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# Title

Synthesis, characterization and application of Zn-doped Fe2O3 nanoparticle for the removal of methylene blue dye from aqueous solution

# Certification

# Dedication

# Acknowlegement

# Abstract

# Table of contents

# List of Tables

# List of Figures

# List of abbreviation

# CHAPTER ONE

## INTRODUCTION

### Background of study

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

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

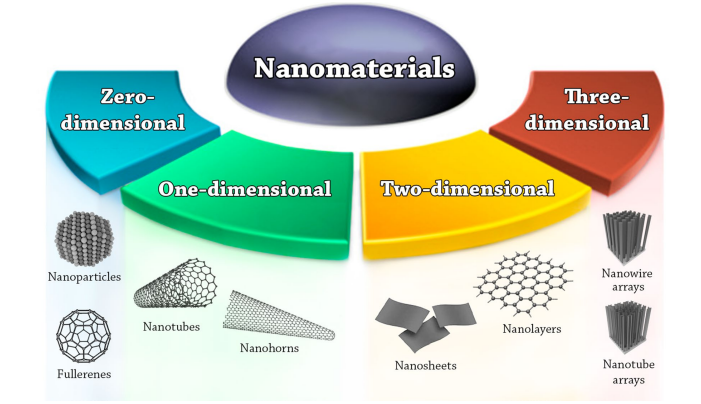


Figure 1: Nanomaterials classification based on dimensionality (Joudeh & Linke, 2022)

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

### AIM OF STUDY

#### 1.2.1 AIM OF STUDY

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

#### 1.2.2 SPECIFIC OBJECTIVES OF STUDY

The specific objectives of this study are as follows:

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

### Justification and significance of the study

# Chapter two

## Literature review

### 2.1 Adsorption

### 2.2 Factors affecting Adsorption capacity

### 2.3 Adsorption Kinetic Model

### 2.4 Adsorption Isotherm model

### 2.5 Adsorption thermodynamics

# Chapter three

## 3.1 Reagent used

1. Potassium hydroxide (KOH)

2. Ferric nitrate (Fe(NO3)₃)

3. Distilled water

4. Methylene blue dye

5. Hydrochloric acid (HCl)

6. Sodium Hydroxide (NaOH)

7. pH buffer

## 3.2 Apparatus and equipment

1. Magnetic stirrer
2. Magnetic bar
3. pH meter
4. Thermometer
5. Electric blender
6. Oven
7. Furnace
8. Glass rods
9. Crucibles
10. Plastic bottles
11. Beakers
12. Conical flasks
13. Volumetric flasks
14. Spatula
15. Dropper
16. Paper tape
17. Whatman no 42 filter papers
18. Hand gloves
19. Nose masks

## 3.3 Synthesis of Zn-doped Fe2O3 nanoparticle using co-precipitation method

The synthesis procedure began with the preparation of a 1 M ferric nitrate (Fe(NO3)₃) solution (50 mL). Zinc precursor solution, which was zinc nitrate (Zn(NO3)₂), was then added in a pre-determined stoichiometric ratio to achieve the desired zinc 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 zinc-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 zinc-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 zinc-doped iron oxide nanoparticles, ready for further characterization and application testing.

## 3.4 Characterization and analysis

## 3.5 Adsorption studies

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

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

### 3.5.1 Determination of the effect of initial concentration

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

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

### 3.5.2 Determination of the effect of contact time

A 10 ppm methylene blue solution, with pH adjusted to 9, was dispensed into 100 mL beakers. Subsequently, 0.04 g of the adsorbent material was introduced into each beaker. The contact duration for each experiment was set at intervals of 10 minutes, specifically at 10 min, 30 min, 60 min, 90 min, and 120 min. Upon completion of each contact period, the mixtures underwent filtration, and the percentage absorbance of the resulting filtrates was determined using a UV-Vis spectrophotometer at a wavelength of 664 nm.

### 3.5.3 Calculation of percentage removal and adsorption capacity

The methylene dye percentage, %R was measured by applying the equation below;

(1)

Where:

= initial concentration of the liquid phase of the dye in (mg/L)

= equilibrium concentration of the liquid phase of dye in (mg/L)

The adsorption capacity is given as:

(1)

Where:

(mg/g) = adsorption capacity

= initial concentration of the liquid phase of the dye in (mg/L)

= equilibrium concentration of the liquid phase of the dye in (mg/L)

V(L) = volume of the solution used for the adsorption

M (g) = the mass of the adsorbent used

# Chapter four

# Reference