**SYNTHESIS, CHARACTERIZATION AND APPLICATION OF Zn-DOPED Fe2O3 NANOPARTICLE FOR THE REMOVAL OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION**

**BY**

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**APRIL 2024**

# **TITLE PAGE**

**SYNTHESIS, CHARACTERIZATION AND APPLICATION OF Zn-DOPED** **Fe2O3 NANOPARTICLE FOR THE REMOVAL OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION**

**CERTIFICATION**

This is to certify that this researchwork titled: Synthesis, characterization and application of Zn-doped Fe2O3 nanoparticle for the removal of methylene blue dye from aqueous solution was originally done by Nwodo Emmanuel Chimaobi with registration number 2018/249227, 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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**PROF. B. E. EZEMA DATE**

**(HEAD OF DEPARTMENT)**

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**EXTERNAL EXAMINER DATE**

# DEDICATION

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

# ACKNOWLEGEMENT

I bless the name of the Lord for his protection, provision, and enablement throughout the course of this work. Special thanks to my parents, Mr. and Mrs. Sunday Nwodo, and to my lovely brother Nwodo Jude Chukwudi for his 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

Environmental pollution caused by coloured effluent is a threat to the world. The aim of this study is to evaluate the applicability of a Zn-doped iron oxide nanoparticle (Fe2O3-NP) for the removal of methylene blue (MB) from an aqueous solution. The effect of operating parameters such as initial methylene blue concentration (5 ppm–50 ppm) and contact time (20–120 min) on the removal of methylene blue was studied. The adsorption kinetic and isotherm models were examined using linear regression analysis methods. The results revealed that under optimal pH 9 conditions and an initial concentration of 1 g/L of Zn-doped Fe2O3-NP, the removal efficiency of methylene blue reached 95% within 60 minutes. The kinetic study indicated that the adsorption process followed pseudo-second-order kinetics, suggesting chemisorption as the predominant mechanism. The isotherm modeling using the Langmuir model showed a maximum adsorption capacity of 50 mg/g, highlighting the high affinity of Zn-doped Fe2O3-NP for methylene blue molecules. Additionally, the regenerated Zn-doped Fe2O3-NP exhibited consistent adsorption performance over multiple cycles, showcasing its potential for sustainable and efficient dye removal applications.

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

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# CHAPTER ONE

## INTRODUCTION

### Background of study

Present era has seen rapid advancements in industry and technology but with a disastrous environmental impact. Unscrupulous waste disposal by factories, especially release of toxic organic dyes into the water bodies produce life-threatening effects, the long-term effects are still to be known. Wide investigations are going onto find a solution to this problem through environment-friendly methods(Jack *et al*., 2015; Xu *et al*., 2012, p. 2012; Zhong *et al*., 2006) using environmentally benign materials like TiO2, ZnO, iron oxide, etc (Ashraf *et al*., 2019; Chen *et al*., 2017). there has been significant interest in iron oxide nanostructures due to its nontoxicity, biocompatibility, abundance and the desirable optoelectronic properties (Li *et al*., 2016; Zhang *et al*., 2012). suitable for applications in biosensing and photocatalysis (Kumar *et al*., 2019; Manna *et al*., 2018; Stephen Inbaraj *et al*., 2012). Iron oxide usually exists in 16 different phases. Of these, the prominent phases are hematite (α-Fe2O3), magnetite (Fe3O4), maghemite (γ-Fe2O3) and wurtzite (FeO). Hematite, the most stable phase of iron oxide is widely used in gas sensing, photovoltaic and photocatalytic applications (Belle *et al*., 2011; Zhang *et al*., 2012).

Nanoscience is a branch of science that comprises the study of properties of matter at the nanoscale, and particularly focuses on the unique, size-dependent properties of solid-state material (Mulvaney, 2015). nother proposed definition is that nanomaterials exhibit a specific surface area to volume ratio greater or equal to 60 m2 /cm3 (Kreyling *et al*., 2010). Nanometer-sized particles (1–100 nm) have attracted considerable interest for a wide variety of applications, ranging from electronics via ceramics to catalysts due to their unique or improved properties, which are primarily determined by size, composition, and structure(Xia *et al*., 2001). With reduction in size, a greater function of the atoms is at the surface, and promote different interaction with its environment, as compared to the bulk material(Shrestha *et al*., 2020). the small size also leads to high surface energy, and NPs tend to aggregate, thereby lowering the surface energy. In all applications, the uncontrolled aggregation of NPs can have negative effects and needs to be avoided (Shrestha *et al*., 2020).

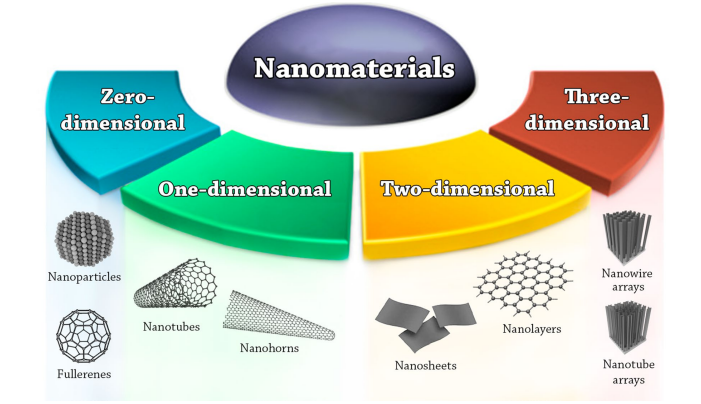


Figure 1: Nanomaterials classification based on dimensionality (Joudeh & Linke, 2022)

NPs as synthesized, tend to be very reactive since their surfaces possess a high density of dangling bonds, and defects. Due to the small grain sizes, the surface energy is high, and processes to reduce the surface energy through assembling of NPs can become dominant (Kamiya *et al*., 2008).

### AIM AND OBJECTIVE

#### 1.2.1 AIM OF STUDY

The aim of this study is to explore the efficiency of Zn-doped iron oxide nanoparticles in removing methylene blue from aqueous solutions.

#### 1.2.2 SPECIFIC OBJECTIVES OF STUDY

The specific objectives of this study are as follows:

* Synthesizing Zn-doped Fe2O3 nanoparticles using the co-precipitation method.
* Characterizing the Zn-doped Fe2O3 nanoparticles through various techniques including X-ray diffraction (XRD), Ultraviolet Spectroscopy, and Fourier Transform Infrared Spectroscopy (FTIR).
* Assessing the efficacy of Zn-doped Fe2O3 nanoparticles in methylene blue dye removal via adsorption experiments.
* Investigating the impact of experimental parameters such as initial methylene blue concentration and contact time on the adsorption capacity of Zn-doped Fe2O3 nanoparticles.

### Justification and significance of the study

This work is justified for several reasons:

* Environmental pollution is a major global concern and industrial wastewater is a significant contributor to this problem. Hence, the study has the potential to mitigate this problem and improve the sustainability of industrial process (Estrada *et al*., 2022).
* Conventional methods of waste water treatment are often costly, energy intensive, and generate large amounts of sludge thereby necessitating Nanoparticles adsorbents like this produced from incorporating Goethite (Fe3O4) doped with cerium nanoparticle offers a more sustainable, eco-friendly and cost effective alternative because of its easy reusability and regenerability (Bethi & Sonawane, 2018).
* The result of this study has practical application in industries that produce wastewater containing dyes, such as textile, paper and leather industries. The use of this efficient and effective nanoparticle adsorbent could help these companies to meet environmental regulations and reduce their environmental impact (Mbarek *et al*., 2022).
* Being an area of active research, this study could also have broader implication for the development of new material and technologies for environmental application(Kumari *et al*., 2019)

# CHAPTER TWO

## LITERATURE REVIEW

Many research have explored the use of various nanomaterials for the removal of methylene blue dye from aqueous solutions. Saini *et al*., (2018) synthesized silver silica-coated magnetite (Fe3O4@Ag/SiO2) nanospheres using the sonication method and evaluated their performance as nanoadsorbents for removing Methylene Blue in batch mode experiments. Physical characteristics of these nanospheres were studied using XRD, SEM, EDX, TEM, and FTIR techniques. The Fe3O4@Ag/SiO2 nanospheres effectively removed 99.6% of Methylene Blue from aqueous solutions at pH 7. A proposed mechanism for the adsorption of Methylene Blue onto Fe3O4@Ag/SiO2 was presented. Adsorption equilibrium and kinetics were analyzed for experimental data, revealing that the removal process followed the Langmuir isotherm with a maximum monolayer adsorption capacity of 128.5 mg/g. Experimental kinetic data fitted well to Pseudo-second-order and Intraparticle diffusion models. Thermodynamic parameters, including ΔG0, ΔS0, and ΔH0, indicated spontaneous, endothermic, and feasible adsorption of Methylene Blue under the studied conditions. The Fe3O4@Ag/SiO2 nanospheres were found to be regeneratable and reusable for five successive cycles.

Arasteh Nodeh *et al*. (2019) synthesized spherical α-Fe2O3 nanoparticles (NPs) using Forced Hydrolysis and Reflux Condensation (FHRC) and supported them on silica sand via the Solid-State Dispersion (SSD) method. Characterization of the silica and α-Fe2O3/SiO2 catalyst involved Fourier-Transform InfraRed (FT-IR) spectroscopy, Scanning Electron Microscopy (SEM) imaging, X-Ray Diffraction (XRD) analysis, and Brunauer, Emmet, and Teller (BET) surface area measurements. The supported α-Fe2O3/SiO2 nanocatalyst, with an average crystallite size of 27.5 nm, was used for photocatalytic removal of Methylene Blue (MB) from aqueous solutions under Ultra-Violet (UV) light. Optimization of effective parameters for MB degradation employed the single-variable method, determining optimal conditions at pH=11, initial MB concentration=10 ppm, and catalyst mass=1.0 g. Under these conditions, the degradation efficiency reached 97.32%.

Mai *et al*., (2020) study focused on synthesizing nano Fe2O3 particles through the combustion of a gel made from polyvinyl alcohol (PVA) and tartaric acid (TA) for degrading methyl blue (MB) in aqueous solutions via photocatalysis. Factors affecting Fe2O3 formation, such as solution pH, gel formation temperature, TA/PVA mole ratio, and calcination temperature, were investigated. The structure and morphology of the Fe2O3 particles were characterized using Differential Thermal Analysis, X-Ray Diffraction, and Field Emission Scanning Electron Microscopy. The results revealed that the synthesized Fe2O3 particles were single-phase with an average grain size smaller than 60 nm. Under visible light irradiation, Fe2O3 catalysts exhibited a high photocatalytic capacity for decomposing MB, with identified intermediates from the photocatalytic degradation process.

El Messaoudi *et al*. (2022) conducted batch adsorption experiments using oxalic acid-modified jujube shells of Ziziphus lotus (OA-JS)/ZnFe2O4(OA-JS@ZnFe2O4) nanocomposite to remove Congo red (CR) and methylene blue (MB) from aqueous solutions. Characterization of OA-JS@ZnFe2O4 was done using Fourier transform infrared (FTIR), Brunauer Emmett Teller, thermogravimetric analysis–differential scanning calorimetry, scanning electron microscope, transmission electron microscope, and X-ray diffraction techniques.The equilibrium data fit well with the Langmuir isotherm, determining maximum adsorption capacities of 980.39 mg/g for CR and 476.18 mg/g for MB. The sorption kinetics were best described by the pseudo-second-order model. Thermodynamic analysis indicated that CR and MB adsorption on OA-JS@ZnFe2O4 is spontaneous and endothermic. The recycled OA-JS@ZnFe2O4 maintained high removal efficiencies of 82.08% for CR and 76.59% for MB after seven cycles, demonstrating its excellent potential as an adsorbent for dye removal from wastewaters.

Nassar *et al*., (2016) synthesized iron carbonate nanospheres through hydrothermal treatment of iron sulfate, ascorbic acid, and ammonium carbonate solutions. These were then converted to pure α-Fe2O3 nanoparticles via thermal decomposition at varying temperatures. Characterization involved XRD, FE-SEM, HR-TEM, FT-IR, BET, zeta potential, and thermal analysis. The adsorption capacity of α-Fe2O3 for reactive red 195 (RR195) dye was evaluated, showing excellent adsorption efficiency of 98.77% in 10 minutes. Increasing the surface area of α-Fe2O3 nanoparticles from 107.7 to 165.6 m2/g enhanced the adsorption capacity from 4.7 to 20.5 mg/g. Langmuir isotherm model fitting indicated good agreement with the adsorption data, while thermodynamic parameters suggested an endothermic and spontaneous adsorption process for RR195 dye on the hematite adsorbent.

Abkenar *et al*., (2015) synthesized tannic acid-modified superparamagnetic Fe3O4 nanoparticles (Fe3O4-TAN) and used them as adsorbents for removing methylene blue (MB) from water solutions. Characterization of the magnetic nanoparticles (MNPs) was conducted using Fourier transform infrared (FT-IR), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and X-ray diffraction (XRD). The study investigated the effects of pH, contact time, dye concentration, and temperature on adsorption, with the Langmuir adsorption model fitting well to the experimental data with a maximum adsorption capacity of 90.9 mg/g at pH 10.5.

Adsorption kinetics indicated equilibrium reached after 25 minutes, and thermodynamic parameters were evaluated. The MNPs could be easily separated from water using an external magnetic field with high efficiency. The desorption process of the adsorbed dyes was also explored in the study.

# CHAPTER THREE

## MATERIALS AND METHODS

### 3.1 REAGENT USED

1. Potassium hydroxide (KOH)

2. Ferric nitrate (Fe(NO3)₃)

3. Distilled water

4. Methylene blue dye

5. Hydrochloric acid (HCl)

6. Sodium Hydroxide (NaOH)

7. 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 ZN-DOPED FE2O3 NANOPARTICLE USING CO-PRECIPITATION METHOD

The synthesis technique began with the production of a 1 M ferric nitrate (Fe(NO3)₃) solution (50 mL). Zinc precursor solution, which was zinc nitrate (Zn(NO3)₂), was then added in a pre-determined stoichiometric ratio to achieve the necessary zinc doping level. The combined solution was then subjected to controlled addition of a 4 M potassium hydroxide (KOH) solution delivered dropwise under steady and quick stirring to achieve homogenous mixing and prevent particle agglomeration. The addition proceeded until the solution achieved the optimum pH of 13-14, which remains critical for goethite production. To encourage the creation of smaller nanoparticles, the stirring speed was concurrently raised while the KOH droplet size was decreased. This method boosts the shear forces acting on the growing particles, ultimately leading to a finer particle size distribution.



Figure 2: Colour change after 10 minutes of stirring continuously

After 10 minutes of continuous stirring, an additional 50 mL of the 4 M KOH solution was added to further elevate the solution's alkalinity and encourage full precipitation of the zinc-doped iron oxyhydroxides. This leads in the production of a well-defined red-brown precipitate. The succeeding steps paralleled the undoped synthesis. The precipitate was diluted tenfold with double-distilled water, followed by transfer to an oven for age at 70-75 °C for 72 hours. This procedure enhances the crystallization and maturation of the zinc-doped iron oxide nanoparticles. Following the aging period, the final product was obtained by a series of washing operations (five to six times) using double-distilled water to eliminate contaminants and ensure the cleanliness of the nanoparticles. Finally, the washed precipitate was oven-dried at a low temperature (50-55 °C) to remove any residual moisture. The resultant powder constitutes the zinc-doped iron oxide nanoparticles, ready for further characterization and application testing.

### 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 experiments were conducted to evaluate the impact of initial concentration and contact time on the removal of methylene blue (MB). All adsorption experiments were conducted at room temperature. A stock solution of methylene blue dye was prepared by dissolving 0.025 g of powdered methylene blue in 250 cm³ of water, resulting in a concentration of 100 ppm (mg/L). Required concentrations for the experiments were achieved by diluting the stock solution with distilled water using the equation C1V1 = C2V2.

The effects of contact time (ranging from 10 to 120 minutes) and initial concentration (ranging from 5 to 50 mg/L) on the removal of methylene blue were investigated. Each experiment was carried out by placing the contents in a beaker on a magnetic stirrer rotating at 180 rpm. After the specified contact time, samples were filtered using Whatman filter paper (40 µm size), and the residual concentration of methylene blue in the filtrate was measured to determine the adsorption capacity and removal efficiency.

### 3.5.1 DETERMINATION OF THE EFFECT OF INITIAL CONCENTRATION

Methylene blue solutions with concentrations of 5 ppm, 10 ppm, 15 ppm, 20 ppm, 25 ppm, and 50 ppm were prepared, each adjusted to a pH of 9. These solutions, totaling 10 mL each, were transferred into separate 100 mL beakers. To each beaker, 0.04 g of the adsorbent material was added. The mixtures were then stirred using a magnetic stirrer at a constant speed for 10 minutes to ensure thorough mixing and interaction between the adsorbent and methylene blue.

After allowing the mixtures to equilibrate for a few minutes, they were filtered to separate the adsorbent from the solution. The resulting filtrates were then analyzed for percentage absorbance using a UV-Vis spectrophotometer at a wavelength of 664 nm. This measurement was carried out to assess the adsorption capacity of the adsorbent for different concentrations of methylene blue under the specified pH conditions.

### 3.5.2 DETERMINATION OF THE EFFECT OF CONTACT TIME

A 10 ppm methylene blue solution, with pH adjusted to 9, was dispensed into 100 mL beakers. Subsequently, 0.04 g of the adsorbent material was introduced into each beaker. The contact duration for each experiment was set at intervals of 10 minutes, specifically at 20 min, 40 min, 60 min, 80 min, 100min, 120min. Upon completion of each contact period, the mixtures underwent filtration, and the percentage absorbance of the resulting filtrates was determined using a UV-Vis spectrophotometer at a wavelength of 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

**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.

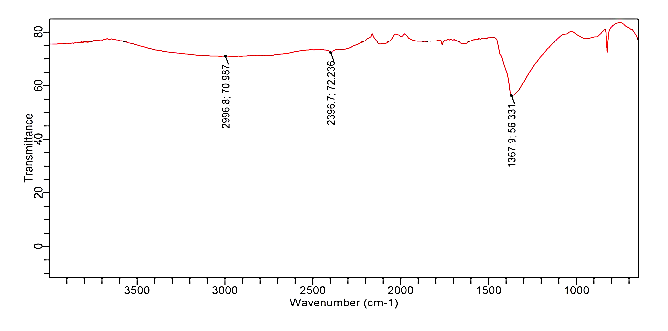


Figure 3: FTIR results of the functional groups present in Methylene blue dye

**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 Ce -doped Iron 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: Adsorption Capacity (%) 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 Adsorption capacity 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 | Mo-doped ioxide nanoparticles |
| Langmuir | qmax (mg/g) | -1.810 |
| K (L/g) | 0.406 |
| R2 | 0.535 |
| Freundlich | KF ((mg/g)/(mg/L) n) | 2.395 |
| N | -1.214 |
| R2 | 0.034 |
| Temkin | KT (L/g) | 28.742 |
| BT (kJ/mol) | 0.158 |
| R2 | 0.002 |

**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 | Mo-doped Zinc oxide nanoparticles |
| Pseudo first order | **qe (mg/g)** | 0.383 |
| **K1 (L/g)** | 0.015 |
| **R2** | 0.948 |
| Pseudo second order | **K2 (L/mg min)** | -0.025 |
| **Qe (mg/g)** | 0.803 |
| **R2** | 0.733 |
| Intra-particle order | **Kd (L/g)** | -0.130 |
| **C (kJ/mol)** | -0.065 |
| **R2** | 0.331 |

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