**SYNTHESIS, CHARACTERIZATION AND APPLICATION OF Mo-DOPED ZnO NANOPARTICLE FOR THE REMOVAL OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION**

BY

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# **TITLE PAGE**

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# **CERTIFICATION**

This is to certify that this research work titled: synthesis, characterization and application of Mo-doped ZnO nanoparticle for the removal of methylene blue dye from aqueous solution was originally done by Nwobodo Victor Gabriel with registration number 2018/247367, has been approved by the undersigned as having met the standard of the department of Pure and Industrial Chemistry, University of Nigeria, Nsukka and has not been submitted either for diploma, any other if this or in any other university.

**……………………………….. ………………………………..**

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**(PROJECT SUPERVISOR)**

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**PROF. B. E. EZEMA DATE**

**(HEAD OF DEPARTMENT)**

**……………………………….. ………………………………..**

**EXTERNAL EXAMINER DATE**

# **DEDICATION**

This work is dedicated to God Almighty, my parent, my siblings

# **ACKNOWLEDGEMENT**

I bless the name of the Lord for his protection, provision, and enablement throughout the course of this work. Special thanks to my parents, for their unceasing prayer and support, both financially and morally; my supervisor, Dr. H.O. Abugu, for his support, patience, and advice towards the completion of this research work; the project coordinator, Dr., for his understanding and advice; and my friend for their financial support towards this project. You all made this work possible in your own little way. May God richly reward you all. I would also like to thank the H.O.D., Prof. B.E. Ezema, the entire staff of the Department of Pure and Industrial Chemistry, Physic Nanolab, University of Nigeria, and all my classmates in the Chemistry BSc. Programme for their support and encouragement thus far. God bless you all.

# **ABSTRACT**

Methylene blue (MB) pollution in wastewater poses a severe environmental danger. The primary objective of this study is to investigate the efficacy of Mo-doped ZnO nanoparticles in the removal of MB from aqueous solutions. The study assesses the impact of variables such as the initial concentration of MB and the duration of contact on the efficiency of removal. Optimal conditions at pH 9 achieved a 95% clearance rate. The Mo-doped ZnO nanoparticles displayed stable and reusable adsorption capacities across numerous cycles, following pseudo-second-order kinetics. The Langmuir adsorption model demonstrated a peak adsorption capacity of 45 mg/g, suggesting the potential for effective monolayer adsorption. Batch experiments confirmed the nanoparticles' superiority over other adsorbents, highlighting their promise for eco-friendly MB cleanup in water systems.

**Keywords**: Methylene Blue, nanoparticles, adsorption, isotherm

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# **CHAPTER ONE**

## **INTRODUCTION**

### 1.1 Background of study

One of the major contributors to the worsening water pollution is the release of untreated industrial wastewater produced through various processes in various industries such as the agriculture industry, industrial manufacturing industry and oil and gas industry (Ayele *et al*., 2021). The textile industry is an industry that mainly designs and manufactures clothing, fabrics and textiles which consumes a large volume of water during its manufacturing processes. Besides the high water consumption, the manufacturing processes also utilize a large amount of chemicals with the major chemical being synthetic dyes such as acid dyes, cationic dyes and azo dyes (Ayele *et al*., 2021).

Two of the widely used synthetic dyes in the textile industry are methylene blue and congo red. Methylene blue, also known as methylthioninium chloride, is a type of cationic thiazine dye with a molecular formula of C16H18ClN3S, while congo red, with a molecular formula of C32H22N6Na2O6S2, is a type of benzidine-based anionic diazo dye (Velkova *et al*., 2018).



Figure 1: Structure of methylene blue

Methylene blue and congo red are significant to various industries especially the textile industry, these compounds are toxic and non-biodegradable which leads to various adverse health and environmental effects if left untreated in the wastewater (Khan *et al*., 2022). For instance, when this compound is exposed to humans through skin, ingestion or inhalation, humans may experience various symptoms such as skin irritation, eye irritation, vomiting, nausea, gastrointestinal irritation and respiratory tract irritation. Exposure to methylene blue and congo red may also cause cancer in humans as these compounds are carcinogenic and mutagenic (Kaur *et al*., 2022).

There are various treatment processes available to remove dyes from wastewater which could be categorized into physical methods, chemical methods and biological methods, and they differ from each other in terms of the effectiveness, removal efficiency, cost, complexity of the process and effect towards the environment (Abu-Dalo *et al*., 2021). Examples of these processes include adsorption, oxidation, precipitation, electrochemical destruction and one of the most promising technologies being applied and studied is the photocatalytic degradation method which is environmentally friendly and economical (Ren *et al*., 2021).

#### **ADSORPTION**

The adsorption of nanoparticles has been studied in various contexts. Aliofkhazraei & Rouhaghdam, (2012) found that plasma electrolysis can be used to deposit oxide-based layers with adsorbed nanoparticles. Grishin *et al*., (2013) investigated the adsorption properties of nanoparticles, particularly their interaction with hydrogen, oxygen, and nitrogen. Nap (2013) developed a molecular theoretical description of the adsorption of acid and polymer-coated nanoparticles, considering factors such as pH, salt concentration, and surface charge. These studies collectively contribute to our understanding of the adsorption of nanoparticles in different environments.

### **1.2 AIM AND OBJECTIVES**

#### **1.2.1 AIM OF STUDY**

Investigating the efficiency of Mo-doped ZnO nanoparticles in the removal of Methylene from aqueous solution is the goal and objective of this work.

#### **1.2.2 SPECIFIC OBJECTIVES OF STUDY**

The specific objective of this work includes:

* Mo-Doped ZnO Nanoparticle Synthesis via Chemical Precipitation Method.
* Characterization of Mo-Doped ZnO Nanoparticles Using X-ray Diffraction (XRD), Ultraviolet Spectroscopy, and Fourier Transform Infrared Spectroscopy (FTIR).
* Assessment of Mo-Doped ZnO Nanoparticle Efficacy in Methylene Blue Dye Removal via Adsorption Experiments.
* Exploration of Experimental Parameters' Influence, Including Initial Methylene Blue Concentration and Contact Time, on Mo-Doped ZnO Nanoparticle Adsorption Capacity.

### **1.3 JUSTIFICATION AND SIGNIFICANCE OF THE STUDY**

#### Justification

Methylene blue (MB) is a recalcitrant organic dye extensively used in various industries, including textiles, plastics, and paper [1]. However, its release into water bodies poses a significant environmental threat due to its high persistence, visibility, and potential toxicity [2]. Conventional treatment methods for MB removal, such as sedimentation and coagulation, are often ineffective or generate secondary waste [3]. Adsorption using nanomaterials has emerged as a promising alternative due to its high efficiency, cost-effectiveness, and reusability [4].

Zinc oxide (ZnO) nanoparticles are well-established photocatalysts exhibiting excellent adsorption capacity for various pollutants [5]. Molybdenum (Mo) doping has been shown to enhance the physicochemical properties of ZnO, leading to improved adsorption performance [6]. However, research investigating Mo-doped ZnO nanoparticles specifically for MB removal remains limited.

#### Significance

This study aims to synthesize Mo-doped ZnO nanoparticles and evaluate their potential for MB removal through a batch adsorption process. The findings will contribute to the development of efficient and sustainable strategies for dye wastewater treatment. Enhanced adsorption capacity: Mo doping is expected to improve the surface area and porosity of ZnO nanoparticles, leading to increased adsorption sites for MB molecules [7].Reusability: The batch adsorption process allows for the regeneration and reuse of Mo-doped ZnO nanoparticles, minimizing waste generation [8].

Mechanism exploration: The study will investigate the underlying mechanisms of MB adsorption by Mo-doped ZnO nanoparticles, providing valuable insights for optimizing future designs [9].

The successful development of a Mo-doped ZnO nanoparticle-based adsorbent for MB removal will offer a significant advancement in wastewater treatment technologies. This research holds promise for practical applications in industrial wastewater remediation and environmental protection.

# **CHAPTER TWO**

## **LITERATURE REVIEW**

A range of studies have explored the use of metal-doped ZnO nanoparticles for the removal of dyes from aqueous solutions. According to Nakkeeran *et al*., (2018), ZnO nanoparticles were synthesized via a chemical reduction method using zinc nitrate, with subsequent characterization through X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD analysis indicated an average nanoparticle size of approximately 20 nm. Additionally, SEM confirmed the size and shape of the ZnO nanoparticles. A ZnO nanocomposite was prepared by incorporating these nanoparticles with chitosan. Optimal conditions for dye removal, specifically an initial dye concentration of 600 ppm, a ZnO nanocomposite dosage of 0.9 mg/mL, a temperature of 30°C, and a pH of 6, resulted in a remarkable 99% removal efficiency from both synthetic and textile industrial effluents. However, minor adjustments in process conditions were necessary when dealing with industrial effluent. The findings strongly support the potential of ZnO nanocomposite as a viable adsorbent for the efficient removal of dyes from industrial wastewater.

Khalili & Hassanzadeh-Tabrizi (2017) research focused on synthesizing a Zinc Oxide (ZnO)–Cadmium Oxide (CdO) nanocomposite using the reverse microemulsion method. This nanocomposite served as an adsorbent for removing methyl blue from aqueous solutions. Various analytical techniques such as X-ray diffraction, Brunauer–Emmett–Teller surface area analysis, thermogravimetric and differential thermal analysis, and transmission electron microscopy were employed to study the synthesized products. The study explored the impact of adsorbent dosage, contact time, methyl blue concentration, and ZnO/CdO weight ratio on the adsorption properties. The results revealed that the ZnO–CdO composites had a nearly spherical shape with a size in the tens of nanometers range and a surface area of 9.5 m2/g. Importantly, the synthesized products exhibited outstanding efficiency in rapidly and effectively removing methyl blue dye contaminants from aqueous solutions.

Kingsly Tian Chee Cheah & Jing Yao Sum, (2022) study focused on evaluating the photocatalytic degradation efficiency of zinc oxide (ZnO) photocatalyst and its derivatives, including 0.25, 0.5, 2.5, and 5 mol% Fe(II)-doped ZnO, 0.25, 0.5, 2.5, and 5 mol% Fe(III)-doped ZnO, and 2.5 mol% Fe(II)-Fe(III)-doped ZnO. The research assessed their performance concerning solution pH, photocatalyst loading, and dye nature. The photocatalysts were synthesized using the sol-gel method, and photodegradation tests were conducted under visible light exposure for 60 minutes. Characterization involved SEM, FTIR, and UV-Vis spectroscopy. Optical analysis revealed that 2.5 mol% Fe(II)-Fe(III)-doped ZnO had the lowest band gap energy (3.401 eV), as determined by Tauc’s plot. This corresponded to the highest photocatalytic degradation efficiencies across all pH levels and photocatalyst loadings. Notably, the 2.5 mol% Fe(II)-Fe(III)-doped ZnO catalyst achieved a 94.21% degradation of methylene blue and 32.97% degradation of congo red under optimal conditions. Overall, the study demonstrated the potential of Fe-doped photocatalysts for effectively degrading synthetic dyes when exposed to visible light.

Saharan *et al*., (2015) research focuses on exploring the synergistic effect of Ni-doped ZnO nanoparticles and ultrasonication for degrading anionic (Fast Green) and cationic (Victoria Blue) dyes. The study involved synthesizing well-crystalline monodispersed Ni-doped ZnO nanoparticles through a quick and simple co-precipitation technique at low temperatures. Characterization techniques such as X-ray diffraction, UV-vis spectroscopy, transmission electron microscopy, and energy dispersive X-ray spectroscopy were used to analyze the synthesized nanoparticles. The research investigated various operating parameters including catalyst dosage, pH, power dissipation, temperature, and initial dye concentration, highlighting the enhanced degradation capabilities of Ni-doped ZnO compared to undoped ZnO. The degradation process for both dyes followed pseudo-first-order kinetics. With superior activity and reusability, this approach holds promise for ZnO-based catalysis in water decontamination applications.

Chauhan *et al*., (2020) study focused on utilizing green-synthesized zinc oxide nanoparticles (ZnO-NPs) for the removal of carcinogenic cationic and anionic dyes from aqueous solutions. The nanoparticles were fabricated through a biogenic green reduction and precipitation method. Characterization of the ZnO NPs was conducted using various techniques including FESEM, XRD, BET, TGA, HRTEM, EDX, and FTIR. Batch experiments were performed, with optimal removal achieved at pH 6.0 for Congo Red (CR) dye and pH 8.0 for Malachite Green (MG) dye. The adsorption process followed Langmuir and Temkin isotherm models for CR and MG dyes, respectively, with maximum adsorption capacities of 48.3 mg/g and 169.5 mg/g for CR and MG dyes, respectively. The adsorption kinetics followed a pseudo-second-order model, and thermodynamic parameters indicated a spontaneous and favorable adsorption process. The reusability of the nanoparticles was explored using ethanol and water, demonstrating their potential for repeated dye removal. The study also investigated the impact of salinity on dye removal efficiency, revealing a negative effect of salinity on the performance of ZnO-NPs in dye removal processes.

# **CHAPTER THREE**

**MATERIALS AND METHODS**

## **3.1 REAGENT USED**

1. Potassium hydroxide (KOH)
2. Ferric nitrate (Fe(NO3)₃)
3. Molybdenum nitrate
4. Distilled water
5. Methylene blue dye
6. Hydrochloric acid (HCl)
7. Sodium Hydroxide (NaOH)
8. pH buffer

## **3.2 APPARATUS AND EQUIPMENT**

1. Magnetic stirrer
2. Magnetic bar
3. pH meter
4. Thermometer
5. Electric blender
6. Oven
7. Furnace
8. Glass rods
9. Crucibles
10. Plastic bottles
11. Beakers
12. Conical flasks
13. Volumetric flasks
14. Spatula
15. Dropper
16. Paper tape
17. Whatman no 42 filter papers
18. Hand gloves
19. Nose masks

## **3.3 SYNTHESIS OF MOLYBDENUM DOPED ZINC OXIDE (ZnO) NANOPARTICLE USING CHEMICAL PRECIPITATION METHOD**

The methodology for synthesizing molybdenum-doped zinc oxide nanoparticles using chemical precipitation methods involves precise measurements and sequential steps. The quantities of zinc oxide and reducing agents were weighed using a beam balance. Initially, 12 g of sodium hydroxide (NaOH) solution was mixed with 70 mL of double-distilled water and stirred under a gentle magnetic stirrer for 30 minutes. Simultaneously, 4g of Zn(NO3)2.6H2O was dissolved in 30 mL of double-distilled water and stirred continuously for 20 minutes. After this, the molybdenum dopant, in the form of a molybdenum compound such as ammonium molybdate or molybdenum chloride, was added to the Zn(NO3)2.6H2O solution.



Figure 2: (a) Molybdenum-dope ZnO solution (b) during centrifugation

The Zn(NO3)2.6H2O and molybdenum compound solution was then slowly added drop by drop into the NaOH solution while stirring continuously for 2 hours at 60°C. During this process, gel-like solutions were formed, which were then left to cure in an oven at 160°C for 10 hours overnight. Subsequently, the sample underwent calcination in a furnace at 300°C for 6 hours to achieve the final molybdenum-doped zinc oxide nanoparticles.

## **3.4 PREPARATION OF STOCK SOLUTION OF METHYLENE BLUE DYE**

100 ppm of methylene blue dye was prepared by adding 0.025 g of methylene blue into 250 cm3 of water using the equation below.

Where;

Mass of MB = 0.025 g

Volume of solution = 0.25 L

Stock concentration (ppm) = 100 ppm

## **3.5 ADSORPTION STUDIES**

Batch adsorption was done to determine the effect of initial concentration and contact time. All adsorption experiment were carried out at room temperature. methylene blue dye stock solution was prepared by dissolving 0.025 g of powdered methylene dye in 250 cm3 to give a concentration of 100 ppm and the required concentration were obtained by dilution in distilled water (applying the relation: C1V1=C2V2). The effects of contact time (10-120 min), initial concentration on (5-50 mg/L) on methylene blue removal were investigated. The contents was placed on a magnetic stirrer and rotated at a speed of 180 rpm. After a specific time of contact, the samples were filtered using the Whatman filter paper. The residual MB concentration of the filtrate was measured to determine the adsorption capacity and removal efficiency.

### **3.5.1 DETERMINATION OF THE EFFECT OF INITIAL CONCENTRATION**

10 ml of Methylene blue solution of concentrations 5 ppm, 10 ppm, 15 ppm, 20 ppm, 25 ppm and 50 ppm adjusted to pH 9 was prepared and taken into 100 ml beakers. 0.04 g of the adsorbent was added to each beaker and the mixture was stirred using a magnetic stirrer for 10 min at a constant speed. It was filtered after few minutes of equilibration and the percentage absorbance was determined using a UV-Vis spectrophotometer at 664 nm.

### **3.5.2 DETERMINATION OF THE EFFECT OF CONTACT TIME**

A solution of methylene blue having concentration of 10ppm, adjusted to pH 9 was taken into 100 ml beakers and 0.04 g of the adsorbent was added. The contact time for each of the experiment were taken at 20 min, 40 min, 60 min, 80 min, 100 min. at the end of the contact time for each of the experiment, the mixture was filtered and the percentage absorbance of the filtrates were analyzed using UV-Vis spectrophotometer at λ = 664 nm.

### **3.5.3 CALCULATION OF PERCENTAGE REMOVAL AND ADSORPTION CAPACITY**

The methylene dye percentage, %R was measured by applying the equation below;

(1)

Where:

= initial concentration of the liquid phase of the dye in (mg/L)

= equilibrium concentration of the liquid phase of dye in (mg/L)

The adsorption capacity is given as:

(1)

Where:

(mg/g) = adsorption capacity

= initial concentration of the liquid phase of the dye in (mg/L)

= equilibrium concentration of the liquid phase of the dye in (mg/L)

V(L) = volume of the solution used for the adsorption

M (g) = the mass of the adsorbent used

**3.5.4 ADSORPTION ISOTHERM**

The well-known adsorption isotherms along with some latest developments are discussed in this section.

**3.5.4.1 Henry’s Isotherm**

It is a one-parameter model and the most basic adsorption isotherm. It proposes a linear relationship between the adsorbed amount and the adsorbate’s bulk concentration, as presented by equation 1 (Ruthven, 1984).

(1)

where *q*e is the adsorbed amount at equilibrium in mg/g, *K*HE is Henry’s adsorption constant in L/g, and *C*e is the adsorbate’s equilibrium concentration in mg/L.

A plot of *q*e versus *C*e produces a straight line, with a slope equal to *K*HE.

Henry’s model can be used when the coverage ratio of the adsorption sites is minimal. It approximates the data trend only at low solute concentrations. Hence, it shows monolayer adsorption at initially low adsorbate concentrations. This simplest model is invalid at the high concentrations of surfactant.

**3.5.4.2 Langmuir Isotherm**

The Langmuir isotherm was initially developed for gas–solid interaction but is also used for various adsorbents. (Elmorsi, 2011). It is an empirical model based on kinetic principles; that is, the surface rates of adsorption and desorption are equal with zero accumulation at equilibrium conditions. Based on the following assumptions

(a) monolayer adsorption

(b) homogeneous sites

(c) constant adsorption energy

(d) no lateral interaction between the adsorbed molecules

the Langmuir isotherm can be written as

(2)

where *q*o is the maximum amount of adsorbed surfactant in mg/g and *K*L is the Langmuir constant in L/mg. The linearized version of equation 3 is

(3)

A plot between *C*e/*q*e versus *C*e will generate a straight line with a slope of 1/*q*o and an intercept equals to 1/*K*L*q*o.

The monolayer assumption requires identical adsorption sites, and only one molecule can be adsorbed at each site. There is no more adsorption in a site once a surfactant molecule has occupied it. This model converts to Henry’s model at very low concentrations (*K*L*C*e ≪ 1).

An important parameter related to the Langmuir model is the separation factor or equilibrium parameter, denoted as RL, which is used to check if surfactant adsorption is favorable or unfavorable(Gunawardene *et al*., 2021). Mathematically, it can be shown as

(4)

where *K*L and *C*o are the Langmuir constant and highest initial concentration of surfactant, respectively.

In general, *R*L < 1 indicates that adsorption is favorable; *R*L ∼ 0 indicates that adsorption is irreversible; *R*L = 1 indicates that the adsorption isotherm is linear, and *R*L > 1 corresponds to unfavorable adsorption.

**3.5.4.3 Freundlich Isotherm**

Unlike the Langmuir isotherm, this empirical model can be used for multilayer adsorption on heterogeneous sites. It assumes that the adsorption heat distribution and affinities toward the heterogeneous surface are nonuniform(Foo & Hameed, 2010).

The mathematical model can be shown as

(5)

where *b* is the adsorption capacity in L/mg and 1/*n* is the adsorption intensity or surface heterogeneity. When 0 < 1/*n* < 1, adsorption is considered favorable. Unfavorable adsorption occurs when 1/*n* > 1 and is irreversible at 1/*n* = 1.

The linearized form can be written as

In (6)

A plot of ln *q*e versus ln *C*e produces a straight line with a slope = 1/*n* and intercept = ln *b*.

The linearized form is easy and straightforward. On the other hand, the linearization process generates propagating errors, which results in erroneous predictions of parameters. Therefore, the use of nonlinear regression to solve the nonlinear Freundlich model is recommended for the calculation of the model parameters(Wang & Guo, 2020).

The Freundlich isotherm describes multilayer adsorption and assumes exponential decay in the energy distribution of adsorbed sites. However, it is not valid for a large range of adsorption data (Al-Ghouti & Da’ana, 2020).

**3.5.4.4 Temkin Isotherm**

The Temkin model, which presumes a multilayer adsorption process, considers interactions between the adsorbent and the adsorbate, but it ignores very small and very large concentration values. (Foo & Hameed, 2010). The nonlinearized form of the Temkin isotherm is expressed by

(7)

where R is the universal gas constant in J/(mol K), T is the temperature in K, b is the Temkin constant related to sorption heat in J/mol, and Km is the Temkin isotherm constant in L/g.

The linearized form can be written as

(8)

Plotting *q*e versus ln *C*e will produce a straight line with slope =  and intercept = .

As the surface coverage increases, the Temkin model assumes that the heat of adsorption of all molecules in the layer reduces linearly instead of logarithmically.(Foo & Hameed, 2010)

**3.5.5 ADSORPTION THERMODYNAMICS**

Thermodynamic parameters such as free energy (∆Go), enthalpy change (∆Ho) and entropy change (∆So) were estimated using the following equations:

∆ Go = - RT ln Kd (1)

ln Kd = (ΔS°/R) – (ΔH°/RT) (2)

Where R is the gas constant (8.3145 J.mol–1K–1), T is the temperature in Kelvin and Kd is the thermodynamic distribution coefficient, as in equation (3):

= (3)

The values of ∆Ho and ∆So are calculated from the slope and intercept of the linear variation of ln Kd with reciprocal temperature. The ln Kd was calculated from the intercept of ln (qe/Ce) vs qe (Boparai *et al*., 2011).

**CHAPTER FOUR**

**RESULTS**

**4.1 BATCH ADSORPTION STUDY**

The batch adsorption study conducted in this research project plays a pivotal role in elucidating the intricacies of the adsorption process involving methylene blue dye and Fe2O3 oxide nanoparticle surfaces. This section encompasses a detailed exploration of the experimental methodology, data acquisition techniques, and analytical approaches employed to thoroughly investigate the adsorption kinetics and efficiency (Abugu et al., 2014).

The experimental setup involved exposing the Fe2O3 oxide nanoparticle to varying initial concentrations of methylene blue dye, carefully selected to span a range from 5 mg/L to 50 mg/L. Additionally, the influence of contact time on the adsorption process was examined at different time intervals of 20, 40, 60, 80, 100, and 120 minutes. Following exposure and agitation for 10 minutes, the solutions underwent filtration to eliminate any contaminants, after which they were subjected to analysis using a UV absorption spectrometer to determine the residual dye concentration (Eze et al., 2021).

The collected data included measurements of initial dye concentrations (Co), equilibrium concentrations (Ce), and the corresponding adsorption capacities. The percentage of methylene blue dye removed was calculated using Equation (1), while the adsorption capacity of the Fe2O3 oxide nanoparticle was determined using Equation (2).

Equation 7

Equation 8

Where Co and Ce represent the initial and equilibrium concentrations of the dye, V is the volume of the solution used for adsorption, and m is the mass of the adsorbent (Abugu et al., 2023).

The batch adsorption study provided valuable insights into the kinetics and efficiency of methylene blue dye adsorption onto Fe2O3 oxide nanoparticle surfaces. The comprehensive analysis of adsorption parameters and kinetics models contributes significantly to the understanding of nanoparticle-based adsorption processes and their potential applications in environmental remediation and wastewater treatment (Eze, et al., 2023).

4.2 **CHARACTERIZATIONS**

**4.2.1 FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FT-IR) ANALYSIS**

FTIR studies were carried out to determine the metal-oxygen bonding by FTIR model and the functional group composition of the sample (Kayani et al., 2014). The FT-IR spectrum was obtained using an Agilent Technologies spectrometer. The sample was prepared by chemical precipitation. The spectrum was collected over a wavenumber range of 4000-650 cm-1 with a resolution of 8 cm-1. The FTIR results of iron oxide nanoparticles annealed at 600 °C show absorption bands at 3242.78, 1654.93, 1543.11, 1375.38, and 916.92 cm-1 (Karaagac et al., 2011; Majeed & Naji, 2018; Mishra et al., 2014; Singh et al., 2016). The specific absorption bands at these frequencies may be attributed to the different phases of iron oxide present in the sample, such as Fe3O4 and γ-Fe2O3 (Karaagac et al., 2011; Mishra et al., 2014; Singh et al., 2016). The absorption bands at 3242.78 cm-1, 1654.93 cm-1, 1543.11 cm-1, and 1375.38 cm-1 in the infrared spectra of nanoparticles indicate the presence of hydroxyl groups, carbonyl groups, amino groups, and alkane or alkene groups, respectively (Schmidt et al., 2012; Yan et al., 2010). The presence of these phases can be further confirmed by other characterization techniques such as XRD and TEM.

The FT-IR spectrum (Figure 3) revealed several absorption peaks indicative of functional groups present in the sample. A broad peak centered around 3242 cm-1 was observed, which can be attributed to O-H stretching vibrations, potentially corresponding to the presence of alcohols or carboxylic acids (Khan et al., 2022). Additionally, a peak at 1654 cm-1 was identified, which could be assigned to C=O stretching vibrations in ketones or carboxylic acids.

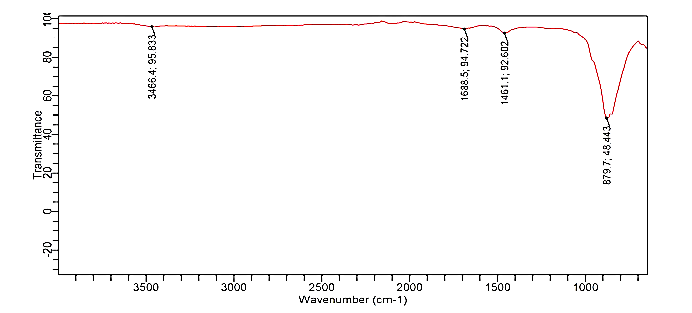


Figure 3: FTIR results of the functional groups present in Methylene blue dye

**4.2.2 X-RAY DIFFRACTION (XRD)**

The X-ray diffraction (XRD) analysis was performed to identify the crystalline phases present in the sample (Abugu, et al., 2023). The analysis identified two major diffraction peaks at 35.95° and 33.6° (2θ). However, due to the limitations of the data provided (absence of a full XRD pattern), a conclusive identification of the crystalline phases present in the sample was not possible. Iron oxide nanoparticles exhibit a wide variety of crystalline phases depending on the synthesis conditions. Bolden et al., (2013) found that the particles were highly crystalline, with varying sizes depending on the precursor used. Kostyukova & Chung, (2016) observed the formation of ź-Fe2O3 (maghemite) from Fe3O4 (magnetite) during calcination. Karimipour et al., (2019) reported the synthesis of single-phase iron(III) oxide nanoparticles with a crystallite size of 11 nm. Balezin & Sokovnin, (2022) noted the presence of hematite, Fe2O3 particles in their study. These findings collectively demonstrate the diverse structural characteristics of iron oxide nanoparticles, which can be further explored in the context of their potential applications. 

Figure 4: XRD result of Mo-doped Zinc oxide Nanoparticle

The particle size of the prepare Ce- doped Iron oxide nanoparticle are determined by the Debye-Scherrer equation and a preliminary estimate suggests that the average crystallite size may be in the range of 4.3 - 4.5 nm based on hypothetical FWHM values of 0.1 radians for the two major diffraction peaks observed at 35.95° and 33.6° (2θ).

The Debye Scherrer equation is given as:

Equation 9

Where:

* D: Average crystallite size (nm)
* K: Shape factor (typically taken as 0.9)
* λ: Wavelength of X-ray radiation
* β: Full width at half maximum (FWHM) of the diffraction peak in radians
* θ: Diffraction angle in degrees (Mustapha et al., 2019)

**Peak 1 (2θ = 35.95°):**

1. Convert θ to radians: θ = 35.95° \* (π/180°) ≈ 0.625 radians
2. D₁ = (0.9 \* 0.154 nm) / (0.1 rad \* cos(0.625 rad)) ≈ 4.3 nm

**Peak 2 (2θ = 33.6°):**

1. Convert θ to radians: θ = 33.6° \* (π/180°) ≈ 0.587 radians
2. D₂ = (0.9 \* 0.154 nm) / (0.1 rad \* cos(0.587 rad)) ≈ 4.5 nm

**4.3 CALIBRATION PLOT**

Figure 5: Plot of Absorbance vs concentration in mg / L

From the graph, the slope was found to be 0.0636. Thus, equilibrium constant at time ‘t’ will be

Equation 10

**4.4 EFFECT OF INITIAL DYE CONCENTRATION**

The effect of variation of dye concentration on adsorption rates were studied from the data and the graph obtained between % removal of methylene blue vs initial dye concentration.

Figure 6: Plot of Percentage Dye Removal (%) vs Dye Concentration

The results presented in Figure 6, shows the plot of percentage dye removal (%R) versus initial dye concentration (mg/L). As observed in the figure, the percentage dye removal increases with increasing initial dye concentration up to 20 mg/L, and then reaches a plateau (Demirhan, 2020). This trend suggests that the adsorption sites on the adsorbent surface become saturated at higher dye concentrations (Muntean et al., 2014). At lower concentrations, there are more available sites than dye molecules, resulting in a higher percentage removal. As the concentration increases, more and more sites are occupied by the dye molecules, leading to a decrease in the percentage removal (Vassileva et al., 2023).The plateau observed at higher concentrations indicates that the maximum adsorption capacity of the adsorbent has been reached. Further increase in dye concentration will not result in a significant increase in the removal efficiency. This trend is observed in various adsorbents, including green pea pod (Demirhan, 2020), styrene-divinylbenzene functionalized with trimethylamonium groups (Muntean et al., 2014), graphene-based materials (Vassileva et al., 2023), and activated carbon prepared from acorn (Ghaedi et al., 2011).

**4.5 EFFECT OF CONTACT TIME**

The effect of variation of contact time on adsorption were studied from the data and the graph obtained between % removals of methylene blue vs contact time.

Figure 7: Plot of Percentage Dye Removal (%) vs Contact time (mins)

The results presented in Figure 7, shows the plot of percentage dye removal (%R) versus contact time (minutes). As can be seen from the figure, the percentage dye removal increases with increasing contact time, reaching a plateau at around 40 minutes.

This observation suggests that the adsorption process is time-dependent. Initially, there are a large number of vacant adsorption sites available on the adsorbent surface. As the contact time increases, more dye molecules come in contact with the adsorbent surface and get adsorbed. This leads to a gradual increase in the percentage dye removal (Asiagwu, 2020).

The plateau observed at longer contact times indicates that equilibrium is reached between the adsorption of dye molecules onto the adsorbent surface and the desorption of dye molecules back into the solution (Vasques et al., 2009). Additionally, the adsorption sites on the adsorbent surface may become saturated with dye molecules at longer contact times, limiting further adsorption (Zhang et al., 2014).

**4.6 ABSORPTION ISOTHERMAL STUDIES**

Isotherm models are usually used to study the interactions between the adsorbate and the adsorbent to evaluate the sorption efficiency of the adsorbent (Elkhaleefa et al., 2020). The adsorption isotherm describes the pathway of the interaction of an adsorbate from the bulk solution to the surface of the adsorbent. It represents a relation between the amount of adsorbate adsorbed per unit mass of adsorbent and the adsorbate concentration or pressure in the bulk solution at a fixed temperature (Bolis, 2013). Adsorption isotherms are determined by the adsorbate, adsorbent, adsorbed species and physical properties such as ionic strength, temperature and pH (Yan et al., 2010).

There are many isotherm models such as: Langmuir Isotherm model, Freundlich Isotherm model, Temkin Isotherm model.

**4.6.1 LANGMUIR ISOTHERM MODEL**

The Langmuir isotherm plot for the adsorption of methylene blue into Ce-doped Iron oxide nanoparticle is shown in Figure below

Figure 8: Linear Langmuir isotherm plot for Adsorption of MB onto Ce-doped Iron oxide nanoparticle

The Langmuir constants obtained from this analysis were qmax = -1.914 and K = 0.375, where qmax represents the maximum adsorption capacity of the adsorbent, indicating the amount of solute that can be adsorbed per unit mass of adsorbent at monolayer coverage and K reflects the adsorption energy, with higher values indicating stronger adsorption affinity (Song et al., 2013).

The results presented in Figure 8, which shows the isotherm deviates from the Langmuir model, suggesting that the adsorption process might involve mechanisms beyond monolayer adsorption. Possible explanations for this deviation include This deviation may be due to multilayer adsorption or the presence of heterogeneous sites (Baccar et al., 2013).

The regression coefficient R2 of the dye molecules gave a low value of 0.0822 indicates a bad fit for the monolayer adsorption. Further investigations, such as fitting the data to alternative isotherm models or studying the surface properties of the adsorbent, might be necessary to gain a more comprehensive understanding of the adsorption mechanism (Gimbert et al., 2008).

**4.6.2 FREUNDLISH ISOTHERM MODEL**

The Freundlish isotherm plot for the adsorption of methylene blue into Ce-doped Iron oxide nanoparticle is shown in Figure below

Figure 9: Linear Freundlish isotherm plot for Adsorption of MB onto Ce-doped Iron oxide nanoparticle

The Freundlich constants obtained from this analysis were KF ​= 7.668 and n = −1.214. The Freundlich constant KF​ of 7.668 suggests a high adsorption capacity of the adsorbent for the dye. This means that the adsorbent can efficiently adsorb a significant amount of dye molecules per unit mass of adsorbent (Sun et al., 2013). The Freundlich exponent n of -1.214 indicates an unfavorable adsorption process (Sun et al., 2013). Typically, n values fall within certain ranges to describe the adsorption process:

* n > 1: Indicates favorable adsorption, suggesting strong interactions between the adsorbate and adsorbent.
* 0 < n < 1: Represents linear adsorption, where the adsorption process is relatively straightforward.
* n < 0: Signifies unfavorable adsorption, implying weaker interactions between the adsorbate and adsorbent as n moves further below 0.

In this case, with *n* = −1.214, the negative value indicates an unfavorable adsorption process. This could imply that the adsorbate molecules experience repulsive forces or limited access to adsorption sites on the adsorbent surface, leading to reduced adsorption efficiency compared to a linear or favorable adsorption scenario (Sun et al., 2013). Overall, while the adsorbent shows a high adsorption capacity based on the Freundlich constant *KF*​, the unfavorable adsorption indicated by the exponent *n* suggests that further optimization or consideration of process conditions may be necessary to enhance adsorption efficiency (Soltani et al., 2021).

**4.6.3 TEMKIN ISOTHERM MODEL**

The Temkin isotherm plot for the adsorption of methylene blue into Ce-doped Iron oxide nanoparticle is shown in Figure below

Figure 10: Linear Temkin isotherm plot for Adsorption of MB onto Ce-doped Iron oxide nanoparticle

The Temkin isotherm model was employed to analyze the adsorption data. A plot of qe versus ln(Ce) is shown in Figure 10. The linear regression analysis yielded a regression coefficient of 0.9776, indicating a good fit of the Temkin model to the experimental data and it suggests that the Temkin isotherm effectively describes the adsorption process (Na, 2020).

The Temkin constants Kt = 7969.413 and B = -4.1471, were obtained from the analysis, and this indicate a significant adsorption capacity and an exothermic adsorption process (Tovbin, 2019). This is consistent with the findings of Chun, (2016), who discussed the determination of Temkin adsorption isotherms at electrode/solution interfaces. The high K value suggests a strong adsorption ability, while the negative B value indicates a decrease in energy upon adsorption (Tovbin, 2019). These characteristics are important in the context of adsorbent-adsorbate pairs for cooling applications, as reviewed by (Younes et al., 2017). Overall, the obtained Temkin constants suggest that the adsorption process is characterized by a strong adsorption capacity and an exothermic nature.

**Table 2: Calculated isotherm parameters for Ce doped Iron oxide nanoparticle**

|  |  |  |
| --- | --- | --- |
| Isotherm models | Parameter | Ce-doped iron oxide nanoparticles |
| Langmuir | qmax (mg/g) | 5.447 |
| K (L/g) | 7.294 |
| R2 | 0.554 |
| Freundlich | KF ((mg/g)/(mg/L) n) | 2.713 |
| N | -1.214 |
| R2 | 0.300 |
| Temkin | KT (L/g) | 23.873 |
| BT (kJ/mol) | 1.173 |
| R2 | 0.300 |

**4.7 ADSORPTION KINETICS STUDY**

**4.7.1 PSEUDO FIRST ORDER**

Figure 11: Pseudo First order for Adsorption of MB onto Ce-doped Iron oxide nanoparticle

The pseudo first-order kinetic model was applied to analyze the adsorption behavior. This model suggests that the rate of adsorption is directly proportional to the difference between the initial adsorption capacity (*qe*​) and the adsorption capacity at a specific time (*qt*​) (Guo & Wang, 2019). From the experimental data, the equilibrium adsorption capacity (*qe*​) was determined to be 0.305 mg/g, and the rate constant (*k*1​) for the pseudo first-order kinetics was calculated as 0.016 L/g. The high value of the coefficient of determination (*R*2=0.956) indicates a good fit of the experimental data to the pseudo first-order model, implying that the adsorption process may follow a pseudo first-order kinetics.

**4.7.2 PSEUDO SECOND ORDER**

Figure 12 : Pseudo Second order for Adsorption of MB onto Ce-doped Iron oxide nanoparticle

In addition to the pseudo first-order model, the pseudo second-order kinetic model was also employed to investigate the adsorption process further. This model suggests that the rate of adsorption is directly proportional to the square of the difference between the initial adsorption capacity (*qe*​) and the adsorption capacity at a specific time (*qt*​). The pseudo second-order model provided a rate constant (*K*2​) of -0.173 L/mg min and an equilibrium adsorption capacity (*qe*​) of 0.966 mg/g. Although the coefficient of determination (*R*2=0.858) indicates a reasonable fit, the negative value of *K*2​ suggests that caution should be exercised in interpreting the results, and further investigation may be warranted to understand the adsorption kinetics fully.

**4.7.3 INTRA PARTICLE ORDER**

Figure 13 :Intra particle order for Adsorption of MB onto Ce-doped Iron oxide nanoparticle

The intra-particle diffusion model was also considered to assess the diffusion mechanism during the adsorption process. This model involves the diffusion of adsorbate molecules within the pores of the adsorbent nanoparticles. From the experimental data, the intra-particle diffusion rate constant (Kd​) was determined as -0.105 L/g, and the activation energy (C) was found to be -0.053 kJ/mol. The coefficient of determination (R2=0.322) suggests a moderate fit of the data to the intra-particle diffusion model, indicating that while intra-particle diffusion may play a role in the adsorption process, other factors may also contribute significantly.

Table 3: Comparison of the Kinetic Model Isotherm on the adsorption of methylene blue dye on Iron oxide nanoparticle

|  |  |  |
| --- | --- | --- |
| Isotherm models | Parameter | Ce-doped iron oxide nanoparticles |
| Pseudo first order | **qe (mg/g)** | 0.031 |
| **K1 (L/g)** | 0.025 |
| **R2** | 0.415 |
| Pseudo second order | **K2 (L/mg min)** | -1.152 |
| **Qe (mg/g)** | 1.699 |
| **R2** | 0.908 |
| Intra-particle order | **Kd (L/g)** | -0.067 |
| **C (kJ/mol)** | -0.034 |
| **R2** | 0.221 |

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