

**SYNTHESIS OF IRON BASED METAL ORGANIC FRAMEWORK
ANCHORED ON THE SURFACE OF REDUCED GRAPHENE OXIDE
FOR THE DEGRADATION OF Cr⁶⁺**

Submitted in partial fulfilment of the requirement for the award of
Bachelor of Technology Degree in Chemical Engineering

by

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**DEPARTMENT OF CHEMICAL ENGINEERING
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**INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)**

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BONAFIDE CERTIFICATE

This is to certify that this project report is the bonafide work of Satish Kumar K (39190029) and Siddharth U (39190031) who carried out the project entitled "SYNTHESIS OF IRON BASED METAL ORGANIC FRAMEWORK ANCHORED ON THE SURFACE OF GRAPHENE OXIDE FOR THE DEGRADATION OF BIODIESEL Cr^{6+} " under my supervision from November 2022 to April 2023

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DECLARATION

We Satish Kumar K (39190029) and Siddharth U (39190031) hereby declare that the Project Report entitled **"SYNTHESIS OF IRON BASED METAL ORGANIC FRAMEWORK ANCHORED ON THE SURFACE OF GRAPHENE OXIDE FOR THE DEGRADATION OF BIODIESEL Cr⁶⁺"** done by me under the guidance of Dr. S. Sathish M.E, Ph.D., SATHYABAMA INSTITUTE OF SCIENCE AND TECHNOLOGY, CHENNAI at is submitted in partial fulfilment of the requirements for the award of Bachelor of Technology degree in Chemical Engineering.

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ABSTRACT

Due to the serious health risks Cr^{6+} poses to both humans and the natural world, hexavalent chromium Cr^{6+} is an extremely dangerous groundwater pollutant. Researcher's interest in Metal-Organic Frameworks (MOFs) for removing pollutants from waterways has increased recently. In the current study, a hybrid amino functionalized MOF@rGO nano catalyst was used to generate $\text{NH}_2\text{-MIL-53 (Fe)}$ which was tested for Cr^{6+} eliminating using an in situ grown nanocrystalline mixed ligand octahedral metal-organic framework with iron metal centers on the outermost layer of reduced graphene oxide (rGO). To describe XRD, MOF, FTIR, FESEM, BET, and EDS studies were used. In the context of a batch system, the impact of a few independent factors on Cr^{6+} removal capability was investigated.

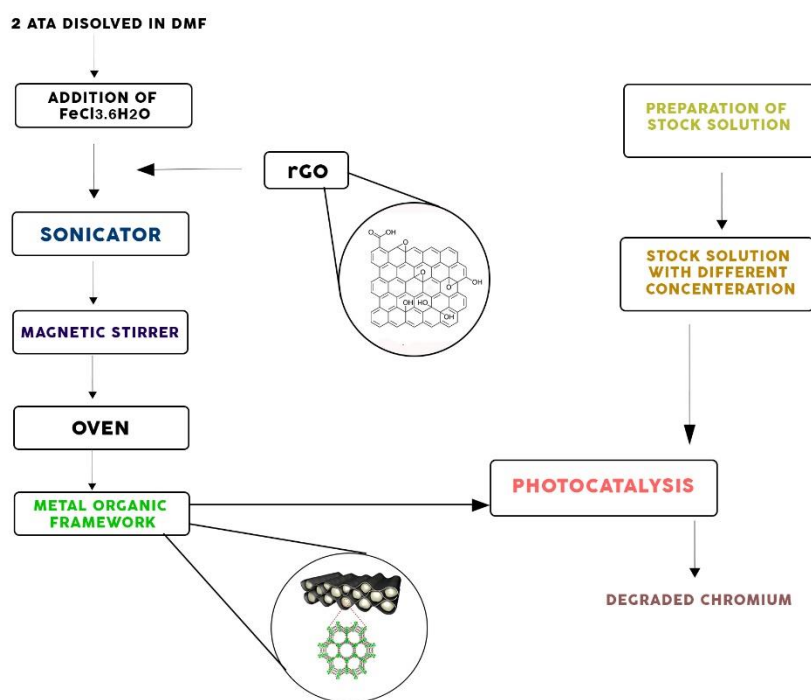


TABLE OF CONTENTS

CHAPTER NO	TITLE	PAGE NO
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	TABLE OF CONTENTS	vi
	LIST OF ABBREVIATIONS	ix
	LIST OF FIGURES	xi
	LIST OF TABLES	xiv
1	INTRODUCTION	1
	1.1 NECESSITY OF WATER	1
	1.2 EXPLANATION ABOUT CHROMIUM	5
	1.3 METAL ORGANIC FRAMEWORK NH ₂ -MIL-53(Fe)	7
	1.4 PHOTOCATALYSIS	11
2	LITERATURE SURVEY	16
	AIM AND SCOPE	18
	3.1 AIM	18
	3.2 SCOPE	18
4	MATERIALS AND METHODS	19
	4.1 REAGENTS	19
	4.2 SYNTHESIS OF NH ₂ -MIL-53(Fe)	19
	4.3 SYNTHESIS OF REDUCED GRAPHENE OXIDE (rGO)	20

	4.4 MODIFICATION OF NH ₂ -MIL-53(Fe) WITH rGO	20
	4.5 PHOTOCATALYTIC DEGRADATION CHROMIUM	21
5	RESULTS AND DISSCUSION	23
	5.1 STRUCTURAL CHARECTERISATION OF	
	NH ₂ -MIL-53(Fe) WITH rGO	23
	5.1.1 X-Ray Diffraction	23
	5.1.2 Field Emission Scanning Electron	
	Microscopy (FE SEM)	23
	5.1.3 Fourier Transform Infrared (FTIR)	24
	5.2 EFFECT OF VARIABLES ON THE DEGRADATION	
	OF CR ⁶⁺	25
	5.2.1 Effect of chromium concentration	25
	5.2.2 Effect of catalyst dosage	26
	5.2.3 Effect of time	27
	5.2.4 Effect of pH	27
	5.2.5 Effect of temperature	28
	5.3 KINETICS	28
	5.3.1 Langmuir Isotherm	29
	5.3.2 Pseudo first order reaction	30
	5.3.3 Arrhenius equation	31
	5.4 STASTICAL ANALYSIS WITH RESPONSE	
	SURFACE METHODOLOGY	32
	5.4.1 Analysis of variance (ANOVA)	34
	5.4.2 central composite design	35
	5.4.3 Interaction effects on operating parameters	

	on optimum conditions	39
	5.4.3.1 Inference from 3-D surface plot	40
	5.4.4 Prediction vs actual	40
	5.5 CHROMIUM DEGRADATION	41
6	SUMMARY AND CONCLUSION	42
	REFERENCES	43

LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
AAS	Atomic Adsorption Spectrometer
BDC	Benzene dicarboxylate
Cr	Chromium
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	Revolution per minute
UV	Ultraviolet
XRD	X-Ray Diffraction

LIST OF FIGURES

FIGURE NO	NAME	PAGE NO
4.1	a) Experimental image of Magnetic stirrer while synthesis of MOF NH ₂ -MIL-53(Fe). b) Experimental image of Sonicator while synthesis of MOF NH ₂ -MIL-53(Fe). c) Experimental image of Conical Flask shaker while synthesis of MOF NH ₂ -MIL-53(Fe).	19
4.2	a) Experimental image of Dropwise addition of alcohol in conical flask mixer while synthesis of MOF NH ₂ -MIL-53(Fe) rGO. b) Experimental image of Slurry pastes mixture of MOF while synthesis of MOF NH ₂ -MIL-53(Fe) rGO.	20
5.1	XRD analysis image of the MOF catalyst NH ₂ -MIL-53(Fe) rGO.	23
5.2	a) SEM analysis image of the MOF catalyst NH ₂ -MIL-53(Fe) rGO. b) SEM analysis image of the MOF catalyst NH ₂ -MIL-53(Fe) rGO.	23
5.3	FT-IR analysis image of the MOF catalyst NH ₂ -MIL-53(Fe) rGO.	24
5.4	Effect of chromium concentration graph which	

	is plotted for time vs percentage degraded.	25
5.5	a) Effect of catalyst dosage graph which is plotted for time vs percentage degraded.	26
5.6	a) Effect of Time graph which is plotted for time vs percentage degraded (0.5g Catalyst dosage). b) Effect of Time graph which is plotted for time vs percentage degraded (1g Catalyst dosage). c) Effect of Time graph which is plotted for time vs percentage degraded (2g Catalyst dosage).	26
5.7	Effect of pH which is plotted for pH vs percentage degraded.	27
5.8	Effect of temperature graph which is plotted for temperature vs percentage degraded.	28
5.9	Langmuir Isotherm Graph plotted for $1/C_e$ vs $1/Q_e$.	29
5.10	Pseudo first order reaction graph for time vs $\ln C$.	30
5.11	Arrhenius equation graph for $1/T$ vs $\ln K$.	30
5.12	RSM graph plotted for Dosage (C) vs Time (D).	36
5.13	RSM graph plotted for pH (A) vs Concentration (B).	36
5.14	RSM graph plotted for pH (A) vs Dosage (C).	37
5.15	RSM graph plotted for pH (A) vs Time (D).	38
5.16	RSM graph plotted for Concentration (B) vs Dosage (C).	38
5.17	RSM graph plotted for Concentration (B) vs Time (D).	39

5.18	RSM graph plotted for Actual vs predicted.	40
5.19	Graph of Chromium degradation plotted for Time vs Degradation concentration percentage.	40
5.20	Graph of Regeneration studies plotted for cycle vs regeneration percentage.	41

LIST OF TABLES

TABLE NO	NAME	PAGE NO
5.1	RSM generated response 1 : degradation.	32
5.2	RSM generated fit statistics.	34

CHAPTER-1 INTRODUCTION

1.1 NECESSITY OF WATER

Of all the valuable resources on Earth, water is necessary for human existence as well as the health of environments, economies, and civilizations. Only a tiny portion of the Earth's surface, or about 2.5%, is covered by freshwater which is suitable for consumption, farming, and other social values. Water is essential for the sustenance of all sentient creatures, so it has an essential role in sustaining life. It is a crucial part of all cells, tissues, and organs in all living things, including people, plants, and animals. It also plays a crucial role in many physiological mechanisms, including digestive process, circulation, and sewage disposal. The largest user of water globally, agriculture, also relies heavily on the water as a resource. Water is needed by crops for watering and pest management, as well as for their development and production. Therefore, access to dependable and sufficient water supplies is essential for both growth in the economy and food security.

Numerous other sectors of the economy, such as manufacturing, electricity generation, and transportation, also depend on water. It is necessary for the creation of numerous products and services and serves the function of refrigerant, solvent, and cleaning substances. Ecological environments depend on water to operate properly. Numerous animals and plants kinds exist in rivers, streams, and coastlines, which also offer habitat and supplies to numerous environments. Various environmental systems, including the nutrient cycle, photosynthesis, and the storing of carbon, involve water. Water resources are under increasing strain due to population growth, climate change, and pollution, despite their importance. Water scarcity is a problem in many parts of the globe, and it can cause problems on the social, economic, and environmental fronts. For the sustainability of human societies and natural ecosystems, water supplies must be managed and protected. A fundamental human value, access to water that is safe and clean is essential for eradicating destitution and enhancing public health. Many individuals lack a source of good drinkable water, which causes waterborne illnesses that can be fatal and cause sickness. According to the United Nations, more than 2 billion people lack access to clean drinking water, and because of growing populations, urbanization, and global warming, this figure is expected to rise.

Water is an essential element of the natural environment as well, sustaining ecosystems as well as biodiversity. It benefits plant development and offers natural habitats for fish, animals, and other living things. It also has an essential role in the water cycle, which moves water around the planet and sustains climate change, and it helps control the Earth's climate by absorbing and releasing heat. Pollution, climate change, excessive use, and unsustainable practices, on the other hand, are dangers to water supplies. Waterways can become contaminated by agricultural, industrial, and residential waste and sewage, and this may damage marine habitats. Floods, droughts, and other severe weather conditions are happening more frequently and with greater severity because of changing the climate. Water is a crucial component of nature as well, supporting ecosystems and the preservation of biodiversity. It promotes the growth of plants and provides animals, fish, and other living creatures with natural ecosystems. It also plays a crucial part in the water cycle, which transports water across the globe and supports environmental issues. By absorbing and releasing heat, it regulates the temperature of the Earth. On the opposite side, threats to water resources include pollution, climate change, inappropriate use, and unsustainably conducted business. Industrial, agricultural, and domestic refuse and effluent can pollute waterways, harming sea life. As a result of climate changes, droughts, floods, and other extreme weather events are occurring more frequently and with greater severity.

Water can be handled sustainably, and it can be conserved in several ways:

1. Minimize water waste: By repairing pipeline leakage, utilizing water-efficient fixtures and equipment, and averting excessive water use, we can conserve water.
2. Use water wisely: We can use water wisely by only using it when necessary, implementing water-saving techniques like xeriscaping and rainwater collection, and utilizing low-flow devices.
3. safeguard water sources: Regulate industrial and agricultural activity and encourage sustainable land use techniques to prevent pollution.
4. Support equitable access: We can encourage equitable access to water supplies by making sure that everyone has access to hygienic utilities and secure, inexpensive drinking water.

5. Invest in water infrastructure: To guarantee that there is enough water available to satisfy both present and future demands, we can make investments in freshwater resources, such as dams, water treatment facilities, and distribution systems.

6. Support study and innovation: We can encourage the development of new methods and technologies that will advance the efficient use and administration of water.

7. Raise awareness: Through support, outreach, and instruction, we can spread the word about the value of water and the necessity of environmentally friendly water-management techniques.

Water is an essential element that sustains nature, life, and economic growth. To guarantee that we have enough water for all of our requirements right now and in the future, water resource control is essential. We can guarantee a clean water future for everyone by conserving water, using it wisely, protecting water sources, supporting equitable access, putting funds into infrastructure, encouraging innovative thinking and research, and increasing awareness.

By repairing pipeline leakage, utilizing water-efficient fixtures and equipment, and averting excessive water use, we can conserve water. We can use water wisely by only using it when necessary, implementing water-saving techniques like xeriscaping and rainwater collection, and utilizing low-flow devices. Regulate industrial and agricultural activity and encourage sustainable land use techniques to prevent pollution. We can encourage equitable access to water supplies by making sure that everyone has access to hygienic utilities and secure, inexpensive drinking water. To guarantee that there is enough water available to satisfy both present and future demands, we can make investments in freshwater resources, such as dams, water treatment facilities, and distribution systems. We can encourage the development of new methods and technologies that will advance the efficient use and administration of water. Through support, outreach, and instruction, we can spread the word about the value of water and the necessity of environmentally friendly water-management techniques. Water is an essential element that sustains nature, life, and economic growth. To guarantee that we have enough water for all of our requirements right now and in the future, water resource control is essential. We can guarantee a clean water future for everyone by

conserving water, using it wisely, protecting water sources, supporting equitable access, putting funds into infrastructure, encouraging innovative thinking and research, and increasing awareness.

Droughts, floods, and storms are becoming more common and severe due to climate change, which has an impact on water availability as well as quality. By adopting water quality management strategies like water rainwater harvesting, conservation, and water recycling, we can tackle this issue and adjust to changing water conditions. Because of excessive use, groundwater levels are rapidly falling in many parts of the globe, endangering the long-term viability of water resources. Adopting laws and rules that support ongoing groundwater management practises, such as lowering pumping rates, increasing water use effectiveness, and applying groundwater recharge methods, is necessary to address this issue. Agriculture, urbanization, and industrial operations all have the potential to pollute freshwater resources and damage marine habitats. We need to embrace sustainable practices that reduce pollution, implement laws that prevent it, and support water purification technologies that can remove pollutants to solve this issue. Sustained water management requires effective water governance. To achieve this, rules and regulations that encourage fair and environmentally friendly water use must be put in place. Additionally, stakeholders must be brought into the judgement process, and organizations that can effectively manage water resources must be built.

In conclusion, efficient water management is a challenging task with many facets that call for cooperation between people, groups, governments, and organizations. We can move towards a water resource future that promotes human well-being, environmental health, and economic prosperity by tackling the specific issues associated with climate change, groundwater depletion, water pollution, and water governance. In conclusion, efficient water management is a challenging task with many facets that call for cooperation between people, groups, governments, and organizations. We can move towards a water resource future that promotes human well-being, environmental health, and economic prosperity by tackling the specific issues associated with climate change, groundwater depletion, water pollution, and water governance.

1.2 ABOUT Cr⁶⁺

Cr⁶⁺ is an extremely hazardous variety of metal that can have detrimental effects on both the health of humans and the environment. In addition to being used in commercial processes like leather tanning, electroplating, and textile production, it is a naturally occurring element that can be discovered in rocks, dirt, and volcanic dust. It can have a number of harmful consequences when it comes into contact with the skin, inhalation, or ingestion. Cr⁶⁺ exposure can cause several health problems, including lung cancer, skin rashes, dry eyes, liver, and kidney harm. Cr⁶⁺ exposure over a long period of time can also affect reproduction, resulting in decreased fertility and birth defects. Additionally, Cr⁶⁺ has been linked to reproductive issues, genetic mutations, and birth deformities. It is regarded as a carcinogen, which means it may result in cancer. The case of Hinkley, California, where people were subjected to tainted water for drinking and experienced a rising cancer rate, is the most well-known illustration of Cr⁶⁺ toxicity. It can harm the ecosystem and negatively affect human health. Cr⁶⁺ can build up in aquatic life after being released into sources of water, harming the environment. Additionally, crops that are contaminated by Cr⁶⁺ in the earth run the risk of contaminating human health when consumed.

Cr⁶⁺ utilization and removal are strictly controlled by several international governmental organizations due to its toxicity and potential risks to both people and the environment. The Environmental Protection Agency (EPA) in the US, for instance, has set the highest contaminant threshold for Cr⁶⁺ in drinkable water. To restrict the use and release of Cr⁶⁺ in manufacturing processes, many nations have also put laws and guidelines in place. It should be eliminated from drinking water that is contaminated as one method of reducing its effects. Cr⁶⁺ can be removed from water using a variety of techniques, such as chemical activation, ion exchange, reverse osmosis, and adsorption. The addition of materials that can bind or capture the Cr⁶⁺ ions from the water is required for adsorption, which is among the most efficient ways to remove Cr⁶⁺ from water. However, one substance that's been utilized extensively to remove Cr⁶⁺ from water is activated carbon. In the elimination of Cr⁶⁺ from water, other compounds like zeolites, clay minerals, and metal-organic frameworks (MOFs) have also demonstrated good results in terms. Given their substantial surface area, adjustable pore size, and unique properties, MOFs are

especially intriguing as adsorbent materials for Cr^{6+} elimination. It is possible to create MOFs with functional groups that can choose to absorb Cr^{6+} ions from water. Numerous works have shown the effectiveness of MOFs in removing Cr^{6+} from tainted water, and the current study is looking into developing new MOFs with improved adsorption capabilities. It has also been investigated for its possible use in several technological and industrial uses in addition to water purification. Cr^{6+} , for instance, may be utilized to make pottery, paints, and dyes, and as a corrosion inhibitor in metals. The usage and removal of Cr^{6+} in such applications, however, must take and into account any possible risks.

There is a continuing study to comprehend the processes of Cr^{6+} toxicity and create remedies for people who are exposed to it in response to clearance and minimization. Antioxidant therapy, for instance, has been suggested as a possible treatment for people who have been exposed to high levels of Cr^{6+} . The reactive oxygen species produced by the metabolism of Cr^{6+} can be neutralized by antioxidants to stop harm to cells and tissues. Additionally, studies are being conducted to determine the variables that affect the absorption and danger of Cr^{6+} . The oxidation state of chromium has been found as one contributing factor. There are various oxidation states in which chromium can occur, with Cr^{6+} proving to be the most hazardous. Recent studies have however demonstrated that specific microbes can convert Cr^{6+} to less harmful forms like chromium $^{3+}$. The clean-up of Cr^{6+} contamination in the environment may be affected by this finding. Cr^{6+} is used in manufacturing applications, so efforts to limit this use have resulted in the creation of substitute technologies and materials. For instance, a few industries have shifted to chromium $^{3+}$ or other less toxic forms of metal. Non-toxic coverings, like those based on zinc or titanium, have taken the position of chromium-based coverings in other industries.

Furthermore, efforts are being made to create environmentally friendly processes for the manufacturing and disposal of chromium-based products. For instance, scientists are looking into how to produce chromium-based materials using sources of clean energy like sun and wind energy. For the disposal of waste containing chromium, they are also investigating the use of bioremediation and other ecologically friendly techniques. Hexavalent chromium also referred to as Cr^{6+} , is a particularly dangerous variety of the chemical chromium. It is a chemical substance

that is frequently utilized in a variety of industrial procedures, such as welding, electroplating, and the production of stainless steel, dyes, and paints. Burning fossil fuels and making cement are two industrial operations that produce Cr^{6+} as a residue.

There are actions that people can take to lower their vulnerability to Cr^{6+} in addition to regulatory modifications. People can, for instance, use a water filtration system that is intended to get rid of Cr^{6+} from their drinking water. Workers in Cr^{6+} using workplaces should also take the necessary security steps, such as donning protective clothing and equipment and adhering to safe handling protocols. Whereas the Cr^{6+} is a recognized toxin, it is essential to remember that there are other dangerous chemicals to which individuals could be subjected daily. Other chemicals and contaminants can also have hazardous impacts on health, so it's critical to take precautions to limit exposure to all potentially dangerous substances. In conclusion, the extremely harmful version of the metal chromium known as Cr^{6+} can have detrimental effects on both human health and the environment. Continuous study is necessary to create efficient reduction, removal, and treatment plans. Additionally, there must be attempts to reduce the use of Cr^{6+} in industrial processes and to create eco-friendly and safer substitute materials and techniques. Working together, scientists, business executives, and governmental organizations can lessen the harmful impacts of Cr^{6+} on the health of people and the environment.

1.3 METAL ORGANIC FRAMEWORK-NH₂-MIL-53(Fe)

Given its distinct characteristics and possible uses, NH₂-MIL-53 (or simply MIL-53-NH₂) is a kind of Metal-Organic Framework (MOF) being extensively researched. A family of substances known as MOFs is composed of metal ions that are linked together by organic ligands to generate porous 3-D structures. An organic ligand with amine (-NH₂) groups surrounds a central metal ion, usually molybdenum (Mo), in NH₂-MIL-53. The mixture of metal and organic elements creates a material that is very porous and has a sizable interior surface area, making it a desirable choice for a variety of uses such as separation, catalysis, and gas storage. The capacity of NH₂-MIL-53 to alter structurally in response to variations in temperature, pressure, or the presence of certain molecules that are guests is one of its most distinguishing

characteristics. The pore's sizes alter as a result of this metamorphosis, which may be utilized to precisely adsorb and release particular vapors or chemicals.

For its possible use in processes including carbon dioxide(CO₂) collection, storing hydrogen, medicine delivery, and catalysis, NH₂-MIL-53 has undergone substantial research. It is a viable contender for a variety of industrial and ecological applications due to its distinctive qualities and tunability. Because of its great thermal stability, it may be used in applications that require high temperatures. It can also endure being subjected to a wide range of chemicals without degrading thanks to its strong chemical stability. Generating an exceptionally high level of crystallinity is one of the key difficulties in the synthesis of NH₂-MIL-53, which is a form of Metal-Organic Framework (MOF) which is extensively researched due to its distinctive features and prospective uses. A family of substances known as MOFs is composed of metal ions that are linked together by organic ligands to create porous structures in three dimensions.

An organic ligand with amine (-NH₂) groups surrounds a central metal ion, usually molybdenum (Mo), in NH₂-MIL-53. This mixture of metal and organic elements creates a material that is very permeable and has a sizable interior area on its surface, making it a desirable choice for a variety of uses such as catalysis, separation, and gas storage. The capacity of NH₂-MIL-53 to alter structurally in accordance with variations in pressure, temperature, or the existence of certain outside molecules is one of its most distinguishing characteristics. The pores' sizes alter as a result of this metamorphosis, which may be utilized to preferentially adsorb and release particular gases or chemicals. It has also been thoroughly researched for its prospective uses in fields including hydrogen storage, catalysis, medicinal delivery, and carbon dioxide capture. It is a viable contender for a variety of industrial use and ecological applications due to its distinctive qualities and tunability. necessary for it to operate at its best. To increase the creation and structural durability of NH₂-MIL-53, researchers have created a number of techniques, including the use of alternative solvents and optimization of the conditions of the reaction. Due to its intriguing characteristics and behaviour, NH₂-MIL-53 is a topic of basic research in besides its possible uses. In order to gain insight into how MOFs may be created and manipulated for particular uses, experts are investigating the fundamental processes of the physical alteration of NH₂-MIL-53 and also how it

communicates with guest molecules. The process of synthesis and accessibility of NH₂-MIL-53 is one of the difficulties in applying it in real-world applications. It can be challenging to scale up to industrial quantities and often necessitates strong reaction conditions for the creation of NH₂-MIL-53. To increase the synthesis and scalability of NH₂-MIL-53, researchers have created a number of techniques, including the use of continuous flow reactors, post-synthetic modifications, and microwave-assisted synthesis.

The long-term viability of NH₂-MIL-53 in various settings presents another difficulty when employing it. Pressure, temperature, and humidity fluctuations can cause structural changes in the material, which can have an impact on how well it performs. However, scientists are striving to comprehend the underlying mechanisms causing these modifications to the structure and to create methods for enhancing NH₂-MIL-53's resilience. NH₂-MIL-53 is still an extremely promising substance with potential uses in a variety of industries despite these difficulties. It is an adaptable material that can be customized for different purposes thanks to its distinctive qualities and tunability. It has also been researched for its possible use in the conversion of energy and storage.

The metal-organic framework (MOF) known as NH₂-MIL-53 (Fe) is composed of iron (Fe) ions connected by biological molecules to form a 3-D porous structure. The "NH₂" in the name alludes to the amino (-NH₂) groups with a function that are present on the molecules of the organic linker. It is also renowned for its structural adaptability and thermal endurance, which make it appropriate for uses like storing gases and extraction that include pressure and temperature variations. The property of NH₂-MIL-53 (Fe) to undergo cyclic structural changes in response to environmental factors as temperature, gas adsorption, and pressure is intriguing. These variations in the porous structure's size and shape can have an impact on the material's characteristics and possible uses.

Application areas for NH₂-MIL-53 (Fe) have included gas storage and split, catalysis, and medication delivery. For instance, it has been demonstrated that NH₂-MIL-53 (Fe) has a high degree of selectivity for the adsorption of carbon dioxide (CO₂), making it a potent substance for the storage and capture of carbon. Additionally, NH₂-MIL-53 (Fe) has been employed as a form of catalyst for a number

of chemical processes, including the production of biofuels from biomass. It is a beneficial substance for gas adsorption and extraction applications because it has comparatively wide pores of roughly 1.4 nm and a high area of coverage. The organic linker molecules' amino functional groups may also make it possible for specific gas molecules to be selectively adsorbed. The capability of NH₂-MIL-53 (Fe) to experience post-synthetic modifications (PSMs), which entail adding fresh chemical functions or changing the ones that already present inside the MOF framework, is additional intriguing characteristic of this material. This enables the material's characteristics and prospective uses to be adjusted. To increase the choice and capability of NH₂-MIL-53 (Fe) for adsorption of gases and separation, for instance, PSMs have been utilized. Researchers are also looking into the use of computer simulations and modeling to enhance the abilities of NH₂-MIL-53 (Fe). These methods provide a more thorough knowledge of the molecular activity and properties of the material, which can guide the development of novel MOFs with enhanced characteristics and prospective uses. Assessing the possible use of MOFs for environmentally friendly uses including water treatment and pollution removal is also gaining popularity. MOFs are a potential material for environmental remediation since they have been found to be excellent at adsorbing a variety of contaminants, including contaminants such as heavy metals, organic chemicals, and dyes.

It is only one of several MOFs that were created and investigated for their special characteristics and possible uses. It is conceivable that additional MOFs with greater advanced characteristics and potential uses will be developed as study in this area expands. Other MOFs, in addition to NH₂-MIL-53 (Fe), have also demonstrated positive outcomes and possible uses in a variety of industries. For instance, MOFs with various metal ions, organic linkers, and pore diameters have been created and their special traits and prospective uses have been investigated. Examples include MOF-177, UiO-66, and ZIF-8, all of which have been studied for their potential in the areas of medication delivery, gas storage and separation, and catalysis. The area of energy storage has recently attracted a lot of interest as a possible use for MOFs. The usage of MOFs as materials for electrodes in supercapacitors and battery packs has been researched. MOFs provide a number of benefits over conventional electrode materials, including increased power density, energy

density, and cycle stability, because of their large surface area, porosity, and customizable characteristics. The ability to scale up and cost-effectiveness of MOF synthesis, their stability under various circumstances, and their possible toxicology and bio compatibility for biomedical uses are only a few of the issues that need to be resolved despite the promise that they hold.

1.4 PHOTOCATALYSIS

A method for catalysing chemical processes is called photocatalysis. A photocatalyst, a substance that absorbs light energy and uses it to initiate a chemical reaction, is used in this process. Metal oxides that can absorb light in the ultraviolet (UV) region, such as titanium dioxide (TiO_2), are the most frequently used photocatalysts. The photocatalyst is subjected to light during a photocatalytic reaction, which activates the material's electrons. As a result, electron-hole pairs are produced, allowing them to interact with the other molecules in the surroundings. The electron-hole couples can create reactive forms of oxygen or other reactive compounds when they interact with specific molecules, such as oxygen or water. These reactive compounds can then interact with organic or inorganic molecules. Manufacturers, most notably pollution clean-up, use photocatalysis. For instance, photocatalysis can be used to purge the air and water of organic pollutants like dyes, pesticides, and medicines. Additionally, it can be applied to clean surfaces and destroy bacteria in the effluent. Photocatalysis has applicability not only in the environment but in a variety of industries. It can be employed to produce energy, for instance, by turning sunlight into power or by producing hydrogen from water.

Although photocatalysis has a lot of possible advantages, there are drawbacks to the method as well. The performance of a reaction, for instance, can be influenced by a variety of elements, including the dimension and form of the photocatalyst particles, the makeup of the natural atmosphere, the intensity and duration of the illumination, and the specific light wavelengths needed to initiate the reaction. The possibility for the formation of by-products or intermediates that could also be detrimental to the surroundings or people's health seems to be another issue with photocatalysis. For instance, the photocatalytic breakdown of some natural contaminants can produce toxic by-products, which need to be closely monitored and managed to reduce their effects. Regardless these difficulties, photocatalysis is

an efficient strategy that shows promise for addressing a range of ecological issues. Photocatalysis is a system that can purify water and is also environmentally friendly because it only uses light and no extra chemicals or power sources. Significant growth has been shown in the creation of new photocatalytic materials and processes in recent years, including the use of novel catalysts like graphene and novel light sources like LEDs. Additionally, investigators investigate how to incorporate photocatalysis into already-in-use technologies like water purification facilities and air ventilation systems. The capacity to function under slight reactions, the relatively inexpensive, and the possibility for use in a variety of applications are some of the main benefits of photocatalysis. Furthermore, photocatalysis is an ecologically sound and financially viable technology that doesn't generate waste or toxic by-products, making it a potential replacement for conventional chemical treatment techniques.

The creation of novel catalysts that are more successful and productive than existing materials is the field of photocatalysis research that is currently in progress. For instance, investigators are looking into the use of novel substances like perovskites and metal-organic frameworks (MOFs), which have demonstrated promising outcomes in laboratory experiments. For instance, scientists are looking into how to modify photocatalytic materials and reaction circumstances to eliminate pollutants from water or air. The creation of self-cleaning areas is a further possible use for photocatalysis. To produce a self-cleaning action, photocatalytic coverings may be added to areas like buildings or textiles because they can aid in the degradation and elimination of contaminants or organic matter that collects on the exterior. In the food industry, where it's feasible to employ it for conservation and protection, and sanitation, photocatalysis may also find use. To stop the development of dangerous bacteria and increase the longevity of food items, for instance, photocatalytic coverings could be applied to the materials used in packaged foods. In conclusion, photocatalysis is a viable technology with a broad spectrum of potential uses in sectors like energy generation and environmental clean-up. Studies is currently being done to increase the effectiveness and productivity of photocatalytic reactions, create novel catalysts, and investigate new uses for this technology. Photocatalysis has the possibility of growing into a potent tool for addressing some of the most

alarming environmental and energy-related problems of our time with ongoing growth and improvement.

Due to their clearly defined and adaptable porous architectures, substantial surface areas, and other characteristics, metal-organic frameworks (MOFs), which exhibit semiconductor-like behavior, have lately attracted widespread fascination with photocatalysis and photothermal catalysis. These benefits serve to overcome the above mentioned difficulties and, in particular, make it easier to determine the structure-activity link. They are useful for logical structural manipulation for enhanced luminescence and separation of charges as well as other impacts. To speed up future progress, it is crucial to summarise this field of study and offer in-depth explanations of MOF-based photocatalysis and photothermal catalysis. MOFs offer several benefits over conventional metal oxide semiconductors, including large specific areas of the surface, rich topology, and readily modifiable porous structure. Metal-organic frameworks (MOFs) are a subclass of permeable crystalline materials made up of organic linkers and metallic vertices (such as metal ions). Fe-MOFs are much more desirable than MOFs with large band gaps. Light may directly excite the large Fe-O clusters, improving the efficiency with which energy is used. Fe-MOFs have reportedly been shown to break down a variety of organic contaminants when exposed to visible light. To speed up the deterioration process, H_2O_2 was often added in most cases as an electron acceptor. Additionally, utilizing $(\text{NH}_4)_2\text{C}_2\text{O}_4$ as the H^+ scavenger, photocatalytic suppression of $\text{Cr}^{(6+)}$ may also be accomplished on MIL-53(Fe). Environmental degradation and the crisis in fossil fuels are now two of the main issues preventing human existence and advancement. When evaluating structure-property connections, the crystal structures of MOFs may easily be used to highlight their highly sequential and crystalline character. Though weak coordination connections, as opposed to the more robust covalent bonds that are seen in typical adsorbent compounds, may result in the breakdown of structure when guest molecules are included in the framework and then removed. Exposure to heat and guest removal cause the MOF structure to change, which may indicate that the material lacks full crystallinity. Numerous MOFs with consistency up to 300 or 400°C have been created, making them appropriate for the majority of applications. This is because a stiff, highly thermostable framework is thought to be of functional benefit. Because of their unique and diverse structural traits, MOFs

can be regarded as being appropriate for innovative practical applications. The mixed-metal/linker technique has been created to create more effective MOFs with desirable features by employing multiple metals in a single (mixed-metal), respectively, due to the adaptability and flexibility of MOFs. A MOF structure may often be modified post-synthesis or solvothermally to include more metal ions or linkers. Regarding MOFs with diverse metals, partial replacement of metal cores may be able to control both their effectiveness as photocatalysts and how effective they are at charging separation. Photoactive visitor species can be integrated into the spaces between molecules or partially stabilised on the exterior of MOFs due to their porous properties. A attractive guest item are metal nanoparticles (MNPs), particularly tiny superior MNPs with varied structures and tailoring potential. Carbon compounds with excellent electrical conductivity were frequently utilized to create hybrid photocatalysts in conventional semiconductor photocatalytic systems. After the introduction of carbon compounds, photogenerated charges may rejoin less frequently. For instance, reduced graphene oxide (rGO), graphene oxide (GO), and carbon quantum dots (CQDs) were typical carbon compounds that might speed up the exchange of photogenerated charges. Similarly to this, combining carbon-based substances with MOFs can improve photocatalytic efficiency by addressing the drawbacks of quick charging recombination in pure MOFs. The release of commercial waste including heavy metal pollutants, which have a significant impact on ecological constituents and their life cycle, has had a negative impact on the health of humans, the environment, and aquatic life. One significant and necessary heavy metal that is employed in the agricultural, industrial, medical, medicinal products, and mining sectors but has a negative interaction and outflow source with water is chromium. The two main oxidised forms of chromium found in the release of wastewater are $\text{Cr}^{(3+)}$ and $\text{Cr}^{(6+)}$, both of which are hazardous elements that can cause cancer in both people and aquatic life. The extremely durable and water-soluble form of $\text{Cr}^{(6+)}$ builds up over time in human and primary algal tissues, straining unavoidable metabolic processes past their allowable limits. Therefore, it is crucial to treat $\text{Cr}^{(6+)}$ from industrial release, and adequate treatment procedures must be established to lower or eliminate these harmful substance's levels in industrial discharges before they are combined with water bodies. The major reason MOFs, a unique class of organic-inorganic hybrid supramolecular structures, may act as photocatalysts is that they combine photosensitizer and catalytic capability in

a single structure. Thus, one solid chemical can assist all three phases of photocatalysis. Photoactive MOFs can operate as more effective photocatalysts by reducing pollution and can quickly be reclaimed and regenerated owing to their solid shape, thereby providing financial benefits, by substituting the conventional photocatalyst, which often comprises heavy metals. The advancements of MOFs in the photo-degradation of organic contaminants in splitting water, wastewater, and photo-reduction of CO₂ are covered in a number of great research. Four core processes are involved in MOF-based photocatalysis, along with other specific properties that are essentially associated with the structure of their crystals. Photoexcitation, charge separation, surface reaction, transfer, transport processes, and charge carrier recombination are these basic operational activities as they pertain to MOF-based photocatalysis. The goal of the current study was to create a very porous MOF that was amino-functionalized. Additionally, it focuses on altering such nanomaterials to enhance their capacity for separating from complicated mixtures. To do this, solvothermal or post-synthetic methods were used to decorate the MOF with carbon material (rGO) to create NH₂-MIL-53(Fe)@rGO. To confirm the nano-sized and mesoporous qualities, the produced catalyst was also characterised for its structural, textural, and functional characteristics. The systematic studies on the elimination of Cr(6⁺) ions.

CHAPTER-2 LITERATURE SURVEY

- A study by **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 TiO_2 has a very high photodegradation rate, according to research. TiO_2 delicate film was created using the sol-gel technique. Only 46.5% of $\text{Cr}^{(6+)}$ was eliminated at the exact same time. At a concentration of 50 ppm, $\text{Cr}^{(6+)}$ 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 TiO_2 . TiO_2 eliminates 80% of the $\text{Cr}^{(6+)}$, but ZnO removes just 45%, making ZnO a less efficient photocatalyst than TiO_2 .
- **Jang et al. (2020)** recorded NH_2 -ASNs, and NH_2 -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 NH_2 -functionalization on the efficiency of adsorption of $\text{Cr}^{(6+)}$. NH_2 -ASNs and NH_2 -MSNs were shown to have maximal $\text{Cr}^{(6+)}$ 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 $\text{Cr}^{(6+)}$ ions from aqueous solutions. With maximal reduction efficiencies of 49.14 and 45.24 mg for MO and $\text{Cr}^{(6+)}$ ions, respectively, the adsorption mechanism of the RGOeHat hybrids for MO and removal of $\text{Cr}^{(6+)}$ follows PSO kinetic and Langmuir isotherm frameworks.
- **Abhilash et al (2018)** said When the photodegradation rate of $\text{Cr}^{(6+)}$ 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 $\text{Cr}^{(6+)}$ 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 $\text{Cr}^{(6+)}$ solution pH.

CHAPTER-3 AIM AND SCOPE

3.1 AIM

The main goal of our project titled “SYNTHESIS AND CHARECTERISATION OF IRON BASED METAL ORGANIC FRAMEWORK AND DEGRADATION OF Cr⁶⁺” is to degrade Cr⁶⁺.

- Synthesis of Metal Organic Framework
- Characterization of Metal Organic Framework
- Degradation studies
- Regeneration studies

3.2 SCOPE

To create an optimum Chromium degradation method for a better environment, choosing an inappropriate method might result in more toxicity. So, Photocatalysis turns to be a better option for Chromium degradation.

Degradation of Chromium from water sources can be reduced.

- Several life-threatening diseases for Humans.
- Harmful to Other creatures and environment.
- Bad quality of water into good and clean water.
- Effects in plants metabolic activities.
- Hampering plant growth and yield.

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.

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°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].



Fig. 4.1: Experimental image of a) Magnetic stirrer while synthesis of MOF $\text{NH}_2\text{-MIL-53(Fe)}$ b) Sonicator while synthesis of MOF $\text{NH}_2\text{-MIL-53(Fe)}$, c) Conical Flask shaker while synthesis of MOF $\text{NH}_2\text{-MIL-53(Fe)}$.

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 muffles 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.

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 NH₂- MIL-53(Fe)/rGO was obtained. These materials are used for photocatalysis removal of Cr(6⁺).



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

4.5 PHOTOCATALYTIC DEGRADATION OF CHROMIUM

A 1000 ppm solution of Cr (⁶⁺) ions was made using Equation (1) as a guide. With 200 rpm of stirring, 2.8574 ± 0.005 g of 99% pure potassium dichromate (K₂Cr₂O₇) salt was mixed in 1000 ml of deionized water. The stock solution was diluted to create the necessary starting concentration of Cr (⁶⁺) ion solutions, which were then examined using an atomic adsorption spectrometer (AAS, SL176, Elico, India).

$$2.8574g \text{ of chromium salt / g of Cr(VI) ions} = \frac{\text{Molar mass of K}_2\text{Cr}_2\text{O}_7}{\text{Atomic weight of Cr} \times 2 \times (\% \text{ Purity of K}_2\text{Cr}_2\text{O}_7)} \quad (1)$$

The chromate stock solution containing 1 L was used for all batch investigations. A chromate solution's absorbance was calculated. At λ_{max} = 540 nm, the calibration curve for Cr(⁶⁺) was discovered. For photocatalytic degradation, the photocatalysts' homogeneous particle sizes ranged from 120 to 500.

To determine the highest % removal under ideal working circumstances, a single-stage steady-state batch experiment was carried out for the elimination of Cr (⁶⁺) from its aquatic mixture. The impact of pH and the catalyst dosage on Cr (⁶⁺) elimination process was examined using 0.5 to 2 g of catalyst in every 250 ml conical flasks which include 100 ml of Cr(⁶⁺) solutions ranging from 100 mg/L to 500 mg/L and including either 0.1 M of HCl which breaks down H⁺ ions converting the resulting solution into acidic or 0.1 M of NaOH which breaks down OH⁻ ions causing it to turn into basic to alter the resultant solution's pH values that vary from 2 to 12 under UV light. By changing the starting Cr(⁶⁺) concentrations at each comparable period of time from 5 to 100 min, the relationship between duration and the initial Cr(⁶⁺) concentrations was examined. During reaching an equilibrium time of 60 min, these flasks were continually stirred by a magnetic stirrer at a rate of 500 rpm. By retaining it on the outside of each flask, the catalyst fragments were segregated from the remaining solutions. After Cr(⁶⁺) adsorption, the final concentrations were examined.

$$\% \text{ Cr}(6+) \text{ removal} = \left(1 - \frac{C_{t=\infty}}{C_{t=0}}\right) \times 100 \quad (2)$$

where C_{t=0}, and C_{t=∞} is the concentrations of Cr (⁶⁺) (mg/L) at initial time and at time t.

Analysis of the metal reduction from aqueous solution during an uninterrupted interval served as the basis for the kinetics investigation. By modifying the pH of the chromium hexavalent mixture with the incorporation of the necessary volume of

NaOH and HCl in the different flask at pH 2-11, a specifically calculated quantity of NH_2 - MIL-53(Fe)/rGO was taken in 100 ml solution in every trial. The flask was then placed under a UV lamp while being constantly stirred by a magnetic stirrer.

CHAPTER-5 RESULTS AND DISCUSSION

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

5.1.1 X-Ray Diffraction (XRD)

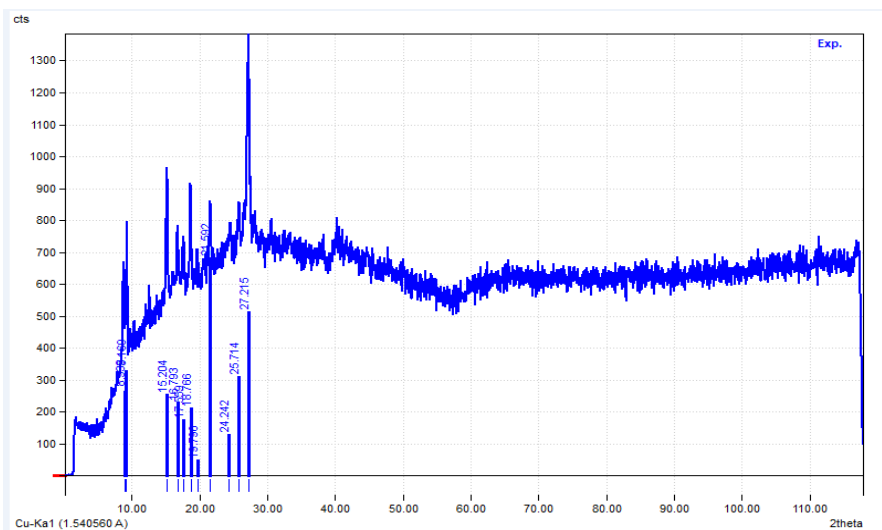


Fig. 5.1: XRD analysis image of the MOF catalyst NH₂-MIL-53(Fe) rGO.

The characteristic points of pure NH₂-MIL-53(Fe) in the XRD spectra at $2\theta = 8.6^\circ$, 10.4° , 15° , 17.5° , 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)

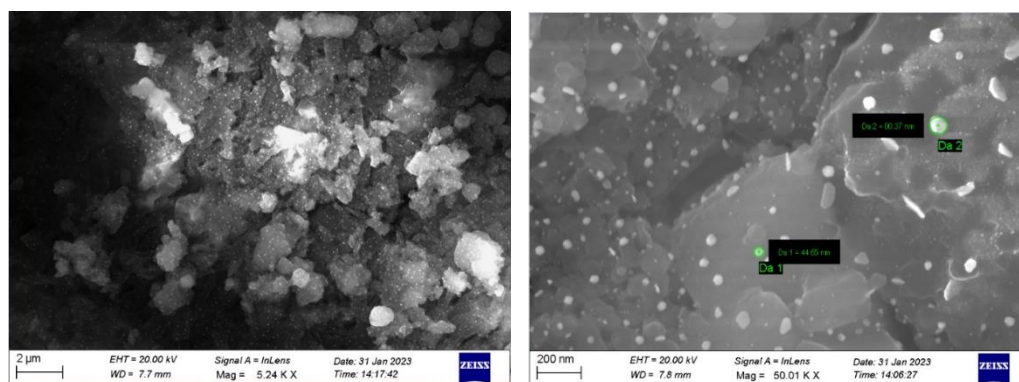


Fig. 5.2: (a)(b) SEM analysis image of the MOF catalyst NH₂-MIL-53(Fe) rGO

Two elements are readily visible on the outermost layer of the a 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)

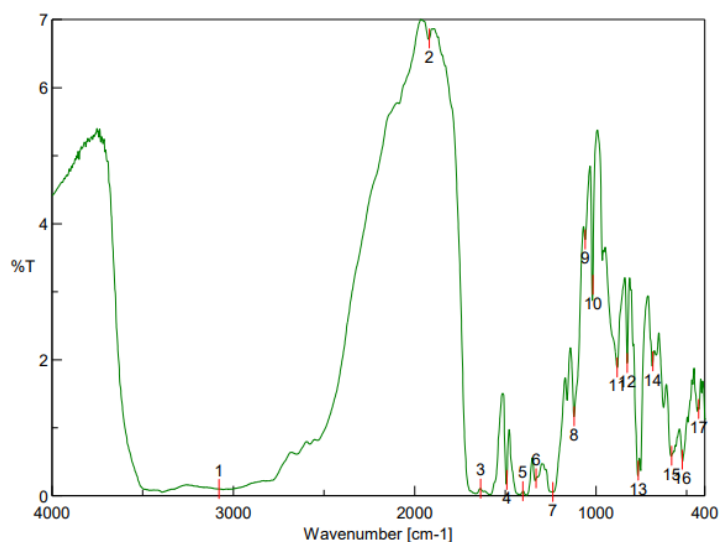


Fig. 5.3: FT-IR analysis image of the MOF catalyst $\text{NH}_2\text{-MIL-53(Fe)}$ rGO

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).

5.2 EFFECT OF VARIABLES ON THE DEGRADATION OF Cr^{6+}

5.2.1 Effect of chromium concentration

To look at how its starting concentration affects degradation. For this study, chromium concentrations ranging from 100 ppm to 500 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 100ppm to 500ppm of chromium, Fig. 5.4 shows the fluctuation in the quantity of chromium degrading with contact time. This concentration's catalyst dose is 0.5g. For various catalyst dosages, the similar pattern was discovered[2, 4].

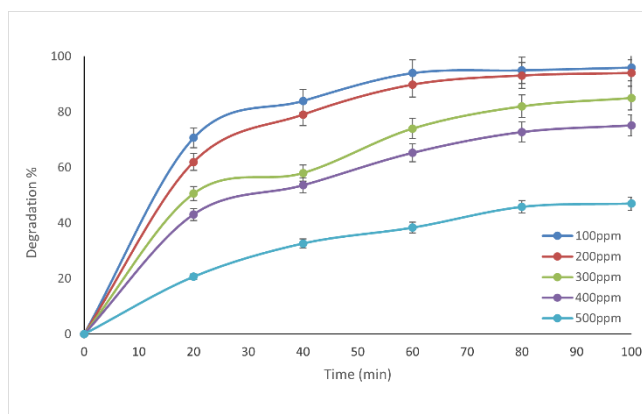


Fig. 5.4: Effect of chromium concentration graph which is plotted for time vs percentage degraded.

5.2.2 Effect of catalyst dosage

The degradation of chromium 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 chromium's 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 for the degradation of Cr^{6+} [5-7].

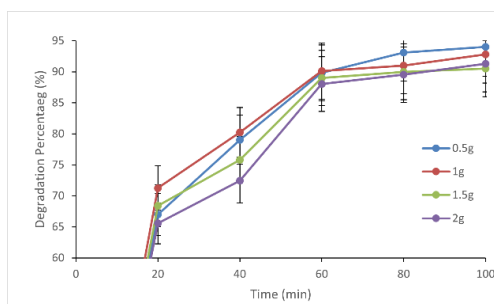


Fig. 5.5: (a) Effect of catalyst dosage graph zoomed version which is plotted for time vs percentage degraded.

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

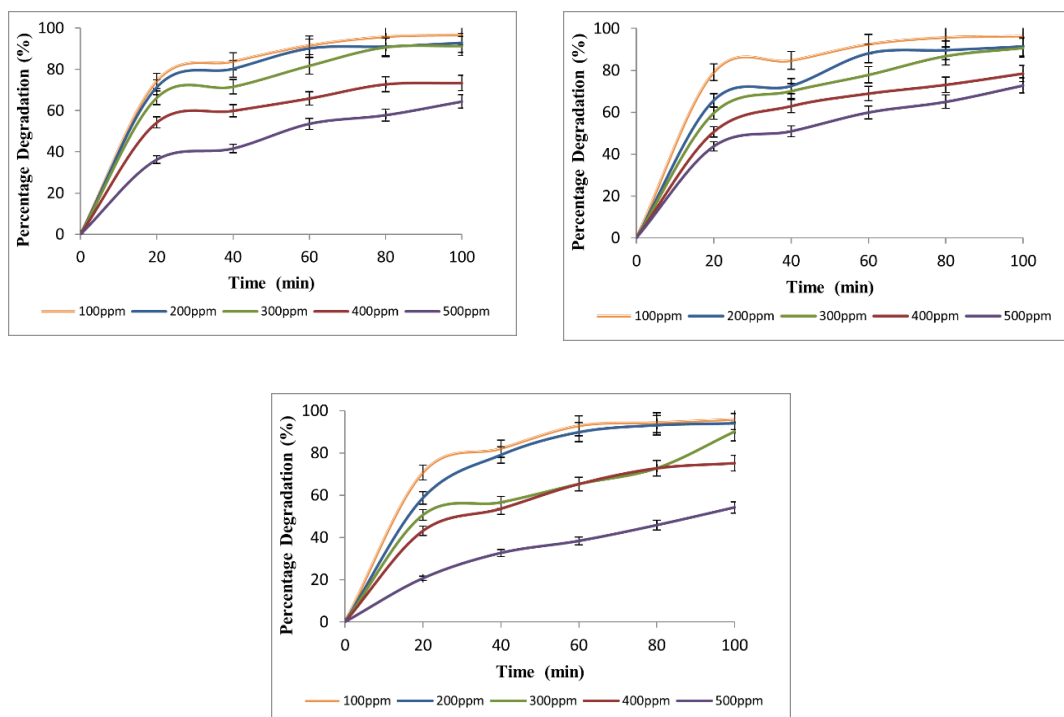


Fig. 5.6: Effect of Time graph which is plotted for time vs percentage degraded (a) 0.5g Catalyst dosage, (b) 1g Catalyst dosage, (c) 2g Catalyst dosage.

5.2.4 Effect of pH

Fig 5.7. shows the influence of pH on chromium degradation when subjected to UV radiation. The chromium 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.

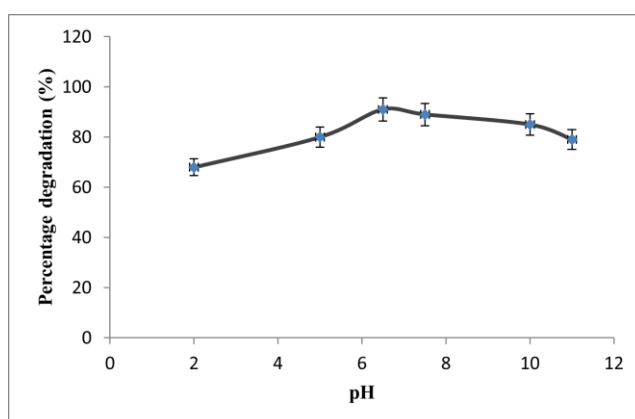


Fig. 5.7: Effect of pH which is plotted for pH vs percentage degraded

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

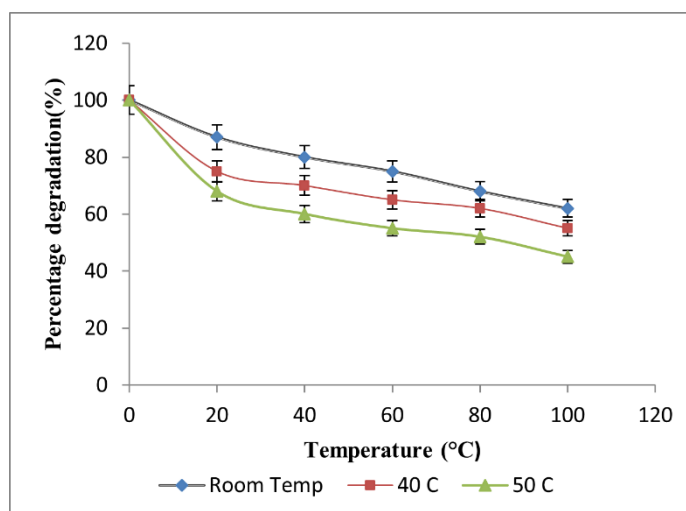


Fig. 5.8: Effect of temperature graph which is plotted for temperature vs percentage degraded.

5.3 KINETICS

Kinetic models that include the pseudo-first-order, Arrhenius equation, and Langmuir isotherm model were used to analyse the process of adsorption.

5.3.1 Langmuir isotherm

Several investigators have used the Langmuir isotherm to model photocatalysis. This model incorporates the observed adsorption characteristics of the base on the photocatalyst surface [9, 10]. According to Langmuir's theory, an adsorption is a form of unimolecular chemical mixture or reaction. A linear plot of C_e/q_e versus C_e must be linear to correspond to the Langmuir isotherm [11, 9]. q_e is the initial chromium concentration (mg/l), and C_e is the equilibrium chromium concentration (mg/l). The Langmuir plots for photocatalysis data are shown in the figure.

The rate of reaction can be expressed as:

$$r = (dC/dt) = (kKC / 1+KC) \quad (3)$$

r is the rate of the reactant (mg/L min), C is the concentration of the reactant (mg/L), t the illumination time, k the reaction rate constant (mg/L min), and K is the adsorption coefficient of the reactant (L/mg).

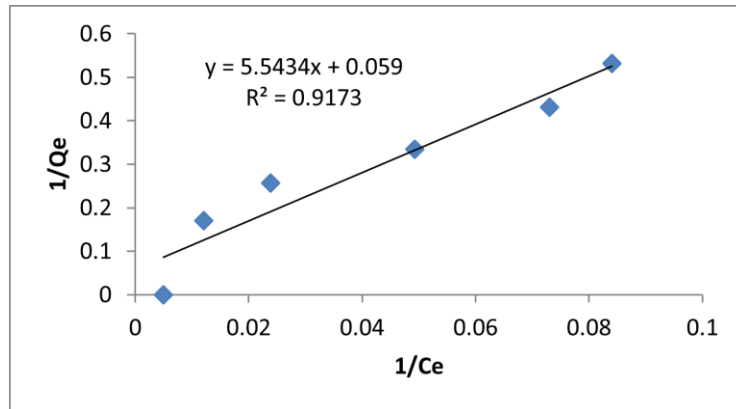


Fig. 5.9: Langmuir Isotherm Graph plotted for $1/C_e$ vs $1/Q_e$

5.3.2 Pseudo first order reaction

If the chemical concentration C is low, equation (3) can be reduced to an obvious first-order equation.

$$\ln (C_o/C_i) = kt \quad (4)$$

$k = [(C_o/C_i) / t]$ is the apparent pseudo-first-order reaction rate constant. (5)

A plot of $\ln C_o/C_i$ 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 $\ln C_o/C_i$ 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.

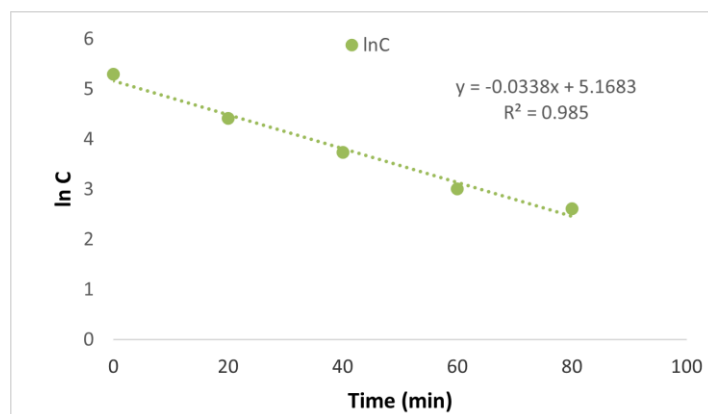


Fig. 5.10: Pseudo first order reaction graph for time vs ln C

5.3.3 Arrhenius equation

Equation (6) was used to study the temperature influence on the kinetic model and compute the activation energy for Cr^{6+} degradation on the $\text{NH}_2\text{-MIL-53(Fe)}$ rGO photocatalyst.

$$k_a = k_2 \exp(-E_a/RT) \quad (6)$$

The logarithmic method of Equation (6) was employed, and the plots of $\ln(k_a)$ vs $1/T$ are given in Fig. The activation energies were calculated using the slopes of the shown graphs. The activation energies (E_a) determined for the $\text{NH}_2\text{-MIL-53(Fe)}$ rGO photocatalyst are 65.58 kJ/mol [14].

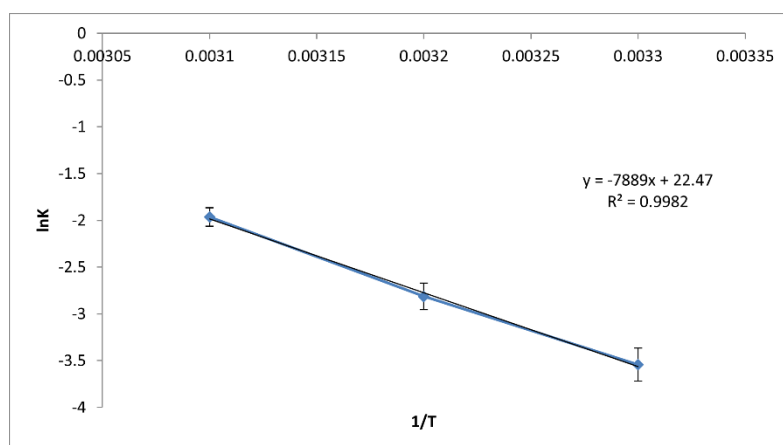


Fig. 5.11: Arrhenius equation graph for 1/T vs ln K.

5.4 STATISTICAL ANALYSIS WITH RESPONSE SURFACE METHODOLOGY

RSM is a method that may be used to explore the cumulative impact of numerous factors and to find the best settings for a multivariate system. RSM is currently actively used for physical conditions, time, dose, pH, and initial concentration process optimization. RSM is a collection of statistical and mathematical instruments for defining the connection between the outcome and the variables that are not dependent. The degradation of chromium in this investigation is carried out utilizing NH₂-MIL-53 (Fe). For the degrading process, RSM with CCD was used to discover potential interactions and select the best operational settings. Physical factors such as dose, pH, duration, and beginning chromium concentration have been optimized.

In traditional experiments, optimization is often performed by altering a single element while holding all other parameters constant under a defined set of conditions. This procedure needs several experiments and is time intensive. To bypass the constraints of the traditional technique, the empirical design of experiments can be utilized to optimize process parameters. RSM is an excellent statistical approach for planning such experiments, developing models, and examining complicated processes for target value optimization. To overcome the constraints of a single-factor optimization procedure, RSM may jointly optimize all influencing parameters. RSM, which comprises factorial structure and regression analysis, aids in evaluating relevant factors, developing models to examine the interactions between variables, and selecting of relevant factors, the development of models to examine the interactions between variables, and the selection of the ideal set of variables or desirable results. Photocatalysis was used in this study to optimize physical parameters for chf. Physical parameters such as dose, duration, pH, and beginning phenol concentration were optimised. RSM is being recommended for determining the impacts of individual elements as well as their interactions. The interplay of potential affecting parameters on the effectiveness of treatment can be examined using RSM a minimal scheduled test. Individual components' relevance, the suitability of this functional form, and the degree of sensitivity of how it reacts to each factor may all be assessed using statistical inference techniques. Many quantitative designs for experiments approaches have recently been used for bioprocess optimization. RSM is the only one that is

adequate for determining the influence of individual variables and effectively obtaining the ideal conditions for a multivariate system. This approach has been used to improve alcoholic fermentation along with various fermentation mediums. RSM is an empirical modulation approach that establishes a link among a set of specified experimental variables and observed outcomes. To create a statistical model, you must first understand the processes. Essentially, the optimization process consists of three primary steps: predicting the coefficients in a mathematical model, forecasting the response, and assessing the model's suitability.

5.4.1 Analysis of variance:

ANOVA (Analysis of Variance) is a statistical approach for analysing data variations across groups. ANOVA may be used in the framework of chromium degradation to find the relevant parameters that affect chromium degradation, such as pH, temperature, catalyst dose, and concentration. A model that is quadratic is a mathematical framework that incorporates a quadratic (squared) element as well as linear terms. A quadratic model may be employed in the framework of chromium deterioration to represent the nonlinear connection between the factors that are entered (such as temperature and time) and the value of the output (such as degradation percentage). When the connection between both the input and the output variables is not linear, this might be advantageous.

Table 5.1: RSM generated response 1 : degradation.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	228.36	14	16.31	71.86	< 0.0001	significant
A-pH	87.13	1	87.13	383.89	< 0.0001	
B-Concentration	0.4082	1	0.4082	1.80	0.1999	
C-Dosage	2.36	1	2.36	10.41	0.0057	
D-Time	0.8177	1	0.8177	3.60	0.0771	

AB	0.3875	1	0.3875	1.71	0.2110	
AC	0.1580	1	0.1580	0.6961	0.4172	
AD	0.0371	1	0.0371	0.1633	0.6919	
BC	0.1351	1	0.1351	0.5950	0.4525	
BD	0.0163	1	0.0163	0.0716	0.7926	
CD	1.31	1	1.31	5.75	0.0299	
A ²	125.58	1	125.58	553.25	< 0.0001	
B ²	0.8795	1	0.8795	3.87	0.0678	
C ²	0.0446	1	0.0446	0.1964	0.6640	
D ²	0.0070	1	0.0070	0.0307	0.8633	
Residual	3.40	15	0.2270			
Lack of Fit	0.9155	10	0.0916	0.1839	0.9887	not significant
Pure Error	2.49	5	0.4978			
Cor Total	231.76	29				

Coding for factors is used.

The sum of squares is of partial Type III.

The predicted result is likely significant given the Model F-value of 71.86. An F-value this big might happen to owe to noise just 0.01% of the time.

Model terms are considered important when the P-value is less than 0.0500. In this instance, key parameters of the model were A, C, CD, and A². The parameters of the model are not essential if the value is higher than 0.1000. Reduced complexity may enhance your model if it has a lot of unnecessary words (except those needed to maintain hierarchy).

The F-value for the lack of fit, 0.18, indicates that the absence of a match is not notable in comparison to the basic error. A significantly inadequate Fit F-value has a 98.87% likelihood of being caused by noise. Since we desire the model to fit, an unimportant failure to fit is desirable.

Fit Statistics

Table 5.2 : RSM generated fit statistics.

Std. Dev.	0.4764	R²	0.9853
Mean	86.87	Adjusted R²	0.9716
C.V. %	0.5484	Predicted R²	0.9618
		Adeq Precision	39.6185

The Predicted R² of 0.9618 and the Modified R² of 0.9716 are reasonably in conformity; that is, the variance between them is under 0.2.

The ratio of signal to noise is measured with Adequate Precision. A ratio of at least 4 is preferred. Your signal is strong enough based on the factor of 39.618. To move about the design space, utilize this model.

5.4.2 Central Composite Design

With a limited number of components, the CCD technique may be effectively used to create the second-order response model. The CCD is divided into three separate elements: (1) the full design, in which the levels of factors are coded to the typical low (1) and high (+1) values; (2) axial points on the axis of each variable away from the designed centre; and (3) centred points that can be copied for determining the error of the experiment's variance [17]. The best value was predicted using a second-order polynomial quadratic equation, which was then used to clarify how the variables interacted. The equation is the quadratic equation model for finding the ideal spot.

$$Y = \beta_o + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1, i < j}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j \quad (7)$$

$$Y = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 \\ + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 \\ + \beta_{34} X_3 X_4 \quad (8)$$

where Y is the anticipated response, X1, X2, X3, and X4 are variables that are independent, b0 is the value of the offset term, and 1, 2, 3, 4 are coefficients of linear effects, 11, 22, 33, 44 are coefficients of squared effects, and 12, 13, 14, 23, 24, 34 are coefficients of interactions. 6 cross-interactions, four quadratic terms, and 4 linear terms make up the regression equation. The 5% level of significant ANOVA was used to assess the empirical mathematical model. The second-order models' importance was examined using ANOVA. F-value is used to gauge the second-order model equation's significance in statistics. To reject the null hypothesis, which states that all of the coefficients of regression are zero, the computed F-value often has to be higher than the tabulated F-value. At a particular level of significance, known as the p-value, tabulated F-values for regress and leftovers are produced using F distributions based on DF, respectively [19, 18]. Chromium deterioration physical parameter optimisation is done using CCD.

5.4.3 Interaction effects on operating parameters at optimum conditions

A 3D surface plot may display the interaction impact between two independent factors on the rate of deterioration. It was demonstrated how two distinct variables along with one additional variable set at an established level affected the rate at which chromium was degraded by NH₂-MIL-53 (Fe) at rGO. According to Fig. 5.12, percentage degradation rose up to the ideal level as dosage (C) and duration (D) were increased. A rise in percentage deterioration was seen as the starting concentration rose from 100 to 500 ppm and the duration increased from 0 to 100min. After that, a rise in starting intensity and duration was accompanied by a drop in the degradation percentage. When the starting concentration was 100 mg/l, the greatest percentage degradation of 93.34% was discovered to occur after 60 minutes. The proportion of degradation reduces if starting concentration or pH are raised further.

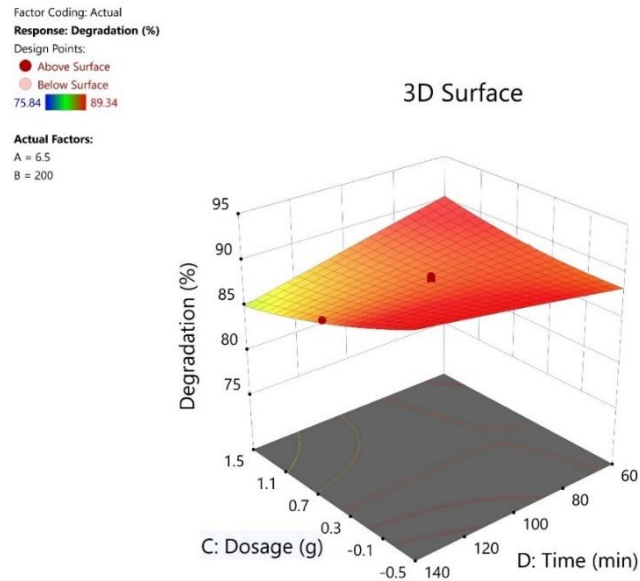


Fig. 5.12: RSM graph plotted for Dosage (C) vs Time (D).

In Fig. 5.13, the influence of two variables—pH (B) and temperature (A)—on deterioration is depicted. As temperature and pH rose, so did the percentage of degradation, which eventually reached its maximum value. A rise in percentage degradation was seen as the temperature reached 30 °C and the pH rose from 2 to 6.5. After that, when temperature and pH increased, the proportion of deterioration decreased. pH 6.5 and a temperature of 30 °C were determined to have the highest degradation percentage of 93.57%. The proportion of deterioration reduces if temperature or pH are raised more.

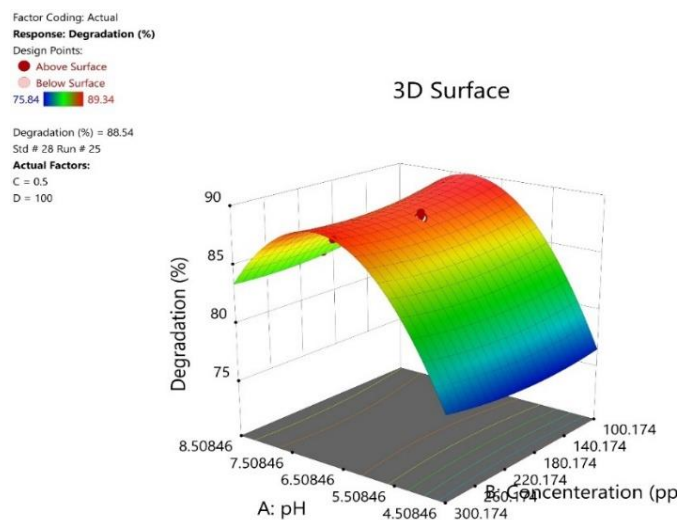


Fig. 5.13: RSM graph plotted for pH (A) vs Concentration (B)

The interaction impact on the starting concentration ratio (C) and temperature (A) is depicted in Fig. 5.14. A rise in the percentage of degradation was seen as the starting concentration went from 100 to 500 mg/l and the temperature went from 30 to 50 °C. Following that, a rise in starting temperature and concentration was accompanied by a drop in the degradation percentage. A temperature of 30 °C and starting concentration of 200 mg/l were determined to have the highest percentage degradation rate of 93.57%. The proportion of degradation reduces if starting concentration or pH is raised further.

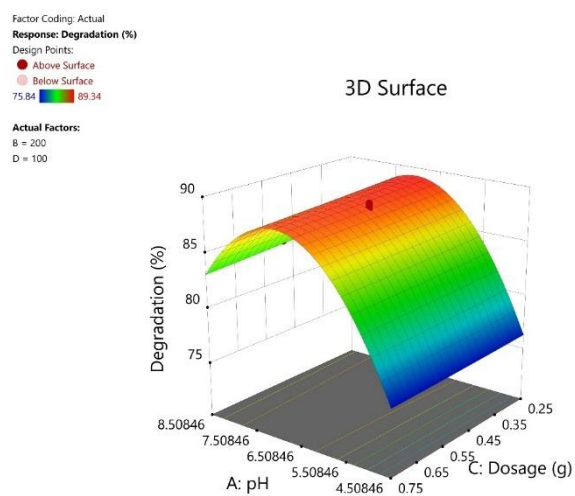


Fig. 5.14: RSM graph plotted for pH (A) vs Dosage (C).

In Fig. 5.15, the interaction between time (D) and temperature (A) was shown to boost percentage deterioration up to the ideal level. A rise in the percentage of deterioration was shown when the period between 0 to 100 min and the temperature rose from 30 to 50 °C. After that, a rise in time and temperature was followed by a drop in percentage deterioration. The temperature of 30 °C and period of 60 min. were determined to have the highest percentage deterioration of 93.54%. The percentage deterioration drops as time or temperature are increased more.

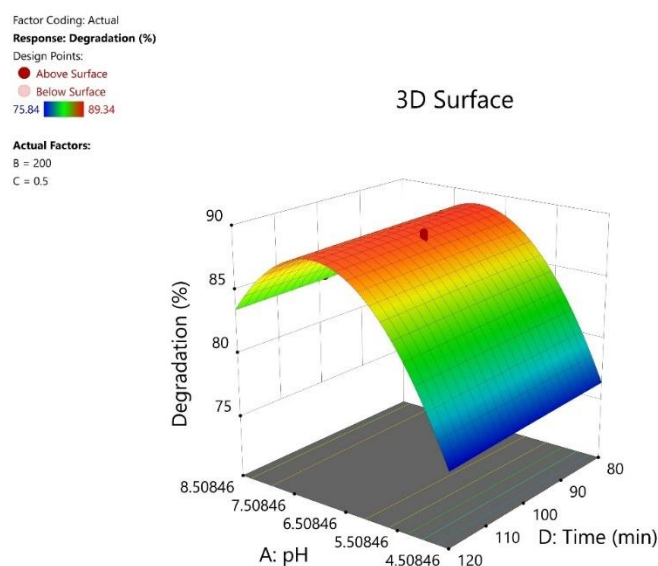


Fig. 5.15: RSM graph plotted for pH (A) vs Time (D).

This is represented as starting concentration (C) and pH (B) in Fig. 5.16. A rise in percentage degradation occurred as the starting concentration was raised from 100 to 500 mg/l and the pH was raised from 2 to 6.5. Following that, a rise in starting concentration and pH was accompanied by a reduction in the percentage degradation. A pH of 5.6 and an initial concentration of 200 mg/l were determined to have the highest percentage of degradation (91.58%). The percentage drops if starting concentration or pH is raised more.

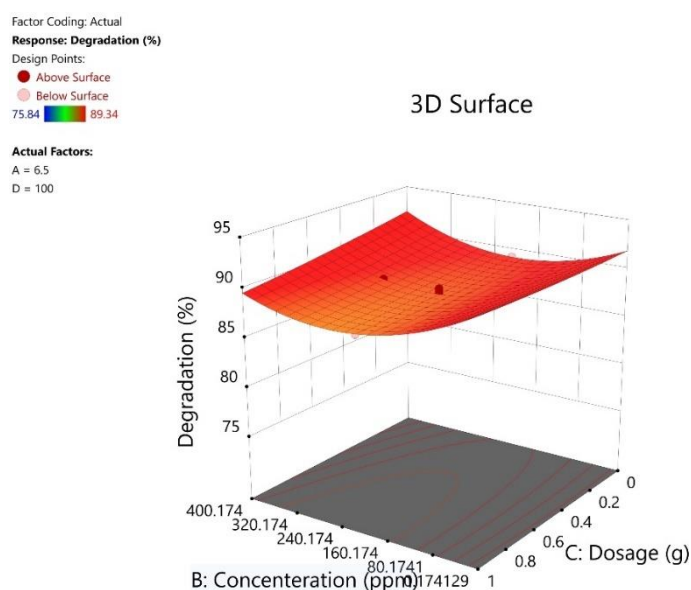


Fig. 5.16: RSM graph plotted for Concentration (B) vs Dosage (C).

Fig. 5.17 depicts the interaction between time (D) and pH (B). A rise in the percentage of deterioration was seen when the period between 0 to 100 min and pH rose from 6.5 to 11. After that, as time and pH increased, a decline in the percentage of deterioration was seen. The greatest degradation rate of 93.57% was discovered at pH 6.5 and 60 minutes. The proportion of deterioration reduces when time or pH are increased further.

Performing the study with an initial concentration of 200 mg/l, pH 6.5 at 30 °C for 60 minutes resulted in an experimentally verified 92.87% degradation, which was used to validate the statistical framework. The experimental results are in good shape with the projected values, as evidenced by the linear correlation plot comparing the adjusted R2 and predicted R2. As a result, it was determined that the models were sufficient for illustrating the response data of % degradation of chromium, allowing for further analysis and forecasting.

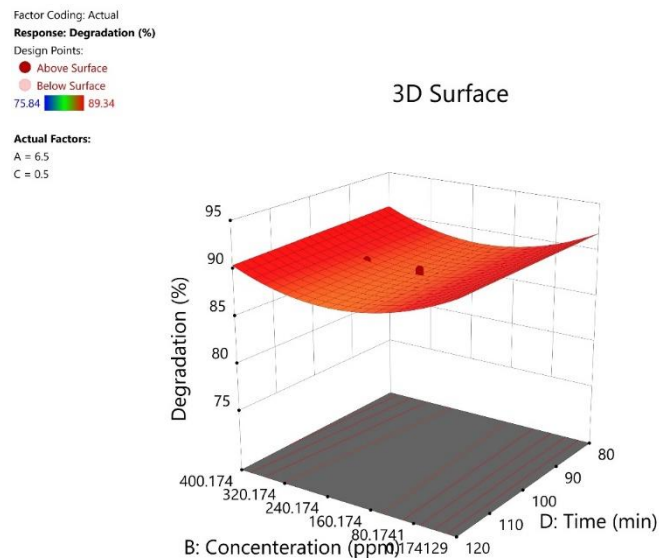


Fig. 5.17: RSM graph plotted for Concentration (B) vs Time (D).

5.4.3.1 Inference from 3D surface plot

Finding relationships among process factors: The 3-D graph may occasionally show connections between various process variables that influence the degradation of chromium. A three-dimensional graph is an invaluable tool for comprehending the

basic links between process factors and deterioration since these interactions might not be visible in two-dimensional contour graphs.

5.4.4 Prediction vs actual

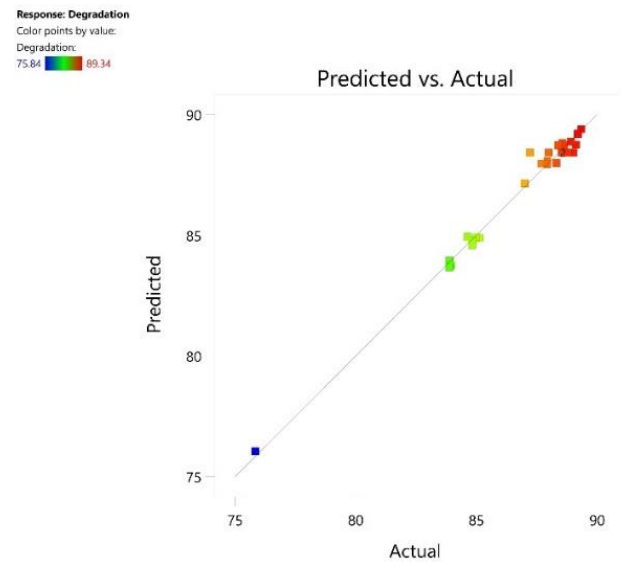


Fig. 5.18: RSM graph plotted for Actual vs predicted.

5.5 CHROMIUM DEGRADATION

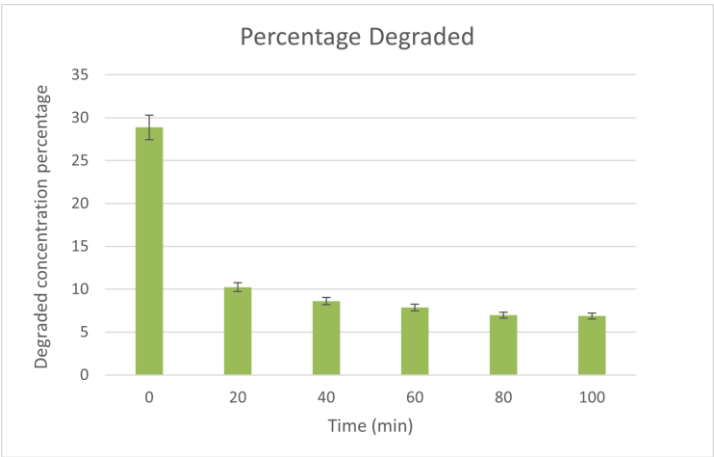


Fig. 5.19: Graph of Chromium degradation plotted for Time vs Degradation concentration percentage.

The amount of chromium in the water is determined from the ICP-OES (Inductively Coupled Plasma - Optical Emission Spectroscopy) results. Fig 5.19 It demonstrates that the amount of chromium in the water decreases as time goes on from 28.87 mg/L as initial concentration to 10.23 mg/L, 8.62mg/L, 7.6mg/L, 6,97mg/L and 6.89mg/L at 20min, 40min, 60min, 80min and 100min respectively. and at 60

minutes it achieves the maximum degradation of 7.43, indicating that 92.57% of the chromium has been eliminated from the water.

5.6 REGENERATION STUDIES

For every of the examined catalysts, the tests were run five times to examine the endurance of the catalyst for chromium oxidation. A constant starting chromium content of 200 mg L⁻¹ was used, along with a pH of 6.5 and a 60-minute irradiation period. The features of the heterogenous catalyst allowed for the recycling process to be carried out without any complications. One benefit of utilizing this type of catalyst is that it is simple to separate the spent catalyst from the testing solvent, and the recyclable components just require washing and oven drying before being reused [18]. The photocatalytic performance of the bare NH₂-MIL-53(Fe) rGO declined by roughly 54 percent in the fifth cycle after lasting continuously for about 2 cycles. The decline may be the result of the synthesized catalyst's surface area aggregating after numerous cycles and going through several heat treatments. For the 200 ppm NH₂-MIL-53(Fe) rGO catalyst, a high level of chromium removal (>90%) was sustained up to the two cycles. The third, fourth, and fifth cycles saw a minor decline in performance. Figure 5.19 depicts chromium degradation, which shows a deterioration of more than 90% from the initial value and a progressive decline. The catalyst can therefore be reused two to three times, depending on the degree of deterioration.

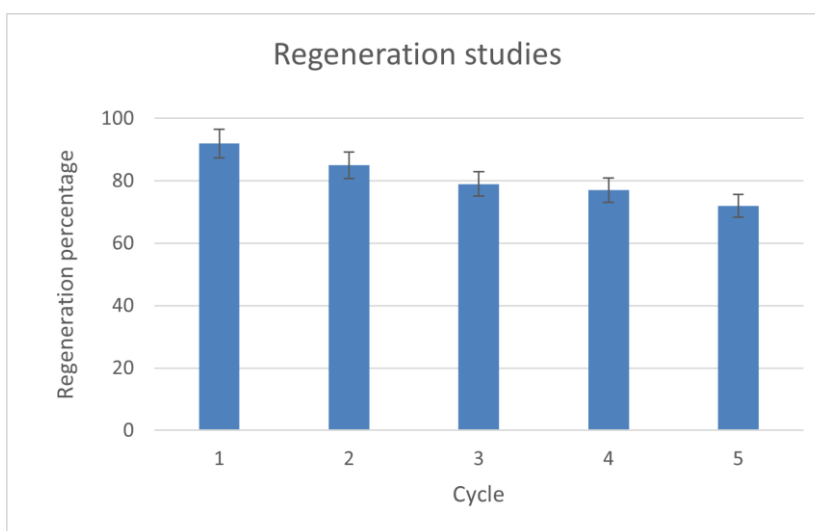


Fig. 5.20: Graph of Regeneration studies plotted for cycle vs regeneration percentage.

CHAPTER-6 SUMMARY AND CONCLUSIONS

Effective synthesis of NH₂-MIL-53(Fe) with rGO is achieved. The MOF was rendered more stable with the addition of an amino group, and the catalyst for the photocatalytic process utilised to degrade chromium was made more effective by the addition of reduced graphene oxide. FE-SEM, XRD, and FT-IR were used to characterise the synthesised MOF catalyst. The usage of NH₂-MIL-53(Fe) with rGO for Cr⁶⁺ degradation has demonstrated encouraging results, according to the existing research. High catalytic activity for the photocatalysis process was shown by the NH₂-MIL-53(Fe) with rGO, which also led to more Cr⁶⁺ degradations. Additionally, NH₂-MIL-53(Fe) with rGO has demonstrated strong stability and reusability, which is crucial for manufacturing at a commercial scale. RSM was used to examine the ideal operating circumstances, which is an efficient and cost-effective method of improving operational conditions. RSM may be used to control operational parameters such as reaction temperature, catalyst dose, pH, irradiation time, and pollutant initial concentration. Additionally, it was discovered that the pH should be kept at 6.5, the initial concentration should be 200 mg/L, the catalyst dosage should be 0.5g, the temperature should be kept at room temperature, and the irradiation time should be 60 minutes, all of which satisfy the actual conditions determined by the UV spectrometer. According to RSM findings, the projected and actual operational conditions values are virtually identical outcomes. Cr⁶⁺ degradation is 92.57%, which was validated by an ICP-OES investigation. In contrast, increasing the catalyst dose doesn't significantly change the degradation percentage. Another crucial step in demonstrating the application of photocatalytic reactions is to investigate their kinetics. According to the analysis of the literature, the most plausible kinetics model for characterising photocatalysis processes is Langmuir-Hinshelwood's pseudo-first-order model. With apparent rate constants (k_{app}) of 0.0338 min⁻¹, the experimental findings for Cr were compatible with the pseudo-first-order kinetics concept (R^2 values near 1). It also creates a linear graph for the 200 mg/L concentration, satisfying the Langmuir isotherm. The potential for NH₂-MIL-53(Fe) reuse with rGO is also encouraging. It is regenerable for a maximum of three times, giving degradation percentages of 92.57%, 88%, and 79%, respectively. The deterioration percentages for the fourth and fifth are 76% and 72%, respectively.

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SYNTHESIS OF IRON BASED METAL ORGANIC FRAMEWORK ANCHORED ON THE SURFACE OF REDUCED GRAPHENE OXIDE FOR THE DEGRADATION OF CHROMIUM 6+

by Rishikiran A

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FOR THE DEGRADATION OF CHROMIUM 6+**

Submitted in partial fulfilment of the requirement for the award of
Bachelor of Technology Degree in Chemical Engineering

by

SATISH KUMAR K (39190029)
SIDDHARTH U (39190031)



**DEPARTMENT OF CHEMICAL ENGINEERING
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BONAFIDE CERTIFICATE

This is to certify that this project report is the bonafide work of Satish Kumar K (39190029) and Siddharth U (39190031) who carried out the project entitled "SYNTHESIS OF IRON BASED METAL ORGANIC FRAMEWORK ANCHORED ON THE SURFACE OF GRAPHENE OXIDE FOR THE DEGRADATION OF BIODIESEL CHROMIUM 6+" under my supervision from November 2022 to April 2023

Internal Guide

Dr. S. SATHISH M.E, Ph.D.

Head of the Department

Dr. S. SATHISH M.E, Ph.D.

Submitted for Viva voce Examination held on _____

Internal Examiner

External Examiner

DECLARATION

We Satish Kumar K (39190029) and Siddharth U (39190031) hereby declare that the Project Report entitled “SYNTHESIS OF IRON BASED METAL ORGANIC FRAMEWORK ANCHORED ON THE SURFACE OF GRAPHENE OXIDE FOR THE DEGRADATION OF BIODIESEL CHROMIUM 6+” done by me under the guidance of Dr. S. Sathish, SATHYABAMA INSTITUTE OF SCIENCE AND TECHNOLOGY, CHENNAI at is submitted in partial fulfilment of the requirements for the award of Bachelor of Technology degree in Chemical Engineering.

DATE:

PLACE: CHENNAI

SIGNATURE THE CANDIDATES

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ABSTRACT

Due to the serious health risks it poses to both humans and the natural world, hexavalent chromium Cr(6+) is an extremely dangerous groundwater pollutant. Researcher's interest in Metal-Organic Frameworks (MOFs) for removing pollutants from waterways has increased recently. In the current study, a hybrid amino functionalized MOF@rGO nano catalyst was used to generate NH₂-MIL-53 (Fe) which was tested for Cr (6+) eliminating using an in situ grown nanocrystalline mixed ligand octahedral metal-organic framework with iron metal centers on the outermost layer of reduced graphene oxide (rGO). To describe XRD, MOF, FTIR, FESEM, BET, and EDS studies were used. In the context of a batch system, the impact of a few independent factors on Cr (6+) removal capability was investigated.

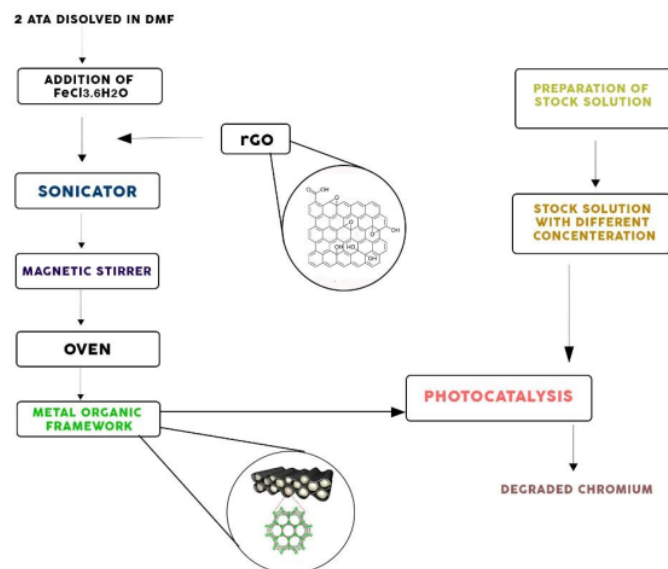


TABLE OF CONTENTS

CHAPTER NO	TITLE	PAGE NO
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	TABLE OF CONTENTS	vi
	LIST OF ABBREVIATIONS	ix
	LIST OF FIGURES	xi
	LIST OF TABLES	xiii
1	INTRODUCTION	1
	1.1 NECESSITY OF WATER	1
	1.2 EXPLANATION ABOUT CHROMIUM	5
	1.3 METAL ORGANIC FRAMEWORK NH ₂ -MIL-53(Fe)	7
	1.4 PHOTOCATALYSIS	11
5 2	LITERATURE SURVEY	16
	AIM AND SCOPE	18
	3.1 AIM	18
	3.2 SCOPE	18
4	MATERIALS AND METHODS	19
	4.1 REAGENTS	19
	4.2 ²⁴ SYNTHESIS OF NH ₂ -MIL-53(Fe)	19
	4.3 SYNTHESIS OF REDUCED GRAPHENE OXIDE (rGO)	20
	4.4 MODIFICATION OF NH ₂ -MIL-53(Fe) WITH rGO	20
	4.5 PHOTOCATALYTIC DEGRADATION CHROMIUM	21
5	RESULTS AND DISSCUSION	23

5.1 STRUCTURAL CHARECTERISATION OF	23
NH ₂ -MIL-53(Fe) WITH rGO	23
5.1.1 X-Ray Diffraction	23
5.1.2 Field Emission Scanning Electron	
Microscopy (FE SEM)	23
5.1.3 Fourier Transform Infrared (FTIR)	24
5.2 EFFECT OF VARIABLES ON THE DEGRADATION	
OF CHROMIUM 6+	25
5.2.1 Effect of chromium concentration	25
5.2.2 Effect of catalyst dosage	26
5.2.3 Effect of time	27
5.2.4 Effect of pH	27
5.2.5 Effect of temperature	28
5.3 KINETICS	28
5.3.1 Langmuir Isotherm	29
5.3.2 Pseudo first order reaction	30
5.3.3 Arrhenius equation	31
5.4 STASTICAL ANALYSIS WITH RESPONSE	
SURFACE METHODOLOGY	32
47	
5.4.1 Analysis of variance (ANOVA)	34
5.4.2 central composite design	35
5.4.3 Interaction effects on operating parameters	
on optimum conditions	39
5.4.3.2 Inference from 3-D surface plot	40
5.4.4 Prediction vs actual	40

	5.5 CHROMIUM DEGRADATION	41
6	SUMMARY AND CONCLUSION	42
	REFERENCES	43

LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
AAS	Atomic Adsorption Spectrometer
BDC	Benzene dicarboxylate
Cr	Chromium
CQDs	Carbon Quantum Dots
CCD	Central Composite Design
DMF	Dimethyl-formamide
Ea	Activation energy
EPC	Environmental Protection Agency
EtOH	Ethanol
Fe	Iron
¹² FE SEM	Field Emission Scanning Electron Microscopy
FT-IR	Fourier Transform Infrared
GO	Graphene Oxide
⁴⁸ 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	Revolution per minute
UV	Ultraviolet
XRD	X-Ray Diffraction

LIST OF FIGURES

FIGURE NO	NAME	PAGE NO
4.1	a) Experimental image of Magnetic stirrer while 4 synthesis of MOF NH ₂ -MIL-53(Fe).	19
	b) Experimental image of Sonicator while 4 synthesis of MOF NH ₂ -MIL-53(Fe).	
	c) Experimental image of Conical Flask shaker while 4 synthesis of MOF NH ₂ -MIL-53(Fe).	
4.2	a) Experimental image of Dropwise addition of alcohol in conical flask mixer while 4 synthesis of MOF NH ₂ -MIL-53(Fe) rGO.	20
	b) Experimental image of Slurry pastes mixture of MOF while 11 synthesis of MOF NH ₂ -MIL-53(Fe) rGO.	
5.1	XRD analysis image of the MOF catalyst 11 NH ₂ -MIL-53(Fe) rGO.	23
5.2	a) SEM analysis image of the MOF catalyst 81 NH ₂ -MIL-53(Fe) rGO.	23
	b) SEM analysis image of the MOF catalyst 28 NH ₂ -MIL-53(Fe) rGO.	
5.3	FT-IR analysis image of the MOF catalyst 28 NH ₂ -MIL-53(Fe) rGO.	24
5.4	Effect of chromium concentration graph which is plotted for time vs percentage degraded.	25

5.5	a) Effect of catalyst dosage graph which is plotted for time vs percentage degraded.	26
	b) Effect of catalyst dosage graph which is plotted for time vs percentage degraded zoomed version.	
5.6	a) Effect of Time graph which is plotted for time vs percentage degraded (0.5g Catalyst dosage).	26
	b) Effect of Time graph which is plotted for time vs percentage degraded (1g Catalyst dosage).	
	c) Effect of Time graph which is plotted for time vs percentage degraded (2g Catalyst dosage).	
5.7	Effect of pH which is plotted for pH vs percentage degraded.	27
5.8	Effect of temperature graph which is plotted for temperature vs percentage degraded.	28
5.9	Langmuir Isotherm Graph plotted for $1/C_e$ vs $1/Q_e$.	29
5.10	Pseudo first order reaction graph for time vs $\ln C$.	30
5.11	Arrhenius equation graph for $1/T$ vs $\ln K$.	30
5.12	RSM graph plotted for Dosage (C) vs Time (D).	36
5.13	RSM graph plotted for pH (A) vs Concentration (B).	36
5.14	RSM graph plotted for pH (A) vs Dosage (C).	37
5.15	RSM graph plotted for pH (A) vs Time (D).	38
5.16	RSM graph plotted for Concentration (B) vs Dosage (C).	38

5.17	RSM graph plotted for Concentration (B) vs Time (D).	39
5.18	RSM graph plotted for Actual vs predicted.	40
5.19	Graph of Chromium degradation plotted for Time vs Degradation concentration percentage.	40
5.20	Graph of Regeneration studies plotted for cycle vs regeneration percentage.	41

LIST OF TABLES

TABLE NO	NAME	PAGE NO
5.1	RSM generated response 1 : degradation.	32
5.2	RSM generated fit statistics.	34

CHAPTER-1 INTRODUCTION

1.1 NECESSITY OF WATER

Of all the valuable resources on Earth, water is necessary for human existence as well as the health of environments, economies, and civilizations. Only a tiny portion of the Earth's surface, or about 2.5%, is covered by freshwater which is suitable for consumption, farming, and other social values. Water is essential for the sustenance of all sentient creatures, so it has an essential role in sustaining life. It is a crucial part of all cells, tissues, and organs in all living things, including people, plants, and animals. It also plays a crucial role in many physiological mechanisms, including digestive process, circulation, and sewage disposal. The largest user of water globally, agriculture, also relies heavily on the water as a resource. Water is needed by crops for watering, fertilization, and pest management, as well as for their development and production. Therefore, access to dependable and sufficient water supplies is essential for both growth in the economy and food security.

Numerous other sectors of the economy, such as manufacturing, electricity generation, and transportation, also depend on water. It is necessary for the creation of numerous products and services and serves the function of refrigerant, solvent, and cleaning substances. Ecological environments depend on water to operate properly. Numerous animals and plants kinds exist in rivers, streams, and coastlines, which also offer habitat and supplies to numerous environments. Various environmental systems, including the nutrient cycle, photosynthesis, and the storing of carbon, involve water. Water resources are under increasing strain due to population growth, climate change, and pollution, despite their importance. Water scarcity is a problem in many parts of the globe, and it can cause problems on the social, economic, and environmental fronts. For the sustainability of human societies and natural ecosystems, water supplies must be managed and protected. A fundamental human value, access to water that is safe and clean is essential for eradicating destitution and enhancing public health. Many individuals lack a source of good drinkable water, which causes waterborne illnesses that can be fatal and cause sickness. According to the United Nations, ⁴² more than 2 billion people lack access to clean drinking water, and because of growing populations, urbanization, and global warming, this figure is expected to rise.

Water is an essential element of the natural environment as well, sustaining ecosystems as well as biodiversity. It benefits plant development and offers natural habitats for fish, animals, and other living things. It also has an essential role in the water cycle, which moves water around the planet and sustains climate change, and it helps control the Earth's climate by absorbing and releasing heat. Pollution, climate change, excessive use, and unsustainable practices, on the other hand, are dangers to water supplies. Waterways can become contaminated by agricultural, industrial, and residential waste and sewage, and this may damage marine habitats. Floods, droughts, and other severe weather conditions are happening more frequently and with greater severity because of changing the climate. Water is a crucial component of nature as well, supporting ecosystems and the preservation of biodiversity. It promotes the growth of plants and provides animals, fish, and other living creatures with natural ecosystems. It also plays a crucial part in the water cycle, which transports water across the globe and supports environmental issues. By absorbing and releasing heat, it regulates the temperature of the Earth. On the opposite side, threats to water resources include pollution, climate change, inappropriate use, and unsustainably conducted business. Industrial, agricultural, and domestic refuse and effluent can pollute waterways, harming sea life. As a result of climate changes, droughts, floods, and other extreme weather events are occurring more frequently and with greater severity.

Water can be handled sustainably, and it can be conserved in several ways:

1. Minimize water waste: By repairing pipeline leakage, utilizing water-efficient fixtures and equipment, and averting excessive water use, we can conserve water.
2. Use water wisely: We can use water wisely by only using it when necessary, implementing water-saving techniques like xeriscaping and rainwater collection, and utilizing low-flow devices.
3. safeguard water sources: Regulate industrial and agricultural activity and encourage sustainable land use techniques to prevent pollution.
4. Support equitable access: We can encourage equitable access to water supplies by making sure that everyone has access to hygienic utilities and secure, inexpensive drinking water.

5. Invest in water infrastructure: To guarantee that there is enough water available to satisfy both present and future demands, we can make investments in freshwater resources, such as dams, water treatment facilities, and distribution systems.

6. Support study and innovation: We can encourage the development of new methods and technologies that will advance the efficient use and administration of water.

7. Raise awareness: Through support, outreach, and instruction, we can spread the word about the value of water and the necessity of environmentally friendly water-management techniques.

Water is an essential element that sustains nature, life, and economic growth. To guarantee that we have enough water for all of our requirements right now and in the future, water resource control is essential. We can guarantee a clean water future for everyone by conserving water, using it wisely, protecting water sources, supporting equitable access, putting funds into infrastructure, encouraging innovative thinking and research, and increasing awareness.

By repairing pipeline leakage, utilizing water-efficient fixtures and equipment, and averting excessive water use, we can conserve water. We can use water wisely by only using it when necessary, implementing water-saving techniques like xeriscaping and rainwater collection, and utilizing low-flow devices. Regulate industrial and agricultural activity and encourage sustainable land use techniques to prevent pollution. We can encourage equitable access to water supplies by making sure that everyone has access to hygienic utilities and secure, inexpensive drinking water. To guarantee that there is enough water available to satisfy both present and future demands, we can make investments in freshwater resources, such as dams, water treatment facilities, and distribution systems. We can encourage the development of new methods and technologies that will advance the efficient use and administration of water. Through support, outreach, and instruction, we can spread the word about the value of water and the necessity of environmentally friendly water-management techniques. Water is an essential element that sustains nature, life, and economic growth. To guarantee that we have enough water for all of our requirements right now and in the future, water resource control is essential. We can guarantee a clean water future for everyone by

conserving water, using it wisely, protecting water sources, supporting equitable access, putting funds into infrastructure, encouraging innovative thinking and research, and increasing awareness.

Droughts, floods, and storms are becoming more common and severe due to climate change, which has an impact on water availability as well as quality. By adopting water quality management strategies like water rainwater harvesting, conservation, and water recycling, we can tackle this issue and adjust to changing water conditions. Because of excessive use, groundwater levels are rapidly falling in many parts of the globe, endangering the long-term viability of water resources. Adopting laws and rules that support ongoing groundwater management practises, such as lowering pumping rates, increasing water use effectiveness, and applying groundwater recharge methods, is necessary to address this issue. Agriculture, urbanization, and industrial operations all have the potential to pollute freshwater resources and damage marine habitats. We need to embrace sustainable practices that reduce pollution, implement laws that prevent it, and support water purification technologies that can remove pollutants to solve this issue. Sustained water management requires effective water governance. To achieve this, rules and regulations that encourage fair and environmentally friendly water use must be put in place. Additionally, stakeholders must be brought into the judgement process, and organizations that can effectively manage water resources must be built.

In conclusion, efficient water management is a challenging task with many facets that call for cooperation between people, groups, governments, and organizations. We can move towards a water resource future that promotes human well-being, environmental health, and economic prosperity by tackling the specific issues associated with climate change, groundwater depletion, water pollution, and water governance. In conclusion, efficient water management is a challenging task with many facets that call for cooperation between people, groups, governments, and organizations. We can move towards a water resource future that promotes human well-being, environmental health, and economic prosperity by tackling the specific issues associated with climate change, groundwater depletion, water pollution, and water governance.

1.2 EXPLANATION ABOUT CHROMIUM 6+

Chromium 6+ is an extremely hazardous variety of metal that can harm detrimental effects on both the health of humans and the environment. In addition to being used in commercial processes like leather tanning, electroplating, and textile production, it is a naturally occurring element that can be discovered in rocks, dirt, and volcanic dust. It can have a number of harmful consequences when it comes into touch with the skin, inhalation, or ingestion. Chromium 6+ exposure can cause several health problems, including lung cancer, skin rashes, dry eyes, liver, and kidney harm. Chromium 6+ exposure over a long period of time can also affect reproduction, resulting in decreased fertility and birth defects. Additionally, chromium 6+ has been linked to reproductive issues, genetic mutations, and birth deformities. It is regarded as a carcinogen, which means it may result in cancer. The case of Hinkley, California, where people were subjected to tainted water for drinking and experienced a rising cancer rate, is the most well-known illustration of chromium 6+ toxicity. It can harm the ecosystem to negatively affect human health. Chromium 6+ can build up in aquatic life after being released into sources of water, harming the environment. Additionally, crops that are contaminated by chromium 6+ in the earth run the risk of contaminating human health when consumed.

Chromium 6+ utilise and removal are strictly controlled by several international governmental organizations due to its toxicity and potential risks to both people and the environment. The Environmental Protection Agency (EPA) in the US, for instance, has set the highest contaminant threshold for chromium 6+ in drinkable water. To restrict the use and release of chromium 6+ in manufacturing processes, many nations have also put laws and guidelines in place. It should be eliminated from drinking water that is contaminated as one method of reducing its effects. Chromium 6+ can be removed from water using a variety of techniques, such as chemical activation, ion exchange, reverse osmosis, and adsorption. The addition of materials that can bind or capture the chromium 6+ ions from the water is required for adsorption, which is among the most efficient ways to remove chromium 6+ from water. However, one substance that's been utilized extensively to remove chromium 6+ from water is activated carbon. In the elimination of chromium 6+ from water, other compounds like zeolites, clay minerals, and metal-organic frameworks (MOFs) have also demonstrated good results in terms. Given their substantial surface area,

adjustable pore size, and unique properties, MOFs are especially intriguing as adsorbent materials for chromium 6+ elimination. It is possible to create MOFs with functional groups that can choose to absorb chromium 6+ ions from water. Numerous works have shown the effectiveness of MOFs in removing chromium 6+ from tainted water, and the current study is looking into developing new MOFs with improved adsorption capabilities. It has also been investigated for its possible use in several technological and industrial uses in addition to water purification. Chromium 6+, for instance, may be utilized to make pottery, paints, and dyes, and as a corrosion inhibitor in metals. The usage and removal of chromium 6+ in such applications, however, must take and into account any possible risks.

There is a continuing study to comprehend the processes of chromium 6+ toxicity and create remedies for people who are exposed to it in response to clearance and minimization. Antioxidant therapy, for instance, has been suggested as a possible treatment for people who have been exposed to high levels of chromium 6+. The reactive oxygen species produced by the metabolism of chromium 6+ can be neutralized by antioxidants to stop harm to cells and tissues. Additionally, studies are being conducted to determine the variables that affect the absorption and danger of chromium 6+. The oxidation state of chromium has been found as one contributing factor. There are various oxidation states in which chromium can occur, with chromium 6+ proving to be the most hazardous. Recent studies have however demonstrated that specific microbes can convert chromium 6+ to less harmful forms like chromium 3+. The clean-up of chromium 6+ contamination in the environment may be affected by this finding. Chromium 6+ is used in manufacturing applications, so efforts to limit this use have resulted in the creation of substitute technologies and materials. For instance, a few industries have shifted to chromium 3+ or other less toxic forms of metal. Non-toxic coverings, like those based on zinc or titanium, have taken the position of chromium-based coverings in other industries.

Furthermore, efforts are being made to create environmentally friendly processes for the manufacturing and disposal of chromium-based products. For instance, scientists are looking into how to produce chromium-based materials using sources of clean energy like sun and wind energy. For the disposal of waste containing chromium, they are also investigating the use of bioremediation and other ecologically friendly techniques. Hexavalent chromium also referred to as chromium

6+, is a particularly dangerous variety of the chemical chromium. It is a chemical substance that is frequently utilized in a variety of industrial procedures, such as welding, electroplating, and the production of stainless steel, dyes, and paints. Burning fossil fuels and making cement are two industrial operations that produce chromium 6+ as a residue.

There are actions that people can take to lower their vulnerability to chromium 6+ in addition to regulatory modifications. People can, for instance, use a water filtration system that is intended to get rid of chromium 6+ from their drinking water. Workers in chromium 6+ using workplaces should also take the necessary security steps, such as donning protective clothing and equipment and adhering to safe handling protocols. Whereas the chromium 6+ is a recognized toxin, it is essential to remember that there are other dangerous chemicals to which individuals could be subjected daily. Other chemicals and contaminants can also have hazardous impacts on health, so it's critical to take precautions to limit exposure to all potentially dangerous substances. In conclusion, the extremely harmful version of the metal chromium known as chromium 6+ can have detrimental effects on both ⁷⁵human health and the environment. Continuous study is necessary to create efficient reduction, removal, and treatment plans. Additionally, there must be attempts to reduce the use of chromium 6+ in industrial processes and to create eco-friendly and safer substitute materials and techniques. Working together, scientists, business executives, and governmental organizations can lessen the harmful impacts of chromium 6+ on the health of people and the environment.

¹⁷1.3 METAL ORGANIC FRAMEWORK-NH₂-MIL-53(Fe)

Given its distinct characteristics and possible uses, ¹⁷NH₂-MIL-53 (or simply MIL-53-NH₂) is a kind of Metal-Organic Framework (MOF) being extensively researched. A family of substances known as MOFs ²⁷is composed of metal ions that are linked together by organic ligands to generate porous 3-D structures. An organic ligand with amine (-NH₂) groups surrounds a central metal ion, usually molybdenum (Mo), in NH₂-MIL-53. The mixture of metal and organic elements creates a material that is very porous and has a sizable interior surface area, making it a desirable choice for a variety of uses such as separation, catalysis, and gas storage. The capacity of NH₂-MIL-53 to alter structurally in response to variations in temperature, pressure,

or the presence of certain molecules that are guests is one of its most distinguishing characteristics. The pore's sizes alter as a result of this metamorphosis, which may be utilized to precisely adsorb and release particular vapors or chemicals.

For its possible use in processes including carbon dioxide(CO₂) collection, storing hydrogen, medicine delivery, and catalysis, NH₂-MIL-53 has undergone substantial research. It is a viable contender for a variety of industrial and ecological applications due to its distinctive qualities and tunability. Because of its great thermal stability, it may be used in applications that require high temperatures. It can also endure being subjected to a wide range of chemicals without degrading thanks to its strong chemical stability. Generating an exceptionally high level of crystallinity is one of the key difficulties in the synthesis of NH₂-MIL-53, which is a form of Metal-Organic Framework (MOF) which is extensively researched due to its distinctive features and prospective uses. A family of substances known as MOFs is composed of metal ions that are linked together by organic ligands to create porous structures in three dimensions.

An organic ligand with amine (-NH₂) groups surrounds a central metal ion, usually molybdenum (Mo), in NH₂-MIL-53. This mixture of metal and organic elements creates a material that is very permeable and has a sizable interior area on its surface, making it a desirable choice for a variety of uses such as catalysis, separation, and gas storage. The capacity of NH₂-MIL-53 to alter structurally in accordance with variations in pressure, temperature, or the existence of certain outside molecules is one of its most distinguishing characteristics. The pores' sizes alter as a result of this metamorphosis, which may be utilized to preferentially adsorb and release particular gases or chemicals. It has also been thoroughly researched for its prospective uses in fields including hydrogen storage, catalysis, medicinal delivery, and carbon dioxide capture. It is a viable contender for a variety of industrial use and ecological applications due to its distinctive qualities and tunability. necessary for it to operate at its best. To increase the creation and structural durability of NH₂-MIL-53, researchers have created a number of techniques, including the use of alternative solvents and optimization of the conditions of the reaction. Due to its intriguing characteristics and behaviour, NH₂-MIL-53 is a topic of basic research in besides its possible uses. In order to gain insight into how MOFs may be created and manipulated for particular uses, experts are investigating

the fundamental processes of the physical alteration of NH₂-MIL-53 and also how it communicates with guest molecules. The process of synthesis and accessibility of NH₂-MIL-53 is one of the difficulties in applying it in real-world applications. It can be challenging to scale up to industrial quantities and often necessitates strong reaction conditions for the creation of NH₂-MIL-53. To increase the synthesis and scalability of NH₂-MIL-53, researchers have created a number of techniques, including the use of continuous flow reactors, post-synthetic modifications, and microwave-assisted synthesis.

The long-term viability of NH₂-MIL-53 in various settings presents another difficulty when employing it. Pressure, temperature, and humidity fluctuations can cause structural changes in the material, which can have an impact on how well it performs. However, scientists are striving to comprehend the underlying mechanisms causing these modifications to the structure and to create methods for enhancing NH₂-MIL-53's resilience. NH₂-MIL-53 is still an extremely promising substance with potential uses in a variety of industries despite these difficulties. It is an adaptable material that can be customized for different purposes thanks to its distinctive qualities and tunability. It has also been researched for its possible use in the conversion of energy and storage.

The metal-organic framework (MOF) known as NH₂-MIL-53 (Fe) is composed of iron (Fe) ions connected by biological molecules to form a 3-D porous structure. The "NH₂" in the name alludes to the amino (-NH₂) groups with a function that are present on the molecules of the organic linker. It is also renowned for its structural adaptability and thermal endurance, which make it appropriate for uses like storing gases and extraction that include pressure and temperature variations. The property of NH₂-MIL-53 (Fe) to undergo cyclic structural changes in response to environmental factors as temperature, gas adsorption, and pressure is intriguing. These variations in the porous structure's size and shape can have an impact on the material's characteristics and possible uses.

Application areas for NH₂-MIL-53 (Fe) have included gas storage and split, catalysis, and medication delivery. For instance, it has been demonstrated that NH₂-MIL-53 (Fe) has a high degree of selectivity for the adsorption of carbon dioxide (CO₂), making it a potent substance for the storage and capture of carbon.

Additionally, ¹¹ NH₂-MIL-53 (Fe) has been employed as a form of catalyst for a number of chemical processes, including the production of biofuels from biomass. It is a beneficial substance for gas adsorption and extraction applications because it has comparatively wide pores of roughly 1.4 nm and a high area of coverage. The organic linker molecules' amino functional groups may also make it possible for specific gas molecules to be selectively adsorbed. The capability of NH₂-MIL-53 (Fe) to experience post-synthetic modifications (PSMs), which entail adding fresh chemical functions or changing the ones that already present inside the MOF framework, is additional intriguing characteristic of this material. This enables the material's characteristics and prospective uses to be adjusted. To increase the choice and capability of ⁴ NH₂-MIL-53 (Fe) for adsorption of gases and separation, for instance, PSMs have been utilized. Researchers are also looking into the use of computer simulations and modeling to enhance the abilities of NH₂-MIL-53 (Fe). These methods provide a more thorough knowledge of the molecular activity and properties of the material, which can guide the development of novel MOFs with enhanced characteristics and prospective uses. Assessing the possible use of MOFs for environmentally friendly uses including water treatment and pollution removal is also gaining popularity. MOFs are a potential material for environmental remediation since they have been found to be excellent at adsorbing a variety of contaminants, including ¹⁷ contaminants such as heavy metals, organic chemicals, and dyes.

It is only one of several MOFs that were created and investigated for their special characteristics and possible uses. It is conceivable that additional MOFs with greater advanced characteristics and potential uses will be developed as study in this area expands. Other MOFs, in addition to NH₂-MIL-53 (Fe), have also demonstrated positive outcomes and possible uses in a variety of industries. For instance, MOFs with various metal ions, organic linkers, and pore diameters have been created and their special traits and prospective uses have been investigated. Examples include MOF-177, UiO-66, and ZIF-8, all of which have been studied for their potential in the areas of medication delivery, gas storage and separation, and catalysis. The area of energy storage has recently attracted a lot of interest as a possible use for MOFs. The usage of MOFs as materials for electrodes in supercapacitors and battery packs has been researched. MOFs provide a number of benefits over

conventional electrode materials, including increased power density, energy density, and cycle stability, ⁶⁵ because of their large surface area, porosity, and customizable characteristics. The ability to scale up and cost-effectiveness of MOF synthesis, their stability under various circumstances, and their possible toxicology and bio compatibility for biomedical uses are only a few of the issues that need to be resolved despite the promise that they hold.

1.4 PHOTOCATALYSIS

A method for catalysing chemical processes is called photocatalysis. A photocatalyst, a substance that ⁴³ absorbs light energy and uses it to initiate a chemical reaction, is used in this process. Metal oxides that can absorb light in the ultraviolet (UV) region, such as titanium dioxide (TiO₂), are the most frequently used photocatalysts. The photocatalyst is subjected to light during a photocatalytic reaction, which activates the material's electrons. As a result, electron-hole pairs are produced, allowing them to interact with the other molecules in the surroundings. The electron-hole couples can create reactive forms of oxygen or other reactive compounds when they interact with specific molecules, such as oxygen or water. These reactive compounds can then interact with organic or inorganic molecules. Manufacturers, most notably pollution clean-up, use photocatalysis. For instance, photocatalysis can be used to purge the air and water of organic pollutants like dyes, pesticides, and medicines. Additionally, it can be applied to clean surfaces and destroy bacteria in the effluent. Photocatalysis has applicability not only in the environment but in a variety of industries. It can be employed to produce energy, for instance, by turning sunlight into power or by producing hydrogen from water.

Although photocatalysis has a lot of possible advantages, there are drawbacks to the method as well. The performance of a reaction, for instance, can be influenced by a variety of elements, including the dimension and form of the photocatalyst particles, the makeup of the natural atmosphere, the intensity and duration of the illumination, and the specific light wavelengths needed to initiate the reaction. The possibility for the formation of by-products or intermediates that could also be detrimental to the surroundings or people's health seems to be another issue with photocatalysis. For instance, the photocatalytic breakdown of some natural contaminants can produce toxic by-products, which need to be closely monitored

and managed to reduce their effects. Regardless these difficulties, photocatalysis is an efficient strategy that shows promise for addressing a range of ecological issues. Photocatalysis is a system that can purify water and is also environmentally friendly because it only uses light and no extra chemicals or power sources. Significant growth has been shown in the creation of new photocatalytic materials and processes in recent years, including the use of novel catalysts like graphene and novel light sources like LEDs. Additionally, investigators investigate how to incorporate photocatalysis into already-in-use technologies like water purification facilities and air ventilation systems. The capacity to function under slight reactions, the relatively inexpensive, and the possibility for use in a variety of applications are some of the main benefits of photocatalysis. Furthermore, photocatalysis is an ecologically sound and financially viable technology that doesn't generate waste or toxic by-products, making it a potential replacement for conventional chemical treatment techniques.

The creation of novel catalysts that are more successful and productive than existing materials is the field of photocatalysis research that is currently in progress. For instance, investigators are looking into the use of novel substances like perovskites and metal-organic frameworks (MOFs), which have demonstrated promising outcomes in laboratory experiments. For instance, scientists are looking into how to modify photocatalytic materials and reaction circumstances to eliminate pollutants from water or air. The creation of self-cleaning areas is a further possible use for photocatalysis. To produce a self-cleaning action, photocatalytic coverings may be added to areas like buildings or textiles because they can aid in the degradation and elimination of contaminants or organic matter that collects on the exterior. In the food industry, where it's feasible to employ it for conservation and protection, and sanitation, photocatalysis may also find use. To stop the development of dangerous bacteria and increase the longevity of food items, for instance, photocatalytic coverings could be applied to the materials used in packaged foods. In conclusion, photocatalysis is a viable technology with a broad spectrum of potential uses in sectors like energy generation and environmental clean-up. Studies is currently being done to increase the effectiveness and productivity of photocatalytic reactions, create novel catalysts, and investigate new uses for this technology. Photocatalysis has the possibility of growing into a potent tool for addressing some of the most

alarming environmental and energy-related problems of our time with ongoing growth and improvement.

Due to their clearly defined and adaptable porous architectures, substantial surface areas, and other characteristics, metal-organic frameworks (MOFs), which exhibit semiconductor-like behavior, have lately attracted widespread fascination with photocatalysis and photothermal catalysis. These benefits serve to overcome the above mentioned difficulties and, in particular, make it easier to determine the structure-activity link. They are useful for logical structural manipulation for enhanced luminescence and separation of charges as well as other impacts. To speed up future progress, it is crucial to summarise this field of study and offer in-depth explanations of MOF-based photocatalysis and photothermal catalysis. MOFs offer several benefits over conventional metal oxide semiconductors, including large specific areas of the surface, rich topology, and readily modifiable porous structure. Metal-organic frameworks (MOFs) are a subclass of permeable crystalline materials made up of organic linkers and metallic vertices (such as metal ions). Fe-MOFs are much more desirable than MOFs with large band gaps. Light may directly excite the large Fe-O clusters, improving the efficiency with which energy is used. Fe-MOFs have reportedly been shown to break down a variety of organic contaminants when exposed to visible light. To speed up the deterioration process, H₂O₂ was often added in most cases as an electron acceptor. Additionally, utilizing (NH₄)₂C₂O₄ as the H⁺ scavenger, photocatalytic suppression of Cr(6+) may also be accomplished on MIL-53(Fe). Environmental degradation and the crisis in fossil fuels are now two of the main issues preventing human existence and advancement. When evaluating structure-property connections, the crystal structures of MOFs may easily be used to highlight their highly sequential and crystalline character. Though weak coordination connections, as opposed to the more robust covalent bonds that are seen in typical adsorbent compounds, may result in the breakdown of structure when guest molecules are included in the framework and then removed. Exposure to heat and guest removal cause the MOF structure to change, which may indicate that the material lacks full crystallinity. Numerous MOFs with consistency up to 300 or 400°C have been created, making them appropriate for the majority of applications. This is because a stiff, highly thermostable framework is thought to be of functional benefit. Because of their unique and diverse structural traits, MOFs

can be regarded as being appropriate for innovative practical applications. The mixed-metal/linker technique has been created to create more effective MOFs with desirable features by employing multiple metals in a single (mixed-metal), respectively, due to the adaptability and flexibility of MOFs. A MOF structure may often be modified post-synthesis or solvothermally to include more metal ions or linkers. Regarding MOFs with diverse metals, partial replacement of metal cores may be able to control both their effectiveness as photocatalysts and how effective they are at charging separation. Photoactive visitor species can be integrated into the spaces between molecules or partially stabilised on the exterior of MOFs due to their porous properties. A attractive guest item are metal nanoparticles (MNPs), particularly tiny superior MNPs with varied structures and tailoring potential. Carbon compounds with excellent electrical conductivity were frequently utilized to create hybrid photocatalysts in conventional semiconductor photocatalytic systems. After the introduction of carbon compounds, photogenerated charges may rejoin less frequently. For instance, reduced graphene oxide (rGO), graphene oxide (GO), and carbon quantum dots (CQDs) were typical carbon compounds that might speed up the exchange of photogenerated charges. Similarly to this, combining carbon-based substances with MOFs can improve photocatalytic efficiency by addressing the drawbacks of quick charging recombination in pure MOFs. The release of commercial waste including heavy metal pollutants, which have a significant impact on ecological constituents and their life cycle, has had a negative impact on the health of humans, the environment, and aquatic life. One significant and necessary heavy metal that is employed in the agricultural, industrial, medical, medicinal products, and mining sectors but has a negative interaction and outflow source with water is chromium. The two main oxidised forms of chromium found in the release of wastewater are Cr(3+) and Cr(6+), both of which are hazardous elements that can cause cancer in both people and aquatic life. The extremely durable and water-soluble form of Cr(6+) builds up over time in human and primary algal tissues, straining unavoidable metabolic processes past their allowable limits. Therefore, it is crucial to treat Cr(6+) from industrial release, and adequate treatment procedures must be established to lower or eliminate these harmful substance's levels in industrial discharges before they are combined with water bodies. The major reason MOFs, a unique class of organic-inorganic hybrid supramolecular structures, may act as photocatalysts is that they combine photosensitizer and catalytic capability in

a single structure. Thus, one solid chemical can assist all three phases of photocatalysis. Photoactive MOFs can operate as more effective photocatalysts by reducing pollution and can quickly be reclaimed and regenerated owing to their solid shape, thereby providing financial benefits, by substituting the conventional photocatalyst, which often comprises heavy metals. The advancements of MOFs in the photo-degradation of organic contaminants in splitting water, wastewater, and photo-reduction of CO₂ are covered in a number of great research. Four core processes are involved in MOF-based photocatalysis, along with other specific properties that are essentially associated with the structure of their crystals. Photoexcitation, charge separation, surface reaction, transfer, transport processes, and charge carrier recombination are these basic operational activities as they pertain to MOF-based photocatalysis. The goal of the current study was to create a very porous MOF that was amino-functionalized. Additionally, it focuses on altering such nanomaterials to enhance their capacity for separating from complicated mixtures. To do this, solvothermal or post-synthetic methods were used to decorate the MOF with carbon material (rGO) to create NH₂-MIL-53(Fe)@rGO. To confirm the nano-sized and mesoporous qualities, the produced catalyst was also characterised for its structural, textural, and functional characteristics. The systematic studies on the elimination of Cr(6+) ions.

CHAPTER-2 LITERATURE SURVEY

- A study by **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 TiO_2 has a very high photodegradation rate, according to research. TiO_2 delicate film was created using the sol-gel technique. Only 46.5% of $\text{Cr}(6+)$ was eliminated at the exact same time. At a concentration of 50 ppm, $\text{Cr}(6+)$ 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 TiO_2 . TiO_2 eliminates 80% of the $\text{Cr}(6+)$, but ZnO removes just 45%, making ZnO a less efficient photocatalyst than TiO_2 .
- **Jang et al. (2020)** recorded NH_2 -ASNs, and NH_2 -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 NH_2 -functionalization on the efficiency of adsorption of $\text{Cr}(6+)$. NH_2 -ASNs and NH_2 -MSNs were shown to have maximal $\text{Cr}(6+)$ 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 $\text{Cr}(6+)$ ions from aqueous solutions. With maximal reduction efficiencies of 49.14 and 45.24 mg for MO and $\text{Cr}(6+)$ ions, respectively, the adsorption mechanism of the RGOeHat hybrids for MO and removal of $\text{Cr}(6+)$ follows PSO kinetic and Langmuir isotherm frameworks.
- **Abhilash et al (2018)** said When the photodegradation rate of $\text{Cr}(6+)$ 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 $\text{Cr}(6+)$ 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 $\text{Cr}(6+)$ solution pH.

3.1 AIM

The main goal of our project titled "SYNTHESIS AND CHARACTERISATION OF IRON BASED METAL ORGANIC FRAMEWORK AND DEGRADATION OF CHROMIUM 6+" is to degrade chromium 6+.

- Synthesis of Metal Organic Framework
- Characterization of Metal Organic Framework
- Degradation studies
- Regeneration studies

3.2 SCOPE

To create an optimum Chromium degradation method for a better environment, choosing an inappropriate method might result in more toxicity. So, Photocatalysis turns to be a better option for Chromium degradation.

Degradation of Chromium from water sources can be reduced.

- Several life-threatening diseases for Humans.
- Harmful to Other creatures and environment.
- Bad quality of water into good and clean water.
- Effects in plants metabolic activities.
- Hampering plant growth and yield.

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.

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

The solvothermal process was used to make $\text{NH}_2\text{-MIL-53(Fe)}$. Normally, 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°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].



Fig 4.1 Experimental image of a) Magnetic stirrer while synthesis of MOF $\text{NH}_2\text{-MIL-53(Fe)}$ b) Sonicator while synthesis of MOF $\text{NH}_2\text{-MIL-53(Fe)}$, c) Conical Flask shaker while synthesis of MOF $\text{NH}_2\text{-MIL-53(Fe)}$.

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 muffles 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.

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 NH₂- MIL-53(Fe)/rGO was obtained. These materials are used for photocatalysis removal of Cr(6+).



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

4.5 PHOTOCATALYTIC DEGRADATION OF CHROMIUM

A 1000 ppm solution of Cr (6+) ions was made using Equation (1) as a guide. With 200 rpm of stirring, 2.8574 ± 0.005 g of 99% pure potassium dichromate ($K_2Cr_2O_7$) salt was mixed in 1000 ml of deionized water. The stock solution was diluted to create the necessary starting concentration of Cr (6+) ion solutions, which were then examined using an atomic adsorption spectrometer (AAS, SL176, Elico, India).

$$2.8574 \text{ g of chromium salt / g of Cr(VI) ions} = \frac{\text{Molar mass of } K_2Cr_2O_7}{\text{Atomic weight of Cr} \times 2 \times (\% \text{ Purity of } K_2Cr_2O_7)} \quad (1)$$

The chromate stock solution containing 1 L was used for all batch investigations. A chromate solution's absorbance was calculated. At $\lambda_{\text{max}} = 540$ nm, the calibration curve for Cr(6+) was discovered. For photocatalytic degradation, the photocatalysts' homogeneous particle sizes ranged from 120 to 500.

To determine the highest % removal under ideal working circumstances, a single-stage steady-state batch experiment was carried out for the elimination of Cr (6+) from its aquatic mixture. The impact of pH and the catalyst dosage on Cr (6+) elimination process was examined using 0.5 to 2 g of catalyst in every 250 ml conical flasks which include 100 ml of Cr(6+) solutions ranging from 100 mg/L to 500 mg/L and including either 0.1 M of HCl which breaks down H^+ ions converting the resulting solution into acidic or 0.1 M of NaOH which breaks down OH^- ions causing it to turn into basic to alter the resultant solution's pH values that vary from 2 to 12 under UV light. By changing the starting Cr(6+) concentrations at each comparable period of time from 5 to 100 min, the relationship between duration and the initial Cr(6+) concentrations was examined. During reaching an equilibrium time of 60 min, these flasks were continually stirred by a magnetic stirrer at a rate of 500 rpm. By retaining it on the outside of each flask, the catalyst fragments were segregated from the remaining solutions. After Cr(6+) adsorption, the final concentrations were examined.

$$\% \text{ Cr(6+) removal} = \left(1 - \frac{C_{t=\infty}}{C_{t=0}}\right) \times 100 \quad (2)$$

where $C_{t=0}$, and $C_{t=\infty}$ is the concentrations of Cr (6+) (mg/L) at initial time and at time t .

Analysis of the metal reduction from aqueous solution during an uninterrupted interval served as the basis for the kinetics investigation. By modifying the pH of the chromium hexavalent mixture with the incorporation of the necessary volume of

10

NaOH and HCl in the different flask at pH 2-11, a specifically calculated quantity of

38

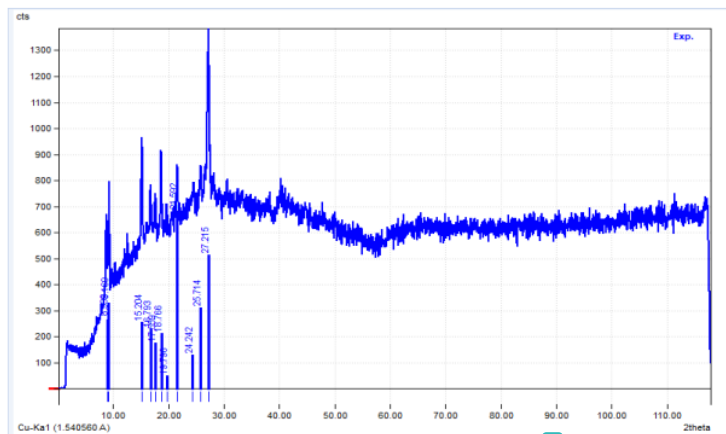
NH₂- MIL-53(Fe)/rGO was taken in 100 ml solution in every trial. The flask was then

placed under a UV lamp while being constantly stirred by a magnetic stirrer.

CHAPTER-5 RESULTS AND DISCUSSION

5.1 STRUCTURAL CHARACTERISATION OF $\text{NH}_2\text{-MIL-53(Fe)/rGO}$

5.1.1 X-Ray Diffraction (XRD)



Two elements are readily visible on the outermost layer of the a 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)

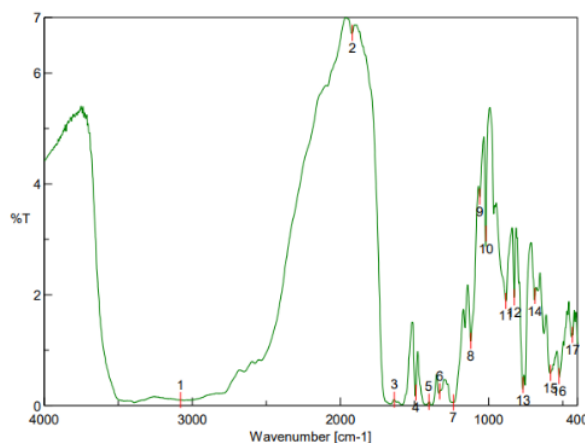


Fig 5.3 FT-IR analysis image of the MOF catalyst $\text{NH}_2\text{-MIL-53(Fe)}$ rGO

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).

5.2 EFFECT OF VARIABLES ON THE DEGRADATION OF CHROMIUM 6+

5.2.1 EFFECT OF CHROMIUM CONCENTRATION

To look at how its starting concentration affects degradation. For this study, chromium concentrations ranging from 100 ppm to 500 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 100ppm to 500ppm of chromium, Fig. 5.4 shows the fluctuation in the quantity of chromium degrading with contact time. This concentration's catalyst dose is 0.5g. For various catalyst dosages, the similar pattern was discovered[2, 4].

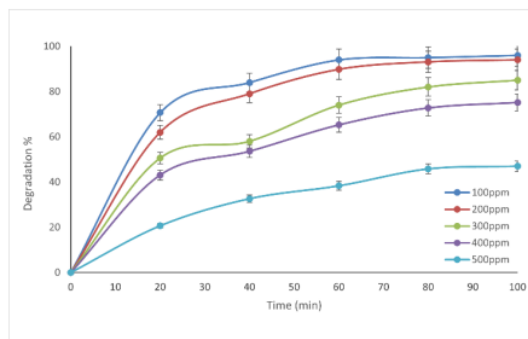


Fig 5.4 Effect of chromium concentration graph which is plotted for time vs percentage degraded.

5.2.2 EFFECT OF CATALYST DOSAGE

The degradation of chromium 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 chromium's 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 for the degradation of chromium 6+ [5-7].

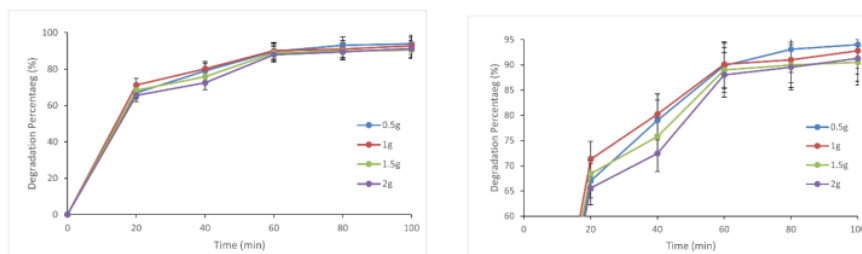


Fig 5.5 (a) Effect of catalyst dosage graph which is plotted for time vs percentage degraded, (b) Effect of catalyst dosage graph zoomed version which is plotted for time vs percentage degraded.

35

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

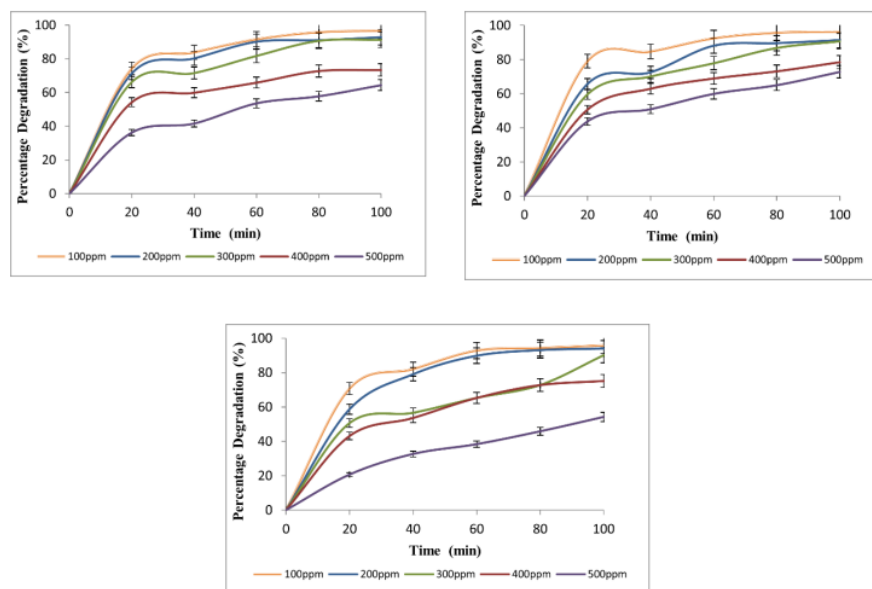


Fig 5.6 Effect of Time graph which is plotted for time vs percentage degraded (a) 0.5g Catalyst dosage, (b) 0.5g Catalyst dosage, (c) 0.5g Catalyst dosage.

³⁵ 5.2.4 EFFECT OF pH

Fig. shows the influence of pH on chromium degradation when subjected to UV radiation. The chromium 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.

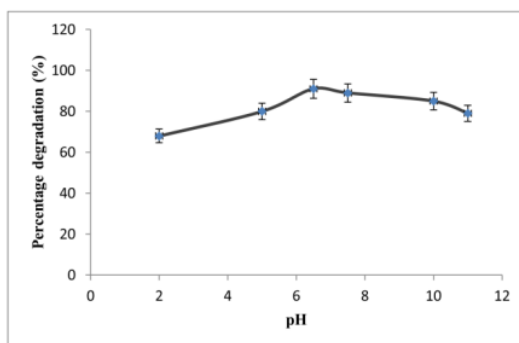


Fig 5.7 Effect of pH which is plotted for pH vs percentage degraded

5.2.5 EFFECT ON 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 93%.

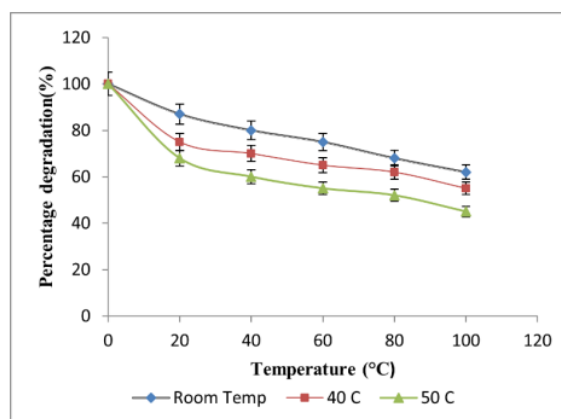


Fig 5.8 Effect of temperature graph which is plotted for temperature vs percentage degraded.

5.3 KINETICS

Kinetic models that include the pseudo-first-order, Arrhenius equation, and Langmuir isotherm model were used to analyse the process of adsorption.

5.3.1 LANGMUIR ISOTHERM

Several investigators have used the Langmuir isotherm to model photocatalysis. This model incorporates the observed adsorption characteristics of the base on the photocatalyst surface [9, 10]. According to Langmuir's theory, an adsorption is a form of unimolecular chemical mixture or reaction. A linear plot of C_e/q_e versus C_e must be linear to correspond to the Langmuir isotherm [11, 9]. q_e is the initial chromium concentration (mg/l), and C_e is the equilibrium chromium concentration (mg/l). The Langmuir plots for photocatalysis data are shown in the figure.

The rate of reaction can be expressed as:

$$r = (dC/dt) = (kKC / 1+KC) \quad (3)$$

r is the rate of the reactant (mg/L min), C is the concentration of the reactant (mg/L), t the illumination time, k the reaction rate constant (mg/L min), and K is the adsorption coefficient of the reactant (L/mg).

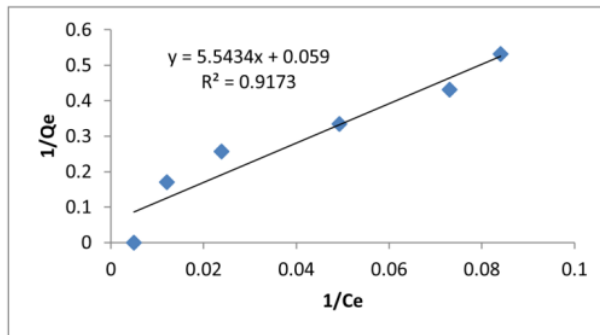


Fig 5.9 Langmuir Isotherm Graph plotted for $1/C_e$ vs $1/Q_e$

5.3.2 PSEUDO FIRST ORDER REACTION

³⁷ If the chemical concentration C is low, equation (3) can be reduced to an obvious first-order equation.

$$\ln (C_o/C_i) = kt \quad (4)$$

⁵⁸ $k = [(C_o/C_i) / t]$ is the apparent pseudo-first-order reaction rate constant. (5)

²⁹ A plot of $\ln C_o/C_i$ vs time yields a straight line, the slope that equals the apparent first-order rate constant k via linear regression [12].

⁹ Figure 5.10 depicts a plot of $\ln C_o/C_i$ 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. ⁹ 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.

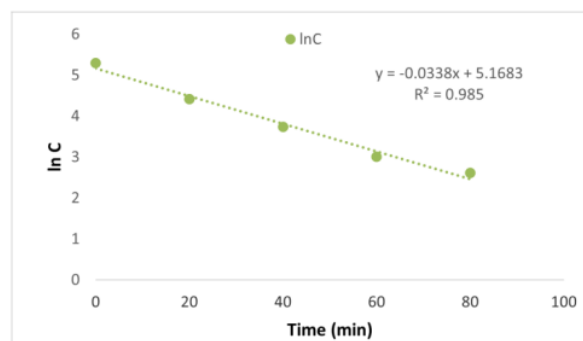


Fig 5.10 Pseudo first order reaction graph for time vs ln C

5.3.3 ARRHENIUS EQUATION

Equation (6) was used to study the temperature influence on the kinetic model and compute the activation energy for Chromium 6+ degradation on the NH₂-MIL-53(Fe) rGO photocatalyst.

$$k_a = k_2 \exp(-E_a/RT) \quad (6)$$

The logarithmic method of Equation (6) was employed, and the plots of ln (k_a) vs 1/T are given in Fig. The activation energies were calculated using the slopes of the shown graphs. The activation energies (E_a) determined for the NH₂-MIL-53(Fe) rGO photocatalyst are 65.58 kJ/mol [14].

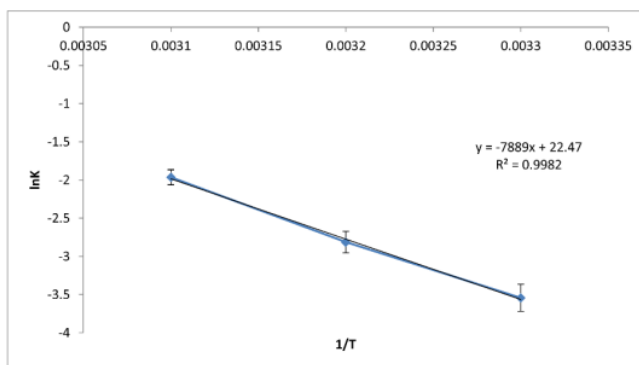


Fig 5.11 Arrhenius equation graph for 1/T vs ln K.

5.4 STATISTICAL ANALYSIS WITH ³¹RESPONSE SURFACE METHODOLOGY

RSM is a method that may be used to explore the cumulative impact of numerous factors and to find the best settings for a multivariate system. RSM is currently actively used for physical conditions, time, dose, pH, and initial concentration process optimization. ¹²RSM is a collection of statistical and mathematical instruments for defining the connection between the outcome and the variables that are not dependent. The degradation of chromium in this investigation is carried out utilizing NH₂-MIL-53 (Fe). For the degrading process, RSM with CCD was used to discover potential interactions and select the best operational settings. Physical factors such as dose, pH, duration, and beginning chromium concentration have been optimized.

In traditional experiments, optimization is often performed by altering a single element while holding all other parameters constant under a defined set of conditions. This procedure needs several experiments and is time intensive. To bypass the constraints of the traditional technique, the empirical design of experiments can be utilized to optimize process parameters. RSM is an excellent statistical approach for planning such experiments, developing models, and examining complicated processes for target value optimization. To overcome the constraints of a single-factor optimization procedure, RSM may jointly optimize all influencing parameters. RSM, which comprises factorial structure and regression analysis, aids in evaluating relevant factors, developing ²²models to examine the interactions between variables, and selecting of relevant factors, the development of ²²models to examine the interactions between variables, and the selection of the ideal set of variables or desirable results. Photocatalysis was used in this study to optimize physical parameters for chf. Physical parameters such as dose, duration, pH, and beginning phenol concentration were optimised. RSM is being recommended for determining the impacts of individual elements as well as their interactions. The interplay of potential affecting parameters on the effectiveness of treatment can be examined using RSM a minimal scheduled test. Individual components' relevance, the suitability of this functional form, and the degree of sensitivity of how it reacts to each factor may all be assessed using statistical inference techniques. Many quantitative designs for experiments approaches have recently been used for bioprocess optimization. RSM is the only one that is

adequate for determining the influence of individual variables and effectively obtaining the ideal conditions for a multivariate system. This approach has been used to improve alcoholic fermentation along with various fermentation mediums. RSM is an empirical modulation approach that establishes a link among a set of specified experimental variables and observed outcomes. To create a statistical model, you must first understand the processes. Essentially, the optimization process consists of three primary steps: predicting the coefficients in a mathematical model, forecasting the response, and assessing the model's suitability.

5.4.1 ANALYSIS OF VARIANCE:

ANOVA (Analysis of Variance) is a statistical approach for analysing data variations across groups. ANOVA may be used in the framework of chromium degradation to find the relevant parameters that affect chromium degradation, such as pH, temperature, catalyst dose, and concentration. A model that is quadratic is a mathematical framework that incorporates a quadratic (squared) element as well as linear terms. A quadratic model may be employed in the framework of chromium deterioration to represent the nonlinear connection between the factors that are entered (such as temperature and time) and the value of the output (such as degradation percentage). When the connection between both the input and the output variables is not linear, this might be advantageous.

Table 5.1 RSM generated response 1 : degradation.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	228.36	14	16.31	71.86	< 0.0001	significant
A-pH	87.13	1	87.13	383.89	< 0.0001	
B-Concentration	0.4082	1	0.4082	1.80	0.1999	
C-Dosage	2.36	1	2.36	10.41	0.0057	
D-Time	0.8177	1	0.8177	3.60	0.0771	

19	AB	0.3875	1	0.3875	1.71	0.2110	
	AC	0.1580	1	0.1580	0.6961	0.4172	
	AD	0.0371	1	0.0371	0.1633	0.6919	
	BC	0.1351	1	0.1351	0.5950	0.4525	
	BD	0.0163	1	0.0163	0.0716	0.7926	
	CD	1.31	1	1.31	5.75	0.0299	
	A ²	125.58	1	125.58	553.25	< 0.0001	
	B ²	0.8795	1	0.8795	3.87	0.0678	
	C ²	0.0446	1	0.0446	0.1964	0.6640	
	D ²	0.0070	1	0.0070	0.0307	0.8633	
	Residual	3.40	15	0.2270			
	Lack of Fit	0.9155	10	0.0916	0.1839	0.9887	not significant
	Pure Error	2.49	5	0.4978			
	Cor Total	231.76	29				

14 Coding for factors is used.

The sum of squares is of partial Type III.

13 The predicted result is likely significant given the Model F-value of 71.86. An F-value this big might happen to owe to noise just 0.01% of the time.

Model terms are considered important when the P-value is less than 0.0500. In this instance, key parameters of the model were A, C, CD, and A2. The parameters of the model are not essential if the value is higher than 0.1000. Reduced complexity may enhance your model if it has a lot of unnecessary words (except those needed to maintain hierarchy).

15 The F-value for the lack of fit, 0.18, indicates that the absence of a match is not notable in comparison to the basic error. A significantly inadequate Fit F-value has a 98.87% likelihood of being caused by noise. Since we desire the model to fit, an unimportant failure to fit is desirable.

Fit Statistics

Table 5.2 RSM generated fit statistics.

³² Std. Dev.	0.4764	R ²	0.9853
Mean	86.87	Adjusted R ²	0.9716
C.V. %	0.5484	Predicted R ²	0.9618
		Adeq Precision	39.6185

⁷The Predicted R² of 0.9618 and the Modified R² of 0.9716 are reasonably in conformity; that is, the variance between them is under 0.2.

The ratio of signal to noise is measured with Adequate Precision. A ratio of at least 4 is preferred. Your signal is strong enough based on the factor of 39.618. To move about the design space, utilize this model.

5.4.2 Central Composite Design

With a limited number of components, the CCD technique may be effectively used to create the second-order response model. The CCD is divided into three separate elements: (1) the full design, in which the levels of factors are coded to the typical low (1) and high (+1) values; (2) axial points on the axis of each variable away from the designed centre; and (3) centred points that can be copied for determining the error of the experiment's variance [17]. The best value was predicted using a second-order polynomial quadratic equation, which was then used to clarify how the variables interacted. The equation is the quadratic equation model for finding the ideal spot.

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1, i < j}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j \quad (7)$$

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 \quad (8)$$

where Y is the anticipated response, X1, X2, X3, and X4 are variables that are independent, b0 is the value of the offset term, and 1, 2, 3, 4 are coefficients of linear effects, 11, 22, 33, 44 are coefficients of squared effects, and 12, 13, 14, 23, 24, 34 are coefficients of interactions. 6 cross-interactions, four quadratic terms, and 4 linear terms make up the regression equation. The 5% level of significant ANOVA was used to assess the empirical mathematical model. The second-order models' importance was examined using ANOVA. F-value is used to gauge the second-order model equation's significance in statistics. To reject the null hypothesis, which states that all of the coefficients of regression are zero, the computed F-value often has to be higher than the tabulated F-value. At a particular level of significance, known as the p-value, tabulated F-values for regress and leftovers are produced using F distributions based on DF, respectively [19, 18]. Chromium deterioration physical parameter optimisation is done using CCD.

5.4.3 Interaction effects on operating parameters at optimum conditions

A 3D surface plot may display the interaction impact between two independent factors on the rate of deterioration. It was demonstrated how two distinct variables along with one additional variable set at an established level affected the rate at which chromium was degraded by NH₂-MIL-53 (Fe) at rGO. According to Fig. 5.12, percentage degradation rose up to the ideal level as dosage (C) and duration (D) were increased. A rise in percentage deterioration was seen as the starting concentration rose from 100 to 500 ppm and the duration increased from 0 to 100min. After that, a rise in starting intensity and duration was accompanied by a drop in the degradation percentage. When the starting concentration was 100 mg/l, the greatest percentage degradation of 93.34% was discovered to occur after 60 minutes. The proportion of degradation reduces if starting concentration or pH are raised further.

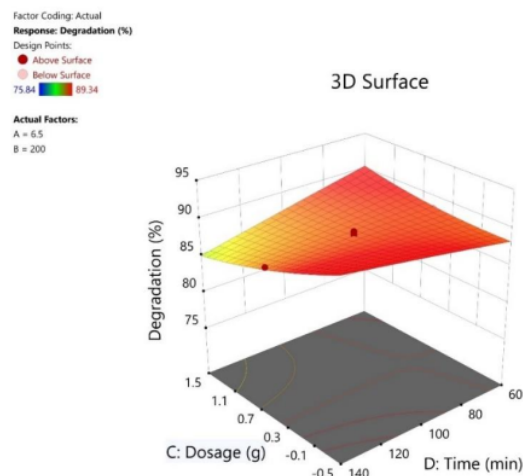


Fig 5.12 RSM graph plotted for Dosage (C) vs Time (D).

In Fig. 5.13, the influence of two variables—pH (B) and temperature (A)—on deterioration is depicted. As temperature and pH rose, so did the percentage of degradation, which eventually reached its maximum value. A rise in percentage degradation was seen as the temperature reached 30 °C and the pH rose from 2 to 6.5. After that, when temperature and pH increased, the proportion of deterioration decreased. pH 6.5 and a temperature of 30 C were determined to have the highest degradation percentage of 93.57%. The proportion of deterioration reduces if temperature or pH are raised more.

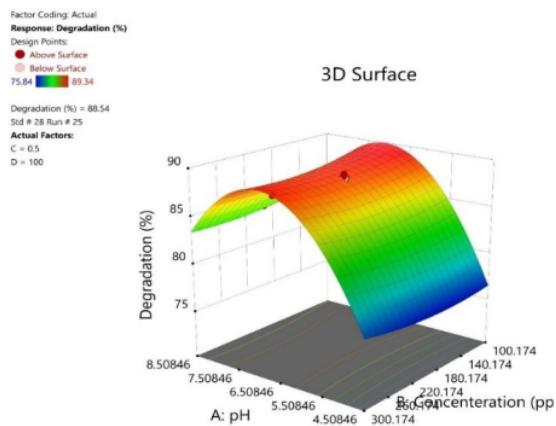


Fig 5.13 RSM graph plotted for pH (A) vs Concentration (B)

The interaction impact on the starting concentration ratio (C) and temperature (A) is depicted in Fig. 5.14. A rise in the percentage of degradation was seen as the starting concentration went from 100 to 500 mg/l and the temperature went from 30 to 50 °C. Following that, a rise in starting temperature and concentration was accompanied by a drop in the degradation percentage. A temperature of 30 C and starting concentration of 200 mg/l were determined to have the highest percentage degradation rate of 93.57%. The proportion of degradation reduces if starting concentration or pH is raised further.

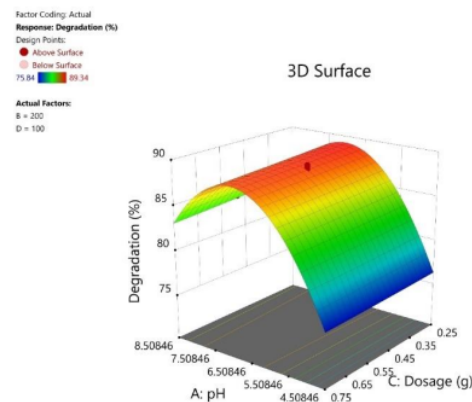


Fig 5.14 RSM graph plotted for pH (A) vs Dosage (C).

In Fig. 5.15, the interaction between time (D) and temperature (A) was shown to boost percentage deterioration up to the ideal level. A rise in the percentage of deterioration was shown when the period between 0 to 100 min and the temperature rose from 30 to 50 C. After that, a rise in time and temperature was followed by a drop in percentage deterioration. The temperature of 30 C and period of 60 min. were determined to have the highest percentage deterioration of 93.54%. The percentage deterioration drops as time or temperature are increased more.

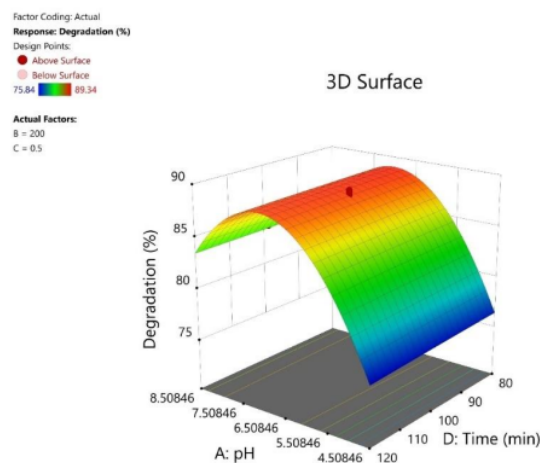


Fig 5.15 RSM graph plotted for pH (A) vs Time (D).

This is represented as starting concentration (C) and pH (B) in Fig. 5.16. A rise in percentage degradation occurred as the starting concentration was raised from 100 to 500 mg/l and the pH was raised from 2 to 6.5. Following that, a rise in starting concentration and pH was accompanied by a reduction in the percentage degradation. A pH of 5.6 and an initial concentration of 200 mg/l were determined to have the highest percentage of degradation (91.58%). The percentage drops if starting concentration or pH is raised more.

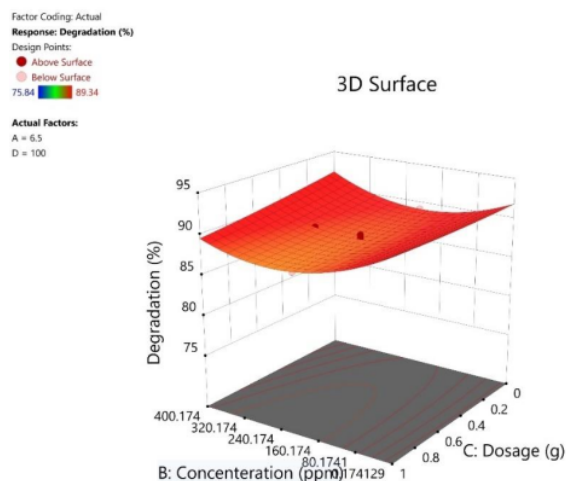


Fig 5.16 RSM graph plotted for Concentration (B) vs Dosage (C).

Fig. 5.17 depicts the interaction between time (D) and pH (B). A rise in the percentage of deterioration was seen when the period between 0 to 100 min and pH rose from 6.5 to 11. After that, as time and pH increased, a decline in the percentage of deterioration was seen. The greatest degradation rate of 93.57% was discovered at pH 6.5 and 60 minutes. The proportion of deterioration reduces when time or pH are increased further.

Performing the study with an initial concentration of 200 mg/l, pH 6.5 at 30 °C for 60 minutes resulted in an experimentally verified 92.87% degradation, which was used to validate the statistical framework. The experimental results are in good shape with the projected values, as evidenced by the linear correlation plot comparing the adjusted R² and predicted R². As a result, it was determined that the models were sufficient for illustrating the response data of % degradation of chromium, allowing for further analysis and forecasting.

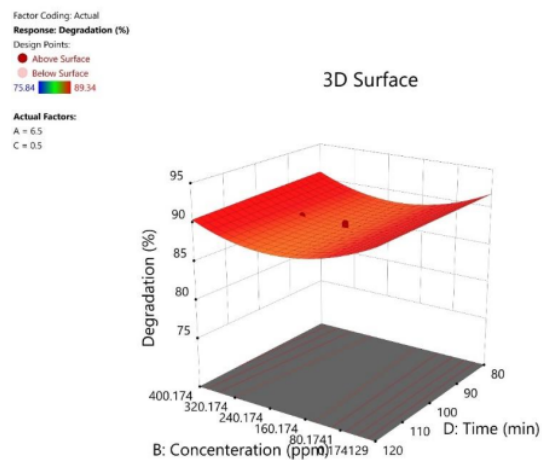


Fig 5.17 RSM graph plotted for Concentration (B) vs Time (D).

5.4.3.2 INFERENCE FROM 3-D SURFACE PLOT:

Finding relationships among process factors: The 3-D graph may occasionally show connections between various process variables that influence the degradation of chromium. A three-dimensional graph is an invaluable tool for comprehending the

basic links between process factors and deterioration since these interactions might not be visible in two-dimensional contour graphs.

5.4.4 PREDICTION VS ACTUAL :

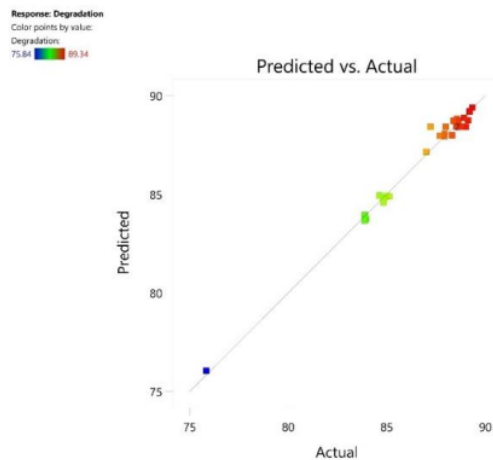


Fig 5.18 RSM graph plotted for Actual vs predicted.

5.5 CHROMIUM DEGRADATION

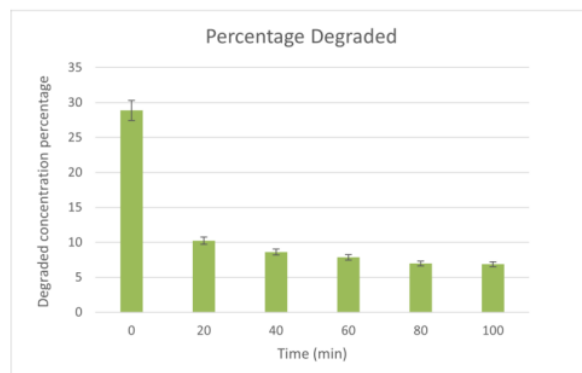


Fig 5.19 Graph of Chromium degradation plotted for Time vs Degradation concentration percentage.

The amount of chromium in the water is determined from the ICP-OES (Inductively Coupled Plasma - Optical Emission Spectroscopy) results. Fig 5.19 It demonstrates that the amount of chromium in the water decreases as time goes on, and at 60 minutes it achieves the maximum degradation of 7.43, indicating that 92.57% of the chromium has been eliminated from the water.

5.6 REGENERATION STUDIES

For every of the examined catalysts, the tests were run five times to examine the endurance of the catalyst for chromium oxidation. A constant starting chromium content of 200 mg L⁻¹ was used, along with a pH of 6.5 and a 60-minute irradiation period. The features of the heterogenous catalyst allowed for the recycling process to be carried out without any complications. One benefit of utilizing this type of catalyst is that it is simple to separate the spent catalyst from the testing solvent, and the recyclable components just require washing and oven drying before being reused [18]. The photocatalytic performance of the bare NH₂-MIL-53(Fe) rGO declined by roughly 54 percent in the fifth cycle after lasting continuously for about 2 cycles. The decline may be the result of the synthesized catalyst's surface area aggregating after numerous cycles and going through several heat treatments. For the 200 ppm NH₂-MIL-53(Fe) rGO catalyst, a high level of chromium removal (>90%) was sustained up to the two cycles. The third, fourth, and fifth cycles saw a minor decline in performance. Figure 5.19 depicts chromium degradation, which shows a deterioration of more than 90% from the initial value and a progressive decline. The catalyst can therefore be reused two to three times, depending on the degree of deterioration.

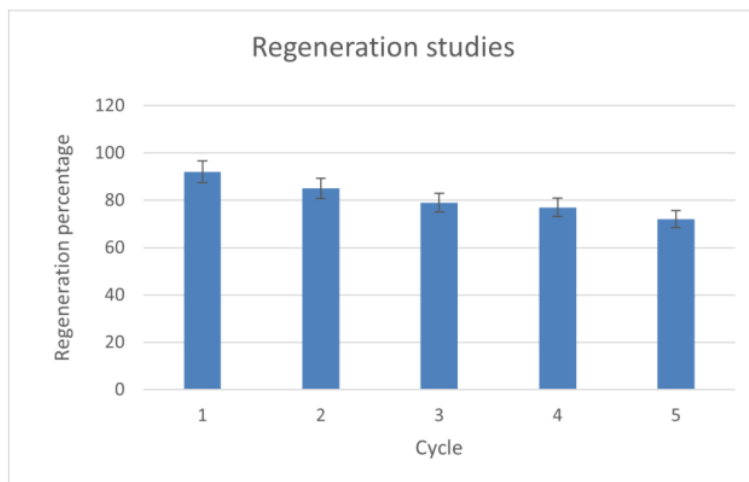


Fig 5.20 Graph of Regeneration studies plotted for cycle vs regeneration percentage.

CHAPTER-6 SUMMARY AND CONCLUSIONS

Effective synthesis of NH₂-MIL-53(Fe) with rGO is achieved. The MOF was rendered more stable with the addition of an amino group, and the catalyst for the photocatalytic process utilised to degrade chromium was made more effective by the addition of reduced graphene oxide. FE-SEM, XRD, and FT-IR were used to characterise the synthesised MOF catalyst. The usage of NH₂-MIL-53(Fe) with rGO for chromium 6+ degradation has demonstrated encouraging results, according to the existing research. High catalytic activity for the photocatalysis process was shown by the NH₂-MIL-53(Fe) with rGO, which also led to more chromium 6+ degradations. Additionally, NH₂-MIL-53(Fe) with rGO has demonstrated strong stability and reusability, which is crucial for manufacturing at a commercial scale. RSM was used to examine the ideal operating circumstances, which is an efficient and cost-effective method of improving operational conditions. RSM may be used to control operational parameters such as reaction temperature, catalyst dose, pH, irradiation time, and pollutant initial concentration. Additionally, it was discovered that the pH should be kept at 6.5, the initial concentration should be 200 mg/L, the catalyst dosage should be 0.5g, the temperature should be kept at room temperature, and the irradiation time should be 60 minutes, all of which satisfy the actual conditions determined by the UV spectrometer. According to RSM findings, the projected and actual operational conditions values are virtually identical outcomes. Chromium 6+ degradation is 92.57%, which was validated by an ICP-OES investigation. In contrast, increasing the catalyst dose doesn't significantly change the degradation percentage. Another crucial step in demonstrating the application of photocatalytic reactions is to investigate their kinetics. According to the analysis of the literature, the most plausible kinetics model for characterising photocatalysis processes is Langmuir-Hinshelwood's pseudo-first-order model. With apparent rate constants (k_{app}) of 0.0338 min⁻¹, the experimental findings for Cr were compatible with the pseudo-first-order kinetics concept (R^2 values near 1). It also creates a linear graph for the 200 mg/L concentration, satisfying the Langmuir isotherm. The potential for NH₂-MIL-53(Fe) reuse with rGO is also encouraging. It is regenerable for a maximum of three times, giving degradation percentages of 92.57%, 88%, and 79%, respectively. The deterioration percentages for the fourth and fifth are 76% and 72%, respectively.

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