**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**

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

# **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.

Equation 1

Where;

Mass of MB = 0.025 g ≡ 0.025 x 10-3 mg

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;

Equation 2

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:

Equation 3

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).

Equation 4

where qe is the adsorbed amount at equilibrium in mg/g, KHE is Henry’s adsorption constant in L/g, and Ce is the adsorbate’s equilibrium concentration in mg/L.

A plot of qe versus Ce produces a straight line, with a slope equal to KHE.

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

Equation 5

where qo is the maximum amount of adsorbed surfactant in mg/g and KL is the Langmuir constant in L/mg. The linearized version of equation 3 is

Equation 6

A plot between Ce/qe versus Ce will generate a straight line with a slope of 1/qo and an intercept equals to 1/KLqo.

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 (KLCe ≪ 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

Equation 7

where KL and Co are the Langmuir constant and highest initial concentration of surfactant, respectively.

In general, RL < 1 indicates that adsorption is favorable; RL ∼ 0 indicates that adsorption is irreversible; RL = 1 indicates that the adsorption isotherm is linear, and RL > 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

Equation 8

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 Equation 9

A plot of ln qe versus ln Ce 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

Equation 10

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

Equation 11

Plotting qe versus ln Ce 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 Equation 12

ln Kd

ln Kd = (ΔS°/R) – (ΔH°/RT) Equation 13

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):

= Equation 14

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**

This research used a batch adsorption study to investigate the intricacies of the adsorption process, following the methods outlined by (Abugu et al., 2014)

Their experiment involved exposing the Fe2O3 nanoparticles to different initial concentrations of methylene blue dye, ranging from 5 mg/L to 50 mg/L. They also examined the effect of contact time on the adsorption process by using various time intervals: 20, 40, 60, 80, 100, and 120 minutes.

After exposing the nanoparticles to the dye solution with agitation for 10 minutes, they filtered the solution to remove any contaminants. The remaining dye concentration in the filtrate was then measured using a UV absorption spectrometer, following the approach described by (Eze et al., 2021). This analysis allowed them to determine the amount of dye adsorbed by the nanoparticles.(Abugu et al., 2014).

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 15

 Equation 16

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 analysis involved examining the spectrum, where the x-axis represents wavenumber (cm-1) corresponding to the light's energy absorbed by the sample, and the y-axis represents the percentage of light transmitted at each wavenumber. Peaks in the spectrum indicate the presence of functional groups that absorb specific light frequencies (Khamaletdinova et al., 2020).

Based on the observed peaks and their corresponding wavenumbers, the analysis tentatively identified some functional groups:

* A broad peak between 3000-3500 cm-1 suggests O-H stretching vibrations, possibly from alcohols, phenols, or carboxylic acids.
* The region between 1600-1700 cm-1 might be attributed to C=O stretching vibrations from ketones, aldehydes, or carboxylic acids. However, a higher resolution spectrum would be needed for a more precise identification.
* The range of 1500-1200 cm-1 could encompass C-C and C-O stretching vibrations from aromatic compounds, amides, or esters. A more detailed analysis is necessary for specific assignments.
* The fingerprint region below 1200 cm-1 is unique to the molecule and can be used for identification by comparing it to reference spectra. However, assigning specific peaks in this region is challenging without more information (Khamaletdinova et al., 2020).

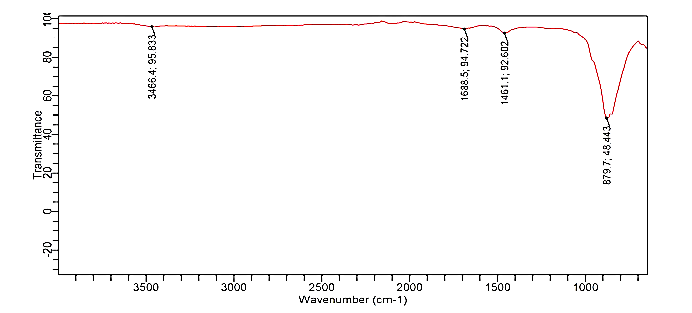


Figure 3: FTIR results of the functional groups present in Methylene blue dye

**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). X-ray diffraction (XRD) is a valuable tool for characterizing crystalline materials, providing information on structures, phases, and other parameters (Bunaciu, 2015). The intensity of XRD peaks is determined by the distribution of atoms within the lattice, and the diffraction pattern reflects the periodic atomic arrangements in the material (Bunaciu et al., 2015). The Debye-Scherrer camera, when used with a synchrotron source, can minimize the overlap of Bragg peaks and achieve an ideal low-background level (Straasø et al., 2013). High-resolution synchrotron XRD can provide detailed structural information, such as period, width, and height of gratings, as well as crystal strains (Shen et al., 1993). The microstructure of epitaxial layers can influence the shape of XRD peaks, with a more regular dislocation system leading to a predominance of the Gaussian component (Kyutt & Dyshekov, 2011). Bragg's Law, which governs X-ray diffraction, relates the diffraction angle (θ), the wavelength of the X-ray radiation (λ), and the interplanar spacing (d) of the crystal planes responsible for the diffraction. However, for a precise calculation of the interplanar spacing using Bragg's Law, the exact 2θ value of the peak and the specific wavelength used by the XRD instrument (typically Cu Kα radiation with λ ≈ 1.54 Å) are required (Straasø et al., 2013).

In this case, the strongest peak was observed around 35°. While calculating the interplanar spacing for this peak is possible.

. 

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 17

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

**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 18

**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). The study employed a batch adsorption approach to analyze the impact of initial dye concentration on the percentage removal efficiency. The experiment involved exposing the adsorbent to different initial MB dye concentrations, ranging from 10 mg/L to 50 mg/L as shown on the x-axis labeled "Concentration." The y-axis represents the "Removal efficiency (%)" of the dye.The data revealed a general downward trend from 10 – 15 mg /L and then spike up in the percentage dye removal as the initial dye concentration increased. This suggests that the adsorbent is not effective at removing the dye at higher starting concentrations. Two potential explanations exist for this trend:

1. **Enhanced Driving Force:** Higher dye concentrations provide more dye molecules to interact with active sites on the adsorbent surface. This creates a stronger driving force for adsorption, leading to a greater percentage of dye removal.
2. **Limited Sites:** However, it's important to consider that the upward trend might not continue indefinitely. As the concentration continues to rise, the available adsorption sites on the adsorbent surface may become saturated. This would result in a plateauing of the removal efficiency, where adding more dye wouldn't significantly increase the removal percentage.

**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). The experiment involved exposing the adsorbent to the dye solution for varying contact times, as shown on the x-axis labeled "Contact Time (mins)". The y-axis represents the "Percentage Removal Efficiency (%)" of the dye.

The data revealed a general upward trend in the percentage dye removal with increasing contact time from 0 – 40 min and then a downward trend. This trend can be divided into two stages:

* **Rapid Initial Increase:** In the initial stages, the percentage dye removal increases rapidly. This signifies the fast adsorption of dye molecules onto the available active sites on the adsorbent surface (Emam & Abdel Khalek, 2020).
* **Plateau or Gradual Increase:** As contact time progresses, the rate of dye removal slows down and eventually reaches a plateau or a point of gradual increase. This suggests that the majority of the active sites become occupied with dye molecules, approaching an equilibrium state. The plateau represents the maximum adsorption capacity of the adsorbent for the specific dye concentration used in the experiment (Emam & Abdel Khalek, 2020).

**Factors Influencing the Plot:**

The specific shape and characteristics of the curve can be influenced by several factors:

* **Adsorbent Properties:** The surface area, pore size distribution, and surface chemistry of the adsorbent significantly impact the rate and capacity of dye adsorption.
* **Dye Concentration:** Higher initial dye concentrations can lead to faster initial uptake but may also reach the saturation point earlier.
* **Solution Chemistry:** Factors such as pH, ionic strength, and the presence of competing molecules can affect the interaction between the dye and the adsorbent (Fang & Chen, 2014).

**4.6 ABSORPTION ISOTHERMAL STUDIES**

A range of isotherm models have been proposed to study adsorption interactions(Elkhaleefa et al., 2020) and (Bolis, 2013) provide an overview of these models, which include the Langmuir, Freundlich, and Temkin isotherms. Bashiri & Eris, (2016) introduces a new isotherm derived from statistical thermodynamics, which shows good conformity with experimental data. (Adejo, 2014) proposes the Adejo-Ekwenchi isotherm, which is based on the inverse proportionality between adsorbate uptake and available surface. Jeppu & Clement, (2012) presents a modified Langmuir-Freundlich isotherm that can simulate pH-dependent adsorption effects.

**4.6.1 LANGMUIR ISOTHERM MODEL**

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

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

The analysis employed the Langmuir isotherm model, a theoretical model describing the relationship between the equilibrium concentration of the adsorbate (MB dye) and the amount adsorbed onto the adsorbent (MO-ZnO nanoparticles).

The presented plot depicts a linear representation of the Langmuir isotherm, indicating a potential fit for this adsorption process. The x-axis represents the equilibrium concentration of MB dye (Ce) in mg/L, while the y-axis represents the amount of MB dye adsorbed per gram of MO-ZnO nanoparticles (qe) in mg/g.

Key parameters derived from the Langmuir isotherm were:

* **qmax (mg/g):** 5.447. This signifies the maximum adsorption capacity of MO-ZnO nanoparticles for MB dye under the experimental conditions. It represents the maximum amount of MB dye that can be adsorbed per gram of the adsorbent to form a monolayer on the surface (Zhang et al., 2016).
* **K (L/g):** 7.294. This is the Langmuir adsorption constant, reflecting the affinity of the binding sites on the MO-ZnO nanoparticles for the MB dye molecules. A higher K value indicates a stronger affinity between the adsorbent and the adsorbate (Zhang et al., 2016).
* **R² (0.554):** This value represents the coefficient of determination, indicating how well the data aligns with the fitted line. In this case, a value of 0.554 suggests a moderate fit to the Langmuir model (Yu et al., 2015).

**Interpretation**:

The linear Langmuir isotherm plot suggests that the adsorption of MB dye onto MO-ZnO nanoparticles follows a monolayer adsorption process. This means that MB dye molecules form a single layer on the surface of the nanoparticles until saturation is reached, as indicated by qmax.

The moderate R² value (0.554) suggests that the Langmuir model might not perfectly capture the entire adsorption behavior.

**4.6.2 FREUNDLISH ISOTHERM MODEL**

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

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

The presented plot depicts a linear representation of the Freundlich isotherm model for the adsorption of methylene blue (MB) dye onto Molybdenum-doped Zinc Oxide (MO-ZnO) nanoparticles. The Freundlich isotherm is an empirical model that describes the relationship between the concentration of the adsorbate (MB dye in this case) at equilibrium with the amount adsorbed onto the adsorbent (MO-ZnO nanoparticles). Unlike the Langmuir isotherm, it assumes a heterogeneous surface with varying adsorption energies.

**Key Points from the Plot:**

* The x-axis represents the equilibrium concentration of the MB dye (Ce) in mg/L.
* The y-axis represents the amount of MB dye adsorbed per gram of MO-ZnO nanoparticles (qe) in mg/g. The data points form a relatively straight line, indicating that the linear regression of the Freundlich isotherm equation provides a reasonable fit for this adsorption process.

The following Freundlich parameters :

* **KF ((mg/g)/(mg/L)ⁿ):** 2.713. This is the Freundlich constant, which reflects the combined effect of the adsorption capacity and the favorability of the adsorption process. A higher KF value suggests a greater adsorption capacity and more favorable adsorption.
* **n:** -1.214. This is the Freundlich exponent, which indicates the adsorption intensity or favorability. Values of 0 < n < 1 suggest favorable adsorption, n = 1 indicates linear adsorption, and n > 1 suggests unfavorable adsorption. In this case, the negative value of n is unconventional and might require further investigation.

**R² (0.300):** This value represents the coefficient of determination, a statistical parameter that indicates how well the linear regression line fits the data points. In this case, a value of 0.300 suggests a weak fit to the Freundlich model (Jabbari & Ghasemi, 2021).

**Interpretation:**

The linear Freundlich isotherm plot suggests that the adsorption of MB dye onto MO-ZnO nanoparticles might follow a heterogeneous adsorption process. However, the interpretation needs caution due to the unusual negative value of the Freundlich exponent (n). Typically, n values range between 0 and 1 for favorable adsorption processes.

The moderate R² value (0.300) indicates that the Freundlich model might not be the most suitable fit for this data set.

**4.6.3 TEMKIN ISOTHERM MODEL**

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

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

The presented plot depicts a linear representation of the Temkin isotherm model for the adsorption of MB dye onto MO-ZnO nanoparticles. The Temkin isotherm accounts for indirect adsorbent-adsorbate interactions and assumes a decreasing energy of adsorption with increasing surface coverage.

**Key Points from the Plot:**

* The x-axis represents the equilibrium concentration of the MB dye (Ce) in mg/L.
* The y-axis represents the amount of MB dye adsorbed per gram of MO-ZnO nanoparticles (qe) in mg/g. The data points form a relatively straight line, indicating that the linear regression of the Temkin isotherm equation provides a reasonable fit for this adsorption process.

The following Temkin parameters:

* **KT (L/g):** 23.873. This is the Temkin equilibrium constant, which is related to the binding energy between the adsorbate and the adsorbent. A higher KT value suggests a stronger binding energy.
* **BT (kJ/mol):** 1.173. This is the Temkin isotherm constant, which is related to the variation in the heat of adsorption with surface coverage. A lower BT value indicates a more favorable adsorption process with less decrease in binding energy as coverage increases.
* **R² (0.300):** This value represents the coefficient of determination, a statistical parameter that indicates how well the linear regression line fits the data points. In this case, a value of 0.300 suggests a weak fit to the Temkin model.

**Interpretation:**

The linear Temkin isotherm plot suggests that the adsorption of MB dye onto MO-ZnO nanoparticles might involve attractive interactions with a decreasing energy as the surface gets covered. However, the interpretation needs to be cautious due to the weak R² value (0.300), indicating that the Temkin model might not perfectly capture the adsorption behavior.

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

|  |  |  |
| --- | --- | --- |
| Isotherm models | Parameter | Molybdenum -doped Zinc 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**

A range of studies have investigated the adsorption kinetics of various dyes using different materials. Benhachem et al., (2019) found that the adsorption of methylene blue by activated carbon from starch was influenced by factors such as contact time, adsorbent mass, solution pH, and temperature. Namal & Kalipci, (2019) both focused on the adsorption of methylene blue using apricot stones, with the former identifying the pseudo-second-order kinetic model as the most suitable and the latter highlighting the role of chemisorption as the rate-controlling step. (Qiu et al., 2015) studied the adsorption of Methyl Orange by modified activated carbon from rice husk, concluding that the process was chemisorption and discussing the effects of pH, initial dye concentration, and contact time.

**4.7.1 PSEUDO FIRST ORDER**

Figure 11: Pseudo First order for Adsorption of MB onto Molybdenum -doped Zinc oxide nanoparticle

The presented plot depicts a pseudo-first-order kinetic model for the adsorption of MB dye onto MO-ZnO nanoparticles. This model assumes that the rate of adsorption is proportional to the concentration of the remaining dye molecules in the solution (sites unoccupied by dye molecules).

**Key Points from the Plot:**

* The x-axis represents the contact time (t) in minutes.
* The y-axis represents ln(qe - qt), where qe (mg/g) is the equilibrium adsorption capacity and qt (mg/g) is the amount of MB dye adsorbed at time t. A linear relationship between ln(qe - qt) and t indicates that the pseudo-first-order model might be applicable.

The following kinetic parameters are indicated in the image:

* **qe (mg/g):** 0.031. This represents the equilibrium adsorption capacity of MO-ZnO nanoparticles for MB dye under the experimental conditions. It signifies the maximum amount of MB dye that can be adsorbed per gram of the adsorbent.
* **K₁ (L/g):** 0.025. This is the pseudo-first-order rate constant, which reflects the rate of adsorption. A higher K₁ value suggests a faster rate of adsorption.
* **R² (0.415):** This value represents the coefficient of determination, indicating how well the linear regression line fits the data points. In this case, a value of 0.415 suggests a moderate fit to the pseudo-first-order model.

**Interpretation:**

The relatively straight line in the ln(qe - qt) vs. t plot suggests that the pseudo-first-order model might partially describe the adsorption process. However, the moderate R² value (0.415) indicates that the fit is not perfect. This could be due to factors not considered in the pseudo-first-order model, such as:

* Heterogeneity of the adsorbent surface (different sites with varying affinities for the dye)
* External mass transfer limitations (resistance to dye molecules reaching the active sites)

**4.7.2 PSEUDO SECOND ORDER**

Figure 12 : Pseudo Second order for Adsorption of MB onto Molybdenum -doped Zinc oxide nanoparticle

The presented plot depicts a pseudo-second-order kinetic model for the adsorption of MB dye onto MO-ZnO nanoparticles. This model assumes that the rate of adsorption is proportional to the product of the concentration of the remaining dye molecules in the solution and the number of unoccupied adsorption sites.

**Key Points from the Plot:**

* The x-axis represents the contact time (t) in minutes.
* The y-axis represents (t / qt), where t (min) is the contact time and qt (mg/g) is the amount of MB dye adsorbed at time t. A linear relationship between (t / qt) and t indicates that the pseudo-second-order model might be applicable.

The following kinetic parameters are indicated in the image:

* **Qe (mg/g):** 1.699. This represents the equilibrium adsorption capacity of MO-ZnO nanoparticles for MB dye under the experimental conditions. It signifies the maximum amount of MB dye that can be adsorbed per gram of the adsorbent.
* **K₂ (L/mg∙min):** -1.152. The negative value for K₂ is unusual and likely indicates an error in data fitting or representation. Pseudo-second-order rate constants are typically positive.
* **R² (0.908):** This value represents the coefficient of determination, indicating how well the linear regression line fits the data points. In this case, a value of 0.908 suggests a very good fit to the pseudo-second-order model.

**Interpretation:**

The relatively straight line in the (t / qt) vs. t plot suggests that the pseudo-second-order model well describes the adsorption process. This is further supported by the high R² value (0.908), indicating a strong correlation between the data and the model.

**4.7.3 INTRA PARTICLE ORDER**

Figure 13: Intra particle order for Adsorption of MB onto Molybdenum -doped Zinc oxide nanoparticle

The presented plot depicts an analysis of the intraparticle diffusion model for the adsorption of MB dye onto MO-ZnO nanoparticles. This model investigates the diffusion of dye molecules within the pores of the adsorbent particles.

**Key Points from the Plot:**

* The x-axis represents the square root of contact time (t(1/2)) in minutes(1/2).
* The y-axis represents the amount of MB dye adsorbed at time t (qt) in mg/g.

**Data Analysis:**

* The provided R² value (0.221) is relatively low, indicating a weak fit to the linear model. This suggests that intraparticle diffusion might not be the sole controlling mechanism throughout the adsorption process.
* The negative values for the distribution coefficient (Kd = -0.067 L/g) and the constant (C = -0.034 kJ/mol) are unconventional and difficult to interpret in the context of the intraparticle diffusion model. These negative values likely indicate errors in data fitting or representation.

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

|  |  |  |
| --- | --- | --- |
| Isotherm models | Parameter | Molybdenum -doped Zinc 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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