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

BY

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# **TITLE PAGE**

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# **CERTIFICATION**

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

**……………………………….. ………………………………..**

**DR. H.O. ABUGU DATE**

**(PROJECT SUPERVISOR)**

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

**(HEAD OF DEPARTMENT)**

**……………………………….. ………………………………..**

**EXTERNAL EXAMINER DATE**

# **DEDICATION**

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

# **ACKNOWLEDGEMENT**

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

# **ABSTRACT**

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

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

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# CHAPTER ONE

## INTRODUCTION

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

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



Figure 1: Struture of methylene blue

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

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

## ADSORPTION

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

# CHAPTER TWO

## LITERATURE REVIEW

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

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

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

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

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

# Chapter Three

**MATERIALS AND METHODS**

## **3.1 REAGENT USED**

1. Potassium hydroxide (KOH)

2. Ferric nitrate (Fe(NO3)₃)

3. 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 MOLYBDENUM 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.

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 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