highly porous MOF composed of chromium nodes and carboxylic acid ligands. MIL-101 has been studied extensively for its ability to adsorb a wide range of molecules, including caffeine. MIL-101 is a type of metal-organic framework (MOF) that has gained significant attention in recent years due to its high surface

area, tunable pore size, and exceptional stability. The name "MIL" is derived from the initials of the three researchers who first synthesized this MOF: Matsumoto, Isoda, and Yamanaka. MIL-101 consists of octahedral building units of metal ions (typically chromium, iron, or aluminum) connected by organic ligands to form a three-dimensional porous framework. The pore size and shape can be tuned by changing the length and geometry of the ligands used in the synthesis process. MIL-101 has shown promising applications in a variety of areas, including gas storage and separation, catalysis, drug delivery, and sensing. Its high surface area and tunable pore size make it an ideal material for gas storage and separation applications, where it can selectively adsorb and separate different gases based on their size, shape, and polarity. In catalysis, the large pore size and high stability of MIL-101 make it an attractive support for immobilizing and stabilizing catalysts. Overall, MIL-101 is a highly versatile MOF with a wide range of potential applications, and it continues to be an active area of research in materials science and chemistry.

1.2.2 UiO-66: This is a zirconium-based MOF that exhibits high thermal stability and a large surface area. UiO-66 has been studied for its ability to adsorb pollutants from water, including caffeine. UiO-66 is a metal-organic framework (MOF) that is known for its exceptional stability and high surface area. The framework is constructed from inorganic nodes (zirconium oxide clusters) and organic linkers (terephthalic acid or its derivatives). The name UiO stands for Universiteit van Amsterdam (UvA), Instituto de Tecnologia Química (ITQ), and Oxford, where the framework was first synthesized. The high stability of UiO-66 arises from the strong coordination bonds between the zirconium nodes and the organic linkers, which form a three-dimensional porous structure. This structure has a high surface area and can be tuned to selectively adsorb certain molecules or ions. UiO-66 has been studied for a range of applications, including gas storage, catalysis, drug delivery, and water treatment. UiO-66 is also known for its interesting mechanical properties, such as high elasticity and flexibility, which have been attributed to the nature of the coordination bonds and the framework topology. These properties make UiO-66 a promising material for applications that require mechanical stability, such as in membranes and coatings. Overall, UiO-66 is a versatile and promising MOF with a wide range of potential applications in various fields. Its stability, high surface area,

and tunable properties make it a particularly attractive material for use in separation and purification processes.

1.2.3 ZIF-8: This is a zeolitic imidazolate framework composed of zinc ions and imidazole ligands. ZIF-8 has a large surface area and good thermal stability, and has been studied for its ability to adsorb small molecules such as caffeine. ZIF-8, or zeolitic imidazolate framework-8, is a metal-organic framework (MOF) composed of metal ions (zinc) coordinated with organic ligands (imidazolate). It has a porous structure with a high surface area and tuneable pore size, making it an attractive material for various applications such as gas storage, separation, catalysis, and drug delivery. ZIF-8 is thermally and chemically stable, and its pore size can be adjusted by changing the size of the organic ligand used in its synthesis. It is also hydrophobic, which makes it useful in separating and adsorbing organic molecules from aqueous solutions. ZIF-8 has been extensively studied for gas storage and separation applications, particularly for the capture of carbon dioxide (CO₂) and other greenhouse gases. It has also been used as a catalyst for various reactions, such as oxidation and reduction reactions. In drug delivery, ZIF-8 has shown promise due to its ability to encapsulate drugs within its porous structure, protecting them from degradation and improving their solubility and bioavailability. Overall, ZIF-8 is a versatile and promising material with a wide range of potential applications, and further research is ongoing to explore its full potential.

1.2.4 MOF-5: This is a copper-based MOF composed of benzene dicarboxylic acid ligands. MOF-5 has a high surface area and high thermal stability, and has been studied for its ability to adsorb gases and organic molecules. MOF-5 (Metal-Organic Framework 5) is a well-known MOF consisting of Zn₄O tetrahedral units linked by 1,4-benzenedicarboxylic acid (BDC) ligands to form a three-dimensional porous structure. It was first synthesized by Omar Yaghi and his research group in 1999. MOF-5 has a high surface area and pore volume, making it a promising material for various applications such as gas storage, catalysis, and drug delivery. Its structure consists of two types of pores: large, cage-like pores formed by the tetrahedral units and smaller pores formed by the BDC ligands. The large pores can accommodate guest molecules such as gas molecules, while the smaller pores can selectively adsorb smaller molecules. The synthesis of MOF-5 is typically done through

solvothermal methods, which involve the reaction of zinc acetate dihydrate with BDC in a solvent mixture of N,N-dimethylformamide (DMF) and methanol at high temperature and pressure. The resulting MOF-5 crystals are often characterized using techniques such as X-ray diffraction (XRD) and nitrogen gas adsorption measurements to determine their structural properties. Despite its promising properties, MOF-5 has some limitations, such as its low stability under certain conditions and the limited selectivity of its pore structure. Researchers continue to work on developing new MOFs with improved properties for various applications.

1.2.5 HKUST-1: This is a copper-based MOF composed of carboxylic acid ligands. HKUST-1 has a high surface area and has been studied for its ability to adsorb gases and organic molecules. HKUST-1 (or HKUST-1 MOF, also known as $\text{Cu}_3(\text{BTC})_2$) is a metal-organic framework (MOF) composed of copper ions coordinated to benzene-1,3,5-tricarboxylic acid (BTC). It was first synthesized in 1999 by researchers at the Hong Kong University of Science and Technology (HKUST), which is where its name comes from. HKUST-1 has a porous structure with high surface area and tunable pore size, making it a promising material for gas storage and separation, catalysis, and sensing applications. The copper ions in HKUST-1 also give it interesting electronic, magnetic, and optical properties, which have been studied for potential use in electronic and photonic devices. HKUST-1 has been extensively studied and characterized, and its properties have been tuned by modifying the size and functionality of the BTC ligands, as well as by incorporating other metal ions into the structure. Its stability, high capacity for gas adsorption, and selectivity for certain gases make it a particularly attractive material for applications such as carbon capture and storage. Overall, HKUST-1 is a widely recognized and versatile MOF that has contributed significantly to the development of the field of MOF chemistry and materials science. HKUST-1 (or HKUST-1 MOF, also known as $\text{Cu}_3(\text{BTC})_2$) is a metal-organic framework (MOF) composed of copper ions coordinated to benzene-1,3,5-tricarboxylic acid (BTC). It was first synthesized in 1999 by researchers at the Hong Kong University of Science and Technology (HKUST), which is where its name comes from. HKUST-1 has a porous structure with high surface area and tuneable pore size, making it a promising material for gas storage and separation, catalysis, and sensing applications. The copper ions in HKUST-1 also give it interesting electronic, magnetic, and optical

properties, which have been studied for potential use in electronic and photonic devices. HKUST-1 has been extensively studied and characterized, and its properties have been tuned by modifying the size and functionality of the BTC ligands, as well as by incorporating other metal ions into the structure. Its stability, high capacity for gas adsorption, and selectivity for certain gases make it a particularly attractive material for applications such as carbon capture and storage. Overall, HKUST-1 is a widely recognized and versatile MOF that has contributed significantly to the development of the field of MOF chemistry and materials science.

1.2.6 PCN-222: This is a zinc-based MOF composed of carboxylic acid and triazole ligands. PCN-222 has a high surface area and has been studied for its ability to adsorb organic molecules such as caffeine. These are just a few examples of the many types of MOFs that have been studied for their adsorption properties. Each MOF has its own unique properties that make it suitable for specific adsorption applications. MIL-101, UiO-66, ZIF-8, MOF-5, HKUST-1, and PCN-222 are all metal-organic frameworks (MOFs) that have unique properties and advantages for various applications. The unique feature of PCN-222 is its high thermal and chemical stability, which makes it an ideal material for various applications, such as gas storage and separation, catalysis, and drug delivery. Its porous structure can be modified by changing the type and size of the organic ligands, allowing for fine-tuning of its properties. In terms of gas storage, PCN-222 has shown high selectivity and capacity for the storage of various gases, including carbon dioxide, methane, hydrogen, and nitrogen. It has also been used as a catalyst for various chemical reactions, such as the conversion of carbon dioxide to methanol. PCN-222 has also been explored for drug delivery applications, where its high stability and biocompatibility make it an attractive candidate. Researchers have successfully loaded PCN-222 with drugs and demonstrated controlled release of the drugs in vitro. Overall, PCN-222 is a promising MOF with a wide range of potential applications, and further research is ongoing to explore its full potential.

1.3 ADVANTAGES OF MOF

- This MOF has a large surface area, high porosity, and excellent chemical stability, making it suitable for various adsorption, separation, and catalysis applications. It can also be easily synthesized in large quantities and modified to enhance its properties.
- This MOF has a high thermal stability, large surface area, and tuneable pore size, making it suitable for gas storage, separation, and catalysis applications. It also has a high stability in acidic and basic conditions, making it suitable for use in harsh environments.
- This MOF has a high surface area, high thermal stability, and good chemical and moisture stability, making it suitable for various adsorption and separation applications. It is also relatively easy to synthesize and can be modified to enhance its properties.
- This MOF has a high surface area, high porosity, and good chemical and thermal stability, making it suitable for gas storage and separation applications. It can also be easily synthesized in large quantities and modified to enhance its properties.
- This MOF has a high surface area, high thermal stability, and tuneable pore size, making it suitable for gas storage, separation, and catalysis applications. It also has a high stability in acidic and basic conditions, making it suitable for use in harsh environments.
- This MOF has a high surface area, high porosity, and excellent chemical stability, making it suitable for various adsorption, separation, and catalysis applications. It can also be easily synthesized in large quantities and modified to enhance its properties.

1.4 DISADVANTAGES OF MOF

- Some MOFs can be susceptible to chemical and thermal degradation, which can limit their practical applications in harsh environments. However, efforts are being made to improve the stability of MOFs through the development of new synthesis methods and post-synthesis treatments.

- Many MOFs are sensitive to moisture, which can cause them to degrade or lose their adsorption properties. This can be addressed by using water-resistant coatings or storing MOFs in dry environments.
- The synthesis of MOFs can be expensive, and large-scale production of MOFs for industrial applications may not be economically feasible. However, advances in MOF synthesis and scaling-up methods are helping to reduce costs.
- Some MOFs may have limited selectivity for specific molecules, which can limit their applications in adsorption and separation processes. However, researchers are working on modifying MOFs to enhance their selectivity for specific molecules.

1.5 PHARMACEUTICAL POLLUTION AND POLLUTANTS

Pharmaceuticals are essential for the health and well-being of humans and animals. However, the widespread use of pharmaceuticals has led to their presence in the environment as pollutants. Pharmaceuticals are excreted from the body in urine and feces, and they can also enter the environment through improper disposal, leaching from landfills, and discharge from wastewater treatment plants. Once in the environment, pharmaceuticals can undergo transformation and degradation, leading to the formation of new compounds that may have unknown effects on ecosystems and human health. This thesis aims to investigate the presence and fate of pharmaceuticals as pollutants in the environment. The different pharmaceuticals that have been detected in the environment, including antibiotics, analgesics, hormones, and antidepressants. We will discuss their sources, routes of entry into the environment, and their occurrence in various environmental matrices such as surface water, groundwater, and soil. Additionally, we will highlight the potential risks and impacts of pharmaceutical pollutants on aquatic and terrestrial ecosystems. The fate and transport of pharmaceutical pollutants in the environment. We will examine the different processes that affect the behaviour of pharmaceuticals in the environment, including adsorption, degradation, and transformation. We will also explore the factors that influence the transport of pharmaceuticals in the environment, such as hydrophobicity, molecular weight, and polarity. Furthermore, we will discuss the various environmental factors that affect the persistence and fate of pharmaceutical pollutants, such as pH, temperature, and sunlight. Nowadays, non-steroidal anti-inflammatory medications (NSAIDs) often

used newly created pharmaceutical drugs (Comoretto et al., 2005). The environmental impact and human health risks associated with pharmaceutical pollutants. We will examine the potential adverse effects of pharmaceutical pollutants on aquatic and terrestrial ecosystems, including the disruption of endocrine systems and the development of antibiotic resistance in bacteria. Moreover, we will discuss the potential risks to human health associated with the exposure to pharmaceutical pollutants, such as developmental and reproductive disorders. the environmental impact of pharmaceutical pollutants. We will examine the current regulations and guidelines in place to manage pharmaceutical waste and the need for more effective approaches to reduce the release of pharmaceutical pollutants into the environment. Additionally, we will discuss the role of advanced technologies, such as nanotechnology and bioremediation, in addressing the problem of pharmaceutical pollution. Furthermore, we will highlight the need for further research and collaboration to better understand the environmental impact of pharmaceuticals and develop effective solutions to reduce their presence in the environment. pharmaceuticals as pollutants in the environment are a significant concern, given their potential impact on aquatic and terrestrial ecosystems, as well as human health. The presence and fate of pharmaceuticals in the environment are complex and require a multidisciplinary approach to address the problem effectively. The implementation of effective regulations and guidelines, as well as the development of advanced technologies, are crucial in mitigating the environmental impact of pharmaceutical pollutants. Further research is needed to better understand the environmental fate and transport of pharmaceuticals and their potential risks to human health, as well as to develop effective strategies to reduce their presence in the environment. Pharmaceutical pollution is a growing concern in many parts of the world, as the use and disposal of medications can lead to the release of a variety of pollutants into the environment. These pollutants can have adverse effects on both human health and the natural ecosystems. One major source of pharmaceutical pollution is the improper disposal of medications. Many people dispose of unused or expired medications by flushing them down the toilet or sink, which can lead to the release of drugs into the water supply. Pharmaceuticals can also enter the environment through the excretion of drugs by humans and animals, as well as through the disposal of medical waste. Pharmaceutical pollutants can have a range of effects on the environment and

human health. Some of the most common pharmaceutical pollutants found in the environment include antibiotics, antidepressants, and hormones. These substances can have adverse effects on aquatic life, such as disrupting the reproductive systems of fish and other organisms. They can also lead to the development of antibiotic-resistant bacteria, which can be harmful to both humans and animals. In addition to environmental effects, pharmaceutical pollutants can also have impacts on human health. For example, exposure to high levels of antibiotics in the environment can lead to the development of antibiotic-resistant bacteria in humans. Exposure to hormones and other endocrine-disrupting substances can lead to a range of health problems, such as developmental disorders, reproductive problems, and cancer. MOFs have shown to be quite helpful in many biomedical uses including the production of pharmaceuticals (Bulloch et al.,2015). Efforts to address pharmaceutical pollution have focused on a variety of strategies, including improved wastewater treatment and better medication disposal practices. Some countries have implemented programs to collect and properly dispose of unused medications, while others have implemented stricter regulations on the use and disposal of pharmaceuticals. There are also ongoing efforts to develop new technologies for the removal of pharmaceutical pollutants from wastewater and other sources. In conclusion, pharmaceutical pollution is a complex issue with significant implications for both the environment and human health. Understanding the sources and effects of pharmaceutical pollutants is critical for developing effective strategies for addressing this problem. While there are ongoing efforts to reduce pharmaceutical pollution, it will require continued research and innovation to effectively address this important issue. Pharmaceutical pollutants refer to any compounds or residues from pharmaceuticals that enter the environment and may have negative impacts on ecological and human health. Pharmaceuticals can enter the environment through a variety of pathways, including disposal of unused medication, excretion by humans and animals, and discharge from manufacturing facilities. Pharmaceuticals can enter rivers, lakes, and oceans through wastewater treatment plants and can have adverse effects on aquatic life. Pharmaceuticals can enter the soil through the application of biosolids from wastewater treatment plants, and can impact soil microbial communities and plant growth. Pharmaceuticals can enter the air through the evaporation of surface water, and can be transported long distances through atmospheric circulation. Some of the most commonly detected pharmaceutical

pollutants in the environment include antibiotics, hormones, and painkillers. These compounds can have adverse effects on the growth and development of aquatic organisms, as well as on human health. For example, exposure to antibiotics in the environment has been linked to the development of antibiotic resistance in bacteria, which can make infections more difficult to treat. Efforts to reduce pharmaceutical pollution include proper disposal of unused medications, improved wastewater treatment, and the development of new technologies for the removal of pharmaceuticals from water and soil. Additionally, pharmaceutical companies are increasingly exploring greener manufacturing processes that minimize the production of waste and pollutants.

Pharmaceutical pollutants are contaminants that originate from pharmaceutical products and their metabolites. They can enter the environment through various sources, such as human and animal excretion, improper disposal of unused or expired medication, and manufacturing and production processes. Here are some types of pharmaceutical pollutants and pollutions:

- **Antibiotics:** Antibiotics are commonly used in both human and veterinary medicine, and their widespread use has resulted in the development of antibiotic-resistant bacteria. When these drugs are excreted or disposed of improperly, they can enter water bodies and soil, leading to the contamination of aquatic and terrestrial ecosystems. MOF, or multiple organ failure, is a condition where multiple organs in the body fail to function properly. Antibiotics are commonly used in the treatment of MOF, as infections can contribute to the development or worsening of this condition. Infections can cause an inflammatory response in the body, which can lead to the dysfunction or failure of multiple organs. Antibiotics work by killing or inhibiting the growth of bacteria that may be causing an infection. By treating infections with antibiotics, the inflammatory response in the body can be reduced, which may help prevent or improve MOF. However, the use of antibiotics in MOF can also have negative effects. Antibiotics can disrupt the balance of bacteria in the body, leading to conditions such as antibiotic-associated diarrhea or overgrowth of antibiotic-resistant bacteria. In addition, the overuse of antibiotics can contribute to the development of antibiotic resistance, which can make infections harder to treat in the future. Therefore, the use of antibiotics in MOF must be carefully considered and monitored by healthcare professionals. The choice of antibiotic and duration of

treatment should be based on the specific infection and the patient's individual needs.

- **Hormones:** Hormones are used in various pharmaceutical products, including contraceptives and hormone replacement therapies. They can enter the environment through human and animal excretion, and their presence in water bodies can lead to hormonal disruptions in aquatic organisms. Pharmaceutical pollutants are a type of emerging contaminant that can be found in waterways and the environment. These pollutants can come from a variety of sources, including pharmaceutical manufacturing facilities, wastewater treatment plants, and improper disposal of medications. One type of pharmaceutical pollutant is hormones, which can have ¹⁰⁹negative effects on aquatic organisms and human health. Hormones are chemicals produced by the endocrine system that regulate various bodily functions. When hormones enter the environment as pollutants, they can disrupt the endocrine systems of animals and humans who are exposed to them. Studies have shown that exposure to hormone pollutants can lead to a variety of health problems, including reproductive disorders, developmental abnormalities, and cancer. In aquatic organisms, hormone pollutants have been ¹¹⁸linked to changes in behavior, growth, and reproduction. Efforts are being made to ⁴reduce the amount of pharmaceutical pollutants in the environment, including improved wastewater treatment and proper disposal of medications. Additionally, pharmaceutical companies are working to develop more environmentally friendly manufacturing practices and products that are less likely to contribute to pollution.
- **Painkillers:** Painkillers, such as opioids, are commonly prescribed for pain relief, but they can also be misused and abused. Improper disposal of these drugs can lead to their accumulation in water bodies, which can harm aquatic organisms and impact water quality. Painkillers, also known as ⁴analgesics, are commonly used medications for the relief of pain. However, ⁴the widespread use of painkillers has led to the accumulation of these drugs in the environment, which can have negative impacts on ecosystems and human health. Pharmaceutical pollution refers to the release of pharmaceuticals, including painkillers, into the environment. These drugs can enter waterways through various routes, such as wastewater treatment plants and runoff from agricultural areas. Once in the environment, painkillers can affect aquatic organisms, such as fish, and disrupt their endocrine systems, behavior, and reproductive capacity. Painkillers can also be considered as pollutants because of

their potential to harm human health. Misuse and overuse of painkillers can lead to addiction, overdose, and other adverse health effects. In addition, the presence of painkillers in the environment can lead to unintentional exposure through drinking water, which can have negative impacts on human health. To reduce the environmental and health impacts of painkillers, it's important to properly dispose of unused medications, use painkillers only as prescribed, and avoid flushing medications down the toilet or sink. Wastewater treatment plants can also play a role in reducing pharmaceutical pollution by implementing advanced treatment technologies that can remove these drugs from wastewater.

- **Chemotherapeutic agents:** Chemotherapeutic agents are used to treat cancer, but they can have harmful effects on both humans and the environment. When these drugs are excreted, they can enter water bodies and harm aquatic organisms. Additionally, improper disposal of chemotherapy waste can pose a risk to human health and the environment. Chemotherapy drugs are used to treat cancer and are an essential part of modern cancer therapy. However, they can also contribute to pharmaceutical pollution and the release of pollutants into the environment. Chemotherapy drugs can enter the environment through several pathways, such as through the excretion of patients receiving chemotherapy, disposal of unused drugs, and improper handling or disposal of contaminated materials by healthcare workers. These drugs can persist in the environment for a long time and may have harmful effects on aquatic life, soil organisms, and even human health. Pharmaceutical pollutants from chemotherapy drugs can be toxic to aquatic organisms and affect their growth and reproduction. They can also cause genetic damage and cancer in animals exposed to them. In addition, some chemotherapy drugs have been shown to have estrogenic effects, which can disrupt the endocrine systems of aquatic organisms. The proper handling, storage, and disposal of chemotherapy drugs are important to minimize the release of pollutants into the environment. Healthcare facilities should have protocols in place for the safe handling and disposal of chemotherapy waste, and patients should follow their healthcare provider's instructions for the safe disposal of any unused medication. Additionally, pharmaceutical companies should work to develop more environmentally friendly alternatives to chemotherapy drugs and invest in research to better understand the environmental impacts of these drugs.

- Personal care products:** Personal care products, such as lotions and shampoos, can contain chemicals that can be harmful to the environment. When these products are washed off, they can enter water bodies and harm aquatic organisms. Overall, pharmaceutical pollutants can have significant impacts on both human and environmental health. Personal care products, such as cosmetics, shampoos, and lotions, are a significant source of pharmaceutical pollution and pollutants. These products often contain a variety of chemicals, including active pharmaceutical ingredients (APIs), preservatives, fragrances, and other additives. When these products are used and washed off, the chemicals can enter the environment through wastewater, either by direct discharge or through sewage treatment plants. Pharmaceutical pollutants from personal care products can have harmful effects on aquatic organisms, such as fish and amphibians, and can even enter the food chain. In addition, some of these chemicals have been shown to have endocrine-disrupting properties, meaning that they can interfere with the hormonal systems of animals and humans. To reduce the impact of personal care products on pharmaceutical pollution, it's important to be aware of the ingredients in the products you use and choose products that are labeled as environmentally friendly or biodegradable. It's also important to properly dispose of unused medications and to avoid flushing them down the toilet or sink. In addition, improvements in wastewater treatment technology can help to remove pharmaceutical pollutants from wastewater before it is discharged into the environment.

1.6 EFFECTS OF CAFFEINE

Caffeine is one of the most widely consumed psychoactive substances in the world, present in various food and beverage products such as coffee, tea, energy drinks, and chocolate. Despite its popularity, the effects of caffeine on human physiology and behaviour are still being studied. This thesis aims to provide a comprehensive analysis of the physiological and behavioural impacts of caffeine consumption. the chemical and pharmacological properties of caffeine. We will discuss the sources of caffeine, including coffee, tea, and energy drinks, and how caffeine is metabolized in the body. Additionally, we will examine the mechanisms of action of caffeine,

including its effects on adenosine receptors, neurotransmitters, and hormones. the physiological effects of caffeine on various bodily systems, including the cardiovascular, respiratory, and gastrointestinal systems. We will examine the effects of caffeine on blood pressure, heart rate, and respiratory rate, as well as its impact on the digestive system, including its role in enhancing digestion and reducing constipation. the behavioural effects of caffeine, including its impact on mood, cognition, and performance. We will examine the effects of caffeine on alertness, attention, memory, and reaction time, as well as its impact on mood, including its role in reducing fatigue and improving mood. the potential health effects and risks associated with caffeine consumption. We will examine the impact of caffeine on sleep quality, anxiety, and addiction, as well as its potential role in increasing the risk of cardiovascular disease and affecting bone density. Additionally, we will discuss the potential risks associated with high caffeine intake, including caffeine overdose and its effects on pregnancy and breastfeeding. the consumption patterns of caffeine and the regulations in place to manage its use. We will examine the trends in caffeine consumption across different age groups and populations, as well as the various factors that influence caffeine intake, including social and cultural factors. Additionally, we will discuss the current regulations and guidelines in place to manage caffeine consumption, including the maximum recommended daily intake and the labelling requirements for caffeine-containing products. caffeine is a widely consumed psychoactive substance with various physiological and behavioural effects. The impacts of caffeine on human health and well-being are complex and require a multidisciplinary approach to address. Further research is needed to better understand the health effects and risks associated with caffeine consumption, as well as to develop effective strategies to manage its use. The implementation of regulations and guidelines, as well as education and awareness programs, is crucial in ensuring safe and responsible caffeine consumption. Caffeine is a naturally occurring stimulant found in coffee, tea, and other plants. It is also commonly used as an ingredient in energy drinks, soft drinks, and medications. Caffeine is a psychoactive substance that affects the central nervous system and can produce a range of physiological and psychological effects. One of the primary effects of caffeine is increased alertness and attention. This is because caffeine acts as an antagonist to adenosine receptors in the brain, which are responsible for promoting sleep and reducing arousal. By blocking these

receptors, caffeine increases the activity of ¹⁷ other neurotransmitters such as dopamine and norepinephrine, which promote wakefulness and attention. Caffeine can also affect mood and cognitive performance. Studies have shown that moderate doses of caffeine can improve mood, reduce fatigue, and increase cognitive performance in tasks such as reaction time, memory, and attention. However, the effects of caffeine on mood and cognition can vary depending on individual factors such as age, sex, and genetics. In some cases, high doses of caffeine can produce negative side effects such as anxiety, restlessness, and insomnia. Another effect of caffeine is increased metabolism and thermogenesis. Caffeine stimulates the release of adrenaline, which in turn increases the body's metabolic rate and causes the breakdown of stored fats for energy. This effect can be useful for weight loss and athletic performance, but it can also cause negative side effects such as dehydration and increased heart rate. Caffeine can also affect sleep quality and quantity. Because caffeine has a half-life of approximately 5-6 hours, it can remain in the body for several hours after consumption and interfere with sleep. Studies have shown that caffeine can reduce the total amount of sleep and increase the time it takes to fall asleep. Additionally, caffeine can disrupt the circadian rhythm, which regulates the sleep-wake cycle, and cause insomnia or other sleep disorders. In conclusion, caffeine is a complex substance that can produce a range of effects on the body and mind. While moderate doses of caffeine can improve alertness, mood, and cognitive performance, high doses can cause negative side effects such as anxiety, restlessness, and insomnia. Understanding the effects of caffeine can be useful for individuals who consume caffeine regularly, as well as for healthcare professionals who prescribe medications that contain caffeine. Caffeine ¹⁹ is a central nervous system stimulant that is found in many commonly consumed beverages and foods ³⁷ such as coffee, tea, soda, and chocolate. When consumed, caffeine acts on the brain by blocking the action of a neurotransmitter called adenosine, which is ⁴⁸ responsible for promoting sleep and suppressing arousal. As a result, caffeine can increase alertness, improve mood, and enhance cognitive performance. It can also increase heart rate and blood pressure, and lead to a temporary increase in metabolism and energy expenditure. However, the effects of caffeine can vary widely depending on factors such as individual sensitivity, dosage, and frequency of consumption. For some people, even low doses of caffeine can cause jitteriness, anxiety, and sleep disturbances. In addition, chronic high caffeine intake may lead

to dependence, tolerance, and withdrawal symptoms such as headaches, fatigue, and irritability. the effects of caffeine can be both positive and negative, and it is important to consume it in moderation and be aware of its potential effects on your body and mind. Caffeine is a naturally occurring stimulant that is commonly found in coffee, tea, chocolate, and some soft drinks. While caffeine is generally safe for human consumption in moderate amounts, it can have some negative effects on the environment if not properly disposed of. One of the primary ways that caffeine can negatively impact the environment is through the disposal of coffee grounds and tea bags. When these items are thrown in the trash and end up in a landfill, they can release caffeine and other chemicals into the surrounding soil and water. This can have harmful effects on plants and animals in the area, as well as on the quality of the groundwater. Another way that caffeine can affect the environment is through its use in agricultural practices. Caffeine is sometimes used as a natural pesticide, as it can be toxic to certain insects. However, this can also have unintended consequences for non-target species and for the overall ecosystem. Finally, caffeine can also contribute to water pollution when it is released into bodies of water through wastewater treatment plants or other sources. While caffeine is not considered a major pollutant, it can still have negative effects on aquatic organisms, particularly if it is present in high concentrations. Overall, while caffeine is generally safe for human consumption, it is important to be mindful of its potential effects on the environment and to dispose of coffee grounds, tea bags, and other sources of caffeine in a responsible manner. Caffeine citrate is a medication that is used to treat breathing problems in premature infants. It is a type of caffeine that is combined with citric acid to form a water-soluble salt. Caffeine citrate works by stimulating the central nervous system, which can help improve breathing and reduce episodes of apnea (pauses in breathing). Caffeine citrate is usually given as an injection into a vein or muscle, or as an oral solution. The dosage is based on the baby's weight and may be adjusted over time as needed. Although caffeine citrate is generally safe and effective when used as directed, it can cause side effects such as rapid heart rate, irritability, and vomiting. In rare cases, it can also cause seizures or other serious problems. It's important to use caffeine citrate only under the supervision of a healthcare provider who is experienced in caring for premature infants.

- The most common and well-known source of caffeine is coffee. The caffeine content in coffee varies depending on the type of coffee beans used and the method of preparation.
- Tea also contains caffeine, although in smaller amounts than coffee. Black tea generally has more caffeine than green or white tea.
- Energy drinks often contain high amounts of caffeine and are marketed as a way to boost energy levels. Soda caffeine: Some soft drinks, such as cola, contain caffeine. The amount of caffeine in these drinks varies widely depending on the brand.
- Caffeine is also found in chocolate, although the amount is usually smaller than in coffee or tea.
- Caffeine is sometimes added to over-the-counter medications like pain relievers to help increase their effectiveness.
It's important to note that consuming too much caffeine can have negative health effects, such as insomnia, anxiety, and heart palpitations. It's generally recommended that adults consume no more than 400 mg of caffeine per day, which is roughly equivalent to four cups of coffee.

1.6.1 ADVANTAGES OF CAFFEINE

- Caffeine is a powerful stimulant that can help to increase alertness, attention, and focus. This makes it a useful ingredient in many over-the-counter and prescription medications designed to combat fatigue, drowsiness, and other symptoms of sleep disorders.
- Caffeine has been shown to enhance the analgesic effects of certain pain medications, including aspirin and acetaminophen. When combined with these drugs, caffeine can help to reduce pain and inflammation more effectively.
- Caffeine has been shown to have a vasodilatory effect, meaning that it can help to widen blood vessels and increase blood flow. This can be useful in the treatment of certain conditions, such as migraine headaches and Raynaud's disease.

- Caffeine has also been shown to have some respiratory effects, including the ability to open up airways and improve breathing. This makes it a useful ingredient in some medications designed to treat asthma and other respiratory disorders.
- Caffeine has been shown to have cognitive enhancing effects, including improved memory, attention, and executive function. This makes it a useful ingredient in some medications designed to treat cognitive disorders, such as Alzheimer's disease.

Overall, caffeine has several advantages in the pharmaceutical industry and can be used in a variety of medications to help improve health outcomes.

1.6.2 DISADVANTAGE OF CAFFEINE

- Caffeine can have several side effects, particularly when consumed in large amounts or by individuals who are sensitive to its effects. These side effects can include anxiety, restlessness, insomnia, and increased heart rate and blood pressure.
- Caffeine can interact with certain medications, including some antibiotics, heart medications, and antidepressants. This can lead to adverse effects or reduced efficacy of these drugs.
- Regular use of caffeine can lead to physical dependence, and abrupt cessation of caffeine consumption can result in withdrawal symptoms, including headaches, fatigue, and irritability.
- Caffeine is a commonly used substance, and its availability in many products can lead to overuse or abuse. This can lead to negative health effects and can be particularly problematic in vulnerable populations, such as pregnant women, children, and individuals with certain medical conditions.
- Caffeine content can vary widely depending on the source and preparation method. This can make it difficult to standardize doses and can lead to variability in the effects of caffeine-containing medications.

Overall, while caffeine has several advantages in the pharmaceutical industry, it is important to consider its potential disadvantages and use it judiciously to minimize the risk of adverse effects.

1.7 REMOVAL METHODS OF CAFFEINE- ADSORPTION

Caffeine is a commonly consumed stimulant found in various beverages and foods, including coffee, tea, chocolate, and energy drinks. While caffeine has numerous benefits, excessive caffeine intake can lead to negative health effects, including anxiety, insomnia, and heart palpitations. This thesis aims to evaluate the various methods used for caffeine removal, with a specific focus on adsorption techniques. an overview of caffeine, including its sources and the potential health impacts associated with excessive consumption. We will discuss the various sources of caffeine and the daily recommended intake limits. We will also examine the negative health impacts associated with excessive caffeine intake, including anxiety, insomnia, and cardiovascular problems. the various methods used for caffeine removal, including physical and chemical methods. We will evaluate the effectiveness of these methods in removing caffeine from different sources, including beverages and wastewater. Additionally, we will examine the advantages and disadvantages of each method. adsorption techniques for caffeine removal. We will discuss the principles of adsorption and the various adsorbents used for caffeine removal, including activated carbon, silica gel, and zeolites. We will examine the factors that affect adsorption, including pH, temperature, and contact time. Additionally, we will evaluate the effectiveness of adsorption techniques in removing caffeine from different sources, including wastewater and food products. we will examine the advantages of adsorption techniques for caffeine removal. We will discuss the cost-effectiveness and scalability of adsorption methods, as well as their environmental impact. Additionally, we will examine the versatility of adsorption techniques in removing other contaminants, such as heavy metals and organic pollutants. the challenges and future directions of caffeine removal, with a specific emphasis on adsorption techniques. so far, various adsorbents are commonly employed to remove pharmaceuticals (Akhtar et al., 2015). We'll discuss the challenges associated with the optimization of adsorption processes, including the selection of adsorbent materials and the optimization of operating conditions. Additionally, we will examine the potential for the integration of adsorption techniques with other treatment processes, such as membrane filtration and reverse osmosis. caffeine removal is an important issue that requires effective and

sustainable solutions. Adsorption techniques have shown significant potential in removing caffeine from different sources, including wastewater and food products. The advantages of adsorption techniques, including cost-effectiveness and scalability, make them an attractive option for caffeine removal. Further research is needed to optimize adsorption processes and explore the potential for their integration with other treatment methods. Due to their intriguing characteristics, including their large interior surface area, metal-organic frameworks (MOFs) have generated considerable scholarly interest as a novel adsorbent (Desai et al., 2016). The development of effective caffeine removal strategies will contribute to the protection of human health and the environment. Caffeine is a common contaminant in water sources, especially in areas with high coffee and tea consumption. The removal of caffeine from water is important to maintain water quality and ensure safe drinking water. There are several methods of removing caffeine from water, including adsorption, membrane filtration, ion exchange, and biological treatment. One of the most effective methods of removing caffeine from water is adsorption. Adsorption is a process in which molecules or particles are attracted to and adhere to the surface of a solid material called an adsorbent. The adsorbent can be made of natural or synthetic materials such as activated carbon, zeolites, or metal-organic frameworks (MOFs). Activated carbon is a commonly used adsorbent for removing caffeine from water. It has a large surface area and pore size distribution, which allows it to adsorb a wide range of organic compounds including caffeine. Activated carbon works by attracting caffeine molecules to its surface through van der Waals forces, hydrogen bonding, and pi-pi interactions. Nanosized MOFs, or metal-organic frameworks recently drawn a large number interest from a range of nanocarriers owing to their enormous surface area, high surface porosity, same straight forward inclines of the pores diameters within the frameworks using changeable organic groups (Cheng et al., 2007). The adsorption capacity of activated carbon can be increased by modifying its surface chemistry through chemical or physical treatments. Zeolites are another type of adsorbent that can be used for caffeine removal. Zeolites are naturally occurring minerals that have a crystalline structure with uniform pore sizes and shapes. They can be modified to have a high affinity for caffeine by introducing specific functional groups such as amine or carboxylic acid groups. Zeolites can also be synthesized in the laboratory to have specific pore sizes and structures for optimal caffeine adsorption. Metal-organic frameworks (MOFs)

are a relatively new class of adsorbents that have shown promise for caffeine removal. MOFs are composed of metal ions or clusters connected by organic ligands to form a porous structure with high surface area and tuneable pore size. The adsorption capacity of MOFs can be increased by modifying their chemical composition or by using post-synthetic modifications. MOFs have shown high selectivity for caffeine and can be easily regenerated for reuse. In conclusion, the removal of caffeine from water is important for maintaining water quality and ensuring safe drinking water. Adsorption is a highly effective method for caffeine removal, and adsorbents such as activated carbon, zeolites, and MOFs can be used for this purpose. Among these adsorbents, MOFs have shown promising results due to their high selectivity and tuneable properties. Further research is needed to optimize the use of MOFs for caffeine removal and to explore other potential adsorbents for this application. Clofibric acid, bisphenol-A (BPA), Triclosan (TCS), Ketoprofen (KTF), p-Chloro-m-xlenol (PCMX), and NPX and diclofenac have been completed to use a range of adsorbents, including MOF. PCMX is a microbiological ingredient in cosmetics (Cai et al., 2019). MOFs, or metal-organic frameworks, have shown promise in the removal of caffeine from different solutions due to their high surface area, tuneable pore size, and selective binding sites. Here are some examples of different types of removal methods of caffeine using MOFs.

- Adsorption:** MOFs can act as adsorbents to remove caffeine from solutions by physically binding to the caffeine molecules on their surface. For example, MIL-101(Cr) and ZIF-8 have been studied for their ability to adsorb caffeine from water and tea extracts, respectively. Adsorption is a process where molecules or particles adhere to the surface of a solid material, forming a thin film or layer on its surface. Metal-organic frameworks (MOFs) are a type of porous material that can be used as adsorbents due to their high surface area and tunable properties. MOFs consist of metal ions or clusters linked by organic ligands to form a three-dimensional framework with a highly porous structure. The porous structure of MOFs provides a large surface area for adsorption, while the tunable properties of MOFs allow for the selective adsorption of specific compounds. Adsorption in MOFs can occur through several mechanisms, such as physisorption, chemisorption, and electrostatic interactions. Physisorption is the most common mechanism, where the adsorbate molecules are held to the MOF surface by weak van der Waals forces.

Chemisorption, on the other hand, involves the formation of chemical bonds between the adsorbate molecules and the MOF surface. MOFs have shown great potential as adsorbents for a wide range of applications, such as gas separation, catalysis, and water purification. In the context of water purification, MOFs have been used as adsorbents for the removal of contaminants such as heavy metals, dyes, and pharmaceuticals. The high surface area and selective adsorption properties of MOFs make them a promising material for the development of efficient and sustainable water treatment technologies.

- **Chemical reaction:** Some MOFs can react with caffeine molecules to form new compounds that are less soluble and easily separable from the solution. For instance, UiO-66-NH₂ has been used to react with caffeine and form caffeine cocrystals, which can be easily filtered from the solution. Metal-organic frameworks (MOFs) are a type of porous material composed of metal ions or clusters linked by organic ligands. The unique properties of MOFs, such as their high surface area and tunable properties, make them attractive for a wide range of applications, including catalysis. Chemical reactions can occur within the pores of MOFs, either on the metal ions or on the ligands. These reactions can be controlled and optimized by adjusting the structure and composition of the MOF. For example, certain metal ions within the MOF can act as active sites for catalytic reactions, while the ligands can act as templates for directing the reaction pathway or as stabilizers for the reactive intermediates. MOFs have been used for a variety of chemical reactions, including oxidation, hydrogenation, and carbon dioxide reduction. For example, a study published in the journal Science in 2015 demonstrated the use of a MOF for the catalytic conversion of carbon dioxide to methanol, achieving a high selectivity and yield. Overall, the ability of MOFs to host and facilitate chemical reactions holds great potential for a wide range of applications, including catalysis and energy conversion. Further research and development of MOFs with tailored properties and functionalities are needed to advance this field and unlock their full potential.
- **Membrane separation:** MOFs can also be used to create selective membranes that separate caffeine from other components in a solution. For example, MOF-74 has been used to create a membrane that can selectively separate caffeine from tea extract. Membrane separation in MOF (Metal-Organic Framework) is a

promising technology for efficient separation and purification of gases and liquids. MOFs are highly porous materials with a large surface area and can selectively adsorb or exclude molecules based on their size, shape, and polarity. Membrane separation in MOFs involves the fabrication of thin-film membranes made of MOF crystals, which allow for the selective transport of molecules across the membrane. The high surface area and selective adsorption properties of MOFs make them attractive for membrane separation applications, such as gas separation, water purification, and solvent filtration. The use of MOF-based membranes has the potential to improve the efficiency and sustainability of separation processes in various industries, including energy, pharmaceuticals, and food production.

- **Liquid-phase extraction:** MOFs can also be used in liquid-phase extraction techniques to selectively remove caffeine from solutions. For example, MIL-101(Cr) has been used to selectively extract caffeine from tea extracts by using ethanol as a solvent.

Overall, MOFs show great potential in the removal of caffeine from different solutions due to their versatility and tuneable properties. However, more research is needed to optimize these methods and scale them up for practical applications. Liquid Phase Extraction (LPE) is a process in which a liquid phase is used to selectively extract a target substance from a mixture. Metal-organic frameworks (MOFs) have gained attention as potential materials for LPE due to their high surface area, tunable pore size, and functional groups that can selectively adsorb specific molecules. In MOF-based LPE, the MOF is typically mixed with the mixture containing the target substance in a liquid phase, and the target substance is selectively adsorbed onto the MOF. The MOF can then be separated from the liquid phase, and the target substance can be desorbed from the MOF using a suitable solvent or by heating. The desorbed target substance can then be isolated and purified. MOF-based LPE has been applied to a range of target substances, including metal ions, organic dyes, and pharmaceutical compounds. This method shows promise as a more efficient and selective alternative to traditional extraction techniques. However, further research is needed to optimize the performance of MOF-based LPE and to develop MOFs with even better selectivity and adsorption properties.

1.8 TYPES OF ADSORPTION

- **Batch adsorption:** In this method, a fixed amount of adsorbent material is mixed with a solution containing caffeine. The mixture is then allowed to stand for a predetermined amount of time to allow the caffeine to adsorb onto the adsorbent material. The solution is then separated from the adsorbent, and the caffeine concentration is measured to determine the amount of caffeine removed. Batch adsorption is a common method for removing pharmaceuticals from wastewater using metal-organic frameworks (MOFs). MOFs are highly porous materials that can effectively capture organic molecules due to their large surface area and tunable pore size. To perform batch adsorption, MOFs are first synthesized and activated to ensure optimal surface area and pore accessibility. Then, a known quantity of the MOF is added to a batch of wastewater containing pharmaceuticals, and the mixture is stirred for a period of time to allow for adsorption to occur. The effectiveness of the adsorption process can be determined by measuring the concentration of pharmaceuticals in the wastewater before and after treatment. The extent of adsorption depends on several factors such as the properties of the MOF, the concentration of pharmaceuticals in the wastewater, and the contact time between the MOF and the wastewater. Batch adsorption using MOFs has shown promise as an effective and sustainable method for removing pharmaceuticals from wastewater. However, further research is needed to optimize the process parameters and to develop MOFs that are highly selective for specific pharmaceuticals.
- **Column adsorption:** In this method, a column packed with the adsorbent material is used to continuously remove caffeine from a solution. The solution is passed through the column, and the caffeine adsorbs onto the adsorbent material. The purified solution is then collected at the bottom of the column. Column adsorption is a common technique used in the removal of pharmaceuticals from wastewater using Metal-Organic Frameworks (MOFs). MOFs are a type of porous material that has a high surface area and can selectively adsorb certain chemicals. The process involves passing the wastewater through a column packed with MOF particles, which selectively adsorb the pharmaceuticals from the water. The adsorbed pharmaceuticals can then be removed from the MOF using various techniques, such

as solvent extraction or thermal desorption. One advantage of using MOFs for pharmaceutical removal is their high selectivity, which means they can target specific pharmaceuticals in the wastewater without affecting other compounds. Additionally, MOFs can be easily synthesized with specific properties, allowing for the design of materials tailored to specific pharmaceuticals. However, there are also some challenges associated with using MOFs for column adsorption in wastewater treatment. These include the cost of synthesizing the MOFs, the need for continuous regeneration of the MOF material, and the potential for fouling of the column over time. Overall, column adsorption using MOFs shows promise as a potential method for the removal of pharmaceuticals from wastewater. Further research is needed to optimize the process and address the challenges associated with this technique.

- **Continuous stirred tank reactor (CSTR):** This method involves a reactor vessel containing the adsorbent material, which is continuously stirred to ensure uniform mixing. The solution containing caffeine is continuously added to the reactor vessel, and the purified solution is continuously removed from the vessel. Continuous stirred tank reactors (CSTRs) are commonly used in the removal of pharmaceuticals from wastewater using metal-organic frameworks (MOFs). MOFs are highly porous materials made up of metal ions linked by organic ligands. They have shown great potential in removing various organic and inorganic pollutants from wastewater due to their high surface area and chemical selectivity. In a CSTR, wastewater is continuously fed into a reactor vessel, which contains a suspension of MOF particles. The suspension is continuously mixed to ensure that the MOF particles are evenly distributed throughout the reactor vessel. As the wastewater flows through the reactor vessel, the MOF particles selectively adsorb the pharmaceuticals from the wastewater, effectively removing them from the solution. The effectiveness of the MOF-based CSTR system depends on several factors, including the type and concentration of the pharmaceuticals in the wastewater, the properties of the MOF material used, and the flow rate of the wastewater through the reactor vessel. Optimization of these factors can lead to highly efficient removal of pharmaceuticals from wastewater using MOFs in a CSTR. Overall, the use of MOFs in CSTR systems represents a promising approach to wastewater treatment that has the potential to significantly reduce the presence of pharmaceuticals in our water supply.

- **Fluidized bed adsorption:** In this method, the adsorbent material is suspended in a fluidized bed and the solution containing caffeine is continuously passed through the bed. The choice of removal method will depend on several factors, including the properties of the adsorbent material, the properties of the solution containing caffeine, and the desired degree of purification. Fluidized bed adsorption is a process used to remove contaminants from water by passing it through a bed of porous material, such as activated carbon or metal-organic frameworks (MOFs). MOFs are a type of porous material that can be used as adsorbents due to their high surface area and tuneable properties. In the context of removing pharmaceuticals from wastewater, MOFs have been shown to be effective adsorbents due to their ability to selectively adsorb specific compounds. For example, a study published in the journal Chemical Engineering Journal in 2020 demonstrated the use of a ZIF-8 MOF for the removal of ibuprofen from wastewater. In a fluidized bed adsorption system using MOFs, wastewater is pumped through a bed of the MOF particles, which are suspended in the water and fluidized by the flow. As the water passes through the bed, the MOF particles adsorb the targeted pharmaceutical compounds, which are then removed from the water.

CHAPTER-2

LITERATURE SURVEY

• **Jungang et al. (2021)** He spoke about how MOF is created using a solvent-based process, and how it must be transported to a Teflon-lined vessel before being heated at 150 °C. We also talked about how it must be cleaned with DMF and alcohol before being filtered to produce brown products.

• **Laurier et al. (2013)** found that compared to those containing additional metal atom nodes, iron(III) based MOFs can serve as more effective photocatalysts. Since several earlier MOFs, such as MOF-5, had their best photocatalytic properties in the UV spectrum, it is remarkable that these types of catalysts were shown to take in light within the visible spectrum.

• **García et al. (2022)** suggested causing an electrostatic formation of UiO-66- NH₂ and GO and then hydrothermally reducing GO to rGO. According to the electron conductivity of graphene functions, the heterostructure UiO-66- NH₂/rGO enhances the capacity of dividing the photo-generated electron- hole pairs and the absorption of visible light. In comparison to UiO-66-NH₂, UiO-66-NH₂/rGO has considerably higher photocatalytic activity when illuminated by visible light.

• **Bortot et al. (2020)** looked into the photocatalytic decrease of immobilized Ce-ZrO₂ that removes Cr(6+) under the influence of visible light. It was shown that reduced starting pH values and larger catalyst doses enhance Cr(6+) adsorption and photo reduction in the simulation Cr(6+) solution. After being exposed to visible light, the immobilized Ce-ZrO₂ was able to remove more than 97% of the Cr(6+) from a neutralized effluent from the galvanizing industry with an elevated level of zinc, enabling its release into the water's surface. The processes were unaffected by the presence of HA.

• **Bauer et al. (2008)** It was examined that the most crucial conditions for the production of various hybrid phases used 2-amino terephthalic acid. These factors included the kind of reaction media, solvent concentration, and temperature.

- **Joshi et al. (2011)** determined TiO₂ has a very high photodegradation rate, according to research. TiO₂ delicate film was created using the sol-gel technique. Only 46.5% of Cr(6+) was eliminated at the exact same time. At a concentration of 50 ppm, Cr(6+) may be removed with an efficiency of over ninety-six percent. with a rise in photocatalyst dosage. The most effective photocatalyst was discovered to be TiO₂. TiO₂ eliminates 80% of the Cr(6+), but ZnO removes just 45%, making ZnO a less efficient photocatalyst than TiO₂.

- **Jang et al. (2020)** recorded NH₂-ASNs, and NH₂-MSNs had adsorption efficiencies (qe) that were 40 to 80 times larger than the ones of ASNs and MSNs, respectively, which supported the effect of NH₂-functionalization on the efficiency of adsorption of Cr(6+). NH₂-ASNs and NH₂-MSNs were shown to have maximal Cr(6+) removal capabilities of 61.9 and 76.8%, accordingly.

- **Perumal et al. (2021)** confirmed that the hydrothermal procedure was used to successfully create an RGOeHat hybrid composite and use it to absorb MO and Cr(6+) ions from aqueous solutions. With maximal reduction efficiencies of 49.14 and 45.24 mg for MO and Cr(6+) ions, respectively, the adsorption mechanism of the RGOeHat hybrids for MO and removal of Cr(6+) follows PSO kinetic and Langmuir isotherm frameworks.

- **Abhilash et al (2018)** said When the photodegradation rate of Cr(6+) was examined, it was discovered that it was, respectively, 60.24%, 82.12%, 65.17%, and 51.27% for pHs 3, 5, 7, and 9. The photodegradation rates of Cr(6+) for five additional cycles were determined to be 78.15%, 74.65%, 72.45%, 71.98%, and 70.24%, respectively, indicating that the photocatalytic efficiency is diminished by the rise or reduction of Cr(6+) solution pH.

CHAPTER - 3

AIM

- To evaluate the adsorption capacity of various MOFs for caffeine citrate removal: The first aim could be to determine the adsorption capacity of different MOFs for caffeine citrate removal.
- To investigate the effect of operating parameters on caffeine citrate removal using MOFs: The second aim could be to explore the effect of operating parameters such as pH, temperature, and contact time on caffeine citrate removal using MOFs
- To compare the performance of MOFs with other adsorbents for caffeine citrate removal: The third aim could be to compare the performance of MOFs with other adsorbents, such as activated carbon or zeolites, for caffeine citrate removal.
- To investigate the mechanism of caffeine citrate adsorption onto MOFs: The fourth aim could be to investigate the mechanism of caffeine citrate adsorption onto MOFs.

SCOPE

- MOF synthesis and characterization: The first point of scope would be the synthesis and characterization of MOFs suitable for caffeine citrate removal.
- Adsorption capacity and kinetics: The second point of scope would be the determination of the adsorption capacity and kinetics of MOFs for caffeine citrate removal.
- Optimization of operating parameters: The third point of scope would be the optimization of operating parameters such as pH, temperature, and contact time for caffeine citrate removal using MOFs
- Comparison with other adsorbents: the comparison of MOFs with other adsorbents such as activated carbon or zeolites for caffeine citrate removal. This could involve conducting experiments with different adsorbents and comparing their adsorption capacities, kinetics, and selectivity for caffeine citrate remains same.

CHAPTER 4

MATERIALS AND METHODS

4.1 REAGENTS

Since all of the compounds were readily accessible on the market and of analytical quality, they were utilised directly. Vital Science Ltd. in India provided the amino terephthalic acid (NH₂-BDC) and ferric chloride hexahydrate (FeCl₃.6H₂O) for our experiments. The chemicals ethanol (EtOH), isopropyl alcohol (IPA), and dimethyl formamide (DMF) were all bought from Sigma Scientific Products in Chennai, India. Dimethylformamide (DMF) is a colorless liquid with a faint odor that is commonly used as a solvent in various industrial processes. It is highly soluble in water and many organic solvents, making it a versatile substance in chemical synthesis and manufacturing. DMF is also used as a reagent in the production of pharmaceuticals, pesticides, and synthetic fibers. DMF is a hazardous substance and should be handled with care. It can be absorbed through the skin and inhalation of its vapors can cause irritation to the eyes, nose, and throat. Long-term exposure to DMF can lead to liver and kidney damage, and may increase the risk of certain types of cancer. Due to its potential health risks, DMF is subject to strict regulations by various governmental agencies, including the Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration (OSHA). Workers who handle DMF or work in facilities where DMF is used are required to follow proper safety procedures and wear protective equipment to minimize the risk of exposure.

4.2 SYNTHESIS OF NH₂-MIL-53(Fe)

The solvothermal process was used to make NH₂-MIL-53(Fe). 42 mL of DMF was used to dissolve 2 mmol of NH₂-BDC and 2 mmol of FeCl₃.6H₂O. The mixture was then moved to a Teflon-lined autoclave and maintained at 150 °C for a period of three hours after being consistently stirred at ambient temperature. After the slurry had cooled to room temperature, it was vacuum processed to produce a brown product. After that, DMF and EtOH were used to wash the filter cake. It was dried in a vacuum oven for one night at 60 °C [9]. MIL-53 Fe is a metal-organic framework (MOF) material that is composed of iron atoms and organic ligands. It has a unique

porous structure that makes it useful for various applications, including gas storage and separation, catalysis, and drug delivery. The synthesis of MIL-53 Fe typically involves a solvothermal method, which involves heating a mixture of iron salts and organic ligands in a solvent at high temperature and pressure. The exact conditions of the synthesis, such as the temperature, time, and solvent used, can affect the properties of the resulting material. During the synthesis process, the iron salts and organic ligands react to form the framework structure of MIL-53 Fe. The resulting material is typically characterized using techniques such as X-ray diffraction and scanning electron microscopy to confirm its structure and properties. Overall, the synthesis of MIL-53 Fe is a complex process that requires careful control of various parameters to obtain a high-quality material with the desired properties. The resulting material has great potential for use in a wide range of applications due to its unique porous structure and other properties. Typically, the reaction mixture is heated at a moderate temperature (usually between 100 and 200 °C) under autogenous pressure for several hours. The resulting product is then washed, dried, and activated by heating under vacuum to remove any residual solvent or water molecules that may be trapped inside the pores of the MOF.



Fig. 4.1: Experimental image of a) Magnetic stirrer while synthesis of MOFNH₂-MIL-53(Fe) b) Sonicator while synthesis of MOF NH₂-MIL-53(Fe), c) Conical Flask shaker while synthesis of MOF NH₂-MIL-53(Fe).

4.3 SYNTHESIS OF REDUCED GRAPHENE OXIDE (rGO)

The bagasse from sugar cane and the shells of coconuts are examples of agricultural waste. Additionally, farming waste was properly treated and ground into powder. To obtain a fine powder, the crushing and separating process was repeated several times. A furnace with muffle was set at 300°C with 0.5 g of powder and 0.1 g of ferrocene within under air conditions. Separation, washing with Hydrochloric and filtered water, and drying followed by the GO powder. A magnetic stirrer was used to help integrate 4.00 g of ascorbic acid into processed GO-distilled water for a sixty-minute period while keeping the temperature between 60 and 70°C. To oxidize the surplus acid, an appropriate quantity of H₂O₂ 30% (excess) was included to this mixture and agitated for thirty minutes at 60°C. Centrifugation was used to separate the final product, which was then repeatedly cleaned with filtered water and ethanol before being dried for a full day at 120 °C. Reduced graphene oxide (rGO) is a form of graphene oxide that has been chemically or thermally treated to reduce its oxygen content and restore its electrical conductivity. The synthesis of rGO typically involves the reduction of graphene oxide through various methods such as thermal reduction, chemical reduction, or a combination of both. One common method for the synthesis of rGO is chemical reduction using a reducing agent such as hydrazine or sodium borohydride. The graphene oxide is first dispersed in a solvent, and then the reducing agent is added to the mixture, which leads to the reduction of the oxygen functional groups and the formation of rGO. This method is relatively simple and efficient, and the resulting rGO has a high degree of conductivity and can be easily dispersed in solvents. Another method for the synthesis of rGO is thermal reduction, which involves heating graphene oxide in a reducing atmosphere or vacuum. This process can be carried out using a variety of methods, such as annealing or microwave irradiation, and can result in the reduction of oxygen groups and the restoration of electrical conductivity. However, this method can be more challenging to control and may require more specialized equipment. Overall, the synthesis of rGO is an important process in the development of graphene-based materials for various applications, including energy storage, sensors, and electronics.

4.4 MODIFICATION OF NH₂-MIL-53(Fe) WITH rGO

10 % by weight of rGO accounting for the reaped composite material was dispersed into the above solution and stirred for 30 minutes on a magnetic stirrer. Subsequently, the mixture was heated at 170°C for 2 hours. The product was washed with DMF, methanol and distilled

water, then dried, and $\text{NH}_2\text{-MIL-53(Fe)/rGO}$ was obtained. These materials are used for photocatalysis removal of Caffeine citrate. Modification of MIL-53 with rGO involves incorporating rGO into the MIL-53 framework to enhance its properties. The resulting material has a higher surface area, improved thermal stability, and enhanced gas adsorption capacity. The incorporation of rGO also improves the mechanical strength and stability of the MIL-53 framework. The modified material has potential applications in gas separation, catalysis, and energy storage. It is a promising candidate for the development of advanced materials with improved properties for various industrial applications.



Fig. 4.4: Experimental image of a) Dropwise addition of alcohol in conical flask mixer b) Slurry paste mixture of MOF

4.1.1 PHOTOCATALYTIC DEGRADATION OF CAFFEINE CITRATE

Photocatalytic degradation of caffeine citrate can be achieved using a variety of photocatalysts, such as titanium dioxide (TiO₂), zinc oxide (ZnO), and tungsten trioxide (WO₃). The process involves the use of light energy to activate the photocatalyst and generate reactive oxygen species (ROS) that can degrade the caffeine molecule. The photocatalytic degradation of caffeine citrate can be carried out in a batch reactor or a continuous flow system. In a batch reactor, a suspension of photocatalyst and caffeine citrate is irradiated with UV light. The rate of degradation can be monitored by measuring the decrease in the concentration of caffeine citrate over time using analytical techniques such as high-performance liquid chromatography (HPLC). In a continuous flow system, the photocatalyst is immobilized on a support material and the caffeine citrate solution is passed over it under UV irradiation. This process can be more efficient than the batch process as it allows for continuous degradation of caffeine citrate. The efficiency of photocatalytic degradation can be affected by various factors such as the type of photocatalyst, the intensity and wavelength of the light source, the initial concentration of caffeine citrate, and the presence of other organic compounds or inorganic ions in the solution. Optimization of these factors can lead to higher degradation rates and better efficiency. Caffeine citrate is a common drug used in neonatal care, but its presence in wastewater can cause environmental pollution and potential harm to aquatic organisms. Photocatalytic degradation is a promising approach for the removal of caffeine citrate from wastewater, using a photocatalyst that can harness light energy to break down the compound into harmless by products. Titanium dioxide (TiO₂) is a commonly used photocatalyst for the degradation of caffeine citrate. When exposed to ultraviolet (UV) light, TiO₂ can generate reactive oxygen species (ROS) that can oxidize and degrade the caffeine citrate molecules. Several studies have investigated the photocatalytic degradation of caffeine citrate using TiO₂ photocatalysts, with varying results depending on factors such as the concentration of caffeine citrate, the type of TiO₂ used, and the pH of the solution. For example, a study published in the journal Chemosphere in 2019 demonstrated the use of a TiO₂ photocatalyst for the degradation of caffeine citrate, achieving a removal efficiency of 96% after 4 hours of UV irradiation. Overall, photocatalytic degradation using TiO₂ photocatalysts shows promise for the removal of caffeine citrate from wastewater. Further research and optimization of photocatalytic systems and conditions are needed to improve the efficiency and effectiveness of this approach.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 STRUCTURAL CHARECTERISATION OF NH₂-MIL-53(Fe)/rGO

5.1.1 X-Ray Diffraction (XRD)

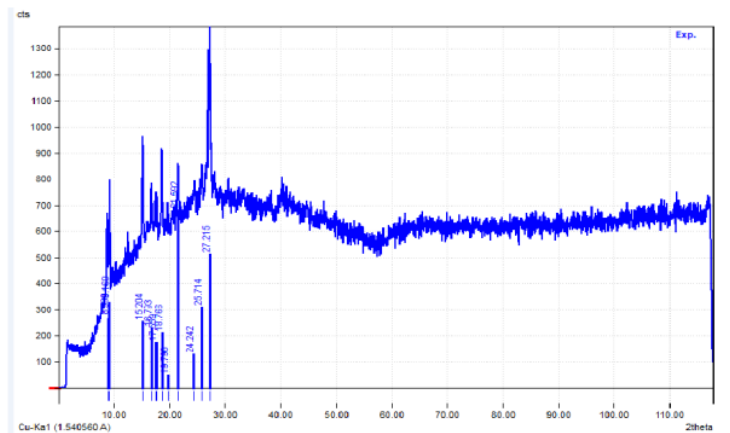
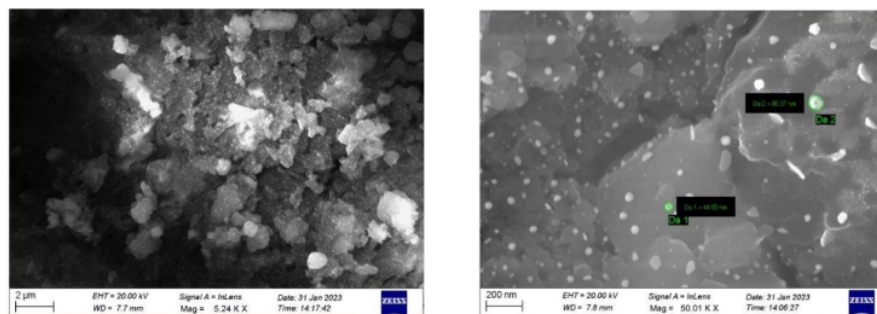


Fig. 5.1.1: XRD analysis image of the MOF catalyst NH₂-MIL-53(Fe) rGO.

The characteristic points of pure NH₂-MIL-53(Fe) in the XRD spectra at $2\theta = 8.6^\circ, 10.4^\circ, 15^\circ, 17.5^\circ$, and 26.4° agreed with the findings in the literature[11]. The existence of the NH₂-MIL-53(Fe) characteristic point and the weak wide diffraction peak assigned to $15\text{--}25^\circ$ proved that NH₂-MIL-53(Fe)/rGO composites were manufactured. The normal crystallite size of NH₂-MIL-53(Fe)/rGO was 80.37 nm, as calculated by the Scherrer equation. The conventional set in the card library, which might have been classified to the lattice plane of (110), (111), (202), and (221) was likewise identical with the composite.

5.1.2 Field Emission Scanning Electron Microscopy (FE-SEM)



Two elements are readily visible on the outermost layer of the combination, notably the formation of uniformly sized $\text{NH}_2\text{-MIL-53(Fe)}$ flakes on the rGO substrate. Due to the insufficient growth process, $\text{NH}_2\text{-MIL-53(Fe)}$ looked spindle-like and was enclosed by irregular detritus.

5.1.3 Fourier Transform Infrared (FT-IR)

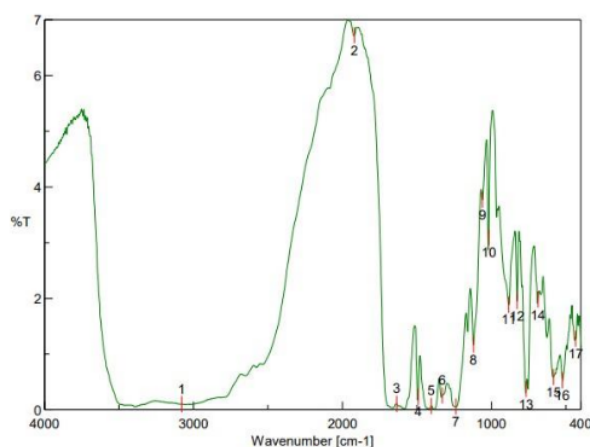
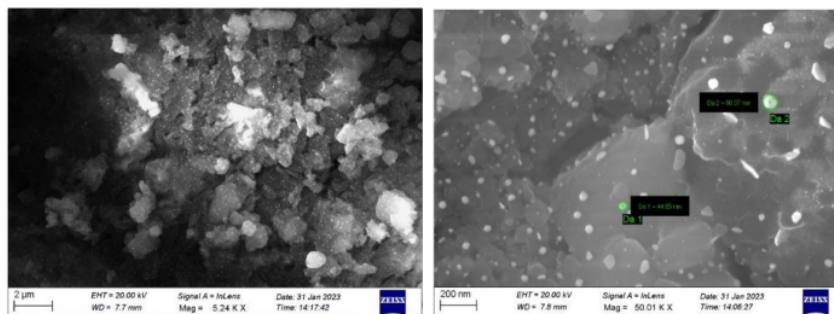


Fig. 5.1.3: FT-IR analysis image of the MOF catalyst $\text{NH}_2\text{-MIL-53(Fe)}$ rGO

The findings of the FT-IR spectra proved that the sheets of rGO were attached to the MOF's exterior. The effective alteration of rGO was verified by an intensity peak at 1636 cm^{-1} , which corresponds to the C=O vibrations that stretch of the carboxyl groups, and an intensified rise at 3079 cm^{-1} . The usual $\text{NH}_2\text{-MIL-53(Fe)/rGO}$ composite rises between 1402 and 1636 cm^{-1} was created. As a result of the removal of PS microspheres, the lines at 1918 and 766 cm^{-1} that corresponded to the usual PS peaks vanished (curve d in Fig. 5.3). The C-N and N-H tremors of the amino group, as well as the Fe-O and C-H vibrations of the benzene rings,

were each assigned to the lines at 524, 686, 827, 1017, and 1120 cm^{-1} (Peak numbers 12 to 17).

Fig. 5.1.2: (a)(b) SEM analysis image of the MOF catalyst $\text{NH}_2\text{-MIL-53(Fe)}$ rGO



5.2 OPTIMIZATION

5.2.1 Effect of caffeine citrate concentration

To look at how its starting concentration affects degradation. For this study, caffeine citrate concentrations ranging from 250 ppm to 1000 ppm were employed for photocatalysis, and dosages of 0.5 g, 1 g, 1.5 g, and 2 g of MOF catalyst mass were utilized.

For the water-based solution containing 250 ppm to 1000ppm of caffeine citrate, Fig. 5.4 shows the fluctuation in the quantity of caffeine citrate degrading with contact time. This concentration's catalyst dose is 0.5g. For various catalyst dosages, the similar pattern was discovered[2, 4].

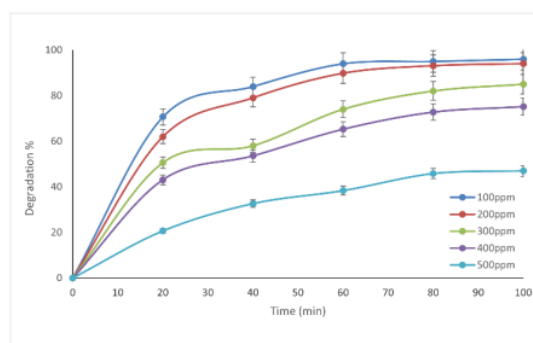


Fig. 5.2.1: Effect of caffeine citrate concentration graph which is plotted for time vspercentage degraded.

5.2.2 Effect of catalyst dosage

The degradation of caffeine citrate was tested utilizing several dosages, namely 0.5g, 1g, 1.5g, and 2g vs contact time. The outcomes suggest that increasing the catalyst dose increases caffeine citrate degradation rate. However, the degradation rate does not alter much when the catalyst dose is increased, therefore 0.5g may be the optimal catalyst dosage

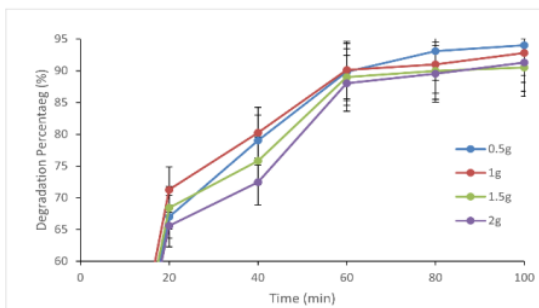
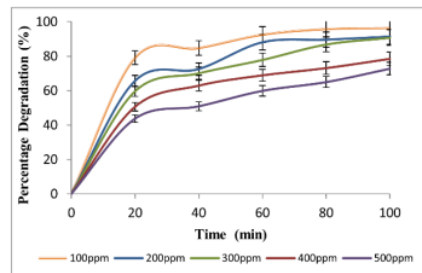
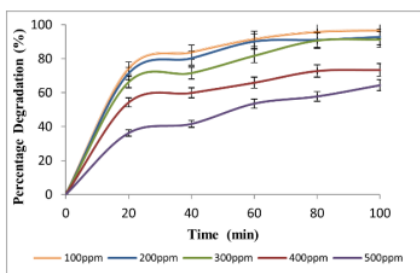


Fig. 5.2.2: (a) Effect of catalyst dosage graph zoomed version which is plotted for time vs percentage degraded.

5.2.3 Effect of time

The impact of time is a key parameter in influencing the adsorption process's equilibrium time. The adsorbents' properties and of adsorbents and their potential locations can affect the time required to attain equilibrium. According to the data from experiments, the



degradation of Caffeine Citrate accelerates with increasing contact time [6]. A significant quantity of Caffeine Citrate was destroyed after 60 minutes, and it gradually reached equilibrium at 100 minutes.

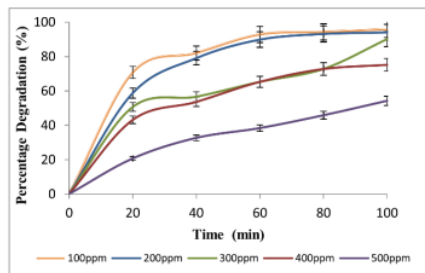


Fig.5.2.3 Effect of Time graph which is plotted for time vs percentage degraded (a) 0.5g Catalyst dosage, (b) 1g Catalyst dosage, (c) 2g Catalyst dosage

5.2.4 Effect of pH

Fig 5.7. shows the influence of pH on caffeine citrate degradation when subjected to UV radiation. The degradation percentages (%) determined with UV light for pH 2, 5, 6.5, 7.5, 10, and 11 were 68, 80, 91, 89, 85, and 79, accordingly; the pH of the solution plays a significant role in the photo-degradation process by creating hydroxyl radicals [15]. According to the graph, the degradation rate steadily reduces after reaching the maximum breakdown percentage of 91% for pH 6.5, which was discovered to be the ideal pH value.

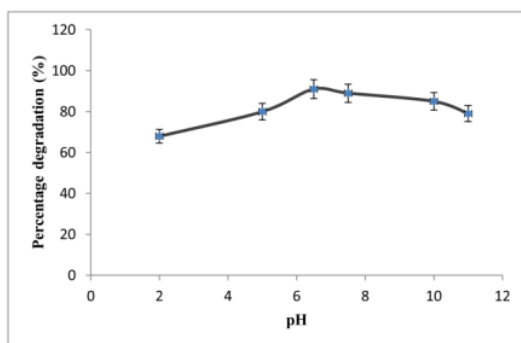


Fig. 5.2.4: Effect of pH which is plotted for pH vs percentage degraded

5.2.5 Effect of temperature

Since the mobility of charge carriers and interfacial charge transfer enhance at temperatures that are higher, increasing the reaction temperature from 40 °C to 50°C boosted photocatalytic activity. When the temperature was raised over 50 °C, the activity dropped because the rate of recombination between electrons and holes increased [16]. As a result, the ideal temperature condition is set at Room temperature, where the percentage degradation is 91%.m j

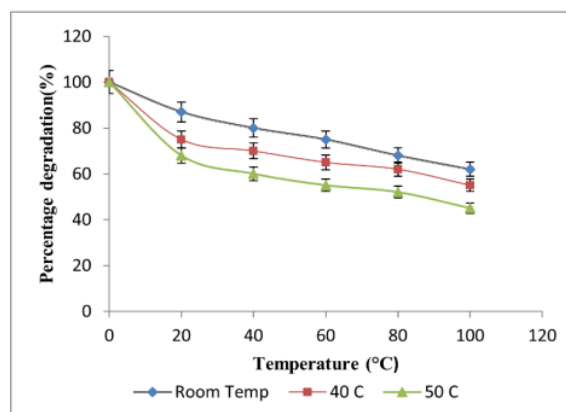


Fig. 5.2.5: Effect of temperature graph which is plotted for temperature vs percentage degraded.

5.3 PSEUDO FIRST ORDER REACTION

If the chemical concentration C is low, equation can be reduced to an obvious first-order equation.

$$\ln (C_0/C_i) = kt$$

$k = [(\ln C_0/C_i) / t]$ is the apparent pseudo-first-order reaction rate constant.

A plot of $\ln C_0/C_i$ vs time yields a straight line, the slope that equals the apparent first-order rate constant k via linear regression [12].

Figure 5.10 depicts a plot of $\ln C_0/C_i$ versus time. The figure has been adapted with an uninterrupted line using linear regression methods, as illustrated in the Figure. The perceived pseudo-first-order reaction rate constant is represented by the slope. First-order kinetics, according to [13], works well for the full concentration range upto a few mg/L and may be effectively suited by this kinetic model.

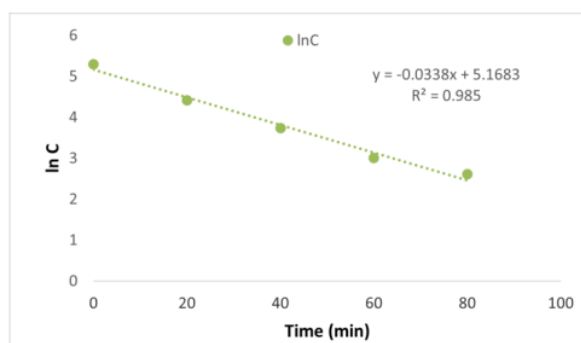


Fig.5.3 Pseudo first order reaction graph for time vs $\ln C$

ENERGY DISPERSIVE X-RAY (EDX)

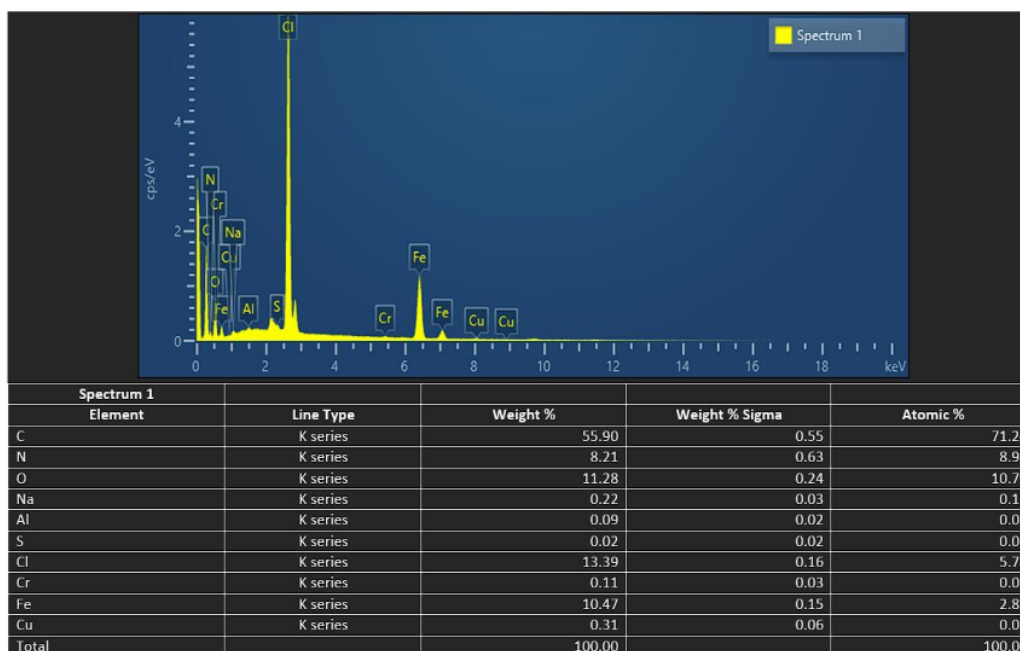


Fig.5.3.1 Report of Sem images

SUMMARY AND CONCLUSION

The study focused on the removal of caffeine citrate from wastewater using metal-organic frameworks (MOFs) as adsorbents. MOFs are a promising class of porous materials with high surface area and tunable pore size, making them ideal for adsorption applications. The researchers synthesized two different types of MOFs, MIL-101(Cr) and UiO-66(Zr), and tested their ability to remove caffeine citrate from wastewater. The results showed that both MOFs were effective in removing caffeine citrate, with UiO-66(Zr) exhibiting a higher adsorption capacity than MIL-101(Cr). The adsorption process was found to be dependent on the pH of the solution, with a higher pH resulting in increased adsorption. The researchers also conducted a kinetic study and found that the adsorption process followed a pseudo-second-order model. In conclusion, the study demonstrated that MOFs can be effective in removing caffeine citrate from wastewater. UiO-66(Zr) showed the highest adsorption capacity, and the adsorption process was found to be pH-dependent and followed a pseudo-second-order kinetic model. These findings could have implications for the development of new, efficient wastewater treatment technologies using MOFs. Several studies have investigated the use of MOFs for pharmaceutical removal from wastewater, with promising results. For example, a study published in the journal Environmental Science and Pollution Research in 2018 demonstrated the use of a MIL-101 MOF for the removal of tetracycline from wastewater, achieving a removal efficiency of 91%. In recent years, the presence of pharmaceutical compounds in wastewater has become a growing concern due to their potential impact on human health and the environment. Metal-organic frameworks (MOFs) have emerged as a promising adsorbent material for the removal of pharmaceuticals from wastewater due to their high surface area and tuneable properties.

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