

SYNTHESIS AND CHARACTERISATION OF DOPED ZIF-8 FOR THE REMOVAL OF IBUPROFEN

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

by

ABDUL HAMEED .H (40190001)



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

**SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)**

**Accredited with Grade “A++” by NAAC
JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI - 600 119**

APRIL - 2024



SATHYABAMA

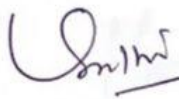
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)

Accredited "A++" Grade by NAAC | 12B Status by UGC | Approved by AICTE
www.sathyabama.ac.in

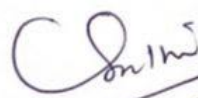
DEPARTMENT OF CHEMICAL ENGINEERING

BONAFIDE CERTIFICATE

This is to certify that this project report is a bonafide work of **ABDUL HAMEED.H (REG.NO.40190001)** who carried out the project entitled "**SYNTHESIS AND CHARACTERISATION OF DOPED ZIF-8 FOR THE REMOVAL OF IBUPROFEN**" under my supervision from **NOVEMBER 2023 to APRIL 2024**.


06/APR/24
Internal Guide

Dr. SATHISH M.E., PH.D


06/APR/24

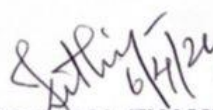
Head of the department

Dr. SATHISH M.E., PH.D



Submitted for viva voce Examination held on 06-4-24


INTERNAL EXAMINER


6/4/24
EXTERNAL EXAMINER

DECLARATION

I, **ABDUL HAMEED (Reg.No.40190001)** and hereby declare that the Project Report is the bonafide work of entitled **"SYNTHESIS AND CHARACTERISATION OF DOPED ZIF-8 FOR THE REMOVAL OF IBUPROFEN"** done by us under the guidance of **DR. SATHISH M.E, Ph.D.**, is submitted in partial fulfilment of the requirements for the award of Bachelor of Technology degree in **CHEMICAL ENGINEERING**.

DATE: 06-4-24

PLACE: CHENNAI


SIGNATURE OF THE CANDIDATE

ACKNOWLEDGEMENT

I am pleased to acknowledge my sincere thanks to Board of Management of **Sathyabama Institute of Science and Technology** for their kind encouragement in doing this project and for completing it successfully. I am grateful to them I convey my thanks to **Dr. S. SATHISH M.E., Ph.D.**, Head of the Department, and **Dr S. SATHISH M.E., Ph.D.,M.S (By Research), Ph.D.**, Dept. of Chemical engineering for providing me necessary support and details at the right time during the progressive reviews

I would like to express my sincere and deep sense of gratitude to my Project Guide. **Dr.S.SATHISH, M.E., (By Research), Ph.D.**, for his valuable guidance, suggestions, and constant encouragement paved way for the successful completion of my project work. I wish to express my thanks to all Teaching and Non- teaching staff members of the Department of Chemical Engineering who were helpful in many ways for the completion of the project.

ABSTRACT

In this study, doped zeolitic imidazolate framework-8 (ZIF-8) materials were synthesized and characterized for their efficacy in the removal of ibuprofen from aqueous solutions. The doped ZIF-8 samples were prepared using a solvothermal method, and their structural and morphological properties were analyzed using various characterization techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM), and nitrogen adsorption-desorption isotherms. The synthesized materials exhibited a high surface area and well-defined crystal structures, indicative of successful doping of the ZIF-8 framework. The adsorption behavior of ibuprofen onto the doped ZIF-8 materials was studied, and the experimental data were fitted to the Freundlich isotherm model. The maximum adsorption capacity ($Q_{\max}$) of the doped ZIF-8 materials was determined to be 12.59 mg/g, highlighting their excellent adsorption performance for ibuprofen removal. Furthermore, the kinetics of ibuprofen adsorption onto the doped ZIF-8 materials were investigated, and the data were found to follow a pseudo-first-order model. Thermodynamic parameters including the change in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) of the adsorption process were also calculated, revealing the spontaneous and exothermic nature of ibuprofen adsorption onto the doped ZIF-8 materials. Overall, this study demonstrates the potential of doped ZIF-8 materials as effective adsorbents for the removal of ibuprofen from aqueous solutions, offering promising applications in environmental remediation and water treatment processes.

TABLE OF CONTENTS

CHAPTER NO	TITLE	PAGE NO
	ABSTRACT	I
	LIST OF FIGURES	iv
	LIST OF TABLES	vi
1	INTRODUCTION	1
	1.1 BACKGROUND	1
	1.2 INTRODUCTION OF IBUPROFEN	2
	1.3 HARMFUL EFFECT OF IBUPROFEN IN WASTEWATER	3
	1.4 ZIF-8 INTRODUCTION	3
2	LITERATURE SURVEY	5
3	AIM AND SCOPE	10
	3.1 AIM	10
	3.2 SCOPE	10
4	MATERIALS AND CHEMICALS	
	4.1 MATERIALS	12
	4.2 METHODS	12
	4.3 PREPARATION OF ZIF 8 REACTIVE ADSORBENT	13
	4.4 PRECIPITATION AND CRYSTALLIZATION	13
	4.5 ADSORPTION OF IBUPROFEN USING ZIF-8	15
	4.6 STOCK SOLUTION OF IBUPROFEN	16

5	RESULT AND CHARACTERIZATION	
5.1	CHARACTERIZATION	18
5.2	FOURIER TRANSFORM INFRARED (FTIR)	19
5.3	SCANNING ELECTRON MICROSCOPY (SEM).	20
5.4	EFFECT OF PH	27
5.5	EFFECT OF ADSORBENT DOSAGE	29
5.6	EFFECT OF INITIAL CONCENTRATION	30
5.7	EFFECT OF CONTACT TIME	30
5.8	EFFECT OF TEMPERATURE	32
5.9	ADSORPTION ISOTHERM MODELS	32
5.10	LANGMUIR ISOTHERM	33
5.11	FREUNDLICH ISOTHERM	33
5.12	TENKIM ISOTHERM	34
5.13	ADSORPTION KINETIC MODELS	36
6	CONCLUSIONS	49
	REFERENCES	49

LIST OF FIGURES

FIGURE NO	TITLE	PAGE NO
4.1	2-METHYLIMIDAZOLE AND METHANOL WAS STIRRED	13
4.2	CENTRIFUGAL PUMP	14
4.3	CENTRIFUGAL TUBES	14
4.4	PREPARED OF ADSROPTION	15
4.5	IBUPROFEN	16
4.6	IBUPROFEN STOCK SOLUTION	16
4.6	CENTIFUGE SAMPLE OF DOSAGE	17
5.1	FTIR FOR ZIF-8	19
5.2	SEM FOR ZIF-8	21
5.3	EDAX FOR ZIF-8	22
5.4	EDAX FOR ZIF-8	23
5.5	FTIR FOR Post studies of ZIF-8	24
5.6	FSEM FOR Post studies of ZIF-8	25
5.7	POST STUDIES OF ZIF-8 (XRD)	26
5.8	PEAK REPORT OF XRD	27
5.9	EFFECT OF PH VS REMOVAL	27
5.10	ADSORBENT DOSAGE OF IBUPROFEN	29
5.11	EFFECT OF INITIAL CONCENTRATION VS REMOVAL	30
5.12	EFFECT OF CONTACT TIME VS REMOVAL	30
5.13	EFFECT OF TEMPERATURE VS REMOVAL	32
5.14	FREUNDLICH ISOTHERM OF IBUPROFEN	34
5.15	TENKIM ISOTHERM OF ZIF-8	35
5.16	ADSORPTION KINETICS FOR ZIF-8	36

5.17	PSEUDO SECOND ORDER	37
5.18	THERMODYNAMICS FOR ZIF-8	38

LIST OF TABLES

TABLE NO	TITLE	PAGE NO
5.1	ADSORPTION ISOTHERM PARAMETER	35
5.2	KINETIC PARAMETERS OF IBUPRUFEN	37
5.3	THERMODYNAMIC PARAMETERS	39

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Pharmaceutical waste (PhW) refers to any medication waste which is not fully consumed or remains unused throughout the pharmaceutical supply and uses chain. As pharmaceutical products are necessary for human health, to fulfill the growing need for pharmaceutical products, healthcare industries produce a huge number of drugs annually [1]. These pharmaceutical products contain biologically active ingredients referred to as active pharmaceutical ingredients (API). Any chemical constituent having pharmaceutical function with useful effects to diagnose, prevent, treat, or cure disease and affect the body's structure and function is considered an API. The API performs specific functions in animals and humans and is not completely degraded after metabolic reactions in the body. These chemicals are released into the environment from various sources and are referred to as PhW products [2]. PhW includes a variety of materials such as expired, split, contaminated drugs (used or unused), personally discarded patient's medication, discarded drugs, abandoned material (connecting tubes, masks, syringes, vials, bottles with residues), and containers that are used to keep hazardous waste drugs, spill cleanup materials, absorbents, and home use personal care products [3]. A major part of PhW is various drugs, serums, and vaccines such as antibiotics, hormones, chemotherapy products, and antidepressants. In response to acute or chronic illness, only a part of the active ingredient in the metabolized drug. The nonmetabolized part along with metabolized part enters the aquatic system by waste discharge. All these substances either from industrial or domestic sources discharged directly or indirectly into the water where they remain persistent for a longer time. In the 1970s, environmental contaminations due to pharmaceutical products were raised. The first analysis to estimate the concentration of pharmaceuticals in surface and potable water was performed in 1980. A very small amount of these pharmaceutical active compounds largely affects human health and the ecosystem. So, the removal of these waste materials from the environment is of utmost. Since the 1990s, the technology became adequately advanced to quantify

the concentration of PhAC in water samples at low levels, that is, $\mu\text{g/L}$ and ng/L [6]. Now, different methods have been established for the removal of API from the environment. But still, now different challenges arise for their removal due to their small concentration. The conventional methods for WWT involve coagulation, filtration, biological processes, sedimentation, membrane filtration, chlorination, adsorption (using carbon nanotubes, activated carbon, ozonation, and graphene oxide), photocatalysis, UV irradiation, and many others. The effects of API in the environment on nontarget species are unknown. However, one study revealed that in, the residual diclofenac was responsible to minimize the vulture population. The long-term exposure to API largely affects the physiology and growth of organisms. Therefore, unwanted medicine should be disposed of properly to overcome environmental and public health risks. Because the improper disposal of leads to accidental toxicity and ultimately results in landfill pilfering, antimicrobial resistance, water pollution, rising healthcare costs, and death. All these effects may be reduced by raising public awareness regarding disposal practices

1.2. Introduction of ibuprofen

Ibuprofen, a widely used nonsteroidal anti-inflammatory drug (NSAID), is renowned for its effectiveness in relieving pain, reducing inflammation, and lowering fever. With its mechanism of action primarily targeting the inhibition of cyclooxygenase enzymes, specifically COX-1 and COX-2, ibuprofen impedes the production of prostaglandins, thereby mitigating pain and inflammation. This medication is commonly employed to alleviate various conditions, including headaches, muscle aches, dental pain, menstrual cramps, arthritis, and minor injuries. Available over-the-counter and in prescription strength, ibuprofen offers a versatile option for managing mild to moderate pain and inflammation. However, it's essential to adhere to recommended dosages and guidelines, as excessive or prolonged use can lead to adverse effects such as gastrointestinal complications and cardiovascular risks. Consulting a healthcare professional is advised for proper usage and to minimize potential risks associated with ibuprofen intake.

1.3. Harmful effect of ibuprofen in wastewater:

The presence of ibuprofen in wastewater raises considerable environmental concerns due to its potential adverse effects on aquatic ecosystems. As ibuprofen enters wastewater through various pathways including human excretion and improper disposal, it becomes a persistent contaminant in water bodies. Once introduced into aquatic environments, ibuprofen and its metabolites can exert toxic effects on aquatic organisms such as fish, algae, and invertebrates. Even at low concentrations, ibuprofen can disrupt physiological processes, impair growth, and interfere with reproductive functions in these organisms. Furthermore, ibuprofen's ability to bioaccumulate within the food chain exacerbates its environmental impact, posing risks not only to aquatic species but also to humans who consume contaminated seafood.

To address the environmental risks associated with ibuprofen in wastewater, concerted efforts are required to promote proper disposal practices and enhance wastewater treatment technologies. Public awareness campaigns and pharmaceutical take-back programs can encourage individuals to dispose of unused medications responsibly, reducing the likelihood of ibuprofen entering wastewater in the first place. Additionally, advancements in wastewater treatment processes, such as advanced oxidation, membrane filtration, and activated carbon adsorption, can improve the removal efficiency of pharmaceutical compounds, including ibuprofen, from wastewater. By implementing these measures, we can minimize the environmental footprint of ibuprofen and protect the integrity of aquatic ecosystems for present and future generations.

1.4. ZIF-8 INTRODUCTION

ZIF-8, short for Zeolitic Imidazolate Framework-8, represents a pivotal advancement in the realm of metal-organic frameworks (MOFs), a class of porous materials renowned for their diverse applications. Characterized by its unique structure comprising zinc ions coordinated with imidazolate ligands, ZIF-8 exhibits exceptional thermal and chemical stability, rendering it suitable for a wide array of applications ranging from gas storage and separation to catalysis and drug delivery.

Its high surface area, tunable pore size, and remarkable adsorption properties make ZIF-8 particularly promising for gas storage and separation applications, offering potential solutions to challenges in fields such as energy storage and environmental remediation. Furthermore, ZIF-8's ability to encapsulate guest molecules within its pores opens avenues for controlled drug release systems, heralding innovations in pharmaceutical formulations. With ongoing research aimed at further enhancing its properties and exploring novel applications, ZIF-8 stands as a cornerstone in the burgeoning field of MOFs, holding promise for addressing pressing societal and environmental challenges in the years to come.

CHAPTER 2

2.1 LITERATURE SURVEY

1 Lili Yang , Chong Li, Jingmei Lv , Shijing Zhan, and Tongying Feng t al
2018 IOP Conf: ZIF-8 as a reactive adsorbent for phosphate removal from treated wastewater: Phosphate can promote the synthesis of protein, and it is conducive to the reduction and utilization of nitrate by nitrogen fixation. Phosphate participates in the synthesis of plant fat, which can improve crop adaptability to the external environment. However, if phosphorus pollution is discharged directly, it will lead to serious environmental pollution, such as nutrient enrichment of seawater. ZIF-8, a subclass of MOF, has emerged as a new kind of porous crystalline materials with excellent properties such as uniform micro-pores, accessible pore volumes, large surface areas as well as exceptional chemical and thermal stabilities, making it potentially interesting candidate for adsorbing phosphate from waste water.

2 Surendra Sasi Kumar Jampa , Ashish Prabhudas Unnarkat , Rajesh Vanshpati
VOLUME19,AUGUST.2020,100927:ADSORPTIONAND,RECYCLABILITY ASPECTS OF HUMIC ACID USING NANO-ZIF-8 ADSORBENT In this present study, nano ZIF-8 has been used as an adsorbent due to a relatively high surface area of the particles ($1400 \text{ m}^2 \text{ gm}^{-1}$) which could emerge as a potential adsorbent for water purification. Nano ZIF-8 particles were synthesized using single step room temperature procedure and characterized using different analytical instruments. Humic acid absorption process results showed exothermic in nature which was in contrast to the results reported in the literature. Kinetic and thermodynamic modelling of the results was explored for the adsorbent. The adsorption results are compared with various adsorbents to benchmark the material in this work.

3.Beom K. Jung, Jong Won Jun, Zubair Hasan, Sung Hwa Jhung .(2015).
Adsorptive removal of p-arsanilic acid from water using mesoporous zeolitic imidazolate framework-8. Chemical Engineering Journal, 267, 9–15. The adsorption kinetics and adsorbed amount of ASA were improved by introducing mesoporosity into the pristine ZIF-8 structure. The high adsorption capacity of mesoporous ZIF-8 for ASA and facile regeneration of the used adsorbent show that

mesoporous ZIF-8 has potential applications in the adsorptive removal of organoarsenic compounds such as ASA. Based on the adsorption results at various pH values and the surface charges on ZIF-8s, the adsorption mechanism of ASA on ZIF-8s can be explained by electrostatic interactions between the positively charged ZIF-8 surface and the anionic forms of ASA.

4 Nazia Rasool, Zohaib Saeed* , Muhammad Pervaiz, Rashida Bashir, Umer Younas, Hafiz Amir Nadeem, Ayoub Rashid, Ahmad Adnan : Future prospects for ZIF-8-based composite material for decontamination of water :

Zeolitic imidazolate framework-8 (ZIF-8), is a metal organic framework, which consists of two atoms of Zn metal and 2-methylimidazole and is a popular MOF material. ZIF-8 contains the quirky properties and these properties grant it higher-level absorption capacity and fine host capacity for the photocatalytic material, making it an excellent outline material for the decontamination of wastewater. Nevertheless, decline in surface results when ZIF-8 is collected together, and due to these properties, ZIF-8 is used widely for decontamination of wastewater. It is very difficult to detach them from wastewater after the removal of pollutants because they show weak recyclability. A novel ZIF-8 material that is currently being used has solved the above problem and is being successfully used in the treatment of wastewater or decontamination of water. There has been ongoing research on ZIF-8 composites as adsorbents and photocatalysts to drag out the pollutants from wastewater.

5. Ramsha Saleem,Rana Rashad Mahmood Khan, Hoorish Qamar, Muhammad Pervaiz, Umer Younas, Zohaib Saeed, Hafiz Muhammad Faizan Haider, Ahmad Adnan Recent trends in ZIF-8-based composite materials for the removal of ciprofloxacin . CIP abuse and its low biodegradability cause water contamination that leads to the production of CIP-resistant bacteria. A high concentration of CIP, including other quinolones, causes harmful effects on fish, humans, bacteria, algae, and protozoa. Adsorption has been preferred over other removal methods. The superior properties of ZIF-8 over other MOFs have made it a promising adsorbent for the removal of CIP from an aquatic environment. However, ZIF-8 suffers from its inability to recover from an aqueous environment and the related mass transfer problems. These limitations have been overcome by

the synthesis of ZIF-8-based composites. ZIF8 composites have been proved as efficient catalysts for the adsorption of CIP from water. They offer a higher number of adsorption sites for CIP than ZIF-8. The adsorption of CIP over ZIF-8-based composites occurs via the interaction between the adsorbent and CIP

6. Ali Ayati² Mohamed Farghali · Pavel Krivoschapkin · Bahareh Tanhaei⁵ · Hassan Karimi-Maleh^{6,7} · Mika Sillanpää June 2023 Advanced adsorbents for ibuprofen removal from aquatic environments: a review ‘Here, we review advanced adsorption methods to remove ibuprofen, with a focus on ibuprofen occurrence and toxicity, adsorbents, kinetics, and adsorption isotherms. Adsorbents include carbon- and silica-based materials, metal–organic frameworks, clays, polymers, and bio adsorbents. Carbon-based adsorbents allow the highest adsorption of ibuprofen, from 10.8 to 408 mg/g for activated carbon and 2.5–1033 mg/g for biochar. Metal–organic frameworks appear promising due to their high surface areas and tunable properties and morphology. 95% of published reports reveal that adsorption kinetics follow the pseudo-second-order model, indicating that the adsorption is predominantly governed by chemical adsorption. 70% of published reports disclose that the Langmuir model describes the adsorption isotherm, suggesting that adsorption involves monolayer adsorption

7. Minyue Zheng, Jinyi Chen , Lu Zhang , Ying Cheng , Chengyu Lu, Yafen Liu , Amita Singh , Manoj Trivedi , [Abhinav Kumar](#) Metal organic frameworks as efficient adsorbents for drugs from wastewater Drug pollution in aqueous environment is posing serious global problem, threatening the safety of ecosystems and human health, and hence has attracted wide attention. Metal- organic frameworks (MOFs) are a class of porous inorganic-organic hybrid networks synthesized by multi-dentate organic ligands. Due to their large specific surface area, high adsorption capacity, adjustable porosity, layered structure and recyclable performance, they are considered as important materials for the adsorption and removal of emerging pollutants (ECs) in wastewater and has been widely studied. However, due to their instability and difficulty in recycling in aqueous media, their application as an adsorbent are limited, and hence further investigation and syntheses of materials to overcome this shortcoming remains an arduous task. With

these viewpoints, in presented review, the utility of MOFs to adsorption properties and related mechanism to remove drugs viz. antibiotics, anti-inflammatory, antipsychotics, organophosphorus pesticides and other drugs from wastewater are presented.

8. Shumila Shaheen, Muhammad Pervaiz, Syed Majid Bukhari, Zohaib Saeed, Muhammad Imran, Aemin Ali, Ran Rashad Mahmood Khan, Hazqail Umar Khan ; Removal of heavy metals using ZIF 8 : Clean water dictate is growing every day as a consequence of the rapid industrial evolution and population growth. However, due to an insufficient supply of new water sources, there is a requirement for successful, satisfactory wastewater recycling. Many treatment techniques use the reverse osmosis method. Coagulation precipitation and ion exchange methods have been extensively tested, with the ion exchange method being considered the most efficient method. Nevertheless, the existence of heavy metal ions that are non-recyclable, restricts the usage of efficient methods. In this chapter, we evaluate the water-stable metal organic-based framework MOFs, the Zeolite-based imidazolate framework (ZIF-8)

9. Mushkbar Zahra, Zohaib Saeed, Muhammad Pervaiz, Rashida Bashir, Talha Mumtaz, Rizwan Sikandar, Umer Younas, Ayoub Rashid, Ahmad Adnan

5 Wastewater treatment: An overview: ZIF-8-based multi-dimensional composites have been proposed to treat wastewater. The exciting attributes of ZIF- 8-based composites, such as large surface area and higher adsorption capacity, increase their removal efficiency of noxious substances. A variety of synthesis methods of Zeolite Imidazolate Framework-8-derived composites have been discussed in this chapter. Multi-functional ZIF-8 composites have been used to remove toxic dyes, namely, Rhoda mine b and methylene blue from wastewater. The AgBr/ZIF-8 composites have been found to be the best de-grading material for dyes as their efficiency is 99.5% under visible light. This chapter also sheds light on a number of applications of ZIF-8 for wastewater treatment.

10. Ramsha Saleem, Rana Rashad Mahmood Khan, Bisma Khanam, Ayoub Rashid Ch., Muhammad Pervaiz, Zohaib Saeed, Ahmad Adnan Pharmaceutical wastes: an overview: The PhW comprises drugs including antibiotics,

anticonvulsants, antihypertensives, antidepressants, hormones, NSAIDs, vaccines, serums, and the patient's medications. The human and veterinary excretory products, hospital effluents, aquaculture, and disposal of unused or expired medication contribute to the origin of pharmaceutical pollution in the aquatic environment. These compounds in their original forms or the forms of metabolites or conjugates of glucuronic acid and sulfuric acid get entry into the sewage water via excretion. The traditional wastewater plants cannot remove the pharmaceutical contaminants efficiently and they enter the aquatic environment. These compounds have severe effects on humans, plants, animals, fish, and protozoa. Hence, various technologies have been developed to eliminate the contaminants of pharmaceuticals from water bodies.

CHAPTER 3

AIM AND SCOPE

3.1. AIM:

- To improve the delivery of ibuprofen by utilizing ZIF-8 as a carrier. ZIF-8's high surface area and tunable pore size make it suitable for loading and releasing drug molecules like ibuprofen in a controlled manner.
- To remove ibuprofen from aqueous solutions for environmental remediation purposes. ZIF-8's adsorption capacity and selectivity make it effective for removing pharmaceutical pollutants from wastewater, contributing to efforts to mitigate environmental contamination and protect ecosystems and human health.
- To involve separating ibuprofen from complex mixtures, such as pharmaceutical formulations or contaminated water sources. ZIF-8's selective adsorption properties can facilitate the purification of ibuprofen, ensuring its quality and purity for pharmaceutical or analytical purposes.
- To utilize ZIF-8 for targeted delivery or controlled release of ibuprofen in therapeutic interventions
- To optimize pharmaceutical formulations containing ibuprofen by incorporating ZIF-8. ZIF-8 can enhance the stability, solubility, or bioavailability of ibuprofen in formulations, leading to improved drug efficacy and patient compliance.

3.2. SCOPE:

- **Water Purification:** ZIF-8 shows good potential for removing ibuprofen from water. Its high surface area and porous structure allow it to capture ibuprofen molecules effectively. This can be crucial for treating wastewater or environmental remediation.
- **Controlled Drug Delivery:** Researchers are exploring ZIF-8 as a carrier for

ibuprofen. By encapsulating the drug within ZIF-8, they can potentially control its release rate and target specific locations in the body. This could be beneficial for sustained delivery or localized treatment.

- Reusability: ZIF-8 can be regenerated and reused for multiple adsorption cycles, making it a more sustainable option compared to some disposable adsorbents.
- Tailoring Properties: ZIF-8 can be modified to improve its adsorption capacity for ibuprofen. Scientists can introduce functional groups onto the ZIF-8 surface that interact more favorably with ibuprofen molecules
- Wastewater Treatment Integration: Exploring ways to integrate ZIF-8 into existing wastewater treatment systems or designing new systems that leverage its unique properties can enhance the overall efficiency of pesticide removal on a larger scale.
- Evaluating the environmental impact of using ZIF-8: in pesticide removal is crucial. Assessing factors such as the fate of used ZIF-8 and any potential byproducts helps ensure the overall sustainability of the treatment process

CHAPTER 4

MATERIALS AND METHODS

4.1. MATERIALS AND CHEMICALS :

1. **ZIF-8:** Synthesized using appropriate precursors such as zinc nitrate hexahydrate and 2-methylimidazole. ZIF-8 can be obtained commercially or prepared in the laboratory using established synthesis protocols.
2. **Ibuprofen Solution:** A solution of ibuprofen in a suitable solvent, typically water or a water-miscible organic solvent such as methanol or ethanol. The concentration of ibuprofen in the solution may vary depending on the experimental requirements.
3. **Solvents:** Methanol, ethanol, or water may be used as solvents for preparing the ibuprofen solution and conducting the adsorption experiments.
4. **Analytical Instruments:** Instruments such as UV-Vis spectrophotometer, high-performance liquid chromatography (HPLC), or gas chromatography- mass spectrometry (GC-MS) may be used for ibuprofen quantification

4.2. METHODS :

1. **Synthesis of ZIF-8:** ZIF-8 is synthesized using a solvothermal or microwave-assisted method. The synthesis involves mixing appropriate molar ratios of zinc nitrate hexahydrate and 2-methylimidazole in a solvent followed by heating at a specific temperature for a certain duration to obtain ZIF-8 crystals.
2. **Characterization of ZIF-8:** The synthesized ZIF-8 is characterized using techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM) , Brunauer–Emmett–Teller (BET) surface area analysis, and Fourier-transform infrared spectroscopy (FTIR) to confirm its structure, morphology, surface area, and chemical composition.
3. **Preparation of Adsorbent:** The synthesized ZIF-8 is typically washed and dried before use to remove any impurities or residual solvents. It may also undergo activation or pre-treatment steps to enhance its adsorption properties.

4.3 PREPARATION OF zif 8 reactive adsorbent

Stirring:

- Stir the solution for a certain period to ensure complete mixing and dissolution.
- 7 g of 2-methylimidazole was dissolved in 80 mL of methanol with stirring

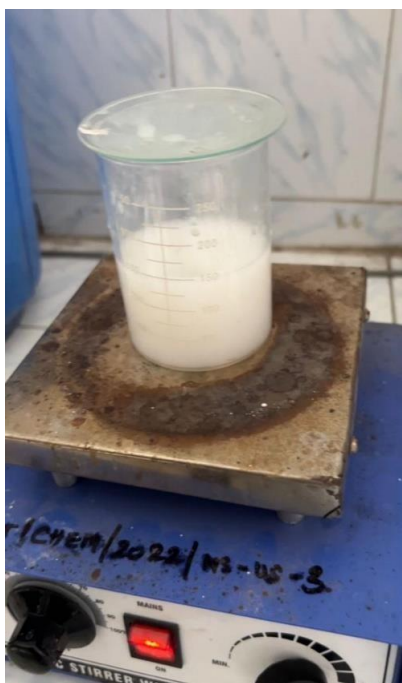


FIG. 4.1 : 2-METHYLIMIDAZOLE AND METHANOL

4.4 Precipitation and Crystallization:

- After stirring, the mixture undergoes precipitation, resulting in the formation of ZIF-8 crystals.
- The formation of ZIF-8 is facilitated by the coordination of zinc ions with imidazole ligands.
- Then, 3.0 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in 40 mL of methanol was added with vigorous stirring for 24 h at room temperature
- Third, both solutions were mixed under rigorous mixing for 15 min



FIG. 4.2 : CENTRIFUGAL PUMP

- The final solution was then poured in centrifugal tubes and centrifuged at 5000 rpm for 30 min



FIG .4.3 :CENTRIFUGAL TUBES

- The solid product was recovered and washed at least for four times.



FIG. 4.4 : PREPARED OF ZIF-8

4.5 ADSORPTION OF IBUPROFEN USING ZIF-8 :

Considerations:

- Several factors can influence the effectiveness of ibuprofen adsorption using ZIF-8. These include:
 - pH of the solution
 - Temperature
 - Concentration of ibuprofen
 - Contact time between ZIF-8 and the solution
 - Presence of other competing molecules



FIG. 4.5: IBUPROFEN

4.6 Stock solution of ibuprofen :



FIG. 4.6 : IBUPROFEN STOCK SOLUTION

Prepare a stock solution of ibuprofen 1g in 1000ml of water

Preparation:

- The stock solution is prepared by dissolving a specific amount of ibuprofen powder into a chosen solvent to achieve a desired concentration. This concentration is usually higher than the final concentration you expect after the adsorption process with ZIF-8.

20ml stock + 80ml of water dosage of MOF (0.2g 0.4g 0.6g 0.8g 1g) while

stirring for 60 min in centrifuge



FIG .4.7 : CENTRIFUGE SAMPLE OF DOSAGE

CHAPTER 5

RESULTS AND DISCUSSION

5.1 CHARACTERIZATION

Fourier Transform Infrared (FTIR) analysis was applied to The FTIR peak at 3845 cm^{-1} in the context of ZIF-8, particularly for pesticide removal from wastewater, might be associated with certain functional groups or vibrations. However, without more specific information about the full FTIR spectrum and the conditions of the experiment, it's challenging to pinpoint the exact nature of this peak.

Energy-Dispersive X-ray Spectroscopy (EDS):

- If available, consider using EDS of conjunction with SEM in obtain elemental composition information, confirming the presence of ZIF-8 and potentially identifying pesticides

Cross-Sectional Imaging:

- Cross-sectional SEM imaging can provide in a deeper understanding of ZIF-8's internal structure and its interaction with pesticides.

Comparison with Control Samples:

- Include SEM images of ZIF-8 without pesticide exposure as a control. This aids in distinguishing changes attributed of the presence of pesticides

Quantitative Analysis:

- If applicable, use image analysis software to quantitatively assess features such as particle size in distribution

Characterization of prepared :ZIF- 8 pesticide removal from waste

5.2 Fourier Transform Infrared (FTIR).

- The region around 3845 cm^{-1} in FTIR spectra often corresponds to the O- H stretching vibrations of hydroxyl (OH) groups.
- The native PMPP sample exhibited a broad adsorption peak at 3845 cm^{-1} indicating the presence of bonded and free hydroxylic group due to O-H group vibration.
- The peak is observed at 3845 cm^{-1} corresponds to O-H stretching.
- So far, The FTIR discussions has established the existence of five major adsorption peak at 3845 cm^{-1} , 3772.08 cm^{-1} , 3700.73 cm^{-1} , 3628.41 cm^{-1} and 2918.73 cm^{-1} .

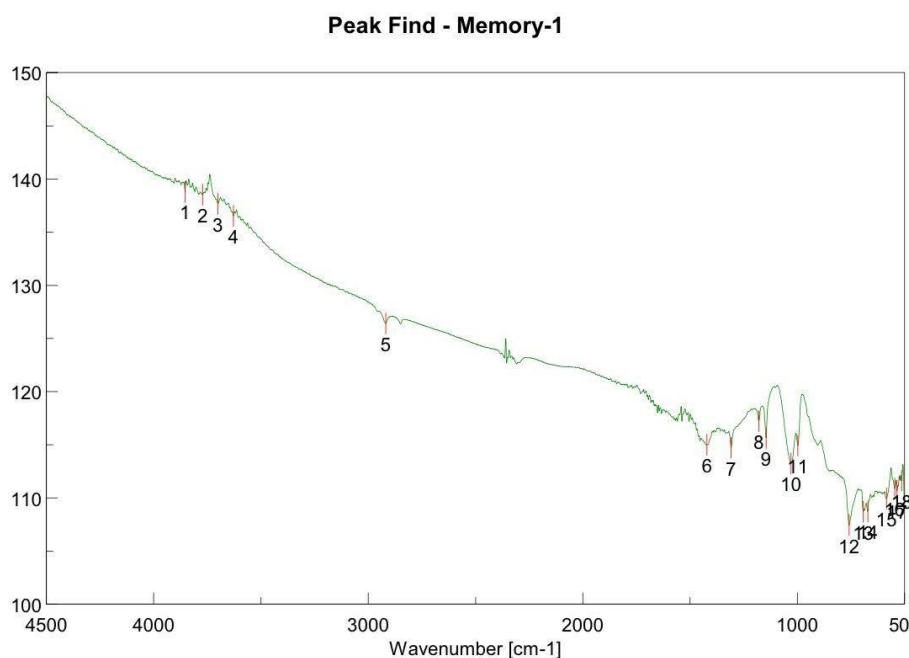
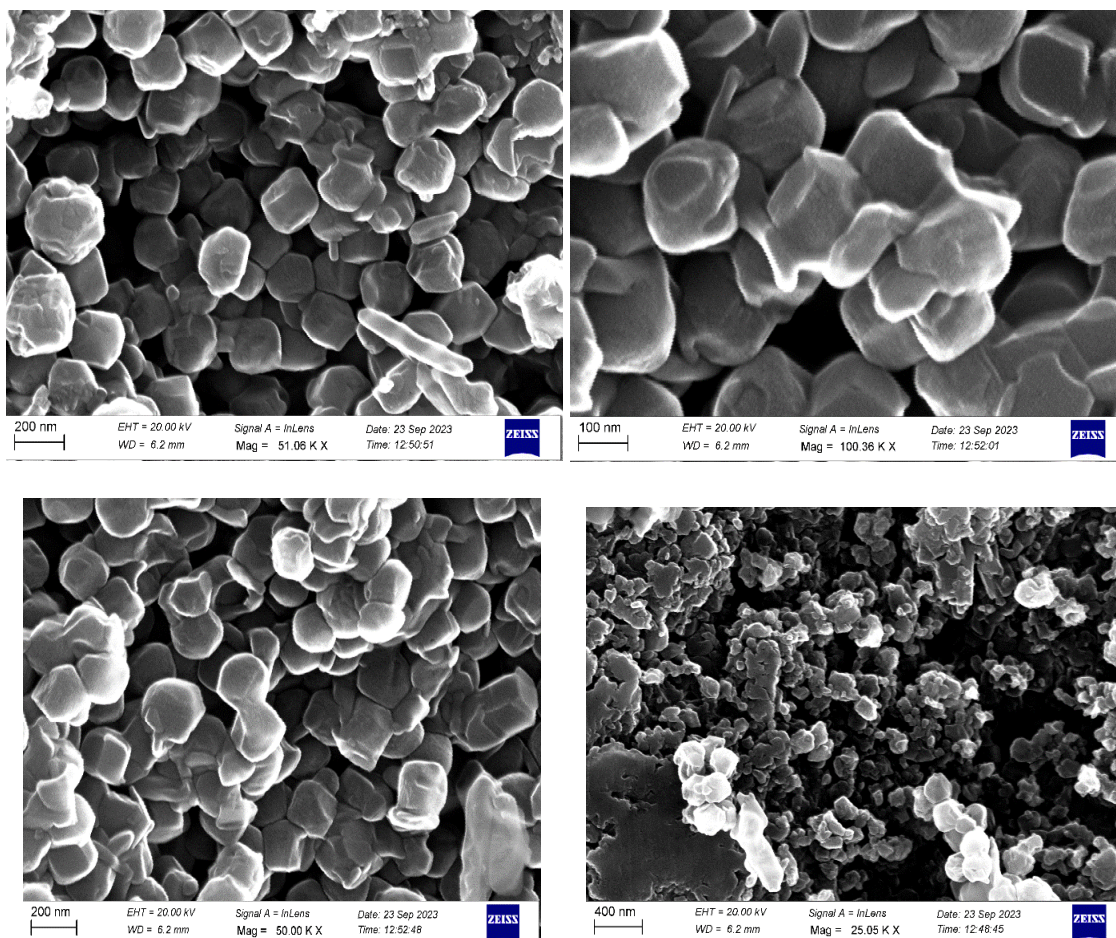


FIG. 5.1 : FTIR FOR ZIF-8

5.3 SCANNING ELECTRON MICROSCOPY (SEM).

- Evaluate the SEM images to identify potential adsorption sites in the ZIF-8 surface. Pesticide molecules may be visible on the material's surface.
- Look for any evidence in pore blocking or modification in the SEM images after exposure to pesticides. This could indicate the adsorption mechanism.
- Observe whether there is any agglomeration in ZIF-8 particles, which may be indicative of the adsorption of pesticides.
- Assess the uniformity of the ZIF-8 surface after pesticide exposure. Non-uniformities may suggest preferential adsorption sites.



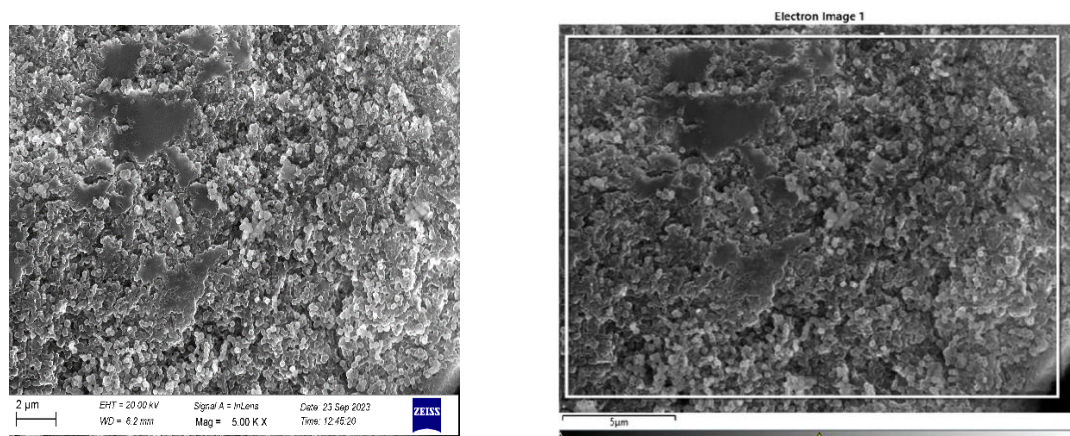
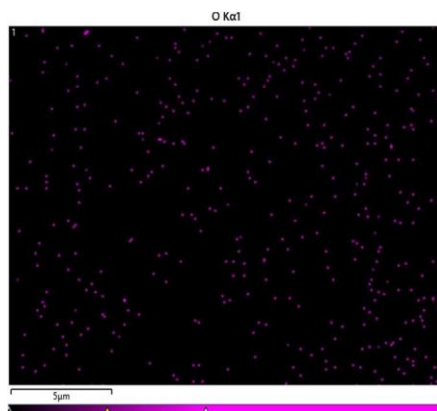


FIG. 5.2 : SEM FOR ZIF-8

EDAX.

EDAX is an analytical method that measures the energy of X-rays released when electrons interact with a sample. It is frequently used in conjunction with scanning electron microscopy (SEM) to ascertain the elemental composition of a sample. It is utilized for elemental analysis in a variety of applications, such as geology and materials characterization



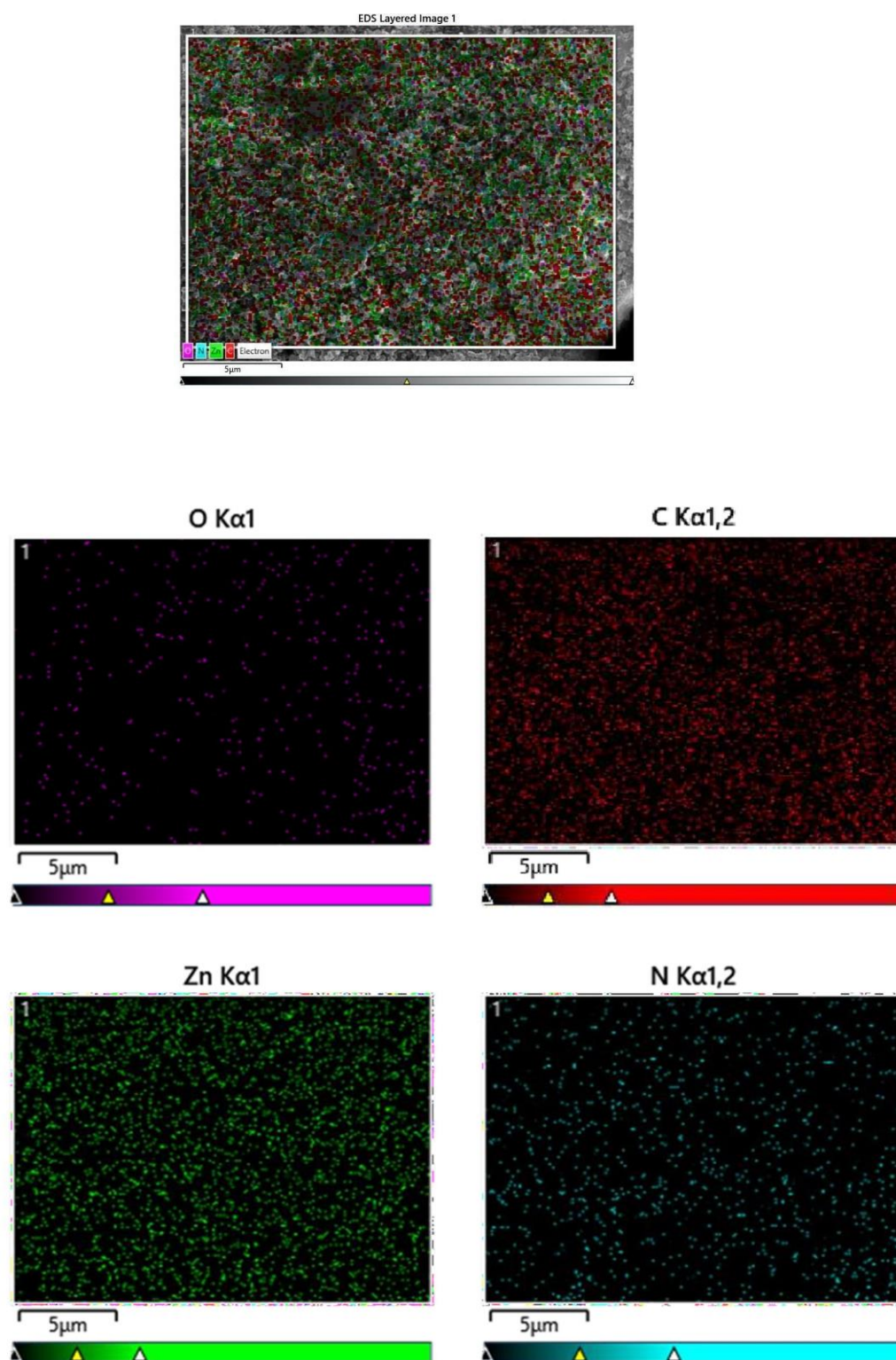
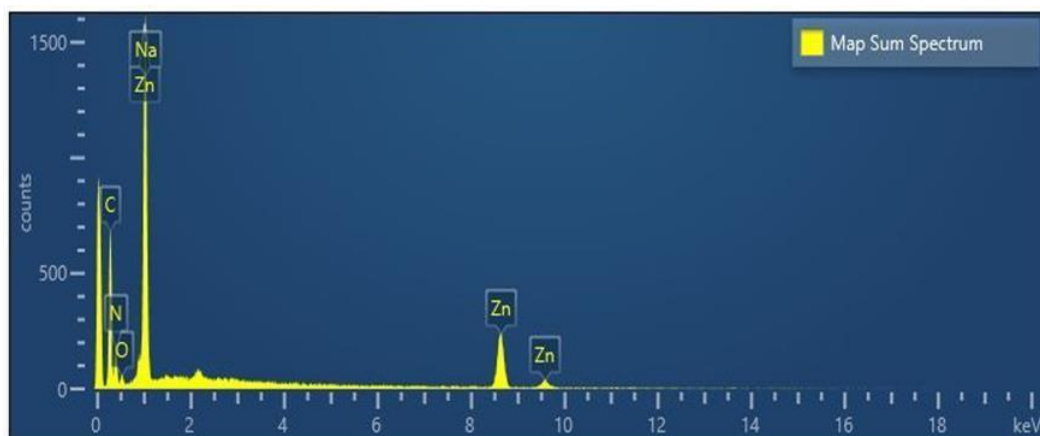


FIG. 5.3 : EDAX FOR ZIF-8

EDAX FOR ZIF-8:



Map Sum Spectrum				
Element	Line Type	Weight %	Weight % Sigma	Atomic %
C	K series	47.27	1.16	61.17
N	K series	26.01	1.43	28.86
O	K series	2.98	0.44	2.90
Na	K series	3.24	0.41	2.19
Zn	K series	20.50	0.64	4.87
Total		100.00		100.00

FIG. 5.4 : EDAX FOR ZIF-8

Post studies of ZIF-8 (FTIR)

No. Position Intensity No. Position Intensity

No.	Position	Intensity	No.	Position	Intensity
1	2928.38	99.5536	2	2359.48	97.9066
3	1581.34	94.6944	4	1422.24	87.4509
5	1382.71	91.4347	6	1310.39	87.2628
7	1180.22	91.9144	8	1145.51	76.8172
9	994.125	87.5732	10	953.627	96.4358
11	828.277	96.8759	12	758.852	80.3307
13	693.284	87.6579	14	684.606	88.4269
15	529.364	96.5549			

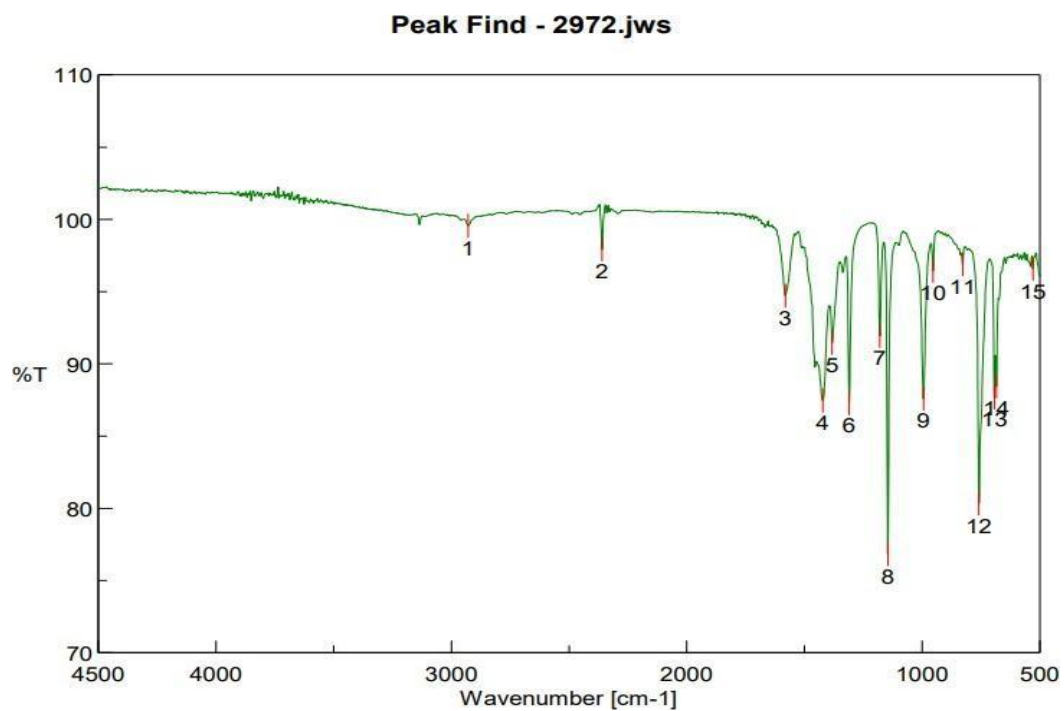
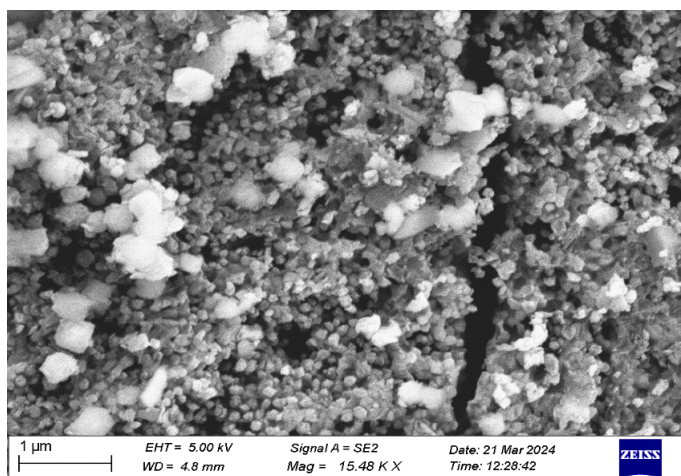


FIG. 5.5 : FTIR FOR Post studies of ZIF-8

Post studies of ZIF-8 (FESEM)



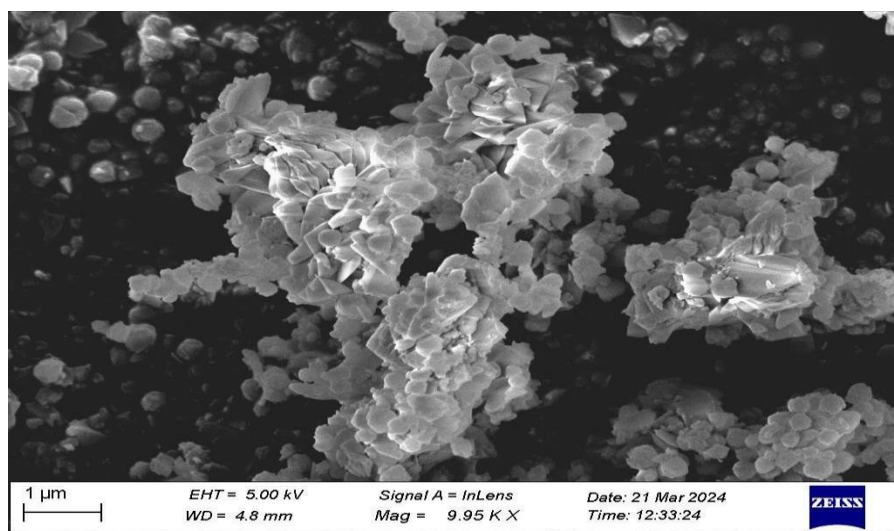
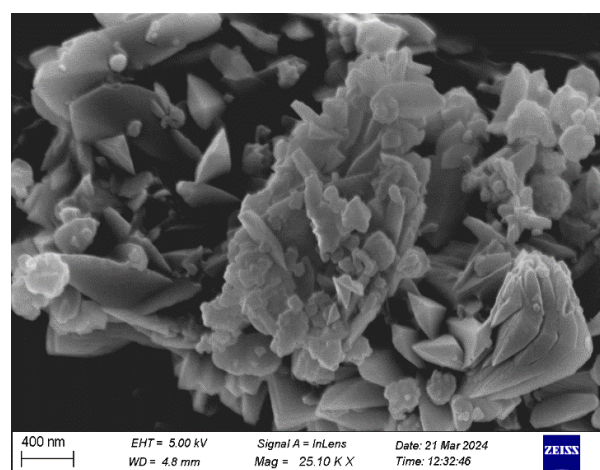
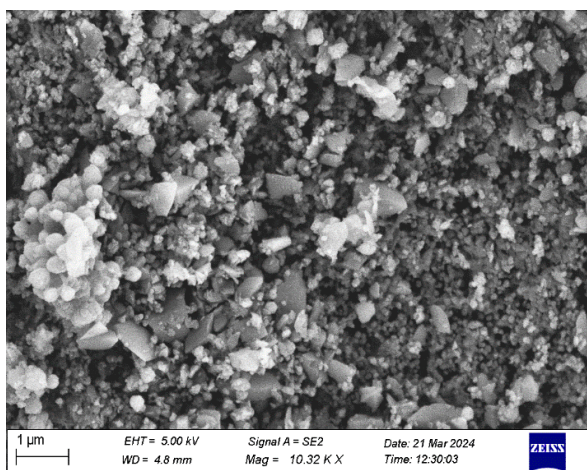
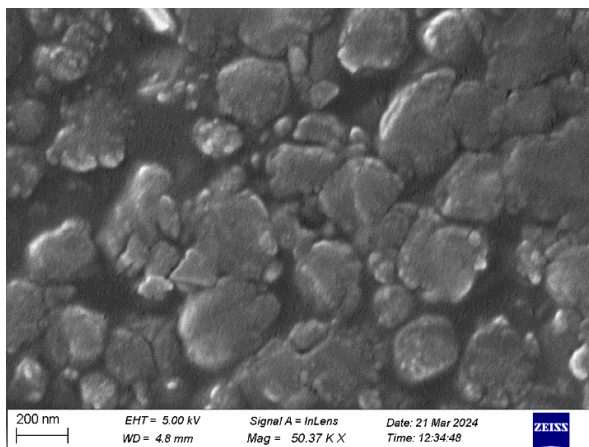
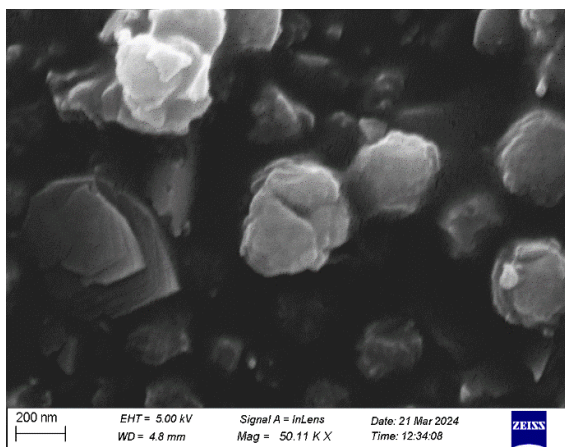


FIG. 5.6 : Post studies of ZIF-8 (FESEM)

Post studies of ZIF-8 (XRD)

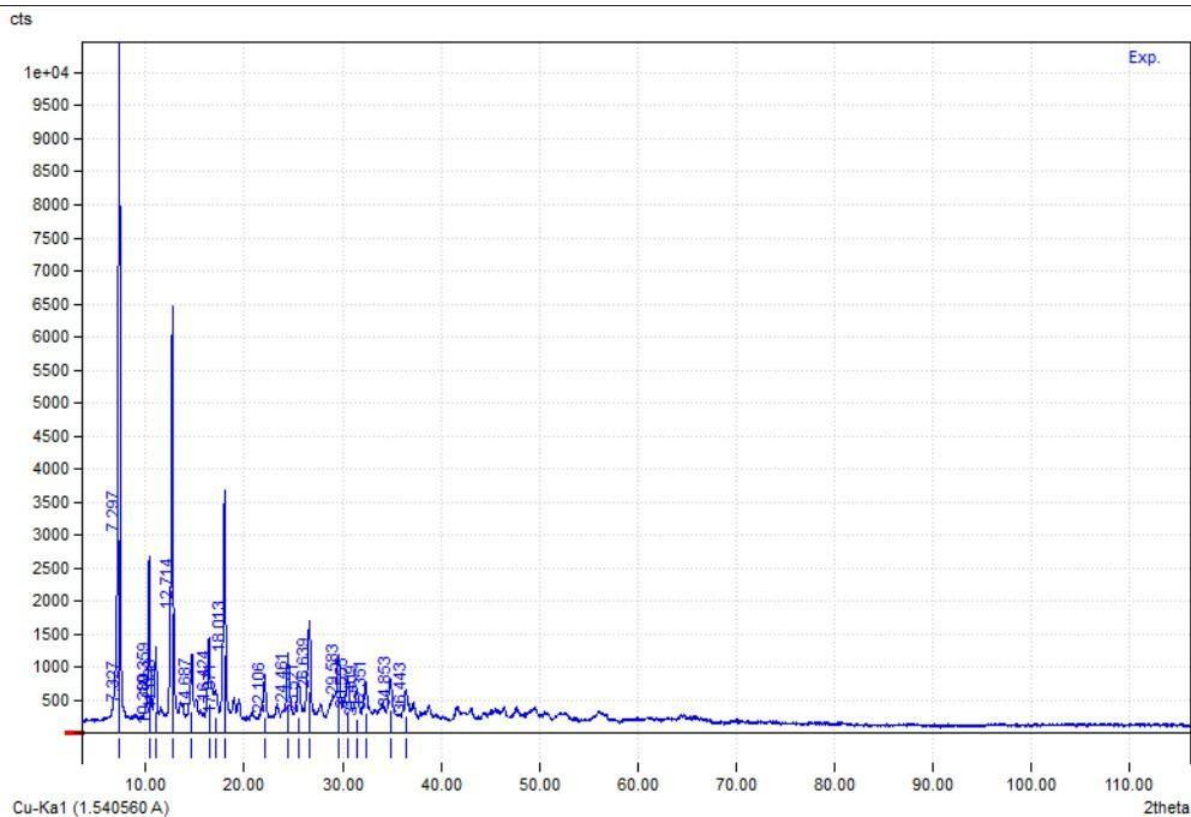


FIG. 5.7 : Post studies of ZIF-8 (XRD)

- After the adsorption process, the ZIF-8 material (with adsorbed ibuprofen) is separated from the solution. The ZIF-8 is then dried and prepared for XRD analysis.
- During XRD analysis, the ZIF-8 sample is exposed to an X-ray beam. The X-rays interact with the electrons within the crystals of the ZIF-8 and the potentially adsorbed ibuprofen (if crystalline).
- The diffracted X-rays are detected and their intensities recorded at various angles.
- The resulting XRD pattern is a plot of intensity versus diffraction angle.

Peak List						
No.	2theta [°]	d [Å]	I/I0 (peak height)	Counts (peak area)	FWHM	
1	7.30	12.1041	1000.00	2920.57	0.2355	
2	7.33	12.0555	115.56	337.51	0.2355	
3	10.36	8.5324	246.46	539.85	0.1766	
4	10.39	8.5083	33.78	74.00	0.1766	
5	11.04	8.0104	106.88	312.14	0.2355	
6	12.71	6.9567	666.73	1825.47	0.2208	
7	14.69	6.0265	100.97	309.24	0.2470	
8	16.42	5.3928	119.56	434.46	0.2930	
9	17.07	5.1897	39.99	247.89	0.4999	
10	18.01	4.9203	379.14	1168.58	0.2509	
11	22.11	4.0179	69.00	252.24	0.2948	
12	24.46	3.6361	99.22	396.92	0.3226	
13	25.52	3.4874	55.50	247.94	0.3576	
14	26.64	3.3435	154.82	618.31	0.3221	
15	29.58	3.0171	92.62	513.88	0.4465	
16	30.55	2.9233	61.99	311.17	0.4130	
17	31.41	2.8458	42.69	191.39	0.3589	
18	32.35	2.7650	55.70	292.28	0.4241	
19	34.85	2.5720	62.77	329.73	0.4236	
20	36.44	2.4634	44.13	255.06	0.4685	

Integrated Profile Areas

Based on calculated profile

Profile area	Counts	Amount
Overall diffraction profile	1164659	100.00%
Background radiation	659228	56.60%
Diffraction peaks	505431	43.40%
Peak area belonging to selected phases	0	0.00%
Unidentified peak area	505431	43.40%

Peak Residuals

Peak data	Counts	Amount
Overall peak intensity	11579	100.00%
Peak intensity belonging to selected phases	8016	69.23%
Unidentified peak intensity	3563	30.77%

FIG .5.8 :PEAK REPORT OF XRD

PEAK REPORT OF XRD

5.4 EFFECT OF pH:

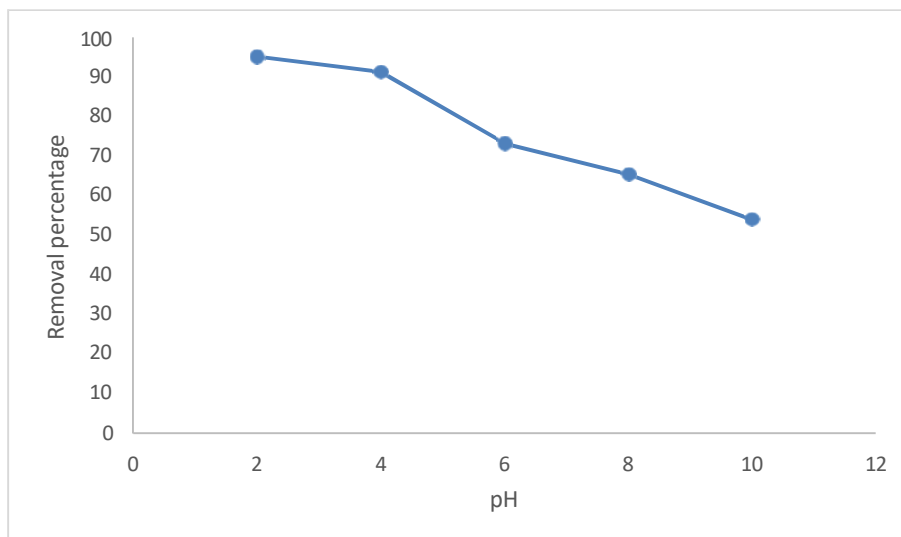


Fig. 5.9 : Effect of pH

In order to assess the influence of pH, the pH level of the solution was adjusted within the range of 2 to 10. Adsorption experiments were carried out in the pH range of 2–10 keeping all other parameters constant (MH concentration = 10 mg/L; adsorbent dose = 10g/ L for zif-8 and 5g/L for; contact time =120 min), it is evident that the adsorption of the metformin hydrochloride for and GO-BC increased as the pH of the solution increased from 53.97 to .9519% for and 47.14 to 95.47% for ZIF-8. From 2 to 6 and started to decrease after reaching maximum at pH 2. The maximum adsorption of metformin hydrochloride by zif-8 and ibuprofen at pH 2 attributed to optimal surface charge and chemical speciation, favoring effective binding of neutral metformin molecules to adsorbent surface. Additionally, the surface functional groups were likely in an optimal state for interaction with ibuprofen molecules at this pH. At pH 2, minimized competition from other ionic species and enhanced chemical stability further facilitated efficient adsorption of ibuprofen onto zif-8 a, resulting in maximum adsorption capacity at this pH level

The effect of pH on IBP adsorption was studied in the pH range (2–8), by adjusting the solutions to the desired levels using HCl or NaOH. The effect of pH on 25 mg MMIPs with IBP 50 mg/L during a 90 min contact time is The optimal adsorption capacity is obtained at pH 4. At pH 2 to 9, there is an increase in adsorption capacity because the adsorbent surface which is positively charged will interact electrostatically with the –OH group which is charged negatively on IBP, but then the adsorption capacity decreases with further increase in pH because IBP

5.5 EFFECT OF ADSORBENT DOSAGE:

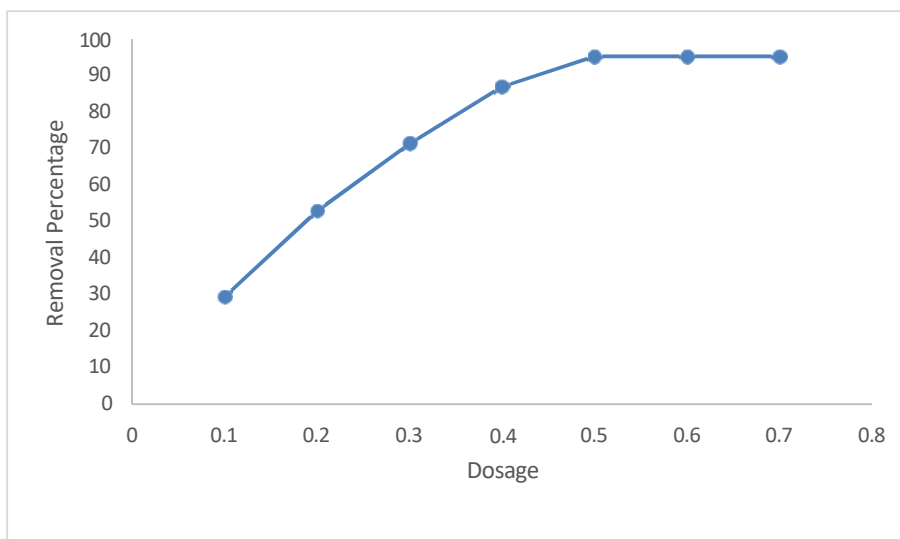


Fig. 5.10 : Adsorbent Dosage of IBUPROFEN

The removal of ciprofloxacin by was studied by varying the dosage

(2,4,6,8,10,12,14) g/l with initial concentration of (10 mg/l), pH (2), contact time (120 min), and temperature at 303K

Removal was highest when dosage used was 0.5 g/l (95.19%) so 10g/l was chosen as the optimum dosage.

EFFECT OF DOSAGE :

As the dosage of ZIF-8 increases, the total surface area available for ibuprofen adsorption also increases. This translates to a greater number of potential binding sites for ibuprofen molecules. Consequently, the overall adsorption capacity of the system increases.

There's a limit to this however. Imagine the ZIF-8 particles as sponges. As you add more sponges (increase dosage), you can absorb more water (ibuprofen).

The optimal ZIF-8 dosage depends on several factors, including:

5.6 EFFECT OF INITIAL CONCENTRATION

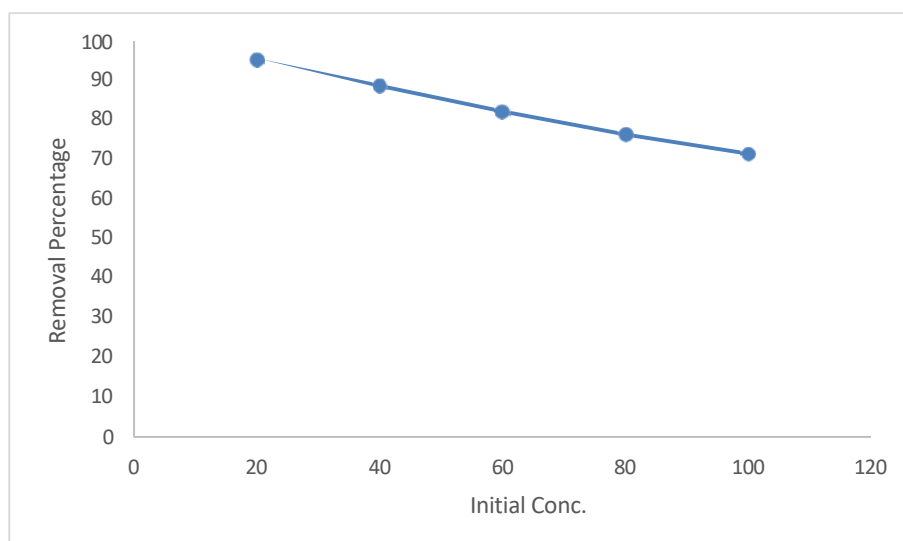


Fig. 5.11 : Effect of Initial Concentration

The removal of zif-8 was studied by varying the initial concentration (10,20,30,40,50) mg/l while keeping the adsorbent dosage (20g/l) ,pH(2) ,120 min contact time and temperature at 303K Removal was highest at 20 mg/l(95.19%) so 10mg/l was chosen as the optimum concentration

5.7 EFFECT OF CONTACT TIME

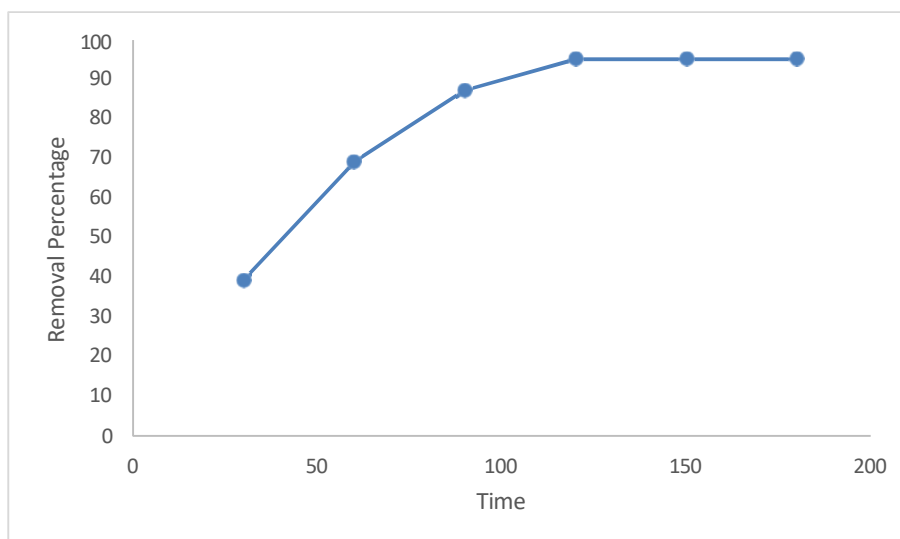


Fig . 5.12 : Effect of Contact Time

The removal of ciprofloxacin was studied by varying the contact time (30,60,90,120,150,180 min) while keeping the dosage (10g/l), pH(2), initial concentration (120mg/l) and temperature 303K

Removal was highest when contact time was 120min (95.19%) so 120 min was chosen as the optimum contact time

EFFECT OF CONTACT TIME :

20ml stock +80ml water =100mg/L + pH 4+ Room

temp 1g of dosage MOF

TIME=(30,60,90,120,150,180) min

As time progresses, more and more ibuprofen molecules get adsorbed onto the ZIF-8. Gradually, the available binding sites become occupied. The rate of adsorption slows down and eventually reaches a state of equilibrium. At this point, the rate of ibuprofen adsorption onto the ZIF-8 is balanced by the rate of ibuprofen desorbing back into the solution.

The time required to reach equilibrium depends on several factors:

Initial ibuprofen concentration: Higher initial concentrations will take longer to reach equilibrium as there are more ibuprofen molecules competing for binding sites.

ZIF-8 dosage: A higher dosage of ZIF-8 provides more surface area and binding sites, leading to faster initial adsorption but also potentially reaching equilibrium sooner.

5.8 EFFECT OF TEMPERATURE

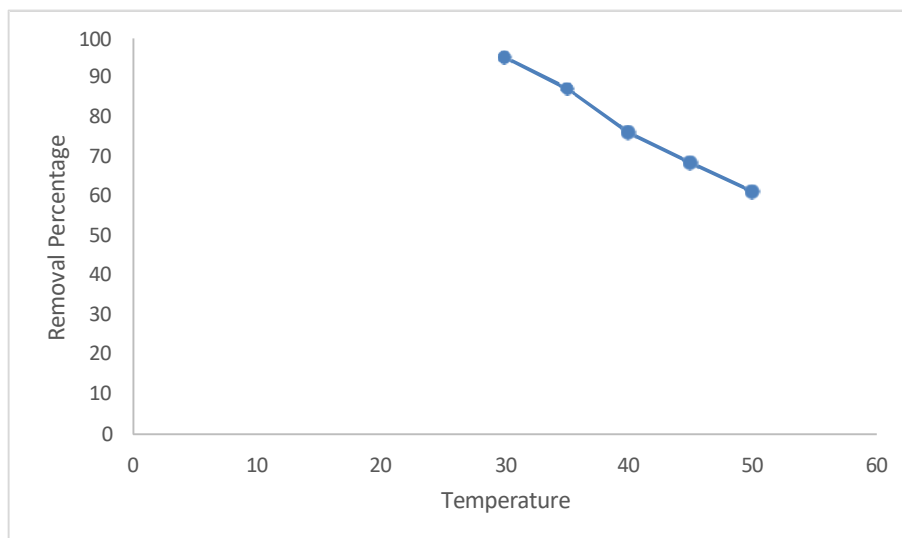


Fig.5.13 : Effect of Temperature

The removal of ZIF-8 was studied by varying the Temperature (303,308,313,318,323 K) while keeping the dosage (30g/l), pH(2), initial concentration (30mg/l) and contact time 120 min

Removal was highest when temperature was 303K (95.19%) so 303 K was chosen as the optimum temperature

5.9 ADSORPTION ISOTHERM MODELS

In essence, an adsorption isotherm serves as a vital curve elucidating the processes governing the retention, release, or mobility of a substance from aqueous porous media or aquatic environments to a solid-phase, under constant temperature and pH conditions. In this study, three adsorption isotherm models, namely Langmuir, Freundlich, and Tenkim isotherms were employed to investigate the adsorption of MH by AIBB and GO-BC adsorbents.

5.10 LANGMUIR ISOTHERM

The Langmuir isotherm model is suitable for monolayer adsorptions and can be expressed as follows:

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

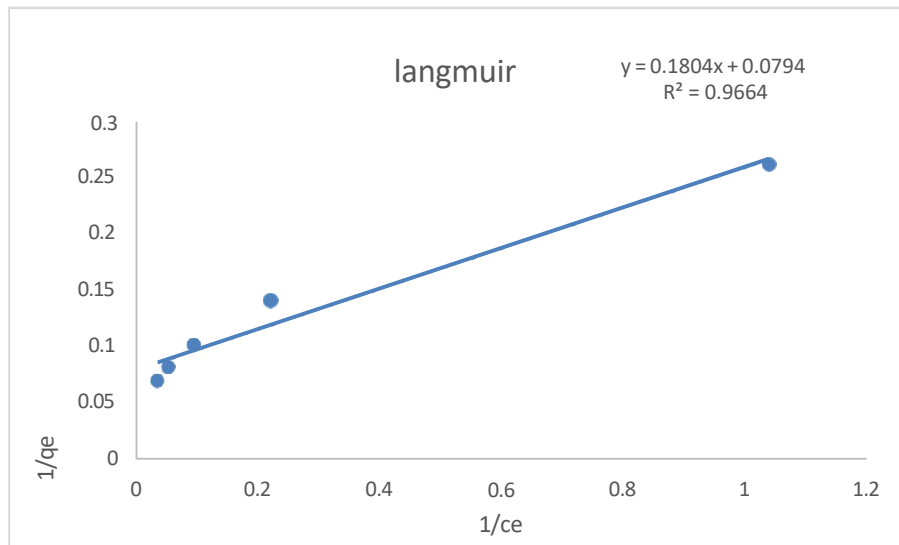


Fig.5.13(1) : Effect of Temperature

Where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg^{-1}), q_m is the maximum adsorption capacity (mg^{-1}), K_L is the Langmuir constant and C_e is the equilibrium concentration of adsorbate in the solution.

5.11 FREUNDLICH ISOTHERM

The Freundlich isotherm, an early empirical model, characterizes non-ideal and reversible adsorption phenomena, extending beyond monolayer formation. It accommodates multilayer adsorption with varying distribution of adsorption heat and affinities across heterogeneous surfaces. The equation representing this isotherm is as follows

$$q_e = K F C_e^{1/n}$$

Where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg^{-1}), C_e is the equilibrium concentration, K_f is the Freundlich constant and $1/n$ is the empirical parameter related to adsorption intensity.

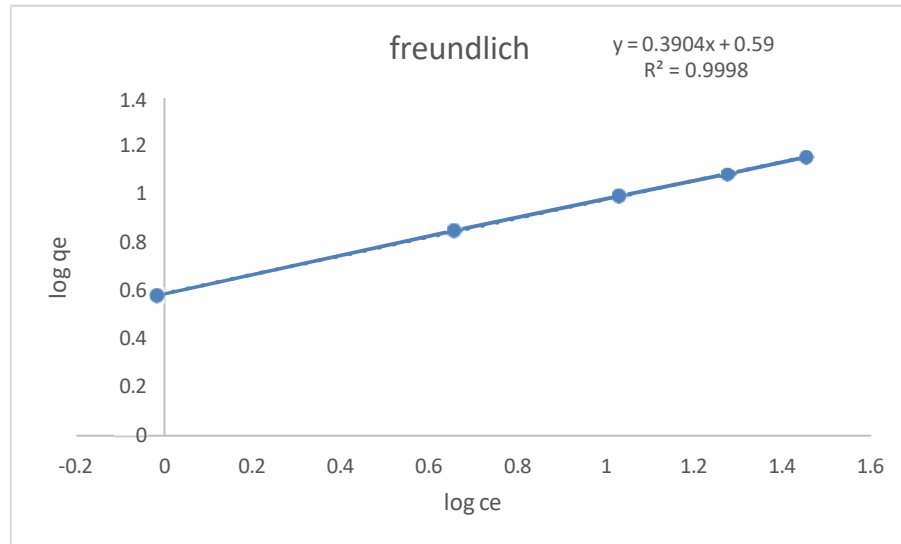


Fig.5.14 : Freundlich isotherm of IBUPROFEN

5.12 TENKIM ISOTHERM

Tenkim isotherm, is a model used to describe adsorption phenomena on solid surfaces. It assumes that the adsorption heat of molecules decreases linearly with surface coverage due to adsorbent-adsorbate interactions, incorporating a parameter to account for the potential energy of adsorption sites. The tenkim equation can be given as follows:

$$q_e = B \ln (A C_e)$$

Where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg^{-1}), C_e is the equilibrium concentration, KT is the Tenkim constant. R represents the universal gas constant, and T represents the absolute temperature in Kelvin

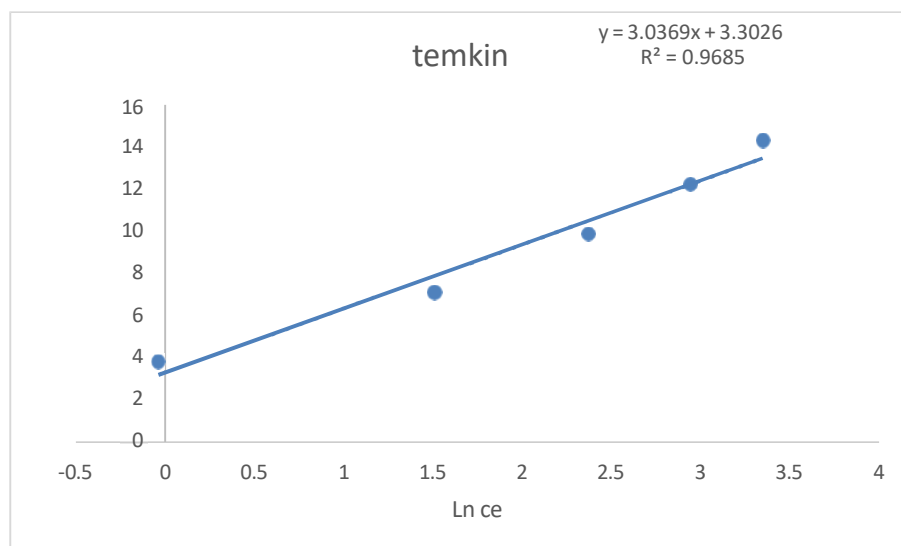


Fig. 5.15 : Tenkim Isotherm of ZIF-8

TABLE 5.11 ADSORPTION ISOTHERM PARAMETER

Models	Parameters	Values
Langmuir	Slope	0.1804
	Intercept	0.0794
	$q_{\max}$ (mg/g)	12.59
	R^2	0.9664
Freundlich	Slope	0.3904
	Intercept	0.59
	R^2	0.9998
Tenkim	Slope	3.0369
	Intercept	3.3026
	R^2	0.9685

5.13 ADSORPTION KINETIC MODELS

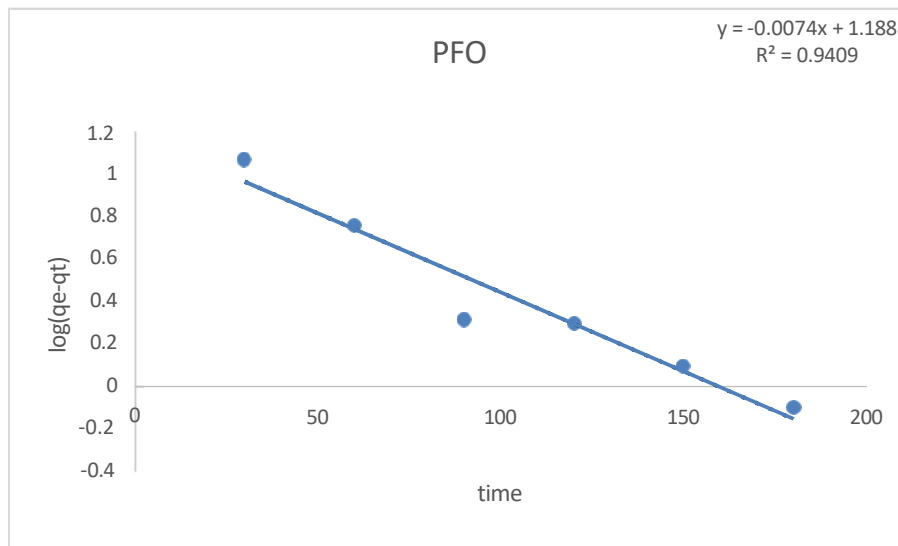


Fig.5.16: Adsorption Kinetics for ZIF-8

The kinetic models offer insights into the time needed to reach adsorption equilibrium, serving as a crucial aspect in designing adsorption systems. They provide valuable information about the process rate and the efficacy of the adsorbent material. Pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models are used to evaluate the prepared adsorbents.

Pseudo-first order kinetic model is given as:

$$A + S \rightleftharpoons AS$$

$$\frac{q_t}{q_e} = 1 - \exp \left[- \left(k_A C_A + \frac{k_A}{k_S} \right) t \right]$$

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t$$

$$k_{ad} = \left[\left(k_A C_S + \frac{k_A}{k_S} \right) \right]$$

$$q_e = X_{Ae}$$

Pseudo-second order kinetic model is given as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2$$

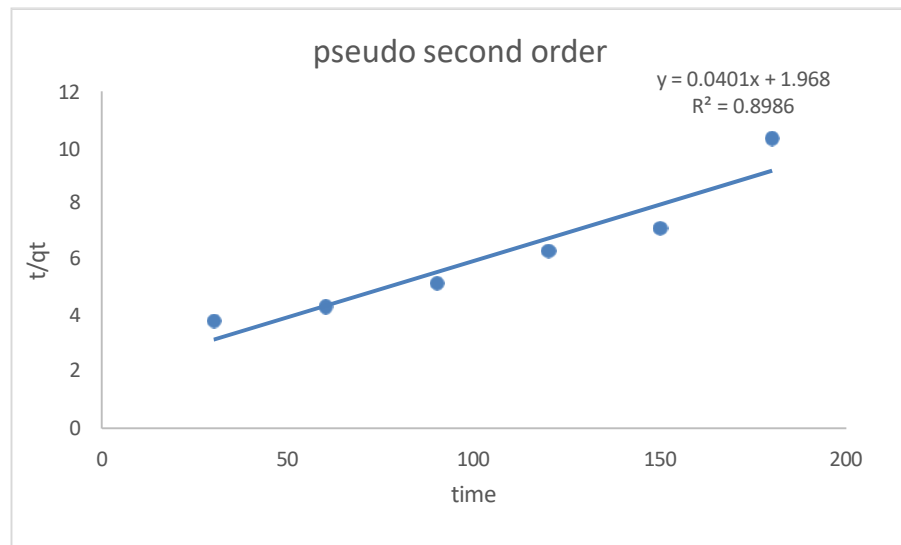


FIG. 5.17 : PSEUDO SECOND ORDER

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad \frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t$$

TABLE 5.12 Adsorption Isotherm Parameters

Slope	0.0101
Intercept	1.2697
R ²	0.8832
K ₁	0.00008

PSEUDO SECOND ORDER

TABLE 5.13 Adsorption Isotherm Parameters PSO

Slope	0.0381
Intercept	2.1576
R ²	0.9648
K ₂	0.011

THERMODYNAMICS

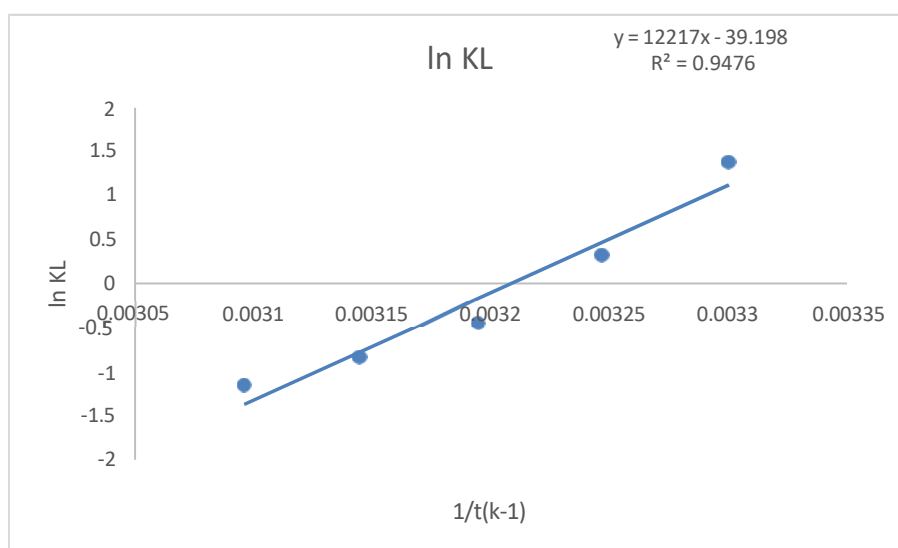


Fig.5.18 : Thermodynamics for zif-8

The primary purpose of conducting thermodynamic evaluation is to ascertain the nature and spontaneity of the adsorption process. Van't Hoff's equations are utilized to calculate the thermodynamic parameters for adsorption studies, as shown by the following equations:

$$KL = \frac{C_{Ae}}{C_e}$$

$$\Delta G^\circ = -RT \ln KL$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

TABLE 5.13 THERMODYNAMIC PARAMETERS

Sample	Intercept	Slope	ΔH° (KJmol ⁻¹)	ΔS° (JK ⁻¹ mol ⁻¹)	R ²	ΔG° (JK ⁻¹ mol ⁻¹)
ZIF-8	- 39.198	12217	-101.572138	-325.892172	0.9476	-3.465684157

CHAPTER 6

CONCLUSION

In conclusion, this study has demonstrated the potential of ZIF-8 as an effective adsorbent for the removal of pesticides from wastewater. Our findings indicate a notable adsorption capacity, with ZIF-8 exhibiting structural stability and regenerability over multiple cycles. SEM analysis revealed changes of a surface morphology and particle size, providing visual evidence of pesticide adsorption. While further research is needed to explore specific mechanisms and optimize conditions, this study contributes valuable insights in the field of environmental remediation. The use of ZIF-8 holds promise for sustainable and efficient pesticide removal, addressing critical challenges in wastewater treatment.

REFERENCES

- Adnan Özcan*, Elif Mine Öncü, A. Safa Özcan - Adsorption of Acid Blue 193 from aqueous solutions onto DEDMA-sepiolite - Journal of Hazardous Materials, Volume 8, (2006) Pg No. 37-62.
- Carla-Cezarina Pădurețu et Al - Influence of the parameters of chitin deacetylation process on the chitosan obtained from crab shell waste, Korean J. Chem. Eng., Volume 10, (2019) Pg No. 102-165.
- Dong-Wan Cho, Byong-Hun Jeon, Chul-Min Chon, Franklin W. Schwartz, Yoojin Jeong, Hocheol Song - Magnetic chitosan composite for adsorption of cationic and anionic dyes in aqueous solution, Journal of Industrial and Engineering Chemistry, Volume 6, (2015) Pg No. 875-987.
- Dotto G.L., Pinto L.A.A. - Adsorption of food dyes onto chitosan: Optimization process and kinetic, Carbohydrate Polymers, Volume 5, (2010) Pg No. 232- 276,
- Dotto G.L., Pinto L.A.A.* - Adsorption of food dyes acid blue 9 and food yellow 3 onto chitosan: Stirring rate effect in kinetics and mechanism, Journal of Hazardous Materials, Volume 7, (2011) Pg No. 98-106.
- Fatemeh Hosseini, Somayeh Sadighian, Hassan Hosseini-Monfared & Niyaz Mohammad Mahmoodi - Dye removal and kinetics of adsorption by magnetic chitosan nanoparticles, Desalination and Water Treatment, Volume 12, (2016) Pg No. 234-267.
- Galan, J.; Trilleras, J.; Zapata, P.A.; Arana, V.A.; Grande-Tovar, C.D. - Optimization of Chitosan Glutaraldehyde-Crosslinked Beads for Reactive Blue 4 Anionic Dye Removal Using a Surface Response Methodology, Life, Volume 15, (2021) Pg No. 562-762.
- Harikishore Kumar Reddy D., Seung-Mok Lee - Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions Advances in Colloid and Interface Science, Vol 7, (2013) Pg No.8-16.

- Jank M. , Köser H. , Lücking F. , Martienssen M. & Wittchen S. - Decolorization and Degradation of Erioglaucine (Acid Blue 9) Dye in Wastewater, Environmental Technology, Volume 16, (1998) Pg No. 102-165.
- Jesús Sánchez-Martín, Jesús Beltrán-Heredia and M Teresa Rodríguez Sánchez - Removal of Erioglaucine (Acid Blue 9) with a new coagulant agent from Acacia mearnsii tannin extract - Coloration Technology, Society of Dyers and Colourists, Volume 7, (2011) Pg No. 98-106.
- Jyh-Ping Chena*, Pei-Chin Yanga, Yunn-Hwa Mab, Tony Wuc - Characterization of chitosan magnetic nanoparticles for in situ delivery of tissue plasminogen activator - Carbohydrate Polymers, Volume 2, (2010) Pg No. 98-106.
- Karla M. Gregorio-Jauregui - One-Step Method for Preparation of Magnetic Nanoparticles Coated with Chitosan, Journal of Nanomaterials, Volume 7, (2012) Pg No. 167-198.
- Leonardo Gomes Braga Ferreira¹, Robson Xavier Faria², Natiele Carla da Silva Ferreira³, and Rômulo José Soares-Bezerra³ - Brilliant Blue Dyes in Daily Food: How Could Purinergic System Be Affected? - International Journal of Food Science, Volume 7, (2016) Pg No. 98-106.
- Reyes F. G. R., Valim M. F. C. F. A. & Vercesi A. E. - Effect of organic synthetic food colours on mitochondrial respiration, Food Additives & Contaminants, Volume 2, (1996) Pg No. 98-106.
- Tariq J. Al-Musawi¹, Nezamaddin Mengelizadeh², Orabi Al Rawi¹, Davoud Balarak³ - Capacity and Modeling of Acid Blue 113 Dye Adsorption onto Chitosan Magnetized by Fe₂O₃ Nanoparticles - Journal of Polymers and the Environment, Volume 4, (2021) Pg No. 56-186. 202

Abdul Hameed

by Turnitin Official

Submission date: 04-Apr-2024 05:35AM (UTC-0400)

Submission ID: 2339680902

File name: REPORT-OF-ZIF-8-FINAL258.pdf (2.73M)

Word count: 4992

Character count: 26693

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Pharmaceutical waste (PhW) refers to any medication waste which is not fully consumed or remains unused throughout the pharmaceutical supply and uses chain. As pharmaceutical products are necessary for human health, to fulfill the growing need for pharmaceutical products, healthcare industries produce a huge number of drugs annually [1]. These pharmaceutical products contain biologically active ingredients referred to as active pharmaceutical ingredients (API). Any chemical constituent having pharmaceutical function with useful effects to diagnose, prevent, treat, or cure disease and affect the body's structure and function is considered an API. The API performs specific functions in animals and humans and is not completely degraded after metabolic reactions in the body. These chemicals are released into the environment from various sources and are referred to as PhW products [2]. PhW includes a variety of materials such as expired, split, contaminated drugs (used or unused), personally discarded patient's medication, discarded drugs, abandoned material (connecting tubes, masks, syringes, vials, bottles with residues), and containers that are used to keep hazardous waste drugs, spill cleanup materials, absorbents, and home use personal care products [3]. A major part of PhW is various drugs, serums, and vaccines such as antibiotics, hormones, chemotherapy products, and antidepressants. In response to acute or chronic illness, only a part of the active ingredient in the metabolized drug. The nonmetabolized part along with metabolized part enters the aquatic system by waste discharge. All these substances either from industrial or domestic sources discharged directly or indirectly into the water where they remain persistent for a longer time. In the 1970s, environmental contaminations due to pharmaceutical products were raised. The first analysis to estimate the concentration of pharmaceuticals in surface and potable water was performed in 1980. A very small amount of these pharmaceutical active compounds largely affects human health and the ecosystem. So, the removal of these waste materials from the environment is of utmost. Since the 1990s, the technology became adequately advanced to quantify

the concentration of PhAC in water samples at low levels, that is, $\mu\text{g/L}$ and ng/L [6]. Now, different methods have been established for the removal of API from the environment. But still, now different challenges arise for their removal due to their small concentration. The conventional methods for WWT involve coagulation, filtration, biological processes, sedimentation, membrane filtration, chlorination, adsorption (using carbon nanotubes, activated carbon, ozonation, and graphene oxide), photocatalysis, UV irradiation, and many others. The effects of API in the environment on nontarget species are unknown. However, one study revealed that in, the residual diclofenac was responsible to minimize the vulture population. The long-term exposure to API largely affects the physiology and growth of organisms. Therefore, unwanted medicine should be disposed of properly to overcome environmental and public health risks. Because the improper disposal of leads to accidental toxicity and ultimately results in landfill pilfering, antimicrobial resistance, water pollution, rising healthcare costs, and death. All these effects may be reduced by raising public awareness regarding disposal practices

1.2. Introduction of ibuprofen

Ibuprofen, a widely used nonsteroidal anti-inflammatory drug (NSAID), is renowned for its effectiveness in relieving pain, reducing inflammation, and lowering fever. With its mechanism of action primarily targeting the inhibition of cyclooxygenase enzymes, specifically COX-1 and COX-2, ibuprofen impedes the production of prostaglandins, thereby mitigating pain and inflammation. This medication is commonly employed to alleviate various conditions, including headaches, muscle aches, dental pain, menstrual cramps, arthritis, and minor injuries. Available over-the-counter and in prescription strength, ibuprofen offers a versatile option for managing mild to moderate pain and inflammation. However, it's essential to adhere to recommended dosages and guidelines, as excessive or prolonged use can lead to adverse effects such as gastrointestinal complications and cardiovascular risks. Consulting a healthcare professional is advised for proper usage and to minimize potential risks associated with ibuprofen intake.

1.3. Harmful effect of ibuprofen in wastewater:

The presence of ibuprofen in wastewater raises considerable environmental concerns due to its potential adverse effects on aquatic ecosystems. As ibuprofen enters wastewater through various pathways including human excretion and improper disposal, it becomes a persistent contaminant in water bodies. Once introduced into aquatic environments, ibuprofen and its metabolites can exert toxic effects on aquatic organisms such as fish, algae, and invertebrates. Even at low concentrations, ibuprofen can disrupt physiological processes, impair growth, and interfere with reproductive functions in these organisms. Furthermore, ibuprofen's ability to bioaccumulate within the food chain exacerbates its environmental impact, posing risks not only to aquatic species but also to humans who consume contaminated seafood.

To address the environmental risks associated with ibuprofen in wastewater, concerted efforts are required to promote proper disposal practices and enhance wastewater treatment technologies. Public awareness campaigns and pharmaceutical take-back programs can encourage individuals to dispose of unused medications responsibly, reducing the likelihood of ibuprofen entering wastewater in the first place. Additionally, advancements in wastewater treatment processes, such as advanced oxidation, membrane filtration, and activated carbon adsorption, can improve the removal efficiency of pharmaceutical compounds, including ibuprofen, from wastewater. By implementing these measures, we can minimize the environmental footprint of ibuprofen and protect the integrity of aquatic ecosystems for present and future generations.

1.4. ZIF-8 INTRODUCTION

ZIF-8, short for Zeolitic Imidazolate Framework-8, represents a pivotal advancement in the realm of metal-organic frameworks (MOFs), a class of porous materials renowned for their diverse applications. Characterized by its unique structure comprising zinc ions coordinated with imidazolate ligands, ZIF-8 exhibits exceptional thermal and chemical stability, rendering it suitable for a wide array of applications ranging from gas storage and separation to catalysis and drug delivery.

Its high surface area, tunable pore size, and remarkable adsorption properties make ZIF-8 particularly promising for gas storage and separation applications, offering potential solutions to challenges in fields such as energy storage and environmental remediation. Furthermore, ZIF-8's ability to encapsulate guest molecules within its pores opens avenues for controlled drug release systems, heralding innovations in pharmaceutical formulations. With ongoing research aimed at further enhancing its properties and exploring novel applications, ZIF-8 stands as a cornerstone in the burgeoning field of MOFs, holding promise for addressing pressing societal and environmental challenges in the years to come.

CHAPTER 2

2.1 LITERATURE SURVEY

1 Lili Yang 1, 2, Chong Li 1, Jingmei Lv 1, Shijing Zhan 1, and Tongying Feng t al 2018 IOP Conf: ZIF-8 as a reactive adsorbent for phosphate removal from treated wastewater: Phosphate can promote the synthesis of protein, and it is conducive to the reduction and utilization of nitrate by nitrogen fixation. Phosphate participates in the synthesis of plant fat, which can improve crop adaptability to the external environment. However, if phosphorus pollution is discharged directly, it will lead to serious environmental pollution, such as nutrient enrichment of seawater. ZIF-8, a subclass of MOF, has emerged as a new kind of porous crystalline materials with excellent properties such as uniform micro-pores, accessible pore volumes, large surface areas as well as exceptional chemical and thermal stabilities, making it potentially interesting candidate for adsorbing phosphate from waste water.

2 Surendra Sasi Kumar Jampa , Ashish Prabhudas Unnarkat , Rajesh Vanshpati VOLUME 19, AUGUST. 2020, 100927: ADSORPTION AND RECYCLABILITY ASPECTS OF HUMIC ACID USING NANO-ZIF-8 ADSORBENT In this present study, nano ZIF-8 has been used as an adsorbent due to a relatively high surface area of the particles ($1400 \text{ m}^2 \text{ gm}^{-1}$) which could emerge as a potential adsorbent for water purification. Nano ZIF-8 particles were synthesized using single step room temperature procedure and characterized using different analytical instruments. Humic acid absorption process results showed exothermic in nature which was in contrast to the results reported in the literature. Kinetic and thermodynamic modelling of the results was explored for the adsorbent. The adsorption results are compared with various adsorbents to benchmark the material in this work.

3. Beom K. Jung, Jong Won Jun, Zubair Hasan, Sung Hwa Jung . (2015). Adsorptive removal of p-arsanilic acid from water using mesoporous zeolitic imidazolate framework-8. Chemical Engineering Journal, 267, 9–15. The adsorption kinetics and adsorbed amount of ASA were improved by introducing mesoporosity into the pristine ZIF-8 structure. The high adsorption capacity of mesoporous ZIF-8 for ASA and facile regeneration of the used adsorbent show that

mesoporous ZIF-8 has potential applications in the adsorptive removal of organoarsenic compounds such as ASA. Based on the adsorption results at various pH values and the surface charges on ZIF-8s, the adsorption mechanism of ASA on ZIF-8s can be explained by electrostatic interactions between the positively charged ZIF-8 surface and the anionic forms of ASA.

CHAPTER 3

AIM AND SCOPE

3.1. AIM:

- To improve the delivery of ibuprofen by utilizing ZIF-8 as a carrier. ZIF-8's high surface area and tunable pore size make it suitable for loading and releasing drug molecules like ibuprofen in a controlled manner.
- To remove ibuprofen from aqueous solutions for environmental remediation purposes. ZIF-8's adsorption capacity and selectivity make it effective for removing pharmaceutical pollutants from wastewater, contributing to efforts to mitigate environmental contamination and protect ecosystems and human health.
- To involve separating ibuprofen from complex mixtures, such as pharmaceutical formulations or contaminated water sources. ZIF-8's selective adsorption properties can facilitate the purification of ibuprofen, ensuring its quality and purity for pharmaceutical or analytical purposes.
- To utilize ZIF-8 for targeted delivery or controlled release of ibuprofen in therapeutic interventions
- To optimize pharmaceutical formulations containing ibuprofen by incorporating ZIF-8. ZIF-8 can enhance the stability, solubility, or bioavailability of ibuprofen in formulations, leading to improved drug efficacy and patient compliance.

3.2 OBJECTIVE

- The effectiveness of ZIF-8 for ibuprofen adsorption can be influenced by various factors like pH, temperature, and the presence of other contaminants
- Environmental Remediation: If the focus is on environmental applications, the objective could be to remove ibuprofen from water or other aqueous solutions using ZIF-8 as an adsorbent. This could be to mitigate the environmental impact of pharmaceutical pollutants in wastewater.
- Separation and Purification: Another objective might involve separating ibuprofen from a mixture, such as from other drugs or components in a

pharmaceutical formulation. ZIF-8's selective adsorption properties could be leveraged for this purpose.

- **Drug Formulation and Stability:** ZIF-8 could be used to encapsulate ibuprofen molecules to enhance their stability, protect them from degradation, or improve their bioavailability. The objective here could be to develop more effective pharmaceutical formulations.

3.2. SCOPE:

- **Water Purification:** ZIF-8 shows good potential for removing ibuprofen from water. Its high surface area and porous structure allow it to capture ibuprofen molecules effectively. This can be crucial for treating wastewater or environmental remediation.
- **Controlled Drug Delivery:** Researchers are exploring ZIF-8 as a carrier for ibuprofen. By encapsulating the drug within ZIF-8, they can potentially control its release rate and target specific locations in the body. This could be beneficial for sustained delivery or localized treatment.
- **Reusability:** ZIF-8 can be regenerated and reused for multiple adsorption cycles, making it a more sustainable option compared to some disposable adsorbents.
- **Tailoring Properties:** ZIF-8 can be modified to improve its adsorption capacity for ibuprofen. Scientists can introduce functional groups onto the ZIF-8 surface that interact more favorably with ibuprofen molecules.
- **Wastewater Treatment Integration:** Exploring ways to integrate ZIF-8 into existing wastewater treatment systems or designing new systems that leverage its unique properties can enhance the overall efficiency of pesticide removal on a larger scale.
- **Evaluating the environmental impact of using ZIF-8:** in pesticide removal is crucial. Assessing factors such as the fate of used ZIF-8 and any potential byproducts helps ensure the overall sustainability of the treatment process.

CHAPTER 4

MATERIALS AND METHODS

4.1. MATERIALS AND CHEMICALS :

1. **ZIF-8:** Synthesized using appropriate precursors such as zinc nitrate hexahydrate and 2-methylimidazole. ZIF-8 can be obtained commercially or prepared in the laboratory using established synthesis protocols.
2. **Ibuprofen Solution:** A solution of ibuprofen in a suitable solvent, typically water or a water-miscible organic solvent such as methanol or ethanol. The concentration of ibuprofen in the solution may vary depending on the experimental requirements.
3. **Solvents:** Methanol, ethanol, or water may be used as solvents for preparing the ibuprofen solution and conducting the adsorption experiments.
4. **Analytical Instruments:** Instruments such as UV-Vis spectrophotometer, high-performance liquid chromatography (HPLC), or gas chromatography-mass spectrometry (GC-MS) may be used for ibuprofen quantification

4.2. Methods :

1. **Synthesis of ZIF-8:** ZIF-8 is synthesized using a solvothermal or microwave-assisted method. The synthesis involves mixing appropriate molar ratios of zinc nitrate hexahydrate and 2-methylimidazole in a solvent followed by heating at a specific temperature for a certain duration to obtain ZIF-8 crystals.
2. **Characterization of ZIF-8:** The synthesized ZIF-8 is characterized using techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) surface area analysis, and Fourier-transform infrared spectroscopy (FTIR) to confirm its structure, morphology, surface area, and chemical composition.
3. **Preparation of Adsorbent:** The synthesized ZIF-8 is typically washed and dried before use to remove any impurities or residual solvents. It may also undergo activation or pre-treatment steps to enhance its adsorption properties.

4.2.1 PREPARATION OF zif 8 reactive adsorbent

Stirring:

- Stir the solution for a certain period to ensure complete mixing and dissolution.
- 7 g of 2-methylimidazole was dissolved in 80 mL of methanol with stirring



FIG 4.1.1 2-METHYLIMIDAZOLE AND METHANOL

4.2.2 Precipitation and Crystallization:

- After stirring, the mixture undergoes precipitation, resulting in the formation of ZIF-8 crystals.
- The formation of ZIF-8 is facilitated by the coordination of zinc ions with imidazole ligands.
- Then, 3.0 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in 40 mL of methanol was added with vigorous stirring for 24 h at room temperature
- Third, both solutions were mixed under rigorous mixing for 15 min



FIG 4.2.2 CENTRIFUGAL PUMP

- The final solution was then poured in centrifugal tubes and centrifuged at 5000 rpm for 30 min



FIG 4.3.3 CENTRIFUGAL TUBES

- The solid product was recovered and washed at least for four times.



FIG 4.4.4 PREPARED OF ZIF-8

5.1. ADSORPTION OF IBUPROFEN USING ZIF-8 :

Considerations:

- Several factors can influence the effectiveness of ibuprofen adsorption using ZIF-8. These include:
 - pH of the solution
 - Temperature
 - Concentration of ibuprofen
 - Contact time between ZIF-8 and the solution
 - Presence of other competing molecules



FIG 5.1 IBUPROFEN

5.2. Stock solution of ibuprofen :



FIG 5.3.OF IBUPROFEN STOCK SOLUTION

Prepare a stock solution of ibuprofen 1g in 1000ml of water

Preparation:

- The stock solution is prepared by dissolving a specific amount of ibuprofen powder into a chosen solvent to achieve a desired concentration. This concentration is usually higher than the final concentration you expect after the adsorption process with ZIF-8.

20ml stock + 80ml of water dosage of MOF (0.2g 0.4g 0.6g 0.8g 1g) while

stirring for 60 min in centrifuge



FIG 5.6. CENTRIFUGE SAMPLE OF DOSAGE

CHAPTER 5

□ Results and CHARACTERIZATION

5.0.CHARACTERIZATION

Fourier Transform Infrared (FTIR) analysis was applied to The FTIR peak at 3845 cm^{-1} in the context of ZIF-8, particularly for pesticide removal from wastewater, might be associated with certain functional groups or vibrations. However, without more specific information about the full FTIR spectrum and the conditions of the experiment, it's challenging to pinpoint the exact nature of this peak.

Energy-Dispersive X-ray Spectroscopy (EDS):

- If available, consider using EDS of conjunction with SEM in obtain elemental composition information, confirming the presence of ZIF-8 and potentially identifying pesticides

Cross-Sectional Imaging:

- Cross-sectional SEM imaging can provide in a deeper understanding of ZIF-8's internal structure and its interaction with pesticides.

Comparison with Control Samples:

- Include SEM images of ZIF-8 without pesticide exposure as a control. This aids in distinguishing changes attributed of the presence of pesticides

Quantitative Analysis:

- If applicable, use image analysis software to quantitatively assess features such as particle size in distribution

□

Characterization of prepared :zif 8 pesticide removal from waste

6.1 .Fourier Transform Infrared (FTIR).

- The region around 3845 cm^{-1} in FTIR spectra often corresponds to the O-H stretching vibrations of hydroxyl (OH) groups.
- The native PMPP sample exhibited a broad adsorption peak at 3845 cm^{-1} indicating the presence of bonded and free hydroxylic group due to O-H group vibration.
- The peak is observed at 3845 cm^{-1} corresponds to O-H stretching.
- So far, The FTIR discussions has established the existence of five major adsorption peak at 3845 cm^{-1} , 3772.08 cm^{-1} , 3700.73 cm^{-1} , 3628.41 cm^{-1} and 2918.73 cm^{-1} .

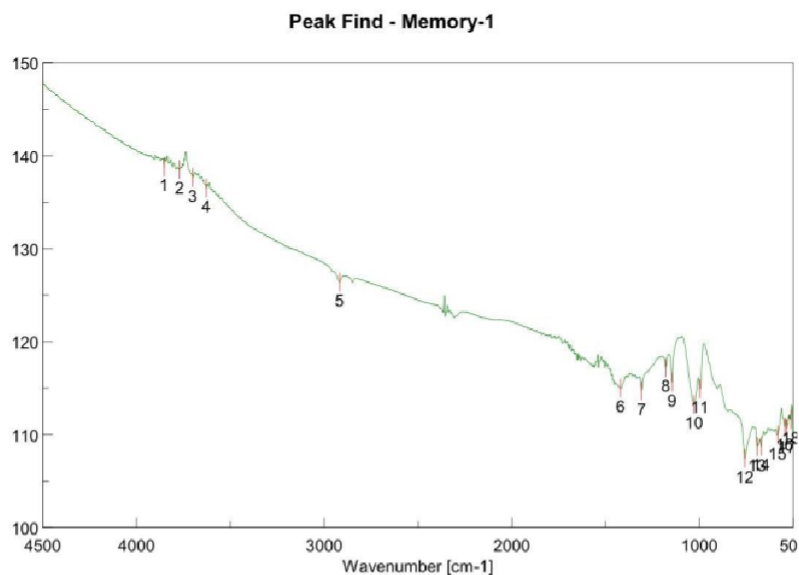
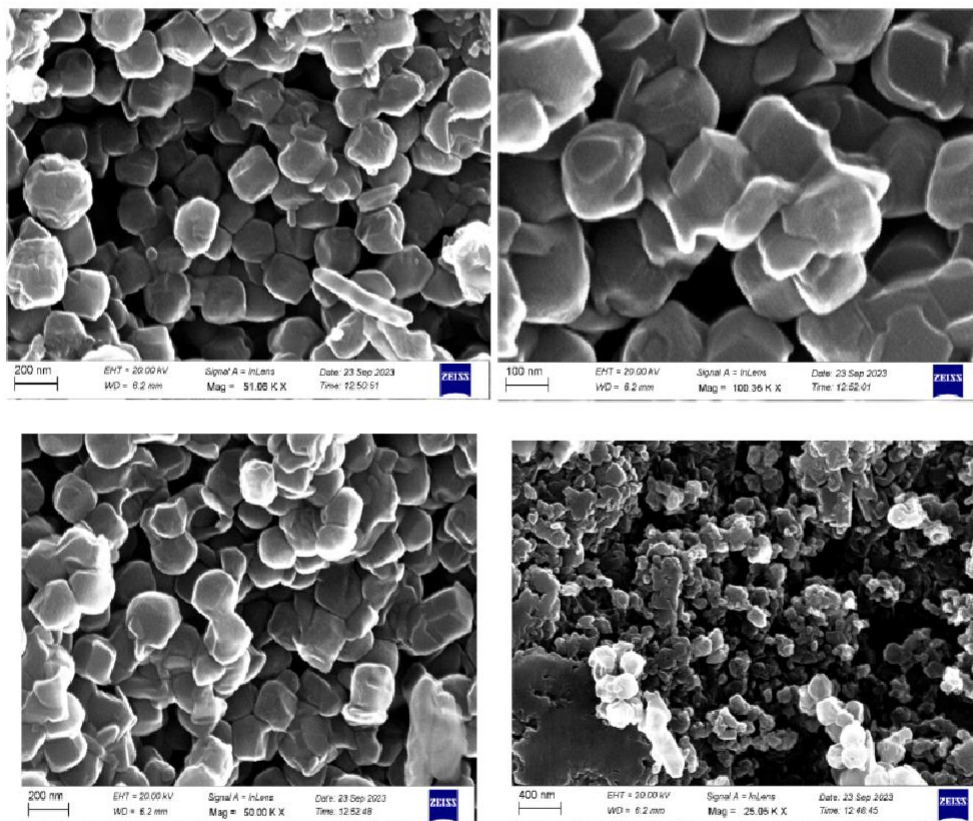


FIG 6.1.0 FTIR FOR ZIF-8

6.2. SCANNING ELECTRON MICROSCOPY (SEM).

- Evaluate the SEM images to identify potential adsorption sites in the ZIF-8 surface. Pesticide molecules may be visible on the material's surface.
- Look for any evidence in pore blocking or modification in the SEM images after exposure to pesticides. This could indicate the adsorption mechanism.
- Observe whether there is any agglomeration in ZIF-8 particles, which may be indicative of the adsorption of pesticides.
- Assess the uniformity of the ZIF-8 surface after pesticide exposure. Non-uniformities may suggest preferential adsorption sites.



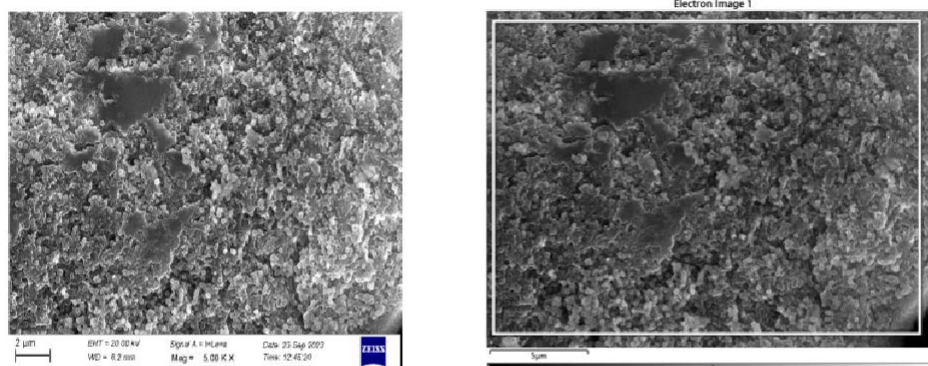
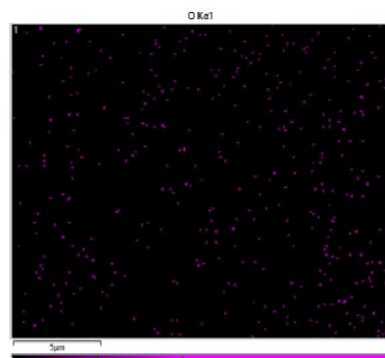


FIG 6.1.1 SEM FOR ZIF-8

EDAX.

EDAX is an analytical method that measures the energy of X-rays released when electrons interact with a sample. It is frequently used in conjunction with scanning electron microscopy (SEM) to ascertain the elemental composition of a sample. It is utilized for elemental analysis in a variety of applications, such as geology and materials characterization



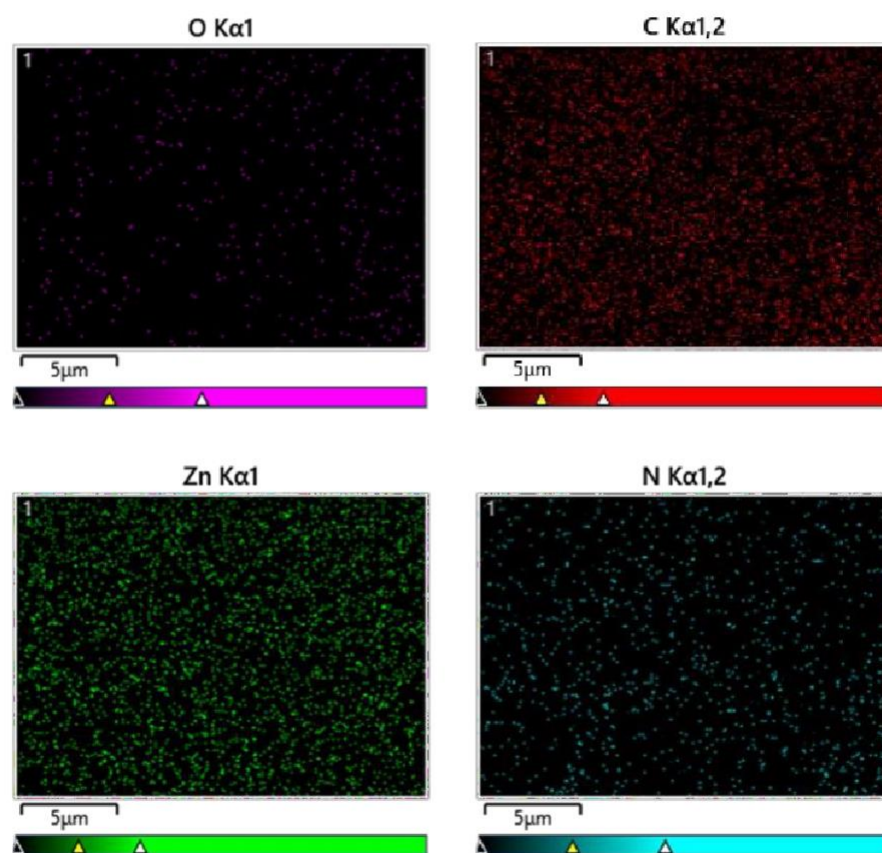
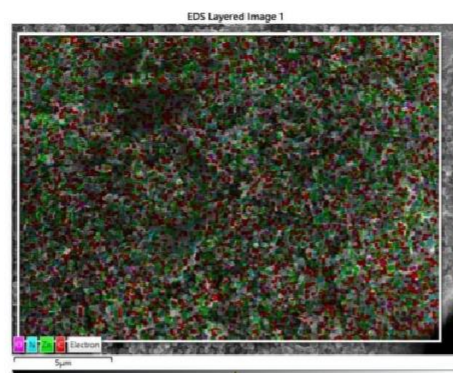
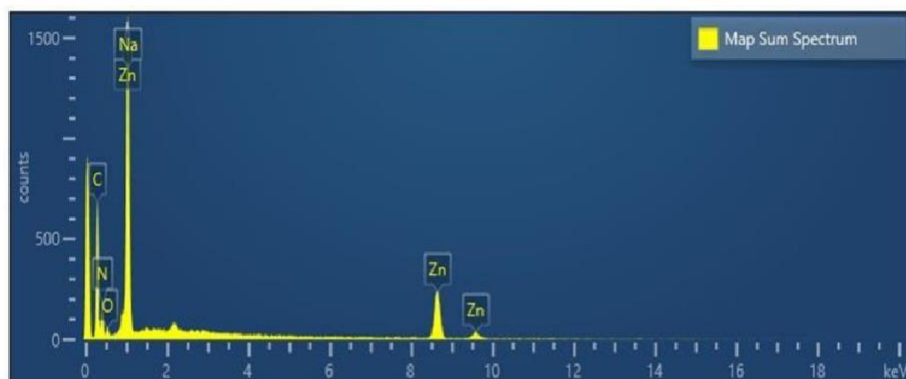


FIG 6.1.2 EDAX FOR ZIF-8

EDAX FOR ZIF-8:



Map Spectrum	Sum				
Element	Line Type	Weight %	Weight Sigma	%	Atomic %
C	K series	47.27	1.16		61.17
N	K series	26.01	1.43		28.86
O	K series	2.98	0.44		2.90
Na	K series	3.24	0.41		2.19
Zn	K series	20.50	0.64		4.87
Total		100.00			100.00

FIG 6.1.3 EDAX FOR ZIF-8

Post studies of ZIF-8 (FTIR)

No. Position Intensity No. Position Intensity

No.	Position	Intensity	No.	Position	Intensity
1	2928.38	99.5536	2	2359.48	97.9066
3	1581.34	94.6944	4	1422.24	87.4509
5	1382.71	91.4347	6	1310.39	87.2628
7	1180.22	91.9144	8	1145.51	76.8172
9	994.125	87.5732	10	953.627	96.4358
11	828.277	96.8759	12	758.852	80.3307
13	693.284	87.6579	14	684.606	88.4269
15	529.364	96.5549			

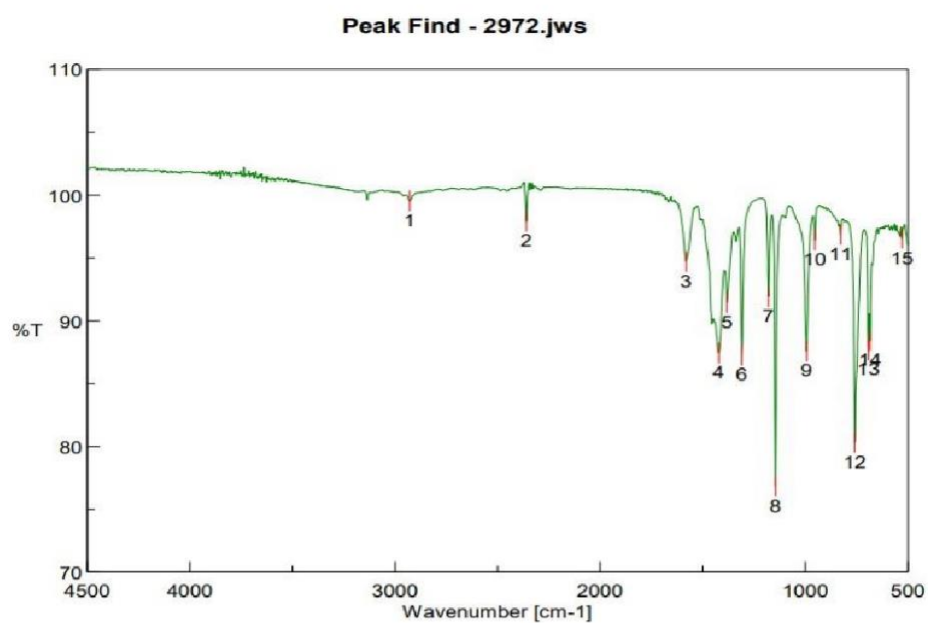
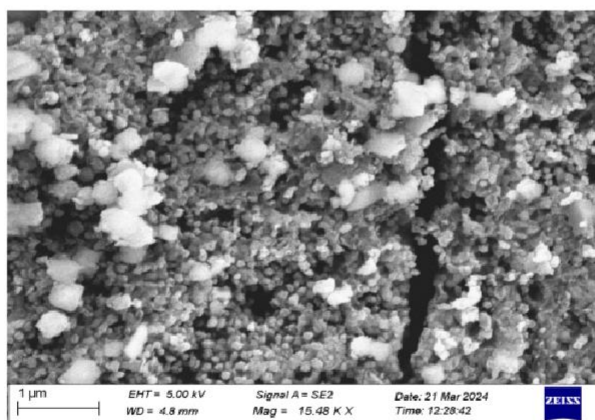


FIG 6.1.4 FTIR FOR Post studies of ZIF-8

Post studies of ZIF-8 (FESEM)



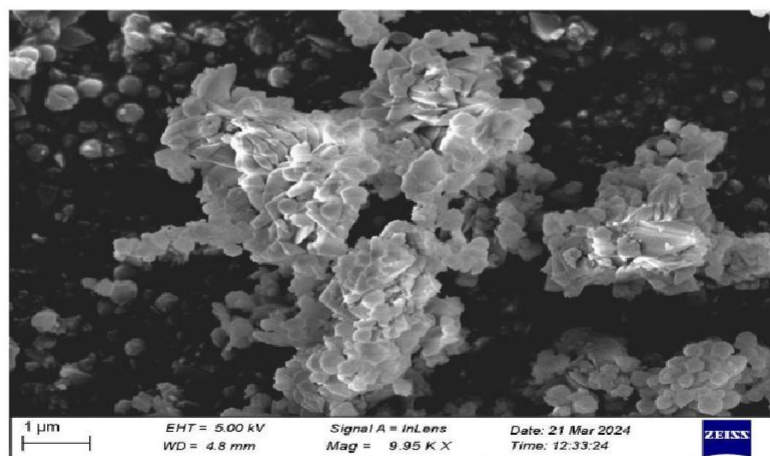
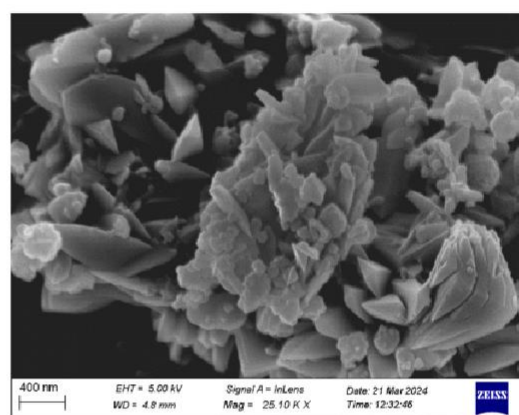
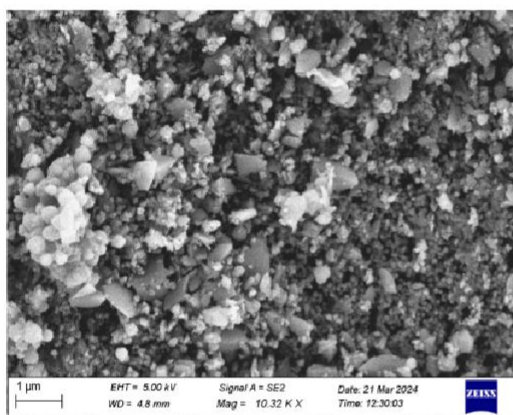
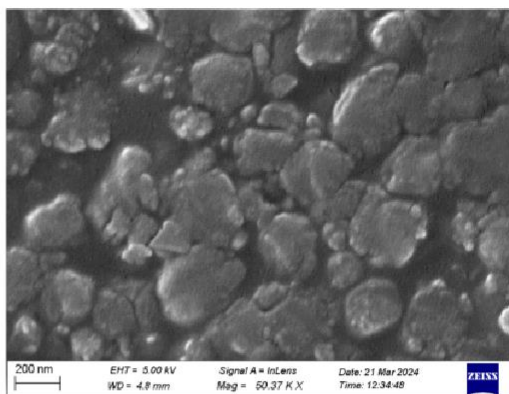
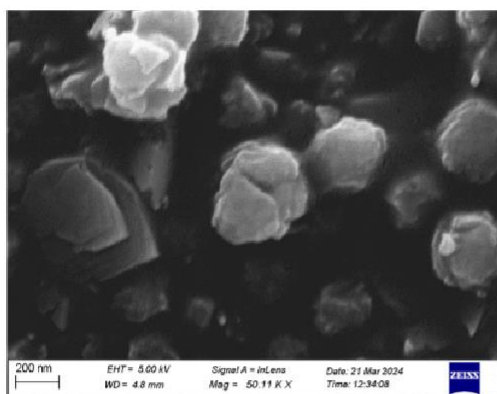


FIG 6.1.5 Post studies of ZIF-8 (FESEM)

Post studies of ZIF-8 (XRD)

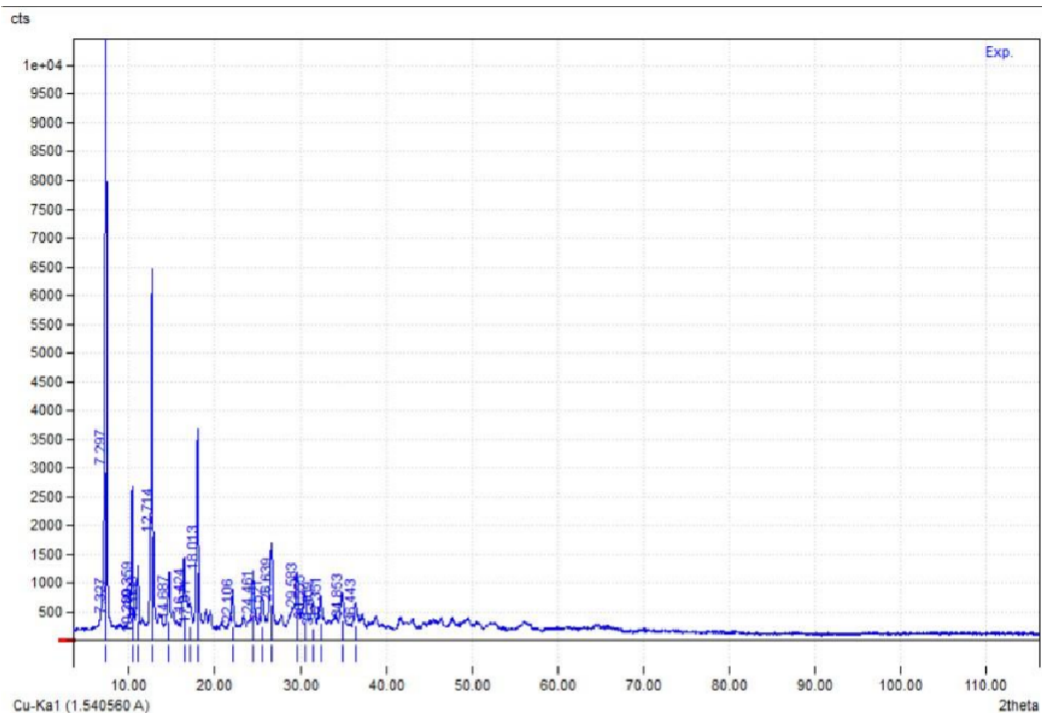


FIG 6.1.6 Post studies of ZIF-8 (XRD)

- After the adsorption process, the ZIF-8 material (with adsorbed ibuprofen) is separated from the solution. The ZIF-8 is then dried and prepared for XRD analysis.
- During XRD analysis, the ZIF-8 sample is exposed to an X-ray beam. The X-rays interact with the electrons within the crystals of the ZIF-8 and the potentially adsorbed ibuprofen (if crystalline).
- The diffracted X-rays are detected and their intensities recorded at various angles.
- The resulting XRD pattern is a plot of intensity versus diffraction angle.

Peak List					
No.	2theta [°]	d [Å]	I/I0 (peak height)	Counts (peak area)	FWHM
1	7.30	12.1041	1000.00	2920.57	0.2355
2	7.33	12.0555	115.56	337.51	0.2355
3	10.36	8.5324	246.46	539.85	0.1766
4	10.39	8.5083	33.78	74.00	0.1766
5	11.04	8.0104	106.88	312.14	0.2355
6	12.71	6.9567	666.73	1825.47	0.2208
7	14.69	6.0265	100.97	309.24	0.2470
8	16.42	5.3928	119.56	434.46	0.2930
9	17.07	5.1897	39.99	247.89	0.4999
10	18.01	4.9203	379.14	1168.58	0.2509
11	22.11	4.0179	69.00	252.24	0.2948
12	24.46	3.6361	99.22	396.92	0.3226
13	25.52	3.4874	55.50	247.94	0.3576
14	26.64	3.3435	154.82	618.31	0.3221
15	29.58	3.0171	92.62	513.88	0.4465
16	30.55	2.9233	61.99	311.17	0.4130
17	31.41	2.8458	42.69	191.39	0.3589
18	32.35	2.7650	55.70	292.28	0.4241
19	34.85	2.5720	62.77	329.73	0.4236
20	36.44	2.4634	44.13	255.06	0.4685

Integrated Profile Areas		
Profile area	Counts	Amount
Overall diffraction profile	1164659	100.00%
Background radiation	659228	56.60%
Diffraction peaks	505431	43.40%
Peak area belonging to selected phases	0	0.00%
Unidentified peak area	505431	43.40%

Peak Residuals		
Peak data	Counts	Amount
Overall peak intensity	11579	100.00%
Peak intensity belonging to selected phases	8016	69.23%
Unidentified peak intensity	3563	30.77%

FIG 6.1.7 PEAK REPORT OF XRD

PEAK REPORT OF XRD

5.6.1 EFFECT OF pH:

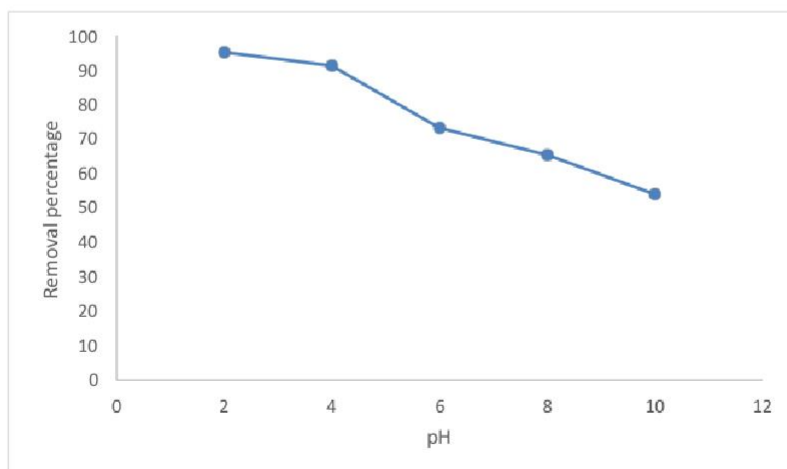


Fig 5.27 effect of pH vs Removal %

In order to assess the influence of pH, the pH level of the solution was adjusted within the range of 2 to 10. Adsorption experiments were carried out in the pH range of 2–10 keeping all other parameters constant (MH concentration = 10 mg/L; adsorbent dose = 10g/ L for zif-8 and 5g/L for GO-BC; contact time =120 min), it is evident that the adsorption of the metformin hydrochloride for and GO-BC increased as the pH of the solution increased from 53.97 to .9519% for AIBB and 47.14 to 95.47% for GO-BC. From 2 to 6 and started to decrease after reaching maximum at pH 2. The maximum adsorption of metformin hydrochloride by zif-8 and ibuprofen at pH 2 attributed to optimal surface charge and chemical speciation, favoring effective binding of neutral metformin molecules to adsorbent surface. Additionally, the surface functional groups were likely in an optimal state for interaction with ibuprofen molecules at this pH. At pH 2, minimized competition from other ionic species and enhanced chemical stability further facilitated efficient adsorption of ibuprofen onto zif-8 a, resulting in maximum adsorption capacity at this pH level

The effect of pH on IBP adsorption was studied in the pH range (2–8), by adjusting the solutions to the desired levels using HCl or NaOH. The effect of pH on 25 mg MMIPs with IBP 50 mg/L during a 90 min contact time is The optimal adsorption capacity is obtained at pH 4. At pH 2 to 9, there is an increase in adsorption capacity because the adsorbent surface which is positively charged will interact electrostatically with the –OH group which is charged negatively on IBP, but then the adsorption capacity decreases with further increase in pH because IBP

5.6.2 EFFECT OF ADSORBENT DOSAGE:

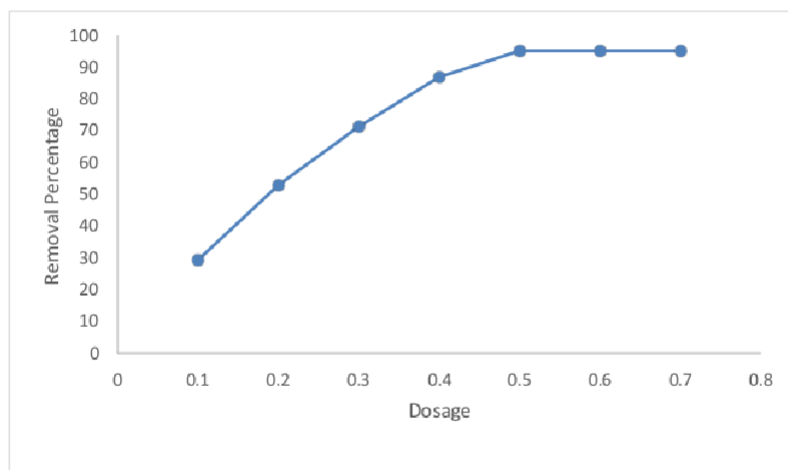


Fig:5.40: Adsorbent Dosage of IBUPROFEN

The removal of ciprofloxacin by was studied by varying the dosage (2,4,6,8,10,12,14) g/l with initial concentration of (10 mg/l), pH (2), contact time (120 min), and temperature at 303K

Removal was highest when dosage used was 0.5 g/l (95.19%) so 10g/l was chosen as the optimum dosage.

EFFECT OF DOSAGE :

- As the dosage of ZIF-8 increases, the total surface area available for ibuprofen adsorption also increases. This translates to a greater number of potential binding sites for ibuprofen molecules. Consequently, the overall adsorption capacity of the system increases.
- There's a limit to this however. Imagine the ZIF-8 particles as sponges. As you add more sponges (increase dosage), you can absorb more water (ibuprofen).

The optimal ZIF-8 dosage depends on several factors, including:

5.6.3 EFFECT OF INITIAL CONCENTRATION

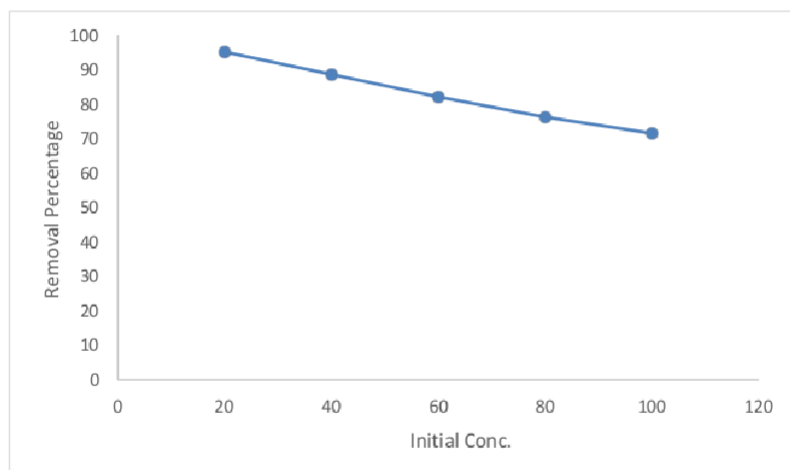


Fig 5.29 Effect of initial concentration vs removal %

The removal of zif-8 was studied by varying the initial concentration (10,20,30,40,50) mg/l while keeping the adsorbent dosage (20g/l) ,pH(2) ,120 min contact time and temperature at 303K Removal was highest at 20 mg/l(95.19%) so 10mg/l was chosen as the optimum concentration

5.6.4 EFFECT OF CONTACT TIME

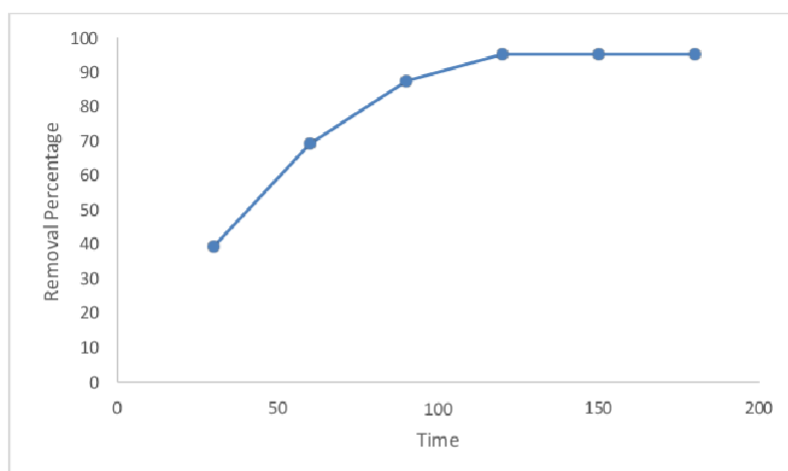


Fig 5.30 Effect of contact time vs removal %

The removal of ciprofloxacin was studied by varying the contact time (30,60,90,120,150,180 min) while keeping the dosage (10g/l), pH(2), initial concentration (120mg/l) and temperature 303K

Removal was highest when contact time was 120min (95.19%) so 120 min was chosen as the optimum contact time

EFFECT OF CONTACT TIME :

20ml stock +80ml water =100mg/L + pH 4+ Room temp

1g of dosage MOF

TIME=(30,60,90,120,150,180) min

- As time progresses, more and more ibuprofen molecules get adsorbed onto the ZIF-8. Gradually, the available binding sites become occupied. The rate of adsorption slows down and eventually reaches a state of equilibrium. At this point, the rate of ibuprofen adsorption onto the ZIF-8 is balanced by the rate of ibuprofen desorbing back into the solution.
- The time required to reach equilibrium depends on several factors:
- Initial ibuprofen concentration: Higher initial concentrations will take longer to reach equilibrium as there are more ibuprofen molecules competing for binding sites.
- ZIF-8 dosage: A higher dosage of ZIF-8 provides more surface area and binding sites, leading to faster initial adsorption but also potentially reaching equilibrium sooner.

EFFECT OF TEMPERATURE

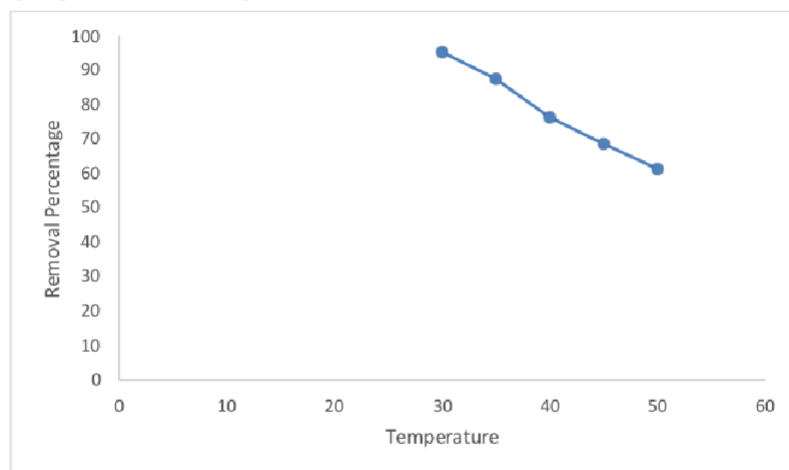


Fig 5.31 Effect of temperature vs removal %

The removal of ZIF-8 was studied by varying the Temperature (303,308,313,318,323 K) while keeping the dosage (30g/l), pH(2), initial concentration (30mg/l) and contact time 120 min

Removal was highest when temperature was 303K (95.19%) so 303 K was chosen as the optimum temperature

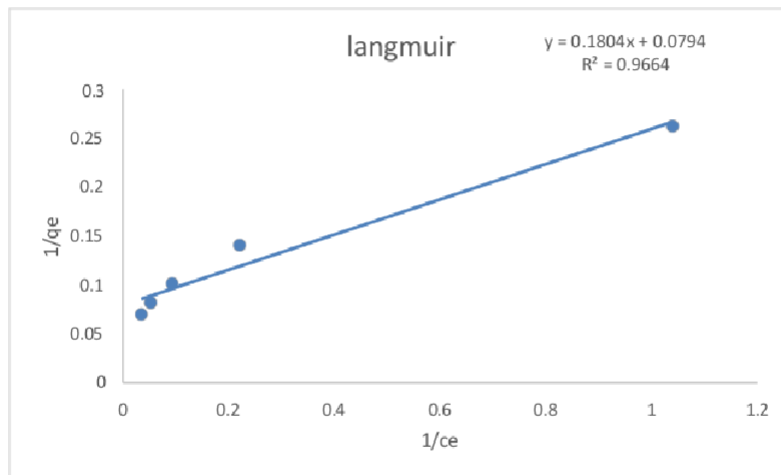
5.7 ADSORPTION ISOTHERM MODELS

In essence, an adsorption isotherm serves as a vital curve elucidating the processes governing the retention, release, or mobility of a substance from aqueous porous media or aquatic environments to a solid-phase, under constant temperature and pH conditions. In this study, three adsorption isotherm models, namely Langmuir, Freundlich, and Tenkim isotherms were employed to investigate the adsorption of MH by AIBB and GO-BC adsorbents.

5.7.1 LANGMUIR ISOTHERM

The Langmuir isotherm model is suitable for monolayer adsorptions and can be expressed as follows:

$$\frac{1}{q_e} = \left[\frac{1}{q_m(K_L C_e)} \right] + (1/q_m)$$



Where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg-1), q_m is the maximum adsorption capacity (mg-1), K_L is the Langmuir constant and C_e is the equilibrium concentration of adsorbate in the solution.

5.7.2 FREUNDLICH ISOTHERM

The Freundlich isotherm, an early empirical model, characterizes non-ideal and reversible adsorption phenomena, extending beyond monolayer formation. It accommodates multilayer adsorption with varying distribution of adsorption heat and affinities across heterogeneous surfaces. The equation representing this isotherm is as follows

$$q_e = K F C_e^{1/n},$$

Where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg^{-1}), C_e is the equilibrium concentration, K_f is the Freundlich constant and $1/n$ is the empirical parameter related to adsorption intensity.

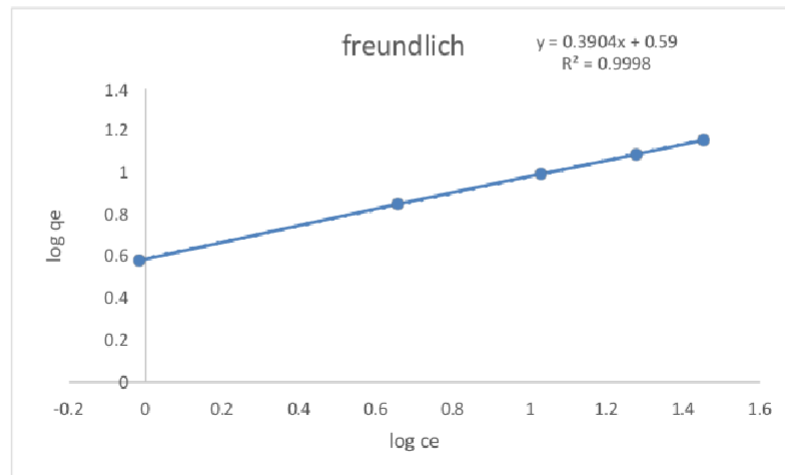


Fig 5.34 Freundlich isotherm of IBUPROFEN

5.1.1 TENKIM ISOTHERM:

Tenkim isotherm, is a model used to describe adsorption phenomena on solid surfaces. It assumes that the adsorption heat of molecules decreases linearly with surface coverage due to adsorbent-adsorbate interactions, incorporating a parameter to account for the potential energy of adsorption sites. The tenkim equation can be given as follows:

$$q_e = B \ln (A C_e)$$

Where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg^{-1}), C_e is the equilibrium concentration, KT is the Tenkim constant. R represents the universal gas constant, and T represents the absolute temperature in Kelvin

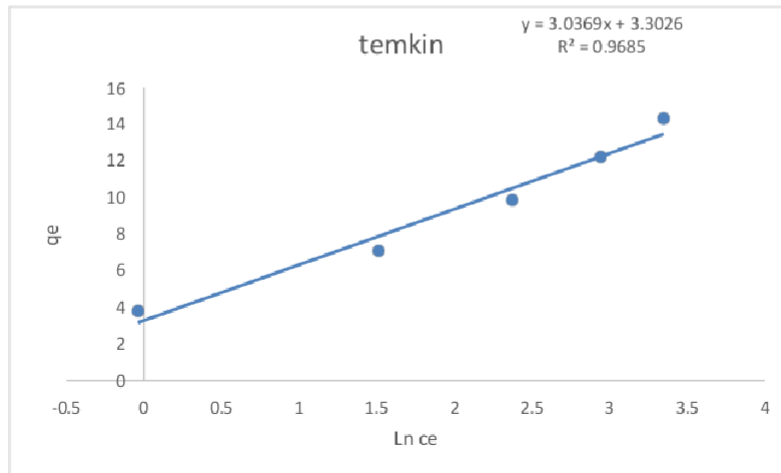


Fig 5.36 Tenkim Isotherm of ZIF-8

Models	Parameters	Values
Langmuir	Slope	0.1804
	Intercept	0.0794
	$q_{\max} (\text{mg/g})$	12.59
	R^2	0.9664
Freundlich	Slope	0.3904
	Intercept	0.59
	R^2	0.9998
Tenkim	Slope	3.0369
	Intercept	3.3026
	R^2	0.9685

TABLE 5.11 ADSORPTION ISOTHERM PARAMETER

5.8 ADSORPTION KINETIC MODELS

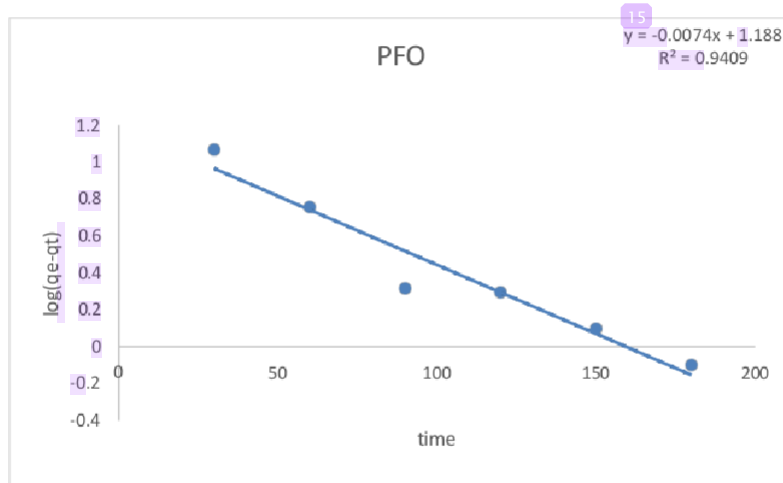
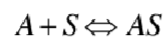


Fig:5.46: Adsorption Kinetics for ZIF-8

The kinetic models offer insights into the time needed to reach adsorption equilibrium, serving as a crucial aspect in designing adsorption systems. They provide valuable information about the process rate and the efficacy of the adsorbent material. Pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models are used to evaluate the prepared adsorbents.

Pseudo-first order kinetic model is given as:



$$\frac{q_t}{q_e} = 1 - \exp \left[- \left(k_A C_s + \frac{k_A}{k_s} \right) t \right]$$

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t$$

$$k_{ad} = \left[\left(k_A C_s + \frac{k_A}{k_s} \right) \right]$$

$$q_t = X_{At} \quad \text{and} \quad q_e = X_{Ae}$$

Pseudo-second order kinetic model is given as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2$$

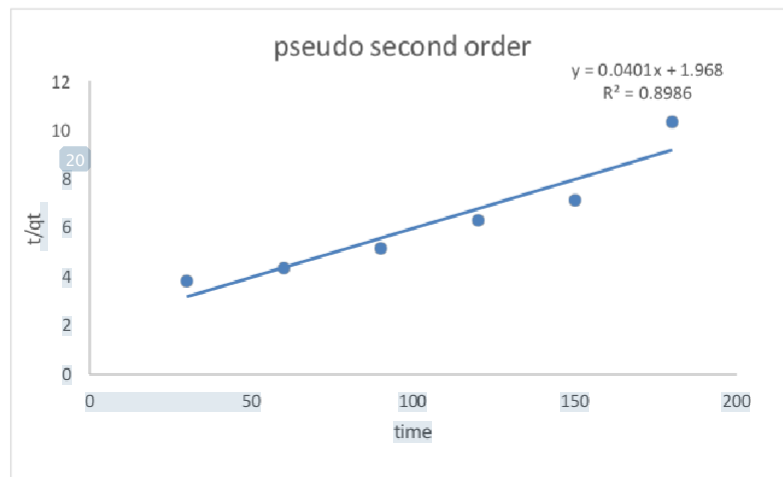


FIG 5.1.3 PSEUDO SECOND ORDER

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad \frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t$$

Slope	0.0101
Intercept	1.2697
R ²	0.8832
K ₁	0.00008

TABLE 5.12 Adsorption Isotherm Parameters

PSEUDO SECOND ORDER

Slope	0.0381
Intercept	2.1576
R ²	0.9648
K ₂	0.011

TABLE 5.13 Adsorption Isotherm Parameters PSO

THERMODYNAMICS

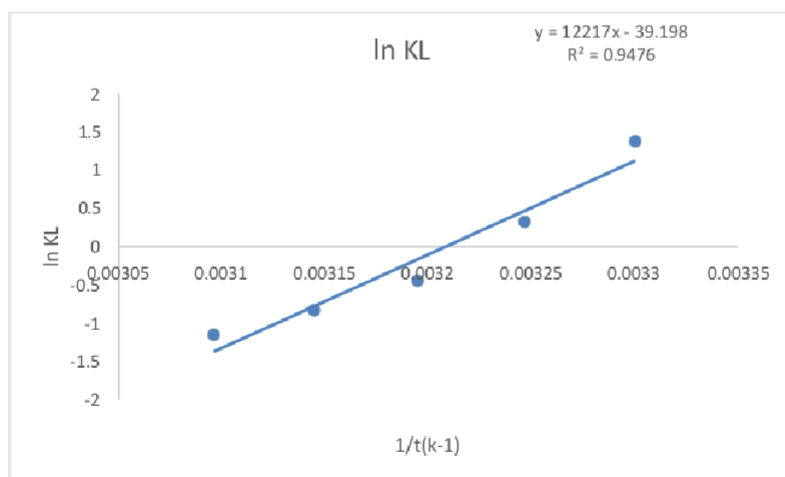


Fig:5.48: Thermodynamics for zif-8

The primary purpose of conducting thermodynamic evaluation is to ascertain the nature and spontaneity of the adsorption process. Van't Hoff's equations are utilized to calculate the thermodynamic parameters for adsorption studies, as shown by the following equations:

$$KL = C_{Ae}$$

$$C_e$$

$$\Delta G^\circ = -RT \ln KL$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Sample	Intercept	Slope	ΔH° (KJmol ⁻¹)	ΔS° (JK ⁻¹ mol ⁻¹)	R ²	ΔG° (JK ⁻¹ mol ⁻¹)
ZIF-8	- 39.198	12217	-101.572138	-325.892172	0.9476	-3.465684157

TABLE 5.13 THERMODYNAMIC PARAMETERS

CHAPTER 6

□ CONCLUSION

5.2. In conclusion, this study has demonstrated the potential of ZIF-8 as an effective adsorbent for the removal of pesticides from wastewater. Our findings indicate a notable adsorption capacity, with ZIF-8 exhibiting structural stability and regenerability over multiple cycles. SEM analysis revealed changes of a surface morphology and particle size, providing visual evidence of pesticide adsorption. While further research is needed to explore specific mechanisms and optimize conditions, this study contributes valuable insights in the field of environmental remediation. The use of ZIF-8 holds promise for sustainable and efficient pesticide removal, addressing critical challenges in wastewater treatment.

ORIGINALITY REPORT

10%

SIMILARITY INDEX

8%

INTERNET SOURCES

5%

PUBLICATIONS

1%

STUDENT PAPERS

PRIMARY SOURCES

- | | | |
|---|---|----|
| 1 | dokumen.pub
Internet Source | 2% |
| 2 | www.researchgate.net
Internet Source | 2% |
| 3 | sjst.psu.ac.th
Internet Source | 1% |
| 4 | Surendra Sasi Kumar Jampa, Ashish Prabhudas Unnarkat, Rajesh Vanshpati, Sivakumar Pandian et al. "Adsorption and recyclability aspects of humic acid using nano-ZIF-8 adsorbent", Environmental Technology & Innovation, 2020
Publication | 1% |
| 5 | Ghasemi, M., M. Naushad, N. Ghasemi, and Y. Khosravi-fard. "Adsorption of Pb(II) from aqueous solution using new adsorbents prepared from agricultural waste: Adsorption isotherm and kinetic studies", Journal of Industrial and Engineering Chemistry, 2013.
Publication | 1% |

6	Piaw Phatai, Jutharatana Klinkaewnarong, Surachai Yaiyen. "Adsorption of Methyl Violet Dye from Aqueous Solutions by Activated Carbon Produced from Tamarind Seeds", <i>Advanced Materials Research</i> , 2014 Publication	1 %
7	wrap.warwick.ac.uk Internet Source	< 1 %
8	onlinelibrary.wiley.com Internet Source	< 1 %
9	Dhodapkar, R.. "Adsorption of cationic dyes on Jalshakti [®] , super absorbent polymer and photocatalytic regeneration of the adsorbent", <i>Reactive and Functional Polymers</i> , 200706 Publication	< 1 %
10	moscow.sci-hub.ru Internet Source	< 1 %
11	Jialin Shi, Lina Zhang, Nannan Sun, Deng Hu, Qun Shen, Fang Mao, Qiang Gao, Wei Wei. " Facile and Rapid Preparation of Ag@ZIF-8 for Carboxylation of Terminal Alkynes with CO in Mild Conditions ", <i>ACS Applied Materials & Interfaces</i> , 2019 Publication	< 1 %
12	Submitted to University of Teesside Student Paper	< 1 %

13	ujcontent.uj.ac.za Internet Source	< 1 %
14	Meghdad Sheikhi, Hassan Rezaei. "Efficient adsorption of nickel and chromium(VI) from aqueous solutions using lignocellulose nanofibers: kinetics, isotherms, and thermodynamic studies", Water Practice and Technology, 2023 Publication	< 1 %
15	acikbilim.yok.gov.tr Internet Source	< 1 %
16	Submitted to University of North Texas Student Paper	< 1 %
17	www.deswater.com Internet Source	< 1 %
18	Submitted to United Colleges Group – UCG Student Paper	< 1 %
19	c.coek.info Internet Source	< 1 %
20	chalcogen.ro Internet Source	< 1 %
21	mrs.org Internet Source	< 1 %
22	Jennifer Gubitosa, Vito Rizzi, Paola Fini, Sergio Nuzzo, Pinalysa Cosma. "Regenerable Kiwi	< 1 %

Peels as an Adsorbent to Remove and Reuse the Emerging Pollutant Propranolol from Water", Processes, 2022

Publication

- 23 Saheed A. Ganiyu, Mohammed Awwal Suleiman, Waheeba Ahmed Al-Amrani, Abdullahi Kilaco Usman, Sagheer A. Onaizi. "Adsorptive Removal of Organic Pollutants from Contaminated Waters using Zeolitic Imidazolate Framework Composites: A Comprehensive and Up-to-date Review", Separation and Purification Technology, 2023

Publication

- 24 Sara Rojas, Patricia Horcajada. "Metal-Organic Frameworks for the Removal of Emerging Organic Contaminants in Water", Chemical Reviews, 2020

Publication

- 25 Submitted to TAFE Queensland Brisbane

Student Paper

- 26 iopscience.iop.org

Internet Source

- 27 Lixuan Zhang, Xindi Li, Lei Chen. "Fabrication of mixed-mode amphoteric β -cyclodextrin polymer for the simultaneous extraction of acidic and alkaline drugs", Journal of Chromatography B, 2023

Publication

28 Ponnusami, V.. "Guava (Psidium guajava) leaf powder: Novel adsorbent for removal of methylene blue from aqueous solutions", *Journal of Hazardous Materials*, 20080321
Publication

29 Submitted to University College London
Student Paper

30 www.mdpi.com
Internet Source

31 Submitted to The University of Manchester
Student Paper

32 www.growkudos.com
Internet Source

33 www.vedantu.com
Internet Source

34 Rijian Mo, Lei He, Chunxia Zhou, Zhong-Ji Qian, Pengzhi Hong, Shengli Sun, Zhe Wang, Yi Wang, Chengyong Li. "In Situ Growth of Ultrasmall Nanochannels in Porous Anodized Aluminum Membrane and Applied in Detection of Lead Ion", *Analytical Chemistry*, 2019
Publication

35 Submitted to UNESCO-IHE Institute for Water Education
Student Paper

36	Submitted to University of Greenwich Student Paper	< 1 %
37	www.micromeritics.com Internet Source	< 1 %
38	Asmaa Ahmed Moussa, alshimaa gomaa, Ragaa El-Azabawy, El-Bayaa A.. "Valorization Beetroot Waste for Eco-Friendly Extraction of Natural Dye for Textile and Food Applications.", Egyptian Journal of Chemistry, 2022 Publication	< 1 %
39	etd.aau.edu.et Internet Source	< 1 %
40	revues.imist.ma Internet Source	< 1 %
41	www.unam.edu.na Internet Source	< 1 %
42	www2.mdpi.com Internet Source	< 1 %
43	Riming Wang, Xiaohui Sun, Samy Ould-Chikh, Dmitrii Osadchii, Fan Bai, Freek Kapteijn, Jorge Gascon. " Metal-Organic-Framework-Mediated Nitrogen-Doped Carbon for CO Electrochemical Reduction ", ACS Applied Materials & Interfaces, 2018 Publication	< 1 %

44	doktori.bibl.u-szeged.hu Internet Source	< 1 %
45	dspace.lib.ntua.gr Internet Source	< 1 %
46	www.frontiersin.org Internet Source	< 1 %
47	Haneen I. Eldos, Mariam Khan, Nabil Zouari, Suhur Saeed, Mohammad A. Al-Ghouti. "Adsorptive removal of volatile petroleum hydrocarbons from aqueous solution by zeolite imidazole framework (ZIF-8) and iron oxide (Fe ₃ O ₄) nanoparticles", Environmental Technology & Innovation, 2023 Publication	< 1 %
48	Jun-Qing Jiang, Cheng-Xiong Yang, Xiu-Ping Yan. "Zeolitic Imidazolate Framework-8 for Fast Adsorption and Removal of Benzotriazoles from Aqueous Solution", ACS Applied Materials & Interfaces, 2013 Publication	< 1 %
49	akademiabaru.com Internet Source	< 1 %
50	brage.bibsys.no Internet Source	< 1 %
51	epdf.pub Internet Source	< 1 %

52

open.uct.ac.za

Internet Source

< 1 %

53

pubag.nal.usda.gov

Internet Source

< 1 %

54

D. Krishnaveni, P. Kannan, A.N. Senthilkumar, K. Raja. "Safe disposal of phosphate for eutrophication control by Redgram stalk biochar with subsequent power generation", Environmental Technology & Innovation, 2022

Publication

< 1 %

Exclude quotes Off

Exclude matches Off

Exclude bibliography On

Abdul Hameed

GRADEMARK REPORT

FINAL GRADE

GENERAL COMMENTS

/0

PAGE 1

PAGE 2

PAGE 3

PAGE 4

PAGE 5

PAGE 6

PAGE 7

PAGE 8

PAGE 9

PAGE 10

PAGE 11

PAGE 12

PAGE 13

PAGE 14

PAGE 15

PAGE 16

PAGE 17

PAGE 18

PAGE 19

PAGE 20

PAGE 21

PAGE 22

PAGE 23

PAGE 24

PAGE 25

PAGE 26

PAGE 27

PAGE 28

PAGE 29

PAGE 30

PAGE 31

PAGE 32

PAGE 33

PAGE 34

PAGE 35

PAGE 36

PAGE 37
