



Faculty of Resource Science and Technology

**Synthesis, Characterization, and Adsorption Study of ZIF-8/NH₂
and GO@ZIF-8/NH₂ for Dye Removal**

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Synthesis, Characterization, and Adsorption Study of ZIF-8/NH₂ and GO@ZIF-8/NH₂ for
Dye Removal

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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 work is 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.

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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/NH₂) and GO-modified ZIF-8/NH₂ (GO@ZIF-8/NH₂) 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/NH₂ 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/NH₂ 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/NH₂, GO@ZIF-8/NH₂, adsorption, dyes

Kajian Sintesis, Penciriran dan Penejerapan ZIF-8/NH₂ dan GO@ZIF-8/NH₂ untuk Penyingkiran 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/NH₂) yang difungsikan amino dan ZIF-8/NH₂ yang diubah suai GO (GO@ZIF-8/NH₂) menggunakan kaedah solvoterma, diikuti dengan penciriran 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/NH₂ 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/NH₂ 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/NH₂, GO@ZIF-8/NH₂ penyerapan, pewarna*

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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	Breunauer-Emmett-Teller

CHAPTER 1

INTRODUCTION

1.1 Study Background

Drinkable water is a significant worldwide concern for the 21st century, as water is the most 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 presence in 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 due to 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/NH₂ 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 with the 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 from researchers. Additionally, the integration of these modifications is expected to improve the adsorption capacity and efficiency, thereby advancing the overall performance of the adsorbent for 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/NH₂ and GO@ZIF-8/NH₂ 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/NH₂ is achieved by adding ammonium hydroxide (NH₄OH) 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/NH₂ 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/NH₂ and GO@ZIF-8/NH₂, to understand their suitability for dye removal

applications. FTIR is used to identify the functional groups present in the absorbents and confirm the successful modification and functionalization of the absorbents. FESEM allows for high-resolution imaging of the adsorbent surface, revealing its morphology, including the size, shape, and uniformity of the nanoparticles. This is critical for understanding how surface characteristics affect adsorption capacity and efficiency. Meanwhile, XRD is used to determine the crystalline structure of the adsorbents, providing insight into the phase compositions and the crystallinity of ZIF-8 and the effect of graphene oxide modification. The XPS provides detailed information on the elemental composition and chemical state of elements on the surface of the adsorbent, helping to identify the presence and oxidation state of functional groups. Zeta potential analysis measures the surface charge of the particles, which influences the adsorbent's interaction with charged dye molecules. A higher zeta potential generally indicates better stability and dispersion of the nanoparticles, which can affect the adsorption efficiency. BET is a crucial technique for evaluating the surface area, pore size and pore volume of ZIF-8/NH₂ and GO@ZIF-8/NH₂. This analysis provides insights into the material's porosity, which is directly linked to its adsorption capacity.

The batch adsorption study evaluates the adsorption efficiency of the nanoparticles for methyl blue dye under varying conditions of pH, initial dye concentration, and contact time. The effect of varying the dye concentration (40ppm –200ppm) is studied to determine how adsorption capacity changes with the number of dyes available. As for contact time, the duration of interaction between the adsorbent and the dye varied (30 minutes-240 minutes) to establish the equilibrium time required for maximum dye adsorption. This parameter is critical for understanding adsorption kinetics and optimizing the process for practical applications. The influence of the solution's pH (pH 1,3,7,9,11,14) is analyzed as

it affects the surface charge of the adsorbent and the ionization state of the dye molecules. The pH optimization ensures maximum interaction between the dye and the adsorbent, leveraging mechanisms such as hydrogen bonding and electrostatic interactions. UV-Vis spectroscopy is employed to measure the concentration of methyl blue in the solution before and after adsorption. By monitoring absorbance at the dye's characteristic wavelength, the removal efficiency and adsorption capacity can be quantitatively determined.

Adsorption mechanisms are determined using isotherm models (Langmuir and Freundlich) and kinetic models (Pseudo First Order and Pseudo Second Order). The study identifies removal efficiencies and adsorption capacities while providing insights into mechanisms such as multilayer adsorption and chemisorption. Langmuir model assumes monolayer adsorption on a homogenous surface with finite binding sites. It provides information on the maximum adsorption capacity ($q_{\max}$) and the binding strength (K_L). The Langmuir model is useful for predicting the saturation point of the adsorbent. Unlike Langmuir model, Freundlich assumes multilayer adsorption on a heterogenous surface, where adsorption strength varies across sites. It introduces parameters such as K_F and n , providing insights on the surface complexity and the feasibility of adsorption. However, for kinetic models, Pseudo First Order assumes the adsorption rate is proportional to the number of unoccupied adsorption sites. It is typically applied to systems where physical adsorption dominates. For Pseudo Second Order, this model suggests that the adsorption rate is proportional to the square of the number of unoccupied sites, often indicative of chemisorption processes involving valence forces or electron-sharing adsorbent and adsorbate.

However, several limitations exist in these processes. The synthesis and

modification procedures are conducted at a laboratory scale and their scalability may be constrained by factors such as cost, time, and control over the size and uniformity of the nanoparticles. Additionally, the reaction conditions like temperature and solvent choice may need further optimization for large-scale production. The use of ammonium hydroxide and graphene oxide in the modification steps also introduces potential environmental and economic concerns, which would need to be addressed for industrial applications. Despite conducting the batch adsorption test, the setup may not accurately reflect adsorption behaviour in the continuous flow systems, which are more relevant for industrial-scale applications. In addition, even though UV-Vis spectroscopy is effective for dye concentration analysis, it may suffer from interference if the sample contains other adsorbent substances, potentially affecting accuracy. The limitations of using isotherm and kinetic models stem from their reliance on simplified assumptions and controlled experimental conditions. Isotherm models such as Langmuir and Freundlich, assume idealized surface properties, either homogeneous or heterogeneous, which may not accurately represent the complexities of real adsorbent surfaces. Therefore, these constraints highlight the need for further investigation to ensure scalability, economic feasibility, and environmental sustainability of the proposed adsorbents for industrial wastewater treatment.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Dyes

Dyes are versatile organic compounds extensively utilized for their ability to impart vibrant and long-lasting colours to a wide range of materials. With over 100,000 different dyes available commercially and global production exceeding 1 million tons annually (Rápó & Tonk, 2021; Bui et al., 2022), the dyes play a crucial role in industries such as textiles, printing, and cosmetics (Kishor et al., 2021; Adesanmi et al., 2022; Al-Tohamy et al., 2022). These dyes are categorized as natural, derived from plants and insects (Ali et al., 2023), or synthetic, produced from complex organic or inorganic chemicals (Das et al., 2023). Due to demand applications, synthetic dyes have dominated the market due to their superior ability, extensive colour range, and adaptability across applications. This massive production and consumption of dyes has led to significant dye contamination in water sources, as illustrated in Figure 2.1 where the consumption of dyes in textile industries is 54%, the highest compared to the other industries.

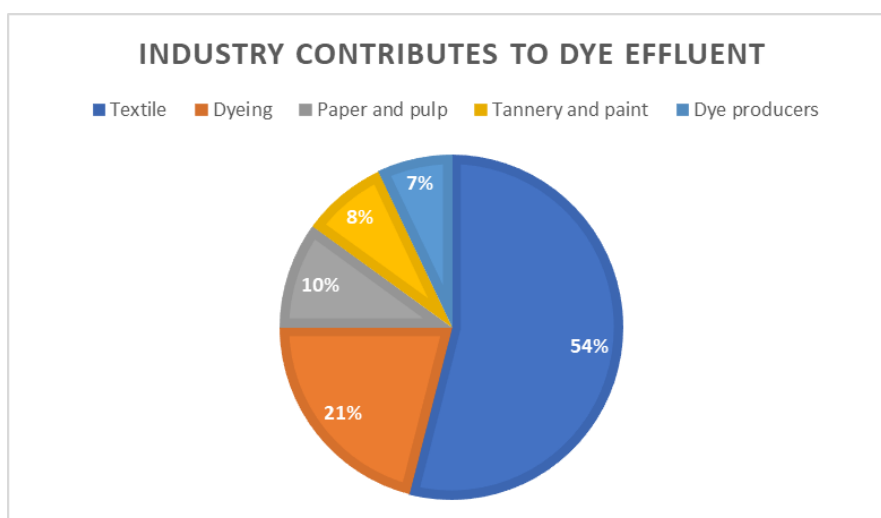


Figure 2.1: The pie chart on the contribution of the industry of dye effluent. Illustration adapted with permission from Velusamy et al. (2021)

The discharge of inadequately treated dye-laden wastewater into aquatic ecosystems contaminates water bodies, jeopardizing both environmental health and biodiversity. This pollution not only impairs photosynthesis in aquatic plants but also introduces toxic and carcinogenic compounds into the environment, causing serious health risks such as skin irritation, respiratory problems, and organ damage (Felista et al., 2020). According to WHO/UNICEF (2021), while progress has been made in improving access to safely managed water services, the challenge of ensuring clean and reliable water for all remains critical.

Dyes are typically categorized based on their chemical structure and ionic charge after dissociation in aqueous solutions (Table 2.1). This review emphasizes the ionic classification of dyes due to its substantial influence on the efficiency of dye removal. Dyes are generally divided into two main categories: ionic and non-ionic. Ionic dyes include cationic (basic) dyes and anionic dyes such as reactive, direct, and acidic dyes (Lu et al., 2023). Non-ionic dyes include vat dyes and dispersed dyes (Ni et al., 2021). Each of these classifications has distinct properties that affect their interaction with various adsorbents and their subsequent removal from water.

In this study, Methyl Blue (Figure 2.2) was selected for investigation due to its widespread use in textile industries and its potential environmental impact. Methyl Blue is an anionic dye. It is also known as Acid Blue 93 and is widely used in laboratories and textile industries. Although it is less toxic, this dye still poses environmental and health risks, particularly due to its persistence in aquatic environments, where it can cause harm to aquatic life and potentially enter the human food chain. In fact, according to Okasha et al. (2019), methyl blue is implicated in irritation of the gut, shortness of breath, and coughing.

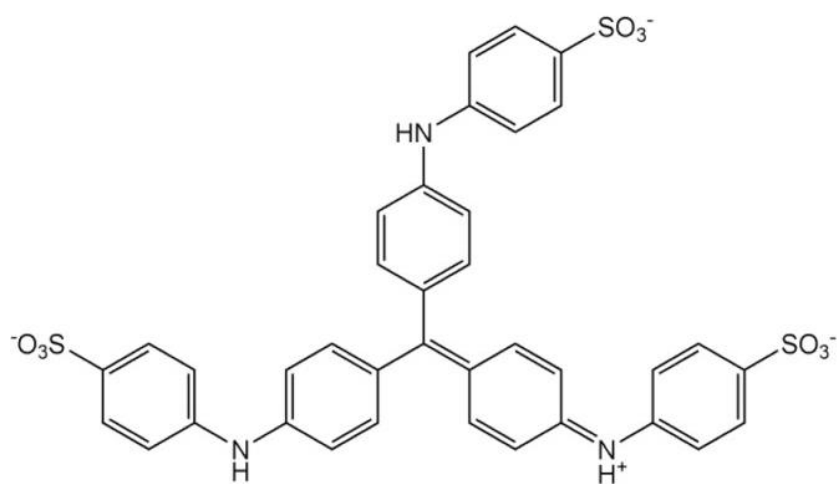


Figure 2.2: Methyl blue chemical structure

Table 2.1: Types of dyes and their application

Dye type	Water solubility	Chromophore groups	Application	Examples	References
Acid	Soluble	Azo, anthraquinone, azine, nitroso, triphenylmethane, xanthene, nitro	Food, silk, leather, wool	Acid Yellow 36 Acid Orange 19	El-Nemr et al. (2023)
Basic	Soluble	Acridine azo, oxazine anthraquinone, azine cyanine, thiazine, triarylmethane	Silk, wood, inks, paper	Crystal Violet Methylene Blue	Mulla et al. (2024) Mosoarca et al. (2022)
Disperse	A type of direct dye	Azo, anthraquinone, nitro, styryl, benzodifuranone groups	Polyester, plastic, nylon,	Disperse Blue 27 Disperse Yellow 3	Rafique et al. (2022)
Azo	Insoluble	Stilbene, pyrazoles, coumarin,	Rayon, cotton, plastics, paints	Acid Red 88 Acid Orange 19	Hidayat et al. (2022)
Direct	Soluble	Polyazo compounds, oxazines, phthalocyanines, stilbenes,	Cotton and paper, rayon, leather	Direct Orange 39 Direct Blue 15	Saeed et al. (2023) Ebrahimi et al. (2019)
Reactive	Soluble	Azo, anthraquinone, triarylmethane, formazan, phthalocyanine, oxazine	Yarn, silk, cellulosic, cotton	Reactive Blue 5	
Vat	Insoluble but soluble with alkali	Anthraquinone (including polycyclic quinones), indigoids, and carbazole	Cotton, fiber, rayon	Vat Orange	Farhan et al. (2021)
Solvent	Insoluble	Azo, anthraquinone, phthalocyanine, triarylmethane	Plastics, gasoline, lubricant	Solvent Red 24 Solvent Yellow 124	
Sulphur	Insoluble	Nitro and amino groups	Cotton, rayon, polyamide, fibres	Sulphur Black 1	Lenninger et al. (2023)

2.2 Effect of Dye on Environment and Health

Lack of evidence suggests that most dyes currently used in the industry and finishing are not hazardous to human health at the levels of exposure experienced by factory workers. However, with long-term and accidental over-exposure, there can be likely health hazards, therefore all dyes and chemicals must be treated with safety and care. The most common hazard of reactive dyes is respiratory problems due to the inhalation of dye particles. Occasionally, these substances have the potential to impact an individual's immune system, and in severe instances, this can lead to a heightened, even dramatic, bodily response when the person is subsequently exposed to the dye through inhalation. This is known as respiratory sensitization, and symptoms can be found in Table 2.2.

Table 2.2: Effects of dyes on human health and its symptoms

Human Health	Symptoms	References
Respiratory problems	• Itching, watery eyes, sneezing	Rápó et al. (2021)
• Respiratory sensitization	• Coughing and wheezing	
• Asthma		
Skin sensitive	• Skin irritation, itchy, or blocked nose, sneezing, and sore eye	Ahmad et al. (2019)

The primary health issues associated with dyeing and finishing processes often stem from exposure to chemicals that function as irritants. These may cause skin irritation, itchy or blocked noses, sneezing, and sore eyes. They include formaldehyde-based resins, ammonia, acetic acid, some shrink-resistant chemicals, some optical whiteners, soda ash, caustic soda, and bleach. Certain reactive, vat, and dispersed dyes are also recognized as skin-sensitive (Ahmad et al., 2019). Textile industries produce large amounts of liquid waste. These textile effluents contain organic and inorganic compounds (WHO\UNICEF, 2021).

In the dyeing processes, not all dyes applied to fabrics adhere permanently, resulting in a portion of these dyes remaining unfixed and getting washed out. These unfixed dyes are often present in high concentrations in textile effluents (Sarojini et al., 2023). The amount of water consumed and released also varies depending on the type of fabrics produced (Kishor et al., 2021). Approximately 0.08 to 0.15 cubic meters of water are utilized to manufacture 1 kg of fabrics. It is estimated that around 1,000 to 3,000 cubic meters of water are discharged following the processing of approximately 12 to 20 tons of textiles per day (Al-Tohamy et al., 2022). These effluents are rich in dyes and chemicals, some of which are non-biodegradable and carcinogenic and pose a major threat to health and the environment. Several primary, secondary, and tertiary treatment processes like flocculation (Ibrahim et al., 2024) and electrodialysis (Tang et al., 2022) have been used to treat these effluents. However, these treatments are not found effective against the removal of all dyes and chemicals used (Zueva, 2018; Rashid et al., 2021).

The discharged effluents not only exhibit elevated concentrations of industry-used dyes but also encompass the chemicals employed in diverse processing stages. Additionally, these effluents contain trace metals like chromium (Cr), arsenic (As), copper (Cu), and zinc (Zn), which have the potential to induce various health issues such as haemorrhage, skin ulceration, nausea, intense skin irritation, and dermatitis (Tang et al., 2022). Textile effluents are also found to contain other organic and microbial impurities (Marszałek et al., 2021). The usage of cotton has been increasing constantly throughout the past century (Anil et al., 2020). Cotton fibres are mainly dyed using azo dyes which are one of the largest groups of synthetic colorants used in the industry.

Azo dyes are difficult to degrade by the current conventional treatment processes. They are characterized by the presence of the nitrogen-nitrogen bond ($-N=N-$) in the center

and hence they are highly electron deficient (Bhayana et al., 2023). These azo dyes are found to be complex and have been found to show carcinogenic evidence on reductive cleavage. These dyes are capable of altering the physical and chemical properties of soil, deteriorating water bodies, and causing harm to the flora and fauna in the environment. It was observed that the toxic nature of dyes causes death to the soil microorganisms which in turn affects agricultural productivity (Pillai et al., 2019).

2.3 Current Wastewater Treatment Methods

Various methods are employed to treat dye-contaminated wastewater, categorized into physical, chemical, and biological approaches. Eliminating colour from industrial dye effluent can be achieved through various techniques. Nevertheless, owing to the diverse array of dyes available and the presence of additional chemicals in industrial effluent besides the dye, many treatment methods may lack effectiveness when applied in isolation. To optimize colour removal, a combination with other treatment options is necessary. The methods for treating dye wastewater can be classified into three categories: physical, biological, and chemical treatments (Table 2.3).

Physical methods function on the principles of mass transfer and typically involve uncomplicated systems designed to extract dye from wastewater. Ion exchange (Türk et al., 2023), adsorption (Xiao et al., 2018), coagulation (Mcyotto et al., 2021), and membrane filtration (Zhang et al., 2021) represent traditional physical processes employed in the separation process. Nonetheless, among chemical, biological, and physical methods, physical approaches are frequently employed for dye removal due to their user-friendly nature, straightforward operating conditions, and enhanced efficiency in the processes (Ganaie et al., 2023).

A cost-effective and straightforward solution for dye removal is the biological

approach (Mojsov et al., 2016), extensively adopted by many countries for treating wastewater contaminated with dyes. This method harnesses the potency of microorganisms such as bacteria, fungi, yeast, and algae, employing anaerobic and aerobic processes to break down dyes (Sahoo et al., 2021). Despite its economic advantages, environmentally friendly nature, lower sludge generation in comparison to alternative methods, and effectiveness in addressing chemical oxygen demand in wastewater, this approach has limitations in efficiently eliminating dyes and toxic pollutants (Madhushika et al., 2022). Supplementary biological methods encompass adsorption by microbial biomass, algae-mediated degradation, enzyme-driven degradation, fungal cultivation, and microbial cultures.

Furthermore, the chemical method is also among the approaches utilized for pollutant removal. However, it is less preferred in industrial applications when compared to biological and physical techniques, primarily due to higher installation and operational costs. Moreover, the expenses associated with chemicals and reagents, along with substantial energy consumption, diminish its attractiveness. Notably, the disposal of secondary toxic byproducts generated during the process is a significant drawback. These processes include advanced oxidation (Kumar & Shah, 2020), ozonation, photochemical irradiation, and ultraviolet radiation (Mukherjee et al., 2023). To address colour removal from wastewater with diverse dyes, cost-effective adsorbents have been employed.

Table 2.3: Advantages and disadvantages of various wastewater treatment

Process	Main Characteristics	Advantages	Disadvantages	Reference
Ion Exchange	Utilization of resins or adsorbents in a non-destructive process	High regeneration, efficient and rapid process	Large volumes require large columns Sensitive to effluent pH	Hassan & Carr (2018)
Chemical Precipitation	Removal of pollutants and separation of the resulting solids	Cost-effective, efficient for removal	Large sludge production volume	Oh et al. (2023)
Membrane Filtration	Non-invasive separation using a semipermeable membrane	A simple, efficient, and fast process that requires no chemicals	High energy requirements High operation and maintenance costs Limited flowrates	et al (2021)
Coagulation/Flocculation	Removal of pollutants and separation of resulting products	Simple process, low capital cost, highly efficient for suspended solids	Requires adjunction of non-reusable coagulants and flocculants Large generation of sludge volume	Ihaddaden et al. (2022)
Solvent Extraction	Separation technology by adding solvent	Suitable for large-scale operations handling high contaminant loads, with minimal operating costs	High capital cost and entrainment of phases in poor effluent quality	Wu et al. (2022)
Biological Methods	Application of either pure or mixed	Effective adsorption with rapid kinetics, using simple equipment, and handling a broad range of contaminants.	The use of organic solvent may be highly toxic and a relatively slow process	Elizaryev et al. (2023)
Adsorption	A mass transfer process where atoms, ions, or molecules move from a liquid to a solid surface through chemical or physical interactions.	A highly effective adsorption process with fast kinetics, a simple procedure, can target a variety of contaminants	Non-selective and relatively high cost of materials such as commercial activated carbon	Awang Chee et al. (2021)

2.4 Adsorption and Adsorbents

2.4.1 Adsorption

Adsorption is a top-quality treatment method for the removal of dissolved dyes. The adsorption method can be defined as the process by which a material collects at the interface between two phases, liquid-solid contact (Zaimee et al., 2021). The term "adsorbate" refers to the material that collects at the contact, and "adsorbent" refers to the solid surface that makes adsorption possible (Figure 2.3). In the chemical engineering processes, adsorption is used as one of the unit operations for the separation of industrial wastewater pollutants.

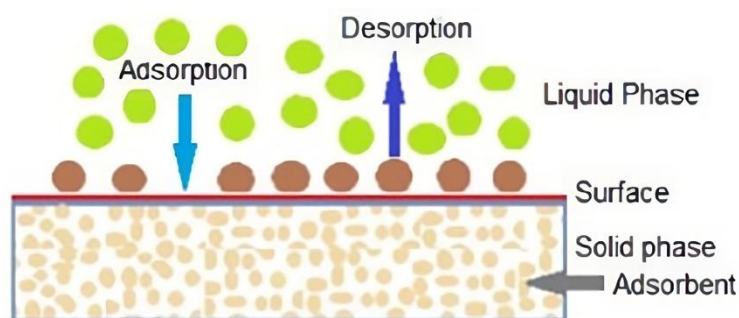


Figure 2.3: Adsorption mechanism adapted with permission from Zaimee et al. (2021)

There are two distinct types of sorption: chemical sorption (chemisorption) and physical sorption (physisorption) (Alaqrbeh et al., 2021). Chemical adsorption involves the formation of solid chemical bonds between molecules or ions of the adsorbate and the surface of the adsorbent. This often results from the exchange of electrons, making chemisorption typically irreversible. On the other hand, physical adsorption is usually reversible, as weak van der Waals intraparticle connections exist between the adsorbate and adsorbent (Patel, 2019). Overall, adsorption, with its capacity for both irreversible and reversible interactions, provides a viable and efficient option for purifying contaminated water.

2.4.2 Adsorbent

2.4.2.1 Metal-Organic Framework (MOF)

Metal-organic frameworks (MOFs) shown in Figure 2.4 are porous crystalline materials constructed by coordinating metal ions or clusters with organic ligands. Their highly tunable nature allows for precise adjustments in pore size, surface chemistry, and stability, making them versatile for a range of applications (Zango et al., 2020; Uddin et al., 2021). A defining feature of MOFs is their remarkably high surface areas, which often exceed those of traditional adsorbents like activated carbon. This property enhances their pollutant adsorption efficiency, as it allows for size and shape-selective interactions with target molecules (Paseta et al., 2019).

The adsorption capabilities of MOFs can be further enhanced through functional modifications, achieved either during synthesis or through post-synthetic strategies. These modifications enable the formation of specific interactions, such as hydrogen bonding, π - π stacking, and electrostatic attractions, which are particularly advantageous for environmental remediation, which are particularly advantageous for environmental remediation applications (Obaid, 2020). The adaptability of MOFs makes them a promising solution for addressing pollution challenges. Beyond adsorption, MOFs have demonstrated immense potential in various fields, including gas storage, catalysis, and drug delivery. Their unique combination of high porosity structural tunability, and chemical functionality underpins their wide-ranging applicability. This growing body of research highlights the transformative role of MOFs in both environment and industry.

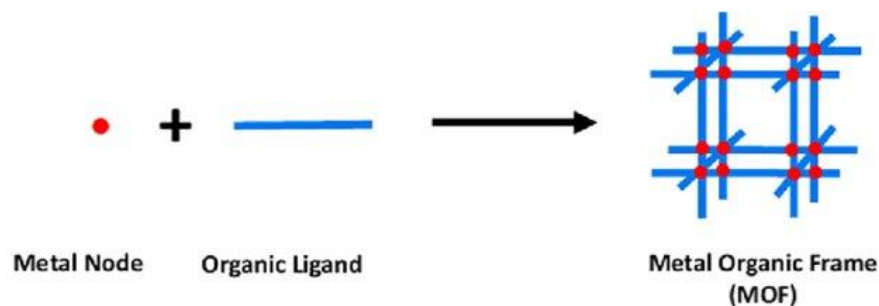


Figure 2.4: The coordination between metal nodes and organic linkers adapted with permission from Zango et al. (2020)

2.4.2.2 Zeolitic Imidazole Framework-8 (ZIF-8)

ZIF-8 (Figure 2.5), a subclass of zinc-based MOFs, has garnered significant attention for wastewater treatment applications. Comprising zinc ions (Zn^{2+}) as metal clusters and imidazole-based ligands, ZIF-8 exhibits a solid-type structure characterized by narrow six-membered ring pore windows ($3.4 \text{ \AA}$) and larger internal pores (Li et al., 2021; Pillai et al., 2019). This unique architecture, combined with its high thermal and chemical stability, 2019; Uddin et al., 2021). Furthermore, the affordability of its constituent components has contributed to its widespread adoption in adsorption and remediation research (Riccò et al., 2018; Uddin et al., 2021).

Recent studies have highlighted the exceptional adsorption performance of ZIF-8 across diverse pollutants, demonstrating its adaptability in environmental remediation. For instance, ZIF-8 achieved a high removal efficiency of 98% for phosphate ions under optimal conditions (initial concentration 10 mg/L , pH 9, and a contact time of 12 hours), attributed to electrostatic interactions between the positively charged ZIF-8 surface and negatively charged phosphate ions, particularly when modified with lanthanum ions. Similarly, ZIF-8 demonstrated remarkable efficiency in removing methyl orange (173 mg/g at pH 6.5) and tetracycline (127 mg/g at pH 5.5), showcasing its versatility in addressing both organic and inorganic contaminants. In addition, ZIF-8 has also been

compared to other MOFs and demonstrated superior adsorption capabilities. For instance, it outperformed ZIF-67 in the adsorption of rhodamine B and exhibited the highest adsorption capacity for acid orange 7 compared to UiO-66 and UiO-66-NH₂ (Yoon et al., 2019). These studies underscore ZIF-8's robustness and efficiency, particularly when used for dye removal. The adsorption of Congo Red, with capacities reaching 1275 mg/g at 308 K, further validates its strong potential in handling industrial dyes (Cao et al., 2021).

However, research gaps remain in optimizing ZIF-8 for complex real-world applications. Pristine ZIF-8 lacks functional groups, limiting its interaction with polar or highly charged pollutants. While functionalized variants like ZIF-8/NH₂ address this limitation, their performance under varying environmental conditions, such as competing ions, diverse pH ranges, and mixed pollutant systems, is not yet fully understood (Li et al., 2021; Paseta et al., 2019).

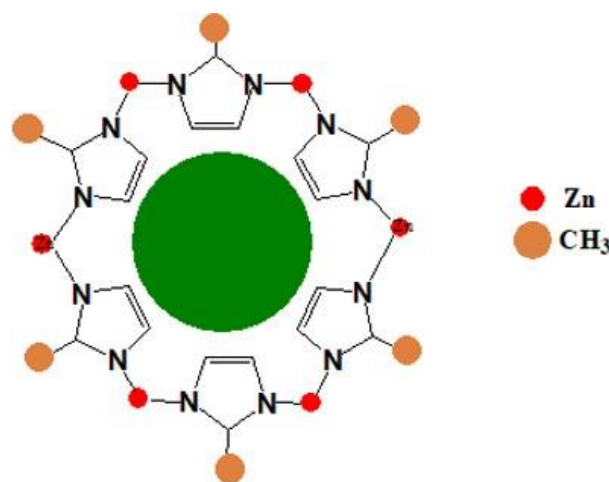


Figure 2.5: Zeolitic Imidazolate Framework-8 structure

2.4.2.3 Functional Modification of ZIF-8

Functional modifications of ZIF-8, particularly the incorporation of amino groups (-NH₂), have emerged as promising strategies to enhance its adsorption performance, especially for ionic and complex dyes. These modifications introduce active sites that improve adsorbate-adsorbent interactions, such as hydrogen bonding, electrostatic attractions, and π - π stacking, significantly enhancing pollutant removal efficiency. For instance, amino-functionalized ZIF-8 (ZIF-8/NH₂) has demonstrated an impressive adsorption capacity of 653.99 mg/g for Congo Red (CR), highlighting its superior performance compared to unmodified ZIF-8 (Ni et al., 2021).

Furthermore, ZIF-8/NH₂ achieved an adsorption capacity of 110 mg/g for methylene blue (MB) at pH 7, outperforming pristine ZIF-8, which exhibited a capacity of only 80 mg/g under similar conditions. The enhanced adsorption performance of amino-functionalized MOFs is not limited to ZIF-8. For example, UiO-66-NH₂ achieved a remarkable adsorption capacity of 393.82 mg/g for Congo Red, significantly surpassing that of its pristine counterpart (Zhang et al., 2019). This underscores the critical role of amino groups in facilitating specific pollutant interactions, thereby improving the adsorbate-adsorbent affinity and overall removal efficiency. The versatility of ZIF-8/NH₂ extends to the adsorption of a broad range of contaminants.

A study by Begum et al. (2020) explored the application of modified ZIF-8 derivatives for chromium (VI) removal, achieving maximum efficiencies of 65% with ZIF-8/NH₂/Mg(OH)₂/GO. These results highlight the synergistic effects of combining amino-functionalization with other materials to further enhance adsorption performance. In an innovative approach, Ma et al. (2021) synthesized ZIF-8/NH₂ crystals on bacterial foams, yielding materials with higher pore volume and surface area than parent ZIF-8. This enhancement resulted in a CO₂ adsorption capacity of 4.91 mmol/g, attributed to

interactions between the amino groups and acidic CO₂ molecules. Similarly, Ni et al. (2021) reported an adsorption capacity of 653.99 mg/g for Congo Red and Eriochrome Black T at room temperature using ZIF-8/NH₂-D, emphasizing the materials's efficiency for dye adsorption under ambient conditions. While ZIF-8/NH₂ and its derivatives have shown exceptional performance, their applicability to a diverse range of pollutants remains an area for further exploration by incorporating GO into this modification.

2.5 Incorporation of Graphene Oxide (GO)

Graphene Oxide (GO) depicted in Figure 2.6 is a derivative of graphene, characterized by oxygen-containing functional groups, such as hydroxyl (-OH), carboxyl (-COOH), and epoxide (-O-), attached to both sides and the edges of its carbon lattice. These groups make GO hydrophilic, enabling easy dispersion in water or organic solvents (Yang et al., 2018). GO's large surface area and its ability to interact with pollutants through covalent bonding, electrostatic attraction, and π - π stacking enhance its adsorption capabilities. Studies have shown GO's potential for removing various pollutants, including heavy metals and dyes. For instance, studies report adsorption capacities ranging from 78 mg/g (GO/ZnTiO₃/TiO₂ composites) to 217.8 mg/g (BC/PVA/GO/APT composites for heavy metal ions) depending on the specific adsorbent properties and preparation methods (Jaramillo & Cuenca, 2024). Additionally, activated graphene oxide has shown high efficiency in methylene blue removal, although exact adsorption values vary depending on surface modifications (Raveena et al., 2024). These findings suggest GO's promising role in wastewater treatment applications, especially when used in hybrid adsorbent systems (Jiříčková et al., 2022).



Figure 2.6: The Graphene Oxide (GO) structure. Image used with permissions of ACS Material (<https://www.acsmaterial.com>)

One of the biggest threats to the environment is water pollution caused by the release of wastewater from industry. Graphene oxide (GO) has been extensively utilized in various applications because of its unique properties, particularly in the removal of harmful pollutants from wastewater (Sunil et al., 2021). This is because GO is capable of covalent or non-covalent due to the oxygen groups decorating the basal planes and the edges (Jiříčková et al., 2022). Figure 2.7 below shows various applications that use GO to approach environmental threats.

Due to its unique properties such as high surface area, biocompatibility, and tunable functional groups, graphene oxide has been used in widely ranging applications (Figure 2.7). One of the applications is related to the environment. GO is extensively used in removing emerging contaminants from water, such as heavy metals (Zhang et al., 2020) and organic pollutants (Velusamy et al., 2021), due to its high adsorption capacity. It acts as a powerful adsorbent to its large surface area and the presence of various functional groups that can interact with pollutants (Anegbe et al., 2024).

Apart from that, the biocompatibility of GO and its ability to interact with

biological molecules make it useful in drug delivery (Itoo et al., 2022), biosensors (Kadhim et al., 2023), and as a scaffold in tissue engineering (Sharifi et al., 2023). Its properties also allow it to function in cancer therapy, where it is employed in targeted drug delivery systems and as a component of therapeutic agents. Furthermore, GO's conductive properties are leveraged in the development of flexible electronics, sensors, and as a material in energy storage devices like supercapacitors (Verma, 2023). The ability to modify its electrical and optical properties through reduction processes adds to its versatility.

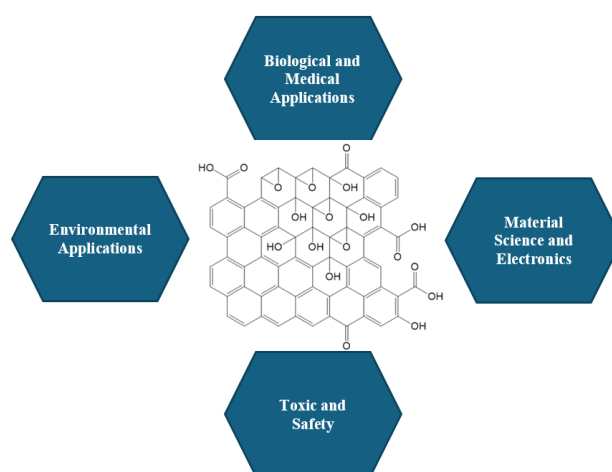


Figure 2.7: The application of graphene oxide (GO)

2.6 Synergistic Potential of GO and ZIF-8

The combination of graphene oxide (GO) with zeolite imidazolate frameworks (ZIF-8) has garnered significant attention due to their complementary properties, offering enhanced performance for pollutant removal and environmental remediation (Kim et al., 2023). GO, a two-dimensional material with high surface area, abundant oxygen-containing functional groups, and excellent mechanical stability, serves as an ideal platform for integrating ZIF-8, a metal-organic framework (MOF) known for its high

porosity, tunable structure, and chemical stability (Abdelhamid et al., 2020). This synergy results in composites with superior adsorption, stability, and reusability compared to their components.

GO provides a large surface area and functional groups such as hydroxyl, carboxyl, and epoxy, which enhance pollutant interaction through mechanisms like pi-pi stacking, hydrogen bonding, and electrostatic interactions (Kim et al., 2023). When combined with ZIF-8, these interactions are further strengthened. ZIF-8's high porosity allows for selective adsorption, while its metal-imidazole framework introduces additional active sites. For instance, ZIF-8/GO composites have shown remarkable efficiency in adsorbing dye molecules. Research by Wang et al. (2018) demonstrated the ZIF-8/GO could achieve an adsorption capacity of 1232 mg/g for methylene blue (MB), surpassing that of the pristine ZIF-8 and GO alone. The improvement was attributed to the synergistic effect of GO's large surface area and ZIF-8's high affinity for pollutants.

Similarly, GO enhances the dispersion and stability of ZIF-8 particles in aqueous environments, reducing aggregation and maintaining accessibility to adsorption sites. This was exemplified in a study by Begum et al. (2020), where ZIF-8/NH₂/GO composites exhibited a 98% removal efficiency for Cr (VI), compared to 65% for unmodified ZIF-8. The addition of GO not only increased the adsorption capacity but also improved the structural integrity of the composite, making it more robust under dynamic conditions.

The incorporation of GO also enhances the thermal and chemical stability of ZIF-8 composites, broadening their applicability in harsh environments. GO's stability in acidic and basic conditions complements the chemical resistance of ZIF-8, creating composites that perform well across a wide pH range. A study by Zhang et al., (2021) highlighted that ZIF-8/GO retained over 90% of its adsorption capacity after five cycles of use in a

wastewater treatment experiment, showcasing its durability. The ZIF-8/GO composites have been extensively explored for their application in wastewater treatment, targeting a variety of pollutants including dyes, heavy metals, and pharmaceuticals. For example, Liu et al., (2019) reported the effective removal of rhodamine B and Congo Red using ZIF-8/GO composites, with adsorption capacities of 965 mg/g and 1275 mg/g, respectively. These composites exhibit rapid adsorption kinetics, attributed to GO's excellent dispersibility and ZIF-8's microporous structure, which facilitates efficient mass transfer. The synergistic integration of GO and ZIF-8 presents a highly effective approach for advanced wastewater treatment. However, despite these promising findings, challenges remain in optimizing the synthesis of GO@ZIF-8/NH₂ composites.

2.7 Factors Affecting Adsorption

Adsorption is a complex process influenced by various factors, including the initial concentration of adsorbates, the pH of the solution, and the contact time. Understanding these factors is critical to optimizing adsorption performance in diverse applications. The initial concentration of adsorbates significantly impacts adsorption capacity. At lower concentrations, a greater proportion of adsorbate molecules come into contact with the active sites of the absorbent, resulting in high removal efficiency. However, as the concentration increases, these active sites become saturated, and the removal efficiency may plateau (Ali et al., 2021). High initial concentrations can also lead to competitive adsorption between molecules, reducing overall adsorption performance (Wang et al., 2022). The relationship between initial concentration and adsorption is often described as adsorption isotherms such as Langmuir and Freundlich models which provide insights into the adsorption mechanism and capacity.

In addition, the pH of the solution is also a crucial factor that can affect the

adsorption, as it influences the ionization state of both the adsorbate and the adsorbent surface. At low pH levels, deprotonation of the adsorbent surface may promote the adsorption of cationic species (Chen et al., 2020). For example, studies have shown that dye molecules and the adsorbent surface promote favourable interactions (Liu et al., 2023). The surface Pzc determines surface characteristics such as adsorption capacity and active centers. This point is directly affected by the pH solution employed, pH_{pzc}, which has a zero-surface charge and is commonly used to characterize the electromagnetic properties of the surface. The pH value used to define Pzc is only valid for systems dominated by H⁺/OH⁻ ions. Many studies have researched the Pzc point of various adsorbents generated from agricultural effluents to improve our knowledge of adsorption's workings. Adsorption of cationic dyes at pH > pH_{pzc} is OH group functional group is beneficial, and the positively charged surface is good for absorption of anionic dyes at pH_{pzc} (Elwakeel et al., 2020). The optimal pH varies depending on the adsorbent and adsorbate properties.

Contact time plays a pivotal role in determining the adsorption equilibrium (Pillai et al., 2019). Initially, adsorption occurs rapidly as abundant active sites are available on the adsorbent surface. Over time, the rate of adsorption decreases as these sites are occupied, eventually reaching equilibrium (Singh et al., 2021). The required contact time to achieve equilibrium depends on factors such as adsorbent porosity, adsorbate concentration, and the natural interactions between the adsorbent and adsorbate. For instance, porous materials like ZIF-8 functionalized with amino groups have been shown to achieve equilibrium faster due to enhanced accessibility of adsorptive sites (Zhang et al., 2023).

2.7.1 Data Analysis of Parameters Affecting the Adsorption

Removal efficiency and capacity are critical parameters in assessing the performance of adsorbents for environmental remediation. These metrics determine the viability of adsorbents in effectively removing pollutants from aqueous solutions and their scalability for real-world applications.

2.7.1.1 Removal Efficiency

Removal efficiency shown as Equation 2.1 refers to the percentage of a pollutant removed from a solution, which is influenced by various factors such as adsorbent surface properties (Rápó & Tonk, 2021). Materials with high specific surface areas and porosity, such as Metal-Organic Frameworks (MOFs) like ZIF-8, demonstrate superior adsorption efficiency. For instance, ZIF-8 has been shown to achieve a phosphate removal efficiency of 98% at pH of 9, due to electrostatic interactions with phosphate ions (Li et al., 2021). Other than that, the chemical nature of the pollutant, such as its molecular size, charge, and functional groups, plays a significant role. Ionic dyes like methylene blue (MB) often exhibit high removal rates when using modified adsorbents that provide specific interactions such as hydrogen bonding or electrostatic attractions (Feng et al., 2016). In addition, the conditions of solution including pH, temperature, and initial concentration significantly impact adsorption efficiency. For instance, studies have shown that ZIF-8 performs optimally for dye removal at near-neutral pH levels, while functionalized variants like ZIF-8/NH₂ enhance efficiency over a broader pH range.

$$\text{Removal Efficiency \%} = \frac{C_0 - C_t}{C_0} \times 100 \quad \text{Equation}$$

2.1

2.7.1.2 Adsorption Capacity

Adsorption capacity measures the amount of pollutant absorbed per unit weight of the adsorbent, often expressed in mg/g shown as Equation 2.2 (Guo & Wang, 2019). It is a critical parameter for evaluating the effectiveness of adsorbents in high-concentration scenarios. Unmodified ZIF-8 typically demonstrates moderate adsorption capacities. For example, it has shown an adsorption capacity of 80 mg/g for methylene blue under optimized conditions (Ni et al., 2021). When functional groups such as amino groups and carboxyl groups are incorporated, these significantly enhance adsorption capacity by introducing additional interaction sites. ZIF-8 has been shown to achieve 110 mg/g for methylene blue and 653,99 mg/g for Congo Red, marking substantial improvements over its pristine material (Rápó & Tonk, 2021). In addition, incorporating graphene oxide (GO) into ZIF-8 further boosts adsorption capacity due to the synergistic effects of GO's large surface area and ZIF-8's selective adsorption properties. For instance, ZIF-8/GO composites demonstrated a significant improvement in Cr(VI) removal, achieving a high adsorption capacity due to the enhanced surface area and functional groups introduced by graphene oxide (Begum et al., 2020).

Adsorption capacity often increases with temperature due to enhanced molecular motion and surface interaction. Kinetic studies reveal that high-capacity adsorbents follow pseudo second order models, indicating chemisorption mechanisms, such as those observed in ZIF-8/NH₂ for rhodamine B, methylene blue and methyl orange (Feng et al., 2016). A comparative assessment of adsorbents highlights the advancements in adsorption capacities also achieved through modification. According to Zhang et al. (2019) study, ZIF-8-loaded UiO-66-NH₂ displayed much better selectivity to MB than its parent MOFs. The adsorption capacity of ZIF-8-loaded UiO-66-NH₂ (173 mg/g) toward MB was found

to be 215% higher than UiO-66-NH₂ (55 mg/g) (Zhang et al., 2019). These findings indicate that functionalization and composite formation significantly enhance adsorption capacities, enabling these materials to address diverse pollutants effectively.

$$qe = \frac{V C_0 - C_e}{m} \quad \text{Equation 2.2}$$

2.8 Adsorption Models Analysis

2.8.1 Isotherm Model

Adsorption isotherms can be defined as the interaction between an adsorbate and an adsorbent, playing a crucial role in optimizing the effectiveness of adsorbents (Alaqarbeh et al., 2021). The shape of an isotherm reveals insights into the stability of these interactions and the adsorption affinity of the molecules involved. These isotherms can be expressed in various mathematical forms, some derived from simplified physical models of adsorption, while others are empirical and designed to align with experimental data (Obaid, 2020). The comparison studies table for methyl blue removal is shown in the Appendices (Table 2.5).

2.8.1.1 Langmuir

The Langmuir theory, introduced by Irving Langmuir in 1916, is based on the premise that adsorption occurs at specific, uniform sites on the surface of an adsorbent (Guo & Wang, 2019). According to this theory, once a site is occupied by an adsorbate molecule, no further adsorption can take place at that site. This model assumes that the adsorbent surface is homogenous and that each site has an equal probability of being occupied (Swenson & Stadie, 2019). Equation 2.3 shows the formula that was used to analyze the adsorption test in this study meanwhile Table 2.4 shows the R_L values which

were used to determine the favourable of the Langmuir isotherm model. Studies have shown that ZIF-8-based adsorbents often align well with the Langmuir model, suggesting uniform adsorption sites and high adsorption capacity for pollutants like dyes and heavy metals (Ni et al., 2021).

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \quad \text{Equation 2.3}$$

Table 2.4: R_L values

R_L value	Type of Isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favourable

2.8.1.2 Freundlich

The Freundlich adsorption isotherm shown as Equation 2.4 is usually employed to quantify the equilibrium relationship between the amount of adsorbate removed per unit weight of the carbon and the adsorbate concentration remaining in the solution (Vigdorowitsch et al., 2021). The Freundlich equation, though empirical, is often employed for data interpretation because of its effectiveness in describing the non-linear adsorption process across various adsorbate concentrations (Alaqarbeh et al., 2021). Its mathematical simplicity makes it easy to use, and it is particularly useful for characterizing adsorption on surfaces with energetically heterogeneous sites. For example, the ZIF-8/GO composite has shown a better fit to the Freundlich model in dye adsorption studies, reflecting their heterogeneous surface properties due to the integration of GO (Begum et al., 2020).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{Equation 2.4}$$

2.8.2 Kinetic Models

Adsorption kinetics are a crucial factor in determining the efficiency of the sorption process (Alaqarbeh et al., 2021). They describe the rate at which solutes are absorbed and the duration that adsorbates remain at the solid-liquid interface (Saleh, 2022). The adsorption rate is influenced by the number of particles adhering to the adsorbent surface per second and the frequency of particle collisions per unit area. The kinetic model assumes that the rate of change in the adsorbate uptake at a given reaction time is directly proportional to the difference in concentration and the rate at which the adsorbate is removed over time (Musah et al., 2022). The comparison studies table for methyl blue removal is shown in the Appendices (Table 2.5).

2.8.2.1 Pseudo First Order

The Lagergren pseudo first order model operates on the premise that the rate of solute uptake over time is directly proportional to the difference between the saturation concentration and the amount of adsorbate absorbed on the solid at any given time (Sahoo et al., 2020). This model is typically applicable during the initial stages of the adsorption process. It is often observed that adsorption kinetics follow this pseudo first order rate equation when the process occurs via diffusion across the interface. The Lagergren pseudo first order model can be described by the following linear form in Equation 2.5 (Musah et al., 2022):

$$\text{Log } (q_e - q_t) = \log q_e + \frac{k_1 p t}{2.303} \quad \text{Equation 2.5}$$

If an adsorption process follows true first-order kinetics, then the intercept of $\log (q_e - q_t)$ versus t plots would be equal to the log of experimentally determined q_e or adjusted to fit the experimental value (Revellame et al., 2020). For a slow adsorption process, true equilibrium can be difficult to reach, making it very difficult to measure q_e accurately.

2.8.2.2 Pseudo Second Order

The pseudo second order kinetic model shown in Equation 2.6 assumes that the rate-limiting step is chemical sorption or chemisorption and predicts the behaviour over the whole range of adsorption (Bullen et al., 2021). In this condition, the adsorption rate is dependent on adsorption capacity not on the concentration of adsorbate (Sahoo et al., 2020). One major advantage of this model over Lagergren's first order is that the equilibrium adsorption capacity can be calculated from the model; therefore, there is theoretically no need to evaluate the adsorption equilibrium capacity from the experiment (Musah et al., 2022).

$$\frac{1}{q_t} = \frac{1}{K_{2p}q_e^2} + \frac{1}{q_e}t \quad \text{Equation 2.6}$$

2.9 Limitations

Despite significant advancements in adsorption research, several limitations persist in the current literature, underscoring the need for further exploration. Most studies on adsorption, including those involving ZIF-8, graphene oxide (GO), and their composites, are conducted under controlled laboratory conditions. These conditions often do not account for the complexities of real wastewater, such as the presence of competing ions, fluctuating pH, and varying pollutant concentrations makes the scalability and practical feasibility of these materials remain uncertain. In addition, while adsorption isotherms and kinetic models provide valuable insights into pollutant-adsorbent interactions, their application is primarily

limited to single-component systems. Multi-component systems, typical of industrial wastewater, introduce competitive adsorption and synergistic effects that are not fully understood or modelled effectively in the existing literature. Furthermore, while some modified adsorbents, such as amino-functionalized ZIF-8 (ZIF-8/NH₂) and ZIF-8/GO composites, have shown promising initial results, their durability under harsh environmental and operational conditions remains uncertain. Functionalization of adsorbents, such as the incorporation of amino groups or GO into ZIF-8, has shown significant improvements in adsorption performance. However, the precise mechanisms by which these modifications enhance adsorption, particularly in multi-component pollutant systems, are not fully elucidated.

CHAPTER 3

MATERIALS AND METHODS

Figure 3 shows the workflow where the research begins with a comprehensive literature review to conceptualize the study. The first phase focuses on synthesizing ZIF-8/NH₂ and GO@ZIF-8/NH₂ composites, to evaluate the impact of graphene oxide (GO) on the physicochemical properties of the synthesized adsorbents using various instrumental techniques. If the synthesis is successful, the study progresses to batch adsorption experiments to assess the performance of these materials in removing methyl blue dye from aqueous solutions under varying conditions such as pH, initial concentration, and contact time. This methyl blue dye was chosen to represent the anionic group of dyes. Following the adsorption studies, the optimum conditions for dye removal are determined. If these conditions are met, the adsorption mechanism is explored through the application of adsorption and kinetic isotherms to identify the interactions and processes involved. The study concludes with data analysis, discussions, and final benchmarking to draw conclusive insights.

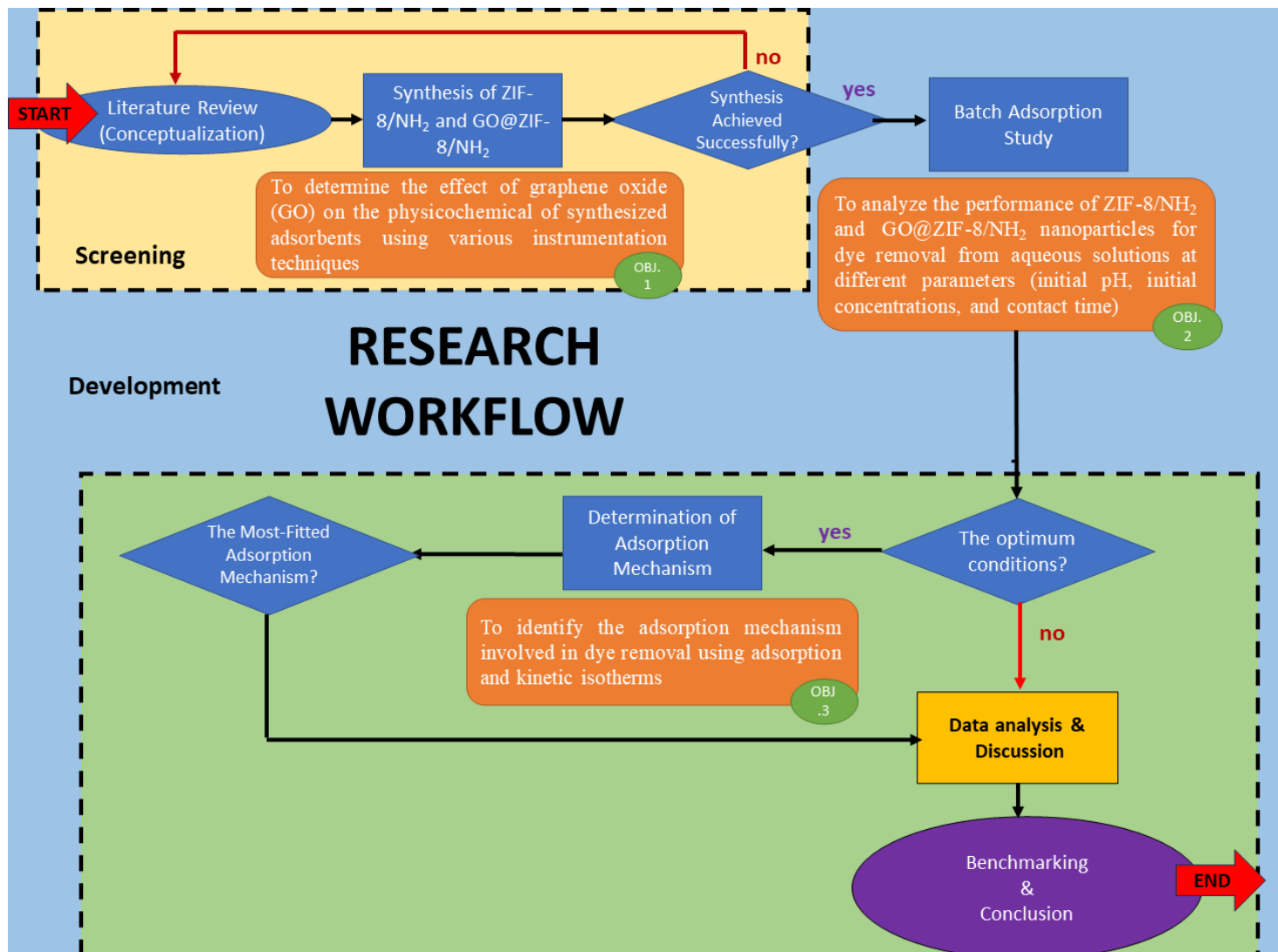


Figure 3: Overall research flow

3.1 Materials

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, Sigma-Aldrich), 2-methylimidazole (Hmim) (99%, Acros Organics), methanol (ACS reagent, Merck), and ammonium hydroxide (NH_4OH) solution, Graphite powder (Sigma-Aldrich), concentrated sulphuric acid (98% H_2SO_4), sodium nitrate powder (NaNO_3), potassium permanganate (KMnO_4), hydrogen peroxide solution (35% H_2O_2), methanol (ACS reagent, Merck), and methyl blue (Bendosen).

3.2 Synthesis of ZIF-8

ZIF-8 synthesis was carried out at room temperature following previous research literature (Oliveira et al., 2023) with some modifications. A mixture of 150 mL methanol containing 4.8501 g (0.05908 mol) of 2-methyl imidazolate and 150 mL methanol containing 2.247 g (0.00756 mol) of zinc (II) nitrate hexahydrate was vigorously stirred for 1 hour to obtain a homogeneous ZIF-8 solution. The mixture turned turbid with a milky white colour. A milky white precipitate formed after allowing the mixture to react for 24 hours. The mixture was filtered, washed in fresh methanol before, and dried for 2 hours in a vacuum oven at 90°C .

3.3 Synthesis of ZIF-8/ NH_2

Modified ZIF-8 was synthesized according to the relevant literature (Begum et al., 2020). About 0.3g (0.00756 mol) of ZIF-8 nanoparticles were dissolved in 25 mL of distilled water. Then, the mixture was added with 5 mL (0.0822 mol) of ammonium hydroxide (NH_4OH) solution. A homogeneous suspension of ZIF-8/ NH_2 was obtained when the mixture was stirred at room temperature for three hours. Then, the ZIF-8/ NH_2 was left at room temperature without stirring for 24 hours to react. After 24 hours, the precipitate was filtered

out and dried for two hours in a vacuum oven at 90°C after being rinsed once with distilled water. Table 3.1 tabulated the sample designation for each synthesized nanoparticle. Figure 3.1 shows the schematic illustration of ZIF-8/NH₂ preparation.

Table 3.1: Preparation method and synthesis duration of ZIF-8 and its modification

Sample Designation	Preparation Method	Synthesis Duration
ZIF-8	<i>In-Situ</i> Solvothermal	1 hour
ZIF-8/NH ₂ -H1	Post-Modification	1 hour
ZIF-8/NH ₂ -H2	Post-Modification	2 hours
ZIF-8/NH ₂ -H3	Post-Modification	3 hours

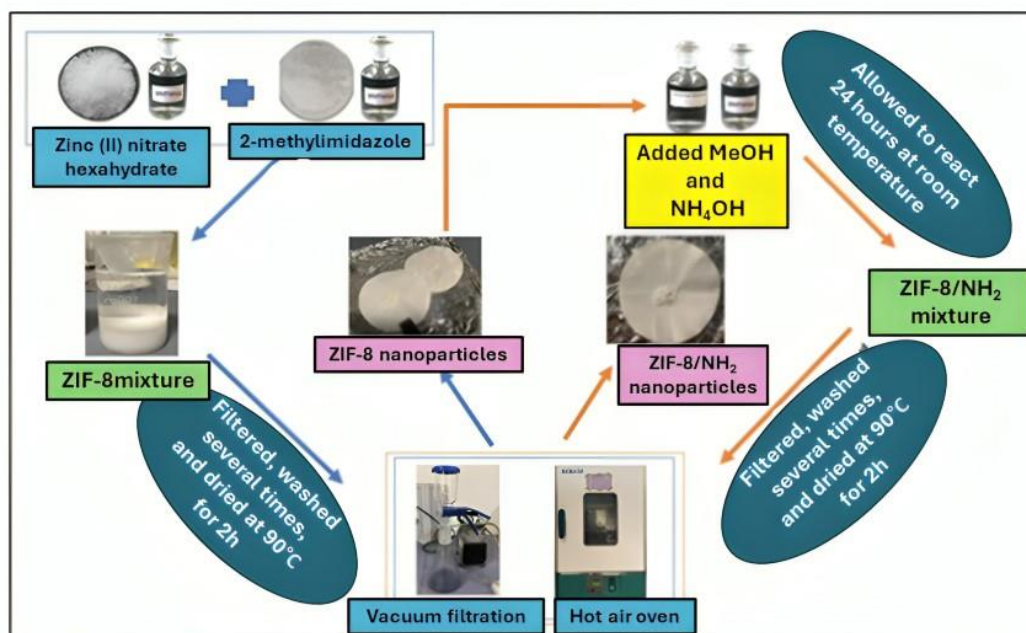


Figure 3.1: Procedure to synthesize ZIF-8 and ZIF-8/NH₂

3.4 Synthesis of GO

Hummers method (Paramasivan et al., 2018) with some modifications used for the synthesis of GO where 23mL (0.422mol) of 98% concentrated H_2SO_4 was cooled down in an ice bath below 0°C for 30 min. 1.0g (0.0833mol) of graphite powder and 0.5g (0.00588 mol) of NaNO_3 were mixed followed by the addition of concentrated H_2SO_4 to the mixture. The exothermic mixture was stirred constantly for another 30 min. The solution was added with 5mL (0.0005mol) KMnO_4 slowly with constant stirring for 15 minutes. Then, the solution was removed and left at room temperature. After that, 140mL of distilled water and 10mL (0.116mol) of 35% H_2O_2 were added to the mixture and stirred for 15 min. The reaction mixture was let overnight. The supernatant was filtered using a vacuum filter, and the residue was washed with ethanol and water numerous times. The residual GO was dried at 60°C in a vacuum oven for 1 hour.

3.5 Synthesis of GO@ZIF-8/ NH_2

The GO@ZIF-8/ NH_2 composite was synthesized via a post-synthesis modification process (Kim et al., 2023). A 100 mg dispersion of graphene oxide (GO) was prepared in water and sonicated for 1 hour to ensure uniform dispersion. In parallel, 100 mg of ZIF-8/ NH_2 was dispersed in methanol. The methanol dispersion was then gradually added to the GO suspension under continuous sonication for an additional hour to facilitate effective interaction between the components. The resulting mixture was filtered, and the residual composite was collected and dried in a vacuum oven at 90°C for 1 hour.

3.6 Characterization of ZIF-8/ NH_2 and GO@ZIF-8/ NH_2

3.6.1 Fourier Transform Infrared Spectroscopy (FTIR)

The chemical characteristics of ZIF-8/ NH_2 and GO@ZIF-8/ NH_2 in this study were

analyzed with a Nicolet IS10 Fourier Transform Infrared (FTIR) spectrophotometer. The powdered sample was first mixed with potassium bromide (KBr), ground for 1 min, and pressed into a translucent pellet before being loaded into the sample holder of the machine. At wavelengths ranging from 400 cm^{-1} to 4000 cm^{-1} , the spectra of the samples were scanned using the OMNIC Spectra software. This FTIR identifies the functional groups that exist in the components by producing an infrared adsorption spectrum.

3.6.2 Field Emission Scanning Electron Microscopy (FESEM-EDX)

The sample preparation was done where nanoparticle adsorbents were adhered onto the 1cm x 1cm platinum plate sample holder. Field Emission Scanning Electron Microscopy (JSM-IT500) was used to determine the surface morphology of the ZIF-8/ NH_2 . Meanwhile, the EDX was determined to characterize the elemental composition of the samples in this study (Nasrollahzadeh et al., 2019).

3.6.3 Zeta Potential Surpass Analyzer

The dispersion of ZIF-8/ NH_2 and GO@ZIF-8/ NH_2 powder in solution was analyzed using the Zeta Potential Surpass analyzer (ELSZ-1000, Otsuka) at Advanced Membrane Technology Research (AMTEC) Universiti Teknologi Malaysia (UTM) to determine the surface charges at different pH conditions.

3.6.4 X-Ray Diffraction Spectroscopy (XRD)

The ZIF-8/ NH_2 and GO@ZIF-8/ NH_2 samples were submitted to be analyzed at Advanced Membrane Technology Research (AMTEC) Universiti Teknologi Malaysia (UTM) for X-ray diffraction Spectroscopy analysis. XRD is a non-destructive analysis to give information on the phase purity, crystallinity, and crystal structure of the synthesized sample. The XRD (MiniFlex, Rigaku) emitted x-rays to the sample and the x-rays were

diffracted at different angles and intensities by using CuK α radiation with a wavelength (λ)= 1.54 Å at room temperature.

3.6.5 X-Ray Photoelectron Spectroscopy (XPS)

The sample in this study was submitted to Advanced Membrane Technology Research (AMTEC) Universiti Teknologi Malaysia (UTM) performed by X-ray Photoelectron Spectrometer Shimadzu Ultra DLD to analyze the composition of the material surfaces and the relative abundances of the components on surfaces.

3.6.6 Brunauer-Emmett-Teller (BET) Analyzer

ZIF-8/NH₂ and GO@ZIF-8/NH₂ nanoparticles were submitted to Advanced Membrane Technology Research (AMTEC) Universiti Teknologi Malaysia (UTM) for BET analysis. BET was performed by using TriStar II 3020 Version 3.02 to determine the specific surface area of solid materials based on adsorption measurements (Ambroz et al., 2018). The analysis was done at a temperature of 77.35K.

3.7 Dye Stock Solution Preparation

The adsorption batch research was conducted with different parameters for the adsorbent. A stock solution of methyl blue dye (MB) was prepared by dissolving 1g of each dye's powder in 1L of distilled water.

3.7.1 Ultraviolet-Visible Spectroscopy (UV-Vis)

Dye batch adsorption analysis, UV-visible was utilized using a Cary 60UV-VIS spectrophotometer which has a wavelength of 190-1100 nm that can be scanned in three seconds.

3.8 Batch Adsorption Study of Methyl Blue

Each conical flask was filled with 80 mL of methyl blue solution and 20 mg of ZIF-8/NH₂. The flasks were then sealed and placed on an orbital shaker, set to 150 rpm, for three hours. Following the shaking period, the dye solution was separated from the adsorbent by centrifugation at 4000 rpm for 10 minutes, effectively isolating the ZIF-8/NH₂ particles from the solution. The concentration of methyl blue in the supernatant was measured using a UV-Vis spectrophotometer with a detection wavelength of 600 nm. A calibration curve, constructed from known dye concentrations, was used to determine the methyl blue concentration in the samples.

Equation 3.1, q_e , was used to determine the equilibrium quantity of dye adsorbed, and Equation 3.2 was applied to determine the efficiency of dye removal (percentage).

$$q_e = \frac{V(C_0 - C_e)}{m} \quad \text{Equation 3.1}$$

$$\text{Removal Efficiency \%} = \frac{C_0 - C_t}{C_0} \times 100 \quad \text{Equation 3.2}$$

where C_0 (mg/L) represented the dye's initial concentration in an aqueous solution, while C_e (mg/L) indicated the equilibrium dye concentration, V (L) represented the volume of dye solution used, and m (g) represented the mass of adsorbent utilized, C_t indicates the dye concentration over time.

The adsorption mechanism was determined using conventional adsorption-equilibrium models, as shown in Table 3.2. The adsorption isotherms, which are Freundlich and Langmuir models, were to explain the material's adsorption rate concerning adsorbent mass per unit. In contrast, kinetic models, pseudo first order, and pseudo second order explained the adsorption rate of the removal (Yoo et al., 2020).

Table 3.2: Adsorption isotherms and kinetics models

Isotherms Models	Linear Equations
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L}$
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$
Kinetics Models	Linear Equations
Pseudo First Order	$\log(q_e - q_t) = \log q_e + \frac{k_{1p} t}{2.303}$
Pseudo Second Order	$\frac{1}{q_t} = \frac{1}{K_{2p} q^2} + \frac{1}{q_e} t$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Synthesis and Characterization of ZIF-8/NH₂

4.1.1 FTIR Analysis

Figure 4.1 presents the FTIR spectra of ZIF-8 and ZIF-8/NH₂, which exhibit characteristic adsorption bands confirming the successful synthesis of the nanoparticle adsorbents. Key bands at 3700 cm⁻¹ and 3158 cm⁻¹ correspond to the C-H stretching vibrations of the methyl and imidazole rings, consistent with findings from Uddin et al. (2021). Additionally, the bands at 1590 cm⁻¹, 750 cm⁻¹, and 690 cm⁻¹ are attributed to the C=N bond vibrations, ring stretching, and aromatic sp² C-H bonding, respectively. These bands align with previous studies that highlight the structural integrity of ZIF-8 frameworks (Zhang et al., 2018). A distinct band at 420 cm⁻¹ confirms the formation of Zn-N bonds, indicating the coordination between zinc ions and nitrogen atoms of the methylimidazole groups, which is a hallmark of ZIF-8 synthesis (Uddin et al., Zhang et., 2018).

For ZIF-8/NH₂, the presence of a pronounced peak at 1650 cm⁻¹ verifies the incorporation of N-H functional groups. This observation is consistent with previous reports demonstrating that amino functionalization enhances adsorption performance due to increased hydrogen bonding sites (Ni et al., 2021). According to the study, FTIR analysis confirmed the presence of key functional groups in the synthesized ZIF-8 materials. The characteristic peaks at 3135 cm⁻¹, 2930 cm⁻¹, and 1585 cm⁻¹ indicate the presence of C-H bonds and C-N stretching vibrations. Additionally, the appearance of an absorption band at 1051 cm⁻¹ suggests successful amino-functionalization of the ZIF-8

framework. Notably, the FTIR spectra ZIF-8-D and NH₂-ZIF-8-D exhibit no significant changes in the primary absorption peaks, confirming that the modification process preserved the material's core structure. This analysis highlights the chemical composition and functional group of the materials, providing critical insights into their successful synthesis and functionalization.

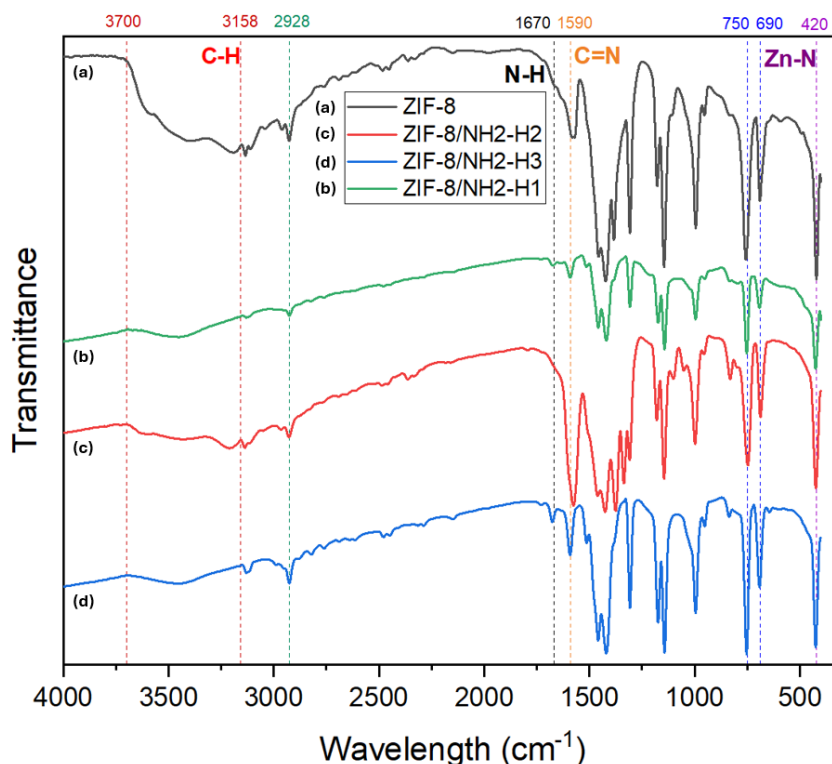


Figure 4.1: ZIF-8 (top) spectrum and ZIF-8/NH₂ spectra (stir duration of the mixture from second top to bottom; 1 hour, 2 hours, and 3 hours) in the FTIR

Figure 4.2 displays the FTIR spectra post-adsorption, revealing subtle yet significant changes in peak positions and intensities. Notable, the peak at 2348 cm⁻¹ emerges prominently, suggesting the formation of new chemical interactions between ZIF-8/NH₂ and methyl blue. The FTIR spectra reveal the emergence of a peak at 2348 cm⁻¹, which is absent in the pristine ZIF-8 materials. This peak is likely associated with the formation of new chemical interactions between the ZIF-8/NH₂ adsorbent and the adsorbed dye molecules, such as methyl blue. Specifically, it may correspond to stretching vibrations of C=O groups

from the dye interacting with the amino-functionalized surface of ZIF-8/NH₂. Alternatively, the peak could signify the formation of hydrogen bonds or π - π stacking interactions, which are known to occur between aromatic dye molecules and the imidazolate framework. The appearance of this peak supports the hypothesis that amino functionalization enhances the material's ability to interact with dye molecules, further validating its potential for effective adsorption applications.

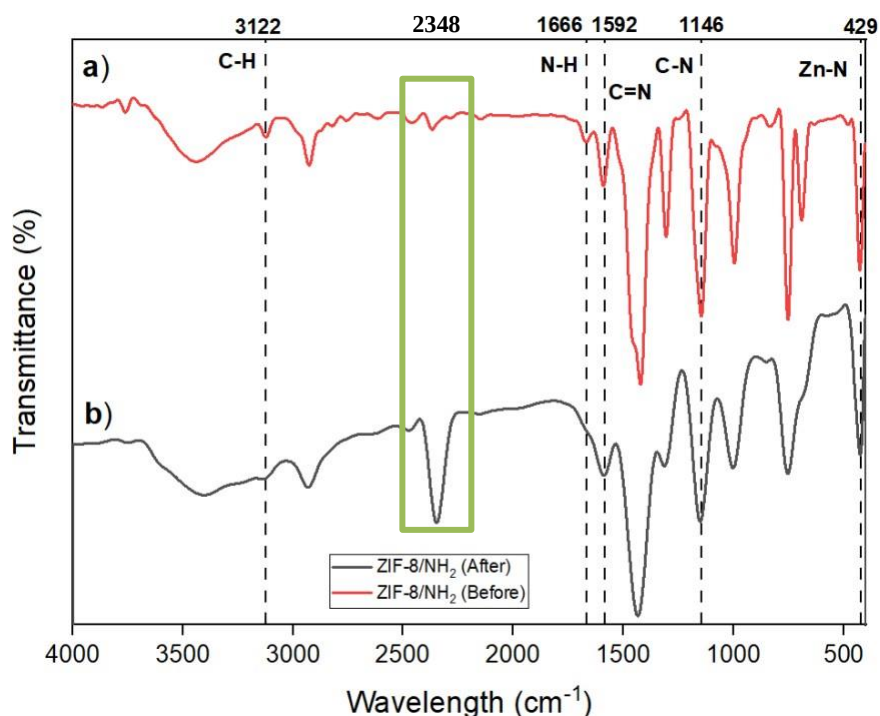


Figure 4.2: FTIR spectrum of ZIF-8/NH₂ before and after adsorption test onto methyl blue dye

4.1.2 FESEM and EDXS Analysis

SEM micrographs provide detailed insights into the morphological characteristics of ZIF-8 and its amino-functionalized derivative, ZIF-8/NH₂. As shown in Figure 4.3a, the unmodified ZIF-8 exhibits relatively small particles with distinct edges and a nearly spherical shape. Upon amino-functionalization, the morphology changes significantly, with ZIF-8/NH₂ displaying a distinct hexagonal shape and well-defined, smooth edges. Figures

4.3b, 4.3c, and 4.3d reveal the impact of synthesis duration on the morphology of ZIF-8/NH₂. The ZIF-8/NH₂-H1 sample (Figure 4.3b) exhibits smaller particle sizes compared to ZIF-8/NH₂-H2 (Figure 4.3c) and ZIF-8/NH₂-H3 (Figure 4.3d). The ZIF-8/NH₂-H2 and ZIF-8/NH₂-H3 nanoparticles, though similar in size, display NH₂ clusters on the ZIF-8 particles' surfaces. These clusters suggest that the NH₂ groups may not have fully crystallized into the hexagonal shape, potentially due to shear forces experienced during intense crystallization stirring, as proposed by Malekmohammadi et al. (2019).

The observed morphological variations align with findings reported by Ni et al. (2021), where the synthesis method and solvent conditions significantly influenced ZIF-8 particle size and distribution. Ni et al. (2021) highlighted that ZIF-8 crystals synthesized in pure methanol resulted in aggregated particles around 80 nm, while those prepared using mixed solutions of methanol and ammonia produced more regular and uniformly distributed crystals, approximately 1 μm in size. They further noted that amino functionalization induced surface roughness and reduced crystallinity, a phenomenon attributed to the coating of a silica gel layer and changes in intercrystallite forces.

In this study, the formation of NH₂ clusters on ZIF-8/NH₂ particles and the potential reduction in crystallinity, as evidenced by morphological irregularities, align with Ni et al.'s observations regarding amino-functionalized ZIF-8 materials. These findings emphasize the critical role of synthesis conditions, including solvent type, ligand interactions, and post-synthesis modifications, in shaping the morphology and structural properties of ZIF-8 and its derivatives. These variations are pivotal in influencing the material's adsorption performance and overall functionality.

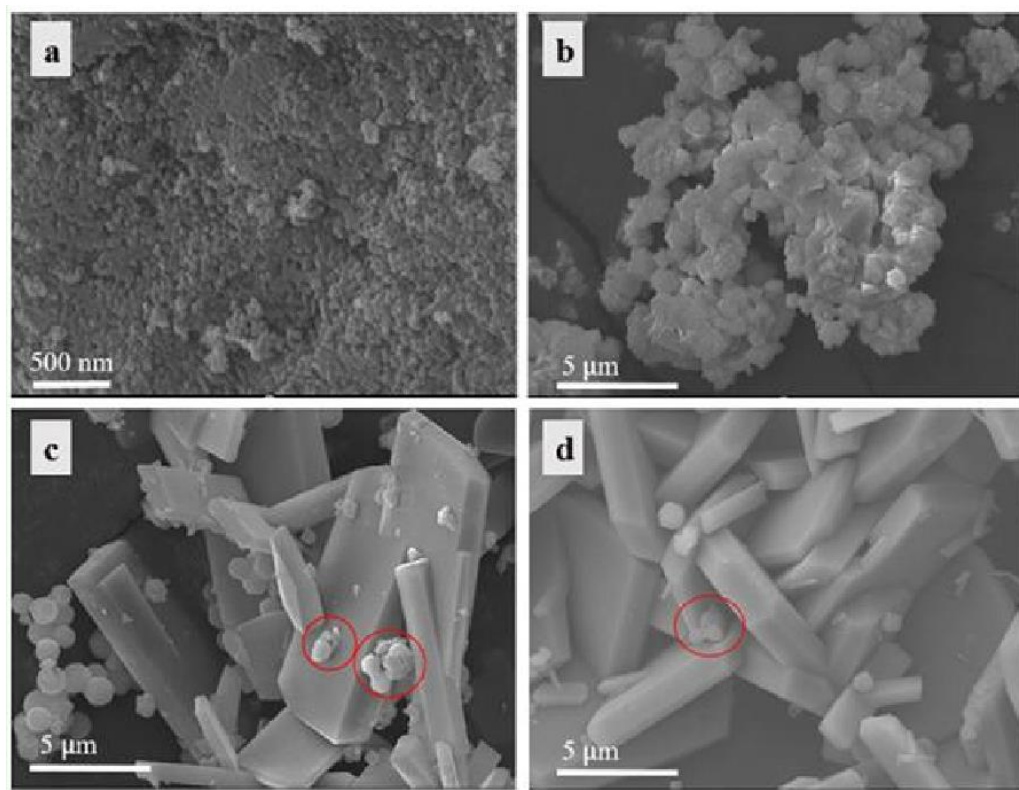


Figure 4.3: SEM figures (a) ZIF-8 and ZIF-8/NH₂ with different stirring hours (b) 1 hour; (c) 2 hours and (d) 3 hours

The SEM micrographs in Figure 4.4 illustrate the morphological changes in ZIF-8/NH₂ after the adsorption of methyl blue. The previously well-defined hexagonal shape of ZIF-8/NH₂ becomes obscured by a voluminous, fluffy substance, suggesting the successful adsorption of methyl blue not the adsorbent surface. This morphological transformation may be attributed to the accumulation of dye molecules forming a dense layer in the adsorbent, further supporting the material's high adsorption capacity for methyl blue. In addition, due to electrostatic interactions and π - π stacking, the methyl blue likely forms a more uniform and voluminous coating after the adsorption.

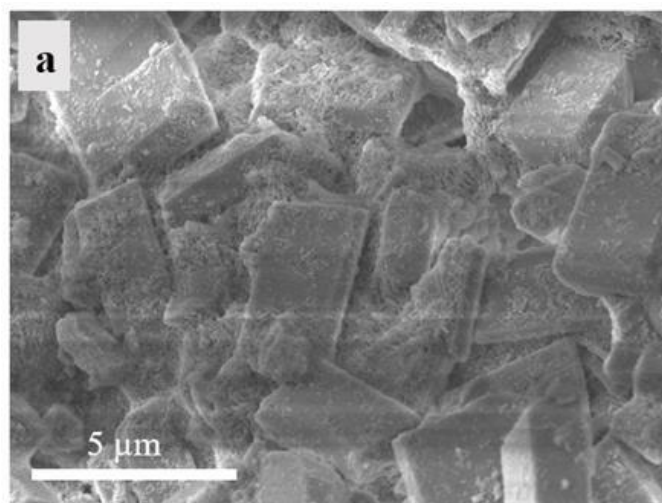


Figure 4.4: FESEM images after adsorption using ZIF-8/NH₂ onto methyl blue dye

Figure 4.5 presents the EDXS analysis of the synthesized ZIF-8/NH₂ before the adsorption process, confirming the presence of nitrogen (N) and zinc (Zn) elements, which are characteristic of the ZIF-8/NH₂ framework. Elemental mapping further supports these findings, demonstrating the uniform distribution of N and Zn on the adsorbent's surface, indicative of a well-synthesized and homogenous material.

After the adsorption of methyl blue, the EDXS spectrum in Figure 4.6 shows a significant change in the elemental composition. The presence of carbon (C) and oxygen (O) elements is now prominent, indicating that the dye molecules, which are rich in carbon, have been absorbed onto the surface of ZIF-8/NH₂. A notable addition is the presence of silicon (Si), which was not detected in the pre-adsorption state. This could suggest the adsorption of silicon-containing species from the dye solution or other impurities, further confirming that the dye molecules have interacted with the adsorbent surface. The distribution of elements shown in the elemental mapping in Figure 4.6 supports this conclusion. Carbon and nitrogen are uniformly distributed across the surface, while oxygen is more concentrated in some regions, likely indicating the locations where methyl blue has been adsorbed. Zinc remains well-distributed, which is expected since it is part

of the ZIF-8 structure, and its presence confirms that the framework integrity of the material remains intact after the adsorption process.

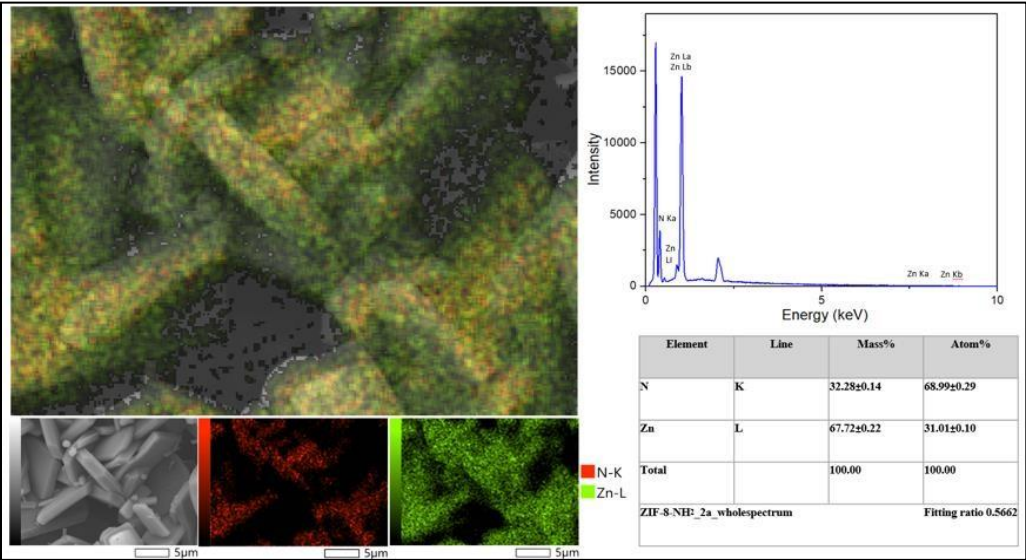


Figure 4.5: EDXS analysis of ZIF-8/NH₂-H3 before adsorption

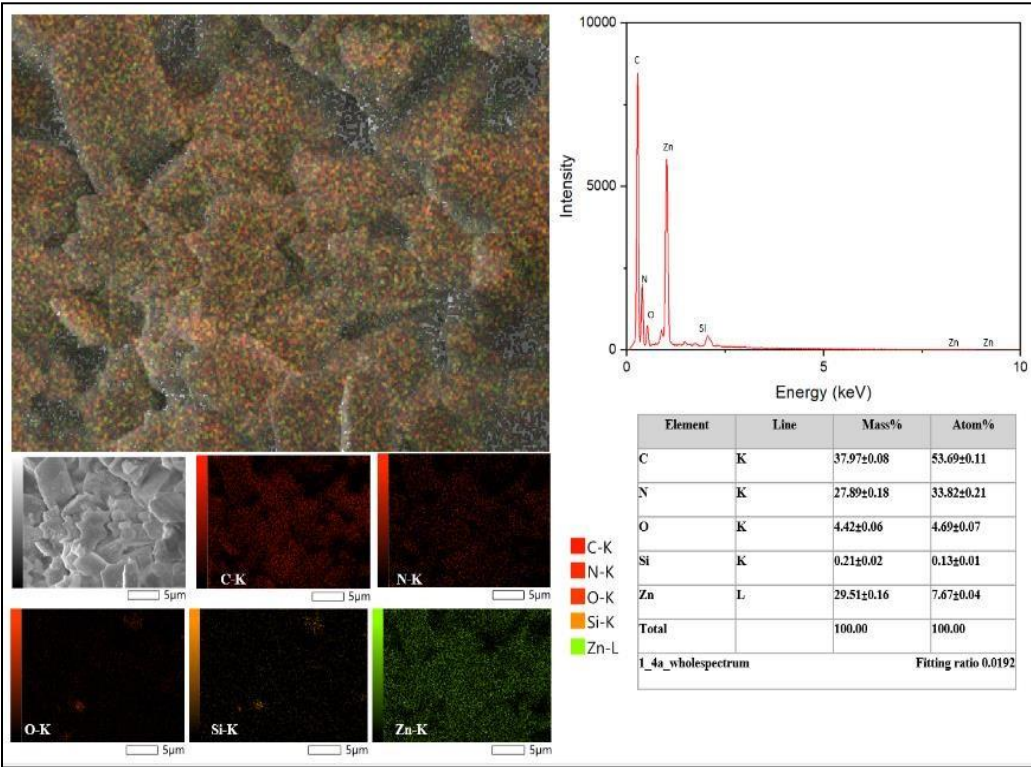


Figure 4.6: EDXS analysis of ZIF-8/NH₂ after adsorption

4.1.3 XRD Analysis

The X-ray diffraction (XRD) analysis of the modified ZIF-8 with an amino group (ZIF-8/NH₂) reveals notable changes compared to the ZIF-8, reflecting structural modifications due to the introduction of amino groups. As shown in Figure 4.7, the XRD peaks of ZIF-8/NH₂ are more pronounced, indicating improved crystallinity and structural integrity. This enhancement is attributed to the ammonium hydroxide treatment, which facilitates the removal of guest molecules from the pores without causing any impregnation, thereby allowing the material to retain its crystalline form. These observations are consistent with the findings of Nordin et al. (2017), who reported that strong diffraction peaks are indicative of high crystallinity, with characteristic peaks appearing at $2\theta = 7.30, 10.35, 12.70, 14.80, 16.40$ and 18.00° , corresponding to the (110), (200), (211), (220), (310), and (222) planes, respectively. Additionally, according to (Ma et al., 2021) the XRD data for ZIF-8/NH₂ show that the diffraction peaks are similar to those of pristine ZIF-8, with a slight rightward shift in the (011) peak, which is commonly attributed to the use of mixed organic ligands in the amino-modified structure. This shift in peak shifts for modified ZIF-8 materials. Specifically, the typical peaks at 2θ of $7.4, 10.2, 12.8, 14.7, 16.5, 18.1, 24.5,$ and 26.7° are ascribed to the (011), (002), (112), (022), (013), (222), (233) and (134) planes of ZIF-8 (Chang et al., 2020).

Following the adsorption of methyl blue dye, the XRD patterns of ZIF-8/NH₂ show minimal changes in the crystallinity of the material, indicating that the structural integrity of the adsorbent is preserved after dye uptake. This stability in crystallinity suggests that the adsorption process does not disrupt the ZIF-8/NH₂ framework, ensuring the material can maintain its structural features and remain effective for subsequent adsorption cycles. The results confirm the potential of ZIF-8/NH₂ as a stable and reusable

adsorbent material for dye removal applications, in line with previous studies on the durability and effectiveness of modified frameworks.

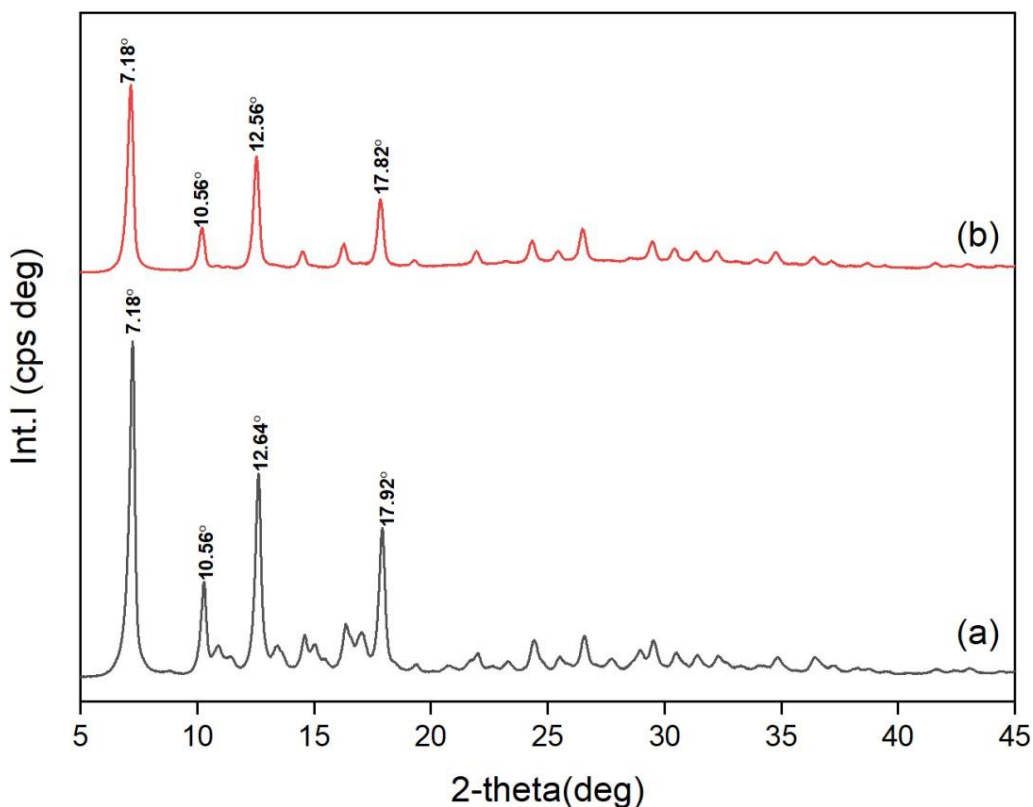


Figure 4.7: The XRD graph of ZIF-8/NH₂ (a) before adsorption and (b) after adsorption

4.1.4 XPS Analysis

The XPS spectra provide significant insight into the surface chemistry and elemental composition of ZIF-8/NH₂ before and after adsorption with methyl blue. The survey spectra (Figures 4.8a and 4.9a) confirm the presence of Zn, O, N, C, and S in the material. After adsorption, shifts in the binding energies, particularly in the N 1s, C 1s, and O 1s regions, suggest interactions between the ZIF-8/NH₂ and the methyl blue dye. A new peak at 533 eV in the O 1s spectrum after adsorption indicates the presence of sulphonate groups (-SO₃H) from methyl blue, confirming successful adsorption.

The Zn 2p spectra (Figures 4.8b and 4.9b) reveal a shift in the Zn 2p $3/2$ and Zn 2p $1/2$ peaks from 1033.12 eV and 155.52 eV to 1033.83 eV and 1061.26 eV, respectively, suggesting interactions between Zn in ZIF-8/NH₂ and methyl blue molecules, likely through coordination or electrostatic interactions. In the N 1s spectra (Figure 4.8c and 4.9c), peaks attributed to NN-Zn (413.5 eV) and N-H (415 eV) shift to 422.51 eV post-adsorption, indicating the involvement of nitrogen atoms in hydrogen bonding or π - π interactions with methyl blue. Similarly, the C 1s spectra (Figures 4.8d and 4.9d) show peaks for C-C/C-H (298.4 eV) and C=N (300.26 eV) in pristine ZIF-8/NH₂, with new peaks appearing at 311.28 eV and 293.62 eV after adsorption, which can be attributed to the aromatic carbons and C-S bonds in methyl blue.

The O 1s spectra (Figures 4.8e and 4.9e) display a distinct shift in binding energy from 547.11 eV to 553.92 eV, indicating interactions between the oxygen atoms in ZIF-8/NH₂ and the sulfonate groups in methyl blue. This shift suggests the formation of hydrogen bonds and electrostatic interactions. Collectively, these changes in binding energies and the appearance of new peaks confirm the adsorption of methyl blue onto ZIF-8/NH₂ through mechanisms such as π - π stacking between the aromatic structures, electrostatic interactions with sulfonate groups, and hydrogen bonding involving amine and hydroxyl groups. These results align with the high adsorption capacity of amine-functionalized ZIF-8 materials, further demonstrating their potential in dye removal applications.

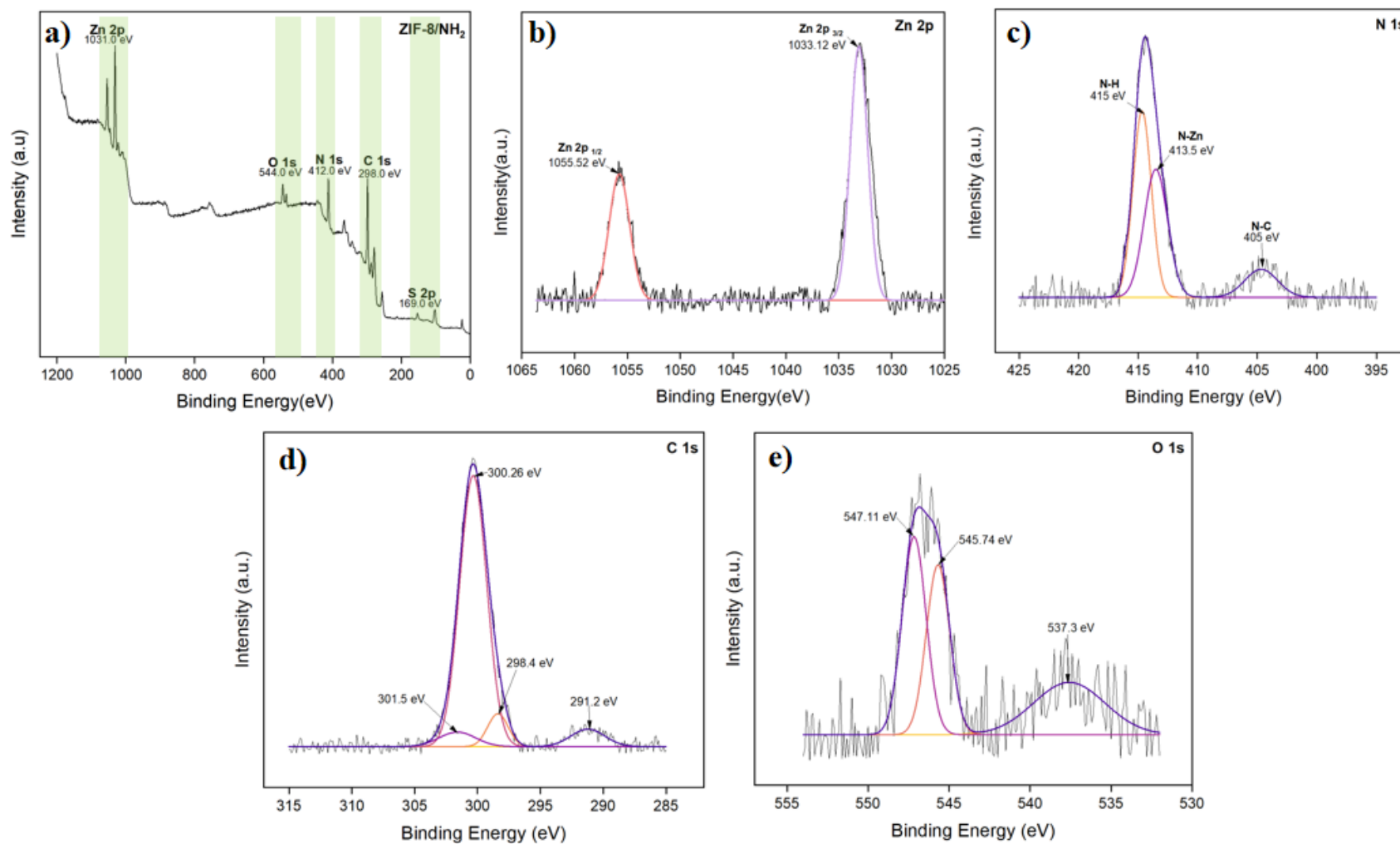


Figure 4.8: XPS spectra of a) ZIF-8/NH₂, b) Zn 2p, c) N 1s, d) C 1s and e) O 1s before adsorption with methyl blue

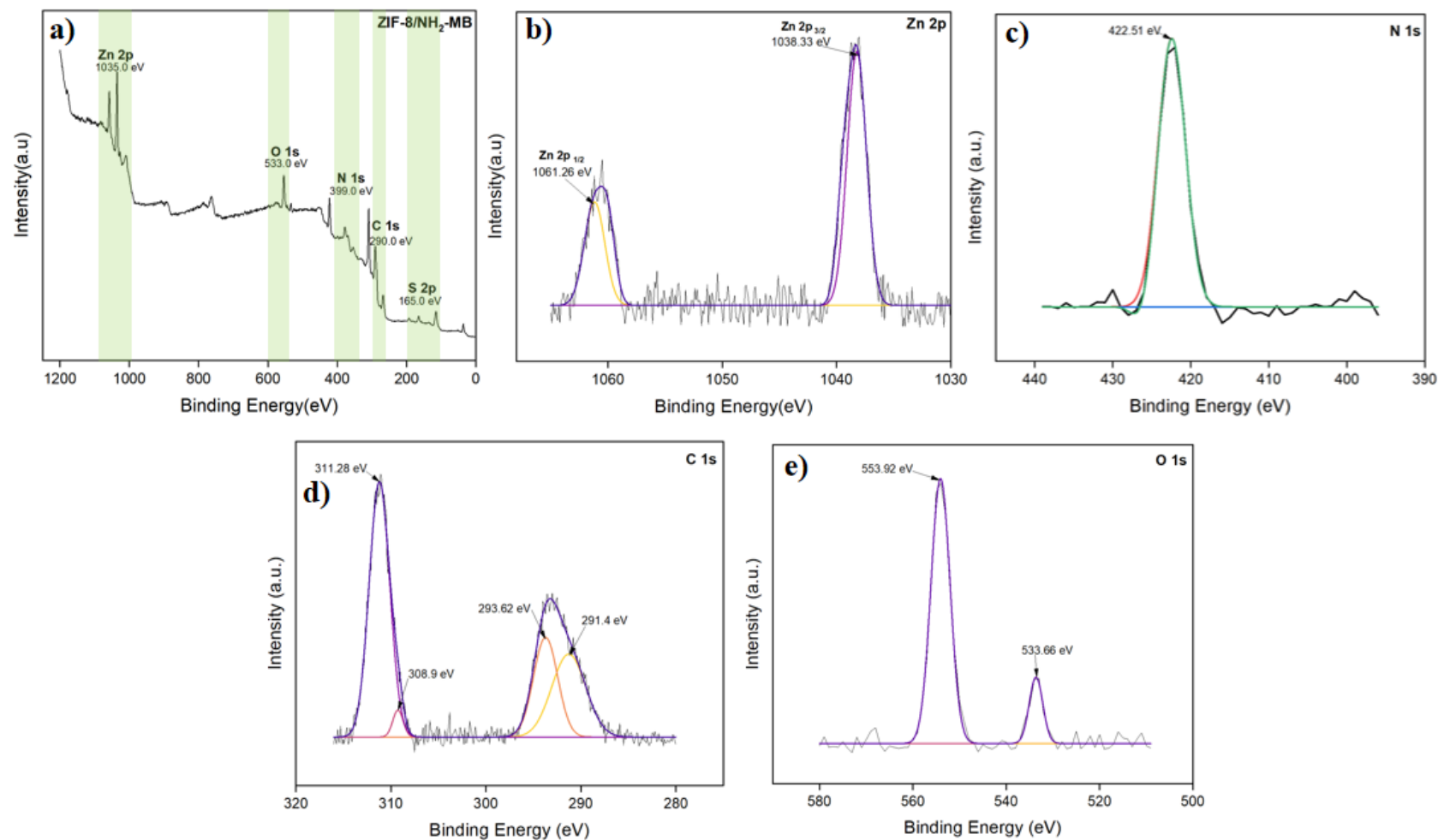


Figure 4.9: XPS spectra of a) ZIF-8/NH₂, b) Zn 2p, c) N, d) C 1s and e) O 1s after adsorption with methyl blue

4.1.5 Zeta Potential Analysis

The zeta potential analysis was conducted to determine the surface charge of ZIF-8/NH₂ and better understand its adsorption mechanism, as illustrated in Figure 4.10. According to Abdelhamid et al. (2020), ZIF-8 materials, except for GO@ZIF-8, typically exhibit positive zeta potential. The solution pH at which the zeta potential of the adsorbent becomes zero is referred to as the pH_{zpc} (Zhang, 2020). In this study, ZIF-8/NH₂ was found to have a pH_{zpc} of 2.79. This indicates that at a pH of 2.79 and below the surface of ZIF-8/NH₂ carries a positive charge, while at pH values above 2.79, the surface charge becomes negative. This transition in surface charge plays a crucial role in the adsorption mechanism, as it determines the material's electrostatic interactions with the oppositely charged species in the dye solution.

The pH-dependent behaviour of ZIF-8/NH₂ suggests that at lower pH values the positively charged surface enhances the adsorption of negatively charged species such as methyl blue, likely due to strong electrostatic attractions. Conversely, at higher pH values, the negative surface charge may reduce such interactions, potentially altering the adsorption efficiency. The influence of methyl blue solution pH on ZIF-8/NH₂ adsorption performance was investigated and is discussed further in Subsection 4.2. For reference, the original isoelectric titration graph from the zeta potential analysis is included in Appendix Figure 4.33.

This observation aligns with findings from Hassanzadeh et al. (2022), who reported that the isoelectric point of nanoparticles typically falls between 2.5 and 3.5. In their study, the pK_a of the drug cefazolin (3.6) closely matched the isoelectric point of the nanoparticles, resulting in a simple surface charge that reduced drug loading due to electrostatic repulsion. However, despite these conditions, a reasonable drug loading was achieved. Similarly, in this

study, the pH_{zpc} of ZIF-8/ NH_2 highlights the importance of charge interactions in influencing adsorption behaviour, further emphasizing the role of pH in tuning the material's adsorption properties.

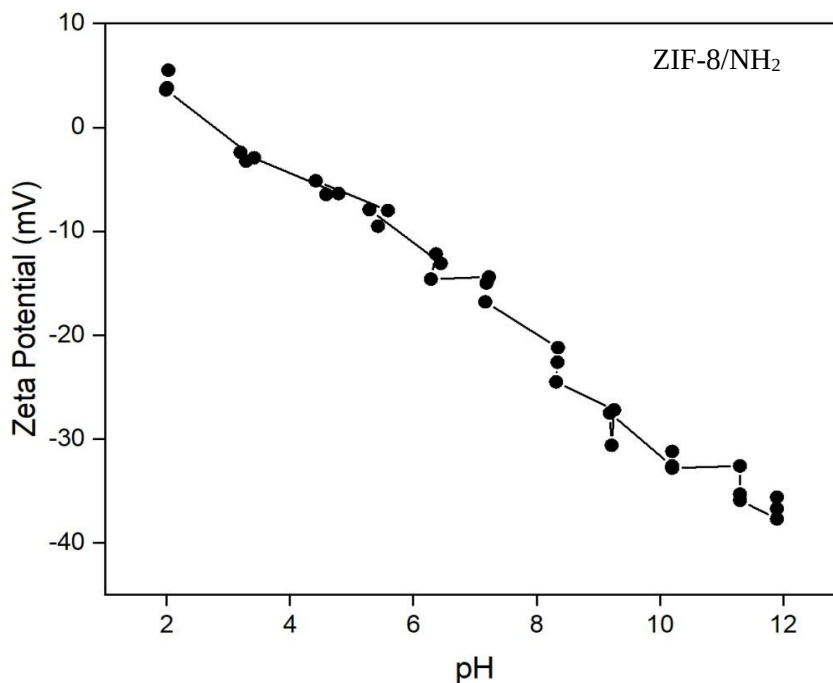


Figure 4.10: Zeta potential of GO@ZIF-8/ NH_2 nanoparticles before adsorption

4.1.6 BET Analysis

For the ZIF-8/ NH_2 nanoparticle, the BET analysis reveals (Table 4.1) a significantly higher surface area of $601.3776 \text{ m}^2/\text{g}$, indicative of the low porosity typical of ZIF structures. This substantial surface area suggests that the material is well-suited for applications that require a lot of active sites for adsorption. The t-Plot micropore area provides a micropore area of $535.2585 \text{ m}^2/\text{g}$, demonstrating that the majority of the surface has come from micropores, which is consistent with the ZIF-8 structure's inherent characteristics. In addition, the BJH adsorption and desorption cumulative surface area are $47.4271 \text{ m}^2/\text{g}$ and $50.4676 \text{ m}^2/\text{g}$, respectively showing a notable presence of mesoporosity, which could enhance the material's performance in applications involving larger molecules or faster

adsorption process. The average pore diameter, as per the BET method, is 3.5121 nm, further confirming the dominance of microporosity with the presence of mesopores as supported by the BJH analysis with pore widths of approximately 24-25 nm. Figure 4.11 shows the plots for ZIF-8/NH₂ BET results.

Table 4.1: BET overall analysis result for ZIF-8/NH₂ nanoparticles

Sample	ZIF-8/NH ₂
Surface Area	
BET surface Area	601.3776 m ² /g
t-Plot external surface area	535.2585 m ² /g
Langmuir Surface Area	712.6069 m ² /g
BJH Adsorption Cumulative Surface Area of Pores between 1.7000 nm and 300.0000 nm width	47.4271 m ² /g
BJH Desorption Cumulative Surface Area of Pores between 1.7000 nm and 300.0000 nm width	50.4676 m ² /g
Pore Volume	
BJH Adsorption Cumulative Volume of Pores between 1.7000 nm and 300.0000 nm width	0.3005 cm ³ /g
BJH Desorption Cumulative Volume of Pores between 1.7000 nm and 300.0000 nm width	0.3029 cm ³ /g
Pore Size	
Adsorption and Desorption average pore diameter (4V/A by BET)	3.5121 nm
BJH Adsorption Average Pore Width (4 V/A)	25.3406 nm
BJH Desorption Average Pore Width (4 V/A)	24.0079 nm

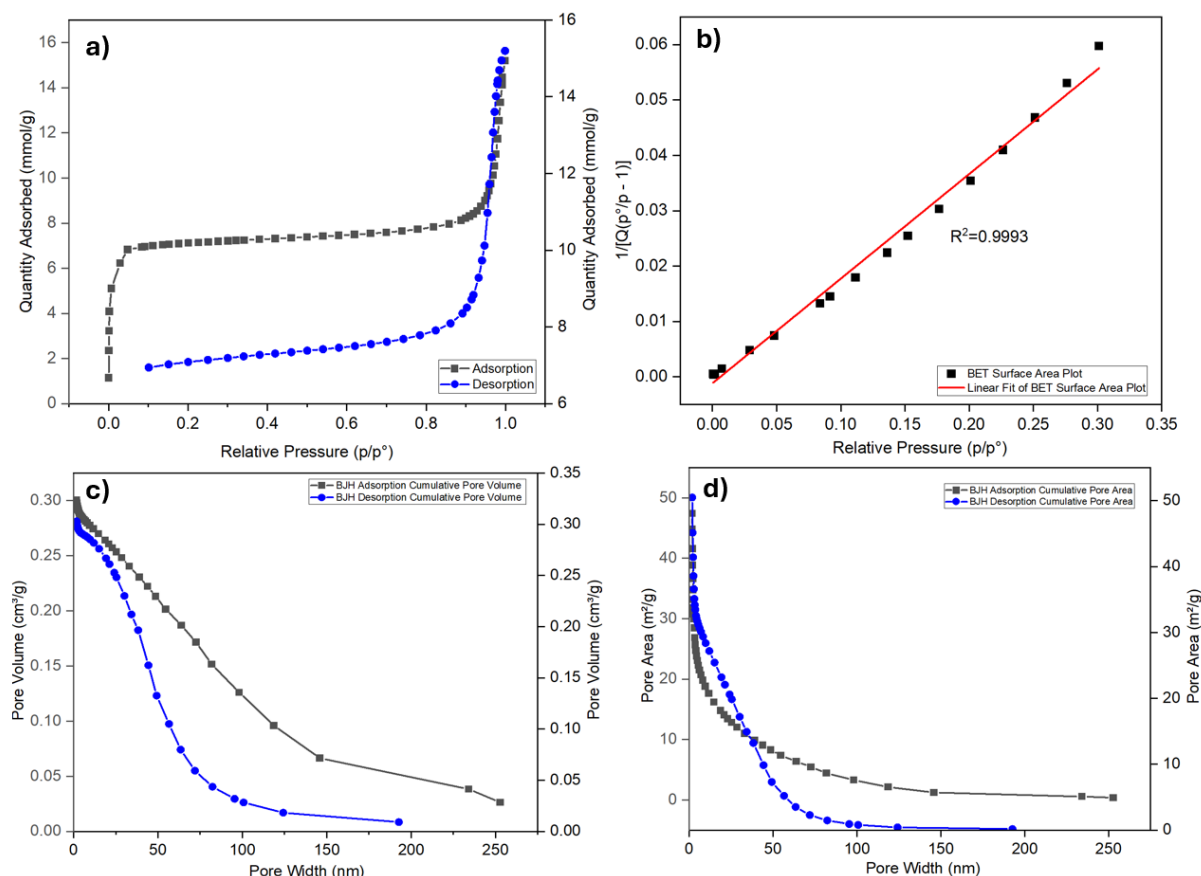


Figure 4.11: Results for ZIF-8/NH₂ nanoparticles of (a) N₂ sorption isotherms, (b) BET surface area plot, (c) BJH adsorption and desorption cumulative pore volume and (d) BJH adsorption and desorption cumulative pore area

4.2 Batch Adsorption Study of ZIF-8/NH₂ onto Methyl Blue Dye

4.2.1 Effect of Contact Time

The removal efficiency of methyl blue (MB) was analyzed over different contact times, as shown in Figure 4.12. The results indicate that the adsorption process occurred rapidly, with the majority of the dye being removed within the first 90 minutes. After this period, the adsorption reached equilibrium, indicating that the adsorption sites were fully occupied by methyl blue. The adsorption of MB onto ZIF-8/NH₂ showed a steady increase in removal efficiency from 79.4% to 82.1% over the first 90 minutes. This rapid adsorption during the initial stage suggests that the adsorbent's surface sites were readily available and

capable of binding MB molecules. After reaching equilibrium, no significant increase in removal efficiency was observed, confirming that the adsorption sites were saturated, and the process had reached its maximum capacity for MB removal.

The initial rapid adsorption can be attributed to the availability of free adsorption sites on the ZIF-8/NH₂ adsorbent. As the contact time increased, these sites gradually became occupied, leading to a slower adsorption rate. The equilibrium time of 90 minutes is consistent with typical adsorption processes, where the rate slows down as fewer unoccupied sites remain. Thus, the results demonstrate that ZIF-8/NH₂ is highly effective for the removal of MB, achieving removal of 82.1% within 90 minutes.

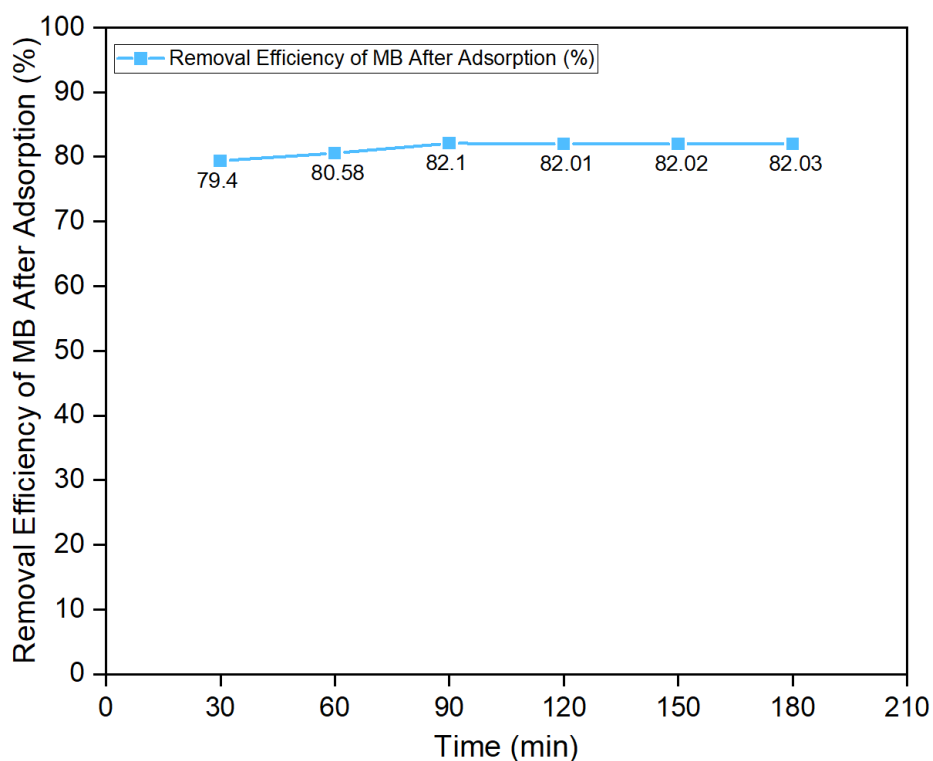


Figure 4.12: Effect of contact time on methyl blue dye removal after adsorption of ZIF-8/NH₂ at pH 7; 160 ppm

4.2.2 Effect of Initial Concentration

In this study, the effect of initial dye concentration on the adsorption capacity of methyl blue (MB) dye was explored. As observed in Figure 4.13, an increase in the initial concentration of the dye resulted in a higher adsorption capacity. This behaviour can be attributed to the increase in the number of dye molecules available for interaction with the adsorbent as the concentration rises. However, as the initial dye concentration continues to increase, the adsorption process experiences a saturation point where the adsorption capacity either stabilizes or decreases due to repulsion between the adsorbed molecules, which hinders further adsorption at the binding sites (Malekmohammadi et al., 2019).

The initial concentration of the dye plays a crucial role in the mass transfer of adsorbate molecules to the adsorbent. As the concentration increases, more dye molecules compete for available adsorption sites on the adsorbent surface (Uddin et al., 2021). This competition limits the number of sites that can be occupied, which explains the observation of a plateau in the removal efficiency at higher concentrations. In this study, the optimum initial concentration for methyl blue (MB) removal was found to be 160 ppm, with a maximum removal efficiency of 83.98%.

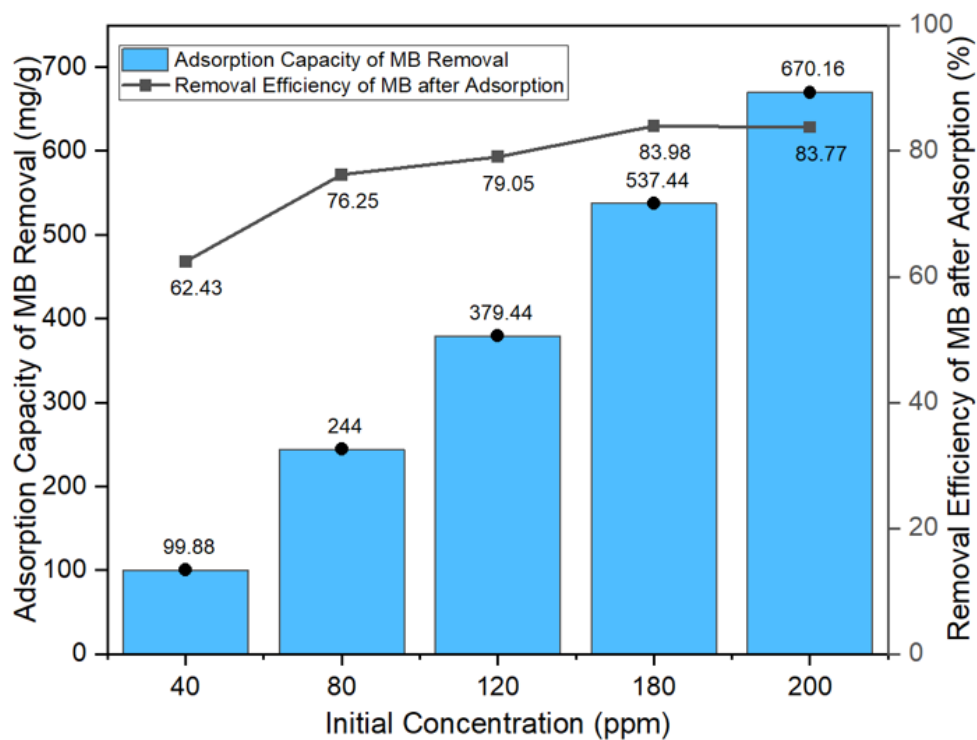


Figure 4.13: Effect of initial concentration on removal efficiency of methyl blue at pH 7 for 90 minutes after adsorption of ZIF-8/NH₂

Figure 4.14 illustrates the colour changes of the dye solution before and after the adsorption test, visually showing the significant reduction in dye concentration due to the adsorption process. These findings highlight the effectiveness of the adsorbent and the importance of optimizing initial dye concentrations to achieve maximum removal efficiency while preventing over-saturation of the adsorbent sites.

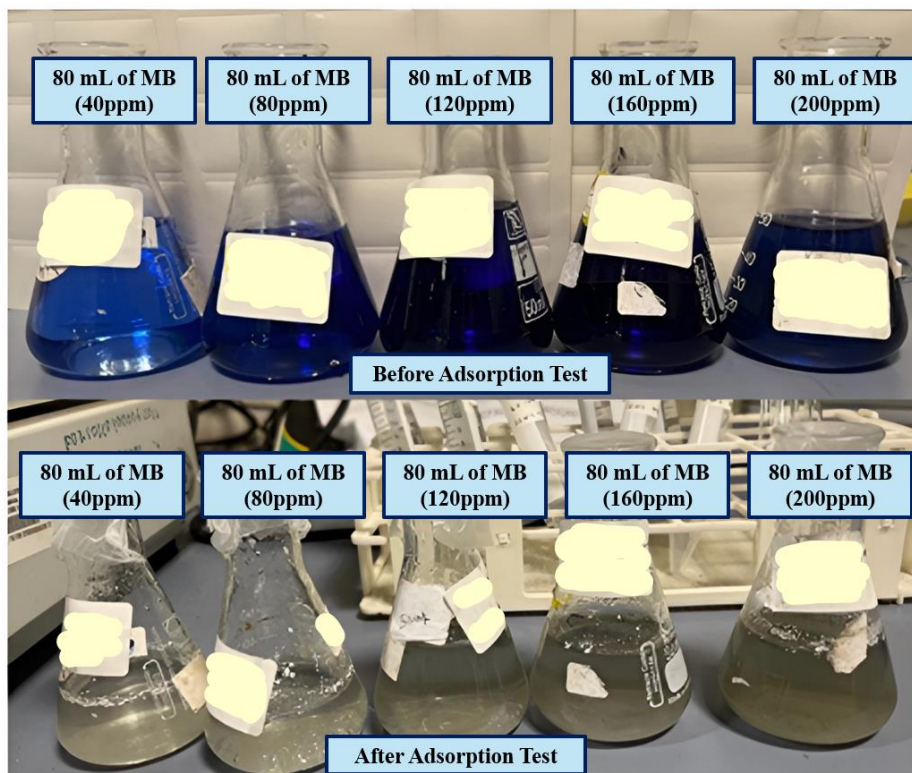


Figure 4.14: The colour changes before and after the adsorption test

4.2.3 Effect of pH Value

Figure 4.15 illustrates the impact of pH on the adsorption efficiency of methyl blue by ZIF-8/NH₂. The study evaluated pH values ranging from 3 to 11, with the dye adsorption pH adjusted using 0.1M HCl and 0.1M NaOH solutions, while other parameters were held constant. As shown in Figure 4.15, the removal efficiency of methyl blue was 18.33% at pH 3, increased significantly to 76.6% at pH 7, and then dropped sharply to 10% at pH 11.

This trend highlights the critical role of pH in influencing the adsorption mechanism. At pH 7, where the removal efficiency peaked, ZIF-8/NH₂ exhibited a negatively charged surface, as discussed in the zeta potential analysis. Despite methyl blue being an anionic dye, the enhanced adsorption efficiency at neutral pH can be attributed to the presence of amine (-NH₂) groups in ZIF-8/NH₂. These functional groups facilitate electrostatic interactions and hydrogen bonding with dye molecules, effectively enhancing adsorption. At lower pH levels,

such as pH 3, the NH_2 groups are likely protonated, resulting in a positively charged surface that weakly interacts with the negatively charged molecules, thereby reducing adsorption efficiency. Conversely, under alkaline conditions (pH 11), excess hydroxide ions compete with methyl blue anions for adsorption sites, further lowering the removal efficiency.

The observed behavior underscores the influence of pH on the availability of functional groups and the competition between dye molecules and the ions in the solution. These findings align with the zeta potential results, which indicate a shift in surface charge with pH. Neutral pH conditions were determined to be optimal for methyl blue adsorption, and this pH was chosen for subsequent adsorption studies involving ZIF-8/ NH_2 .

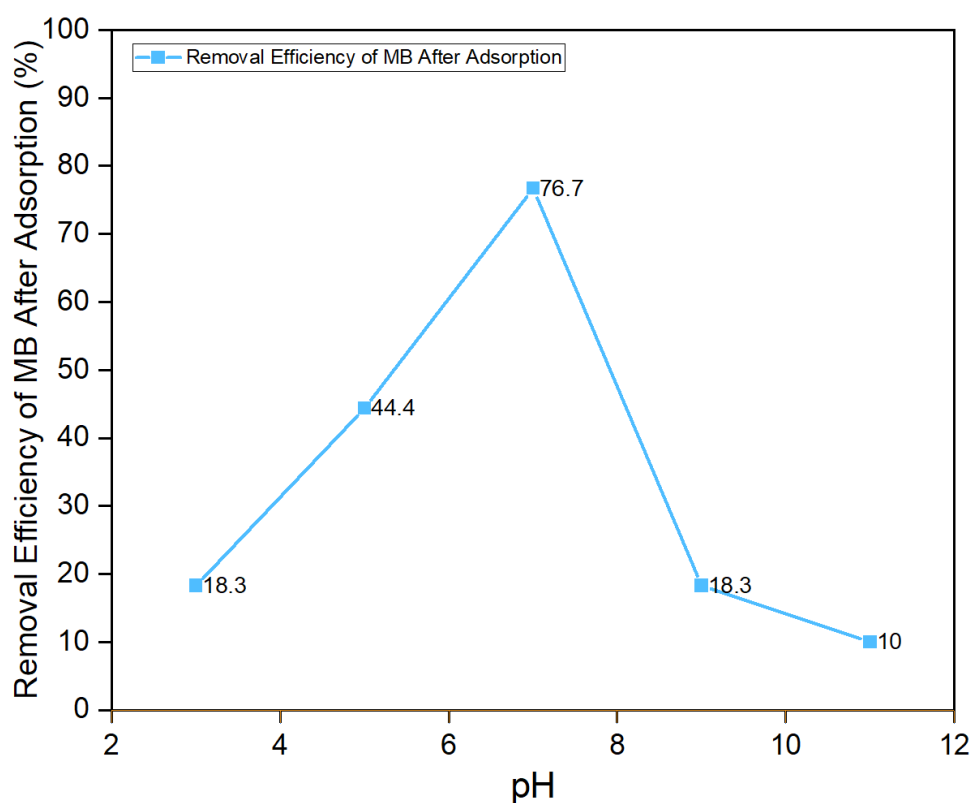


Figure 4.15: Effect of pH on the adsorption of methyl blue dye removal after adsorption onto ZIF-8/ NH_2

4.3 Adsorption Isotherms and Kinetic onto ZIF-8/NH₂ for Methyl Blue Dye

4.3.1 Adsorption Isotherm Model

The adsorption isotherms of methyl blue onto ZIF-8/NH₂ were analyzed using the well-established Langmuir and Freundlich models to understand the adsorption mechanism and surface interactions. The Langmuir and Freundlich adsorption isotherm models for methyl blue are illustrated in Figures 4.16(a) and 4.16(b), respectively, and the derived isotherm parameters are summarized in Table 4.2. Additional data related to plotting these isotherm models can be found in Tables 4.8 and 4.9 in the Appendices.

Based on the analysis, the calculated maximum adsorption capacity ($q_{\max}$) for methyl blue using the Langmuir model was 186.57 mg/g, while the Langmuir constant (K_L) was determined to be 0.0062. The separation factor (R_L) for methyl blue was also computed to be 0.0062, suggesting that the adsorption process is favorable. However, the regression coefficient (R^2) for the Langmuir model was 0.7180, indicating only a moderate fit to the experimental data. In contrast, the Freundlich isotherm model exhibited a better fit with an R^2 value of 0.9453, highlighting that this model better describes the adsorption process of methyl blue onto ZIF-8/NH₂. The Freundlich constant (K_F) of the heterogeneity factor ($1/n$) further suggests that the adsorption process is favorable and occurs on a heterogeneous surface, as indicated by $1/n$ values less than 1.

The favorability of adsorption as described by the Freundlich model indicates that the adsorption process is multilayered and occurs on a heterogenous surface rather than following the monolayer adsorption mechanism proposed by the Langmuir model. These findings align with the multilayer adsorption mechanism where the dye molecules interact with multiple adsorption sites on the ZIF-8/NH₂ surface. The results of this study are

consistent with findings reported by Feng et al. (2016) who studied the adsorption of empty blue using ZIF-8. While their results demonstrated a better fit with the Langmuir model, this study shows that the addition of amino functional groups (NH_2) to ZIF-8 nanoparticles significantly altered adsorption behavior, making it more suited to the Freundlich model. This suggests that the presence of NH_2 groups enhances surface heterogeneity, promoting multilayer adsorption. Overall, the adsorption of methyl blue onto ZIF-8/ NH_2 nanoparticles is better represented by the Freundlich isotherm model, implying a multilayer adsorption process on a heterogeneous surface.

Table 4.2: Adsorption isotherms parameters for the adsorption of the dye on ZIF-8/ NH_2

Type of Isotherms	Parameters of Methyl Blue Dye	
Langmuir	q_{max}	186.57
	K_L	1
	R_L	0.0062
	R^2	0.7180
	X^2	38.03452
Freundlich	n	2.4611
	K_F	0.0122
	R^2	0.9453
	X^2	0.6044

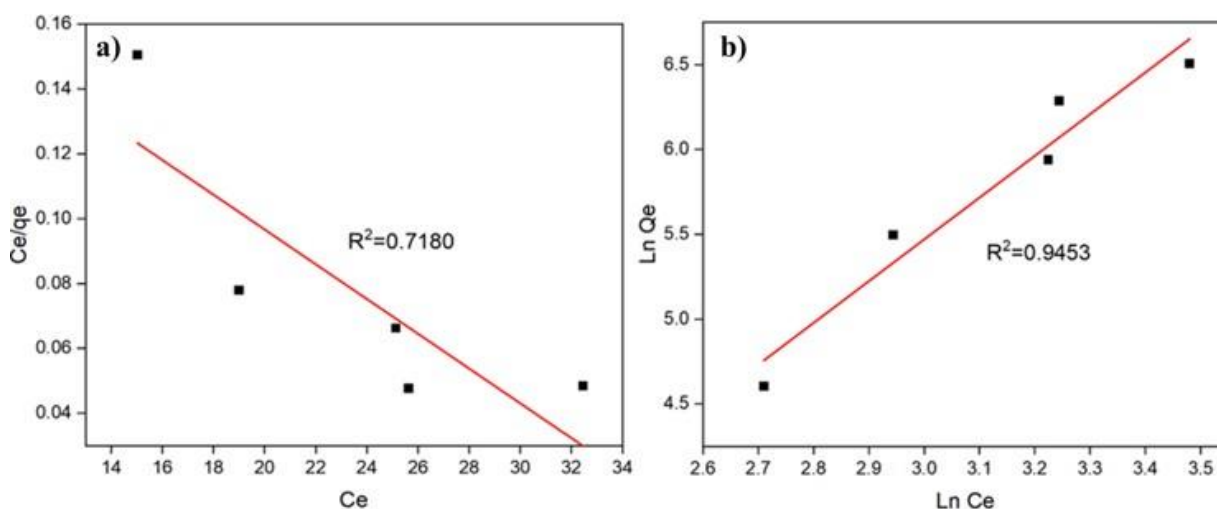


Figure 4.16: The (a) Langmuir model and (b) Freundlich plots of methyl blue dye on ZIF-8/NH₂

4.3.2 Kinetics Model

The kinetics of methyl blue adsorption onto ZIF-8/NH₂ were investigated using an initial methyl blue concentration of 160 ppm over 90 minutes duration. The kinetic data were analyzed using pseudo first order (PFO) and pseudo second order (PSO) models. The linear plots of $\log(q_e - q_t)$ vs t and $1/q_t$ vs t , representing the PFO and PSO models respectively, are presented in Figure 4.17. A completely linear trend in these plots indicates that both surface adsorption and intraparticle diffusion processes occur simultaneously during adsorption (Etim, 2019). The kinetic parameters derived from the PFO and PSO models are summarized in Table 4.3, while the detailed data and graph plotting are included in Tables 4.8 and 4.9 in the Appendices.

For methyl blue adsorption, the R^2 values for the PFO and PSO models were found to be 0.6871 and 0.9999, respectively. The higher R^2 value of the PSO model suggests that it provides a better fit to the experimental data compared to the PFO model, indicating that the adsorption of methyl blue onto ZIF-8/NH₂ follows the pseudo second order kinetic model. This finding implies that chemisorption, involving the formation of chemical bonds between the adsorption and the dye molecules, is the dominant adsorption mechanism.

Furthermore, the theoretically calculated equilibrium adsorption capacity (q_e) from the PSO model was 537.4 mg/g, which closely matched the experimental q_e value of 529.10 mg/g. This agreement further supports the applicability of the PSO model in describing the adsorption kinetics of methyl blue onto ZIF-8/NH₂.

These results align with a study conducted by Jia et al. (2021), in which MIL-100 (Fe) was used as an adsorbent to remove methylene blue and methyl blue. Similar to the current study, the PSO kinetic model exhibited a higher linear regression coefficient (R^2) compared to the PFO model, indicating a better fit to the adsorption kinetics. This reinforces the conclusion that the adsorption of methyl blue onto ZIF-8/NH₂ primarily occurs via a chemisorption mechanism, characterized by the exchange or sharing of electrons between the adsorbent and the dye molecules.

Table 4.3: Adsorption kinetics parameters for dye adsorption on ZIF-8/NH₂

Order of Reaction	Parameters of Methyl Blue Dye	
Pseudo First Order	q_e	0.9976
	k_1	0.9976
	R^2	0.6871
	X^2	596.403
Pseudo Second Order	q_e	529.1
	k_2	8.67E-01
	R^2	0.9999
	X^2	1.3334

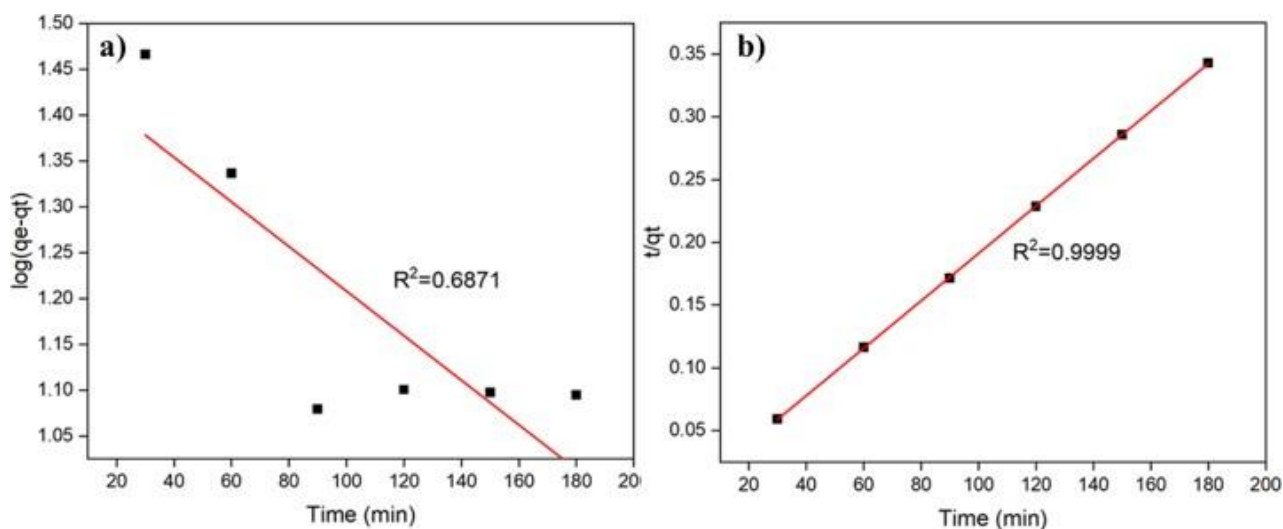


Figure 4.17: The plots of (a) pseudo first order and (b) pseudo second order of MB onto ZIF-8/NH₂

4.4 Synthesis and Characterization of GO@ZIF-8/NH₂

A modification of ZIF-8/NH₂ nanoparticles with graphene oxide (GO) was conducted to enhance the adsorbent's performance in dye removal. The incorporation of GO aimed to improve critical properties such as surface area, porosity, and chemical reactivity, which directly affect the efficiency of the adsorption process. The resulting modified adsorbent, GO@ZIF-8/NH₂, was tested for its ability to remove methyl blue dye, allowing for direct comparison with the adsorption performance of unmodified ZIF-8/NH₂.

The modification with GO introduces additional functional groups and structural heterogeneity, which can significantly influence the adsorption mechanism. For example, GO provides oxygen-containing functional groups, such as hydroxyl, epoxy, and carboxyl groups, which may enhance electrostatic interactions and hydrogen bonding with dye molecules. Furthermore, the increased surface area and pore volume of GO@ZIF-8/NH₂ potentially improves the accessibility of adsorption sites, thereby increasing dye removal efficiency.

This comparative study highlights the benefits of incorporating graphene oxide, offering valuable insights into how surface modification influences adsorption performance. The enhanced efficiency observed with GO@ZIF-8/NH₂ underscores its potential for practical applications in wastewater treatment, where improved adsorption capacity and selectivity are crucial for removing anionic dyes like methyl blue. These findings also provide a foundation for further strategies to optimize adsorbent materials for diverse environmental applications.

4.4.1 FTIR Analysis

Figure 4.18 shows the FTIR spectra of ZIF-8/NH₂, GO, and GO@ZIF-8/NH₂ composite, highlighting the differences in functional group characteristics after the incorporation of graphene oxide (GO) into ZIF-8/NH₂. These spectral analyses provide insights into the successful modification and how it impacts the adsorbent's chemical structure. For ZIF-8/NH₂, the spectrum shows characteristic peaks including a strong band at 1576 cm⁻¹ corresponding to C=N stretching vibration of the imidazole ring and ends at 757 cm⁻¹ and 684 cm⁻¹, indicating Zn-O and Zn-N bonds, respectively. These peaks confirm the structural integrity of ZIF-8/NH₂ and the successful incorporation of amino groups (NH₂) into the framework. Additionally, the O-H stretching at 3429 cm⁻¹ suggests the presence of surface hydroxyl groups, which contribute to adsorption interactions.

In contrast, the spectrum of GO@ZIF-8/NH₂ exhibits notable changes that confirm the successful integration of GO into the ZIF-8/NH₂ framework. The broadening of the O-H band at 3429 cm⁻¹ indicates enhanced hydrogen bonding due to the functional groups of GO interacting with ZIF-8/NH₂. Furthermore, the intensity of the C=O stretching band at 1110 cm⁻¹, a hallmark of GO, is slightly reduced in GO@ZIF-8/NH₂, suggesting chemical interactions between GO carboxyl groups and ZIF-8/NH₂. These interactions likely

improve the overall surface functionality and reactivity of the composite.

Notably, the Zn-N stretching band at 684 cm^{-1} , indicative of the ZIF-8 framework, is retained in GO@ZIF-8/NH₂, confirming that the fundamental structure of ZIF-8/NH₂ remains intact after modification. This retention is crucial as it preserves the structural stability of the adsorbent while enhancing its adsorption properties. Compared to unmodified ZIF-8/NH₂, the addition of GO introduces additional surface-active sites and increases the heterogeneity of the adsorbent surface, as evidenced by the changes in the FTIR spectra. These modifications are expected to enhance the adsorption capacity of methyl blue by providing more interactions for electrostatic and hydrogen bonding interactions. These FTIR findings align with studies by Begum et al., (2020), demonstrating that incorporation of GO into metal-organic framework like ZIF-8 improved adsorption performance without comprising structural integrity.

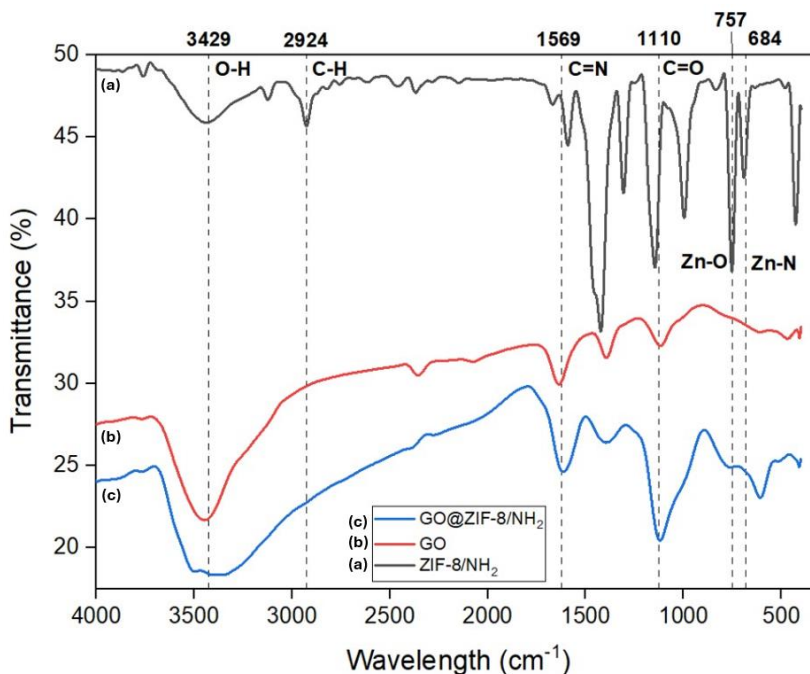


Figure 4.18: Comparison of FTIR analysis for ZIF-8/NH₂, GO, and GO@ZIF-8/NH₂

4.4.2 FESEM and EDXS Analysis

Figure 4.19 presents the FESEM images of (a) graphene oxide, and (b) GO@ZIF-8/NH₂ before adsorption of methyl blue dye. These images provide insights into the structural characteristics of the materials and the changes induced by the adsorption process. In Figure 4.19a, the FESEM image of GO exhibits its characteristic wrinkled and layered morphology. The stacked layers of GO are indicative of its high surface area and the presence of oxygen-containing functional groups, such as hydroxyl and carboxyl groups, which contribute to its excellent adsorption properties when incorporated with ZIF-8NH₂. Figure 4.19b shows the FESEM image of GO@ZIF-8/NH₂ before adsorption. The hexagonal crystal structure of ZIF-8/NH₂ is evident with GO successfully deposited onto its surface. The integration of GO onto ZIF-8/NH₂ enhances the composite's surface area and provides additional capabilities of GO with the structural stability and functional groups of ZIF-8/NH₂, particularly the ammino groups (-NH₂), which facilitate electrostatic interaction and hydrogen bonding with the dye molecules.

Following the absorption of methyl blue dye, Figure 4.19c reveals significant changes in the surface morphology of GO@ZIF8/NH₂. The image illustrates the uniform distribution of methyl bleu molecules on the composites' surface. The originally visible hexagonal structure is less distinct, as the adsorbed dye molecules obscure the surface. This observation confirms the strong interaction between methyl blue dye and the functional sites on GO@ZIF-8/NH₂. The primary adsorption mechanisms likely involve π - π staking, electrostatic interactions, and hydrogen bonding between the dye molecules and the composite. The morphological transformation after adsorption suggests the high adsorption efficiency of GO@ZIF-8/NH₂ for the blue dye. The even coverage of dye molecules across the surface indicated the availability of sufficient active sites on the absorbent, which were

effectively utilized during the adsorption process.

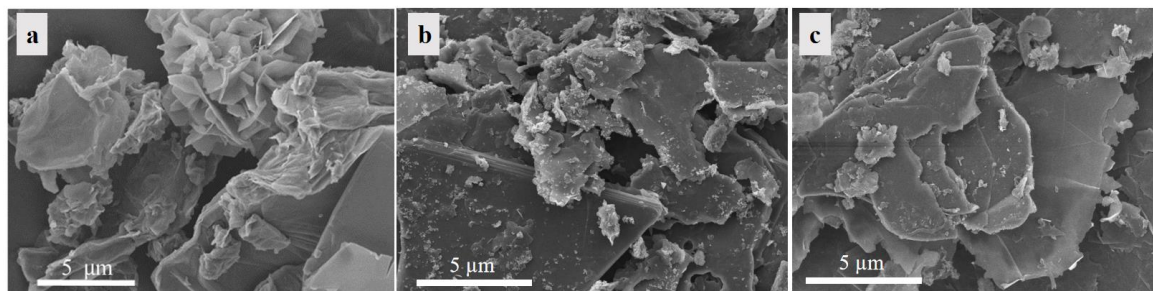


Figure 4.19: FESEM images of (a) GO and before adsorption using (b) GO@ZIF-8/NH₂ and (c) after adsorption of methyl blue dye

The EDXS (Figure 4.20) analysis provides important insights into the synthesis and adsorption performance of the materials. For GO, the high carbon (C) and oxygen (O) content observed in the elemental composition aligns with its expected structure. The uniform distribution of C and O indicates the purity of the GO sample, with no detectable sulfur (S) or zinc (Zn), as expected. This confirms that the GO precursor does not contain unwanted contaminants. In the GO@ZIF-8/NH₂ sample, the incorporation of zinc (Zn) and nitrogen (N) is evident, verifying the successful functionalization of GO with ZIF-8/NH₂. The reduction in oxygen content compared to pure GO suggests partial coverage of its surface by ZIF-8, which could influence its adsorption capacity. However, the elemental mapping reveals an uneven distribution of Zn, hinting at non-uniform coverage. This inconsistency suggests that the synthesis process might need optimization to ensure better homogeneity.

After adsorption with methyl blue (MB), the GO@ZIF-8/NH₂-MB sample exhibits a detectable sulfur (S) signal, indicating the successful interaction between the adsorbent and the dye. The persistent Zn and N signals confirm the structural stability of ZIF-8/NH₂ post-adsorption. However, the weak sulfur intensity implies either a low adsorption efficiency or incomplete interaction between MB and the adsorbent. This could be attributed to limited

functional groups on the adsorbent surface or steric hindrance during the adsorption process. These results align with the findings of Mirzajani et al. (2019), where the successful incorporation of ZIF-8 into GO was confirmed through morphological and elemental analysis. In this study, the SEM and EDXS analyses collectively demonstrate that GO@ZIF-8/NH₂ was successfully synthesized, as evidenced by the presence of Zn and N signals, consistent with ZIF-8. The partial reduction in oxygen content further supports the conclusion that ZIF-8 covered portions of the GO surface, a result also observed in Mirzajani et al.'s work. This indicates that the synthesis method employed effectively mirrors the structural and compositional characteristics reported in the literature, strengthening the reliability of the current findings.

Despite these findings, some limitations are apparent in the analysis. The overlapping regions between Zn and O in the elemental maps may interfere with accurate quantification, while the relatively low fitting ratios suggest challenges in spectrum resolution and background noise. These issues highlight the need for synthesis optimization to achieve uniform functionalization and enhanced adsorption performance.

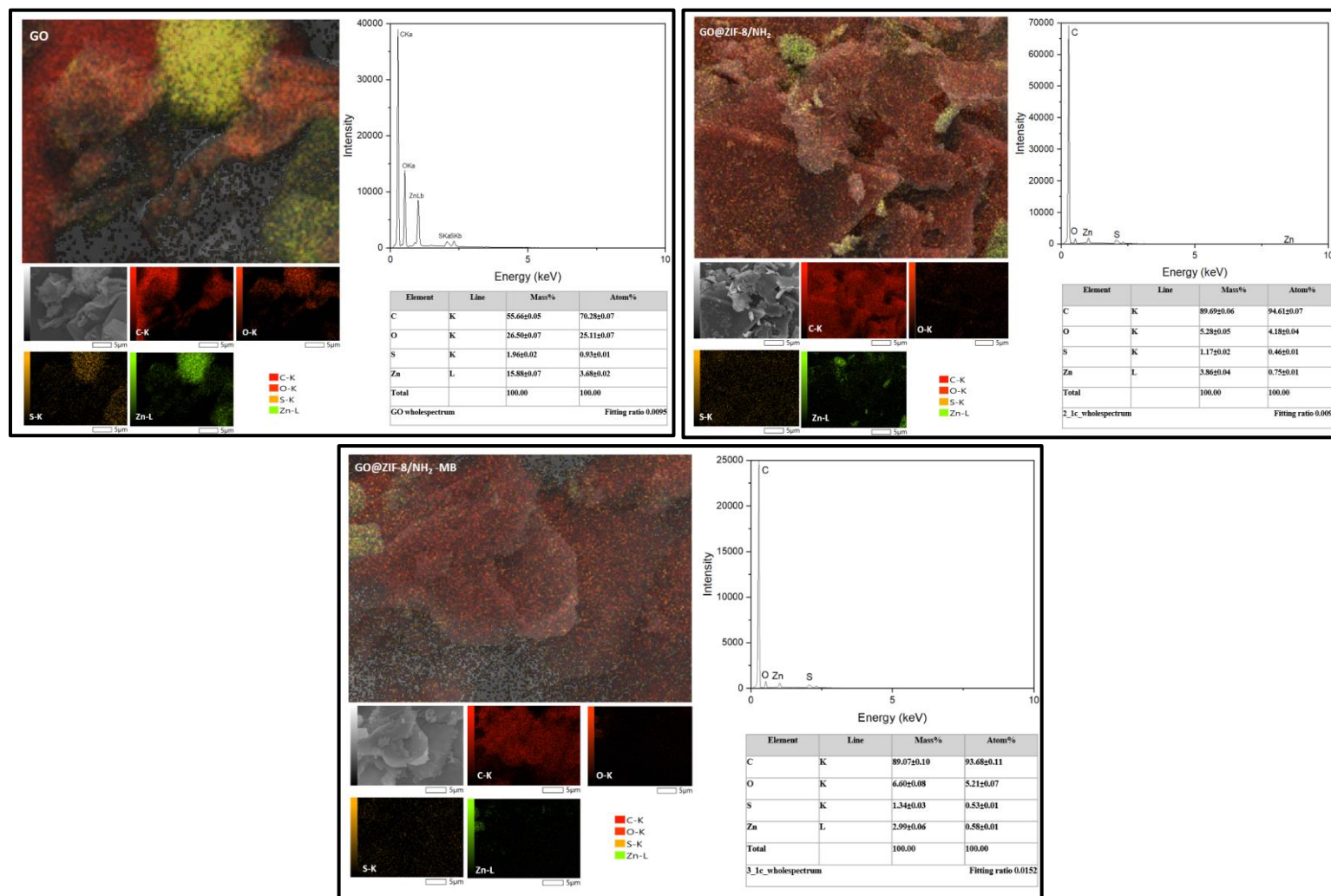


Figure 4.20: EDXS analysis of (a) GO, (b) GO@ZIF-8/NH₂, and (c) GO@ZIF-8/NH₂-MB

4.4.3 XRD Analysis

Figure 4.21 presents the X-ray diffraction (XRD) patterns of GO@ZIF-8/NH₂ (a) before and (b) after the adsorption process. These patterns provide insights into the structural and crystallinity changes of the composites it interacts with methyl blue dye.

In the XRD pattern of GO@ZIF-8/NH₂ before adsorption (Figure 4.20a) characteristic peaks of ZIF-8/NH₂ are observed at 7.18°, 12.38°, and 15.44°, confirming the retention of the soladite-like crystalline structure. The additional broad peak at 26.28 indicates the presence of graphene oxide (GO) within the composite, signifying the successful integration of GO into the ZIF-8/NH₂ framework. This peak corresponds to the (002) plane of GO, further highlighting its layered structure. After the adsorption of methyl blue dye (Figure 4.20b), notable changes in the XRD pattern are observed. The intensity of peaks, particularly at 7.18° and 26.28, increased, indicating enhanced crystallinity. This change suggests that the adsorption process promotes a more ordered arrangement within the composite material. The sharper peaks are likely due to the interaction between the dye molecules and the functional groups on the surface of GO@ZIF-8/NH₂, leading to secondary structural reorganization.

The increase in crystallinity after adsorption may be attributed to the interaction of methyl blue molecules with abundant oxygen-containing functional groups on GO such as hydroxyl, carboxyl, and epoxy groups and the amino-functionalized ZIF-8 framework. The dye molecules form strong hydrogen bonds and electrostatic interactions with the composite surface, which may stabilize the overall structure and improve its periodicity. These confirm that the incorporation of GO into ZIF-8/NH₂ does not compromise the structural intensity of the composite. Instead, the adsorption of methyl blue enhances the crystallinity of GO@ZIF-8/NH₂, likely due to the uniform distribution of dye molecules across the adsorbent surface.

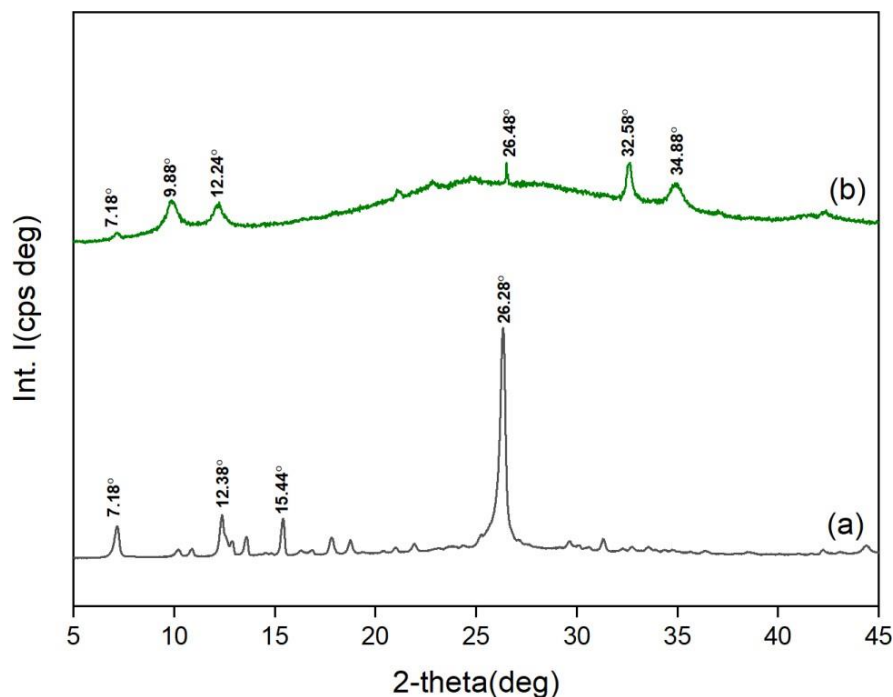


Figure 4.21: The XRD graph of GO@ZIF-8/NH₂ (a) before adsorption and (b) after adsorption onto methyl blue dye

4.4.4 XPS Analysis

The chemical composition and bonding environment of GO@ZIF-8/NH₂ were examined using XPS to investigate the interactions before and after dye adsorption (Figures 4.22 and Figure 4.23). Before adsorption (Figure 4.22c), the C 1s spectrum of GO@ZIF-8/NH₂ revealed four distinct peaks corresponding to the C-C bond at 284.4 eV, the C-N bond at 287.2 eV, the C-H bond at 286.1 eV, and the C=O bond at 290.13 eV. These peaks confirm the coexistence of GO and ZIF-8/NH₂ in the composite highlighting the characteristic oxygen and nitrogen-containing functional groups derived from both materials. After adsorption (Figure 4.23c), the C 1s peaks showed a slight shift to lower binding energies. This shift suggests strong interactions between the methyl blue dye and the functional groups on GO@ZIF-8/NH₂ likely mediated by hydrogen bonding, π - π interactions, and electrostatic forces.

In the O 1s spectrum before adsorption (Figure 4.22d), distinct peaks at 533.6 eV, 534.9 eV, and 535.6 eV were observed, which correspond to various oxygen-containing functional groups such as hydroxyl, carboxyl, and epoxy groups in GO. These peaks indicate the successful incorporation of oxygen functionalities in the GO structure within the composite. Following adsorption (Figure 4.23d), a leftward shift in the O 1s peaks was observed, accompanied by a slight intensity change. This shift suggests the active participation of oxygen groups in bonding with dye molecules, confirming their role in enhancing adsorption performance. Furthermore, the Zn 2p XPS spectra (Figures 4.22b and 4.23b) displayed two prominent peaks corresponding to Zn 2p $3/2$ and Zn 2p $1/2$, located at approximately 1024.0 eV and 1048.5 eV, respectively before adsorption. These peaks are characteristic of Zn²⁺ in the ZIF-8 framework. After adsorption, the peaks shifted slightly toward lower binding energies, reflecting an interaction between Zn sites and the dye molecules, possibly through electrostatic interactions or coordination bonding.

The XPS analysis provided conclusive evidence of the adsorption mechanism at the molecular level. The shifts in binding energies for C 1s, O 1s, and Zn 2p spectra suggest that the adsorption process is dominated by the functional groups of GO@ZIF-8/NH₂, which interact with the dye molecules through multiple mechanisms. These interactions, including hydrogen bonding, π - π stacking, and electrostatic forces, contribute to the efficient removal of methyl blue by the composite material. Furthermore, the chemical shifts and peak intensity variations indicate a strong affinity between the adsorbent and the dye, affirming the high adsorption efficiency of GO@ZIF-8/NH₂.

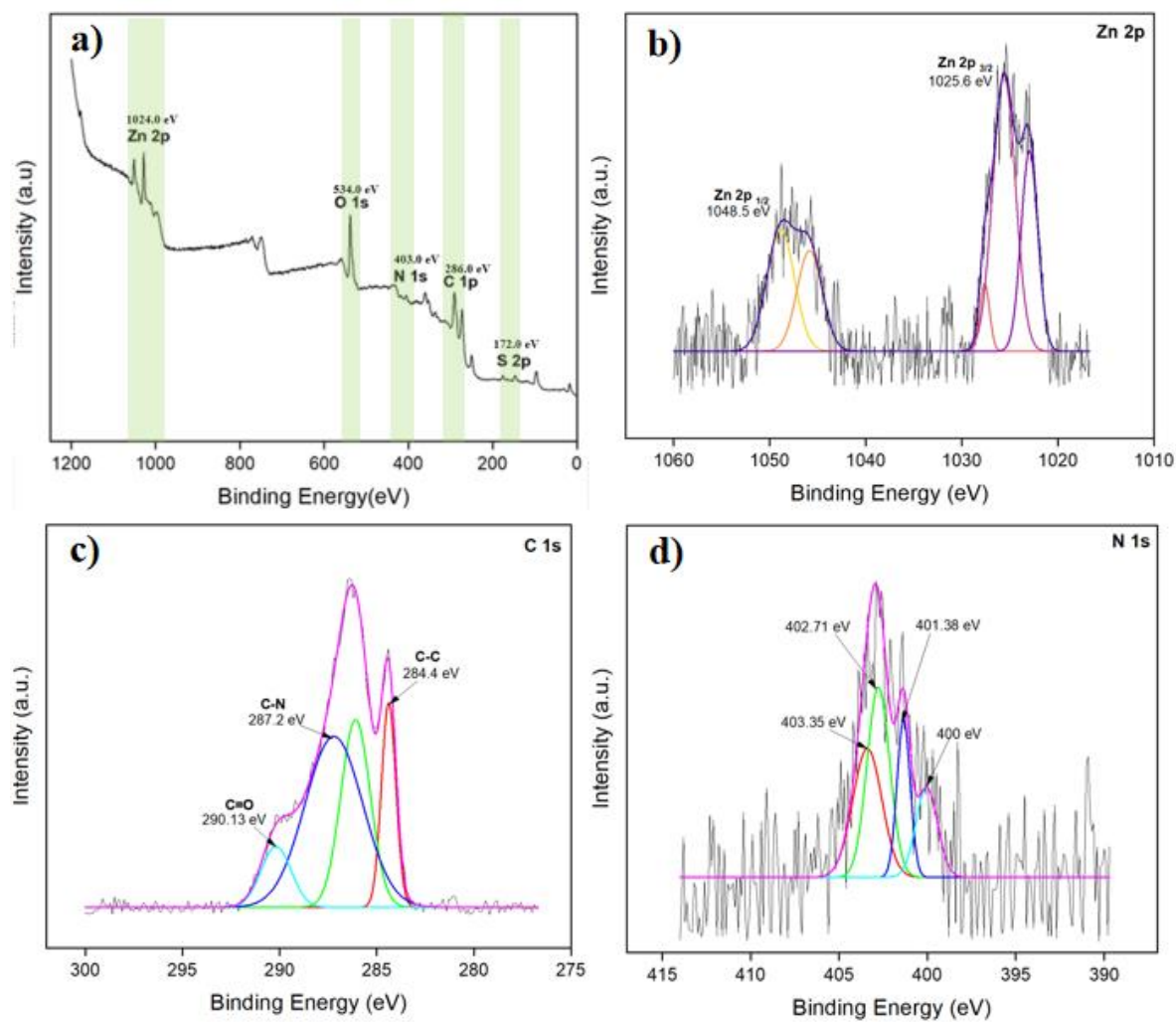


Figure 4.22: XPS spectra of a) GO@ZIF-8/NH₂, b) Zn 2p, c) C 1s and d) O 1s before adsorption with methyl blue

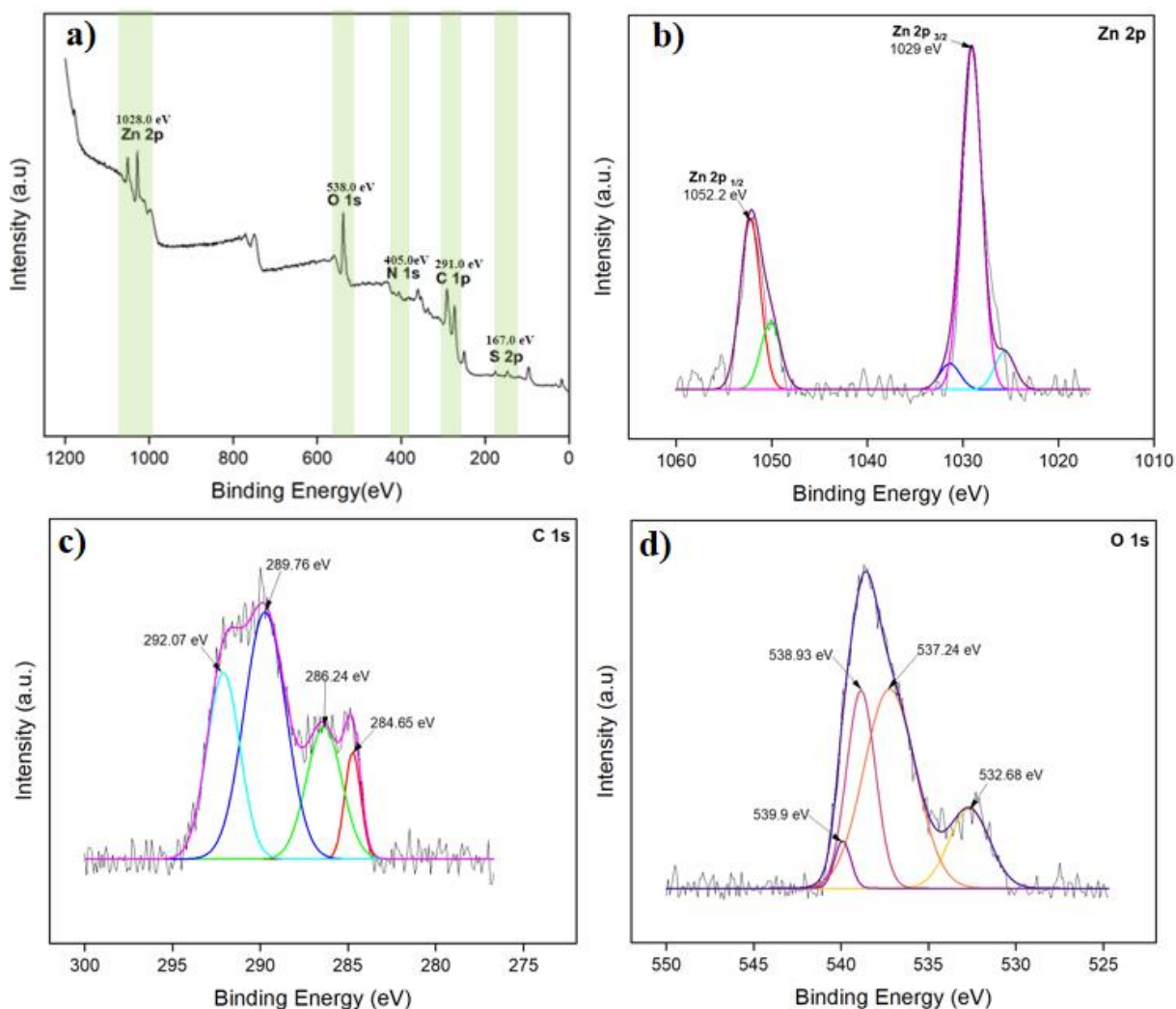


Figure 4.23: XPS spectra of a) GO@ZIF-8/NH₂, b) Zn 2p, c) C 1s and O 1s after adsorption with methyl blue

4.4.5 Zeta Potential Analysis

The zeta potential analysis GO@ZIF-8/NH₂ (Figure 4.24) revealed a point zero charge (pH_{zpc}) at 2.57, indicating the pH at which the material's surface exhibits a neutral charge. Below this pH, the surface of GO@ZIF-8/NH₂ is positively charged due to the protonation of amino groups and other protonated functional groups present in the composite. Conversely, with a pH value exceeding 2.57, the surface charge becomes negative, attributed to the deprotonation of amino groups and dissociation of other

oxygen-containing functional groups, such as hydroxyl (-OH), carboxyl (-COOH), and epoxy groups from the GO component. These functional groups significantly enhance this surface charge behavior, as evidenced by the pronounced negative shift to higher pH values.

The negative surface charge at pH values above 2.57 plays a critical role in the adsorption of methyl blue, which is an anionic dye. Electrostatic interactions are diminished at pH values below the pH_{zpc} due to repulsion between positively charged functional groups and the dye molecules. However, as the pH increases, the surface deprotonates, resulting in a stronger electrostatic attraction between the negatively charged surface of GO@ZIF-8/NH₂ and the cationic components of the dye. The behavior emphasizes the importance of surface chemistry and pH-dependent charge characteristic adsorption studies. It is crucial to align the operating pH of the methyl blue solution to a range above the pH_{zpc} to maximize adsorption efficiency, as discussed in subsection 4.5.3. The original isoelectric titration graph for ZIF-8/NH₂ is shown in Figure 4.33 (Appendices). Provide a baseline comparison to assess the impact of graphene oxide incorporation on the surface charge dynamics.

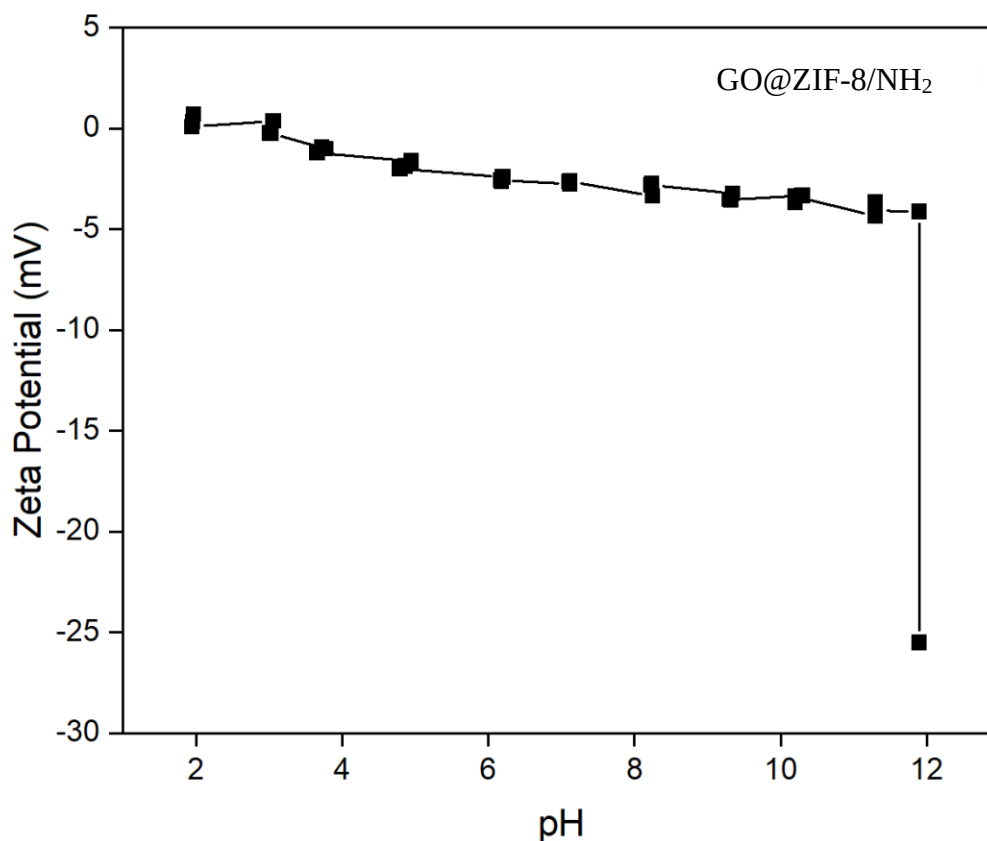


Figure 4.24: Zeta potential of GO@ZIF-8/NH₂

4.4.6 BET Analysis

In contrast to the ZIF-8/NH₂ nanoparticles, the BET analysis (Table 4.4) of GO@ZIF-8/NH₂ composite yielded a BET surface area of 87.7159 m²/g, which is significantly lower than that of pristine ZIF-8/NH₂. This relatively moderate surface area suggests that the incorporation of graphene oxide (GO) into the ZIF-8/NH₂ framework did not significantly enhance the accessible surface area, potentially due to the agglomeration of GO or partial blockage of ZIF-8 pores by the GO sheets. The t-plot analysis shows a micropore area of 63.9508 m²/g, indicating that a significant portion of the surface area is attributed to micropores, characteristics of the ZIF-8 framework. However, this is a reduction compared to the ZIF-8/NH₂, again suggesting that GO might be obstructing some of these microporous sites.

Additionally, the BJH analysis revealed a cumulative pore surface area of 17.4728 m²/g for adsorption and 19.3929 m²/g for desorption, which points to the presence of mesopores within the composite, albeit in lower qualities. The presence of these mesopores can be beneficial for applications that require faster adsorption kinetics. The average pore diameter, determined by the BET method, is 5.5562 nm, suggesting that the material exhibits mesoporosity alongside its microporous structure. The BJH method further supports this, with an average pore width of approximately 18-19 nm. Figure 4.25 shows the plots of BET analysis for ZIF-8/NH₂.

Table 4.4: BET overall analysis result for GO@ZIF-8/NH₂ nanoparticles

Sample	GO@ZIF-8/NH ₂
Surface Area	
BET surface Area	87.7159 m ² /g
t-Plot external surface area	63.9508 m ² /g
Langmuir Surface Area	110.0924 m ² /g
BJH Adsorption Cumulative Surface Area of Pores between 1.7000 nm and 300.0000 nm width	17.4928 m ² /g
BJH Desorption Cumulative Surface Area of Pores between 1.7000 nm and 300.0000 nm width	19.3929 m ² /g
Pore Volume	
BJH Adsorption Cumulative Volume of Pores between 1.7000 nm and 300.0000 nm width	0.0816 cm ³ /g
BJH Desorption Cumulative Volume of Pores between 1.7000 nm and 300.0000 nm width	0.0923 cm ³ /g
Pore Size	
Adsorption and Desorption average pore diameter (4V/A by BET)	5.5562 nm
BJH Adsorption Average Pore Width (4 V/A)	18.6624 nm
BJH Desorption Average Pore Width (4 V/A)	19.0371 nm

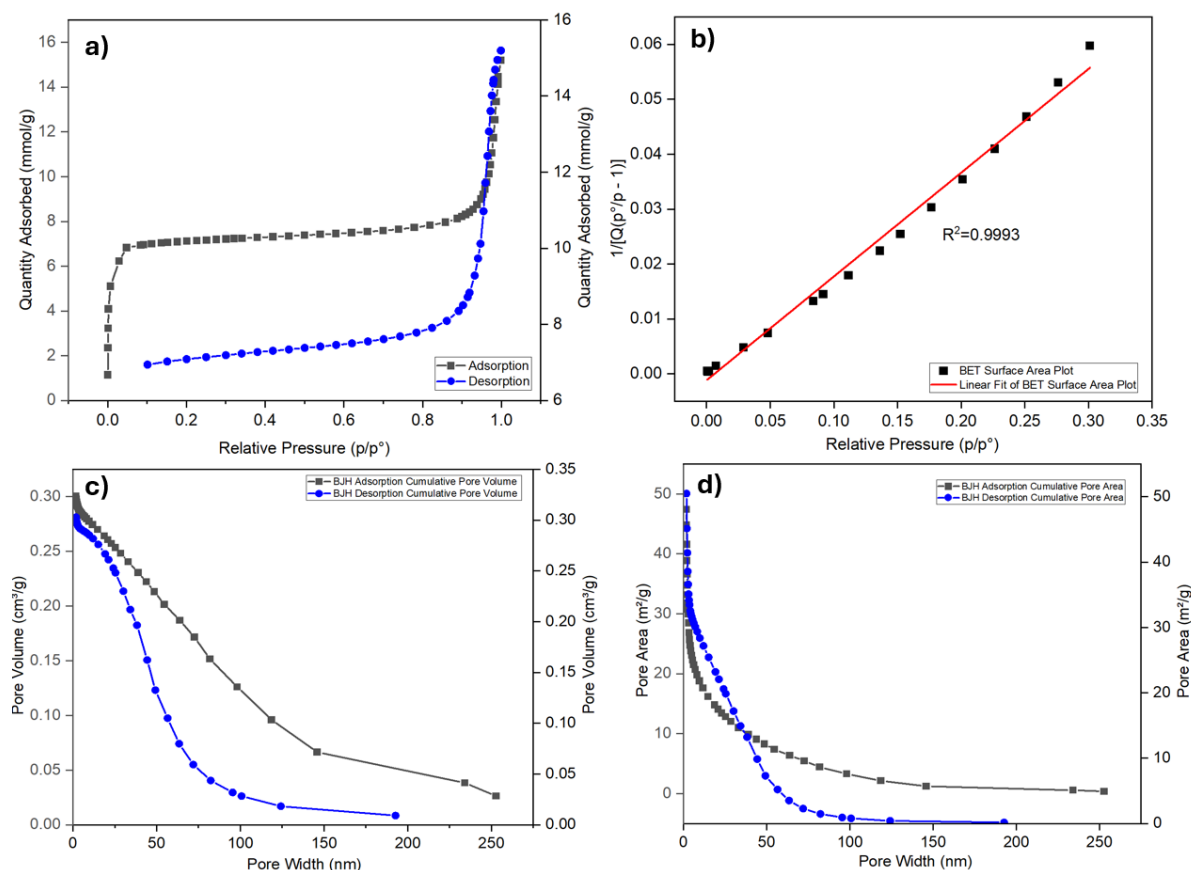


Figure 4.25: Results for GO@ZIF-8/NH₂ nanoparticles of (a) N₂ sorption isotherms, (b) BET surface area plot, (c) BJH adsorption and desorption cumulative pore volume and (d) BJH adsorption and desorption cumulative pore area

Thus, when comparing the GO@ZIF-8/NH₂ composite with the pristine ZIF-8/NH₂, it becomes clear that the incorporation of GO results in a trade-off. The composite introduces additional mesoporosity, which can be advantaged for certain applications, so at the expense of reducing the overall surface area and microporosity. This implies that GO@ZIF-8/NH₂ might be more suitable for this dye removal process as it requires faster adsorption kinetics due to its mesopores.

4.5 Batch Adsorption of GO@ZIF-8/NH₂ onto Methyl Blue Dye

4.5.1 Effect of Contact Time

The adsorption kinetics of methyl blue onto GO@ZIF-8/NH₂ were evaluated under optimal conditions of pH 9 and an initial dye concentration of 200 ppm. The results,

illustrated in Figure 4.26, show that the equilibrium was achieved within 60 minutes. This marks a significant improvement over previous studies using ZIF-8/NH₂ alone, where longer times were required to reach equilibrium. GO@ZIF-8/NH₂ demonstrated the capability to remove up to 90% of methyl blue in a shorter timeframe, highlighting its superior adsorption performance. This enhancement is directly related to the structural and surface modifications confirmed through characterization. The XPS analysis revealed that the incorporation of graphene oxide (GO) into ZIF-8/NH₂ introduced oxygen-containing functional groups (such as hydroxyl, carboxyl, and epoxy) and enhanced the presence of amino groups. These groups increase the availability of active sites for adsorption and enable stronger interaction with the dye molecule through hydrogen bonding, electrostatic interactions, π - π stacking.

Moreover, the zeta potential analysis indicated that the surface charge of GO@ZIF-8/NH₂ changes based on pH, with a point of zero charge (pH_{zpc}) at 2.57. At pH 9, the surface is negatively charged, promoting electrostatic interactions with the positively charged methyl blue dye, further accelerating adsorption kinetics. The BET surface area and porosity of GO@ZIF-8/NH₂, determined in prior studies, also highlight the increased surface area and pore volume compared to ZIF-8/NH₂ alone. This enhanced porosity facilitates dye diffusion into the composite, complementing the fast adsorption kinetics. Therefore, the combined results from XPS, zeta potential, and structural characterization confirm that the incorporation of GO into ZIF-8/NH₂ not only improves the functional group availability but also modifies surface charge and diffusion dynamics, making it a highly efficient adsorbent for rapid methyl blue dye removal.

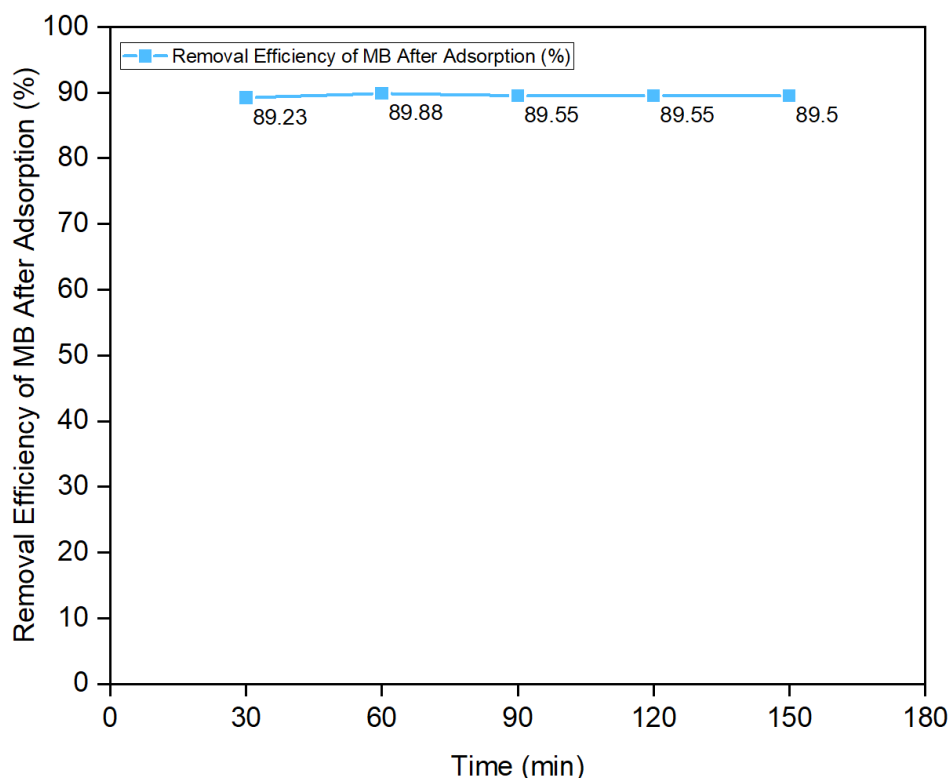


Figure 4.26: The effect of contact time of (a) methyl blue dye removal onto GO@ZIF8/NH₂ at pH 7 for 200 ppm

4.5.2 Effect of Initial Concentration

Under the conditions of pH 9 and 60 minutes of contact time, the adsorption behaviour of methyl blue onto GO@ZIF-8/NH₂ was studied across various initial concentrations. These parameters were kept evaluating the influence of concentration on adsorption performance. Based on the adsorption performance of GO@ZIF-8/NH₂ for methyl blue at various initial concentrations presented in Figure 4.27, the results demonstrate a significant removal efficiency of up to 90.45% at an optimal initial concentration of 200 ppm. Correspondingly, the adsorption capacity increased with higher initial concentrations, reaching a maximum of 867.44 mg/g at 240 ppm. This trend highlights the strong adsorption capability of GO@ZIF-8/NH₂, which can be attributed to its enhanced surface area and the abundance of functional groups introduced by graphene

oxide (GO).

At pH 9, the GO@ZIF-8/NH₂ surface becomes negatively charged due to the deprotonation of amino groups and other functional groups. Despite this, the high adsorption capacity for anionic methyl blue suggests that other mechanisms dominate the adsorption process. The effective removal of methyl blue can be attributed to π - π stacking interactions between the aromatic rings of the dye molecules and the aromatic framework of GO@ZIF-8/NH₂, as well as hydrogen bonding between the functional groups of the adsorbent and the dye. These mechanisms overcome the electrostatic repulsion that might arise at higher pH values, enabling efficient adsorption even for negatively charged dye molecules.

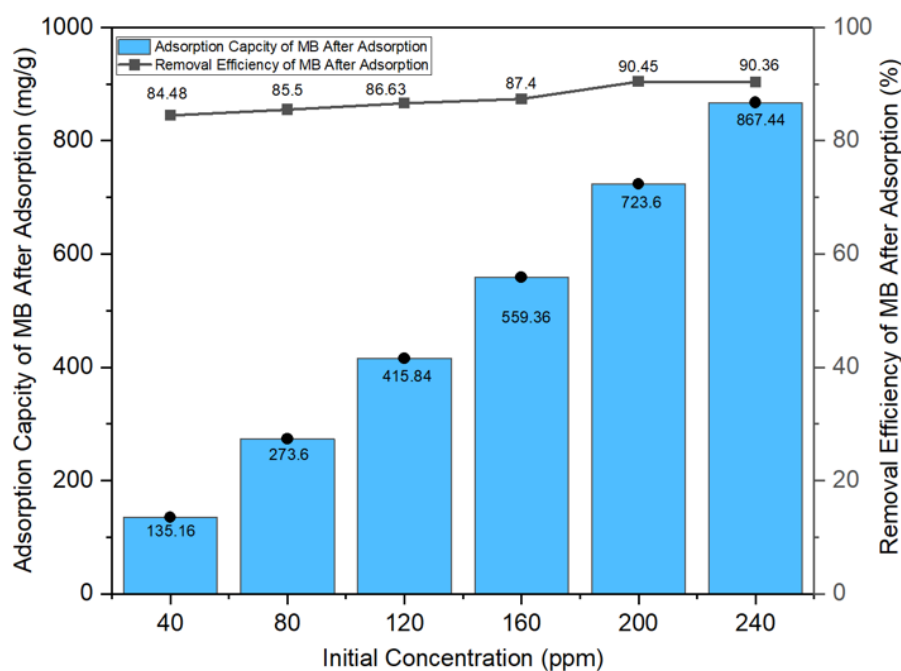


Figure 4.27: The effect of initial concentration on (a) methyl blue dye removal onto GO@ZIF-8/NH₂ at pH 7 for 60 minutes

4.5.3 Effect of pH Value

The effect of pH on the adsorption of methyl blue (MB) dye onto GO@ZIF-8/NH₂ was evaluated, and the results are illustrated in Figure 4.28. The removal efficiency of MB

increased with increasing pH, reaching a maximum value of 91% at its optimal pH of 7. Beyond this optimal pH, the removal efficiency decreased, which is consistent with the zeta potential of GO@ZIF-8/NH₂. The material becomes increasingly negatively charged at its isoelectric point (pH 2.57), influencing the electrostatic interactions between the adsorbent surface and the molecules. For MB, as an anionic dye, the removal efficiency trend aligns with electrostatic attraction at lower pH levels, where the adsorbent surface remains positively charged. As the pH increases, the negatively charged GO@ZIF-8/NH₂ surface enhances the interaction with MB molecules. However, at pH levels higher than 7, the adsorption efficiency decreases, possibly due to increased competition between hydroxide ions and the dye molecules for adsorption sites. The observed trend demonstrates that the presence of functional groups such as amino, hydroxyl, and carboxyl groups in GO@ZIF-8/NH₂ facilitates efficient interaction with the anionic dye molecules. These functional groups, combined with the material's high porosity and mesoporous structure, enable effective dye removal across a range of pH levels. Thus, this proves that the ability to achieve high removal efficiency at pH 7 underscores its potential for practical wastewater treatment applications involving anionic dyes.

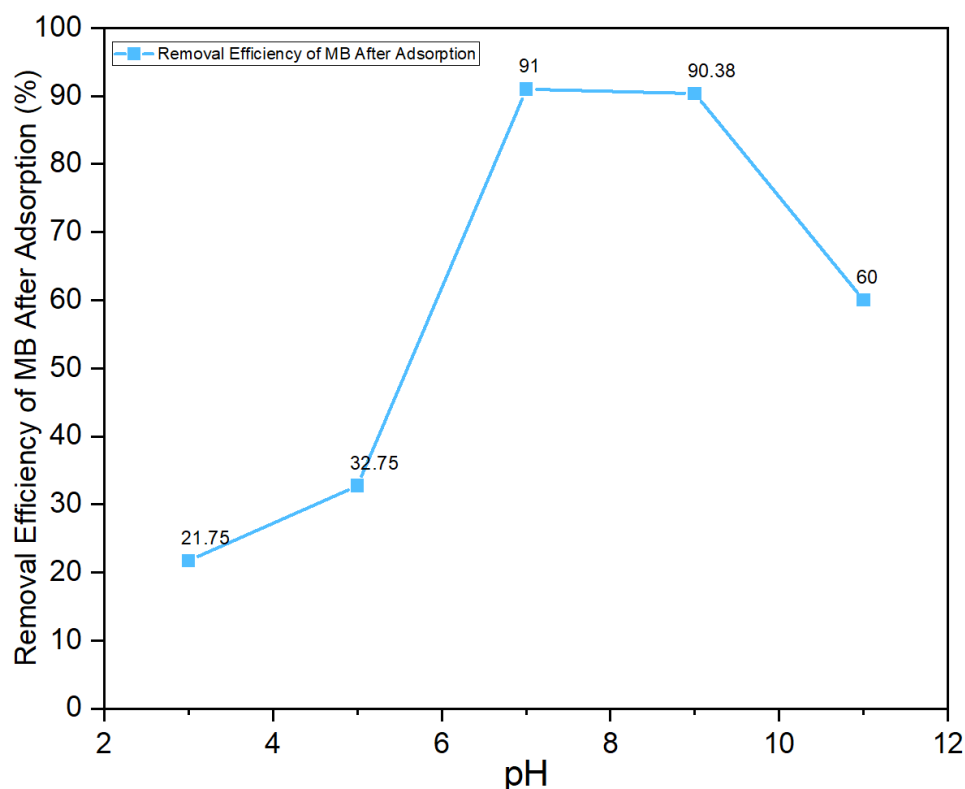


Figure 4.28: Effect of pH on the adsorption of methyl blue dye removal after adsorption onto GO@ZIF-8/NH₂

4.6 Adsorption Isotherm and Kinetic of GO@ZIF-8/NH₂ onto Methyl Blue

4.6.1 Adsorption Isotherm Model

The adsorption isotherm for methyl blue removal using GO@ZIF-8/NH₂ was found to be favorable, with data better fitting the Freundlich isotherm model compared to the Langmuir model. This is evident from the higher R^2 value of 0.9687 for the Freundlich model, compared to 0.9598 for the Langmuir model, as shown in Table 4.5 and Figure 4.29. The isotherms were plotted based on the data from Table 4.10 in the Appendices. The Freundlich isotherm model indicated that adsorption occurs on a heterogeneous surface with multiple layers and a non-uniform distribution of adsorption sites. This aligns with the observed high adsorption capacity of GO@ZIF-8/NH₂, as the incorporation of graphene oxide (GO) enhances the surface area and provides abundant functional groups. The high R^2 value for the Freundlich model confirms that the adsorption of methyl blue is more

accurately described by multilayer adsorption.

In contrast, the lower R^2 value for the Langmuir model suggests adsorption is not limited to a monolayer on a finite number of identical sites. However, the Langmuir isotherm model still indicates favorable adsorption, as the computed R_L value for methyl blue is 0.005, which is within the range of $0 < R_L < 1$, signifying a favorable adsorption process. Moreover, the Freundlich constant (n) was found to exceed 1, further confirming that the adsorption process is effective and advantageous. When $n > 1$, it suggests that the adsorbent exhibits a high affinity for the adsorbate, supporting the conclusion that GO@ZIF-8/NH₂ provides enhanced adsorption performance for methyl blue. Thus, the findings demonstrate that the adsorption of methyl blue onto GO@ZIF-8/NH₂ involves a multilayer adsorption process, driven by the heterogeneous nature of the adsorbent surface. The results underscore the effectiveness of GO@ZIF-8/NH₂ in achieving high removal efficiency through enhanced surface properties and diverse adsorption sites.

Table 4.5: Adsorption isotherms parameters for dye adsorption on GO@ZIF-8/NH₂ at 200 mg/L, 60 minutes

Type of Isotherms	Parameters of Methyl Blue Dye	
Langmuir	$q_{\max}$	869.56
	K_L	1
	R_L	0.005
	R^2	0.7809
	X^2	47.4160
Freundlich	n	1.1389
	K_F	199.03
	R^2	0.9598
	X^2	-1.6549

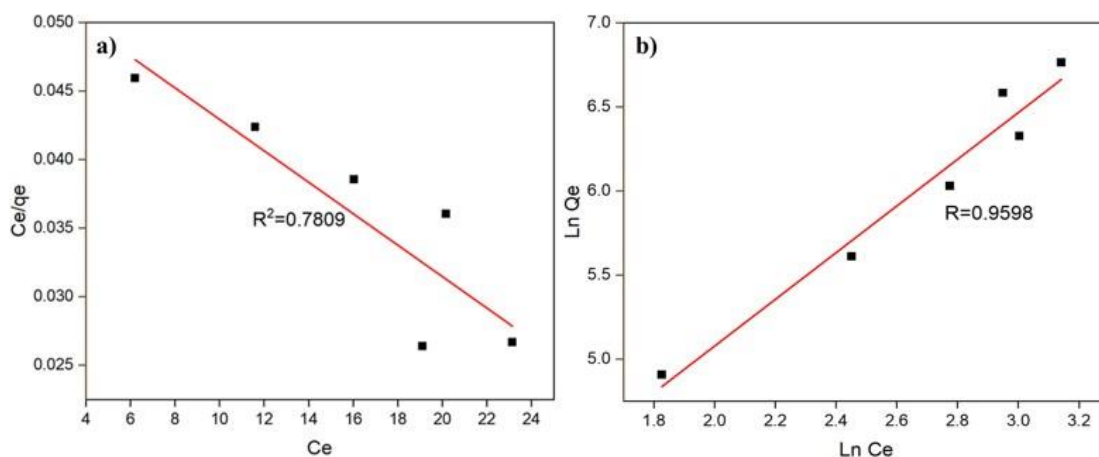


Figure 4.29: The (a) Langmuir model and (b) Freundlich for methyl blue dye removal onto GO@ZIF-8/NH₂

4.6.2 Kinetics Model

The results of the adsorption kinetics analysis from methyl blue are presented in Table 4.6 and Figure 4.30. These graphs were potted using data obtained from Table 4.10 in the appendices. Based on the findings, GO@ZIF-8/NH₂ nanoparticles are highly effective for the removal of methyl blue. The R² value of 0.9999 indicates that the adsorption process aligns well with the pseudo second order kinetic model, outperforming the pseudo first order model. The suitability of the pseudo second order model suggests that chemisorption is the dominant mechanism governing the adsorption process. Chemisorption typically involves the formation of chemical bonds between the adsorbate molecules and active sites on the adsorbent surface. This aligns with the high adsorption capacity of GO@ZIF-8/NH₂, which is enhanced by the incorporation of graphene oxide, providing a large number of functional groups and active sites.

Additionally, the theoretically calculated q_e value for methyl blue (723.6 mg/g) is slightly higher than the experimentally determined q_e at equilibrium (719.42 mg/g). This agreement further supports the applicability of the pseudo second order kinetic model for describing the adsorption process.

Table 4.6: Adsorption kinetics parameters for dye adsorption on GO@ZIF-8/NH₂ at 200 mg/L, 60 minutes

Order of Reaction	Parameters of Methyl Blue Dye	
Pseudo First Order	q _e	0.9924
	k ₁	0.9924
	R ²	0.6574
	X ²	177.78534
Pseudo Second Order	q _e	719.42
	k ₂	3.42E-03
	R ²	0.9999
	X ²	-0.40689

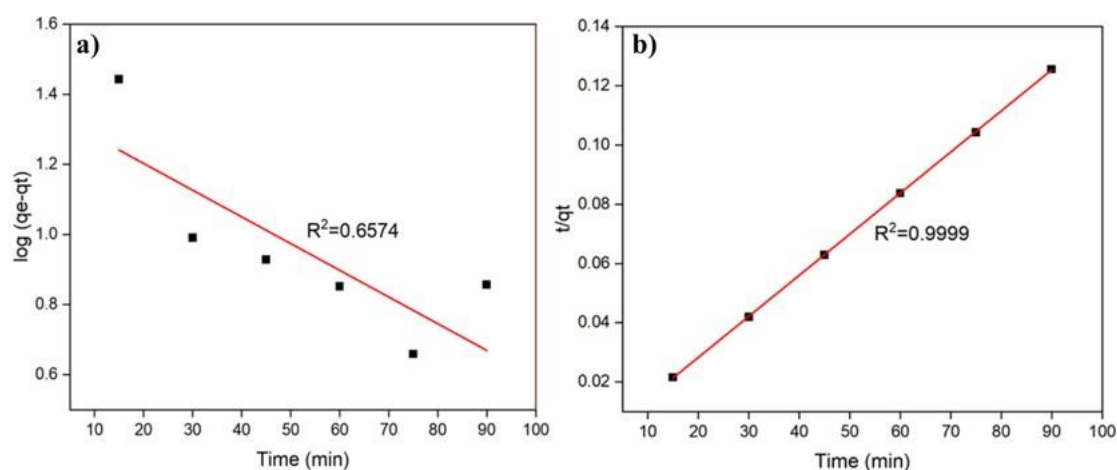


Figure 4.30: The plots of (a) pseudo first order and (b) pseudo second order kinetics for the adsorption of methyl blue on GO@ZIF-8/NH₂

Figure 4.31 below provides a schematic illustration of the adsorption of MB dye on the GO@ZIF-8/NH₂. It can be concluded that both adsorbents demonstrated excellent efficacy in removing methyl blue dye, as evidenced by the analysis results. Thus, Table 4.7 summarizes the overall findings of this study.

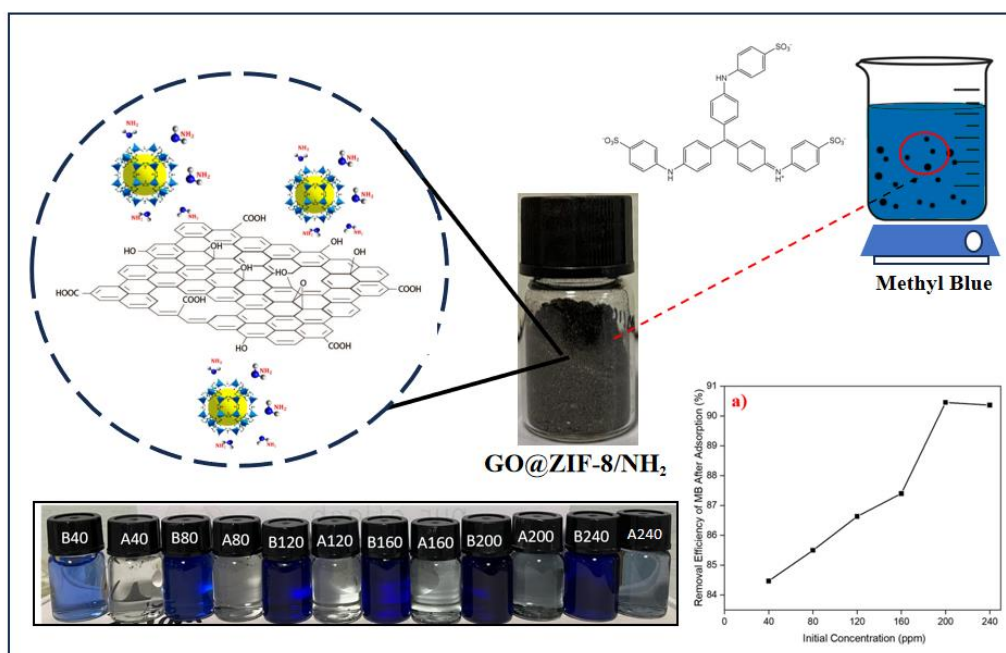


Figure 4.31: Schematic illustration of MB adsorption into GO@ZIF-8/NH₂

Table 4.7: Overall results of this research

Adsorbent			ZIF-8/NH ₂	GO@ZIF-8/NH ₂
Dye			Methyl Blue	
Adsorption Capacity (mg/g)			537.4	723.6
Removal Efficiency (%)			83.98	90.45
Optimum	Concentration (ppm)		160	200
Parameters	Time (min)		90	60
	pH		7	7
Isotherms	Langmuir	$q_{\max}$	186.57	869.57
		K_L	1	1
		R_L	0.0062	0.0050
		R^2	0.7180	0.7809
		X^2	38.0345	47.4160
	Freundlich	n	2.4611	1.3892
		K_F	0.0122	199.03
		R^2	0.9453	0.9598
		X^2	0.6044	-1.6549
Kinetics	Pseudo	q_e	0.9976	0.9924
	First Order	k_1	0.9976	0.9924
		R^2	0.6871	0.6574
		X^2	596.04	177.78534
	Pseudo	q_e	529.1	719.42
	Second Order	k_2	8.67E-01	3.42E-03
		R^2	0.9999	0.9999
		X^2	1.3334	-0.40689

4.7 Possible Adsorption Mechanisms

The possible adsorption mechanisms of ZIF-8/NH₂ and GO@ZIF-8/NH₂ for methyl blue (MB) as shown in Figure 4.32 can be attributed to several key interactions and structural features, which are closely linked to their pore characteristics and surface properties. For ZIF-8/NH₂, the high BET surface area (601.3776 m²/g) and predominantly microporous structure facilitate the adsorption of smaller dye molecules like MB, with a capacity of 537.4 mg/g and a removal efficiency of 83.98%. The smaller pores, with an average diameter of 3.5121 nm, create a favorable environment for the formation of strong hydrogen bonds between the hydroxyl and amino groups on the adsorbent surface and the dye molecules. This hydrogen bonding interaction enhances the attraction between the adsorbent and the dye, improving the overall adsorption capacity. Additionally, electrostatic interactions play a key role, as the positively charged amino-functionalized surface of ZIF-8/NH₂ strongly attracts the negatively charged MB molecules, further improving adsorption performance.

In contrast, GO@ZIF-8/NH₂, with a lower BET surface area (87.7159 m²/g) but significant mesoporosity, exhibits a higher adsorption capacity for MB (723.6 mg/g and 90.45% efficiency). The mesopores in GO@ZIF-8/NH₂ provide larger diffusion pathways, enhancing the adsorption of dye molecules. The graphene oxide (GO) modification further improves the material's adsorption capacity by introducing additional functional groups, such as hydroxyl and carboxyl groups, that facilitate hydrogen bonding interactions. These functional groups strengthen the interaction between the adsorbent and dye molecules, enhancing the overall adsorption performance. The presence of GO also contributes to π - π stacking interactions between the aromatic structure of MB and the adsorbent, increasing the binding affinity.

Electrostatic interactions remain significant for GO@ZIF-8/NH₂ as well. The amino-functionalized ZIF-8 and the functional groups on graphene oxide create positively charged adsorption sites that effectively attract the negatively charged MB molecules. At pH 9, the slightly alkaline environment promotes stronger electrostatic interactions, further enhancing the adsorption efficiency. From the isotherm data, the Langmuir model indicates that GO@ZIF-8/NH₂ has a higher maximum adsorption capacity ($q_{\max} = 869.57$ mg/g) for MB compared to ZIF-8/NH₂ ($q_{\max} = 186.57$ mg/g), reflecting the higher binding affinity and capacity of GO@ZIF-8/NH₂. The RL values close to 0 for both materials suggest favorable adsorption conditions. The Freundlich model further supports the enhanced adsorption behavior of GO@ZIF-8/NH₂, as its higher n values indicate the presence of stronger adsorption sites. In terms of adsorption kinetics, both materials follow a pseudo second order model, with high correlation coefficients ($R^2 = 0.999$), suggesting that chemisorption is the dominant mechanism. This supports the idea that the adsorption process is largely governed by the formation of chemical bonds between the adsorbent and the dye molecules. The faster adsorption of MB on GO@ZIF-8/NH₂, as indicated by the BET results, can be attributed to the larger mesopores and enhanced surface interactions, which allow for quicker dye diffusion and binding.

In summary, the adsorption mechanisms of ZIF-8/NH₂ and GO@ZIF-8/NH₂ are driven by hydrogen bonding, electrostatic interactions, and π - π stacking. The microporous structure of ZIF-8/NH₂ favors the adsorption of smaller dye molecules like MB, while the mesoporosity and functionalized surface of GO@ZIF-8/NH₂ enhance the adsorption of MB molecules. These interactions, coupled with the favorable pore structure and surface area, make both materials highly effective in removing the dye, as demonstrated by their adsorption capacities and removal efficiencies.

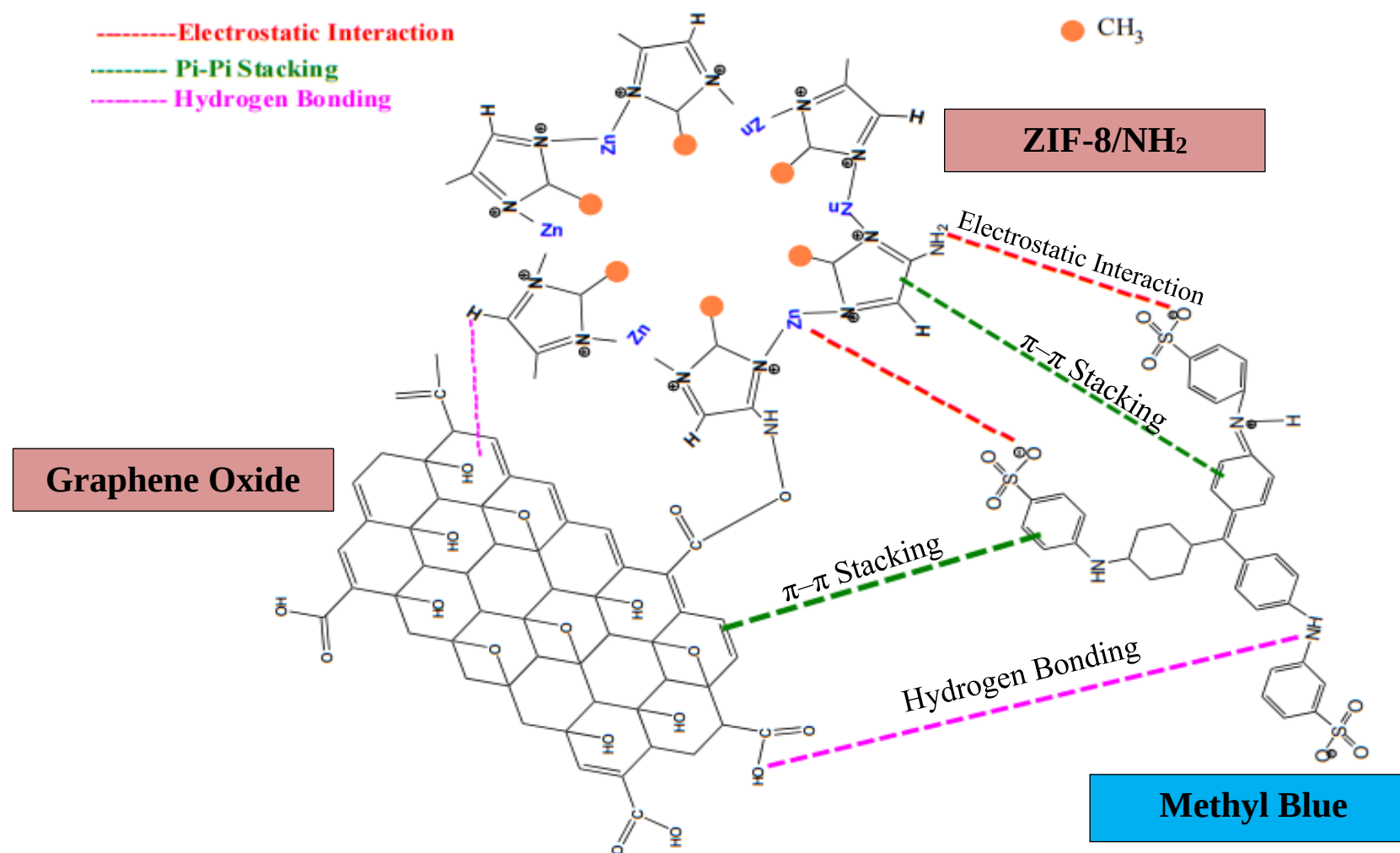


Figure 4.32: Possible mechanism for adsorption of methyl blue dye on the ZIF-8/NH₂ and GO@ ZIF-8/NH₂

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In summary, the incorporation of graphene oxide (GO) into ZIF-8/NH₂ significantly enhanced the physicochemical properties of the synthesized adsorbents. Characterization techniques confirmed the presence of amino groups in ZIF-8/NH₂ and oxygen-containing functional groups, including hydroxyl, carboxyl, alcohol, and epoxy groups, in GO@ZIF-8/NH₂, indicating the successful integration of GO. Additionally, surface morphology analysis revealed nanoparticles with diverse size distributions and shapes, further highlighting the unique characteristics of GO@ZIF-8/NH₂ that contribute to its superior adsorption performance compared to ZIF-8/NH₂ alone.

The batch adsorption study for methyl blue (MB) demonstrated a clear improvement in adsorption performance with the incorporation of GO. While ZIF-8/NH₂, with its high BET surface area of 601.38 m²/g and predominantly microporous structure, achieved a maximum adsorption capacity of 537.4 mg/g at pH 7, an initial dye concentration of 160 mg/L, and a contact time of 90 minutes, GO@ZIF-8/NH₂ outperformed it significantly. GO@ZIF-8/NH₂, with its enhanced mesoporosity and additional functional groups, achieved an adsorption capacity of 723.6 mg/g under the same optimized conditions, reaching equilibrium faster in just 60 minutes. The mesoporosity and functionalized surface of GO@ZIF-8/NH₂ facilitated better diffusion of dye molecules and stronger interactions with MB, contributing to its higher removal efficiency of 90.45%, compared to 83.98% for ZIF-8/NH₂.

The adsorption mechanism involved key interactions such as hydrogen bonding, electrostatic attraction between the negatively charged MB and the positively charged

amino-functionalized surfaces, and π - π stacking interactions between the aromatic structures of MB and the adsorbents. Both adsorbents conformed to the Freundlich isotherm, indicating multilayer adsorption, and followed the pseudo second order kinetic model, suggesting that chemisorption was the dominant mechanism. However, the inclusion of GO significantly enhanced the number and strength of adsorption sites, as evidenced by the higher adsorption capacity and faster kinetics of GO@ZIF-8/NH₂.

In conclusion, the study highlights the substantial improvements achieved by incorporating graphene oxide into ZIF-8/NH₂. GO@ZIF-8/NH₂ exhibited superior adsorption capacity, faster kinetics, and higher removal efficiency for methyl blue compared to ZIF-8/NH₂ alone. These enhancements are attributed to the synergistic effects of increased mesoporosity and the introduction of additional functional groups provided by GO. This research underscores the potential of GO@ZIF-8/NH₂ as a promising adsorbent for effective and sustainable dye removal from wastewater, offering significant advancements in environmental remediation technologies.

5.2 Recommendations

In moving forward with this study, it is recommended to delve deeper into exploring additional parameters such as adsorbent dosage, temperature, and adsorbent ratio that may influence adsorption to improve the quality of the adsorption test. Hopefully, this current work will encourage further experimental and theoretical studies in this area. It also would be interesting if molecular docking could be included in this study in the future. Furthermore, investigates the regeneration and reusability techniques for long-term performance and economic viability can be considered in terms of scalability, economic feasibility, and environmental impact. This deeper exploration is essential to ensure that findings can be applied effectively in large-scale industries. It is

also significant to conduct a test in large-scale wastewater, as this step holds great promise for advancing sustainable wastewater management practices. Hence, the batch adsorption process using modified ZIF-8 with amino group and GO exhibited instant removal of MB dye, thereby presenting a promising potential for future applications in treating wastewater contaminated with synthetic dyes.

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APPENDICES

Table 2.5: The methyl blue dye removal using different adsorbents according to different published studies

Adsorbents	R^2	Adsorption capacity ($q_{\max}$) mg/g	Fitted adsorption isotherm and kinetic model	Removal efficiency (%)	References
ZIF-8		2500	Langmuir Pseudo Second Order	Not mentioned	(Feng et al., 2016)
Commercial ZIF-8		0.19	Not mentioned	95	(Cheng et al., 2020)
SA/PEI hydrogel		400	Langmuir Pseudo Second Order	99	(Godiya et al., 2020)
Magnetic mesoporous activated carbon (MMAC)		Not mentioned	Freundlich Not mentioned	82	(Azam et al., 2020)
Water stable D-camphorate-based MOFs with Co ions		671	Langmuir Pseudo Second Order	85	(Tsai & Wu, 2019)
Water-stable cationic Fe-based metal-organic framework, CPM-97-Fe		304	Freundlich Pseudo Second Order	75.3	(Tian et al., 2019)
Trimetallic Cu-Co-Ni nanoparticles (NPs) anchored to amino-modified MOF MIL-101(Fe)		Not mentioned	Not mentioned	99	(Chen et al., 2020)
Ground Nut Waste		4.00	Langmuir Pseudo Second Order	Not mentioned	(Etim, 2019)

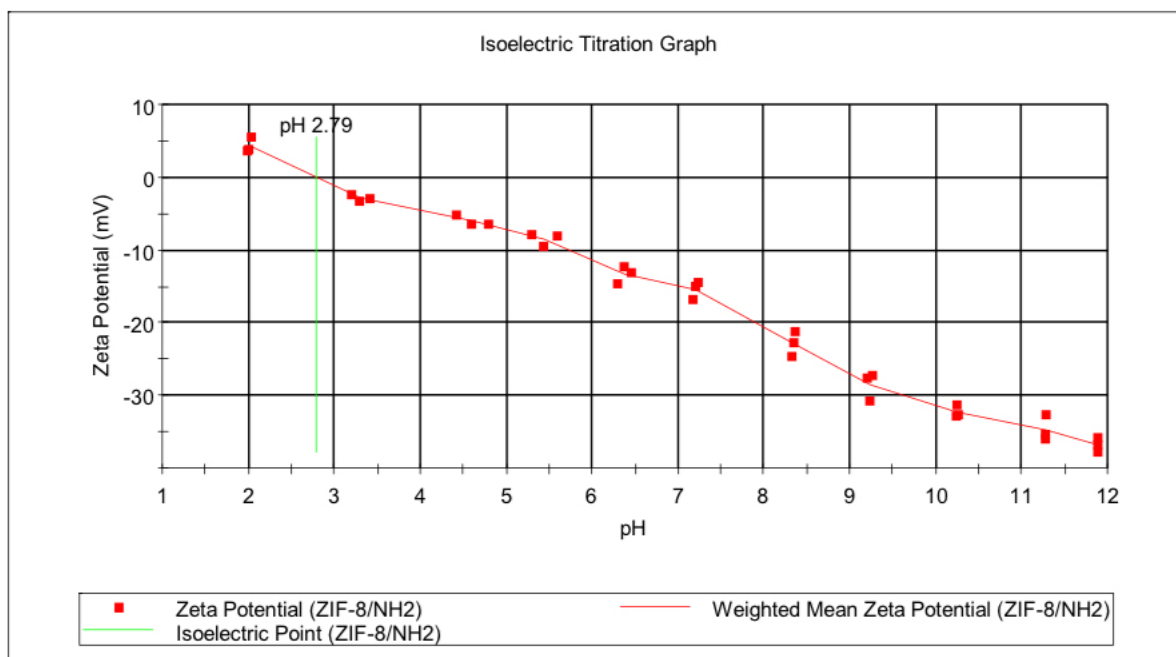


Figure 4.33: The isoelectric titration graph of ZIF-8/NH₂



Figure 4.34: The isoelectric titration graph of GO@ZIF-8/NH₂

Table 4.8: Data collected for adsorption of ZIF-8/NH₂ onto methyl blue

Initial Concentration (ppm)	Contact time	Removal Efficiency	Adsorption Capacity	Removal Efficiency	Adsorption Capacity	Ce	Ce/Qe	Ln Ce	Ln Qe	t/qt	log (qe-qt)
20	30	62.43	99.88	79.4	508.16	15.03	0.15048	2.71005	4.60397	0.05904	1.46657
40	60	76.25	244.00	80.58	515.72	19.00	0.07787	2.94444	5.49717	0.11634	1.33686
60	90	79.05	379.44	82.1	525.44	25.14	0.06626	3.22446	5.93870	0.17129	1.07918
80	120	83.98	537.44	82.01	524.84	25.64	0.04771	2.44154	6.28682	0.22864	1.10037
100	150	83.77	670.16	82.02	524.92	32.46	0.04844	3.48001	6.50752	0.28576	1.09760
	180			82.03	525.00					0.34286	1.09482

Table 4.9: Data collected for adsorption of GO@ZIF-8/NH₂ onto methyl blue

Initial Concentration (ppm)	Contact time	Removal Efficiency	Adsorption Capacity	Removal Efficiency	Ln Ce	Ln Qe	t/qt	log (qe-qt)
40	0	84.475	135.16		1.82616	4.90646	0.02156	1.44342
80	15	85.5	273.6		2.45101	5.61167	0.04203	0.99123
120	30	86.63333	415.84	89.225	2.77509	6.0303	0.06293	0.9284
160	45	87.4	559.36		3.0037	6.32679	0.08374	0.85248
200	60	90.45	723.6	89.88	2.94969	6.58424	0.10431	0.65896
	75	90.35833	867.44		3.14156	6.76555	0.12563	0.85733
	90			89.55			0.02156	1.44342
	120			89.55				
	150			89.5				

