Faculty of Resource Science and Technology

Synthesis, Characterization, and Adsorption Study of ZIF-8/NH_2 and GO@ZIF-8/NH_2 for Dye Removal

Nur Afiqah Binti Kamaludin

Master of Science
2024

Synthesis, Characterization, and Adsorption Study of ZIF-8/NH_2 and GO@ZIF-8/NH_2 for Dye Removal

Nur Afiqah Binti Kamaludin

A thesis submitted

In fulfillment of the requirements for the degree of Master of Science

(Environmental Chemistry)

Faculty of Resource Science and Technology
UNIVERSITI MALAYSIA SARAWAK
2024

DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak, except where due acknowledgments have been made, the workis that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Nur Afiqah

……………………………

Signature

Name: Nur Afiqah Binti Kamaludin

Matric No.: 22020228

Faculty of Science and Technology

Universiti Malaysia Sarawak

Date:10th December 2024

ACKNOWLEDGEMENT

First and foremost, I am profoundly grateful to Allah SWT for His countless blessings and the strength granted to me throughout this research journey, enabling me to complete my studies successfully. I wish to extend my heartfelt gratitude to my research supervisor, Dr. Dayang Norafizan Binti Awang Chee, for her unwavering guidance, insightful advice, and encouragement throughout this project. Her dedication and expertise have been a source of constant inspiration, and it has been a privilege to work under her mentorship.

I am deeply indebted to my parents, Kamaludin Bin Gabut and Ramunah Binti Mohram, for their endless love, prayers, and sacrifices. Their unwavering support has been my greatest motivation and the foundation of my achievements. My gratitude also goes to my family for their understanding and encouragement during the challenges of this journey. I would also like to thank my colleagues for their camaraderie, advice, and invaluable assistance throughout this project. Your encouragement and support have made this journey more meaningful.

My sincere appreciation goes to the Faculty of Resource Science and Technology and the Centre for Graduate Studies at Universiti Malaysia Sarawak for their guidance and support during my studies. Finally, I would like to acknowledge Universiti Malaysia Sarawak for providing me with the opportunity and resources to pursue and complete my research here. To everyone who contributed to this journey in ways big or small, I extend my heartfelt thanks. This achievement would not have been possible without your support.

ABSTRACT

Zeolitic Imidazole Framework (ZIF-8) is a metal-organic framework known for its high porosity and large surface area, making it a promising adsorbent for pollutant removal. However, its efficiency in removing complex dye molecules is limited by the lack of specific functional groups necessary to enhance interactions with pollutants. To address this limitation, ZIF-8 was functionalized with amino groups and further modified with graphene oxide (GO) to improve its adsorption performance. This study explores the synthesis of amino-functionalized ZIF-8 (ZIF-8/NH_2) and GO-modified ZIF-8/NH_2 (GO@ZIF-8/NH_2) using a solvothermal method, followed by extensive characterization through FTIR, FESEM-EDXS, Zeta Potential, XRD, XPS, and BET analysis. Batch adsorption experiments were conducted to evaluate the removal efficiency of methyl blue (MB) under varying conditions of pH, dye concentration, and contact time. The adsorption mechanisms were analyzed using Langmuir, Freundlich, Pseudo First Order, and Pseudo Second Order models. Results showed that ZIF-8/NH_2 achieved an adsorption efficiency of 83.98% for MB under optimal conditions (160 ppm, pH 7, 90 minutes). The incorporation of GO significantly enhanced the performance, with GO@ZIF-8/NH_2 achieving a removal efficiency of 90.45% at 200 ppm, pH 7, within 60 minutes. The improved performance was attributed to the increased mesoporosity, functional group availability, and stronger interactions such as hydrogen bonding, electrostatic attraction, and π-π stacking. The adsorption processes of both adsorbents were best described by the Freundlich isotherm model, indicating multilayer adsorption, and followed the pseudo second order kinetic model, suggesting chemisorption as the dominant mechanism. In conclusion, the incorporation of graphene oxide into amino-functionalized ZIF-8 enhanced its physicochemical properties and adsorption efficiency, demonstrating its potential as an effective and sustainable adsorbent for dye removal in wastewater treatment applications.

Keywords: Metal organic framework, ZIF-8/NH_2, GO@ZIF-8/NH_2, adsorption, dyes

Kajian Sintesis, Penciriran dan Penejerapan ZIF-8/NH_2 dan GO@ZIF-8/NH_2 untuk Penyikiran Pewarna

ABSTRAK

Rangka Kerja Imidazole Zeolitik (ZIF-8) ialah rangka kerja logam-organik yang terkenal dengan keliangan yang tinggi dan luas permukaan yang besar, menjadikannya penjerap yang menjanjikan untuk penyingkiran bahan pencemar. Walau bagaimanapun, kecekapannya dalam mengeluarkan molekul pewarna kompleks dihadkan oleh kekurangan kumpulan berfungsi tertentu yang diperlukan untuk meningkatkan interaksi dengan bahan pencemar. Untuk menangani had ini, ZIF-8 difungsikan dengan kumpulan amino dan diubah suai dengan graphene oxide (GO) untuk meningkatkan prestasi penjerapannya. Kajian ini meneroka sintesis ZIF-8 (ZIF-8/NH_2) yang difungsikan amino dan ZIF-8/NH_2 yang diubah suai GO (GO@ZIF-8/NH_2) menggunakan kaedah solvoterma, diikuti dengan pencirian yang meluas melalui FTIR, FESEM-EDXS, Potensi Zeta, XRD, XPS dan analisis BET. Eksperimen penjerapan kelompok telah dijalankan untuk menilai kecekapan penyingkiran metil biru (MB) di bawah pelbagai keadaan pH, kepekatan pewarna, dan masa sentuhan. Mekanisme penjerapan dianalisis menggunakan model Langmuir, Freundlich, Pseudo First Order, dan Pseudo Second Order. Keputusan menunjukkan bahawa ZIF-8/NH_2 mencapai kecekapan penjerapan sebanyak 83.98% untuk MB dalam keadaan optimum (160 ppm, pH 7, 90 minit). Penggabungan GO telah meningkatkan prestasi dengan ketara, dengan GO@ZIF-8/NH_2 mencapai kecekapan penyingkiran 90.45% pada 200 ppm, pH 7, dalam masa 60 minit. Prestasi yang lebih baik itu disebabkan oleh peningkatan mesoporositi, ketersediaan kumpulan berfungsi dan interaksi yang lebih kuat seperti ikatan hidrogen, tarikan elektrostatik dan susunan π-π. Proses penjerapan kedua-dua penjerap paling baik diterangkan oleh model isoterma Freundlich, menunjukkan penjerapan berbilang lapisan, dan mengikuti model kinetik *tertib pseudo-saat, mencadangkan kemisorpsi sebagai mekanisme dominan. Kesimpulannya, penggabungan graphene oksida ke dalam ZIF-8 yang berfungsi amino meningkatkan sifat fizikokimia dan kecekapan penjerapannya, menunjukkan potensinya sebagai penjerap yang berkesan dan mampan untuk penyingkiran pewarna dalam aplikasi rawatan air sisa.*

Kata kunci: *Rangka bentuk logam organik, ZIF-8/NH_2, GO@ZIF-8/NH_2 penyerapan, pewarna*

TABLE OF CONTENT

LIST OF FIGURES

Page

LIST OF TABLES

LIST OF ABBREVIATIONS

MB	Methyl Blue
MOF	Metal Organic Framework
ZIF-8	Zeolitic Imidazolate Framework-8
ZIF-8/NH_2	Amino Functionalized Zeolitic Imidazolate Framework
GO	Graphene Oxide
PFO	Pseudo First Order
PSO	Pseudo Second Order
FESEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersed X-ray
XRD	X-ray Diffraction
FTIR	Fourier Transform Infrared Spectroscopy
XPS	X-ray photoelectron spectroscopy
BJH	Barrett-Joyner-Halenda
BET	Breuneur-Emmet-Teller

CHAPTER 1

INTRODUCTION

1.1 Study Background

Drinkable water is a significant worldwide concern for the 21st century, as water is themost essential element for life on Earth. More than 71% of the earth's surface is covered with water, yet according to international standards, less than 1% is drinkable due to various contaminations (Singh, 2018). The contamination of water resources by synthetic dyes has become a critical environmental and public health issue. These dyes are commonly used in various industries, including textiles, food, and cosmetics, leading to their widespread presencein wastewater. According to Gupta and Suhas (2019), there are over 100,000 commercially available dyes, and the yearly global output is between 700,000 and 1,000,000 tonnes.Conventionally water treatment methods often fall short of efficiently removing these dyes dueto their complex chemical structures and high stability. Consequently, there is a pressing need for advanced materials capable of effectively absorbing and removing dyes from contaminated water.

Wastewater treatment is the most important process to remove and eliminate contaminants from wastewater. There are many techniques for removing dyes from industrial effluents, which include physical methods such as adsorption (Xiao et al., 2018), membrane separation (Yang et al., 2024) coagulation (Mcyotto et al., 2021), and ion exchange (Türk et al., 2023) on synthetic adsorbents, chemical methods such as ozonation (Lanzetta et al., 2023) Fenton reagents (Moghadam & Nori Kohbanan, 2018), electro-chemical destruction(Beddai et al., 2022), and photocatalysis processes (Kucukcongar et al., 2023), biological processes (Mojsov et al., 2016). However, among the techniques, adsorption is the most preferred method to be used by researchers because of its operating conditions with low-cost operation, also it has high adsorption capacity. Therefore, to utilize this method, an effective absorbent such as subclasses of Metal-Organic Frameworks is needed.

Zeolitic Imidazolate Framework-8 (ZIF-8) is a type of metal-organic framework (MOF) known for its high surface area, tuneable pore size, and chemical stability. Its potential for adsorptive applications has been well-documented, but there is room for improvement needed in its performance. Therefore, by modifying the ZIF-8 nanoparticles by incorporating amino groups, the material's adsorption properties can be enhanced due to increased interaction sites and improved affinity for various pollutants. Additionally, Graphene oxide (GO) is a two-dimensional (2D) material that is also very advantageous to be used as an adsorbent due to its high surface-to-volume ratio and abundant oxygenated-functional groups (hydroxyl, carbonyl, carboxyl, and epoxy groups).

Hence, with the use of modified adsorbents, a combination of GO and amino-functionalized ZIF-8 through hybridization which produces GO@ZIF-8/NH_2 could synergistically enhance the properties of both materials, offering a composite with superior adsorption capabilities. Moreover, these groups can enhance their hydrophilicity in aqueous solutions and provide reactive sites for covalent bonding, dipole-dipole interactions, or electrostatic interactions withthe adsorbate (Ahmad et al., 2020). Therefore, this hybrid material is expected to leverage the high surface area and functional groups of ZIF-8 and the excellent dispersion and surface modification possibilities of GO.

Thus, in this study, the removal of methyl blue dye was focused on using a modified ZIF-8 as an adsorbent through an adsorption approach. This method is particularly effective for decolorizing water due to its straightforward operational requirements. Adsorption is widely recognized as one of the most effective techniques for removing dyes and heavy metals from wastewater, and it has garnered significant interest fromresearchers. Additionally, the integration of these modifications is expected to improve the adsorption capacity and efficiency, thereby advancing the overall performance of the adsorbentfor treating dye-contaminated water.

1.2 Problem Statement

The escalating demand in both industrial processes and daily human activities has led to a significant increase in the volume and intricacy of wastewater in our environment. Among the pollutants, synthetic dyes are particularly challenging due to their chemical stability, toxicity, and resistance to conventional wastewater treatment methods (Lin et al., 2023). These dyes, often ionic in nature, interact strongly with water and are difficult to remove, especially because their charged molecules are highly soluble and persistent in the environment. Persistence poses severe risks to aquatic life and can also have detrimental effects on human health.

While various adsorbent materials have been developed to address the problem of dye removal, the effectiveness of these materials varies significantly depending on the specific dye in question. Different dyes interact differently with adsorbents due to variations in their molecular structures, charges, and chemical properties. This variation makes it challenging to develop a one-size-fits-all solution for dye removal from wastewater. Due to this, an advanced adsorbent material such as ZIF-8, a subgroup of MOFs widely chosen by researchers for wastewater treatment.

Zeolitic imidazolate framework-8 (ZIF-8), a metal-organic framework (MOF), has shown promise in adsorption applications due to its large surface area and tunable properties (Panda et al., 2019). However, to effectively adsorb and remove a wide range of charged dye molecules, the performance of ZIF-8 can be further enhanced through functionalization. Modifying ZIF-8 with amino groups introduces additional functional sites that can interact more effectively with different types of charged dye molecules, potentially improving its adsorption capacity. Furthermore, incorporating graphene oxide (GO) into this framework can enhance its adsorption performance by providing more active sites and increasing its affinity for a variety of dyes. Despite these advancements, there is still a lack of comprehensive research on the synthesis, characterization, and adsorption capabilities of these modified materials, particularly in understanding how they interact with different types of dyes under varying conditions. The complexity of dye-adsorbent interactions necessitates a more nuanced approach to developing adsorbents that can effectively target a wide range of dyes.

This thesis aimed to address this gap by focusing on determining the effect of graphene oxide on the physicochemical of synthesized adsorbents using various instrumentation techniques. Following this, an extensive batch adsorption study was conducted to analyze their performance in removing synthetic dye specifically methyl blue from aqueous solutions. By optimizing these materials and gaining insights into their adsorption mechanism, particularly about the varying interactions between different dyes, and the adsorbents, this research seeks to develop more efficient and sustainable solutions for the treatment of dye-contaminated water

1.3 Objectives

The study focused on producing modified ZIF-8 nanoparticles as adsorbents to remove methyl blue dye from aqueous solutions. The objectives of the study were as follows:

i. To synthesize and modify ZIF-8 with amino group and graphene oxide (GO).

ii. To determine the effect of graphene oxide (GO) on the physicochemical of synthesized adsorbents using various instrumentation techniques.

iii. To evaluate the performance of ZIF-8/NH_2 and GO@ZIF-8/NH_2 nanoparticles for dye removal from aqueous solutions at different parameters such as initial pH, initial concentrations, and contact time using batch adsorption test.

iv. To identify the adsorption mechanism involved in dye removal using adsorption and kinetic isotherms.

1.4 Scope of Study

The synthesis of ZIF-8 involves reacting 2-methylimidazolate and zinc (II) nitrate hexahydrate with methanol, followed by stirring for 1, 2, and 3 hours to optimize the formation process. The stirring duration is critical because it influences the crystallization and morphology of ZIF-8, which directly impacts its adsorption performance. Next, the modification of ZIF-8 to synthesize ZIF-8/NH_2 is achieved by adding ammonium hydroxide (NH_4OH) to introduce amino groups. This modification enhances the adsorbent's ability to interact with pollutants. Following this, graphene oxide (GO) is incorporated into ZIF-8/NH_2 using a modified Hummer method, which improves the material’s surface area and introduces additional functional groups, enhancing its adsorption capacity.

Advanced characterization techniques, including FTIR, FESEM, XRD, XPS, and Zeta Potential analysis, are used to assess the morphology and functional properties of the ZIF-8/NH_2 and GO@ZIF-8/NH_2, to understand their suitability for dye removal