**SYNTHESIS, CHARACTERIZATION AND APPLICATION OF CE-DOPED FE2O3 NANOPARTICLE FOR THE REMOVAL OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION**

BY

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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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**EXTERNAL EXAMINER DATE**

# **DEDICATION**

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

# **ACKNOWLEDGEMENT**

# **ABSTRACT**

Methylene blue (MB) is a hazardous chemical that is widely found in wastewater, and its removal is critical. One of the most common methods to remove MB is adsorption.

# **TABLE OF CONTENTS**

[**TITLE PAGE** 3](#_Toc163721451)

[**CERTIFICATION** 4](#_Toc163721452)

[**DEDICATION** 5](#_Toc163721453)

[**ACKNOWLEDGEMENT** 6](#_Toc163721454)

[**ABSTRACT** 7](#_Toc163721455)

[**TABLE OF CONTENTS** 8](#_Toc163721456)

[**LIST OF TABLES** 10](#_Toc163721457)

[**LIST OF FIGURES** 11](#_Toc163721458)

[**LIST OF ABBREVIATION** 12](#_Toc163721459)

[**CHAPTER ONE** 13](#_Toc163721460)

[**INTRODUCTION** 13](#_Toc163721461)

[**1.1** **BACKGROUND OF STUDY** 13](#_Toc163721462)

[**1.2** **AIM AND OBJECTIVES** 16](#_Toc163721463)

[**1.3** **JUSTIFICATION AND SIGNIFICANCE OF THE STUDY** 16](#_Toc163721464)

[**CHAPTER TWO** 18](#_Toc163721465)

[**LITERATURE REVIEW** 18](#_Toc163721466)

[**2.1** **ADSORPTION** 22](#_Toc163721467)

[**2.2**  **FACTOR AFFECTING ADSORPTION CAPACITY** 24](#_Toc163721468)

[**2.3** **ADSORPTION KINETIC MODEL** 26](#_Toc163721469)

[**2.4** **ADSORPTION ISOTHERM MODEL** 30](#_Toc163721470)

[**2.5** **ADSORPTION THERMODYNAMICS** 35](#_Toc163721471)

[**CHAPTER THREE** 36](#_Toc163721472)

[**3.1** **REAGENT USED** 36](#_Toc163721473)

[**3.2** **APPARATUS AND EQUIPMENT** 36](#_Toc163721474)

[**3.3** **SYNTHESIS OF CERIUM DOPED IRON (FE2O3) NANOPARTICLE USING CO-PRECIPITATION METHOD** 37](#_Toc163721475)

[**3.4** **CHARACTERIZATION AND ANALYSIS** 38](#_Toc163721476)

[**3.5** **ADSORPTION STUDIES** 39](#_Toc163721477)

[**3.5.1**  **DETERMINATION OF THE EFFECT OF INITIAL CONCENTRATION** 39](#_Toc163721478)

[**3.5.2** **DETERMINATION OF THE EFFECT OF CONTACT TIME** 39](#_Toc163721479)

[**3.5.3 CALCULATION OF PERCENTAGE REMOVAL AND ADSORPTION CAPACITY** 40](#_Toc163721480)

[**CHAPTER FOUR** 41](#_Toc163721481)

[**RESULTS AND DISCUSSION** 41](#_Toc163721482)

[**4.1** **SYNTHESIS OF IRON NANOPARTICE** 41](#_Toc163721483)

[4.2 **CHARACTERIZATIONS** 41](#_Toc163721484)

[**REFERENCES** 42](#_Toc163721485)

# **LIST OF TABLES**

# **LIST OF FIGURES**

# **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 the human eyes once they are released to the water bodies but are not easily removed. However, most synthetic dyes are properly 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, which 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 water courses. Hence, a promising treatment techniques is required to overcome such challenge for a safe disposal. Oxidation of such dyes from aqueous industrial discharges is considered a difficult technique since dyes show resistance to various oxidants, chemical, 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). Amongst the different physical and chemical processes, adsorption is an effective technique, which is successfully used for the removal of colors 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 in adsorbing organic compounds especially colors from wastewater and sewage tanks due to their high 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 the interstitial gaps of cotton fibers and remains stable on fabric. Hence, MB is one of the most used apparel colors.

Methylene blue dye-containing effluent from various industries such as textile, rubber, plastic, paper-making are established to be carinogenic and also create toxic effects on living organisms (P. S. Kumar et al., 2014). Methylene blue is a cation color with a complex aromatic structure, which 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 local burns, nausea and vomiting, mental disorders, and Methemoglobinemia (Mulugeta & Belisti, 2014; Rafatullah et al., 2010).

However, because MB is poisonous, carcinogenic, and non-biodegradable, it may create a variety of environmental hazards in 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, diarrhea, vomiting, cyanosis, and other symptoms (Al-Tohamy et al., 2022)

In the present work Cerium-doped Fe2O3 nanoparticles with different concentration were prepared with co-precipitation method. Structural and adsorbing properties were studied for the prepared particles. Then Cerium-doped Fe2O3 nanoparticle were efficiently used to adsorbed organic dye Methylene blue. These organic dyes are released in to water streams by textile, food, printing industries etc. The dye polluted water is harmful for aquatic life and is carcinogenic to human beings (Phuruangrat et al., 2018).

#### **1.1.2 ADSORPTION**

Adsorption is a phenomenon that describes the interaction between two different phases that forms an interface layer by transfer of 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, so the interfacial layer 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 adsorption process is 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 ZnO 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 Fe2O3 nanoparticle 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 Fe2O3 nanoparticles.

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

This work is justified for several reasons:

1. 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).
2. 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).
3. 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).
4. 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)

Overall, the study is justified and significant due to its potential in address a pressing environmental issue, develop more available, sustainable and cost effective water treatment options and contribute to the advancement of nanotechnology for environment applications.

# **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 synthesis and characterization of Fe3O4 reduced graphene oxide composite via the hydrothermal method, focusing on its catalytic efficacy in removing methylene blue (MB) from water solutions. The study highlighted the composite's notable attributes, including high removal efficiency and favorable catalytic properties, positioning it as a potential precursor for future graphene-based material production. Graphene oxide (GO) was successfully derived from graphite using a modified Hummer's method, resulting in uniform particle sizes ranging from 1 to 4 μm. Additionally, the study explored the synthesis of rGO-PP and mGO-PP composites through a straightforward hydrothermal approach, followed by their application in MB removal from aqueous solutions. Notably, under optimized conditions, the mGO-PP composite exhibited a significant MB removal efficiency of 65%, surpassing that of PP, GO-PP, and rGO-PP composite materials. This finding underscores the potential of mGO-PP composite for effective color removal, thereby contributing to the diversification of materials used in water treatment applications.

Malatji et al. (2021) reported on recent studies focused on the removal of methylene blue (MB) from aqueous solutions utilizing biopolymer-based hydrogel nanocomposites. The adsorption method, known for its advantages such as low cost and ease of design, was highlighted as the most promising treatment technique for MB dye removal. The work delved into the underlying principles of the adsorption method, discussed common adsorbent materials utilized, and outlined the advantages associated with this approach.

Lima et al. (2017) provided an overview of the fundamental properties of Fe3O4@C core-shell nanoparticles, highlighting their synthesis methods and potential applications as adsorbents. These nanoparticles are utilized in environmental remediation to address water pollution concerns and protect human health from various harmful substances, including dyes, pharmaceuticals, oils, and heavy metals. Their notable features include a high adsorption capacity and easy separation due to their magnetic properties, making them a promising material for wastewater treatment applications.

Wu et al., (2016) conducted a study where magnetic Fe3O4 C nanocomposites, featuring a well-defined core shell structure, were synthesized through a simple solvothermal process using ferrocene as both the iron and carbon source in the presence of hydrogen peroxide (H2O2). These Fe3O4@C nanocomposites were then applied as adsorbent materials for removing methylene blue (MB) from aqueous solutions. Various experimental parameters, including contact time, solution acidity, and initial MB concentration, were systematically investigated. The findings revealed that the equilibrium uptake of MB depended on both the initial MB concentration and the acidity of the solution. The adsorption kinetics of MB followed a pseudo-second-order reaction model, indicating a significant role of chemical interactions during the adsorption process. Importantly, the synthesized Fe3O4 C nanocomposites exhibited excellent reusability and could be easily separated from the adsorption system after capturing MB. Overall, the results suggested that the prepared Fe3O4@C composites have promising potential as effective adsorbents for removing dye pollutants from wastewater, owing to their well-defined structure, magnetic properties facilitating separation, and robust adsorption capabilities.

Tran et al., (2017) explored the potential of a chitosan/Fe3O4/graphene oxide (CS/Fe3O4/GO) nanocomposite for effectively removing methylene blue (MB), a cationic dye, from aqueous solutions. The process involved the initial preparation of graphene oxide (GO) from graphite obtained from pencils using Hummer's method. Subsequently, the CS/Fe3O4/GO nanocomposite was synthesized through a chemical co-precipitation method using a mixture solution of GO, Fe3+, Fe2+, and chitosan. The synthesized CS/Fe3O4/GO nanocomposite underwent characterization using XRD, VSM, and SEM techniques to understand its structural and magnetic properties. Various parameters influencing dye removal were investigated, and the equilibrium data for dye adsorption were well-fitted to the Langmuir isotherm, indicating monolayer adsorption behavior rather than multilayer adsorption described by the Freundlich isotherm. The maximum monolayer capacity (qmax) determined from the Langmuir isotherm was calculated as 30.10 mg. The study concluded that the CS/Fe3O4/GO nanocomposite demonstrated promise as a cost-effective and efficient adsorbent for removing cationic dyes from aqueous solutions, highlighting its potential for practical applications in wastewater treatment.

Xiang et al. (2021) conducted research on the preparation and application of Fe3O4@C nanoparticles for the decolorization of high concentrations of methylene blue (MB). The nanoparticles were synthesized through an in situ, solid-phase reaction using FeSO4, FeS2, and PVP K30 without any precursor materials. The study found 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 explored the use of H2O2 as an initiator for a Fenton-like reaction to enhance MB removal efficiency. The results showed that the Fe3O4@C nanoparticles achieved approximately 99% removal efficiency for 100 mg/L MB, whereas pure Fe3O4 nanoparticles only achieved around 34% removal. The study also discussed the mechanism of H2O2 activation on Fe3O4@C nanoparticles and proposed potential degradation pathways for MB. Importantly, the Fe3O4@C nanoparticles maintained high catalytic activity even after five usage cycles, indicating their potential for repeated use. Overall, the research presents a straightforward method for producing Fe3O4@C nanoparticles with excellent catalytic reactivity, suggesting a promising avenue for industrial-scale production of these nanoparticles for treating high concentrations of dyes in wastewater.

Abdelrahman et al. (2019) conducted a study on the synthesis of Fe2O3 (hematite) nanoparticles with varying crystallite sizes (40-59 nm) derived from Egyptian insecticide cans via the combustion method. The organic fuels employed in the synthesis were urea, glycine, L-alanine, and L-valine. The Fe2O3 nanoparticles underwent comprehensive characterization using various techniques including BET, PL, FT-IR, XRD, HR-TEM, FE-SEM, UV-Vis, and DTG. The study focused 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 effectively modeled by the first-order kinetics. Furthermore, the Fe2O3 nanoparticles exhibited consistent photocatalytic activity even after being reused three times, highlighting their stability and potential for practical applications.

Osorio-Aguilar et al., (2023) study focuses on the adsorption and photodegradation of organic dyes, using methylene blue (MB) as a model. It traces historical and current trends in research, emphasizing the environmental impact, removal, and degradation using nanomaterials. The study highlights China's dominance in research on dye photodegradation using carbon nanomaterials. While these materials show promise in efficiently removing MB, safety concerns regarding byproducts and CNT handling require attention for responsible application in environmental remediation. The study emphasizes the need for comprehensive risk assessments and safety measures in nanomaterial synthesis 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. 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 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). 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 was 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 3: (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. This results in the formation of a well-defined red-brown precipitate. The subsequent steps mirrored the undoped synthesis. The precipitate was diluted tenfold with double-distilled water, followed by transfer to an oven for aging at 70-75 °C for 72 hours. This step facilitates the crystallization 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 the 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 10 min, 30 min, 60 min, 90 min, 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:

(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 Fe2O3 nanoparticles. In order to establish the nature and the strength of the adsorption process involved, data obtained from ultraviolent measurements was fitted to adsorption isotherms; The linearized form of Langmuir, and Freundlich isotherms are shown in equations 3.9-10 respectively.

The equilibrium constant values (Kads) was computed from the intercept of the plots

**3.5.5 ADSORPTION THERMODYNAMICS**

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

∆ Go = - RT ln Kd (1)

ln Kd = (ΔS°/R) – (ΔH°/RT) (2)

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

= (3)

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

# **CHAPTER FOUR**

## **RESULTS AND DISCUSSION**

### **4.1 SYNTHESIS OF IRON NANOPARTICE**

### 4.2 **CHARACTERIZATIONS**

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