Synthesis of Eu^{3+}-doped ZnONanocomposite for Photocatalytic Degradation of Methylene blue dye

GenaNura

A Thesis Submitted to the Department of Applied Chemistry
College of Applied Natural Science

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Applied Chemistry (Industrial Chemistry)

Office of Graduate Studies
Adama Science and Technology University

Dec, 2025
Adama, Ethiopia

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DECLARATION

I hereby declare that this Master Thesis entitled "**Synthesis of Eu^{3+}-doped ZnO Nanocomposite for Photocatalytic Degradation of Methylene blue dye**" is my original work. That is, it has not been submitted for the award of any academic degree, diploma or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation

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Name of student	Signature	Date

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I, the major advisor of this thesis, hereby certify that we have read the revised version of the thesis entitled "**Synthesis of Eu^{3+}-doped ZnO Nanocomposite for Photocatalytic Degradation of Methylene blue dye**" prepared under my/our guidance by **GenaNura** submitted in partial fulfillment of the requirements for the degree of Masters of Science in Applied Chemistry (Industrial Chemistry). Therefore, we recommend the submission of revised version of the thesis to the department following the applicable procedures.

Gemmechu Deressa (Ph.D.)	_____	_____
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I, the advisor of the thesis entitled "**Synthesis of Eu^{3+}-doped ZnO Nanocomposite for Photocatalytic Degradation of Methylene blue dye**" and developed by **GenaNura**, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

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We, the undersigned, members of the Board of Examiners of the thesis by **Gena Nura** have read and evaluated the thesis entitled "**Synthesis of Eu^{3+}-doped ZnO Nanocomposite for Photocatalytic Degradation of Methylene blue dye**" and examined the candidate during open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Applied Chemistry (Industrial Chemistry).

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF ACRONYMS

CB	Conduction band
DRS	Differential reflectance spectroscopy
EZO	Europium doped Zinc oxide
FT-IR	Fourier Transforms Infrared
MB	Methylene blue
NPs	Nanoparticles
PL	Photoluminescence
PVA	Polyvinyl alcohol
VB	Valence band
XRD	X-ray diffractometer

ABSTRACT

The doping of rare earth element like europium ions into the ZnO matrix and can considerably enhance photocatalytic performance. Here in this study, Eu^{+3}-doped ZnO (EZO) Nano composite was prepared by using simple solution combustion method. The nanostructured materials that contain different amount of europium ion were synthesized starting from zinc and Europium nitrate as precursor of sol. The disappearance of independent Europium oxide peaks on the XRD pattern of composite and the presence of a low-angle peak shift confirm the successful inclusion of Europium ion within ZnO lattice. The slightly reduction of direct and indirect DRS-UV-vis bandgap energy for EZO nanocomposites relative to ZnO (3.21eV) supports the evidence ofEuropium ion inclusion in ZnO matrix interpretation. Moreover, the Eu^{+3}-doped ZnO (EZO) Nanocompositewave length shift of photoluminescence spectra and intensity reduction compared to ZnO also confirms the improvement of visible light absorption and the hindrance of electro-holes recombination. Thus, it's possible to deduce that, the Eu^{+3}-doped ZnO (EZO) Nanocomposite has better charge transfer and visible light absorption properties than ZnO nanoparticles (NPs). The Fourier Transform Infrared (FTIR) spectral investigation provides the information about the presence of expected chemical bonding and functional groups attached to Europium ion (Eu^{3+}) doped and undoped zinc oxide (ZnO) nanoparticles. The prepared EZO nanocomposites exhibited advanced photocatalytic activities ($k=0.03\ min^{-1}$) relative to ZnO ($k=0.02\ min^{-1}$). The enhanced of photocatalytic degradation of methylene blue dye is attributed to the improved light absorption and charge transfer ability of Eu^{+3}-doped ZnO (EZO) Nanocomposite.

Keywords: Eu^{+3}-doped ZnO nanocomposite, methylene blue, photocatalysis

CHAPTER ONE

1. INTRODUCTION

1.1.Background of Study

Much of industrial pollutants that are found in the environment particularly in water pose critical health risks to human life. Nowadays, the removal of these harmful pollutants, mainly organic dyes, is the critical environmental challenge(Ahmad et al., 2020). Methylene blue (MB) is a widely used synthetic dye in the textile, paper, and pharmaceutical industries. However, its recalcitrant nature makes it difficult to remove by traditional methods, such as adsorption or coagulation (Xia et al., 2020). Recently photocatalysis, which involves the use of semiconductor materials is a promising method to degrade organic contaminants under light irradiation(Balapure et al., 2024). Among several semiconductor photocatalysts, zinc oxide (ZnO) has got significant consideration because of its good photocatalytic performance, harmlessness and chemical stability.ZnO is a wide-bandgap (3.37 eV) semiconductor material that exhibits excellent photocatalytic properties under ultraviolet (UV) light.It has attracted wide attention in this area due to their exceptional structural and functional properties which are applied for potential applications in energy, environmental nanotechnology and photocatalytic degradation of pollutants to change harmful and toxic organic pollutants into harmless products(Kshirsagar et al., 2024). Herein, the photocatalytic process valence band holes and conduction band electrons are produced on the surface of semiconductors when photons from the light source such as UV and visible light interact with catalyst, thus these photon induced holes are further react with H_2O or OH^-, which are attached on the catalytic surfaces to generate hydroxyl radical (·OH), and electrons in the conduction band interact with adsorbed O_2 to yield superoxide radical ($\cdot O_2$) (Rong et al., 2022).Despite these advantages ZnO's photocatalytic activity is primarily limited to UV light, which accounts for only a small portion of the sunlight range.

However, ZnO's inadequate visible light absorption limits its photocatalytic efficiency under the irradiation of natural sunlight. In order to overcome this drawback, doping ZnO with rare-earth metal such as europium (Eu^3) have been explored. The doping of Eu^{3+} ions into ZnO can improve its light absorption, particularly in the visible region, and enhance its photocatalytic properties (Al Rifai & Kulnitskiy, 2013; Applications, 2022; Armelao et al., 2008). This limitation can be solved by modifying the surface of ZnO by introducing dopants that extend its visible light absorption. Rare-earth metal ions like Eu^{3+} are ideal candidates due to their

exceptional optical belongings, containing good fluorescence performance and the ability to sensitize the material for enhanced photocatalytic activity. The inclusion of Eu^{3+} ions in the ZnO lattice enhances its photocatalytic activity by facilitating the formation of more photon induced electron-hole pairs under the irradiation of visible light, improving the overall material's catalytic performance. The incorporation of dopants within host materials results in the improvement of surface area and generates lattice defects and modifies bandgap energy of the host ZnO (M. Kumar et al., 2021). Most lanthanides elements ions show high luminescent intensity due to their 4f- intra shell shifts can produce bright luminescence spectrum. From those elements, europium ion (Eu^{3+})shows a robust release because of the 4f– 4f transition of electrons(Gemechu et al, 2022).

Numerous ZnO-based catalyst implementation possibilities improvements through doping procedures were well studied and reported. Al Rifai et al. synthesized Europium-doped ZnO by a chemical vapor deposition method. The successful preparation of the material was confirmed by the XRD, SEM-EDX, and more photoluminescence analysis (Al Rifai & Kulnitskiy, 2013). Kumar et al. synthesized Europium Eu^{+3}-doped ZnO nanomaterial via facial co-precipitation method. In this study the improvement in photonic properties of doped material was explained through invoking the presence of Eu^{+3} electron in the band gap of ZnO (M. Kumar et al., 2021). El Jouad et al. synthesized europium doped ZnO thin films using a spray pyrolysis method for optoelectronics applications. Besides, the inclusion of europium ion in the ZnO lattice was also confirmed from the slight angle peak shift compared to the single ZnO (El Jouad et al., 2020).

The porosity nature of materials improves surface area which helps for good collaboration of catalysts with pollutants. Solution incineration synthesis method has an efficient approach for preparing porous materials (Perego et al., 2013). Though, it produces high amounts of heat and facilitates the aggregation of NPs because of high surface energy(Saxena et al., 2017). Accordingly, become stable agent such as polyvinylpyrolidone (PVP)and polyvinyl alcohol (PVA) should be used. The polymer PVA is widely used as a surfactant due to its good mechanical characteristic and non-toxicity. Moreover, it can participate in exothermic reactions and provide heat needed during combustion synthesis (Abebe et al., 2022). Mohammed et al. synthesized a porous Co-doped ZnO/Ag heterostructure using a PVA

capping agent. In addition, the PVA polymer used as fuel that helps the combustion process and generates a wormhole-like porous material(Mohammed et al., 2025).

Based on the over head evidences, the situation is fascinating to synthesize Eu^{+3}-doped ZnO (EZO) Nanocomposite through solution combustion approach for overcoming ZnO's drawback and advancing this one Photocatalytic cefficiency. Besides, the Eu^{+3}-doped ZnO (EZO)Nanocomposite, which is prepared through solution combustion approachhas not yet been reported for degradation of methylene blue. The inclusion of europium in the ZnO lattice was found to boost the photocatalytic degradation application. This degradation efficiency enhancement is connected with the photonic property improvement due to the insertion Eu^{+3}within ZnO matrix.

1.2.Statement of the Problem

The main sources of water pollution and the intensification in fabrication of synthetic dyes are attributed on the way to their high consumption in others industries, typically the textile industries are the primary cause for water pollution by methylene blue dye. Methylene blue dye is stable against water, temperature and light, as a result it cannot be frequently removed during the traditional wastewater handling methods (Ahmad et al., 2020), because this dye has continuing to exist in our environment. As MB dye present in food source and drinking water, it can seriously damage a person's physical and nervous system. Therefore, the elimination of this pollutant has become the serious issue currently (Alanazi et al., 2021).

Essentially, there are a lot of traditional wastewater treatment methods that work based on chemical and physical principles, however due to the intricate technique and processes involved, the prerequisite of expensive equipment and chemicals and secondary pollutant generation their practical advantages is often constrained and cost of existing removal methods (Cheng et al., 2020). Currently, heterogeneous photocatalytic oxidation through ZnO catalyst is an advisable method of MB removal. But, the main problems of using ZnO as photocatalysts photon induce electrons-holes recombination (EHR) and are lack of harvesting visible light. As a result, to solve these drawbacks of ZnO, doping with transition metals was used in the previous works (Mengistu et al., 2023). These problems are expected to be overcome by developing Eu^{+3}-doped ZnO (EZO) nanocomposite material via a solution combustion synthesis method.

1.3.Objective of the Study

1.3.1. General objective

The general objective of this study is to synthesize and characterize Eu^{+3}-doped ZnO (EZO) Nanocomposite for Photocatalytic degradation of methylene blue dye.

1.3.2. Specific objective

- To synthesize ZnO NPs
- To synthesize Eu^{+3}-doped ZnO (EZO)Nanocomposite
- To characterize the synthesized NPs and composites using different systematic techniques such as XRD, DRS-UV-vis, PL and FTIR.
- To investigate those methylene blue dye degradation capabilities of synthesized ZnO NPs and Eu^{+3}-doped ZnO (EZO)Nanocomposite.

1.4.Significance of the Study

This study showed a low-cost, environmentally sustainable solution for degrading methylene blue dye using Eu^{+3}-doped ZnO (EZO) Nanocomposite. Moreover, Eu^{+3}-doped ZnO (EZO)Nanocomposite catalytic performance was enhanced by using solution combustion method to produce porous material, providing efficient pollutant degradation. From the result of this study, all communities, industries, the scientific community, and future researchers will be benefited. This research opens the chance for further research on the development of advanced methods for the water purification.

1.5.Scope of the Study

The scope of this study was restricted to the fabrication in connection with ZnO, and Eu^{+3}-doped ZnO (EZO) Nanocomposite, using a portion solution combustion techniques; the characterization of as prepared nanoparticles and composites utilizing XRD, UV-Vis- DRS, PL, and FTIR analytical technique. UV-Vis spectroscopy also applied for the investigation photocatalytic activity of as-synthesized nanomaterial's on synthetic methylene blue dye.

CHAPTER TWO
2.LITERATURE REVIEW

2.1. The pollution of Water

Water pollution is occurred commonly associated with the discharge of industrial effluents which consist extensive amount of dyes, aromatic, heavy metal ions and the decomposed product of herbicides and pesticide (S. Naseer et al., 2022). The pollution of water by toxic dyes is a considerable environmental problematic throughout the world recently. A lot of industries like textile, leather, printing, paper, etc. discharge a large amount of hazardous pollutant to water bodies(Mondal et al., 2019). The discharge of toxic dyes to water parts usually results in the unwanted coloring of the water surface, which commonly resists sunlight from passing the water surface and used in the photochemical and biological functions important for aquatic life (Lam et al., 2012). Rafi et al (2021) reported that, based on the World Bank report, around 17-20% of contamination of water came from textile industries and treatment; therefore, textile industries represents the pollution of water problem internationally because of accidental discharge of polluted water in to the water bodies, which shows a major influence on the cleanliness of water resources.

The pollution of water bodies due to water-borne pathogen and also related diseases; are a serious problem that concern around the world. Pollution of water by pathogens is a severe problem for all form of water bodies is critical issue(Magana-Arachchi& Wanigatunge, 2020). Besides, rivers have been polluted by incomplete treated and/or untreated discharge from petrochemicals, rolling steel mills oil spills, and pesticides pollutant. In addition, it should be known that the comparative high stability synthetic dyes results health and environmental difficulties because of their carcinogenic poisonous and mutagenic properties (Sarkar Phyllis et al., 2022).

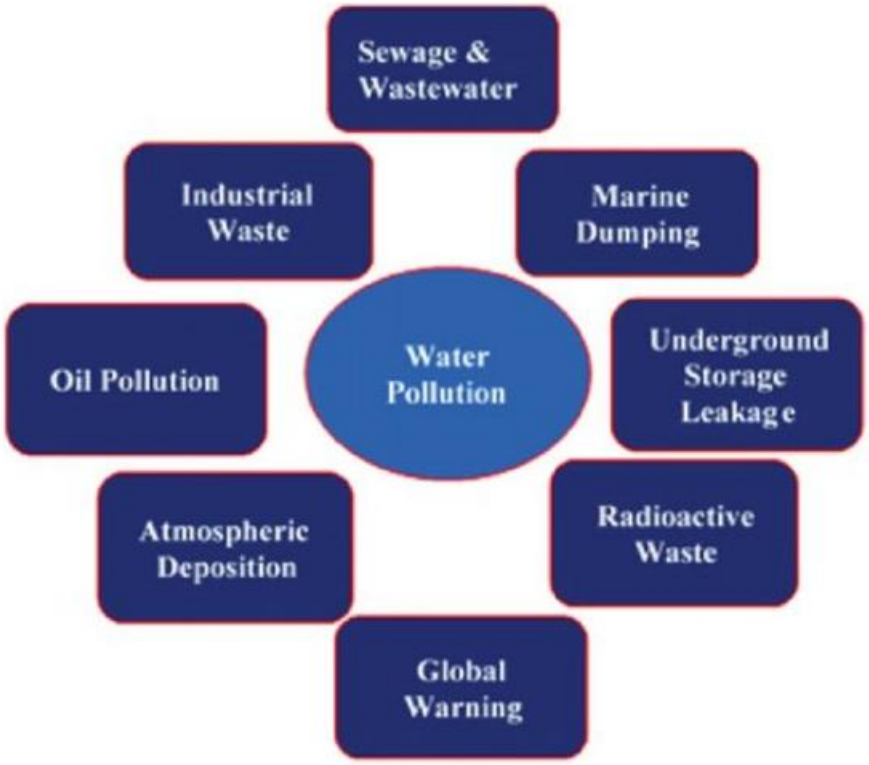


Figure 1: Different sources of water pollution(Koduru et al., 2019)

2.1.1. Properties of methylene blue (MB) dye

The organic dye compounds have been released from different industries as effluents are the main cause of pollution and eutrophication in aquatic environment. Synthetic dyes are commonly applied in large amounts in the textile industries, which are physically and chemically stable compounds and hazardous to our environment (Adeel et al., 2021). From synthetic organic dyes; methylene blue (MB) is a famous cationic and thiazine organic dye with chemical formula-($C_{16}H_{18}ClN_3S$), and having λ_{max} of 664 nm, is a solid dark blue powder at room temperature and forms blue solution after complete dissolution in water; soluble in water, ethanol, methanol, acetone and ethyl acetate (Hamad & Idrus, 2022). MB is carcinogenic dye that has been prepared and used in several industries for different purposes like dyeing of cotton, coloring of paper, wool and fabrics hair, and indicator of redox reaction (Riggert et al., 2001). It induces a grave problem to human health such as damaging nervous system and eyes. Besides, it results nausea, breathing difficulty, diarrhea, and vomiting. Thus, it is important to eradicate this toxic pollutant from water bodies. In Photocatalytic degradation of Methylene blue study, UV-Vis analysis is very essentialtoanalyze the change in absorbance curve due to the presence of catalyst and to compare the efficiency of catalyst

by calculating the degradation efficiency and reaction rate constant (Akhmal Saadon et al., 2016).

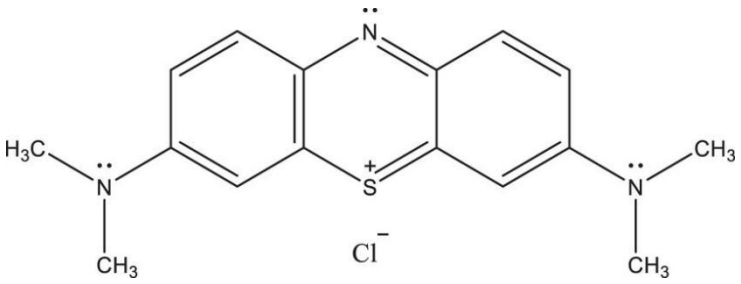


Figure 2:MolecularStructure of methylene blue

2.1.2. Methods used to remove MB from water

Usually, the treatment waste water follows four main stages, such as preliminary, primary, secondary and tertiary processes. In detailed, preliminary processes used for the elimination of large substances like grits, plastics, papers, wood etc fundamental remediation includes skimming to eradicate frothy solids and flotation and sedimentation to eliminate settable impurities. Then, secondary treatment includes the fail of dissolved microbial and colloidal equipment(Hamad& Idrus, 2022). Tertiary treatments involves an advanced method especially, applied for methylene blue removal, which includes biological agent (aerobic, anaerobic, anoxic or facultative), chemical agents (chemical precipitation, ozonation, ion exchange, photocatalysis and ultrasound) and physical (sedimentation, coagulation, membrane filtration, flocculation filtration, and adsorption) (Collivignarelli et al., 2019). Though, previous studies reported several techniques that used waste water treatment application as demonstrated in Fig.3.Whereas, photocatalysis provides an extensive variety of advantages due to its simple set up, cost effectiveness, lower energy consumption, high pollutant degradation efficiency without the generation of hazardous by-products (Sarkar Phyllis et al., 2022).

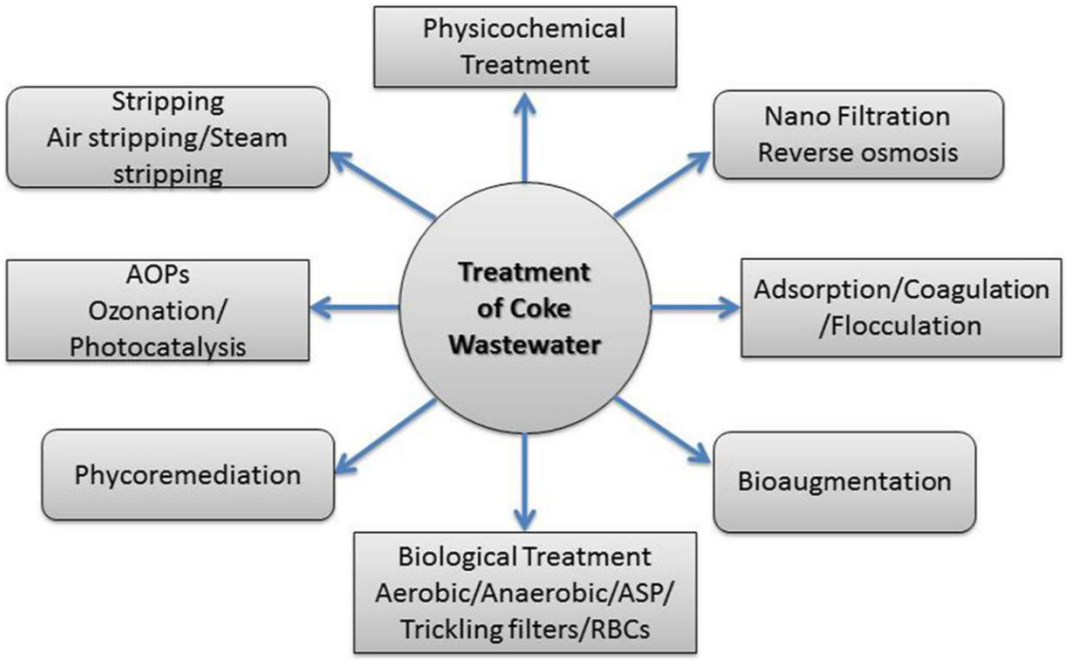


Figure 3: Most common waste water treatment methods(Mishra et al., 2021)

2.2. Introduction to Nanotechnology and Nanomaterial's

Nanotechnology refers to a technology of propose manufacture and application of nanostructure materials, as well as also an crucial empathetic of physical property and phenomenon of Nanomaterial's(Köhler & Fritzsche, 2008). It is a fast developing field in science and technology for the application of fabricating material in nanoscale. Many companies in the world are presently trying to use nanotechnology to create their inventions more productivein terms of structure, functioning, and designing of materials (Khin et al., 2012). It has allowed the civilization of all industrial domain, starting from small-scale production and processing units in the medicine ,agriculture and food industries to larger-scale production units (Xia et al., 2020).

Nanomaterial's, compare to bulk substances, have the scales ranging from individual atoms or molecules to submicron scope at least in one dimension (Policy, 2015). They have unique chemical and physical properties that able to be used for different purpose. The important of nanotechnology was firstly described by Feynman, during the science lecture allowed ''There is plenty of room at the bottom'' at the annual meeting of the American Physical Society in 1959 (Reed et al., 2014). A lot of discoveries and innovation in the manufacturing of nano objects have been established. The fabrication of novel materials, processes and phenomena at the nanoscale, and also the improvement of new experimental and theoretical techniques for research work give many new opportunities for the establishment of innovative nanostructures

materials. Nanostructured materials can be fabricated with exception nanostructures and properties. This field has predictable to open new era in science and technology.

2.3. Nanoparticles (NPs)

Nanoparticles (NPs) are a types of nanomaterial's that have the size 1-100nm in diameter in all dimension(Vasyliev et al., 2020).It is hard to observe nanoparticles by standard optical microscopes, needing the use of laser microscopes or electron microscopes.They have an exceptional size-dependent feature known as high 'aspect ratio', refers to the high surface area to volume ratio..Particle size with aspect ratio has indirect relationships; when small size descends the aspect ratio will ascends. That means they have a high surface area than volume. The enlarged outside Local of the smaller nanoparticles will increases their reactivity (Khin et al., 2012)).

2.3.1. Zinc oxide (ZnO) nanoparticles

Zinc oxide (ZnO) is an extended band gap II-VI semiconductor known used for high electron mobility, optical transparency, and room-temperature luminescence. It has a white color appearance, is usually known as zinc white or zincate, as well as it is insoluble in water and alcohol, however it soluble in acids like hydrochloric acid. Due to ZnO turns yellow when heated and white when cooled, it is thermochromic in its crystalline form (Puspitasari et al., 2018). It has three crystal forms such as hexagonal wurtzite, the cubic zinc blende, and the cubic rock salt. The most known structure is wurtzite, which shows the high stability under normal conditions. Each individual anions in wurtzite hexagonal structure has a pattern parameter of a = 0.3296 nm and c = 0.520 nm, with space group P63mc and point group C6v4, is surrounded by four Cations in the corners of the tetrahedron, displaying tetrahedral coordination and sp^3 covalent bonding (Liu et al., 2019).

ZnO provides a lot of attractive features, including high electron mobility, non-toxicity, biocompatibility, outstanding transparency, high photocatalytic activity, high stability and strong room-temperature luminescence (Abebe & Ananda Murthy, 2022). UV lasers, Solar cells, optoelectronics, laser diodes, transparent conductive contacts, beam emitter diodes, gas probes, surface acoustic wave devices, and piezoelectric devices and thin-film transistors are all use ZnO nanoparticles in some way. ZnO nanomaterial's have been employed in a multiple implementations such as cosmetics, electronics, optics, and photocatalytic degradation of organic dyes(Klingshirn et al., 2010). Compared to other semiconductor metal oxides, ZnO has a greatest degree of lattice defects, allowing it an excellent photocatalysts material.

Surface area, Phase purity, crystallite size, synthesis procedures and dopants kind are all key factor in determining photocatalytic efficiency(Yang et al., 2013).

2.4. Photocatalysis

The word photocatalysis combines the terms “phos,” which means light, and “katatalyo, ” which means to decompose. Generally, photocatalysis describes alteration in the speed of a chemical process caused by visible light or ultraviolet light in the occurrence of a material that captures light and participates in chemical change of reactants. A material that captures visible or ultraviolet light and produces reactive species when excited is called a photocatalysts (Chong et al., 2024).

The photocatalytic reactions can occur in either homogeneous systems or heterogeneous; but, heterogeneous photocatalysts have obtained a lot more interest due to its ability uses in several fields, including the generation of energy and cleanup of environments. Moreover, heterogeneous photocatalysts are simply separated from a reaction mixture, allowing them appropriate for application in additional reactions(Perego et al., 2013).

2.4.1. Mechanism of photocatalytic degradation

The photocatalytic degradation of pollutant mostly involvea few steps starting from adsorption-desorption, electron-hole pair production and chemical reaction. The overall mechanism of photocatalytic degradation of organic molecules best described in the equations below (Thennarasu & Sivasamy, 2013). Once the photocatalysts is irradiated with light energy with required band gap energy of PC, then electrons are jump from the valence band (VB) to the conduction band (CB) nm it the concurrent formation of holes (h^+) in the VB:

$$PC + hv \longrightarrow e_{CB}^- + h_{VB}^+$$

The electrons producedby irradiation could be easily trapped by O_2molecule which is absorbed on the photocatalyst surface to give superoxide radicals ($^{\bullet}O_2^-$):

$$e_{CB}^- + O_2 \longrightarrow {}^{\bullet}O_2^-$$

Thus, $^{\bullet}O_2^-$ could react with H_2O molecule to generatehydroperoxyl radical ($HO_2\bullet$) and hydroxyl radical ($^{\bullet}OH$), those are strong oxidizing agents to degrade the organic molecule:

$$^{\bullet}O_2^- + H_2O \longrightarrow HO_2\bullet + {}^{\bullet}OH$$

At the same time, the photon induced holes could be trapped by surface hydroxyl groups (or H_2O) to give hydroxyl radicals ($^{\bullet}OH$):

$$h_{VB}^{+} + H_2O \longrightarrow {}^{\bullet}OH + H^{+}$$

Lastly, the organic molecules will be decomposed to give carbon dioxide and water as follows:

$$^{\bullet}OH + \text{organic molecules} + O_2 \longrightarrow \text{Products } (CO_2 \text{ and } H_2O)$$

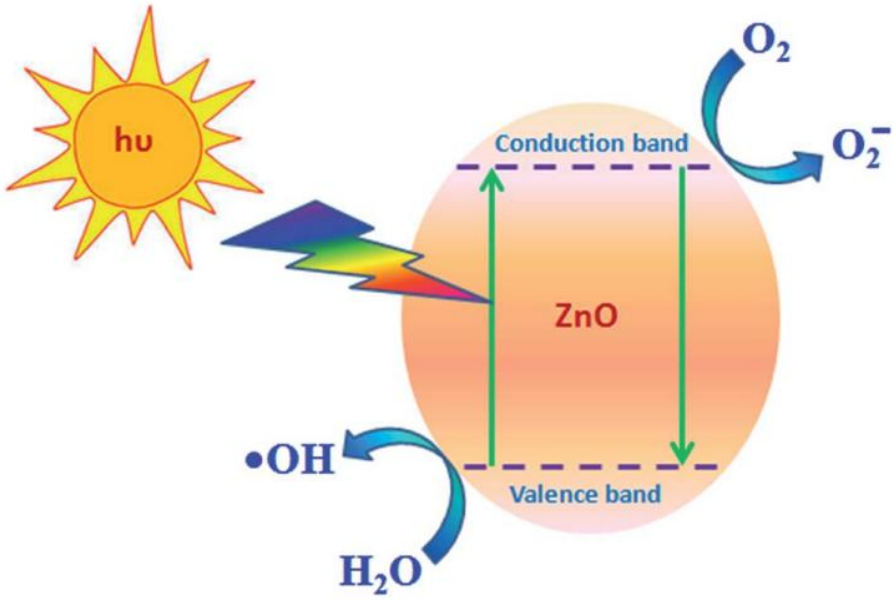


Figure 4: Diagrammatic representation of photocatalytic degradation mechanism(Adhikari et al., 2014)

2.5. Doping

Nowadays,nanotechnology has proceed to improvement in fabricating nanomaterials for waste water treatment through doping, can advanced the optoelectronic properties of metal oxide semiconductors (Molavi et al., 2024). Doping of transitin metals can tune optical properties of host materials and absorption of visible light(Abebe & Ananda Murthy, 2022). Doping ZnO with rare earth elements like Europium can significantly improve its photocatalytic properties throughencouraging charge separation and resisting electron-hole recombination. Europium (Eu^{+3}) ions, due to their luminescent properties can improve the band structure of ZnO. Furthermore, Europium doping assists for inhibiting the recombination of photon induced electron-holes pairs; which helps to increasing a lifetime of electron-hole pairs. Then, this separation of charges used to facilitate more effective electron transfer to the dye molecules

leading to a more efficient degradation process (El Jouad et al., 2020). Besides, it is used for bandgap energy modification; Europium ions also play a crucial role in modifying the ZnO bandgap, making it more appropriate for photocatalysis beneath visible light which is more prominent than UV light. This helps for better utilization of solar energy in photocatalytic degradation applications (Armelao et al., 2008).

When Eu^{+3} ions are inserted into ZnO lattice, they may occupy Zn^{+2} sites within the ZnO matrix. The inclusion of Eu^{+3} ions introduces new energy levels within the bandgap of ZnO, which can change both the optical and electronic characteristics of the material.Eu^{+3}naturallyassist to photoluminescence spectrum in the red-orange region associated with $5D^0 \rightarrow 7F^2$electron transitions, while Eu^{2+} may give to blue or green emissions; the emission properties dependent on the concentration of dopant, the local environment of the Eu ions, and the synthesis conditions (Al Rifai & Kulnitskiy, 2013).The maineffect of doping with Eu is the improvement of the luminescent properties. Europium dopingadvances the photoluminescence characteristics, leading the material to release light at specific wavelengths. These fascinating luminescent properties are valuable for several applications in optoelectronics, like in phosphors for displays or light-emitting diodes (LEDs). Moreover, doping can affect the morphology and crystalline of ZnO nanoparticles(Applications, 2022).

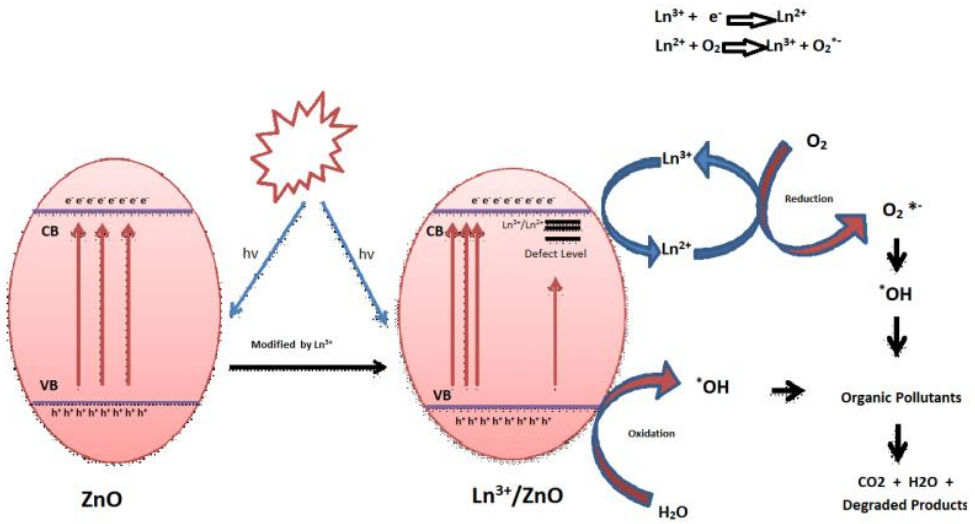


Figure 5: Photocatalytic degradation mechanism ZnO and rare earth element doped-ZnO(R. Kumar & Dosanjh, 2022)

2.6. Synthesis methods

The synthesis of nanostructured materials involves several approaches were applied to achieve high catalytic efficiency and structural integrity (Iqbal et al., 2012). The synthesis methods can be top down or bottom up approaches, as illustrated in Fig. 6.

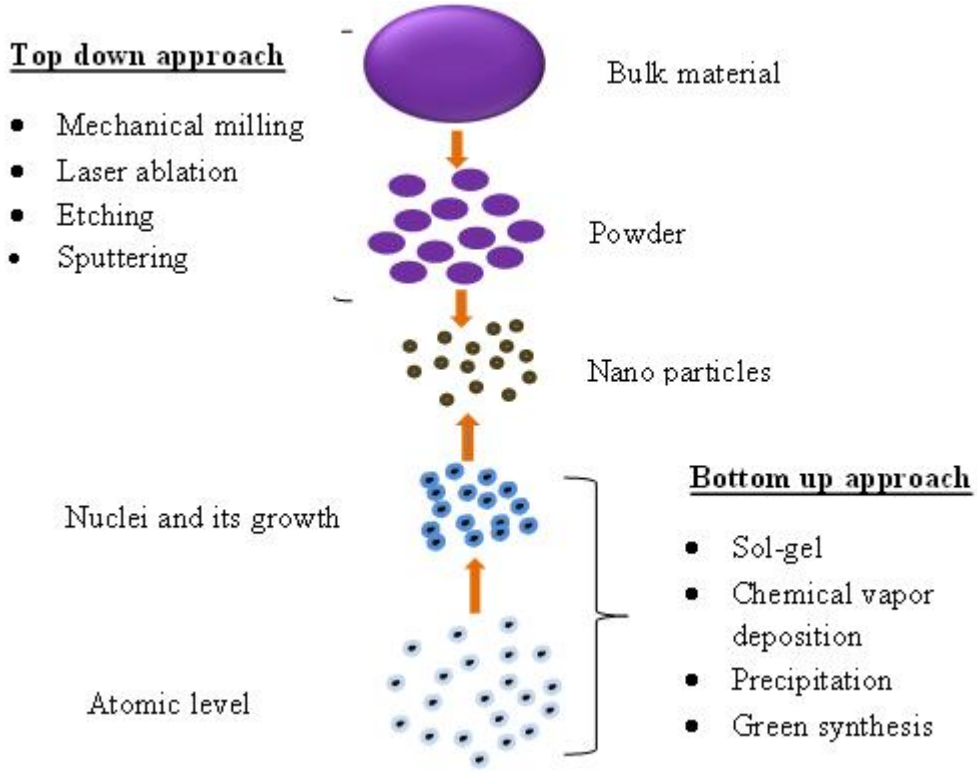


Figure 6:Synthesis of nanostructured materials by bottom-up and top-down approaches

a) Solution combustion synthesis approach

The synthesis method which is solution combustion synthesis is a fast, simple, time/energy effective process; it works based on propellant chemistry and the stoichiometric ratio fuel to oxidant (precursor). In this method the reaction between organic fuel (reducer) and metal precursors (oxidizer)results exothermic reaction, which produce intense evolution of gases(Chen et al., 2021), has a good compensation as a liquid phase chemical method. The emission of NO_2 and CO_2 gases allows self-sustained and auto-catalytic combustion reaction between intermediate phases. Solution combustion reaction is conducted when the reaction temperature surpasses the ignition temperature of redox (oxidant and fuel) solution (Siddique et al., 2022).. The reaction carried out at high speed and nanomaterial is created with uniform porous structure(Nersisyan et al., 2017). The main stages of this synthesis method are formation of collodial solution of oxidant and fuel (reducer), transformation of sol to gel and

combustion of gel to produce metal oxide nanoparticles (Yin et al., 2023).Fig. 7,Summarizes the steps involved in solution combustion synthesis method.

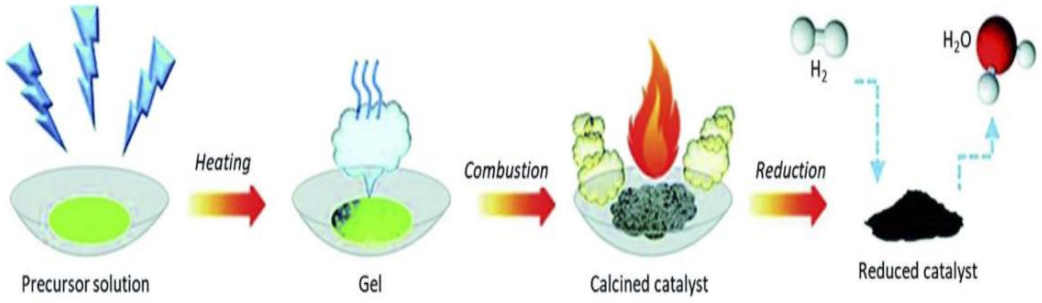


Figure 7:Diagrammatic representation of solution combustion synthesis method (Abebe et al., 2022)

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Experimental Site

This research was carried out in Adama Science and Technology University (ASTU); Applied chemistry, Materials Science and Engineering and Applied Physics laboratories. Moreover, chemicals were purchased from a well-known market. The synthesis of materials was conducted at Adama Science and Technology University in applied Chemistry laboratory. XRD, photocatalytic degradation of MB and UV-Vis DRS spectroscopy analysis was performed in ASTU Materials Science and Engineering laboratory. Photoluminescence analysis was carried out in ASTU applied physics laboratory. In addition, FT-IR was carried out at Addis Ababa Science and Technology University at industrial chemistry department laboratory.

3.2. Chemicals and Reagents

The chemicals that used in this study are; Analytical grade chemicals such as Zinc nitrate hexa-hydrate ($Zn(NO_3)_2.6H_2O$, 99.5%, Sigma Aldrich, Germany), Europium nitrate ($Eu(NO_3)_3$, 99.5%, Sigma Aldrich, Germany), Polyvinyl alcohol (PVA, Thermo Fisher Scientific India Pvt) and Reagents such as ethanol (97%), Ammonium hydroxide (NH_4OH), distilled water and HCl and methylene blue dye (82%, Sigma Aldrich) for the investigation of photocatalytic activities of the as-synthesized catalysts.

3.3. Equipment and Instruments

The powder X -ray diffractometer (XRD) is used for the crystallinity analysis of the as-synthesized powders. To study the optical properties of samples DRS-UV-Vis, and PL spectrophotometer was used. FTIR also used to study the functional bonding and chemical bonding between metal and oxygen, and other functional groups that found in synthesized samples.

3.4. Synthesis of Photocatalysts

Synthesizing nanomaterials using simple approaches like combustion reduces time and cost and makes it easier for scaling up production. Herein, the solution combustion chemical strategies(Abebe, et al., 2023)with a certain modifications was used to synthesize photocatalysts. To synthesize single ZnO NPs, 0.5g of PVA was dissolved in 50 mL of distilled water and stirred continuously for about 15 minutes at 70°C. After the complete dissolution of PVA polymer, the aqueous solution was cooled down to room temperature. The

zinc precursor solution was prepared by adding Zn $(NO_3)_2.6H_2O$ salt in the cooled PVA surfactant solution along with thecontinuous stirring on a magnetic stirrer at about 65 °C. After the full liquefaction of suspension, the final sol was permitted to cool to room temperature. Then, the evaporation was takes placed on hot plate at 100°C to form a gel. Additional heating the gel to the zinc salt precursor-PVA polymer ignition temperature of 150-240°C, the combustion/self-propagation process occurred. The final combusted material was crushed and calcined in the muffle furnace at 450°C for about 1hr. The calcination helps in removal of different impurities in order to produce a stable ZnO nanocrystal.

Likewise, with varying concentrations of Zinc and Europium precursors, a series of 1%, 3%, and 5% Eu^{+3}-doped ZnO nanostructured materials are also synthesized following the same solution combustion approach. In detailed, 0.5 g of PVA was dissolved in 50 mL of water and cooled to room temperature. Then, three samples with various zinc nitrate and Europium nitrate salt precursor percentages were synthesized by liquefaction in a pre-dissolved and cooled PVA polymer solution. The precursor's percentages used to synthesize catalysts are 99, 97 and 95%, for zinc and equal 1%, 3% and 5% percentages for europium nitrate salt. The prepared samples were then coded as 1%, 3%, and 5%, respectively. When the synthesis was carried out, the mixtures were dissolved at 70 °C to form a sol; the water was dehydrated at 100°C to form a gel and finally combusted in the temperature range of 150-240°C and calcined at 450°C for 1 hr. The diagrammatic illustration of the synthesis procedure that shows PVA polymer liquefaction, mixing of the precursors in PVA aqueous solution to form a sol, drying to form gel, and finally calcining to obtain stable nanomaterials was shown in Fig. 8.

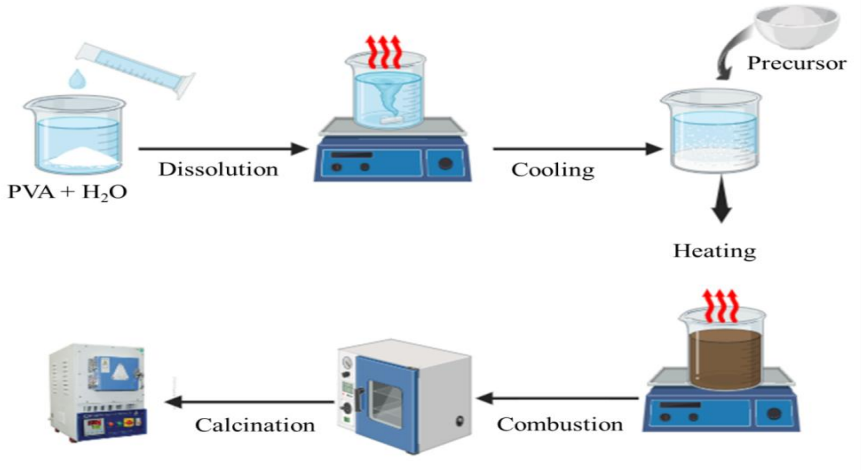


Figure 8: Schematic illustration of synthesis of ZnO and Eu-doped ZnO

3.5. Characterization of as Synthesized Photocatalysts

The solidity structure and size of the nanomaterials influenced by several factors including precursor salts, surfactant additives, temperature and reactant concentrations. To progress consistent synthesis of nanomaterials, characterization is found to be important. Characterization deals with the study of structure, composition and properties of prepared samples (Mudalige et al., 2019).

3.5.1. X-Ray diffraction (XRD)

The structural characteristics of synthesized sample was investigated by the X-ray diffractometer (XRD-7000, SHIMADZU Corporation, Japan) using Cu-Kα radiation (λ = 0.15404 nm) at scan rate of 3°/min. The XRD data was recorded in terms of peaks intensity and 2θ values from 10° to 80° and those data was plotted using origin software. The miller indices of diffraction peaks were indexed according to their corresponding JCPDS files; the diffracted X-rays were then being detected, processed, and counted. Besides, the average crystalline size was calculated from XRD spectra by using Debye-Scherrer equation (Domingues et al., 2024).

$$D = \frac{K\lambda}{\beta cos\theta} = \frac{0.9\ x0.15406}{\text{FWHM}\ cos\theta} \qquad (6)$$

Where, *D*= particle size of the crystal; K = Sherrer constant (usually 0.9); λ = wavelength of X-Ray source, Cu Kα radiation (1.5406 Å); β = full width at half-maximum (FWHM) of the diffraction peak in radian; θ = Bragg's diffraction angle

3.5.2. UV-Vis DRS

The band gap of the prepared materials estimated utilizing UV-Vis diffuse reflectance spectrophotometric technique, which give the information about the optical absorption efficiency of as-synthesized nanomaterials materials (Ray et al., 2022). The optical property of samples was investigated with the ultraviolet-visible disperse reflectivity spectroscopic technique (Carry 100 UV-Vis, Agilent Technologies). The solid sampleswere placed in the sample holder of the DRS instrument, then the reflectance spectrum were collected and the band gap energy of nanomaterials was estimated with help of Kubelka-Munk function plot (Joy et al., 2024).

3.5.3. Photoluminescence (PL)

The emitted light'swavelength of prepared nanomaterials was investigated under optical excitation by a photoluminescence instrument (Cary Eclipse, Agilent Technologies), which gives information about the emission wavelength shift and the reduction of electron holes

recombination (EHR). Lastly, the data was plotted and interpreted in relative to the material's properties and applications (Albert manoharan et al., 2018).

3.5.4. Fourier transform infrared spectroscopy (FT-IR)

The chemical bonding and functional groups which present in fabricated nanomaterials whereconducted by Fourier Transform Infrared spectrometer (FTIR-6600typeA, Jasco). The sample preparation was proceed by mixing small amount of sample with potassium bromide, squeezing it to make a pellet, and putting it on a specimen holder, thus the data was recorded from 400-4000 cm^{-1} (Thennarasu & Sivasamy, 2013).

3.6. Photocatalytic degradation of Methylene Blue Studies

According to the method of recent trails (D. Singh et al., 2024), the photocatalytic efficiency of prepared samples was tested by the degradation of methylene blue dye . The experiments were carried out by taking 100 mL of methylene blue dye in an aqueous solution (10 mg/L) with a required amount of the prepared photocatalysts. In detailed, before illumination, the reaction mixture was stirred continuously in the dark condition for around 30 minutes to formthe adsorption/desorption equilibrium of the dye on the photocatalysts. After 30 minutes, depending on the UV-Vis DRS characterization results of the nanomaterials, a 150 W tungsten halogen lamp as the light source was used. The samples were irradiated directly by focusing light into the reaction mixture at a standard distance from the reactor. Magnetic stirring was applied to continuously mix the solution. The temperature of the overall reactor controlled by a water circulation. With ten (10) minutes interval approximately 4 mL MB solution was withdrawn, the solution was centrifuged to remove the photocatalyst from the sample. The methylene blue dye concentration was measured by UV-vis spectrophotometer (UV-3600 Plus series) at the absorption maximumu wavelength at λ_{max}= 664 nm and reaction dynamics study also understood from the reaction kinetic equation.In this study the mathematical treatment of the reactions was simplified by Pseudo-first-order kinetics equation. This equation enhances data analysis and helps for determination of reaction rate constant.

3.6.1. Effect of some operational parameter

Effects of few operational parameters which are photocatalyst dosage (10, 20 and 30 mg) and percentages (1%, 3% and 5%) of dopants were investigated for the selected catalyst in order to optimize the degradation performance.

CHAPTER FOUR

RESULT AND DISCUSSION

4.1. X-Ray diffraction (XRD) Pattern Analysis

The purity if phases and crystal graphic structure of prepared single and EZOnanomaterials were investigatedusing XRD technique. The X-Ray diffraction pattern peaks of single ZnO, and Eu_2O_3match with the hexagonal wurtzite (JCPDS# 00-036-1451) and monoclinic (JCPDS# 00-043-1008) structures, respectively. The detected diffraction patterns for ZnO NPs occurred at 31.5, 34, 36, 47.5, 56.5, 63, and 67° 2θ values, as corresponding to (100), (002), (101), (102), (110), (103), and (112) lattice planes, correspondingly as depicted in (Fig. 9a). At all percentages of dopant concentration (1, 3, and 5%), the Eu^{+3}-doped ZnO (EZO) NanocompositeXRD peaks revealed only a scattering patterns similar to the wurtzite structure of ZnO, confirms the fascinating incorporation of Eu^{+3} rare earth metal ion within the ZnO lattice. Besides, there are no scattering peaks of Eu_2O_3observed in the X-Ray diffraction patterns of Eu^{+3}-doped ZnO (EZO) Nanocomposite. All the diffraction patterns of doped materials are shifted to lower 2θvalue, this is due to the increase in lattice strain by doping ofEu^{+3} ions which have greater ionic size (0.95 c) than ionic radius of ZnO (0.74 Å) in tetrahedral coordination (Al Rifai & Kulnitskiy, 2013). According to the above facts, it's reasonable to deduce that the solubility of europium ion in the ZnO matrix is much better. Therefore, the nonappearance of the Eu_2O_3crystal phase is also described to be associated its high dispersion and minimum density distribution (Wang et al., 2022).

The average crystalline size of ZnO NPs and Eu^{+3}-doped ZnO (EZO) Nanocompositewas calculated using the Debye-Scherer equation.($K\lambda/\beta cos\theta = (0.9\ x\ 0.15406)/(\text{FWHM}\ cos\theta)$ where, *D*denotes the crystal average particle size; *k*denotes the Sherrer constant, which is taken as 0.9 for this study; λ represents a wavelength of X-ray source at Cu Kα radiation (0.15406 nm); β denotes diffraction peaks full width at mid-peak; and θ is Bragg's angle of diffraction.

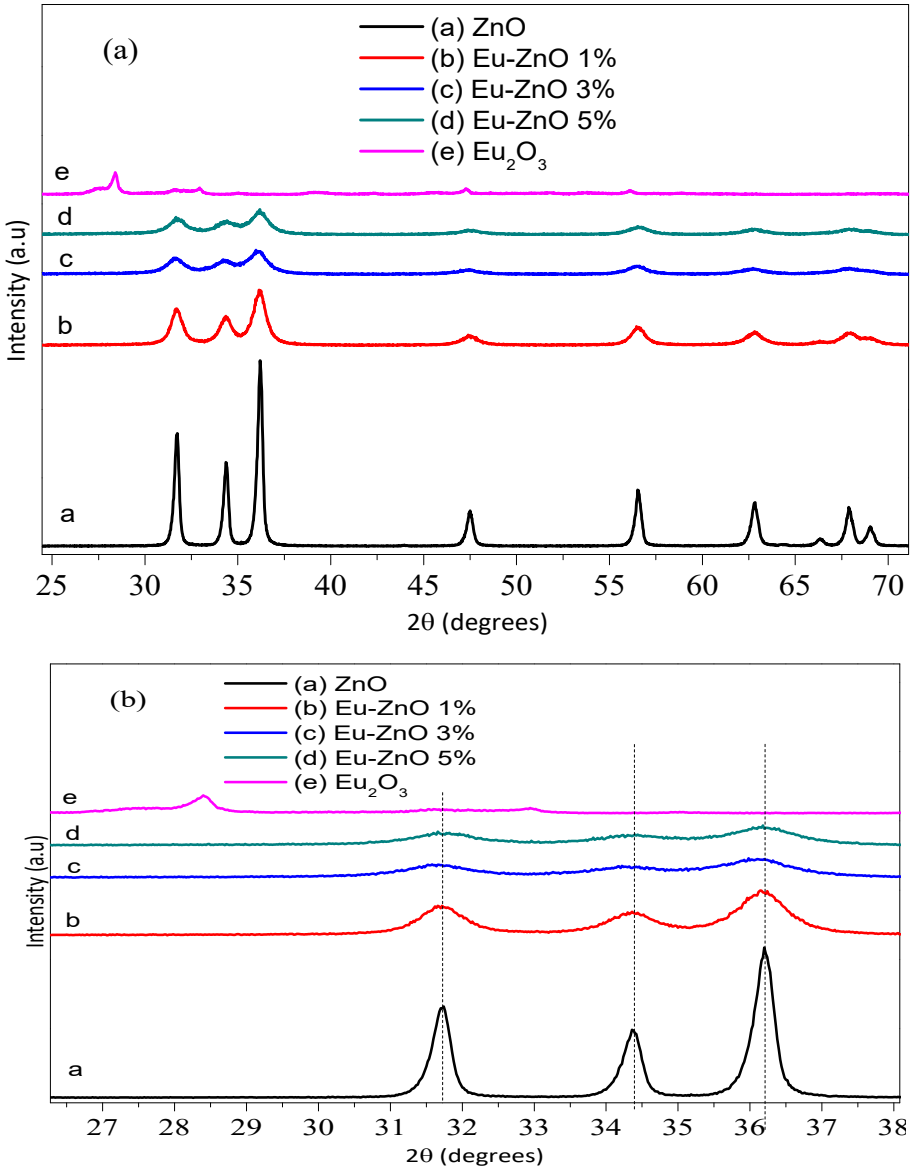


Figure 9:(a) XRD pattern plots of ZnO, and doped ZnO with 1, 3 and 5% of europium ion; (b) the magnified view of the plots.

4.2. UV Visible-DR-Sanalysis

The DRS-UV-Vis spectra analyses were used for the investigation of optical propertiesof the prepared ZnO and different percentage of Eu^{+3}-doped ZnO (EZO) Nanocomposite is presented in Fig. 10 (a-c). As shown Fig.10a; the strong reflection band at about 380-400nm is due to the ZnO's near band vergedistinctive reflection. The reflection bands at higher wavelength are also reported to be 4f → 4felectron transition, confirming the inclusion of europium ion with in ZnO lattice(El Jouad et al., 2020).

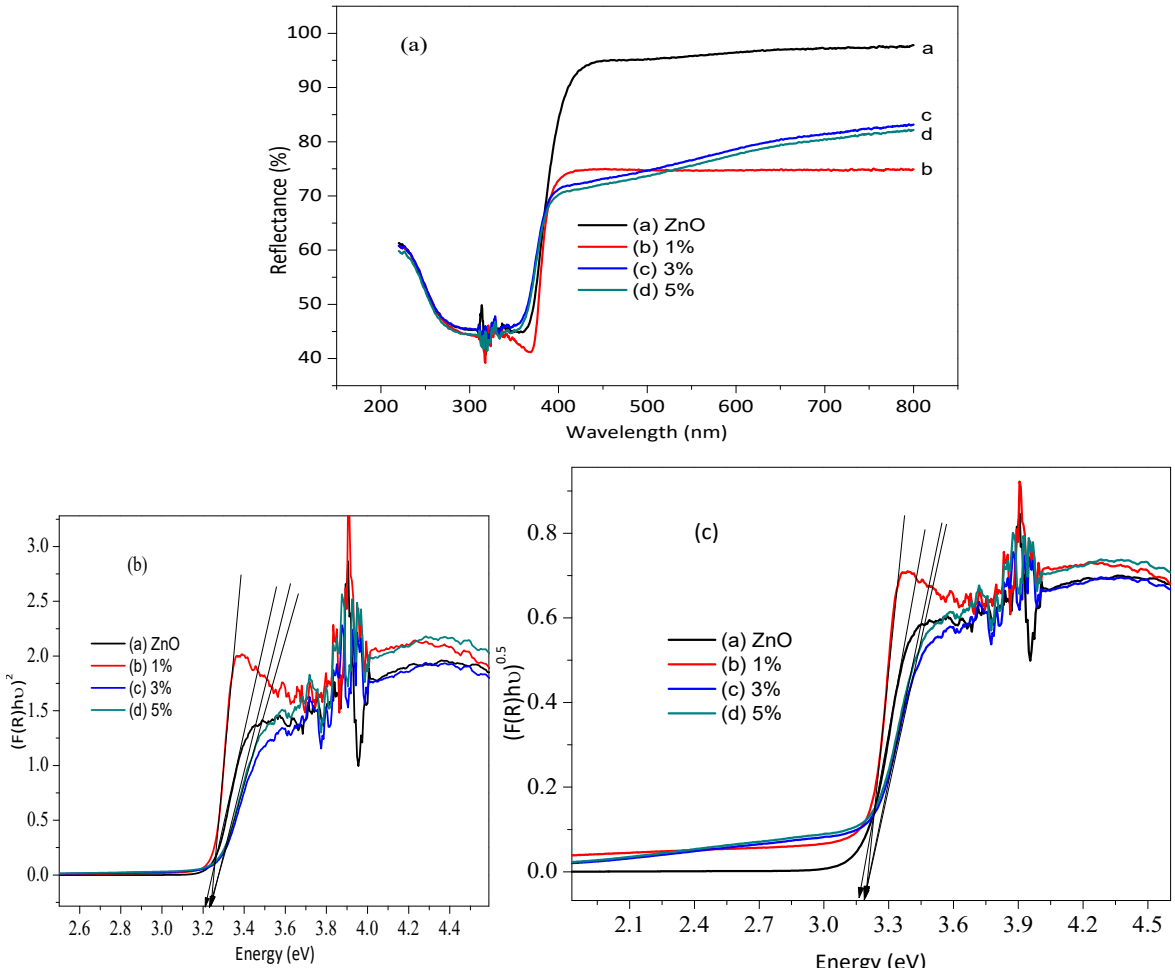


Figure 10: (a) DRS-UV-vis analysis spectrum of ZnO and Eu^{+3}-doped ZnO (b) respective indirect ZnO and EZO Nanocomposite Kubelka–Munk function plot,(c) the direct ZnO and EZO Nanocomposite Kubelka–Munk function plot.

The semiconductor materials are classified in to direct and indirect based on the precious stone momentum (*k-factor*) values. When the *k-factor* value in the maximum valence band (VB) and minimum conduction band (CB) is equal the materials said to be direct semiconductor materials. Then, the electron at higher level pairs up and directly emits the absorbed light. Conversely, in the indirect materials, the *k-factor* value turn out to be different, thusthe excited electron gets relaxation time. Throughout this relaxation time theholes react with waterand also electron interact with oxygen to produce the highly reactive species, hydroxyl radicals (•OH). In the Eu^{+3}-doped ZnO nanocomposites, the incorporation of europium in the ZnO matrixforms defects within the VB and CB, which helps electron relaxation. Therefore, the direct and indirect bandgap energy of synthesized Eu^{+3}-doped ZnOwas considered and

calculated based on the Kubelka–Munk function plot (Fig. 10 a-b). The estimated direct band gap energy for Eu^{+3}-doped ZnO was found to be slightly comparable to that of ZnO (3.22 eV) and also the direct band gaps are found to be approximately 3.19 eV.

4.3. Photoluminesence (PL)

Photoluminesence is produced from a semiconductor materials when excited electrons in higher energy level back to lower energy level by the releasing of energy difference via photon emission (Tebyetekerwa et al., 2020). The instrument used in this study was a Fluoresence Spectrometer, here in principle this type of instrument when the samples experiencing internal energy transition by releasing photon energy before returns to ground state some amount of absorbed energy get released such that the emitted light has minimum energy than the absorbed light. The photoluminescence spectra for ZnO NPs and Eu^{+3}-doped ZnO (EZO) Nanocomposites are presented in Fig. 11. The spectral analysis was conducted at excitation wavelength of 325nm. As the information obtained from the spectra, the samples have broad emission spectrum from 360nm to 550nm. The near-band edge (NBE) emission peak occurred at 395nm, it is typical electron-hole recombination emission peak of ZnO(Kandasamy et al., 2024). The others additional three important emission peaks in the visible region are associated with internal imperfections of the interstitial of Zn and O (Zn_i and O_i), antisites (Zn_O, O_{Zn}) and vaccancies (V_{Zn}, V_O) (Sedky et al., 2023).The violet emissions peaks at about (420-423nm) is related to an electron transition from donor level to the valence band of ZnO (H. Naseer & Iqbal, 2024). The blue emission peaks at about 441nm is due to an electron transition between acceptor levels and conduction band of ZnO. The green emission (484-486nm) related to the transition of electrons between vaccancy of oxygen (V_O) and vaccancy of zinc (V_{Zn}) (Gebretsadik et al., 2024). Moreover,Fig. 11.revealed the two important effect of Eu^{+3}-doped ZnO (EZO) Nanocompositeon emission peaks, those are shifting of peaks toward higher wavelength with increasing dopants concentration and reduction in intensity of peaks. A reduction in intensity confirms minimum electron-holes recombination rate (Gebretsadik et al., 2024). Furthermore, there is a slight shifting of spectrum to higher wavelength for the Eu^{+3}-doped ZnO (EZO) Nanocomposite compared to the ZnO.

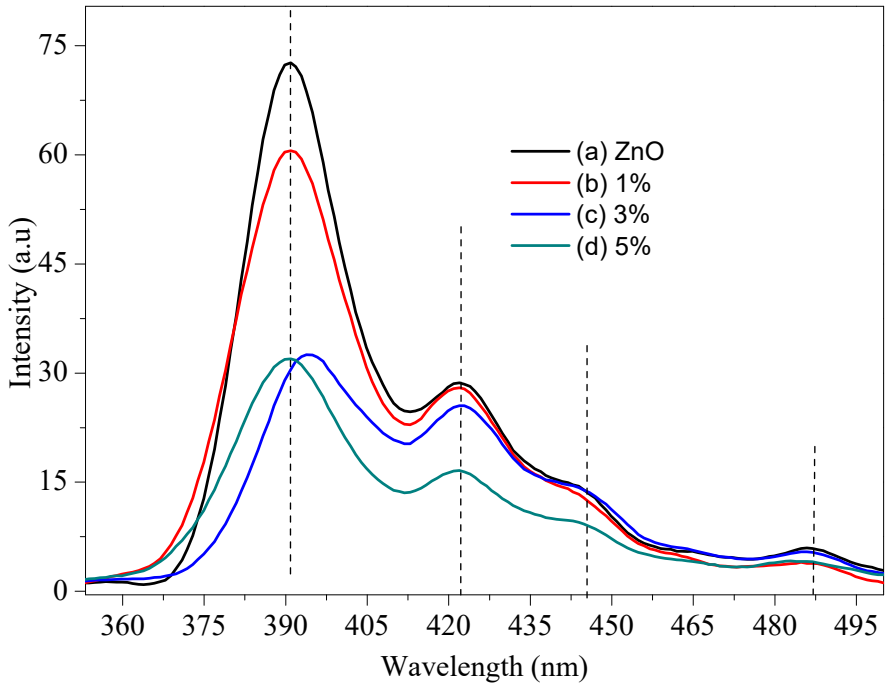


Figure 11: Photoluminescence spectra plot of ZnO and Eu^{+3}-doped ZnO (EZO)Nano composite. 1%, 3% and 5% represent the percentage of Eu^{+3} ions.

4.4. Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

The functional group and chemical bonding information were investigated using the FTIR instrument, as depicted in Fig. 12. The band occurred at around 3500cm^{-1} is due to the O-H stretching vibration band associated tothe interstitial or surface adsorbed water molecules. The metal-oxygen (M-O) bond bending vibration were detected in the fingerprint region, which is below 1000cm^{-1} are due to transverse optical stretching modes (Anžlovar et al., 2011). The strong absorption bands occurred at about720$cm^{-1}$is due to the vibration of ZnO(Xiong et al., 2006). There are numerous bands occurred in the range of 3500-900cm^{-1}, these maybe associated with the leftover impurities that appearedwhen the synthesis was conducted. The broad absorption band detected at 1450cm^{-1} is associated with the C-H bending vibration (Gemmech et al, 2022),

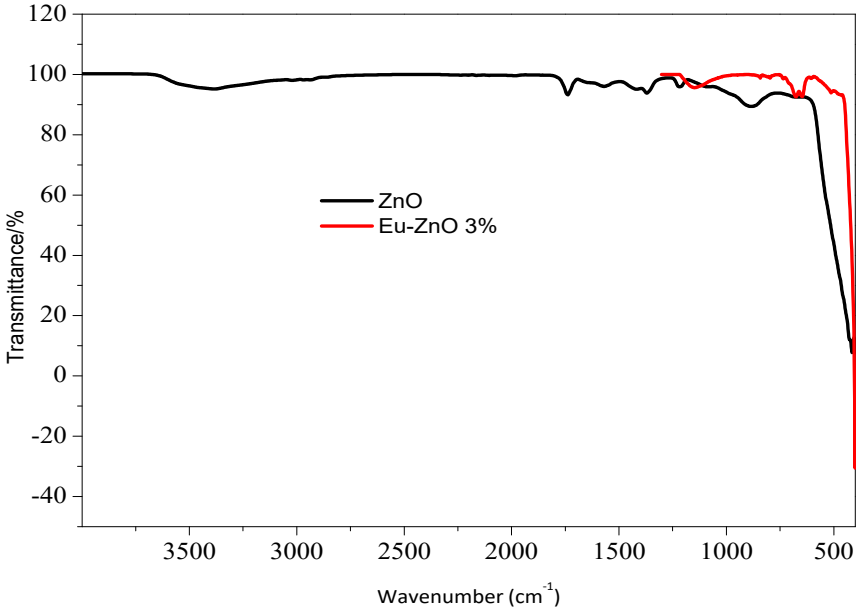


Figure 12: FTIR spectra plot of ZnO and Eu^{+3}-doped ZnO (EZO) Nanocompositeafter calcinations of prepared samples.

4.5. Photcatalytic Activities

The photocatalytic degradation performance enhanced withthe formation of more defects on the surface of porous nanomaterials (Sun et al., 2016). Recently, metal oxide semiconductor catalysts were playing important role in photocatalytic decomposition of methylene blue; ZnO has been studied widely for the decomposition of organic dyes(Khalid et al., 2023). It is certain that, during ZnO photocatalyst exposed to a light that have sufficient energy forms electron - holes pairs on the catalyst surface. The resulting holes interact with water producing strong oxidizing agent hydroxyl radicals (·OH) and also the electrons react with oxygen provides super-oxide radicals, subsequentlyit forms more hydroxyl radicals (Cheng et al., 2020). Then, MB adsorbed on the photocatalyst, the hydroxyl radicals react with MB and converts to harmless products. Though, the issue of electron-hole recombination will be occurred when using ZnO NPs as a photocatalyst (Meky et al., 2023). The doping of rare earth elements is among the recent reasonable trialstosolve these limitation of ZnO catalyst(Gebretsadik et al., 2024,).

The synthesized ZnO NPs and Eu^{+3}-doped ZnO (EZO)Nanocomposite were utilized as a photocatalyst for methylene blue degradation. The maximum absorption wavelength of methylene blue dye is at about 664nm. The degradation curve of methylene blue dye in aqueous solution by prepared photocatalysts is depicted in Fig. 13 and 15. The amount of

photocatalystswas kept 10mg in 10g/mL of Methylene blue and the experiment was conductedat pHabout 10. Hereinthis study, an adsorption test was carried out in the dark condition for 30min. Thus, the samples were centrifuged and the absorbance was collected by UV-Vis spectrophotometer. When absorption of light carried out the blue color of methylene blue converts to colorless slowly as the time increases. Based on the information obtained from the graphs, the absorbance of solution in the presence of ZnO NPs was greater relative to other composites, which confirms the less degradation efficiency of ZnO ($k=0.025\ min^{-1}$) as compared to other composites. But, when ZnO was doped with different percentages of europium ion, the absorbance were decreased with the correlatedamounts, which indicate excellent degradation ability of methylene blue dye. These improvement in degradation of methylene blue is related with the enhancement of absorption of light through doping of Europium ion (M. Kumar et al., 2021).

4.5.1.Percentage effect

The absorbances of suspension in the existence of different percentages of Europium dopant(1%, 3% and 5% EZO) was reducedcompared to ZnO NPs, which confirms high degradation efficiency of blends. The enhanced photocatalytic efficiency of EZOdue to visible light absorption advancement associated to dopants effect (Das et al., 2021).Moreover, the photocatalytic activity of EZO blends was reduced with the dopant amounts increased from 1% to 5% EZO, this is related to the formation of more defects on the ZnO crystals, which improves surface area and slightly disturbance crystallinity of catalysts(Hanh et al., 2024). Nano compositesthat have good crystallinity and larger surface area provides more active site for catalytic reaction center, ultimately the photocatalytic degradation efficiency was enhanced (Chong et al., 2024).

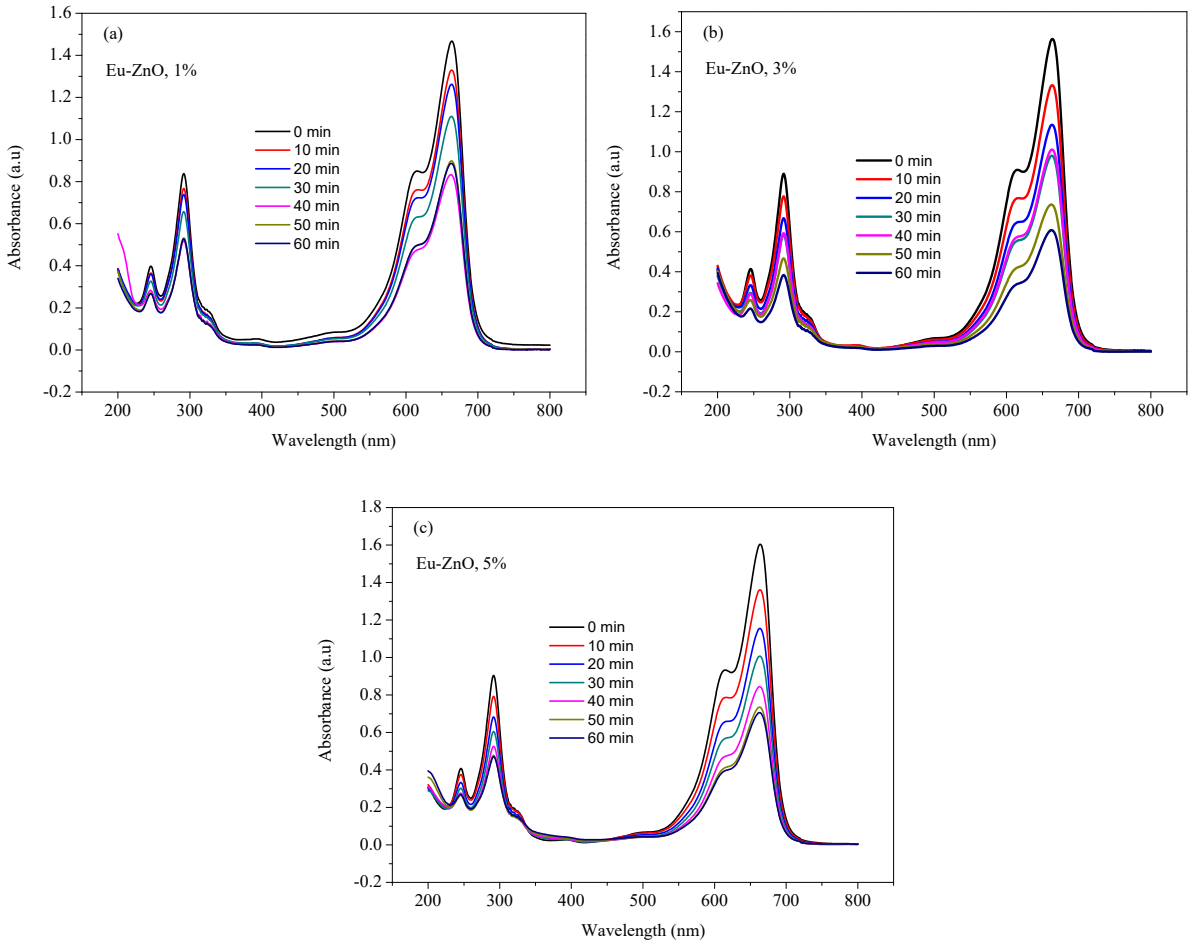


Figure 13:The percentage effect plots of absorbance versus wavelength (nm) of (a) 1% EZO, (b) 3% EZO, and (c) 5% EZO;

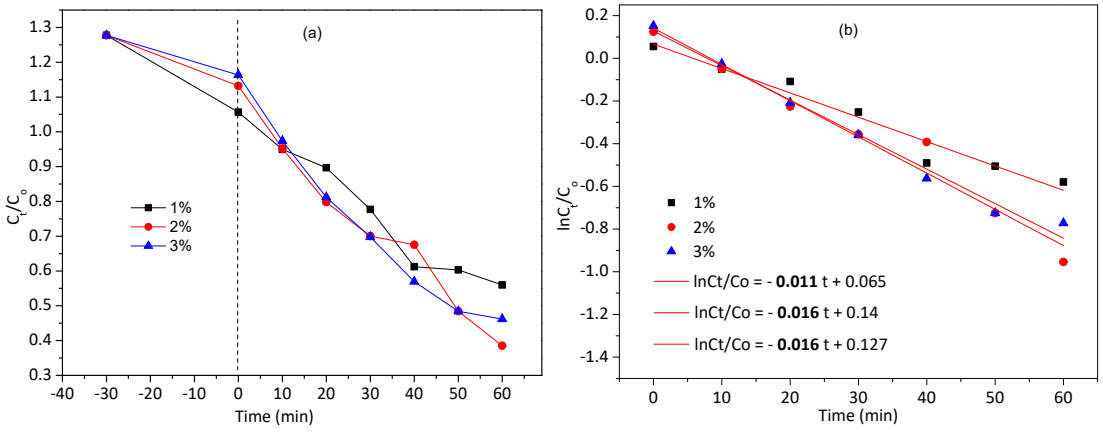
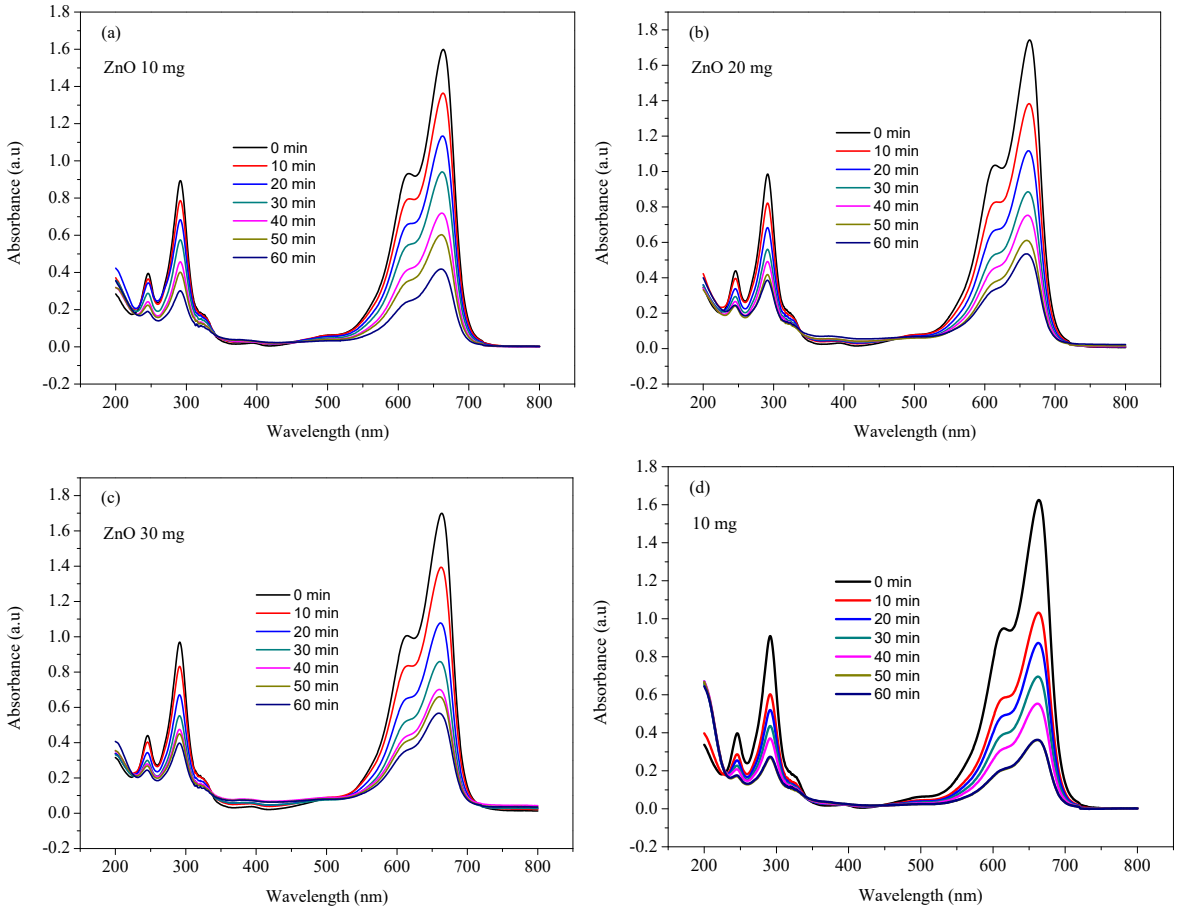


Figure 14: (a) the $\frac{Ct}{C_0}$ versus time (min) plot of different percentages of nanocomposites, (b) $ln\frac{c_t}{c_0}$versus time (min) plot of NPs and heterostructures

4.5.2. Dosage effect

The amount of photocatalyst is the considerable operational parameter in the photocatalytic degradation of pollutants(Ahmad et al., 2020). In this study, the dosage effect of ZnO NPs and EZO catalysts on photocatalytic degradation of MB was investigation as presented in Fig. 15 (a- f). As the dosage of ZnO or EZO photocatalyst increases beyond an optimal point, the rate constant decreases due to several factors. Higher catalyst loading leads to excessive light scattering and shielding, reducing the penetration of photons into the solution and limiting electron–hole pair generation. Moreover, agglomeration of particles at higher concentrations decreases the effective surface area and active sites, while increased turbidity causes mass transfer limitations. These combined effects lower photocatalytic efficiency, explaining the decrease in the reaction rate constant with excessive catalyst dosage(Akpan& Hameed, 2009), which decrease the number of active sites on the surface of catalyst that are open to light exposure.



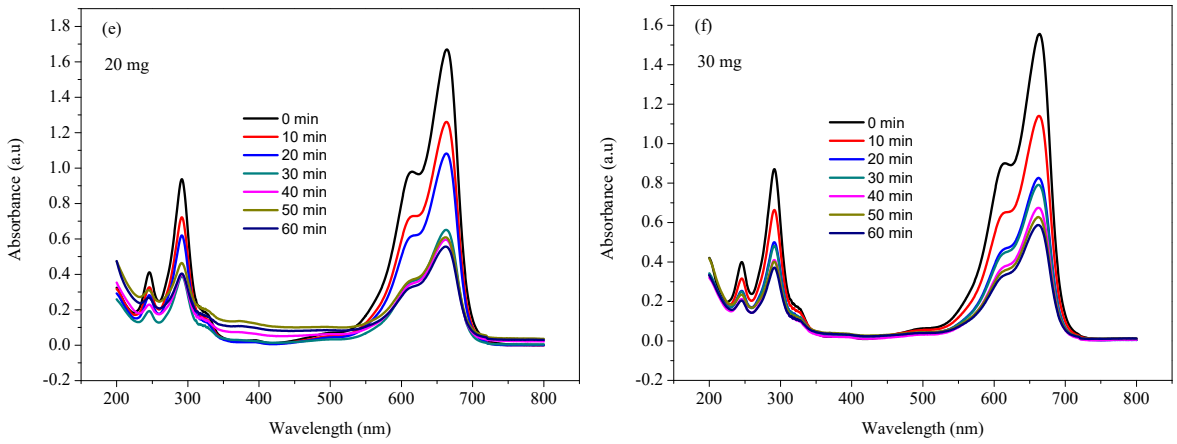


Figure 15:The dosage effect plots of absorbance versus wavelength (nm) of EZOnanocomposites; (a) 10 mg ZnO, (b) 20 mg ZnO, (c) 30 mg ZnO, (d) 10 mg 1% EZO, (e) 20 mg 3% EZO, and (f) 30 mg 5% EZO

The determination of the pseudo-first-order rate constant for degradation ofmethylene blue dye was conducted by plotting $ln\frac{c_t}{c_0}$ versus irradiation time (Das et al., 2021). The graphs of $ln\frac{c_t}{c_0}$vs irradiation time as shown in Fig. 16,provides the rate constant for each photocatalysts from the slope of curves. The estimated rate constant for 10mg ZnO, 20mg ZnO,30mg ZnONPs, 10 mg of 1% EZO, 20mg of 3% EZO, 20 mg of 5% EZOwere found to be 0.025, 0.023, 0.021, 0.03, 0.02 and 0.01 min^{-1}.

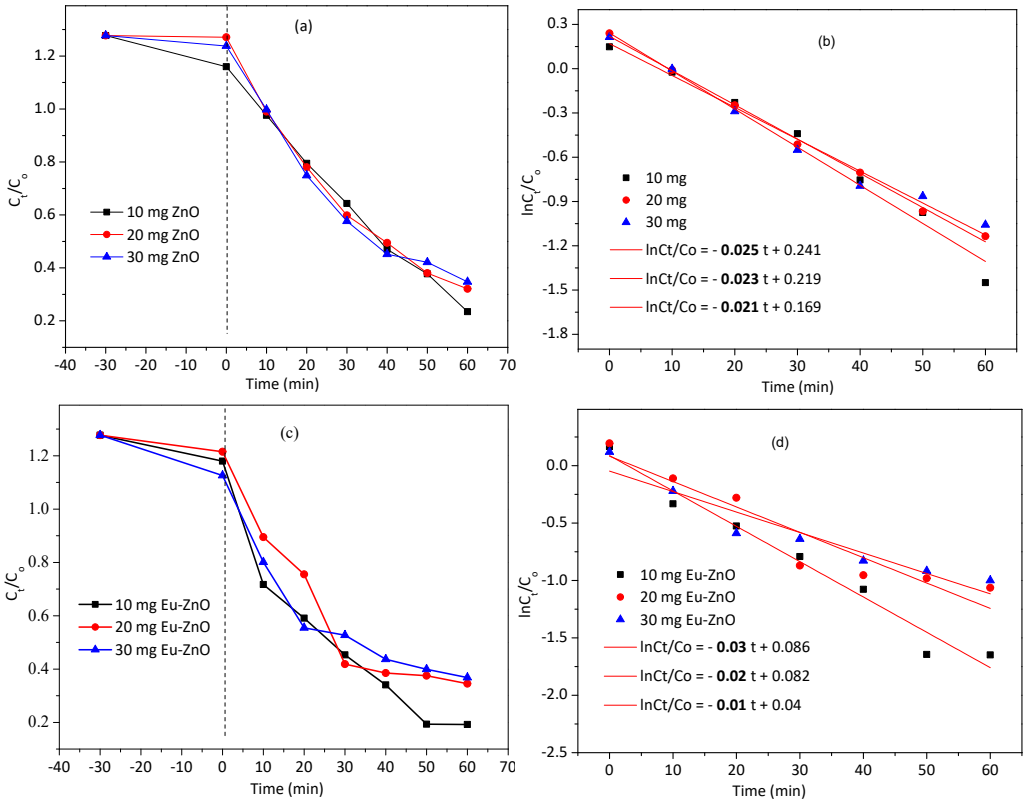


Figure 14: (a) the plots $\frac{Ct}{C_0}$ versus time (min) of NPs and composites, (b) $ln\frac{c_t}{c_0}$versus time (min) plot of NPs and composites

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Here, a single phase hexagonal wurtizite ZnO and Eu^{+3}-ZnO nanocomposite with the percentages of (1%, 3%, and 5%) were successfully synthesized using the simple solution combustion synthesis method. The effective doping of europium ions within the ZnO lattice is ensured by the shifting of ZnO XRD patterns and the disappearance of an independent europium oxide peak. UV-Visible diffuse reflectance spectroscopic and photoluminescence investigations confirmed the enhanced optical properties of ZnO through the doping of Europium. FTIR spectral analysis revealed the expected functional groups and chemical bonding in Eu^{+3}-doped ZnO nanocomposites, typically the metal-oxygen bonds.

Finally, the photocatalytic degradation efficiency of the prepared samplewas tested on methylene blue (MB) dye; Eu^{+3}- doped ZnO nanocomposite ($k=0.3\ min^{-1}$) showed better photocatalytic degradation ability than single ZnO nanoparticles ($k=0.02\ min^{-1}$). This is associated to the advancement of ZnO optical properties through the incorporation of Europium ion within ZnO lattice.

5.2. Recommendation

According to the findings of this study, it is recommended that further research be carried out to optimize more operational parameter of photocatalytic degradation efficiency, the use of another types of dopants and the application of synthesized nanomaterials different areas such as biological activities (antibacterial, antifungal, anticancer) energy and sensors applications. This research tested only photocatalysis potential of prepared samples on real dye. Then, further research should be tested on dyes that are released from different factories and to be conducted on other type of synthetic dyes. In addition, to get more clear information about the formation of doping with metals, an advanced analytical technique like SEM,HR-TEM, and X-ray photoelectron spectroscopy (XPS) are advisable techniques.Besides, In order to ascertain which reactive species are typically involved in the photodegradation of the methylene blue dye, scavengers test is recommended to conduct that used during photoreaction.

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