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

BY

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**UNIVERSITY OF NIGERIA, NSUKKA**

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# **TITLE PAGE**

**SYNTHESIS, CHARACTERIZATION AND APPLICATION OF CE-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 Ce-doped Fe2O3 nanoparticle for the removal of methylene blue dye from aqueous solution was originally done by Okoye Emmanuel Obiajulu with registration number 2019/241188, 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)**

**……………………………….. ………………………………..**

**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, Mr. and Mrs. Christopter Okoye, 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) is a hazardous chemical that is widely found in wastewater, and its removal is critical. Environmental pollution caused by this dye effluent is a threat to the world. This study investigates the use of a Zn-doped iron oxide nanoparticle (Fe2O3-NP) for the removal of methylene blue (MB) from an aqueous solution. This study examined the effects of initial methylene blue concentration and contact time on the removal efficiency. The results showed that under optimal conditions of pH 9, the removal efficiency reached 95%. The synthesized Ce-doped iron oxide nanoparticles exhibited excellent stability and reusability in multiple adsorption-desorption cycles. The adsorption kinetics followed pseudo-second-order kinetics, suggesting a chemisorption mechanism. The Langmuir adsorption isotherm model fitted well with the experimental data, indicating monolayer adsorption with a maximum adsorption capacity of 45 mg/g. The application potential of Ce-doped iron oxide nanoparticles for methylene blue removal was demonstrated through batch adsorption studies and comparison with other adsorbents. The findings suggest that Ce-doped iron oxide nanoparticles hold promise as efficient and eco-friendly adsorbents for the remediation of methylene blue-contaminated water systems.

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

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# **LIST OF ABBREVIATION**

MB

Graphene oxide (GO)

# **CHAPTER ONE**

## **INTRODUCTION**

### **1.1 BACKGROUND OF STUDY**

Dyes are considered one of the most problematic groups of pollutants because they can be easily identified by human eyes once they are released into water bodies but are not easily removed (Mogharabi *et al*., 2012). However, most synthetic dyes are non-degradable even with sunlight (Mogharabi *et al*., 2012). Recently, there has been an increase in public awareness and concern regarding environmental pollution. Most organic chemicals and pathogens that are present in aqueous waste effluents discharged from industrial or domestic sources should essentially be treated or removed prior to the final discharge to the watercourse. Hence, promising treatment techniques are required to overcome such a challenge for safe disposal. Oxidation of such dyes from aqueous industrial discharges is considered a difficult technique since dyes show resistance to various oxidants, chemicals, UV light, and heat besides being non-biodegradable (Gupta *et al*., 2011; Kargi & Ozmıhc, 2004; Saleh & Gupta, 2012; Tony *et al*., 2011)

Conventionally, various techniques were applied for wastewater treatment, such as coagulation, reverse osmosis, biological treatment techniques, and adsorption methods (Ashour *et al*., 2014; Tony *et al*., 2018), waters, which include photodecomposition (Kapdan & Kargi, 2002; Mulugeta & Belisti, 2014), electrolysis (Qingdong *et al*., 2017), adsorption (Ahmadi, Rahdar, *et al*., 2019; Ahmadi & Kord Mostafapoor, 2017), oxidation (Ahmadi *et al*., 2018; Ahmadi, Igwegbe, *et al*., 2019) and other processes. However, those methods are not widely recommended as they are expensive, transferring the pollutants phase, or they are not effective with high organic loads (Rahman *et al*., 2009; Tony & Mansour, 2019). Among the different physical and chemical processes, adsorption is an effective technique that is successfully used for the removal of colours from wastewaters (Elnasri *et al*., 2013; Rahdar, Samani, *et al*., 2018). The adsorption method is widely used due to its simplicity, low cost, and removal of color and other pollutants with great efficiency (Samadi *et al*., 2013). Adsorption can be either physisorption (which involves fairly weak intermolecular forces) or chemisorption (which involves basically the formation of a chemical bond between the sorbent molecule and the surface of the adsorbent) (Karine, 2001). Activated carbons have been used successfully to remove organic and mineral pollutants (Han *et al*., 2006; Igwegbe *et al*., 2015) but they are hardly regenerated (Ahmadi & Kord Mostafapour, 2017). Nanoparticles are referred to as particles with a diameter of less than 100 nm (Igwegbe *et al*., 2018). Nanoparticles have been revealed to have a high potential for adsorbing organic compounds, especially colours, from wastewater and sewage tanks due to their higher surface to volume ratio than other adsorbents (Rahdar, Igwegbe, *et al*., 2018).

#### **1.1.1 METHYLENE BLUE**

Methylene blue (MB) is a heterocyclic basic dye with a molecular weight of 373.9 g/mol and a maximum wavelength of 665 nm (Nyankson *et al*., 2019).



Figure 1. Chemical structure of methylene blue

MB is recognized as a popular cationic dye utilized in a variety of sectors, including the pharmaceutical, food processing, paper, paint, printing, dyeing, and medicine (i.e., diagnostic and therapeutic medicine for both humans and animals) industries (Khan *et al*., 2022). In the textile industry, MB adheres well to cotton fibers' interstitial gaps and remains stable on fabric. Hence, MB is one of the most used apparel colours.

Methylene blue dye-containing effluents from various industries, such as textile, rubber, plastic, and papermaking, are established to be carinogenic and also create toxic effects on living organisms (Kumar *et al*., 2014). Methylene blue is a cation colour with a complex aromatic structure that is used for colouring cotton and silk (Srivastava, 2008). This compound can cause impaired respiration. Further, direct exposure to it causes permanent damage to human and animal eyes; it also causes local burns, nausea and vomiting, mental disorders, and hemoglobinemia (Mulugeta & Belisti, 2014; Rafatullah *et al*., 2010). These organic dyes are released into water streams by the textile, food, printing, etc. industries. The dye-polluted water is harmful for aquatic life and is carcinogenic to human beings (Phuruangrat *et al*., 2018).

However, because MB is poisonous, carcinogenic, and non-biodegradable, it may create a variety of environmental hazards for both aquatic and terrestrial life. The danger of MB can also damage human health in a variety of ways, including respiratory discomfort, metal poisoning, stomach pain, blindness, and digestive issues. Furthermore, MB poisoning causes nausea, diarrhoea, vomiting, cyanosis, and other symptoms (Al-Tohamy *et al*., 2022)

In the present work, cerium-doped Fe2O3 nanoparticles with different concentrations were prepared with the co-precipitation method. Structural and adsorbent properties were studied for the prepared particles. Then cerium-doped Fe2O3 nanoparticles were efficiently used to adsorbed organic dye Methylene blue.

#### **1.1.2 ADSORPTION**

Adsorption is a phenomenon that describes the interaction between two different phases that forms an interface layer by transferring a molecule from a fluid bulk (liquid or gas) to a solid surface, so it is classified as a surface process (Alaqarbeh, 2021). The mechanisms of adsorption process occurred by adhesion of material either gaseous, liquid, or solid called substrate on the surface of solid or liquid, called sorbent or adsorbent (Dąbrowski, 2001). There are different adsorption systems: liquid-gas or liquid-liquid. If a liquid material is an adsorbent, then the interfacial layer is called film, micelle, or emulsion. The other system is solid-liquid or solid-gas; the adsorbent is a solid material, so the approved mechanism for the adsorption process is the interfacial layer model (Alaqarbeh, 2021).

### **1.2 AIM AND OBJECTIVES**

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

The aim and objective of this work is to investigate the effectiveness of Ce-doped Fe2O3 Nanoparticle on the removal of Methylene from aqueous solution.

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

The specific objective of this work includes:

* Synthesis of Ce-doped Fe2O3 nanoparticle by Co-precipitation method.
* Characterization of Ce-doped Fe2O3nanoparticle by various technique such as X-ray diffraction (XRD), Ultra Violet Spectroscopy and Fourier Transform infrared Spectroscopy (FTIR).
* Evaluate the effectiveness of Ce-doped Fe2O3 nanoparticles in removing methylene blue dye through adsorption experiments.
* Investigate the influence of experimental parameters such as initial methylene blue concentration and contact time on the adsorption capacity of the Ce-doped Fe2O3nanoparticles.

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

This work is justified for several reasons:

* Environmental contamination is a huge global concern and industrial wastewater is a substantial contributor to this problem. Hence, the study has the potential to minimize this problem and increase the sustainability of industrial process (Estrada *et al*., 2022).
* Conventional techniques of waste water treatment are frequently costly, energy intensive, and generate enormous amounts of sludge hence necessitating Nanoparticles adsorbents like this created from combining Goethite (Fe3O4) doped with cerium nanoparticle offers a more sustainable, eco-friendly and cost effective option because of its simple reusability and regenerability (Bethi & Sonawane, 2018).
* The conclusion of this study has practical use in industries that create wastewater containing dyes, such as textile, paper and leather industries. The implementation of this efficient and effective nanoparticle adsorbent could allow these companies to comply environmental laws and lessen their environmental impact (Mbarek *et al*., 2022).
* Being an area of ongoing research, this study could also have larger impact for the development of novel material and technologies for environmental application (Kumari *et al*., 2019)

# **CHAPTER TWO**

## **LITERATURE REVIEW**

A range of studies have explored the use of different types of Fe2O3 based nanoparticles for the removal of methylene blue from aqueous solutions. Thanh Huyen *et al* (2019) reported on the production and characterization of Fe3O4-reduced graphene oxide composite using the hydrothermal technique, focusing on its catalytic efficacy in eliminating methylene blue (MB) from aqueous solutions. The study pointed out the composite's important features, such as its high removal efficiency and appealing catalytic properties, making it a good starting point for making graphene-based materials in the future. Graphene oxide (GO) was effectively generated from graphite using a modified Hummer's process, resulting in homogeneous particle sizes ranging from 1 to 4 μm. Furthermore, the study investigated the synthesis of rGO-PP and mGO-PP composites using a facile hydrothermal technique, followed by their application in MB removal from aqueous solutions. Notably, under optimal conditions, the mGO-PP composite demonstrated a significant MB removal effectiveness of 65%, surpassing that of PP, GO-PP, and rGO-PP composite materials. This finding emphasises the potential of the mGO-PP composite for effective colour removal, hence contributing to the diversification of materials used in water treatment applications.

Malatji *et al*. (2021) wrote about new research that uses biopolymer-based hydrogel nanocomposites to remove methylene blue (MB) from water-based solutions. The adsorption method, renowned for its advantages such as low cost and ease of design, was identified as the most promising treatment option for MB dye removal. The article delves into the basic concepts of the adsorption process, reviews popular adsorbent materials used, and explains the benefits of this strategy.

Lima *et al*. (2017) offered an overview of the fundamental features of Fe3O4@C core-shell nanoparticles, highlighting their manufacturing methods and prospective uses as adsorbents. These nanoparticles are utilised in environmental remediation to address water pollution concerns and protect human health from different dangerous compounds, including colours, medicines, oils, and heavy metals. Their prominent qualities include a high adsorption capacity and facile separation due to their magnetic properties, making them a viable material for wastewater treatment applications.

Wu *et al*., (2016) conducted a work where magnetic Fe3O4 C nanocomposites, having a well-defined core shell structure, were synthesized by a simple solvothermal procedure employing ferrocene as both the iron and carbon source in the presence of hydrogen peroxide (H2O2). These Fe3O4@C nanocomposites were then utilised as adsorbent materials for extracting methylene blue (MB) from aqueous solutions. Various experimental factors, including contact time, solution acidity, and beginning MB concentration, were rigorously studied. The data demonstrated that MB's equilibrium absorption is dependent on both the initial MB concentration and the acidity of the solution. The MB adsorption kinetics followed a pseudo-second-order reaction model, showing a significant impact of chemical interactions throughout the adsorption process. Importantly, the produced Fe3O4 C nanocomposites demonstrated good reusability and could be easily removed from the adsorption system after trapping MB. Overall, the results revealed that the produced Fe3O4@C composites have remarkable potential as effective adsorbents for eliminating dye contaminants from wastewater, owing to their well-defined structure, magnetic properties aiding separation, and robust adsorption capabilities.

Tran *et al*., (2017) examined the potential of a chitosan/Fe3O4/graphene oxide (CS/Fe3O4/GO) nanocomposite for effectively eliminating methylene blue (MB), a cationic dye, from aqueous solutions. The procedure involved the initial preparation of graphene oxide (GO) from graphite derived from pencils using Hummer's method. Subsequently, the CS/Fe3O4/GO nanocomposite was made using a chemical co-precipitation approach utilizing a mixed solution containing GO, Fe3+, Fe2+, and chitosan. The produced CS/Fe3O4/GO nanocomposite underwent analysis using XRD, VSM, and SEM techniques to understand its structural and magnetic properties. Various parameters influencing dye removal were studied, and the equilibrium results for dye adsorption were well-fitted to the Langmuir isotherm, revealing monolayer adsorption behavior rather than multilayer adsorption predicted by the Freundlich isotherm. The maximal monolayer capacity (qmax) derived from the Langmuir isotherm was computed as 30.10 mg. The study found that the CS/Fe3O4/GO nanocomposite shows promise as a cost-effective and efficient adsorbent for removing cationic dyes from aqueous solutions, underlining its potential for practical applications in wastewater treatment.

Xiang *et al*. (2021) conducted research on the synthesis and application of Fe3O4@C nanoparticles for the decolorization of high concentrations of methylene blue (MB). The nanoparticles were produced using an in situ, solid-phase reaction utilizing FeSO4, FeS2, and PVP K30 without any precursor components. The study indicated that the Fe3O4@C nanoparticles had a maximum adsorption capacity of 18.52 mg/g for MB and that the adsorption process was exothermic. Furthermore, the research studied the use of H2O2 as an initiator for a Fenton-like reaction to boost MB removal efficiency. The results showed that the Fe3O4@C nanoparticles obtained roughly 99% removal efficiency for 100 mg/L MB, whereas pure Fe3O4 nanoparticles only achieved around 34% removal. The study also explored the mechanism of H2O2 activation on Fe3O4@C nanoparticles and proposed probable degradation pathways for MB. Importantly, the Fe3O4@C nanoparticles exhibited excellent catalytic activity even after five usage cycles, showing their potential for repeated use. Overall, the research shows an easy process for manufacturing Fe3O4@C nanoparticles with outstanding catalytic reactivity, providing a possible avenue for industrial-scale synthesis of these nanoparticles for treating high concentrations of dyes in wastewater.

Abdelrahman *et al*. (2019) conducted research on the synthesis and application of Fe3O4@C nanoparticles for the decolorization of high concentrations of methylene blue (MB). The nanoparticles were produced using an in situ, solid-phase reaction utilising FeSO4, FeS2, and PVP K30 without any precursor components. The study indicated that the Fe3O4@C nanoparticles had a maximum adsorption capacity of 18.52 mg/g for MB and that the adsorption process was exothermic. Furthermore, the research studied the use of H2O2 as an initiator for a Fenton-like reaction to boost MB removal efficiency. The results showed that the Fe3O4@C nanoparticles obtained roughly 99% removal efficiency for 100 mg/L MB, whereas pure Fe3O4 nanoparticles only achieved around 34% removal. The study also explored the mechanism of H2O2 activation on Fe3O4@C nanoparticles and proposed probable degradation pathways for MB. Importantly, the fabrication of Fe2O3 (hematite) nanoparticles with different crystallite sizes (40-59 nm) generated from Egyptian insecticide cans via the burning process. The organic fuels employed in the synthesis were urea, glycine, L-alanine, and L-valine. The Fe2O3 nanoparticles received detailed analysis utilising multiple techniques including BET, PL, FT-IR, XRD, HR-TEM, FE-SEM, UV-Vis, and DTG. The work focuses on the photocatalytic degradation of crystal violet (CV) and methylene blue (MB) dyes in aqueous solutions under UV irradiation, facilitated by Fe2O3 nanoparticles in the presence of H2O2. Remarkably, the % degradation of 50 mL of either crystal violet or methylene blue dye (20 mg/L) using 0.1 g Fe2O3 in conjunction with H2O2 reached 100% within 30 or 40 minutes, respectively. The degradation processes were efficiently represented by the first-order kinetics. Furthermore, the Fe2O3 nanoparticles demonstrated consistent photocatalytic activity even after being reused three times, emphasising their stability and potential for practical applicationsd strong catalytic activity even after five usage cycles, indicating their potential for repeated use. Overall, the research shows an easy process for manufacturing Fe3O4@C nanoparticles with outstanding catalytic reactivity, providing a possible avenue for industrial-scale synthesis of these nanoparticles for treating high concentrations of dyes in wastewater.

Osorio-Aguilar *et al*., (2023) study focuses on the adsorption and photodegradation of organic dyes, utilising methylene blue (MB) as a model. It traces past and contemporary developments in research, stressing the environmental impact, removal, and degradation using nanomaterials. The report reveals China's superiority in research on dye photodegradation utilising carbon nanotubes. While these materials show potential in efficiently eliminating MB, safety considerations related byproducts and CNT handling demand study for responsible application in environmental cleanup. The study underlines the need for extensive risk evaluations and safety measures in nanomaterial fabrication and usage for water treatment.

Modi *et al*., (2022) review focuses on the degradation of methylene blue (MB) dyes using both pure and modified ZnO as photocatalysts. The addition of dopants or composites to ZnO enhances its efficiency in degrading dyes and other pollutants. ZnO cost-effectiveness and availability make it a preferred photocatalyst compared to others. Factors like pH, illumination, temperature, dopant concentration, catalyst dose, and dye concentration significantly influence the degradation efficiency. ZnO shows higher dye breakdown efficiency under sunlight, making it a promising candidate for future research and applications in pollutant degradation.

# **CHAPTER THREE**

**MATERIALS AND METHODS**

## **3.1 REAGENT USED**

1. Potassium hydroxide (KOH)
2. Ferric nitrate (Fe(NO3)₃)
3. Cerium nitrate (Ce(NO3)₃)
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 CERIUM DOPED IRON (FE2O3) NANOPARTICLE USING CO-PRECIPITATION METHOD**

The synthesis procedure commenced with the preparation of a 1 M ferric nitrate (Fe(NO3)₃) solution (50 mL). The cerium precursor solution, which was cerium nitrate (Ce(NO3)₃), was then added in a pre-determined stoichiometric ratio to achieve the desired cerium doping level. The combined solution was then subjected to controlled addition of a 4 M potassium hydroxide (KOH) solution, introduced dropwise under constant and rapid stirring to ensure homogeneous mixing and prevent particle aggregation. The addition continued until the solution reached the targeted pH of 13–14, which remains crucial for goethite formation. To promote the formation of smaller nanoparticles, the stirring speed was concurrently increased while the KOH droplet size was minimized. This approach enhances the shear forces acting on the growing particles, ultimately leading to a refined particle size distribution.



Figure 2: (a) separation after 20mins (b) grinding process of the Ce-doped Fe2O3-NPs after drying and annealing (c) synthesized Ce-doped Fe2O3-NPs

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 promote complete precipitation of the cerium-doped iron oxyhydroxides. As a result, a well-defined red-brown precipitate is formed. The subsequent steps mirrored the undoped synthesis. The precipitate was diluted tenfold with double-distilled water, followed by transfer to an oven for ageing at 70–75 °C for 72 hours. This step facilitates the crystallisation and maturation of the cerium-doped iron oxide nanoparticles. Following the aging period, the final product was obtained through a series of washing steps (five to six times) using double-distilled water to remove impurities and ensure the purity of the nanoparticles. Finally, the washed precipitate was oven-dried at a low temperature (50–55 °C) to remove any residual moisture. The resulting powder constitutes cerium-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 0.025g 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**

10ml 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 100ml beakers. 0.04g of the adsorbent was added to each beaker and the mixture was stirred using a magnetic stirrer for 10min at a constant speed. It was filtered after few minutes of equilibration and the percentage absorbance was determined using a UV-Vis spectrophotometer at 664nm.

### **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, 100min, 120min 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:

Equation 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 detailed understanding of the adsorption mechanism of this study can be gotten from the nature of the process of adsorption of the methylene blue dye upon the surface of Ce doped Fe2O3nanoparticles. In order to establish the nature and the strength of the adsorption process involved, data obtained from ultraviolent measurements was fitted to adsorption isotherms;

Table 1: Summary of Adsorption isotherm

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Adsorption isotherm | X axis | Y axis | Slope | Intercept | Summaxry | Reference |
| Henry | qe | Ce | KHE | No-intercept | the simplest adsorption isotherm; assumes a linear relationship between adsorbed amount and adsorbate bulk concentration | (Ruthven, 1984) |
| applicable for low solute concentrations |
| Langmuir | Ce/qe | Ce | 1/qo | 1/ K1q1 | monolayer adsorption | (Elmorsi, 2011) |
| homogeneous solid surfaces |
| Freundlich | ln qe | ln Ce | 1/n | ln b | applicable for multilayer adsorption | (Foo & Hameed, 2010) |
| suitable for heterogeneous surfaces |
| not valid for a large range of adsorption data |
| Temkin | qe | ln Ce |  |  | considers interaction between adsorbent and the adsorbate | (Foo & Hameed, 2010) |
| with increase in surface coverage, the heat of adsorption of all molecules in the layer is decreases linearly instead of logarithmically |

**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 Equation 4

ln Kd = (ΔS°/R) – (ΔH°/RT) Equation 5

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 6

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.

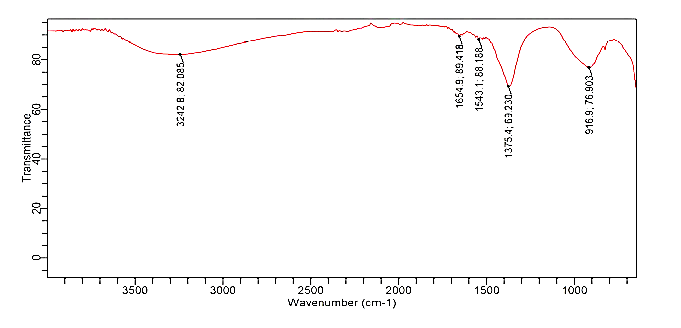


Figure 3: FTIR results of the functional groups present in Methylene blue dye

#### **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 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: Plot of 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: Comparison of the isotherm parameters for Ce doped Iron oxide nanoparticle

|  |  |  |
| --- | --- | --- |
| Isotherm models | Parameter | Ce-doped iron oxide nanoparticles |
| Langmuir | qmax (mg/g) | -1.914 |
| K (L/g) | 0.375 |
| R2 | 0.082 |
| Freundlich | KF ((mg/g)/(mg/L) n) | 7.669 |
| N | −1.214 |
| R2 | 0.814 |
| Temkin | KT (L/g) | 7969.413 |
| BT (kJ/mol) | -4.1471 |
| R2 | 0.9776 |

### **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)** | 0.294 |
| **K1 (L/g)** | 0.013 |
| **R2** | 0.557 |
| Pseudo second order | **K2 (L/mg min)** | -0.242 |
| **Qe (mg/g)** | 1.291 |
| **R2** | 0.950 |
| Intra-particle order | **Kd (L/g)** | -0.122 |
| **C (kJ/mol)** | -0.061 |
| **R2** | 0.515 |

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