

***Moringa Stenopetala* (Shiferaw) Seed Extract Mediated Synthesis of α -Fe₂O₃
Nanoparticle for Photocatalytic Degradation of Methylene Blue Dye**



Olika Mamo Raga

A Thesis Submitted to the Department of Applied Chemistry

School of Applied Natural Science

Presented In Partial Fulfillment of the Requirement for the Degree of

Master of Science in Applied Chemistry (Industrial Chemistry)

Office of Graduate Studies

Adama Science and Technology University

June, 2023

Adama, Ethiopia

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Advisor: Gemechu Deressa (Ph.D.,Associate Professor)

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DECLARATION

I declare that this thesis entitled “***Moringa Stenopetala* Seed Extracted Mediated Synthesis of Hematite Nanoparticles for Photocatalytic Degradation of Methylene Blue Dye**” is my original work. That is, has not been submitted for the award of any academic degree, diploma or certificate to any of the university. All sources of this material that are used in this thesis are duly acknowledged through proper citations.

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Name of student

Signature

Date

RECOMMENDATION

I, the advisor of this thesis, hereby certify that I have read the revised version of this thesis entitled “*Moringa Stenopetala* Seed Extract Mediated Synthesize of Hematite Nanoparticles for Photocatalytic Degradation of Methylene Blue Dye” prepared under my guidance by **Olika Mamo Raga** submitted for partial fulfillment for the requirements for the degree of Master of Science in Applied Chemistry (Specialization in Industrial Chemistry). Therefore, I recommend the revised version of the thesis to the Department following the applicable procedures.

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APPROVAL PAGE

I, the advisor of this thesis entitled “***Moringa stenopetala* Seed Extract Mediated Synthesis of α -Fe₂O₃ Nanoparticles for Photocatalytic Degradation of Methylene Blue Dye**” and developed by **Olika Mamo Raga**, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated in to the final version of this thesis.

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We, the undersigned, mebers of the boards of examiners of the thesis by Olika Mamo Raga have read and evaluate the thesis entitled “***Moringa stenopetala* Seed Extract Mediated Synthesis of α -Fe₂O₃ Nanoparticles for Photocatalytic Degradation of Methylene Blue Dye**” and exmained the candidate about during open defense. This is, therefore, to certify that this thesis is accepted for partial fulfillments of the requirement of Degree of Master of Science in Applied Chemistry (Specilaization in Industrial Chemistry).

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LIST OF ABBREVIATIONS AND ACRONYMS

CB	Conduction band
COD	Chemical oxygen demand
e-	electron
FTIR	Fourier transform infrared spectroscopy
IONPs	Iron oxide nanoparticles
MB	Methylene blue
MSS	Moringa Stenopetala seed
NPs	Nanoparticles
PZC	Point of zero charge
SNNRP	South Nations & Nationalities' Representative of People
rad	Radian
rpm	Revolution per minute
SEM	Scanning electron microscope
TGA	Termogravimetric analysis
UV-VIS	Ultraviolet-visible spectroscopy
VB	Valence band
XRD	X-ray diffractometry

ABSTRACT

Photocatalytic degradation of organic pollutants is an effective technology for the treatment of industrial wastewater. This study focused on the green synthesis of hematite nanoparticles using Moringa stenopetala seed extract for effective photocatalytic degradation of methylene blue dye under sunlight irradiation. Hematite (α -Fe₂O₃) NPs were synthesized via precipitation process with seed extract acting as a capping and reducing agent. The synthesized α -Fe₂O₃ nanoparticles were characterized using thermo gravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-visible spectroscopy (UV-Vis), and Fourier transform infrared (FTIR) spectroscopy. TGA confirms the synthesized hematite nanoparticles were calcinated at 600 °C. The XRD result confirmed the formation of a rhombohedral centered hexagonal structure of α -Fe₂O₃ NPs with an average crystallite size of 32.57 nm. From UV-Vis analysis, the appearance of the maximum peak at 313 nm and the calculated band gap energy of 2.744 eV highly confirm the development of α -Fe₂O₃ NPs. From the FT-IR data, the peak at 538 cm⁻¹ indicates the formation of characteristic Fe-O bonds. The functional group responsible for the formation of α -Fe₂O₃ nanoparticles was revealed by Fourier transform infrared radiation. The photocatalytic application of α -Fe₂O₃ NPs for photocatalytic degradation of methylene blue dye using direct solar light irradiation. The degradation efficiency of 98.33% was achieved at pH 12, catalyst dosage of 0.05 gm, and 30 mg/L of dye at 90 minutes. The degradation efficiency of MB dye was varied with the pH of the solution, concentrations of dye, and dose of α -Fe₂O₃ NPs for a certain interval of time. The calculated chemical oxygen demand (COD) value indicates the elimination of the dye, and the recyclability experiment indicates the fabricated α -Fe₂O₃ NPs have high stability and can be used for several times.

Keywords: α -Fe₂O₃, Photocatalytic degradation, moringa stenopetala seed, green synthesis

1. INTRODUCTION

1.1. Background of the Study

The most important natural resource on earth for maintaining life is water. For better health and ecological function, providing clean water is the most important thing for human beings. Water contamination results when pollutants are dumped into water bodies without being properly treated. Plants and animals that live in bodies of water are affected by contaminated water. It also affects individual species, populations, natural biological communities, and consumers. Water bodies have been contaminated by various types of pollutants, which lower the quality of water due to the rapid growth of industries, increased human population, agricultural activities, and excessive use of chemicals (Fouda et al., 2021). The discharge of large quantities of contaminants including fertilizers, pesticides, dyes, surfactants, phenols, and nutrients could potentially affect the well-functioning of the ecosystem. Among all chemicals, dyes are the most noticeable aquatic hazardous substances responsible for environmental pollution released by a variety of industries, including textile, cosmetics, rubber, food, printing, paper, and pharmaceuticals (An et al., 2019). The textile industry uses about 700,000 tons of dye annually worldwide (Aguayo-Villarreal et al., 2020). There are more than 10,000 dyes used in textile manufacturing alone, which are complex in structure and synthetic in nature (M. Hassaan et al., 2017). During printing and dyeing processes, about 10-20% of dyes are discharged from textile industries and discharged into the natural environment and water bodies without proper treatment (Amsayazhi & Mohan, 2018). Untreated dyes cause serious health problems for aquatic living organisms as well as the environment due to their toxic, carcinogenic, and mutagenic effects. They form harmful hazardous diseases, such as allergies, skin diseases, mutations, and cancer, and also affect the kidneys, liver, brain, and central nervous system. Dyes in the water system prevent the penetration of light, which affects the photosynthesis of aquatic life and decreases the amount of dissolved oxygen (Samchetshabam et al., 2017).

Among the different classes of dyes, methylene blue is a basic synthetic dye that is largely applied as a coloring agent in the textile, pharmaceutical, paper, dyeing, and food industries. It has been widely used for a number of medicinal purposes, both in the human and veterinary sectors. Methylene blue has toxic, carcinogenic, non-degradability, and stability properties. As a

result, it can lead to health problems including anemia, nausea, vomiting, abdominal disorders, blindness, respiratory distress, and gastrointestinal problems (Sagadevan et al., 2021). Degradation of MB dye from industrial wastewater is an important issue due to its characteristics of being non-degradable easily and persistent for a longer period in the environment. To respect environmental norms, the toxic materials should be degraded before their disposal.

Numerous conventional methods have been employed to treat industrial wastewater, including adsorption, precipitation, electrochemical treatment, filtration, coagulation, biodegradation, ozonization, flocculation and so on (Y. Zhou et al., 2019). However, the majorities of these technologies have issues with secondary pollution problems, operation requires a long time, is expensive, and requires the disposal of large amounts of sludge. Therefore, it is important to develop an efficient and environmental-friendly technology for treating of industrial effluents.

Advanced oxidation processes are defined as oxidation processes involving the formation of reactive species, mainly hydroxyl radicals, as successful methods for organic pollutant degradation. Advanced oxidation processes are effective for the destruction of organic pollutants include photolysis, ozonization, the photo-fenton process, and the photocatalytic process. Among advanced oxidation processes, photocatalytic processes has become the best successful techniques, for breaking down the majority of organic pollutants (Aaga & Anshebo, 2023). Because of their relative low-cost and high stability, low-toxicity, operation in an ambient environment, and increased ability to degrade organic pollutants into harmless compounds (Khaki et al., 2017). In this regard, photocatalytic degradation of persistent organic pollutant is applied by activation of a photocatalyst using sunlight. The photocatalytic degradation mechanism involves the activation of semiconductor materials by light energy, mostly in the ultraviolet and visible regions of light, to generate electron and hole (e^-/h^+ pairs) semiconductors in the CB and VB, respectively. These photogenerated (e^-/h^+ pairs) react with dissolved oxygen and water to produce superoxide radicals and hydroxyl radicals respectively. Then, the produced radicals attack the organic pollutant in wastewater and decompose into smaller, harmless products. The total mineralization of organic pollutants does not generate secondary pollution, a simple and easy treatment procedure, or complete degradation to produce water and carbon dioxide (Shenoy et al., 2021). However, this photocatalytic technology is affected by a wide

band gap energy, poor light absorption, fast recombination rates of photo-induced electrons and holes, and pH dependence (Koe et al., 2019).

The photocatalytic process using semiconducting metal oxides and sunlight generates very reactive hydroxide radicals, which could attack the toxic organic contaminants and convert them into nontoxic products. The dye molecules in the water were degraded through the electron hole pair process (M. A. Hassaan & Nemr, 2017). For photocatalytic degradation of organic dyes, there is a need to prepare different nanomaterials, including metal and metal oxide nanoparticles such as titanium (IV) oxide (TiO_2), zinc oxide (ZnO), iron (III) oxide (Fe_2O_3), and copper (II) oxide. Among this metal oxide, $\alpha\text{-Fe}_2\text{O}_3$ is an n-type semiconductor photocatalyst that has the advantage of being abundant, cheap, and environmental-friendly (Domacena et al., 2020). Hematite shows rhombohedrally centered hexagonal structure of the corundum type with a densely packed oxygen lattice. It is thermodynamically stable iron oxide with a narrow band gap, which theoretically allows it to absorb light energy at a wide range of wavelengths. It is an important material for the photocatalytic system due to its suitable band gap, low cost, non-toxic, environmental friendliness and magnetic nature (Liu et al., 2013). It is economical and resistant to corrosion, which marks it a potential candidate for photocatalytic applications, which could collect up to 40 % of the solar spectrum energy. There are a number of methods available to synthesize $\alpha\text{-Fe}_2\text{O}_3$ NPs, including co-precipitation, hydrothermal, sol-gel, solvothermal, ultrasonication, and microwave methods (Asoufi et al., 2018). However, the above techniques require toxic chemicals, specialized equipment, energy-consuming operating conditions, high costs, high temperatures, and pressure. The toxic byproducts generated from the chemical methods lead to environmental pollution. Hence, there is a need for a cheap and clean process of synthesis to produce nanoparticles (Bishnoi et al., 2018).

This research focused on green synthesis of $\alpha\text{-Fe}_2\text{O}_3$ NPs using *Moringa stenopetala* seeds aqueous extract for the photocatalytic degradation of MB dye in wastewater under visible light irradiation. *Moringa stenopetala* is a member of the Moringaceae family, which includes shrubs and trees grown across the tropical zone, including Ethiopia. There are 13 species in the genus *Moringa*, but only *Moringa oleifera* has received research and development attention. *Moringa* is a multipurpose tree of significant economic importance, as it has vital nutritional, industrial, and medicinal applications (Caudell et al., 2015). *Moringa stenopetala* is a tree

indigenous to East Africa, mainly present in northern Kenya and the southern part of Ethiopia, and it is known by different vernacular names: ‘Haleko’ in Gofa and Wolayta areas, ‘Shelagta’ in the Konso language, ‘Shiferaw’ in Amharic: and cabbage tree in English (Addis et al., 2014). Because of its high nutritional content and appearance towards the end of the dry season, *Moringa stenopetala* is particularly important as a significant source of food for humans. *Moringa stenopetala* grows naturally in well-drained soils at altitudes of 900-1200 m. The species is quite drought resistant. In southern Ethiopia, it has been found in areas with mean annual rainfall ranging from 500-1400mm.

The seeds of *Moringa stenopetala* powder, which is the best natural coagulant used for wastewater purification and is easily available and effective for the removal of heavy metals, could be an innovative and economical approach for the treatment of industrial wastewater (Melsse & Berihun, 2013). The *Moringa stenopetala* seed is an important source of oil that could be used for cooking or for different industrial applications (Ejigu et al., 2010). *Moringa stenopetala* seed extracts could be promising natural antimicrobial agents with potential applications in controlling bacteria that cause water-borne diseases. The presence of secondary metabolites in the *Moringa stenopetala* seed, such as alkaloid, steroids, isobutyl thiocyanate, glucosinolates, and protein, is responsible for the reducing and stabilizing agents (Habtemariam, 2017). The presence of bioactive chemicals contributes to *Moringa stenopetala* seeds anti-cancer properties. Isothiocyanates are of major interest for their biological activities, such as their anticancer, antidiabetic, antimicrobial, and anti-inflammatory effects. The *Moring stenopetala* seed, which has therapeutic potential along with the socioeconomic significance of the plant, has been used recently for study.

1.2. Statement of the Problem

Organic dyes are the main pollutant discharged to the environment, especially from the textile, leather, tanning, paper, pharmaceutical, cosmetic, and plastic industries. These organic dyes are stable and persistent, and they are hazardous and toxic compounds that cause abnormal urine and stool color, burning eyes, and irritation of the gastrointestinal tract with symptoms of nausea, diarrhea, and vomiting. Also affect aquatic bodies because they block sunlight and thereby reduce dissolved oxygen concentrations (Nagajyothi et al., 2020). Methylene blue is a common organic dye used primarily for coloring, printing, and medical treatment in different industries.

The discharge of methylene blue dye pollutants without treatment can cause serious problems for environmental and human health. Due to its intricate aromatic structure, hydrophilic makeup, and great light stability, it is not biodegradable. The removal of this dye from industrial wastewater using conventional wastewater treatment is time-consuming, costly, and poses disposal problems, and often transfers pollutants from one phase to another, causing other serious health problems (Solomon et al., 2012).

Therefore, heterogeneous photocatalysis is a promising technique for effective photocatalytic degradation of these pollutants. Photocatalytic degradation is currently an effective, simple, low-cost, and environmental friendly process that converts pollutants into harmless products. For this purpose, several metal oxide nanoparticles have been synthesized and applied. But most of them require high-energy irradiation, which is not cost effective and energy consuming. Among several metal oxides, α -Fe₂O₃ has the advantage of using solar energy for photocatalytic applications because of its lower bandgap and thus could absorb a significant portion of light over a wider range of wavelengths (Sebatini et al., 2020). In addition, α -Fe₂O₃ exhibits better physio-chemical stability in the aqueous medium, it is economical, and non-toxic which makes it a potential candidate for photocatalytic applications that could collect up to 40 % of the solar spectrum energy (Alagiri & Hamid, 2014).

1.3. Objectives of the Study

1.3.1. General Objectives

The general objectives of the study are to synthesize, characterize, and study the photocatalytic degradation efficiency of α -Fe₂O₃ nanoparticles.

1.3.2. Specific objectives

- To synthesize α -Fe₂O₃ nanoparticles through a green synthetic pathway using *Moringa stenopetala* seed extract.
- To characterize the synthesized α -Fe₂O₃ NPs using TGA, XRD, FTIR, UV-Vis, and SEM.
- To determine the optimum parameters such as pH, catalyst dosage, exposure time, and initial concentration of the dye for complete degradation.
- To evaluate the degradation efficiency of the synthesized photocatalysts for the degradation of MB.
- To investigate the mechanism of the photocatalytic degradation process.

- To determine the chemical oxygen demand (COD) of the degraded product
- To regenerate the used catalyst.

1.4. Scope of the Study

In this study, preparation of α -Fe₂O₃ NPs using *Moringa stenopetala* seed extract, characterization of α -Fe₂O₃ NPs using TGA, XRD, FTIR, UV-Vis, and SEM, and their application for photocatalytic degradation of MB were studied. Chemical oxygen demand determination and catalyst regeneration after degradation.

1.5. Significance of the study

This study provides knowledge on biosynthesis of α -Fe₂O₃NPs using *Moringa stenopetala* seed extract and the way to treat organic dye polluted water before discharging it to the environment. It gives direction on how to prepare a cost effective and environmental friendly photocatalyst, and it can initiate the use of the green synthesis method of metal oxide nanoparticles by using different parts of plant extract. This study provides the uses of solar energy source for photocatalytic degradation of organic dyes by preparing metal oxide nanoparticle with a suitable band gap. It initiates the utilization of solar radiation as a sources of energy.

2. REVIEW LITRATURE

2.1. Water Pollution

Water is vital to almost all life forms for existence. Water makes up 65% of our bodies and covers more than 71% of the surface of the earth. The bulk of the water is unfit for supporting human life, and there are a few sources of potable water. Numerous organic and inorganic pollutants were released into water system as a result of the widespread use of chemicals for various pourposes in daily life and the expansion of different industries, causing unintended contamination of our existing natural resources.

Water pollution is the condition in which there are too many pollutants present for it to be safe to use for drinking, bathing, cooking, or other purpose (Owa, 2014). Most of the water bodies in the ecological system are affected by contaminants that are released from industries and agricultural activity. One of the main contaminants found in the wastewater from textile and other industries is organic dyes. During the production process, 10–20% of the worlds total dye product is lost as textile waste and released as effluents into the environment.

2.1.1. Methylene Blue Dye (MB)

Methyl thioninium chloride is the chemical name for methylene blue. It has the chemical formula $C_{16}H_{18}N_3SCl$ and a molecular weight of 319.87 g/mol. It is the basic cationic dye known by the IUPAC name 3, 7-bis (dimethyl amino)-phenothiazin-5-ium-chloride. Because of the amine and sulfur functional groups in this dye, dissolving in an aqueous solution results in a net positive charge. Methylene blue is a solid, odorless, dark green powder that dissolves in water to produce a blue solution (Livy Laysandra, 2017). In addition to its medical uses in medicine, pharmaceutical formulation, pesticide production, and varnish. This dye is used in a variety of applications, including coating, coloring of paper, wool and printing (Olusakin et al., 2022).

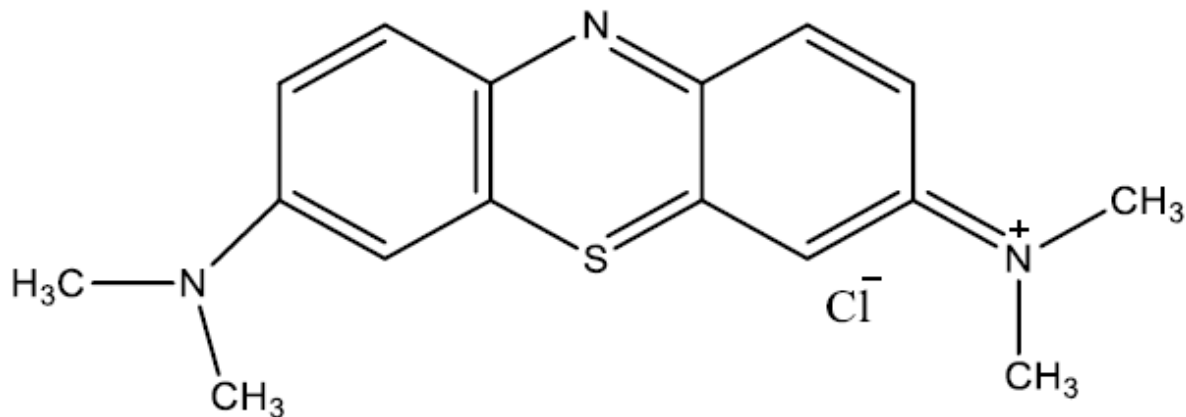


Figure : Structure of Methylene blue dye.

2.1.2. Impacts of methylene blue dye on living things

Methylene blue is the most often used dye for dyeing cotton, silk, wood, and printing. It has a negative impact on human health: it causes eye burns that result in long term eye damage. Additionally, swallowing these chemicals through the mouth causes a burning feeling, nausea, and vomiting, as well as a physiological state that makes breathing difficult. Adsorption, chemical flocculation, photodegradation, and ozonization are a few of the treatment methods that have been employed to minimize the severity of the potential harm to individuals and the environment caused by water containing dyes.

2.2. Sources wastewater containing organic dye

Without proper treatment, the textile sector discharges wastewater, including dye, into the environment. The discharge of wastewater containing dye chemicals into water sources considerably decreases the quality of the water. They often have a complex molecular structure and a synthetic origin, making them inert and incapable of degrading in waste streams (T. A. Khan et al., 2013). The presence of very small concentrations of colors in water (less than 1 ppm for some dyes) is highly apparent and alters transparency and water-gas solubility. Additionally, decreasing light's ability to pass through water reduces photosynthesis activity, leading to an oxygen shortage and destabilizing the biological cycle of aquatic biota (El Haddad et al., 2013). Dye effluent and its degradation products are frequently carcinogenic, toxic, and mutagenic, which harm both human and aquatic life.

2.3. Treatment of Organic Dye Polluted Aqueous System

Recently, a variety of techniques for removing dyes from textile wastewater have been developed, including physical, chemical, and biological methods. Many of these traditional technologies for treating textile wastewater dye effluents have not typically been employed on a large scale in the textile and paper sectors due to their high cost and final disposal problems. Because of their high cost and final disposal problems, many of these conventional methods for treating textile wastewater containing dye effluents have not been applied on a large scale in the textile and paper industries (Hasan, 2008). These factors have led to the investigation of advanced oxidation processes as a new technique to eliminate toxic organic dye molecules without releasing any harmful byproducts at the ends of the organic effluent removal process (Alshehri et al., 2017).

In advanced oxidation processes, the photocatalytic materials form reactive species during dye degradation processes. The reactive species will degrade the organic molecules by oxidizing them with a continuous photocatalytic reactive species generation process to nontoxic products (e.g., carbon dioxide and water) through mineralization (Deng & Zhao, 2015).

2.4. Wastewater Treatment Method

There are different industries that use dyes and pigments to pollute water, including the textile, paper, rubber, and food industries. These dyes contain a variety of hazardous chemicals with uncertain environmental behavior, such as aromatic amines ($C_6H_5-NH_2$), which are thought to have cancer causing properties. Chemical, physiochemical, and biological processes such as adsorption, chemical precipitation, electrochemical oxidation, and aerobic and anaerobic biological processes have been examined to remove dyes from wastewater (Jemal, 2015).

2.4.1. Physical methods

A treatment that does not contribute to chemical reactions or biological changes is considered a physical treatment. There are several physical methods, such as adsorption and membrane filtration technology (nanofiltration and reverse osmosis). Membrane filtration is a technique used to treat wastewater from industrial effluents. Separation has been achieved by preventing particles larger than the pore on the film from entering the wastewater stream. The drawbacks of

membrane processes are their cost for periodic membrane replacement and their short lifespan before membrane fouling starts.

2.4.2. Chemical method

Chemical treatment includes coagulation, precipitation-flocculation with $\text{Fe}^{2+}/\text{Ca}(\text{OH})_2$, electro floatation, electrokinetic-coagulation, ozonization, and electrochemical processes. These chemical techniques are expensive, and they involve the usage of extreme chemicals, additional treatment may be required because there is the possibility that some secondary pollution problems like sludge will arise after the removal of dyes.

2.4.3. Biological method

Biodegradation methods like fungal decolonization, microbial degradation, adsorption by microbial biomass, and bioremediation systems are frequently employed to treat industrial wastewater. This is because a variety of microorganisms, including bacteria, yeast, algae, and fungi, can accumulate and degrade various pollutants. Many organic molecules can be degraded using biological treatment methods but are not capable of removing dyes due to their complex chemical structure and synthetic organic origin.

2.4.4. Advanced oxidation process for wastewater treatment

Due to the large variety of contaminants that can be oxidized, researchers that assessed alternative treatments for harmful contaminants came to the conclusion that the advanced oxidation processes are quite effective (Byrne et al., 2018). These procedures use a variety of techniques, such as chemical oxidation, photocatalysis, and ozonization. This process works by generating highly reactive hydroxyl radicals that are non-selective and encourage the mineralization of organic pollutants that produce carbon dioxide, water, and inorganic compounds that are harmless or biodegradable.

2.5. Nanoparticles

Nanotechnology is one of the most significant and rapidly growing areas of research that uses biosynthetic and environmental-friendly technology for the synthesis of nanoparticles (NPs). It is the ability to measure, manipulate, and manufacture things on an atomic level, usually between

1-100 nm. They have a large surface area to volume ratio, which is their most important feature and responsible for the widespread use of these nanomaterials. NPs have attracted the special attention of the scientific community due to their fascinating properties, including physical, mechanical, optical, magnetic, electronic and sensing which considerably vary in many aspects from their bulk counterparts. NPs have been significantly used in diverse disciplines, including food, cosmetics, medicine, engineering, agriculture, and energy (Paulson & Jothibas, 2021).

2.5.1. Metal oxide nanoparticles

Metal oxide NPs have received great attention due to their excellent electrical, optical, magnetic, and catalytic properties in various fields such as photocatalysis, catalysis, sensors, and heavy metal removal (Khalafi et al., 2019). Metal oxides such as TiO_2 , ZnO , SnO_2 , and Fe_2O_3 are usually used as photocatalysts for the photocatalytic degradation of organic dyes due to their wide band gap and high photosensitivity (Umar et al., 2013). Metal oxide nanomaterials are a diverse category of materials that have a wide range of applications, such as water purification, environmental remediation, energy, personal care products, and medical technology.

2.5.2. Iron oxide nanoparticles

Among various nanoparticles, iron-oxide nanoparticles (IONPs) have attracted the attention of the community due to magnificent properties such as high catalytic and adsorption ability, reactivity, biocompatibility, mechanical, thermal, and chemical stability (Bibi et al., 2019). IONPs are used in many fields such as wastewater treatment for the elimination of many pollutants like dyes, heavy metals, and drugs; the petroleum industry for remote detection and directional transport; and local heating; and biomedical fields for anticancer and antimicrobial drugs (K. Zhou et al., 2020). IONPs have magnetic properties that can be rapidly removed from the solutions and reused many times, reducing the total operating cost. Iron oxide NPs exist in diverse polymorphs like magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), and $\beta\text{-Fe}_2\text{O}_3$. Among them, hematite is the most stable iron oxide with a high resistance to corrosion, low cost; and it is also biocompatible, environmentally friendly, and non-toxic.

2.5.3. Hematite (α -Fe₂O₃) nanoparticles

Hematite is an n-type semiconductor photocatalyst that has the advantage of being abundant, cheap, and environmental-friendly (Liu et al., 2013). It is the most thermodynamically stable iron oxide with a narrow band gap of 2-2.2eV and it directly acts as a visible light active photocatalytic material. It exhibits a rhombohedrally centered, hexagonal structure of the corundum type with a densely packed oxygen lattice (Basavegowda et al., 2017). It is a promising material for the photocatalytic system due to its suitable bandgap, low cost, low toxicity, high abundance, and magnetic nature. α -Fe₂O₃ is a very important material extensively used in catalysis, pigments, battery cathodes, photo electrodes, gas sensors, electrochromic films, environmental protection, biomedicine, and magnetic devices (Rufus et al., 2017).

2.5.4. Magnetic properties of hematite

In bulk hematite, two magnetic transitions are observed: the Néel temperature at $T_N \approx 960$ K and the Morin transition at the temperature $T_M \approx 263$ K. Below T_M , the spins are order antiparallel, and the hematite acts as an antiferromagnetic material. Above T_M , the spins display canted ordering and weak-ferromagnetism with soft magnetic properties. The magnetic properties of hematite depend on its crystallinity, particle size, subparticle structure, cation substitution, and morphology. Nanosized hematite particles show a variety of peculiar magnetic properties when compared to the properties of hematite bulk material. Hematite has revealed very interesting magnetic properties in nanoparticle forms, such as superparamagnetism, spin glass, memory effects, high coercivity, high magnetization, and a decrease in the Morin and Curie temperatures (Teja & Koh, 2009).

2.5.5. Synthesis method of hematite

Many methods have been proposed for the synthesis of α -Fe₂O₃ nanoparticles, including sol-gel, electrochemical deposition, hydrothermal and solvothermal co-precipitation, and microwave irradiation. These chemical techniques, have a number of limitations, including the use of toxic chemicals, high energy consumption, the use of organic solvents, and high temperature and pressure conditions. Green synthesis approaches, which avoid using toxic chemicals through the synthesis processes, can be used to overcome the challenges created by chemical methods (Alajmi et al., 2018).

2.5.6. Green synthesis of hematite

Green synthesis approaches to hematite nanoparticles are gaining importance due to their being eco-friendly, cost-effective, simple, easy to perform, and involving no toxic agent. Hematite nanoparticles can be produced by different microorganisms (yeast, fungi, bacteria, etc.) and plant tissues (leaves, fruit, latex, peel, flower, root, stem, etc.) as reducing and capping agent. Among these, plants seem to be the best candidates, and they are suitable for the large-scale biosynthesis of nanoparticles. Green synthesis methodologies based on biological precursors depend on various reaction parameters such as solvent, normal temperature, pressure, and pH conditions (acidic, basic, or neutral). For the synthesis of hematite nanoparticles, plant biodiversity has been broadly considered due to the availability of effective phytochemicals in various plant extracts. α -Fe₂O₃ NPs have been successfully synthesized with extracts of various parts of plant species that include Psidium guajava (Rufus et al., 2016), Sida cordifolia (Pallela et al., 2019), Aloe vera (Mukherjee et al., 2016), Pistacia vera (Abusaleem et al., 2019), Ailanthus excels (Asoufi et al., 2018), and so on. To the best of my literature survey, hematite is not prepared using *Moringa stenopetal* seed extract, yet this plant is the most abundant in the south and reported to be rich in different phytochemicals. Therefore, this work was focused on the green synthesis of α -Fe₂O₃ NPs using moringa stenopetala seed aqueous extract and its application for the photocatalytic degradation of methylene blue dye in wastewater under visible light irradiation.

2.5.7. Photocatalytic activity of hematite

Hematite (α -Fe₂O₃) is a promising semiconductor photocatalyst that has the advantage of being abundant, cheap, and environmentally friendly. Hematite assisted photocatalysis and photo oxidation of organic contaminants were found to be highly effective, environmentally compatible, low-cost, and less complicated techniques for converting pollutants into relatively harmless byproducts (Weldemariam et al., 2015). The green synthesis of hematite nanoparticles with different morphologies promises to be a visible-light photocatalyst for the degradation of organic pollutants in water. Lassoued et al. (Lassoued et al., 2018) reported the photocatalytic activity of α -Fe₂O₃ NPs, under visible irradiation, and achieved 89% photocatalytic degradation of MB dye. The photocatalytic activity of α -Fe₂O₃ NPs, under visible light irradiation for 120 min achieved 90.2% photocatalytic degradation of MB dye. The photocatalytic activity

of hematite synthesized from Arabic gum was achieved at 90 % congo red degradation in 90 min under sunlight irradiation.

2.6. Heterogeneous Photocatalysis

Photocatalysis is one of the advanced oxidative processes whose principle involves the activation of a catalyst through sunlight or artificial light irradiation. It involves the degradation of organic pollutants by the initiation of redox transformations, and has been proven to be an efficient tool for the degradation of aqueous as well as atmospheric organic pollutants. This technique involves the initiation of photoreactions in the presence of a semiconductor photocatalyst. Photocatalytic action is the light-induced redox reaction of semiconductors. A semiconductor has an energy band structure composed of a low energy valence band (VB) and a high energy conduction band (CB), and the band gap between a conduction band and a valence band is called a forbidden band. When the energy of the incident light is larger than the band gap of the semiconductor, the electrons in the VB of the semiconductor are excited to the CB by photons, and the corresponding holes are generated in the VB. Photogenerated electrons and holes are separated by an electric field and move to the surface of semiconductor particles. The photogenerated pores have strong oxidizing properties and can oxidize substances adsorbed on the surface. The photogenerated e^-/h^+ pairs will take part in the red-ox reactions to produce the final products (Moniz et al., 2015).

2.6.1. Mechanism of heterogeneous photocatalysis

Heterogeneous photocatalysis is conducted by using semiconductors, which allow the complete mineralization for great variety of organic pollutants. This process is able to degrade water pollutants such as various types of organic dyes or complex mixtures of water contaminants into carbon dioxide, water, and mineral acid. A photocatalytic reaction proceeds as follows: When light has a particular energy, electrons on a VB are excited and jump to a CB, while the holes remain on the VB. The electrons on the CB move to the surface of the catalyst and participate in a reduction reaction, and the holes on the VB diffuse to the photocatalyst surface and are involved in an oxidation reaction. In the course of the reaction, the electrons can form H_2O_2 or a superoxide radical O_2^- with H^+ and dissolved O_2 in the aqueous solution, and the holes can oxidize OH^- to produce a hydroxyl radical, and, as a result, accomplish the goal of decomposing

contaminants (Zhang et al., 2019). Figure 2: illustrates the basic principle of photocatalytic reaction.

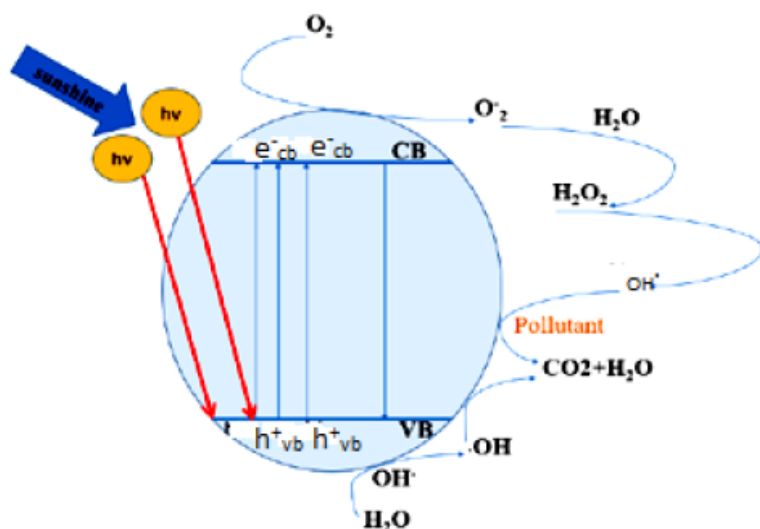


Figure : Photocatalytic reaction mechanism (Zhang et al., 2019)

2.6.1.1. Oxidation mechanism

In the oxidation mechanism, when the light is irradiated, a hole (h^+) is generated in the VB as a result of an electron (e^-) shifting to the CB. This hole (h^+) oxidizes the water molecule on the photocatalyst surface, allowing for the formation of hydroxyl radicals, which have a potent oxidative decomposing capability. This hydroxyl radical reacts with the organic matter in the dye. The organic dyes eventually break down into carbon dioxide and water (M. M. Khan et al., 2015).

2.6.1.2. Reduction mechanism

In the reduction mechanism, CB electrons react with dissolved oxygen species to form superoxide anions (O_2^-). These superoxide anions attach to the intermediate products in the oxidative reaction, forming peroxide or changing to hydrogen peroxide and then to water. The reduction is likely to occur more easily in organic matter than in water. Therefore, a higher concentration of organic matter tends to increase the number of positive holes. This reduces the carrier recombination and enhances the photo-catalytic activity (Archana et al., 2021).

2.6.2. Factor affecting photocatalytic degradation

The rate of photodegradation of an organic compound by a photocatalyst can be influenced by variables like pH, catalyst dosage, initial concentration of dye, and light intensity.

2.6.2.1. Effect of solution pH

The photocatalytic degradation efficiency is affected by the solution pH. This was because of the catalyst facilitated the adsorption between the dye and the catalyst, depending on the nature of the catalyst and the charges of the dyes (Reza et al., 2017a).

2.6.2.2. Effect of catalyst dosage

The amount of catalyst also influences the efficiency of photocatalytic degradation. If there is an increase in the quantity of catalyst, the number of active sites on the semiconductor surface increases, which in turn increases the number of hydroxyl and superoxide radicals. As a result, the photocatalytic degradation rate increases. However, as the catalyst loading is improved beyond an optimum concentration, the degradation rate is unfavorable because there is a decrease in the light penetration depth into the solution and consequently a diminishing of light scattering.

2.6.2.3. Effect of initial dye concentrations

The photocatalytic degradation rate of a certain dye or pollutant depends on its concentration, nature, and the presence of other existing compounds in the water matrix. Kumar and Pandey (Kumar & Pandey, 2017) reported that the photocatalytic degradation processes are contributed by the dyes that are adsorbed on the catalyst surface but not in the bulk of the solution. They stated that the initial concentration of dye played an important role in the photocatalytic degradation efficiency and was generally favored at low dye concentrations.

2.6.2.4. Effect of light intensity

The light intensity has a major impact on the photocatalytic degradation process. The quantum yield, which is the ratio of the rate of reaction to the rate of radiation absorption, determines the quantum of light absorbed by any photocatalyst. The photocatalytic reaction responses varied depending on the light source wavelength (Reza et al., 2017b)

2.7. Moringa Stenopetala Seed

As a multifunction tree with significant economic value, moringa has vital nutritional, industrial, and medicinal applications (Gore, 2018). *Moringa stenopetala* seeds are a significant source of oil and are utilized in a variety of industrial applications. According to recent reports, *Moringa stenopetala* seed oil is used as potential feedstock for biodiesel production (Ejigu et al., 2010). The plant *Moringa stenopetala* is well known for having a large number of bioactive compounds that are frequently utilized in popular culture to treat a variety of diseases, including hypertension, diabetes mellitus, stomach pain, etc. The amount of organic compounds and absorption capacity of *Moringa stenopetala* seed have increased due to the presence of hydroxyl and carbonyl in the seed. According to this study, the functional groups present in the seed include O-H stretching, C-H stretching in the aliphatic chain, C=O stretching of carboxylic acid, C-C bond, and N-H mode of amine, which contribute to reducing and stabilizing purposes.

For the preparation of metal and metal oxide nanoparticles in the current work, *Moringa stenopetala* seed is recommended due to the variety of bioactive molecules that exist in the seed that can function as reducing agents as well as stabilizers in favor of converting metal salt into metal oxide nanoparticles.



Figure : Moringa Stenopetala plant and Seed

3. METHODOLOGY

3.1. Study Sites Description

The green synthesis of hematite nanoparticles using *Moringa stenopetala* seed extract and evaluation of their photocatalytic activity and characterizations were carried out at Adama Science and Technology University (ASTU). *Moringa stenopetala* Seeds were collected from the SNNRP region, Gedeo zone, around the Dilla University main campus, 359 km away from Addis Ababa.

3.2. Chemical and Reagent

Iron (III) nitrate nonahydrate (TECHNO PHARM CHEM. India, 98%), methylene blue 82 % (Sigma-Aldrich, Japan) , sulfuric acid ,98 % (Merric company), potassium dichromate (LOBA CHEMIE), silver sulfate, mercuric sulfate (Alpha chemika), ferrous ammonium sulfate (LOBA CHEMIE), Phenanthroline ferrous sulfate, moringa stenopetala seed extract, Hydrochloric acid ,HCl, 37 % (Sigma-Aldrich) and NaOH (Abron Experts-133 001, India) that are of analytical grade were purchased for this study.

3.2.1. Instrument and Apparatus

Instrument and apparatus that were used include: pipette, Muffle furnace, spatula, test-tube , electronic balance (Model JA103P, Japan), beaker (100 mL, 500 mL and 1000 mL, magnetic stirrer with hot plate (UK), conical flask (250 mL), volumetric flask (50 mL, 100 mL, 250 mL, 500 mL and 1000 mL) and funnels, measuring cylinder (25 mL, 50 mL, 100 mL) electrical shaker (Heidolph UNIMAX 2010), Whatman no 42 filter paper , refrigerator, crucible, mortar and pestle, centrifuge (L-600), and Thermogravimetric analysis, (model DTA-60H, Shimadzu Co, Japan), X-ray Diffractometer (XRD-700, Shimadzu Co, Japan), Fourier Transform Infrared Radiation (Perkin Elmer, Spectrum 65 FTIR, and USA), Scanning Electron Microscopy ((JEOL/EO-JCM-6000 PLUS, Japan) and Double beam Ultraviolet-Visible Spectrophotometer (SM-1600 Dualbeam UV-Vis Spectrophotometer, azota Corp., USA) instruments were used.

3.3. Preparation of *Moringa stenopetala* seed extract

Moringa stenopetala seed was collected from around Dilla University's main campus, Gedeo Zone, SNNRP region, Ethiopia. The hull was removed from the seed surface and the wings from the kernels. The seed was cleaned with tap water to remove the dust particles, followed by

distilled water. The seed was air dried at room temperature to remove the residual moisture. The kernels were ground into medium fine powder using a mortar and pestle to achieve solubilization of the active ingredients in the seed. The aqueous extract of the sample was prepared by boiling the finely powdered seeds (50 g) with 500 mL of distilled water at 80°C for 20 minutes, until the color of the aqueous solution changes to milk like liquid. Then the extract was cooled to room temperature and filtered using whatman no 42 filter paper. Finally, extract was stored in a refrigerator in order to be used for further experiments (Gebino & Govindan, 2018).



Figure : Flow diagram for the preparation of moringa stenopetala seed extract.

3.4. Synthesis of Hematite Nanoparticles using Moringa Stenopetala Seed

Ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was used as a precursor for the synthesis of $\alpha\text{-Fe}_2\text{O}_3$ NPs via the precipitation method. 0.1 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to the beaker and heated it at 60 °C on the hot plate by stirring for 10 minutes to homogenize the solution. Next, a solution of aqueous extract of moringa seed powder was added dropwise to 0.1 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution in 3:1, 2:1, and 1:1 volume ratios while stirring. Following this, 1M NaOH was added till pH was adjusted to 11 and stirred continuously for 2 hours till a red-brown color formed. The

solution was cooled at room temperature until precipitates were formed. After that, the precipitate was collected via centrifuge at 6000 rpm and washed with distilled water several times to remove impurities. The collected powder of hematite was dried in the oven at 80 °C for 10 hours. The red-brown $\alpha\text{-Fe}_2\text{O}_3$ was transferred into the silica crucible and calcinated at 600 °C for 5 hours in a muffle furnace (Weldegebrail & Sibhatu, 2021). Finally, the calcinated products have been evaluated for their catalytic activity, and by comparing their crystalite sizes, the one with the best efficiency was selected for further application.

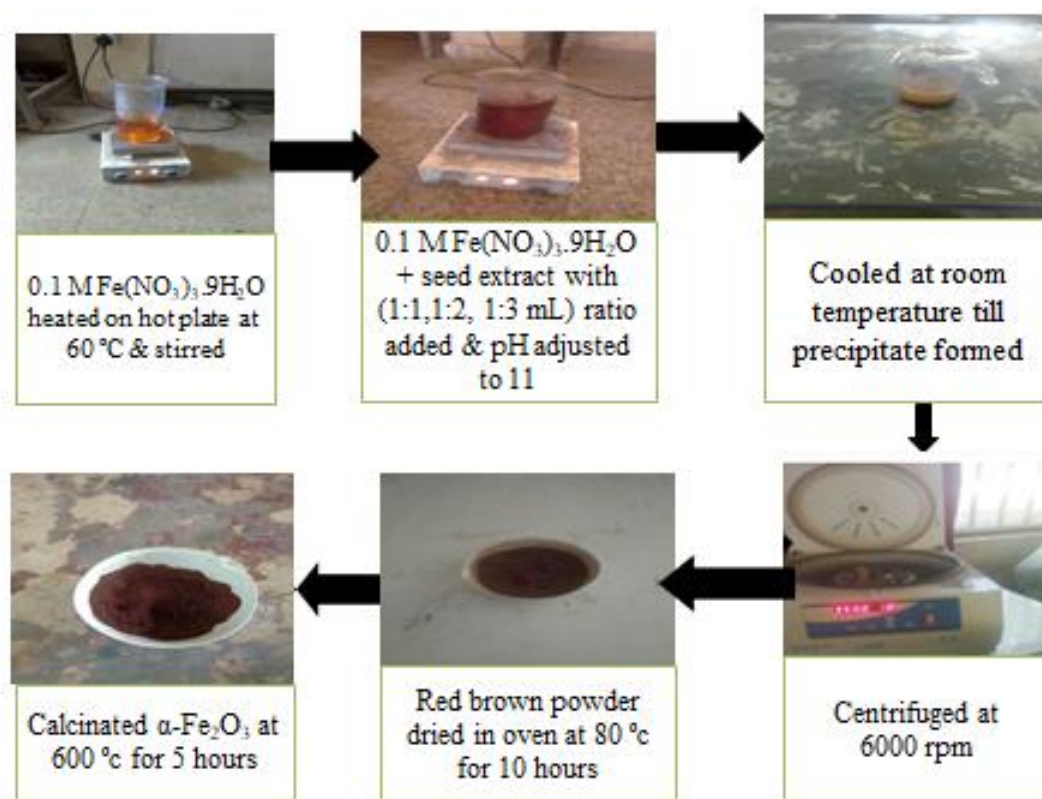


Figure : Flow diagram for the synthesis of hematite nanoparticle.

3.5. Characterization of Synthesized $\alpha\text{-Fe}_2\text{O}_3$ NPs.

Thermogravimetric Analysis (TGA), Fourier Transform Infrared Radiation (FT-IR), Ultraviolet-Visible (UV-Vis) Spectroscopy, powder X-ray Diffract meter (XRD) and Scanning Electron Microscopy (SEM) were used to characterize the synthesized $\alpha\text{-Fe}_2\text{O}_3$ NPs.

3.5.1. Thermogravimetric thermal analysis (TGA)

The thermal analysis of hematite has been carried out in the temperature range of 31°C to 800°C. TGA model (DTG-60H) for the determination of the calcination temperature and weight loss. 10 mg of synthesized α -Fe₂O₃ NPs were taken and placed on the alumina crucible for TGA analyzed at heating rate of 20°C/min with a constant non-stop glide of nitrogen.

3.5.2. X-ray Diffractometry (XRD)

The crystalline phase of synthesized α -Fe₂O₃ NPs was identified using X-ray diffractometry (XRD-700 Shimadzu Co., Japan). A Cu target for generating a CuK α (λ = 0.15406 nm) accelerating voltage 40 kV and current 30 mA. X-ray diffraction of α -Fe₂O₃ powders was measured for the 2θ angles ranging from 10° to 80° with scans step 0.02°. The sample was measured at room temperature, with a scan speed of 3°/min, an angular step of 0.02°, and a counting time of 0.40 sec.

3.5.3. Scanning electron microscopy (SEM)

Scanning electron microscopy was used to analyze the morphology, size, crystalline structure and orientation of hematite nanoparticle. Images are created by scanning electron microscopy (SEM -JEOL JCM 6000 PLUS, Japan) identifying the secondary electrons that are released from the surfaces as a result of the primary electron beams excitation. A small amount of sample powder was dissolved in acetone and briefly sonicated. Additional drop of the sample was put on the conducting carbon tape that has been applied on scanning electron microscopy stub. A thin sheet of gold was further coated with sputter coater to improve conduction. The microstructure of the synthesized α -Fe₂O₃ NPs was captured at various magnifications.

3.5.4. Fourier transform infrared radiation (FTIR)

The FT-IR analysis was carried out to find out the functional groups present in the nanoparticles and to check whether Fe-O bond is formed. It is also applied to examine the possible significant functional groups existing in the seed extract that are responsible for reducing and capping in the preparation of α -Fe₂O₃ NPs with the scanning range of 4000 cm⁻¹ to 400 cm⁻¹. For the FT-IR characterization, the sample was mixed with solid KBr uniformly and properly, which was

compressed to settle down on a thin transparent film and this thin transparent film was used for FT-IR analysis which was kept in the chamber of the instrument for scanning.

3.5.5. Ultraviolet-Visible Spectroscopy (UV-Vis)

Optical absorption and optical band gap energy measurement were carried out on synthesized α -Fe₂O₃ NPs. Double beam UV-Vis spectrophotometry (SM-1600 Dual beam UV-Vis Spectrophotometer, azzota Corp., USA) was used to obtain the absorption spectrum of the synthesized nanoparticles. The optical absorption was measured in wavelength range of 200-800 nm using BaSO₄ reference standard material. Optical properties characterize the response of materials to incident electromagnetic radiation. The sample was dissolved in appropriate solvent and fills in to sample holder cuvette and used for analysis.

3.6. Double beam UV-Vis Spectrophotometer Calibration

The standard stock solutions of MB dye was taken for calibration of the instrument. For the instrument calibration, first 1000 mg/L of stock solution of each dye was prepared and an intermediate standard solution containing 100 mg/L was prepared in 500 mL volumetric flask from the standard stock solution that contained 1000 mg/L of interest to be analyzed. Then, five working standards of the dye solution in 100 mL volumetric flask were prepared for calibration purpose. The objective of calibration of the instrument was to see the linearity of the instrument response and also for calculation of the remaining concentration of the dyes after degradation in investigating the kinetics of the degradation experiment.

3.7. Photocatalytic Experiment

The photocatalytic activity of the synthesized α -Fe₂O₃ NPs was studied by photocatalytic degradation of MB dye solution under natural sunlight irradiation. For effective degradation, various experimental parameters such as pH, catalyst dose, initial concentration of dye, and exposure time have been optimized. The photocatalytic degradation reaction was carried out in an open system containing 50 mL of prepared MB solution (at different concentrations: 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, and 50 mg/L) and 0.05 gm of synthesized α -Fe₂O₃ NPs. Before irradiation, the beaker containing the mixture of MB dye and α -Fe₂O₃ NPs was stirred for 10 minutes in the dark. This was done to maintain equilibrium between the desorption and adsorption processes between the dye molecule and α -Fe₂O₃ NPs surface. After 30 minutes, the solution was exposure to sunlight irradiation within time, with the strongest light intensity from

5:30 to 8:30 (local time). The photocatalyst was separated from the degraded methylene blue solution using Whatman filter paper no.42, and the absorbance was measured before and after degradation using a double beam UV-Vs spectrophotometer at 665 nm for Methylene blue dye. Finally, the photodegradation efficiency of MB dye was calculated using equation 1.

$$\text{Degradation percentage} = \frac{A_o - A_t}{A_o} \times 100\% \quad (1)$$

Where, A_o is initial absorbance of dye solution before degradation and A_t is absorbance of dye solution at time, t after degradation.

3.7.1. Effect of solution pH

To study the effect of pH on photocatalytic degradation of MB dye, 50 mL of 30 mg/L of MB solution was taken, and pH was adjusted to 2, 4, 6, 8, 10, and 12 by using 0.1 M HCl and 0.1 M NaOH. 0.05 g of synthesized $\alpha\text{-Fe}_2\text{O}_3$ NP was added to each solution in the beaker. Then the solution was stirred using a stirrer for 10 minutes and kept in the dark to maintain the desorption or adsorption for 30 minutes. After 30 minutes, the solution was exposed to sunlight for 3 hours. The photocatalyst left was separated from the degraded solution using whatman filter paper no. 42, and its absorbance was measured before and after degradation using a double beam UV-visible spectrophotometer at 665 nm for methylene blue dye.

3.7.2. Effect of catalyst dosage

To study the effect of catalyst dosage on photocatalytic degradation of MB dye, 50 mL of 30 mg/L of MB solution was adjusted to a pH of 12. Then different dosage of $\alpha\text{-Fe}_2\text{O}_3$ (0.01 g, 0.05 g, 0.1 g, 0.15 g, 0.2 g, and 0.25 g) were added to the solution, keeping other parameters constant. Then the solution was stirred using a stirrer for 10 minutes and kept for 30 minutes in the dark to maintain desorption or adsorption. After 30 minutes, the solutions were exposed to visible light irradiation for 180 minutes. The photocatalyst left was separated from the degraded solution using Whatman filter paper no.42, and the absorbance before and after degradation was measured using a double beam UV-Visible spectrophotometer at 665nm.

3.7.3. Effect of initial concentration

To study the effect of initial concentration on photocatalytic degradation of MB dye, 50 mL of MB solution with various concentrations (10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, and 50 mg/L) was used, and the other parameters were kept constant. Then, the solution was stirred for 10 minutes and kept for 30 minutes in the dark to maintain the desorption or adsorption.

3.7.4. Effect of exposure time

To optimize the exposure time, the range of time intervals (30 min, 60 min, 90 min, 120 min, 150 min, and 180 min) was investigated while keeping other parameters constant.

3.7.5. Point of Zero Charge (PZC)

The point of zero charge is the pH at which the photocatalyst surface of α -Fe₂O₃ NPs has an equal distribution of total positive and total negative charges on its surface site. The total charge on the surface of the hematite nanoparticle becomes zero at this pH. The surface charge of α -Fe₂O₃ NPs might be positive or negative with respect to the pH of the reaction component. Using 0.1 M NaCl solutions, the PZC of synthesized α -Fe₂O₃ NPs was studied. Then 50 mL of a different pH 0.1 M NaCl solution in a conical flask containing 0.05 g of α -Fe₂O₃ NPs was added. The solution was adjusted to pH of 2, 4, 6, 8, 10, and 12 using 0.1M HCl and 0.1M NaOH on a digital pH meter. The solution was stirred at 500 rpm for 48 hours for pH stabilization at room temperature. After 48 hours of equilibration, the final pH of each solution was measured, and a plot was constructed between the initial pH and the change in pH. PZC is the point at which this curve intersects the initial pH, which equals the change in pH in a straight line.

3.7.6. Regeneration of α -Fe₂O₃ nanoparticle.

A regeneration experiment was done to confirm the reusability of α -Fe₂O₃ NPs for practical application in real systems. It is one of the important parameters used for photocatalytic application in the simple treatment method. This experiment was achieved through filtration using Whatman filter paper no 42. The entire operating cost is decreased by the magnetic nature of α -Fe₂O₃ NPs, which are easily removed from the solutions and reused numerous times. The photocatalyst left on filter paper was washed carefully many times with distilled water and dried for 24 hours. The dried photocatalyst was regenerated four times in succession. The stability was

assessed by recycling the photocatalyst with the same quantity of newly prepared MB solution after each run.

3.7.8 Chemical Oxygen Demand (COD) Determination.

COD is a parameter used to measure the amount of organic matter in water, and it can be used to represent the total decomposition of all chemically degradable organic pollutants in water. The higher the COD level, the higher the oxidation in an organic compound in the sample, which will eventually reduce the dissolved oxygen levels. The subsequent reduction in dissolved oxygen can further lead to anaerobic conditions, which are harmful to aquatic life. The quantity of potassium dichromate used in the reaction is equivalent to the oxygen (O_2) used to oxidize the organic matter in wastewater (Norouzi & Nezamzadeh-ejhieh, 2020).

The determination of COD is made by using 50 mL of MB dye solution after the degradation reaction is added to the refluxing flask. To the solution, 0.1 g $HgSO_4$ and 5 mL of 18.4M H_2SO_4 were slowly added until mercury sulfate dissolved completely. 25 mL of 0.025 M $K_2Cr_2O_7$ and 0.1g of Ag_2SO_4 were added with continuous stirring. Then 20 mL of H_2SO_4 was slowly added with stirring to the flask, followed by boiling chips. The solution refluxed for 2 hours. After reflux was completed, the flask was cooled, and the solution was transferred into a 250 mL conical flask. 8 to 10 drops of phenanthroline ferrous ammonium sulfate indicator were added to the solution and titrated against 0.025 M ferrous ammonium sulfate until the blue –green color changed into reddish blue. 24.5 mL of ferrous ammonium sulfate are consumed until the end point. The same procedure is applied for blank preparation, and distilled water is used instead of a sample. For the blank titration, 31.6 mL of ferrous ammonium sulfate are consumed.

The concentration of COD is calculated from the difference between the volumes of ferrous ammonium sulfate consumed in blank and sample titrations. Blank solution is the solution without analyte (methylene blue solution).

4. RESULT AND DISCUSSION

4.1. Characterization of Synthesized Nanoparticle

4.1.1. Thermogravimetric Analysis (TGA)

The thermal stability, decomposition temperature, and decomposition phase of synthesized hematite nanoparticles were analyzed using thermogravimetric analysis. The thermal analysis of synthesized $\alpha\text{-Fe}_2\text{O}_3$ nanoparticle has been carried out from 31 °C to 800 °C and the total percentage of mass loss in the sample is 43.6%. There are three mass loss steps in the given temperature ranges. The first weight loss (5.4 %) was observed in the temperature range of 31°C to 200 °C due to the removal of water molecules present in the sample. The second step corresponds to mass loss (30.34 %) occurring between 200 to 345 °C which is due to the elimination of organic molecules in plant extract. The third step of weight loss (7.86 %) occurring in the temperature range of 345 to 600°C was due to the complete conversion of the mixed phase into $\alpha\text{-Fe}_2\text{O}_3$. Beyond 600 °C, the curve is parallel to the temperature axis which conforming the stable $\alpha\text{-Fe}_2\text{O}_3$ product.

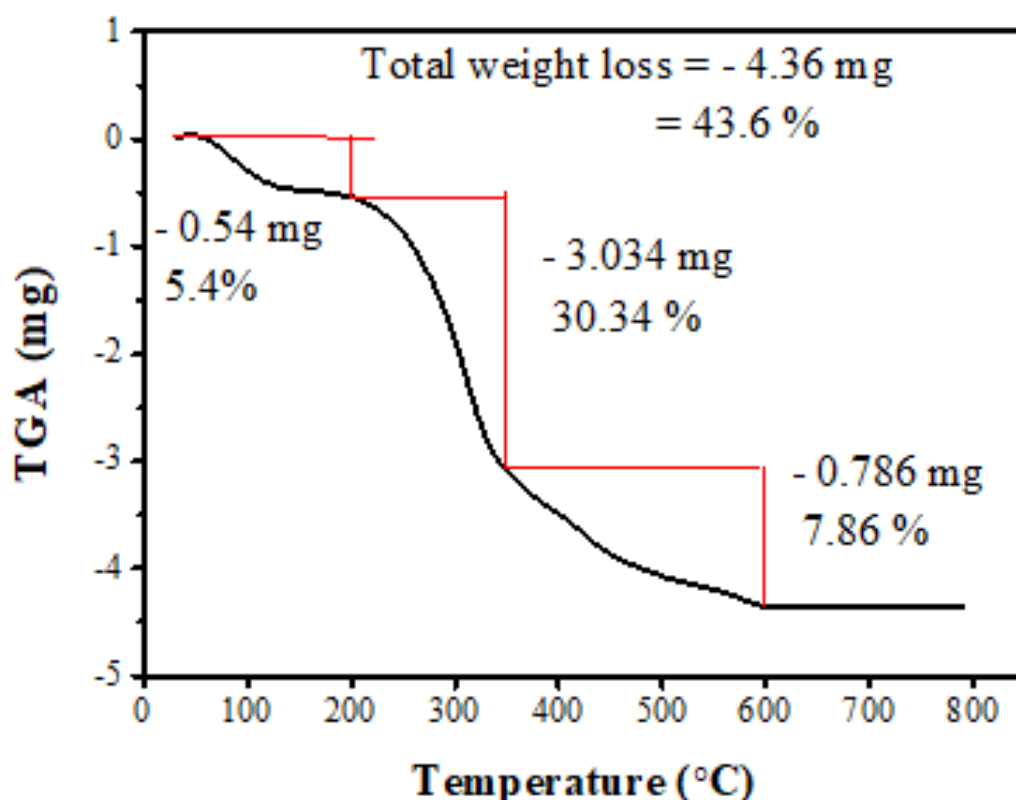


Figure : The TGA graph of synthesized of $\alpha\text{-Fe}_2\text{O}_3$ NPs.

4.1.2. X-ray Diffraction (XRD) Analysis

By using X-ray diffraction techniques, the phase purity and crystallinity of green prepared α -Fe₂O₃ NPs were examined. Figures 7a, 7b, and 7c comprise the XRD pattern of synthesized α -Fe₂O₃ NPs with precursor concentration to seed extract ratio (1:2, 1:1, and 1:3), respectively. The green synthesized α -Fe₂O₃ NPs to the seed extract ratios of 1:2, 1:1, and 1:3 were revealed by the XRD pattern as standard α -Fe₂O₃ NPs with the same plane value. The diffraction peak 2θ of 24.31°, 33.34°, 35.81°, 41.00°, 49.66°, 54.27°, 57.21°, 62.65°, and 64.20° which can be matched to miller indices' (012), (104), (110), (113), (024), (116), (018), (214), and (300) planes, respectively. All the diffraction peaks were consistent with space group R-3c (JCPDS card no.33-0664) and 2θ of 24.17°, 33.19°, 35.67°, 40.93°, 49.50°, 54.11°, 57.43°, 62.50°, and 64.06°, which clearly indicates α -Fe₂O₃ NPs are crystalline and exhibits a rhombohedra centered hexagonal structure (Rajendran et al., 2014). This XRD data confirms that the synthesized nanoparticles are pure, as there is no peak observed other than those in JCPDS file of α -Fe₂O₃ NPs.

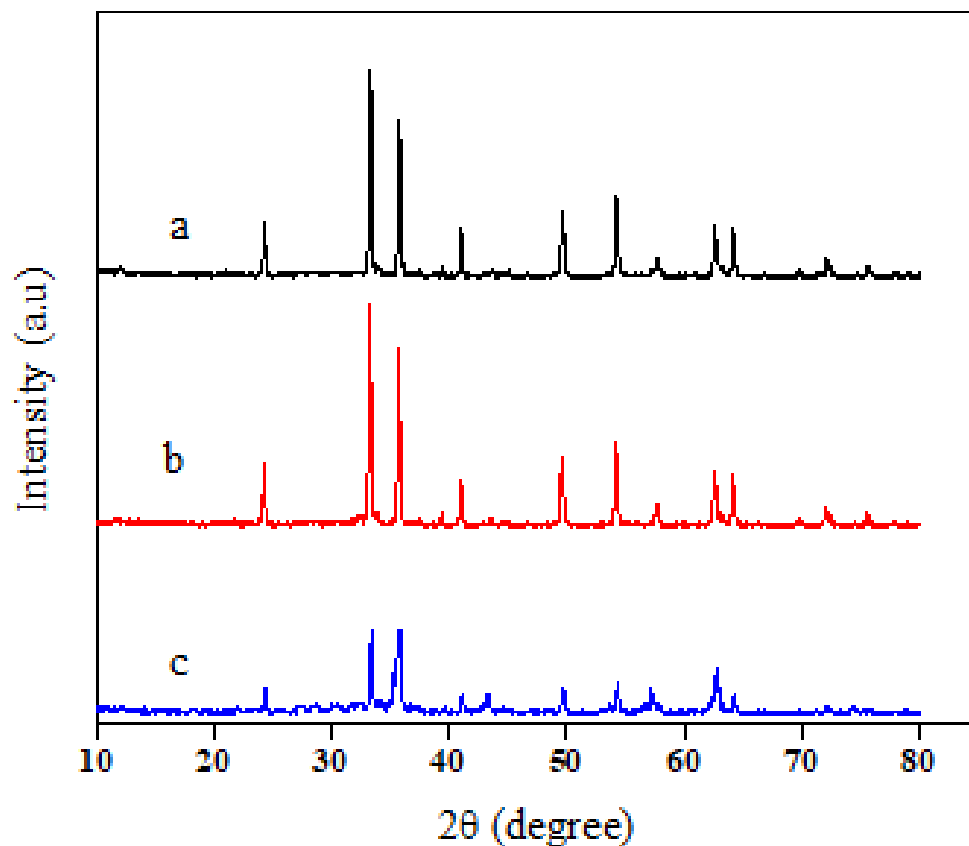


Figure : The XRD patterns of a) 1:2 α -Fe₂O₃ b) 1:1 α -Fe₂O₃ and c) 1:3 α -Fe₂O₃ NPs

The crystallite size of α -Fe₂O₃ NPs was determined from the full width at half maximum (FWHM) of the XRD pattern by the Scherer formula:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

Where, D is the average crystallite size (nm), k is the shape factor (0.9), λ is the X-ray wavelength of Cu K α = 0.15406 nm, β is the full width at half maximum of the peak (FWHM), and θ is the Bragg angle. The calculated average crystallite size of synthesized α -Fe₂O₃ NPs with precursor to seed extract ratios of 1:2 α -Fe₂O₃ NPs, 1:1 α -Fe₂O₃ NPs, 1:3 α -Fe₂O₃ NPs) was found to be 32.57nm, 33.60 nm, and 29.35 nm, respectively. It is thus observed that the size of pure α -Fe₂O₃ NPs synthesized decreases as the concentration of *Moringa stenopetala* seed extract increases. This is due to the capping agent playing the role of stabilizing and functionalizing the nanoparticle. The capping agent imparts the desired properties of nanoparticles by controlling size and protecting the surface area and morphology. Hence, the average crystallite size of all samples synthesized with a precursor to plant extract ratio was computed and compiled in Table 1.

Table : Shows the typical crystallite size of α -Fe₂O₃ NP with ratio precursor to plant extract

Sample Code	2 θ (deg)	θ (deg)	θ (rad)	FWHM (rad)	hkl value	Crystallite size	Average Crystallite size
α -Fe ₂ O ₃ 1:2 ratio	24.314	12.157	0.212	0.00379	012	37.37	32.57 nm
	33.344	16.672	0.290	0.00374	104	38.726	
	35.819	17.909	0.312	0.004	110	36.395	
	41.00	20.475	0.358	0.0041	113	35.996	
	49.662	24.831	0.433	0.0048	024	31.767	
	54.272	27.136	0.473	0.0051	116	30.478	
	62.656	31.328	0.546	0.0069	214	26.904	
	64.204	32.102	0.56	0.006	300	28.860	
α -Fe ₂ O ₃ 1:1 ratio	24.268	12.134	0.211	0.0036	012	38.809	33.60 nm
	33.290	16.645	0.290	0.0037	104	38.750	
	35.767	17.883	0.311	0.0039	110	36.830	
	41.06	20.425	0.356	0.004	113	36.736	
	49.614	24.807	0.432	0.0048	024	31.400	
	54.223	27.116	0.472	0.0051	116	30.398	
	62.608	31.304	0.546	0.0059	214	27.380	
	64.161	32.080	0.559	0.0057	300	28.547	
α -Fe ₂ O ₃ 1:3 ratio	24.393	12.196	0.212	0.0037	012	37.939	29.35 nm
	33.412	16.706	0.291	0.0042	104	34.113	
	35.729	17.864	0.311	0.0095	110	15.358	
	41.006	20.485	0.357	0.0041	113	37.00	
	49.736	24.868	0.433	0.0047	024	32.328	
	54.337	27.168	0.473	0.0053	116	29.565	
	62.764	31.382	0.547	0.0082	214	19.807	
	64.234	32.117	0.560	0.0057	300	28.720	

4.1.3 Fourier Transform Infrared Radiation (FTIR) Analysis

The various functional groups present in the synthesized $\alpha\text{-Fe}_2\text{O}_3$ NPs are identified with the help of an FT-IR instrument, given that every particular chemical bond frequently has a distinct energy absorption band. Using the KBr pellet approach, the FI-TR was captured in the solid phase in $400\text{--}4000\text{ cm}^{-1}$ range. The FT-IR spectrum of hematite ($\alpha\text{-Fe}_2\text{O}_3$) NPs is illustrated in Figure 8. The absorption band at 3435 cm^{-1} attributed to O-H stretching, and a vibration band at 1638 cm^{-1} is assigned to C=C stretching due to capping by bioactive molecules present on the surface of the hematite nanoparticles. The peaks obtained at 538 cm^{-1} and 474 cm^{-1} were assigned to the Fe–O group, which is typical for $\alpha\text{-Fe}_2\text{O}_3$ due to metal oxygen stretching vibrational modes. This FT-IR result strongly confirms the formation of Fe-O bond, and hence it gives information about the desired material ($\alpha\text{-Fe}_2\text{O}_3$ NPs).

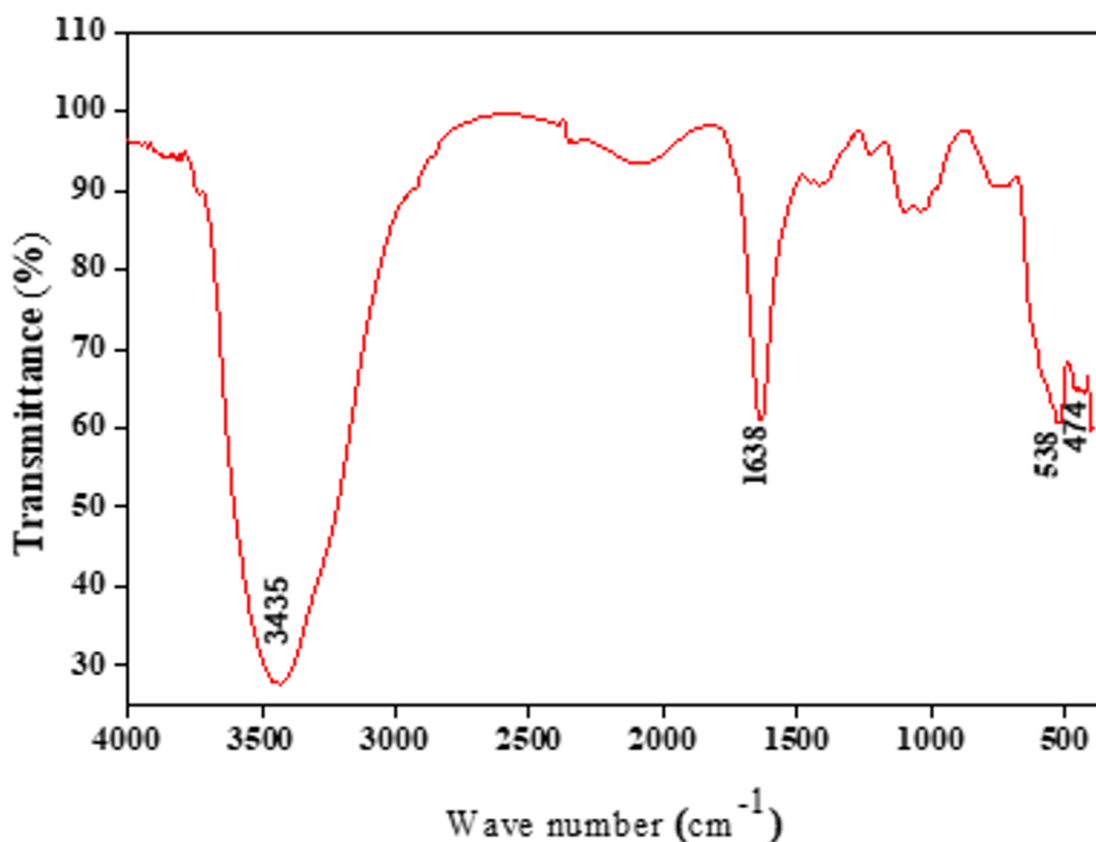


Figure : FTIR spectrum of green synthesized $\alpha\text{-Fe}_2\text{O}_3$ NPs

The FI-TR spectra for the *Moringa stenopetala* seed extract are displayed in Figure 9. The peak at 3451 cm^{-1} can be attributed to the O-H and N-H from water molecules. The bands at 2927

cm^{-1} and 2856 cm^{-1} correspond to asymmetric and symmetric C-H stretching vibrations of the aliphatic chain. The peak at 1744 cm^{-1} is related to the C=O of stretching carbonyl. The bands at 1643 and 1552 cm^{-1} are N-H stretch modes in amine. The peak at 1041 cm^{-1} is due to the C-N stretching functional group. The peak at 621 cm^{-1} indicates N-H bending. From the listed functional groups, those with high electron sharing capacity, such as carbonyl carbon, hydroxyl, etc., are believed to act as reducing agents in the preparation of hematite NPs.

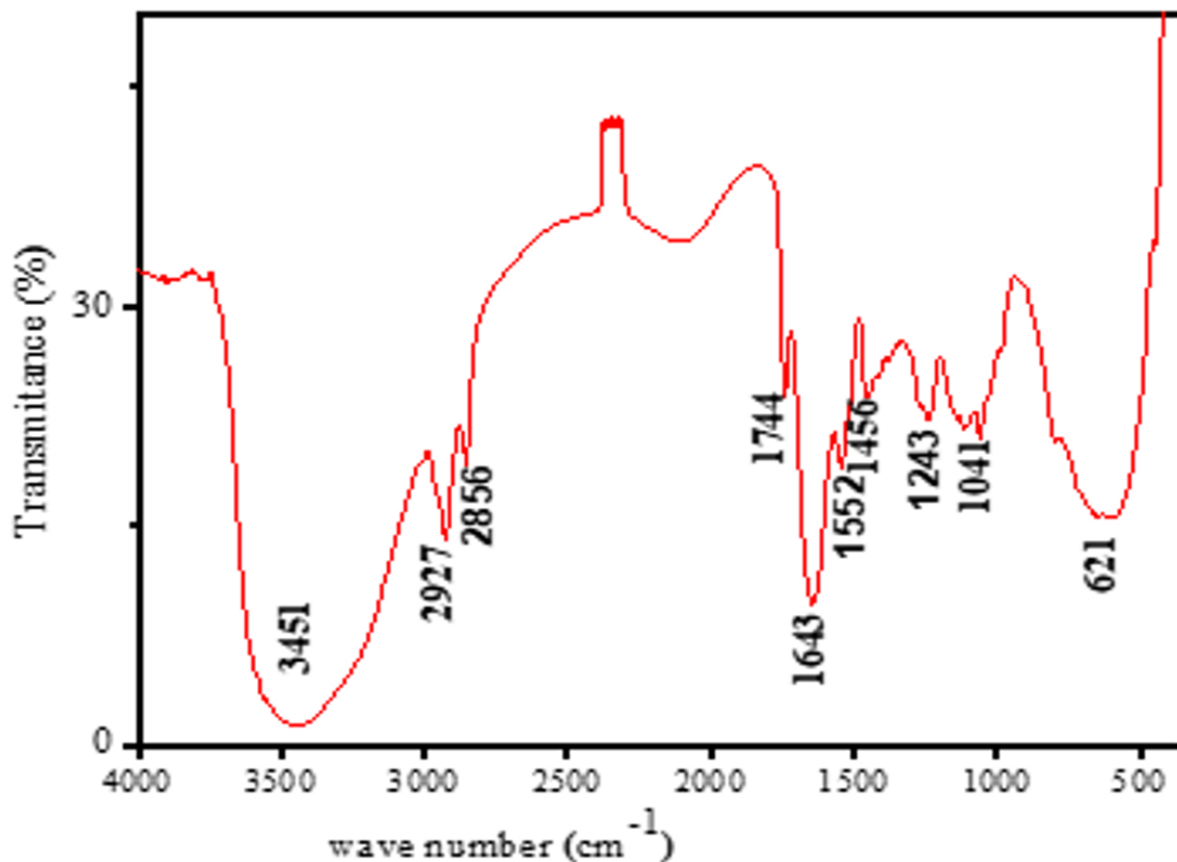


Figure : FTIR spectrum of moringa stenopetala seed extract.

4.1.4. Ultraviolet-visible Spectroscopy (UV-Vis) Analysis.

Moringa stenopetala seed aqueous extract mediated green synthesized $\alpha\text{-Fe}_2\text{O}_3$ NPs were characterized by UV-Visible spectroscopy. The Optical properties of green synthesized $\alpha\text{-Fe}_2\text{O}_3$ NPs were analyzed between 200 nm to 800 nm wave length range using their absorbance measurement. The sharp absorption peak was found at 313 nm in the visible region. Due to the ligand-to-metal charge-transfer transitions (direct transitions), the absorption peak appeared in the region between 250-400 nm with combined contributions from the Fe^{3+} ligand field

transitions (Ali et al., 2017) . The absorbance peak for the formation of α -Fe₂O₃ NP is illustrated in Figure 10.

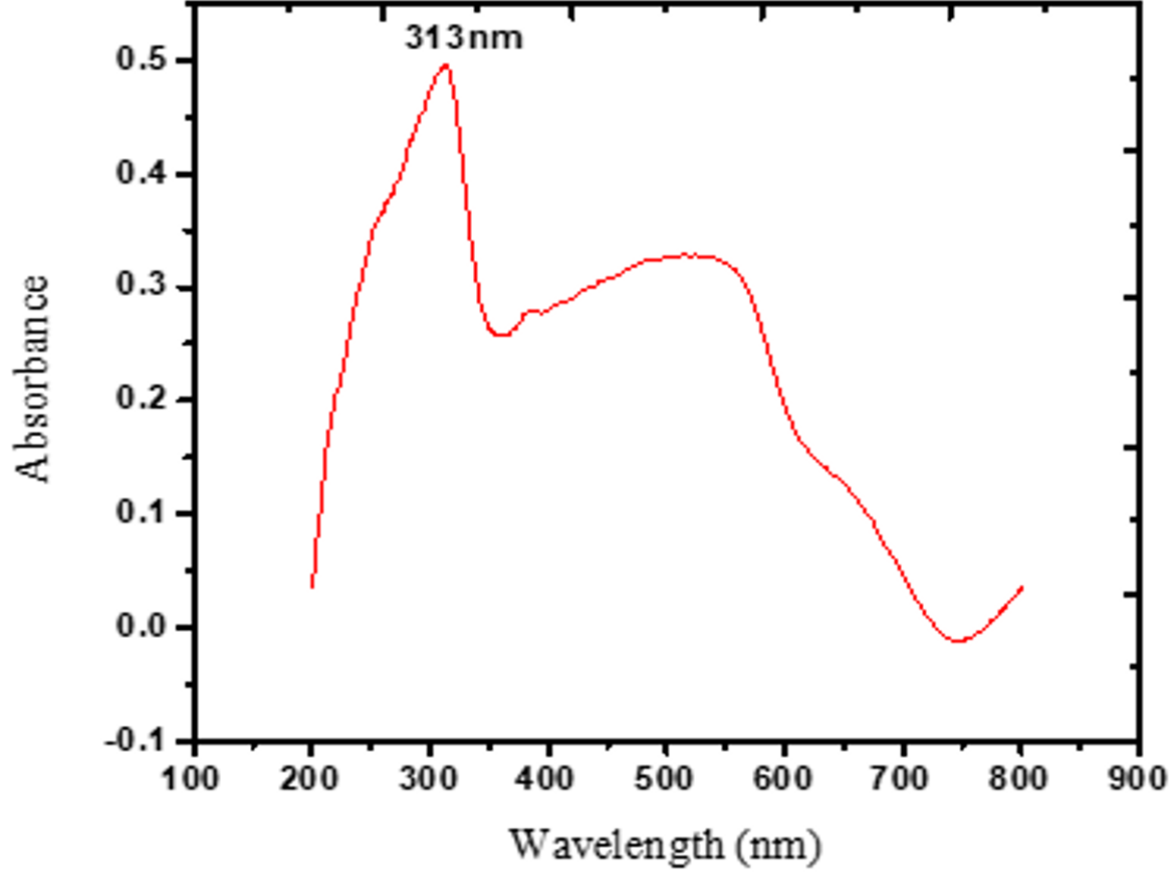


Figure : UV-Vis spectrum of synthesized α -Fe₂O₃ NPs.

The energy band gap of α -Fe₂O₃ NPs was examined in the current work on optical characterization. The Tauc plot was used to calculate the energy band gap.

$$(\alpha h\nu)^{1/n} = k(h\nu - E_g) \quad (3)$$

Where α is the absorption coefficient, $h\nu$ is the energy of the photon, E_g is the optical band gap, k is constant. n takes the value $\frac{1}{2}$ or 2, depending on whether the transition is direct or indirect respectively. The energy band gap of the synthesized nanoparticles was obtained By projecting linear components of $(\alpha h\nu)^2$ versus $h\nu$ to the plot $\alpha = 0$, we were able to determine the energy band gap of the synthesized hematite nanoparticles. The energy band gap is the minimum energy difference between the valance band and conduction band. It has also been reported that α -Fe₂O₃

exhibits both direct band gaps and indirect band gaps (Sundara Selvam et al., 2021). The energy band gap of the green synthesized α -Fe₂O₃ NPs was found to be 2.744 eV, which can be seen from Figure 11.

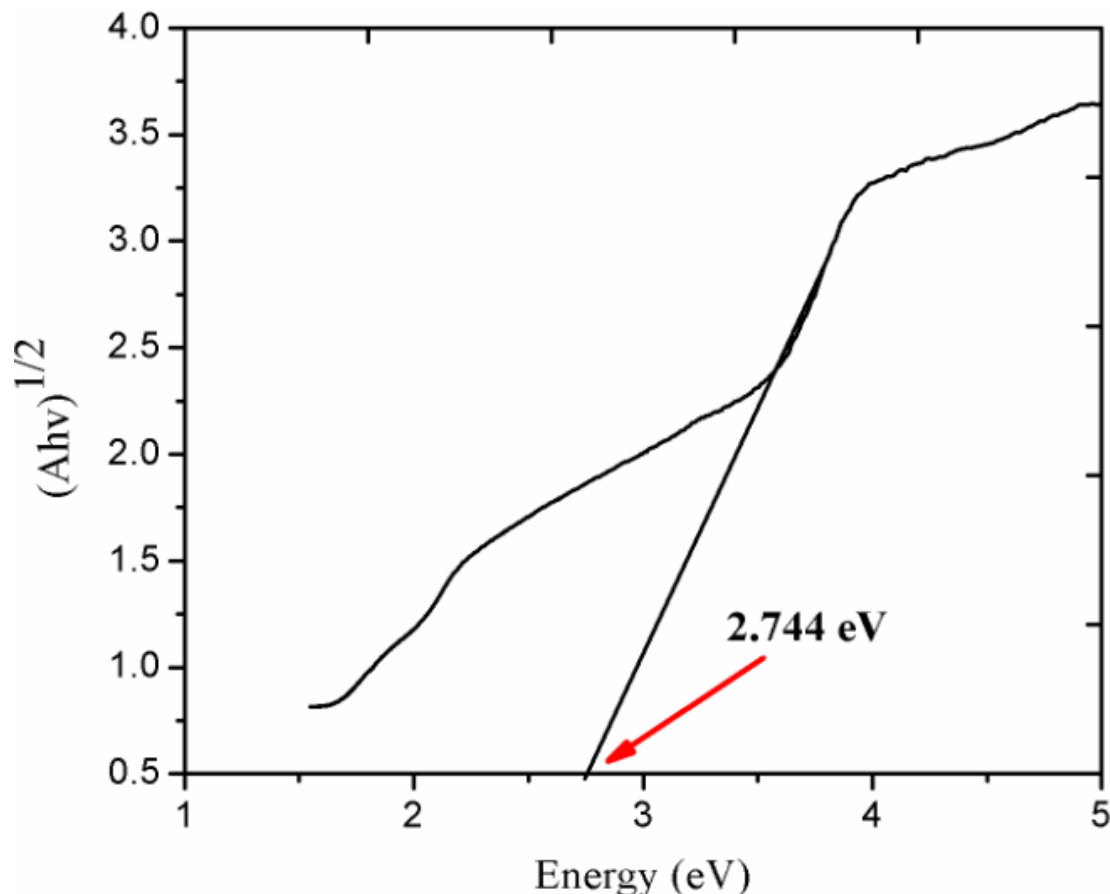


Figure : $(Ah\nu)^{1/2}$ for α -Fe₂O₃ NPs vs. photon energy.

4.1.5. Scanning Electron Microscopy (SEM) Analysis.

SEM is the most common analytical technique employed in the characterization of α -Fe₂O₃ NPs. Information about the sample surface morphology is revealed by signals resulting from the interaction between light and sample. The SEM images of green synthesized hematite nanoparticles are shown in Figure 12. The image shows the grain like morphology, irregular distribution, and spherically random orientation. The fact that there was less particle aggregation than expected suggests that the biomolecules in the seed extracts were effective in reducing particle aggregation and agglomeration.

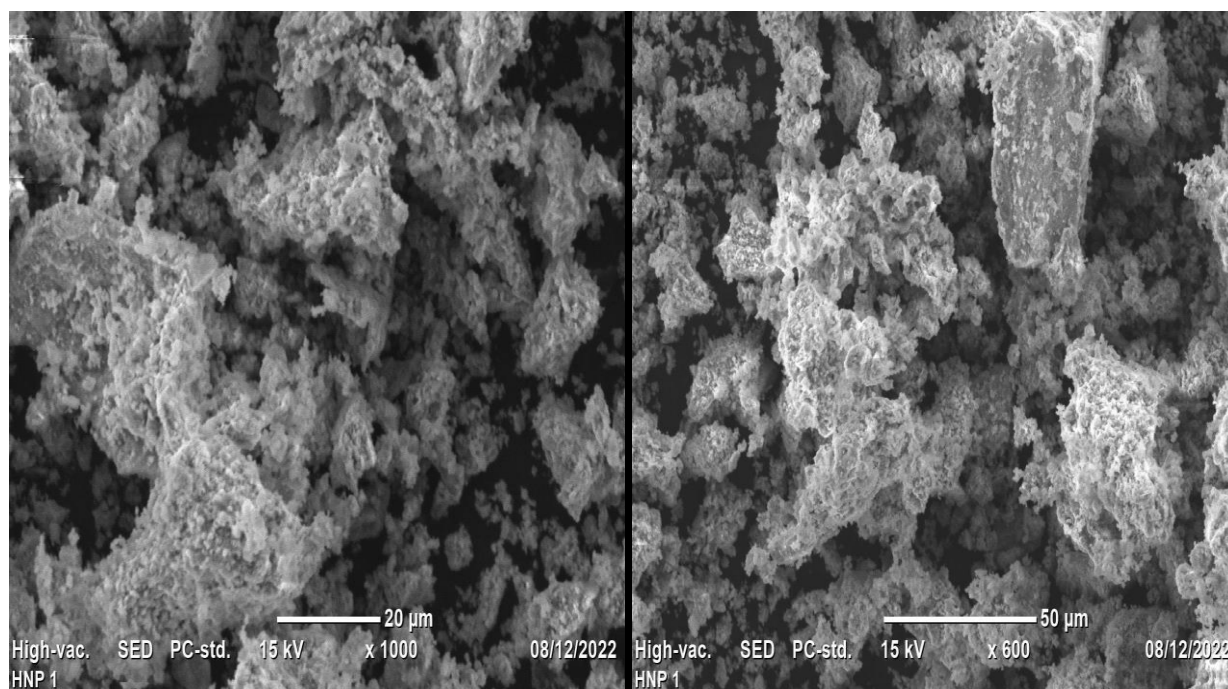


Figure : The SEM image of green synthesized α -Fe₂O₃ NP.

4.2. Photocatalytic Study

Photocatalytic activity of green synthesized α -Fe₂O₃ NPs was evaluated by photodegradation of methylene blue dye pollutant under natural sunlight irradiation. The synthesized α -Fe₂O₃ NPs with different ratios of precursor to plant extract (1:2, 1:1, and 1:3) were optimized to select the one with the highest photocatalytic degradation efficiency. The degradation efficiency of precursors to plant extract (1:2, 1:1, and 1:3) was found to be 98.23 %, 96 %, and 93.5 %, respectively. Based on preliminary tests, a precursor to plant extract with a ratio of 1:2 was selected for further study for photocatalytic degradation of MB dye. The typical method for detecting dye degradation was a slow transition from colored to colorless solutions. By adjusting experimental variables such as pH of the solution, catalyst dosage, initial concentration of dye, and exposure time, the degradation process aided by α -Fe₂O₃ NPs was examined.

4.2.1. Point of zero charge

The point of zero charge is the pH at which the photocatalyst surface of α -Fe₂O₃ NPs has an equal distribution of total positive and total negative charges on its surface site. The surface charge of hematite nanoparticles is zero at this pH. The point of zero charge of α -Fe₂O₃ NPs was found to be 8 in agreement with the literature (Kusior et al., 2019). The surface of the

photocatalyst is positively charged when pH is less than 8, and the surface of the photocatalyst is negatively charged when pH is greater than 8. So at higher pH values (particularly 12), strong attractive forces between the negatively charged photocatalytic surface and cationic methylene blue dye favor higher photocatalytic degradation. The electrostatic forces between positively loaded MB (cationic dye) and positively loaded photocatalyst sites cause MB degradation to decrease at lower pH.

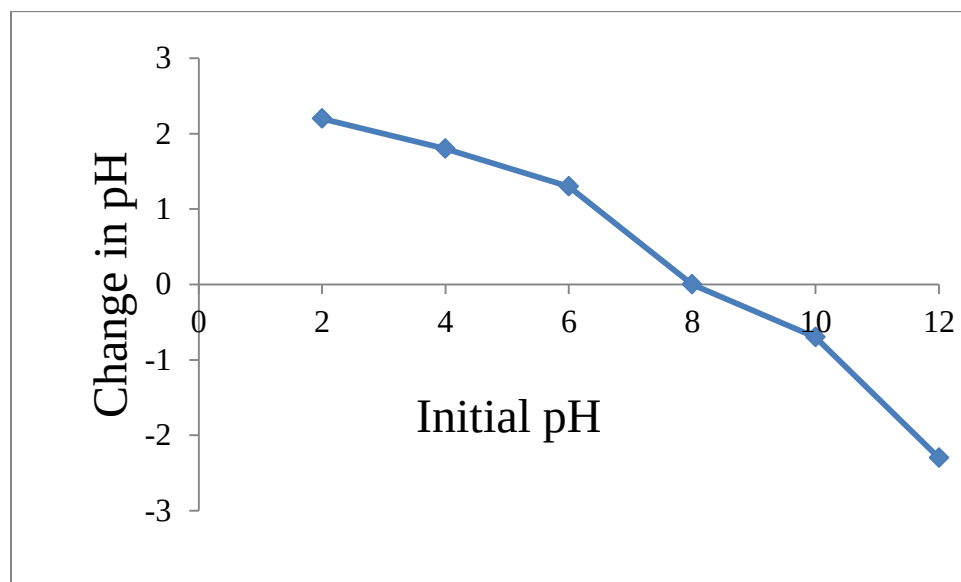


Figure : The point of zero charge graph of $\alpha\text{-Fe}_2\text{O}_3$ NPs

4.2.2. Effects of solution pH

The effect of pH of the solution on photocatalytic degradation of MB dye was tested at pH ranges of 2, 4, 6, 8, 10, and 12 while maintaining other factors constant, including catalyst dosage, initial concentration of dye, and exposure time. The adsorption of dye molecules on the surface of a photocatalyst can be influenced by solution pH. Figure 14 showed that the percentage degradation of MB dye molecules increased with increasing pH of the reaction mixture. At pH 2 in an acidic condition, the degradation efficiency of MB dye was found to be 31.9%, whereas at pH 12 in a basic solution, the percentage degradation was increased to 98.25 %. So the maximum degradation efficiency of MB was obtained at pH 12. At lower pH (below pzc), the surface of the photocatalyst is positively charged and electrostatic repulsion between the photocatalyst and the cationic MB dye and a high concentration of proton hinder the degradation efficiency. At higher pH (greater than pzc), the surface of the photocatalyst is negatively charged, and more reactive radicals can be generated for significant electrostatic interaction

between positively charged MB dyes that enhances higher photocatalytic degradation efficiency. Therefore, due to an increase in the interaction between the solution and the surface of $\alpha\text{-Fe}_2\text{O}_3$ NPs: the degradation efficiency of MB is higher in alkaline media.

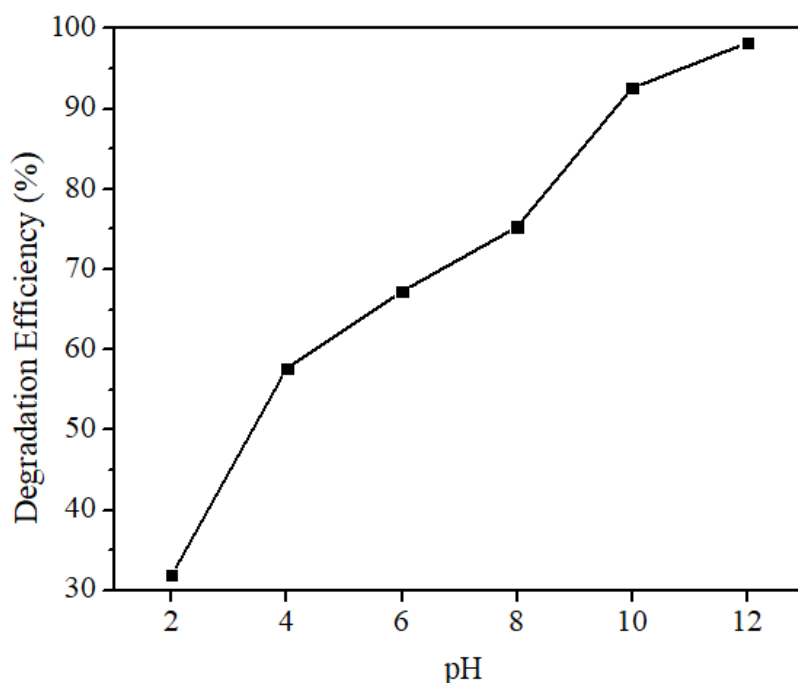


Figure : Effect of pH on photo degradation of MB dye.

4.2.3. Effects of catalyst dosage

By varying the dosage of 0.01 g, 0.05 g, 0.1 g, 0.15 g, 0.20 g, and 0.25 g on pH 12 at an initial MB dye concentration of 30 mg/L, the effect of photocatalyst dosage on the degradation of MB using $\alpha\text{-Fe}_2\text{O}_3$ NPs was studied. Figure 15 showed that the dosage of 0.05 g resulted in the maximum degradation efficiency of MB (98.28 %). After optimum value, increasing dosage tends to decrease the degradation efficiency of MB dye. Dye degradation increases initially as catalyst dosage increases due to more active sites on the photocatalytic surface, where there are more hydroxyl and superoxide radicals, which accelerate dye degradation. However, when the numbers of photocatalysts increases above the optimum value, the turbidity of the reaction mixture blocks light irradiation from reaching the catalytic surface, As a result, fewer photocatalyst active sites are generated, which leads to a decrease in the rate of degradation.

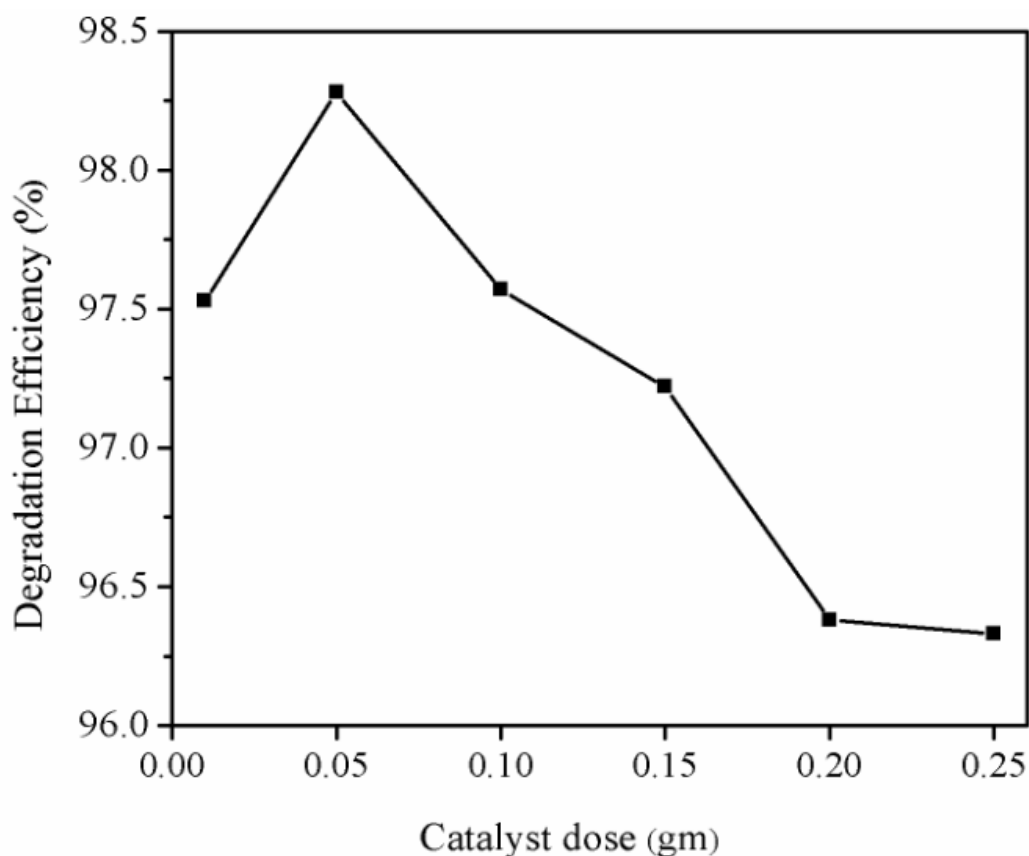


Figure : Effect of catalytic dosage on Photodegradation of MB dye.

4.2.4. Effect of initial concentration

An additional important factor in photocatalytic degradation was the initial concentration of dye. The effect of initial concentrations of dye degradation efficiency was investigated by varying the concentration of dye to 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, and 50 mg/L at a catalyst dosage of 0.05 g, pH 12, and a 180 minute irradiation time. Figure 16 shows that increasing the initial concentration of dye result in increased dye degradation up to the optimum value. The maximum degradation percent of MB was 98.13 %, which was achieved at an initial concentration of 30 mg/L. Up to the optimum value of the initial concentration of the dye, increasing the concentration increases the degradation efficiency because more dye molecules become available to be degraded. As the initial concentration of MB dye increases more and more, dye molecules are adsorbed on the surface photocatalyst, and a significant amount of light irradiation is adsorbed by dye molecules rather than by $\alpha\text{-Fe}_2\text{O}_3$ NPs. This problem inhibits the penetration of light to the catalyst surface by decreasing the generation of radicals since the active sites are occupied by dye molecules. As a result, for a given number of hematite sites, the degradation

efficiency of $\alpha\text{-Fe}_2\text{O}_3$ NPs decreases as the methylene blue dye concentration in the solution increases. This issue was associated with the lack of sufficient surface sites to support higher concentrations of methylene blue dye already present in the solution. All dye molecules in the solution might interact with binding sites at lower concentrations, making them more susceptible degradation than those at higher concentrations.

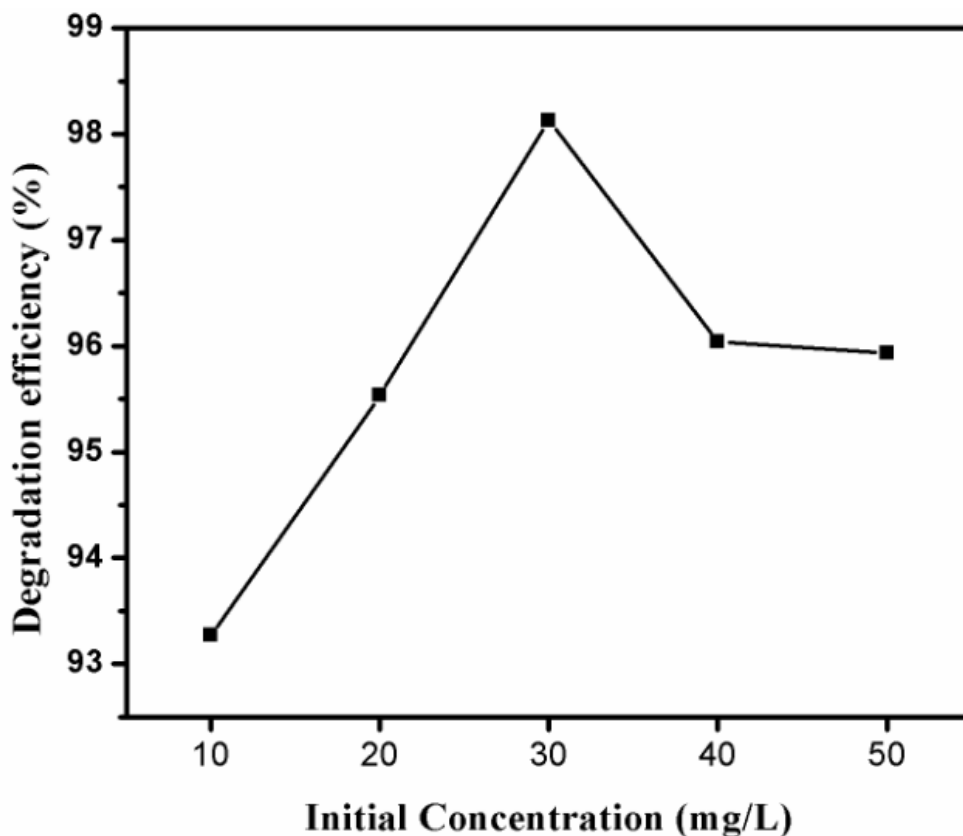


Figure : Effect of initial concentration on MB dye photodegradation.

4.2.5.. Effects of exposure time

At constant experimental conditions, such as pH 12, initial MB dye concentration 30 mg/L, and catalyst dosage of 0.05 g, the impacts of exposure duration on photocatalytic degradation of MB dye were studied by increasing the exposure time from 30 min to 180 min with 30 minute intervals. The degradation efficiency of MB increases from 88.57% to 98.33% as the time of irradiation increases from 30 to 90 minute, and after the optimum time, the degradation efficiency seems to attain a constant value.

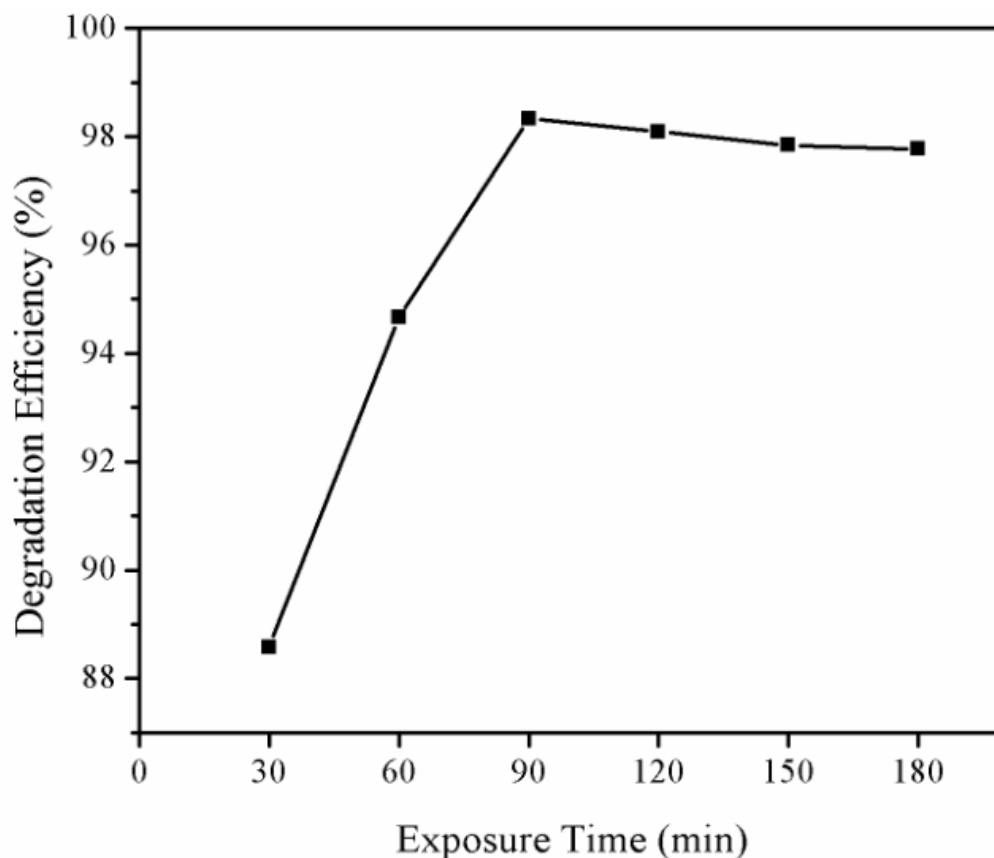


Figure : Effect of exposure time on Methylene blue degradation.

4.3. Kinetic Study of photocatalytic reaction

The Langmuir–Hinshelwood (L–H) mechanism can be used to evaluate the kinetics of chemical degradation. In this model, the rates of reactions increase linearly with the concentration of organic compounds at low concentrations and are independent of the concentration at high concentrations, which is the kinetics observed for photodegradation of organic compounds in aqueous solution. It also contains several pieces of information about the reactions that occurred at the surface of the photocatalyst. The photodegradation rate can be predicted with the help of kinetic parameters, which also provide information for developing and modeling the degradation process. To predict the photodegradation data of the dye, the pseudo zero-order, pseudo first-order and pseudo second-order kinetics models have been investigated in the present study. To measure the activity of heterogeneous photodegradation, the Langmuir–Hinshelwood (L-H) model is considered as the following equation:

$$r = -\frac{dc}{dt} = \frac{kKC}{1+KC} \quad (4)$$

Where K and k denote the thermodynamic adsorption constant and photodegradation rate constant, respectively, and C denotes the dye concentration.

For investigating the pseudo kinetics, a calibration curve was constructed to calculate the remaining concentration of the dyes after degradation at different time intervals. By making serial dilutions from 100 mg/L of MB dye (1 mg/L, 2 mg/L, 3 mg/L, 4 mg/L, and 5 mg/L), data for the calibration curve were obtained. Then, an absorbance calibration curve versus MB dye concentration was drawn. A straight line was used to match the experimental data shown in Figure 18 and has a high regression coefficient value ($R^2 = 0.9992$).

Table : Calibration curve of methylene blue dye

concentration	Measuremet of absorbance(Ao)			
	Ao	Ao	Ao	Av
0	0	0	0	0
1mg/L	0.097	0.099	0.098	0.098
2mg/L	0.190	0.191	0.192	0.191
3mg/L	0.291	0.292	0.290	0.291
4mg/l	0.399	0.40	0.401	0.40
5mg/L	0.504	0.50	0.502	0.502

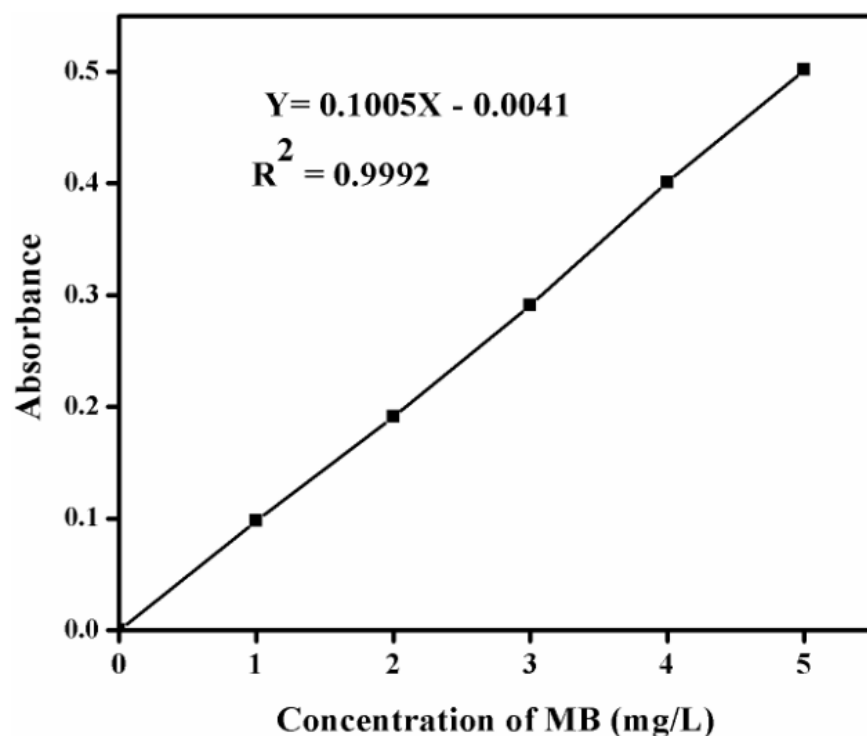


Figure : Calibration curve for methylene blue dye.

The pseudo kinetics experiment was conducted, and the calibration curve was used for calculating the remaining concentration of the dyes. The photodegradation pseudo kinetics studies were conducted with an initial methylene blue concentration of 30 mg/L and exposure times ranging from 30 to 90 minutes, while all other experimental parameters were held constant.

Table : Data for determining pseudo kinetics model

Dye	C _i (mg/L)	Time (min)	C _t (mg/L)	C _i -C _t	C _i /C _t	Ln(C _i /C _t)	1/C _t -1/C _i
MB	30	30	3.379	26.621	8.878	2.183	0.262
		60	1.7353	28.27	17.34	2.853	0.544
		90	0.782	29.218	30.07	3.40	1.245

4.3.1. Pseudo zero order kinetic model

The reaction kinetics can be simplified because one of the reactants functions as a photocatalyst whose concentration does not vary. Since the photodegradation rate is independent of dye concentration, the rate at low dye concentration can be simplified to $KC \gg 1$ and the kinetics can be considered pseudo zero-order at high dye concentrations, where the photocatalyst surface is completely covered.

$$r = -\frac{d_c}{d_t} = k \quad (5)$$

Integrating the equation $C = C_i$ at $t = 0$ and $C = 1/2C_i$ respectively yields.

$$C_i - C_t = K_0 t \quad (6)$$

Pseudo zero-order kinetics is represented by a plot of $C_i - C_t$ vs. irradiation time, where C_i is initial concentration before degradation and C_t is the concentration at time t after degradation. As a result, saturation coverage on the photocatalyst surface is observed, and the photodegradation rate is independent of the dye concentration. For pseudo zero-order, the correlation coefficient (R^2) is 0.956.

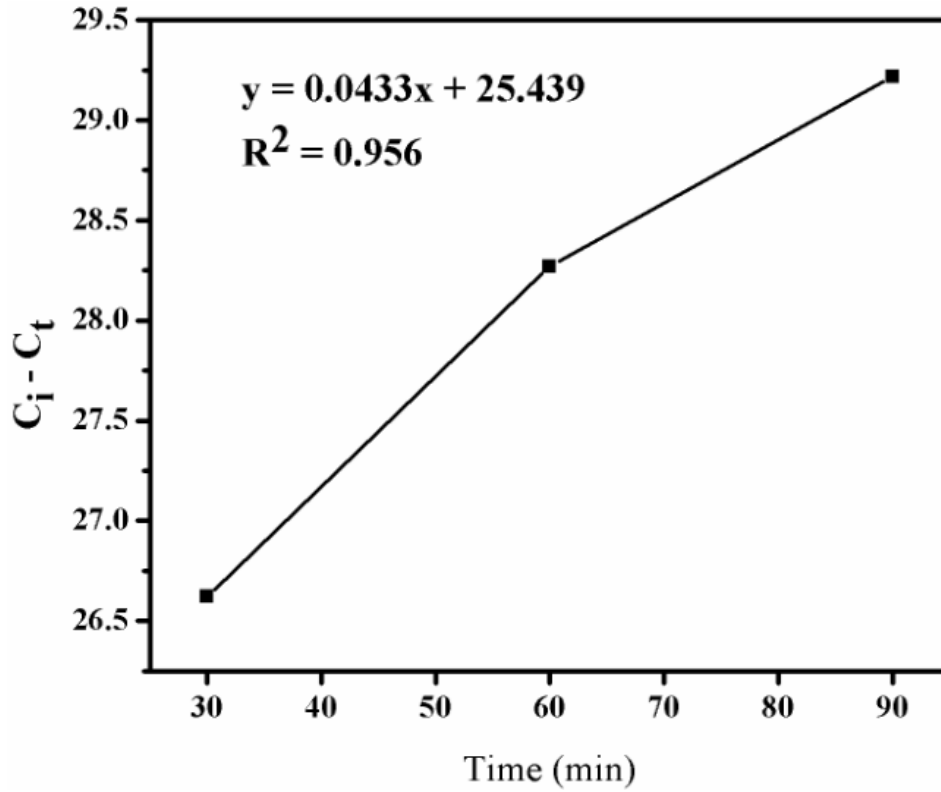


Figure : Pseudo zero order kinetic model of methylene blue

4.3.2. Pseudo first order kinetic model

The rate law can be simplified considering that $KC \ll 1$ and the kinetics can then be considered as apparent first order:

$$r = -\frac{dc}{dt} = K_1 C \quad (7)$$

Where k_1 is representing the first order rate constant, integrating the equation becomes:

$$\ln \left(\frac{C_i}{C_t} \right) = K_1 t \quad (8)$$

The pseudo first order kinetics of MB dye degradation and the results confirm that the appropriate model to describe the photodegradation reaction of MB dye is given below.

$$\ln \left(\frac{C_i}{C_t} \right) = kt \quad (9)$$

Where C_i and C_t (mg/L) of MB concentrations at the initial and any time in the solution, respectively. Plotting the $\ln. (C_i/C_t)$ versus t gave a straight line of slope k , indicating that the reaction is first order in MB dye.

The kinetics study for photodegradation of methylene blue was investigated at pH 12, catalyst dosage of 0.05g/50mL, MB concentration of 30 mg/L, and exposure time ranging from 30 to 90 min with a 30 min interval. Figure 20 shows the photodegradation kinetics of MB dye of α -Fe₂O₃ NPs in the pseudo-first-order kinetic model.

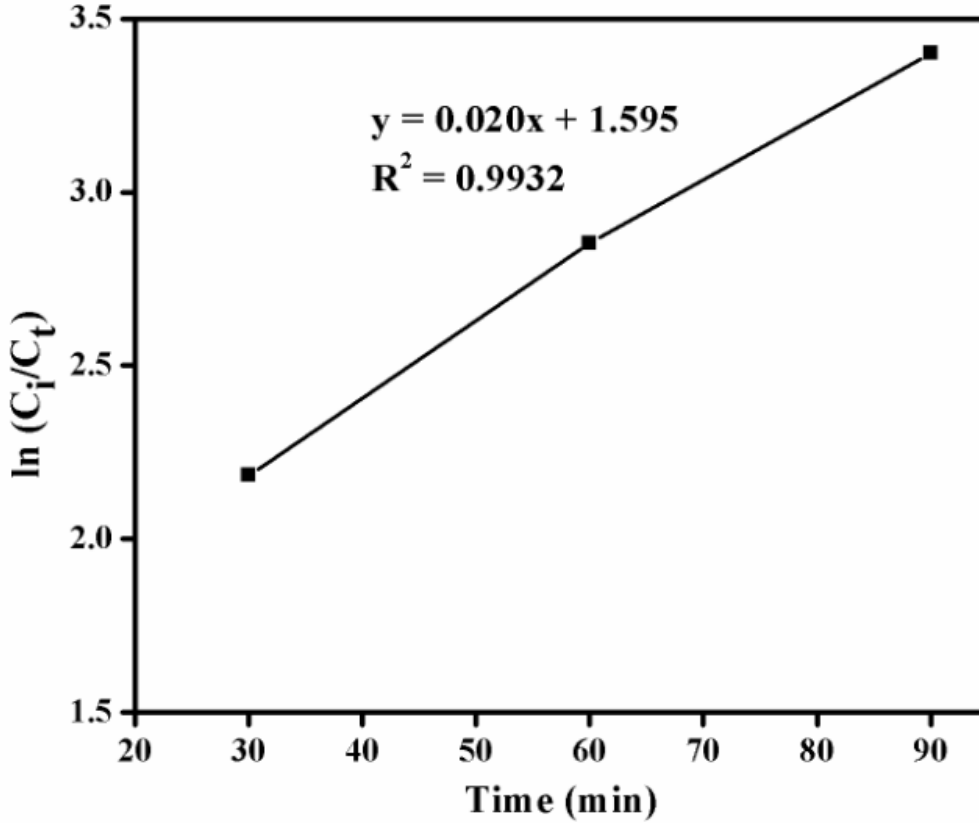


Figure : Pseudo-first order kinetics for MB.

4.3.3. pseudo second order model

For the pseudo-second order kinetics, the model can be expressed by the following linear equation 10:

$$\frac{1}{C_t} - \frac{1}{C_i} = k_2 t \quad (10)$$

where C_t is the amount of MB adsorbed at time t , k_2 is the pseudo-second order rate constant, and C_i is the amount of MB adsorbed at time $t = 0$. The pseudo-second order correlation coefficient is 0.885.

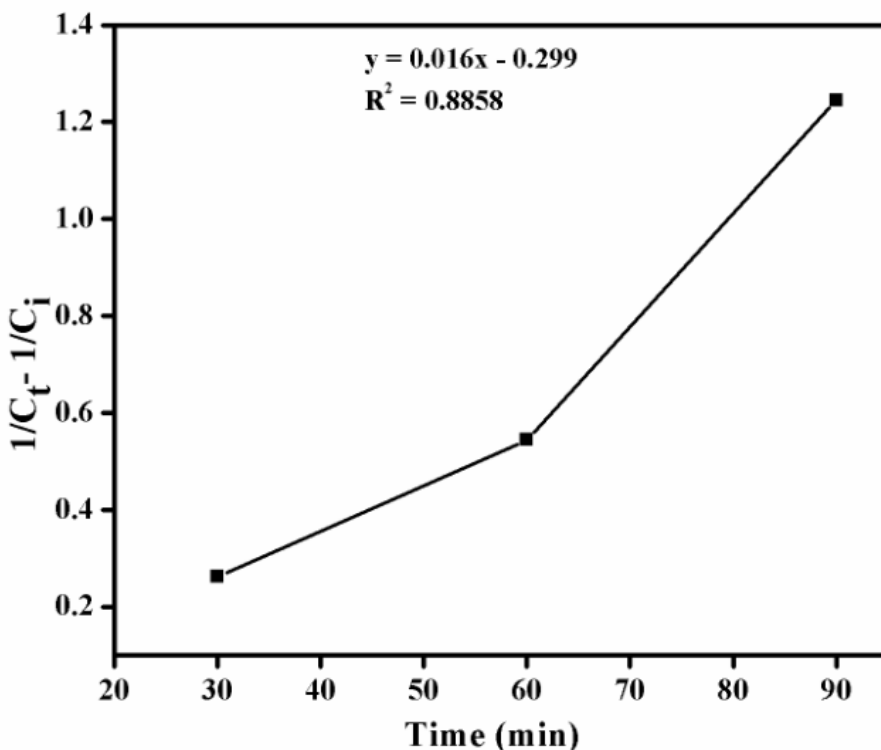


Figure : Pseudo second order kinetic model for MB dye.

Table : Rate constant (k) correlation coefficient (R²) for kinetic models

Types of Model	Methylene Blue Dye	
	k	R ²
Pseudo zero order	0.311	0.952
Pseudo first order	0.031	0.993
Pseudo second order	0.0075	0.885

4.4. Chemical Oxygen Demand(COD) Determination.

The value of COD was calculated by following formula:

$$\text{COD} \left(\frac{\text{mg}}{\text{L}} \right) = \frac{8(V_{bl} - V_s) * M}{V} * 1000 \quad (11)$$

Where V_{bl} and V_s are the volumes of ferrous ammonium sulfate consumed in titration for the blank and the sample, respectively. M is the Molarity of a standardized ferrous ammonium sulfate solution. V is the volume of the degraded solution of MB dye. The COD value is calculated to be 28.4 mg/L. This value indicates that the degradable organic material is almost

successfully degraded, and the synthesized material can be applied for the degradation of methylene blue dyes.

4.5. Regeneration of the synthesized $\alpha\text{-Fe}_2\text{O}_3$ NPs

The regeneration of a photocatalyst is crucial for its industrial application. One of the purposes of the synthesized nanocatalyst was to be regenerated by simple treatment after the experiment. In this experiment, the hematite nanoparticle was recovered from the solution through filtration, and the powder of the nanocatalyst was left on filter paper. The solid nanocatalyst on filter paper was washed several times with distilled water and dried for 24 hours before being used for another cycle. Finally, the paste mass was reused in the successive photodegradation experiments. After degradation, the regenerated nanoparticles were used as photocatalysts for four times in succession. Figure 21 indicated that the performance of the synthesized nanocatalyst was 97.55 %, 96.02%, 93.83%, and 92.62% in successive four recycles. However, the gradual decrease in photocatalytic degradation efficiency with the number of repeated uses results from the waste of catalyst during washing processes.

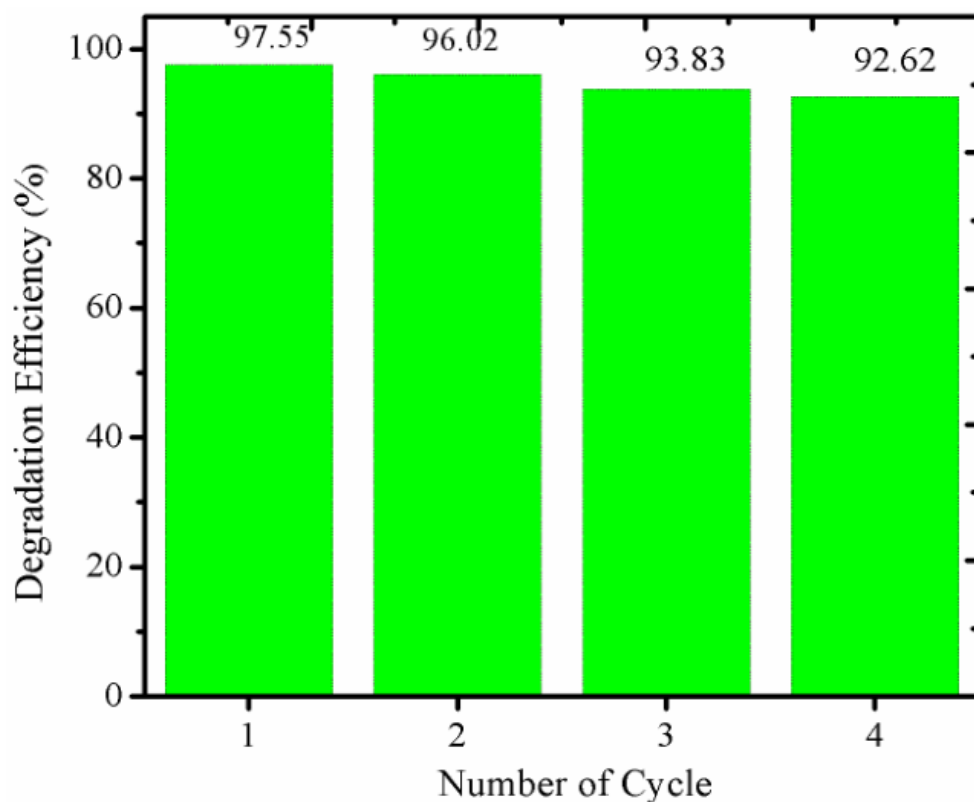


Figure : Regeneration of synthesized $\alpha\text{-Fe}_2\text{O}_3$ NPs.

4.6. Mechanism of photodegradation

Photocatalytic degradation using a semiconductor metal oxide involves mainly electron-hole pair production and chemical reactions. When the system contains a photocatalyst and an organic pollutant is exposed to a photon of energy equal to or greater than that of the band gap energy of the photocatalyst, the electrons (e^-) of $\alpha\text{-Fe}_2\text{O}_3$ are excited from the valance band (VB) to the conduction band (CB) by creating holes (h^+) in VB. Such electron transfer prevents recombination of the electron-hole pair, which increases the effectiveness of photodegradation. The superoxide radicals ($\text{O}_2^{\cdot -}$) created when the electron in CB $\alpha\text{-Fe}_2\text{O}_3$ was captured by molecular oxygen that was present on the surface of CB. While hydroxide ions, with the formation of active species such as hydroxyl radicals, were able to trap photo-induced holes in VB. The complete mineralization of MB in CO_2 and H_2O results from the free radical reaction with MB. For synthesized $\alpha\text{-Fe}_2\text{O}_3$ NPs, the band gap using the Tauc plot was calculated to be 2.744 eV. Based on this result, the proposed photocatalytic degradation mechanism of MB under sunlight irradiation shown in Figure 23.

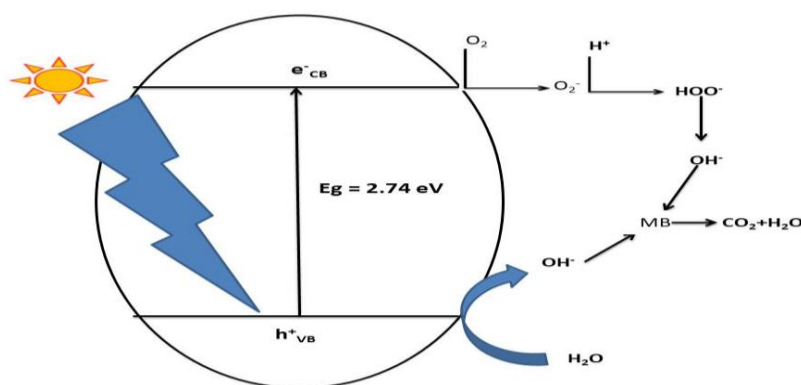
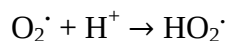
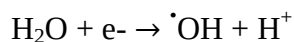
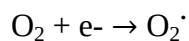
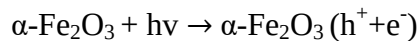
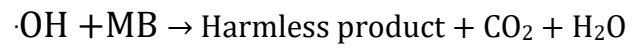
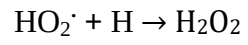


Figure : Proposed photocatalytic degradation mechanism of hematite nanoparticle.

In the proposed mechanism, the following reaction will happen.





5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

In this study, α -Fe₂O₃ NPs were synthesized using green techniques with *Moringa stenopetala* seed extract and ferric nitrate nonahydrate as a precursor. The synthesized α -Fe₂O₃ NPs were applied for photocatalytic methylene blue dye under sunlight irradiation. Hematite nanoparticles were characterized using analytical tools such as TGA, XRD, FT-IR, SEM, and UV-visible spectrophotometry. TGA confirms the synthesized α -Fe₂O₃ NPs were calcinated at 600 °C. The XRD result confirmed the formation of a rhombohedral centered hexagonal structure of hematite nanoparticles with a crystallite size of 32.57 nm. FT-IR spectra confirm characteristics peaks of Fe-O bonds and functional groups present in seed extracts that are assumed as reducing and capping agents in the formation of α -Fe₂O₃ NPs. The optical band gap energy of synthesized hematite nanoparticles was 2.744 eV. It is possible to conclude that the green synthesized α -Fe₂O₃ nanoparticle is effective for potodegradation of methylene blue dye from aqueous solution under exposure to natural sun light from a photocatalytic degradation study. It was concluded that the photocatalytic degradation efficiency of methylene is highly influenced by the pH of the dye solution, catalyst dose, initial dye concentration, and exposure time. The degradation efficiency of α -Fe₂O₃ NPs against MB dye at pH 12, 0.05 g of catalyst dose, and 30 mg/L of initial dye concentration was 98.33% within 90 minutes of sunlight irradiation. Photocatalytic degradation of methylene blue dye follows pseudo first order kinetics. Generally, it is possible to conclude that hematite nanoparticles can be fabricated using *Moringa stenopetala* seed extract as a reducing and capping agent and they can be used for the degradation of methylene blue dye under sunlight irradiation.

5.2. Recommendation

There is little recommendation on the characterization of hematite nanoparticles that will provide complete information for future studies. SEM-EDX should be used to characterize the elemental distribution of hematite nanoparticles. Hematite nanoparticles should be analyzed using TEM and BET instruments in order to determine the particle size, morphology and surface area of the nanoparticles.

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7. APPENDIXES

7.1. Raw Data

Table 5: Effect of solution pH for photodegradation efficiency of Methylene blue dye using 0.05gm/50mL of catalyst dosage and 30 mg/L of dye concentration

PH	Absorbance after degradation (At)				Absorbance before degradation (Ao)				Degradation efficiency (%)
	At	At	At	Av	Ao	Ao	Ao	Av	
2	1.821	1.825	1.822	1.822	2.671	2.677	2.682	2.676	31.907±0.13764
4	1.133	1.133	1.131	1.132	2.671	2.677	2.682	2.676	57.69593±0.12538
.6	0.874	0.874	0.878	0.875	2.671	2.677	2.682	2.676	67.2632±0.04727
8	0.655	0.664	0.666	0.661	2.671	2.677	2.682	2.676	75.3038±0.2117
10	0.199	0.197	0.199	0.199	2.671	2.677	2.682	2.676	92.6235±0.0669
12	0.046	0.046	0.048	0.046	2.671	2.677	2.682	2.676	98.25±0.0395

Table 6: Effect of catalyst for photo degradation efficiency of Methylene Blue dye using pH=12, 30 mg/L dye concentration in 50 mL of solution volume

Dosage	Absorbance after degradation(At)				Absorbance before degradation(Ao)				Degradation efficiency (%)
	At	At	At	Av	Ao	Ao	Ao	Av	
0.01g	0.067	0.068	0.063	0.066	2.671	2.677	2.682	2.676	97.5341±0.124
0.05g	0.044	0.046	0.048	0.046	2.671	2.677	2.682	2.676	98.28±0.071
0.1g	0.064	0.065	0.066	0.065	2.671	2.677	2.682	2.676	97.5716±0.0323
0.15g	0.071	0.075	0.077	0.074	2.671	2.677	2.682	2.676	97.2230±0.1085
0.2g	0.097	0.097	0.096	0.096	2.671	2.677	2.682	2.676	96.3884±0.028
0.25g	0.097	0.099	0.098	0.098	2.671	2.677	2.682	2.676	96.3387±0.0338

Table 7: Effect of initial concentration for photodegradation efficiency of MB using catalyst dosage = 0.05 gm/50 mL and at pH =12

Initial con.	Absorbance after degradation(A_t)				Absorbance before degradation(A_o)				Degradation efficiency
	A_t	A_t	A_t	A_v	A_o	A_o	A_o	A_v	
10pm	0.074	0.074	0.073	0.0736	1.089	1.096	1.099	1.094	93.268 $\pm$ 0.080
20pm	0.095	0.099	0.096	0.0966	2.160	2.168	2.170	2.166	95.536 $\pm$ 0.090
30pm	0.051	0.048	0.051	0.050	2.671	2.677	2.682	2.676	98.13 $\pm$ 0.0667
40pm	0.112	0.115	0.116	0.1143	2.884	2.886	2.889	2.886	96.038 $\pm$ 0.069
50pm	0.119	0.121	0.123	0.121	2.972	2.983	2.975	2.976	95.934 $\pm$ 0.065

Table 8:Effect of contact time for photodegradation of MB dye using 30 mg/L initial concentration,catalyst dosage=0.05gm/50mL at pH=12

time	Absorbance after degradation(A_t)				Absorbance before degradation(A_t)				Degradation Efficiency(%)
	A_t	A_t	A_t	A_v	A_o	A_o	A_o	A_v	
30min	0.304	0.308	0.305	0.3056	2.671	2.677	2.682	2.676	88.579 $\pm$ 0.074
60min	0.139	0.141	0.140	0.140	2.671	2.677	2.682	2.676	94.663 $\pm$ 0.161
90min	0.043	0.045	0.046	0.0446	2.671	2.677	2.682	2.676	98.33 $\pm$ 0.0540
120mn	0.051	0.050	0.052	0.051	2.671	2.677	2.682	2.676	98.09 $\pm$ 0.0289
150mn	0.056	0.058	0.059	0.0576	2.671	2.677	2.682	2.676	97.84 $\pm$ 0.0425
180mn	0.058	0.060	0.061	0.0596	2.671	2.677	2.682	2.676	97.77 $\pm$ 0.0421

Table.9. Point of zero charge for α -Fe₂O₃ NPs

Initial pH	Final pH	Change in pH
2	4.2	2.2
4	5.8	1.8
6	7.2	1.2
8	8	0
10	9.3	-0.7
12	9.7	-2.3

Table 10. Recycling of synthesized α -Fe₂O₃ NPs

No of cycle	Absorbance after degradation (At)				Absorbance before degradation (Ao)				Degradation Efficiency (%)
	At	At	At	Aav	Ao	Ao	Ao	Aav	
Cycle 1	0.063	0.066	0.067	0.0653	2.671	2.677	2.682	2.676	97.55±0.03
Cycle 2	0.105	0.106	0.108	0.1063	2.671	2.677	2.682	2.676	96.02±0.05
Cycle 3	0.161	0.166	0.168	0.165	2.671	2.677	2.682	2.676	93.83±0.123
Cycle 4	0.197	0.196	0.199	0.1973	2.671	2.677	2.682	2.676	92.62±0.049