Green Synthesis of Nickel Oxide and Zinc Ferrite Nanoparticles and Their Catalytic Applications

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ABSTRACT
The traditional method of synthesizing nanoparticles is being replaced with sustainable and environmentally friendly methods. These environmentally friendly methods create nanoparticles using plant extract and microorganisms. To create nanoparticles, plant extracts made from various plant parts are typically utilized. Calotropis procera leaf extract was used to create NiO and ZnFe2O4 nanoparticles using a microwave-assisted technique. Numerous phytochemicals included in Calotropis procera leaf extract serve as capping and reducing agents during the creation of nanoparticles. FTIR and UV-visible spectroscopy were used for characterisation.
ZnFe2O4 has peaks at 372 and 460 nm, whereas NiO nanoparticles have a peak at 387 nm. These methods are the most effective for confirming that the synthesis process was successful and that the produced nanoparticles included a variety of functional groups. A UV-visible spectrophotometer was used to examine the photocatalytic activity of NiO and ZnFe2O4 nanoparticles for the breakdown of 4-notrophenol. For 4-nitrophenol, NiO nanoparticles exhibit 78% degradation and ZnFe2O4 exhibits 85%. 4-nitrophenol must be broken down since it has a negative impact on the environment and is released by a number of companies.
The successful and effective catalytic performance of green synthesized NiO and ZnFe2O4 nanoparticles demonstrates that the green synthesis method using plant extract has been shown to be a good catalyst and that a green route has been identified for the successful development of eco-friendly materials for various applications.

1. Introduction

One of the major challenges facing environmentalists today is the handling of industrial waste water. Wastewater from the food, pharmaceutical, and textile sectors, including organic dyes, is the primary source of environmental pollution [1]. These stable dyes show resilience to degradation and can linger in water for a long time if untreated. Along with organic dyes, industrial effluent also contains heavy metals that are harmful to human health and pollute water, such as lead, chromium, nickel, and arsenic [2].

1.1. Nanotechnology

Many academics from many fields have been interested in nanotechnology, which is the study of altering matter at the microscopic level [7, 8]. Because of their unique qualities, nanomaterials are a promising solution for environmental issues such the elimination of organic waste, heavy metals, dyes, microbes, and other pollutants. Moreover, nanoparticles exhibit remarkable sensitivity and a larger surface area [9]. It suggests that nanotechnology is linked to its inventive uses in electronics, health, food, and other sectors, demonstrating how important it would be for creating new technologies and solving global issues.

1.2. Nanomaterials

Nanoparticles, which range in size from 1 to 100 nanometers, are extremely small chemical groupings that exist on the nanoscale [10]. Because of their small size, they exhibit distinct traits and behaviors that distinguish them from larger particles. The potential of nanoparticles in a variety of fields, including electronics, materials science, medicine, and the environment, is being intensively investigated by researchers [11]. One of the main benefits of tiny nanoparticles is their higher surface area to volume ratio, which leads to both better characteristics and increased reactivity.

1.3. Metal Nanoparticles

Metal nanoparticles between 1 and 100 nm are found to have special physical, chemical, and biological characteristics that allow them to be used in a variety of sectors, such as environmental research, electronics, and medicine. Gold, silver, iron oxide, copper, and platinum are a few examples of metal nanoparticles that have various characteristics including biocompatibility, antibacterial activity, or catalytic efficiencyA. For instance, gold nanoparticles are often employed in medication administration and medical imaging, whereas silver nanoparticles are frequently used in antibacterial applications because they may harm microbial cell membranes [14].

Zinc ferrite ($ZnFe_2O_4$) and nickel oxide (NiO) are crucial components of metal nanoparticles. Because of its magnetic, electrical, and optical properties, zinc ferrite nanoparticles can be used in energy storage devices, sensors, magnetic storage media, and catalysis [15]. Zinc ferrite nanoparticles can be used as a photocatalyst or in Fenton-like reactions, which generate reactive species that degrade dye molecules, to effectively remove synthetic dyes [16Nickel oxide nanoparticles are used in many different fields, such as catalysis, environmental remediation, energy generation and storage, and biomedical applications, because of their superior electrical conductivity, heat resistance, ability to produce reactive species under light for dye degradation, and capacity to adsorb a large number of dye molecules due to their large surface areas.

[17, 18].

The breakdown of synthetic colors, which are discharged into waste water from many sources, mainly the textile industry, due to their non-biodegradable nature and dangerous impacts, is one of the major environmental uses of zinc ferrite and NiO nanoparticles. Because of their effective catalytic qualities, zinc ferrite and NiO nanoparticles provide an ecologically and financially viable water treatment option.

1.4. Importance of Nanoparticles

Catalysis was one of the first uses of nanoparticles. Silica, metal oxide, and metal ferrites are just a few of the materials and minerals that have been employed as nanoscale catalysts over the years. From academic research to commercial applications, catalysis plays a crucial role in chemical reactions and numerous chemical processes. In addition to having a definite favorable impact on reaction rate, large surface area nanoparticles may also make sense in terms of reactant transport.

Numerous industries employ nanoparticles. From a medical standpoint, they are used in the development of vaccinations, imaging tools like CT and MRI scans, cancer therapies like chemotherapy and extreme heat, and the administration and targeting of medications. Nanoparticles are essential to drug delivery systems because they bind to pharmaceuticals to target certain cells, minimize adverse side effects, and allow regulated drug release [20].

They are utilized in the energy sector for solar and photovoltaic cells, fuel cells, batteries, and energy conversion and storage. Numerous components of electrical devices, including semiconductors, transistors, memory storage devices, LEDs, and displays, employ nanomaterials [21–23].

Additionally, they are utilized in everyday consumer goods including sunscreen and cosmetics, textiles and accessories, and food processing and packaging [24–26]. Nanoparticles are widely used in environmental cleaning, including soil remediation, air pollution management, and water purification and treatment [27–29]. They are widely used in agriculture. They are employed in agricultural disease prevention and control, fertilizer development, and pesticide targeting and delivery. For commercial use in chemical reaction catalysts, surface modification, coatings, and composites, nanomaterials are crucial [33, 34].

It is difficult to create highly functionalized catalysts, and the development and improvement of catalysts still depend on the use of high-throughput technologies [35]. By turning this information into useful applications, researchers are able to create custom catalyst materials that are purposefully manufactured with a carefully regulated combination of certain features. Nanoparticles are particularly helpful in biological sensing, transport, and imaging of live cells and tissues because their surface characteristics may be modified and a wide variety of core materials are easily accessible.

1.5. Methods and strategies for creating nanoparticles

Although there are several ways to produce nanomaterials, top-down and bottom-up approaches are the most often used (figure 1.1). The top-down method breaks down larger bulk materials into nano-sized particles, whereas the bottom-up method employs individual atoms to construct larger nanomaterials. For certain particular qualities and uses, the production of nanoparticles primarily uses a variety of techniques. These techniques may be roughly divided into three categories: physical, chemical, and biological (hybrid or green).

1.5.1. Physical methods

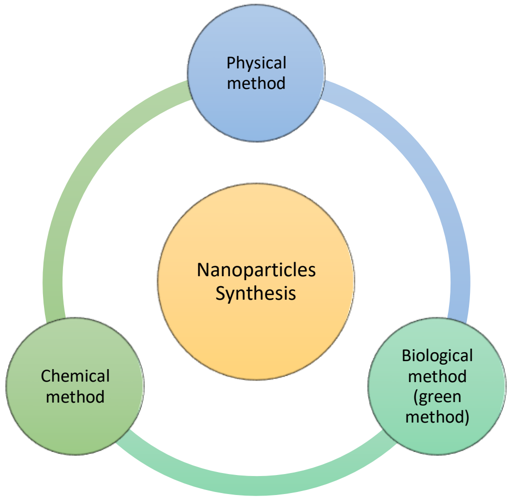
Physical methods, such as ball milling and laser ablation, employ mechanical or physical forces to convert bulk materials into nanoscale particles. Because the synthesis of nanoparticles is reliant on mechanical and physical energy, which includes certain excitation forces among materials, they are referred to as physical techniques. The most common methods are ultra sonication, lithography, UV irradiation, and laser ablation [36].

1.5.2. Chemical Methods

The manufacturing of nanoparticles is based on a chemical reaction process, which is why it is referred to as the "chemical method." Using this process, a nanoparticle is created by combining two or three chemical agents in one or more phases. Chemical vapor deposition (CVD), the sol-gel technique, and polymerization are the three chemical processes used to create nanoparticles [37].

15.3. Biological Methods

The biological approach is the third primary technique for creating nanoparticles. In order to prepare nanoparticle synthesis, this approach uses plant or microorganism extracts (and certain animal extracts for particular nanoparticles) as biological agents [38]. This approach's primary benefit is its eco-friendliness. Figure 1.2 below provides a list of the primary techniques.



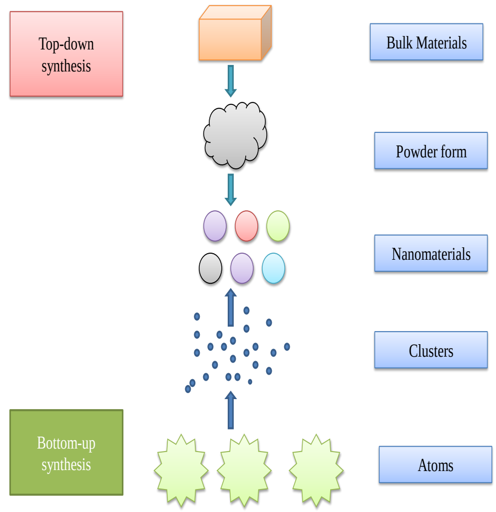


Figure 1.1: Diagram for several nanoparticle synthesis techniques

Figure 1.2: Synthesis of nanoparticles by physical, chemical, and biological approaches

1.5.4. Hybrid methods

In between physical and chemical synthesis, hybrid techniques like hydrothermal synthesis and micro emulsion offer previously unheard-of control over the size, shape, and content of nanoparticles. For example, green synthesis techniques include stabilizers or reducing agents that come from natural sources, including microbes, plant extracts, or biodegradable polymers, in an effort to reduce their negative effects on the environment [39]. To reduce the environmental contamination and energy consumption that result from the production of nanoparticles, benign solvents, renewable resources, and energy-efficient procedures are used.
Depending on the type of function, toxicity, and manufacturing size of the intended uses, it is selected based on the particular application requirements. In addition to its sustainability benefits, green synthesis is known to produce nanoparticles with special qualities and a smaller environmental impact than traditional synthesis methods. By merging green techniques with other synthesis processes, the creation of nanoparticles is further enhanced with greater flexibility and ecologically beneficial uses. This increases the nanoparticles' suitability for a number of uses, such as biomedical applications and environmental pollution clearance.

1.6Green nanoparticle synthesis

Due to their economical and environmentally beneficial material processing, green synthesis nanoparticles are becoming favored. Numerous efforts have been undertaken to enhance the efficacy of methods for creating, modifying, and studying functional nanomaterials with specific physicochemical characteristics [40]. Numerous organisms, including bacteria, fungi, actinomycetes, yeasts, viruses, algae, and plants, are employed in the green synthesis of nanomaterials [30, 41, 42]. In order to replace non-toxic chemicals in the production of nanoparticles and their subsequent use (as antiviral, photocatalyst, antibacterial, nano-catalyst, and other therapeutic materials), many researchers and environmentalists are interested in employing plant extract and other microorganisms. Figure 1.3 illustrates the biological synthesis of nanoparticles and their applications.

There has been a lot of interest in the production of NPs using plant base extracts and their subsequent uses as antiviral, photocatalyst, antibacterial, nanocatalyst, and other medicinal materials.
This interest stems from the increasing need for non-toxic compounds in these procedures [43, 44]. One creative area of nanobiotechnology is the synthesis of nanomaterials from different plant parts, such as leaves, flowers,

roots, and stems. The creation of nanomaterials depends on natural reductants and biostabilizers such as flavonoids, alkaloids, proteins, carbohydrates, enzymes, and polyphenols [45].

Different plant extracts have different amounts and combinations of chemicals. Plant extracts can behave as reducing agents, surfactants, and precipitants due to their composition. Plant extracts have been known to be able to synthesis nanomaterials since the early 1900s, despite the fact that the process that produces nanoparticles was not well understood at the time. Vegetable barriers, fruits, cereals, herbs, and other plant parts including seeds, leaves, stems, and roots are among the many plant extracts that are frequently rich in polyphenol chemicals that can act as reducing or surfactant agents during the synthesis of nano-compounds.

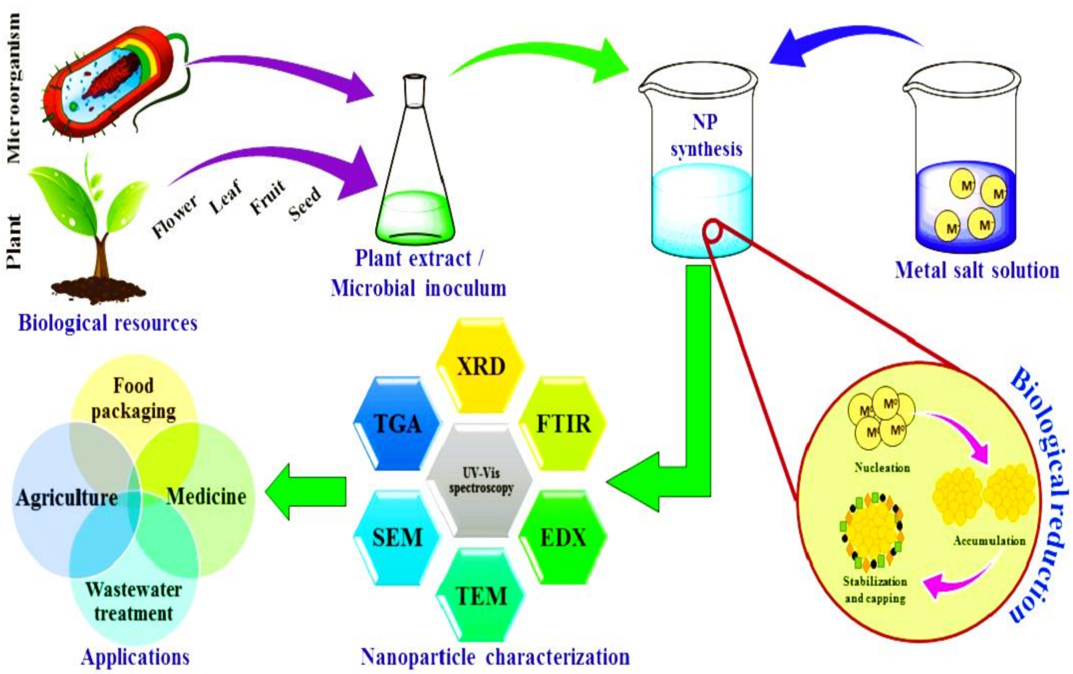


Figure 1.3: Biologically based green production of nanoparticles [38]

1.6.1. Plant extract-based green production of nanoparticles

One significant development in nanotechnology is the creation of nanoparticles using plant extracts. It offers a sustainable and environmentally friendly alternative to conventional chemical or physical processes. By using the natural reducing and stabilizing agents present in many plants, this green synthesis approach produces nanoparticles with unique features that are suitable for a range of applications. There are several crucial elements in the green synthesis process that set it apart from other approaches.

In addition to acting as stabilizing agents and reducing metal ions, the phytochemicals cap the nanoparticles to prevent aggregation, which would otherwise jeopardize stability. By attaching particular molecules to them, these nanoparticles may be further functionalized and tailored for various uses. advantages of green synthesis over other synthesis techniques. It employs readily accessible natural ingredients, doesn't produce harmful waste, and produces comparatively less byproducts than conventional processes, making it more environmentally friendly.

1.6.2. Preparation of plant extract

The following stages are involved in making plant extract. The first step is to carefully choose the plant material since different plants have different phytochemicals that stabilize and reduce nanoparticles. Aloe vera, green tea, neem, and turmeric are some of the plant species that are commonly utilized for this purpose. Following selection, the plant material is thoroughly cleaned, dried, and ground into a fine powder.

1.6.3. Calotropis procera leaves extract

The Calotropis procera plant, sometimes known as milkweed, contains a wide range of phytochemicals, including as cardenolides, steroid glycosides, flavonoids, lignans, terpenes, coumarins, phenolic acids, and reducing sugars. These phytochemicals support the plant's antibacterial, anti-inflammatory, antioxidant, and anticancer properties [50, 51]. Twine, bow strings, and lines are made from the bark fiber of this evergreen plant, which also produces white latex with medicinal and pesticidal qualities [52].

Calotropis procera extract has been successfully employed in many studies to create nanoparticles. Ag-NPs may be produced quickly and efficiently with the help of Calotropis procera flower extract. These particles show significant biological activities such as anti-inflammatory, antibacterial, and antifungal qualities, and they have uniform, stable, and well-dispersed features [53]. Additionally, magnetite nanoparticles made from Calotropis procera leaf extract showed antibacterial efficiency against a range of illnesses but no action against Escherichia coli [54, 55].

1.7. Calotropis procera leaf characteristics and phytochemical analysis

Calotropis procera is a member of the Plantae kingdom. It belongs to the group of plants called Streptophyta, which also includes vascular plants. It is thus included under the class Equisetopsida, which comprises a collection of plants having hollow stems. Calotropis procera is a member of the Magnoliidae subclass, which is characterized by berry-like fruits and flowering plants.

Figure 1.4: Calotropis procera plant

Calotropis procera, commonly known as the Aak in Pakistan, is a member of the Apocynaceae family. Other names for it include Aiton, Milkweed, Calotrope, Giant milkweed, Indian milkweed, wild cotton, rubber tree, Usha, Aak, and Madar. This plant thrives in the southern coasts of Iran, North Africa, Southeast Asia, and Middle East Asia, as well as on coastal sand dunes in tropical climates [52, 58]. Each part of the plant, such as the root, stem, leaf, and flower, has a specific purpose in a variety of sectors, including food processing, medicine, fuel generation, textiles, paper, rubber, plant care, and nanoparticle synthesis [59–61].

C. procera contains functional groups like OH and C = O that function as reducing and capping agents for the synthesis of nanoparticles. The specific organic chemicals, or metabolites, found in Calotropis plants rely on the extraction circumstances, including the plant's genus, the parts of the plant used for the extraction, and the polarity of the solvent. Methanolic C extractions.

1.8. Green synthesis of Zinc ferrites nanoparticles

Green synthesis is a useful and non-toxic approach for producing $ZnFeO_4$ nanoparticles. In this process, plant extracts serve as natural reducing and stabilizing agents that aid in the creation of nanoparticles. The procedure is intended to be straightforward, long-lasting, and effective. To make plant extracts, some plant parts—such as flowers, leaves, fruits, roots, or stems—are first dissolved in an aqueous or hydroalcoholic solution. Once the bioactive components have been properly extracted, the solution is heated to around 80°C and stirred for one to four hours.

. It is noteworthy that the extract's phytochemical contributes to the reduction and stabilization of metal ions. Precursor salts for zinc (Zn) and iron (Fe) are then added to a solution. Iron chloride, zinc nitrate, and zinc acetate are often utilized salts for this purpose. Before adding the plant extract, the mixture is heated to 60°C while being stirred for an hour. The phytochemicals in the plant extract help reduce metal ions and create nanoparticles. After reduction, the mixture is filtered or centrifuged to extract the nanoparticles from the liquid.

The nanoparticles are cleaned using ethanol or distilled water after contaminants have been eliminated by filtering or centrifugation. After that, the nanoparticles are dried at temperatures between 80°C and 100°C to ensure that no moisture remains. This procedure is shown in Figure 1.5.

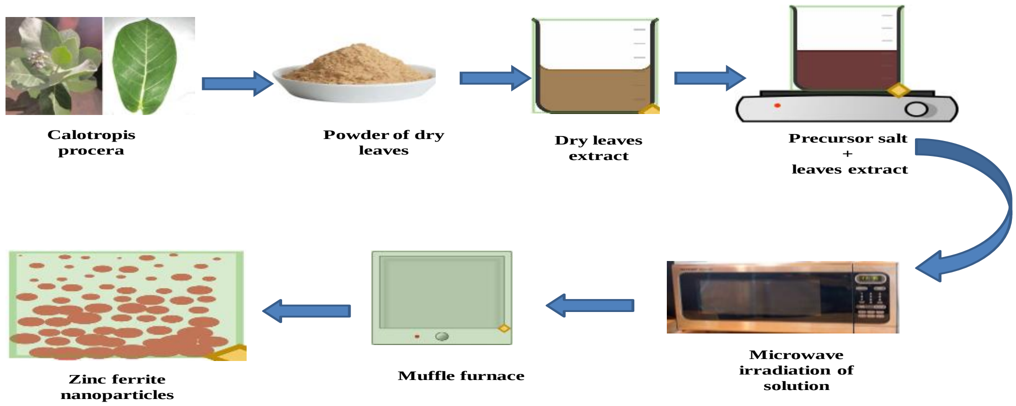


Figure.1. 5 Green production of $ZnFeO_4$ nanoparticles from Calotropis procera leaves

Furthermore, the dried nanoparticles are calcined at temperatures higher than 400 °C. For ZnFeO4 nanoparticles to have the appropriate crystalline structure, the calcination step is crucial. The high temperature transforms the precursor into well-crystallized ZnFe2O4 nanoparticles, improving their magnetic and structural characteristics. In addition to using fewer dangerous chemicals, this green synthesis method aligns with the principles of ecologically friendly and sustainable production. The method produces nanoparticles with remarkable properties suitable for a range of applications, such as catalysis, magnetic storage, and biological fields, while reducing environmental effect through the use of plant extracts.

1.8.1. Properties of Zinc ferrites nanoparticles

The use of $ZnFe_2O_4$ nanoparticles in technology is made possible by a few important physical characteristics. These particles range in size from 9.8 to 12 nanometers on average, and they have a magnetic property that can be either ferromagnetic or superparamagnetic. On the other hand, their saturation magnetization (Ms) reaches 64 emu/g. This measurement demonstrates the high magnetism of $ZnFe_2O_4$ nanoparticles.

A specific class of transition metal oxides known as zinc ferrites is used in many different fields, including energy storage, biomedicine, sensing, and catalysis [65, 66[]. They belong to the class of materials known as perovskites, which are characterized by a structure that may be altered by a little change in temperature. It has been shown to be multiferroic with a band gap of 1.8–2.5 eV. High saturation magnetization, surface-area-to-volume ratio, and shape and size-dependent magnetic properties are the main features of $ZnFe_2O_4$ nanoparticles in a spinel structure [67].

1.8.2. Application of zinc ferrite nanoparticles

The significant potential of $ZnFeO_4$ nanoparticles for dye photodegradation has been shown in several research. $ZnFeO_4$ nanoparticles, including nickel-zinc spinel ferrite modified with lanthanum and $ZnFeO_4$ replaced with cobalt

, have been successfully synthesized and characterized for effective dye degradation, according to research. The work sheds light on the potential technique of visible-light-induced $ZnFe_2O_4$ photocatalysis for good degradation

of hazardous dyes, such as methylene blue from water resources and Remazol brilliant violet 5R (RBV-5R). Under certain operating conditions, RBV-5R was nearly completely degraded (99.9%), indicating this photocatalyst's potential for environmental remediation [69, 70].
When visible light activates these nanoparticles, organic colors like methyl orange and methylene blue are broken down extremely effectively. $ZnFe_2O_4$ has also been added to silver and silver chloride nanocomposites, which are appropriate for photocatalytic dye degradation applications in environmental pollution remediation and have improved thermal diffusivity and visible light activity.

1.9. Green synthesis of NiO nanoparticles

An ecologically safe and sustainable method of going green is the green production of NiO nanoparticles utilizing plant or microbe extracts that function as capping and reducing agents. It is the greatest choice for mass manufacturing and provides a greener, cleaner, and more sustainable approach than the traditional method. This approach doesn't use dangerous chemicals and requires less energy than other procedures. Usually, a nickel salt precursor is combined with a plant extract or microbial culture, heated to improve reduction, and then exposed to microwave radiation.

1.9.1. Properties of NiO nanoparticles

The production process and additives employed affect the characteristics of NiO nanoparticles. Calotropis procera leaf extract-derived nickel oxide nanoparticles have intriguing properties for a range of uses. Through XRD analysis, the characterisation of these nanoparticles in several studies indicated a face-centered cubic structure [72]. NiO nanoparticles have homogeneous spherical shapes and are usually less than 100 nm [73]. Although reported sizes and surface coatings vary, NiO nanoparticles usually agglomerate when dispersed in water, which impacts their surface area and hydrodynamic diameter. NiO nanoparticles are appealing for a range of scientific applications due to these combined characteristics [75].
Moringa oleifera flowers are used to create NiO nanoparticles with a face-centered cubic structure, various crystallite sizes, 3.42 eV band gaps, and unique morphologies.
seeds, and leaves [76]. Green-synthesised NiO nanoparticles derived from Acacia Nilotica bark exhibit antimicrobial properties, form a protective layer on surfaces, and alter emission bands when oxygen levels are low [77].

1.9.2. Application of NiO nanoparticles

Fungi, bacteria, and even certain viruses have been demonstrated to be susceptible to the antibacterial properties of nickel oxide nanoparticles [78, 79]. Their antibacterial properties are caused by a variety of methods. When NiO NPs come into contact with microorganisms, one of the main processes is the release of reactive oxygen species (ROS). These ROS, which include hydrogen peroxide and superoxide radicals, cause oxidative stress and harm the body's cellular components, including lipids, proteins, and nucleic acids.
There has been a lot of study interest in the photocatalytic destruction of several pollutants employing nickel oxide nanoparticles (NiO NPs), such as 4-chlorophenol, Methylene blue, p-nitrophenol dye, Congo red, and others [81–83]. NiO NPs have proven successful in accelerating the breakdown of these various pollutants under photocatalytic conditions because to their special catalytic qualities. Exposure to light facilitates the interaction between NiO NPs and the target pollutants, producing reactive species that start degradation processes [84]. This study greatly extends our knowledge of the use of NiO NPs for hazardous chemical reduction and advanced oxidation processes for environmental remediation, demonstrating the promise of these nanoparticles in addressing environmental challenges connected to water pollution.

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1.10. Industrial waste water

The recent fast advancement of industrialization has led to a rise in the discharge of toxins into the environment. Water bodies become contaminated when untreated pollutants from municipal and other businesses are put there [85]. To put it another way, companies discharge either fully or partially treated effluent into the environment, contaminating both land and water. This particular industrial sector is quite significant.

The primary steps of the textile industry's manufacturing cycle are bleaching, dyeing, and washing, where water usage is most noticeable. The pharmaceutical, textile, paper, and cosmetics sectors are the primary users of synthetic dyes [87].

Water is often utilized in the mending, washing, and dying processes in textile manufacturing. The dyes are a result of soluble organic molecules, particularly those classified as basic, acidic, reactive, and direct.

1.10.1 4-Nitrophenol

4-nitrophenol, also known as 4-hydroxynitrobenzene or p-nitrophenol, is an aromatic substance. C6H5NO3 is its chemical formula. It has a strong smell and is a crystalline solid that ranges in color from yellow to colorless. It is soluble in water and other organic solvents and poisonous by nature.

2. Materials and Methods

For catalysts to be successful in catalytic applications, synthesis and characterisation are essential processes. This chapter includes the tools, supplies, and procedures necessary to synthesize $ZnFe_2O_4$, NiO, and ZSM-Catalyst. It then goes into depth about the characterisation methods used to examine their morphological, structural, and chemical characteristics.

2.1. Equipment Beakers, measuring cylinders, filter paper, pH paper, China dishes, pipettes, pipette suckers, and conical flasks Glass funnel, quartz cuvette, magnetic stirrer, test tube, glass rod, spatula, thermometer, glass viols, aluminum foils, and stopwatch

2.2. Chemical reagents

Distilled water, Nickel nitrate Ni (NO3)2.6H2O, Zinc nitrate Zn (NO3)2.6H2O, Iron nitrate Fe (NO3)2.9H2O, 4-nitrophenol, Sodium borohydride NaBH4

2.3. Instruments

Weighing balance, Hot plate, Double beam spectrometer, Single beam spectrometer, Hot air oven, Muffle furnace, Fourier transform infrared spectrophotometer

2.4. Experimental Work

2.4.1. Preparation of plant extract

In the Lahore region, fresh Calotropis procera plant leaves were gathered. Distilled water was used to thoroughly clean the leaves. Dust and dirt must be removed off the leaves in order to prevent them from altering the intended outcome. The leaves were cleaned and then oven-dried.

2.4.2. Phytochemical analysis of leaf extract from Calotropis procera:

To find bioactive components, a qualitative phytochemical investigation of Calotropis procera leaf extract was carried out. A conventional phytochemical screening test was performed on the extract. The phytochemical examination of plant extracts is a crucial stage in the production of nanoparticles because it reveals the presence of biomolecules that can reduce and stabilize metal ions, leading to the development of nanoparticles. The test and techniques are covered in table 2.1.

Name of phytochemical	**Name of test**	**Procedure**
Alkaloids	Wagner's test	A mixture of 2% H2SO4 and 3 ml of plant extract was boiled for two minutes. The 100 ml beaker was then filled to the brim with a few drops of Wagner's reagent (2 g of KI and 1.27 g of I2 in 5 ml of water)
Flavonoids	Shinoda test	3 pieces of magnesium chips were added to 3ml of plant extract, followed by a few drops

		of concentrated HCl. Fehling's solutions A and B were heated with 5 ml of plant extract in equal amounts.
Reducing sugar	Fehling's test	1% FeCl3 solution and 1% K3 [Fe(CN)6] solution was combined with 5 mL of extract.
Phenolic compounds	Ferric chloride test	5 mL of extract was mixed with 1% FeCl3 solution and 1 mL of 1% K_3 $[Fe(CN)_6]$ solution.
Saponins	Frothing test	After mixing 3 mL of extract with 10 mL of distilled water and shaking vigorously for 5 minutes, the mixture was allowed to sit at room temperature for 30 minutes.
Tannins	Braemer's test	3 mL of extract was added in 10% alcoholic $FeCl_3$ solution
Terpenoids	Salkowski test	3 ml of H_2SO_4 and 2 ml of $CHCl_3$ were carefully added to 5ml of extract to create a layer.

Table 2.1: Tests for identification of different phytochemicals present in Calotropis procera leaves extract [117]

By knowing the specific phytoconstituents involved, we can optimize the synthesis process and create nanoparticles with the right properties for use. Plant-based nanoparticle synthesis offers a cost-effective and eco-friendly alternative to traditional methods, paving the way for innovative uses in fields including electronics, medicine, and catalysis.

2.4.2. Green Synthesis of NiO nanoparticles

Using a hot plate, magnetic stirrer, and 40 °C, a stoichiometric quantity of Ni(NO3)2.6H2O was homogeneously mixed with 50 ml of Calotropis procera leaf extract solution for approximately two hours. NiO nanoparticles are synthesized using a home microwave oven once the string is finished. The mixture was put in the convection setting of the microwave oven and exposed to radiation for twenty minutes. The final product was calcined for three hours at 400 °C in a muffle furnace.

2.4.3. Green synthesis of $ZnFe_2O_4$ nanoparticles

50 milliliters of Calotropis procera leaf extract were mixed with zinc nitrate hexahydrate and ferric nitrate-6-hydrate in a 1:2 M ratio. While these metal nitrates function as oxidizers, the extract from Calotropis procera leaves acts as a reducing agent. To create a homogenous mixture, the solution was stirred for 60 minutes on a hot plate using a magnetic stirrer while maintaining a temperature of 80 °C. The mixture was then exposed to a microwave oven until a gel-like substance was formed.

2.5. Characterization techniques

2.5.1. UV-Vis Spectroscopy

UV-Vis spectroscopy is a useful analytical technique that compares a sample's transmittance or absorption of a certain UV or visible light wavelength to a reference or blank. UV-visible spectroscopy measures how much light is absorbed by the sample when a beam of light with a certain wavelength—typically between 200 and 800 nanometers—is passed over it. The Beer-Lambert law, which describes a linear connection between the sample's concentration, absorbance, and route length, is the foundation of this technique. UV-Vis spectroscopy may get significant information on the molecular makeup and structure of the sample by employing this approach to measure the optical properties of the sample.

These peaks help the researchers to tell when and where NPs are present, how large they are, how closely packed they are, and whether they are in an aggregated state or dispersed. Figure2.1 gives a general outlook of a common double beam UV-visible spectrophotometer.

Figure 2.1: UV-Vis spectrophotometer

2.5.2. FT-IR spectroscopy

Fourier transform infrared spectroscopy is a useful analytical method for detecting and characterizing unknown materials, including nanoparticles. This method scans the samples with infrared light to reveal their chemical composition and structure. Using FTIR spectroscopy, researchers can analyze nanoparticles in the following ways:

Identify the different kinds of nanoparticles and their chemical composition.

Check for surface changes and functionalization.

Determine any potential contaminants and investigate the interactions between nanoparticles and their environment.

Describe the molecular structure and bonding of nanoparticles.

By scanning particles across a wavelength range of 400 to 4000 cm-1, you may obtain a fingerprint of their chemical structure. Because of its many advantages, including non-destructive examination, little sample preparation, and rapid data collection, the Fourier Transform Infrared (FTIR) method is an essential tool in the research and development of nanoparticles.

Figure 2.2: FT-IR spectrophotometer

2.6. Photocatalytic reduction of 4-nitrophenol

In the catalytic reduction experiment, 4-nitrophenol was broken down using sodium borohydride and green-synthesized nanoparticles as a catalyst. In a quartz cuvette with a one-centimeter path length, the reaction mixture included 1.4 milliliters of dye (0.06 mM), 0.7 milliliters of sodium borohydride (12 mM), 40 milligrams of the nanoparticle catalyst, and 0.35 milliliters of deionized water.

By frequently scanning the mixture's absorption spectra between 200 and 800 nanometers in wavelength, the UV-Vis spectrophotometer tracked the progress of the reaction. It was monitored until the absorbance leveled off, indicating the end of the process. When the pale yellow hue disappeared, the reaction was over. By altering the concentrations of $NaBH_4$, 4-nitrophenol, and the catalyst, reduction rates were ascertained.

3. Results and Discussion

This section discusses the production of $ZnFe_2O_4$ and NiO nanoparticles using green plant extract, their characterization results, and the kinetics and mechanism of 4-nitrophenol degradation.

3.1. Green NiO nanoparticle synthesis utilizing leaf extract from Calotropis procera: Calotropis procera leaf powder was used to make plant extract. Using a hot plate, magnetic stirrer, and 40 °C, a stoichiometric quantity of Ni (NO3)2.6H2O was uniformly mixed with 50 ml of Calotropis procera leaf extract solution for approximately two hours. NiO nanoparticles are synthesized using a home microwave oven once the string is finished. The mixture was exposed to radiation in a microwave oven for twenty minutes.

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Figure 3.1: NiO nanoparticles from Calotropis procera leave extract

3.2. Green Synthesis of $ZnFe_2O_4$ nanoparticles using Calotropis procera leave extract

Zinc ferrites nanoparticles are synthesized using the extract from Calotropis procera leaves as a capping and reducing agent. Calotropis procera leaf extract is used to create highly efficient, less hazardous, and more cost-effective nanoparticles. When zinc nitrate and iron nitrate precursor were added to the extract during the green synthesis technique for $ZnFe_2O_4$ nanoparticle generation, the extract's bright yellow hue turned to dark brown. 50 milliliters of Calotropis procera leaf extract were mixed with zinc nitrate and zinc ferrite in a 1:2 M ratio.

Zn (NO3)2.6H2O + Fe (NO3)3.9H2O $ZnFe_2O_4$ gel

$ZnFe_2O_4$ gel $ZnFe_2O_4$ $ZnFe_2O_4$ (nanoparticles)

Figure 3.2: Zinc ferrite nanoparticles using Calotropis procera plant leaves extract

Zinc ferrite nanoparticles are very important due to their unique properties such as larger surface area and optical properties. Clear visual changes involved in each step of green synthesis process. These visual changes occurred when $ZnFe_2O_4$ NPs were synthesized from zinc nitrate hexahydrate and ferrous nitrate hexahydrate precursor salt using Calotropis procera leaves extract. Dark brown colored zinc ferrite NPs were obtained as end product.

3.3. Analysis of green $ZnFe_2O_4$ nanoparticles

3.3.1. Phytochemical analysis of the Calotropis procera leaves extract

Phytochemical tests were conducted to determine whether plant extract included metabolites such as terpenoids, saponins, tannin, alkaloids, and flavonoids. The extract of Calotropis procera leaves contains the main phytochemicals.

Flavonoids like luteolin and apigenin and tannins like ellagic and gallic acids are among the phytochemicals present in the extract.

Polyphenols, including catechins and chlorogenic acid

Terpenoids, including limonene and pinene
The synthesis and stability of nanoparticles depend on the following phytochemicals: As reducing agents, flavonoids and polyphenols reduce Ni2+ and Zn2+ ions to create NiO and ZnFe2O4 nanoparticles.

Tannins and terpenoids act as capping agents, keeping the nanoparticles stable and preventing them from clumping together. The antioxidant qualities of these phytochemicals help to prevent oxidation and nanoparticle degradation.

These phytochemicals aid in the production of targeted nanoparticles and extend their shelf life. The resulting ZnFe2O4 and NiO nanoparticles exhibit unique properties such improved biocompatibility and biodegradability, high surface area, enhanced catalytic activity, and outstanding reactivity.

3.3.2. Results of phytochemical analysis

Wagner's Test
Plant extract and Wagner reagent with 2% sulfuric acid were combined, and the process for this alkaloids test was followed. Reddish-brown precipitates were seen, suggesting that our plant extract contained alkaloids.

Fehling's Test
Fehling's test was used to determine whether reducing sugar was present. Brick-red precipitates are the result of this test. Based on this information, we may deduce that our plant extract contains reducing sugars.

Frothing Test
Saponins are confirmed by the Frothing test. The creation of honeycomb froth was the test's outcome. This indicates the presence of saponins.

Braemer's Test
The experiment's test tube featured greenish-gray hues. This illustrates our plant extracts' tannin concentration.

Salkowski Test
In this test, the interface turned reddish-brown. A reddish-brown ring was observed in a test tube. This indicates the presence of terpenoids in the surroundings. The table displayed the phytochemical data. 3.1

Table 3.1: Results of phytochemical analysis of *Calotropis procera* leave extract

Name of phytochemical	**Name of test**	**Result**
Alkaloids	Wagner’s test	+
Flavonoids	Shinoda test	+
Polyphenolic compounds	Ferric chloride test	+
Reducing sugar	Fehling’s test	+
Saponins	Frothing test	+
Tannins	Braemer’s test	+
Terpenoids	Salkowski test	+

Table 3.1: Results of phytochemical analysis of Calotropis procera leave extract

3.4. Fourier Transform Infrared Spectroscopy

Efficient functional groups in the 4000-400 cm-1 range were found using FTIR. Figure 3.3 displays the FTIR of NiO NPs made with leaf extract from Calotropis Procera. The notable vibrational stretching frequency at 431 cm−1 is caused by the distinctive metal-oxygen (Ni-O) interaction, which guarantees the creation of the crystalline NiO phase. The origins of the broad band at 3428 cm-1 were determined to be atmospheric adsorbed water molecules and a chemically connected hydroxyl group.

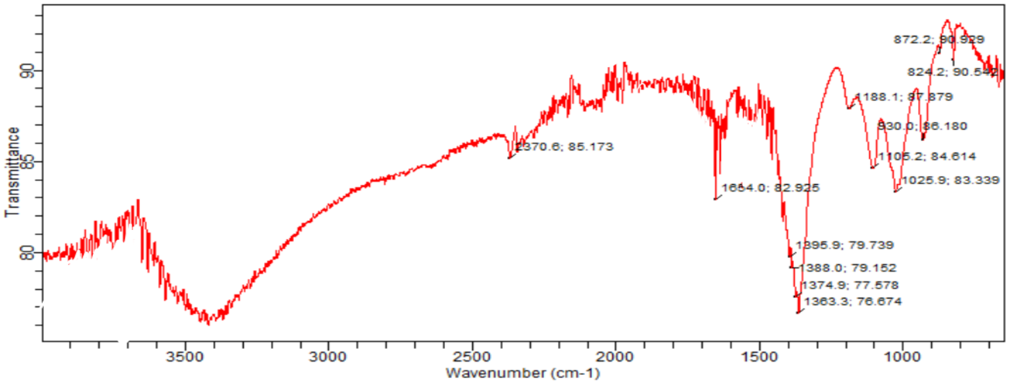


Figure 3.3: FT-IR of green synthesized NiO nanoparticles by Calotropis procera leave extract

Figure 3.4's FTIR spectra were used to identify the functional groups found in the green produced $ZnFe_2O_4$ nanoparticles made from Calotropis procera leaf extract, which were utilized as reducing and capping agents. The main amine's N-H stretching is seen at about 3400 cm-1. At lower wave numbers (822 and 797 cm−1), Zn-O and Fe-O at their respective tetrahedral and octahedral locations of $ZnFe_2O_4$ nanoparticles show two noticeable absorbance peaks. Thus, C.

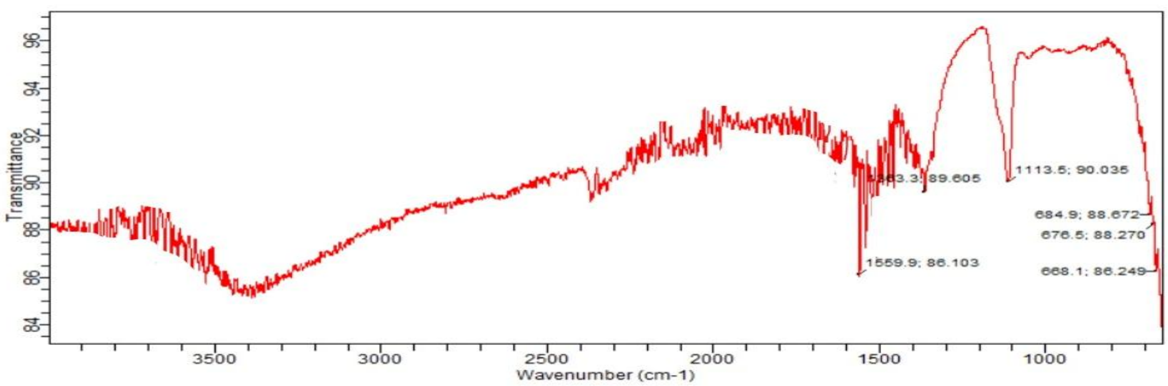


Figure 3.4: FT-IR spectra of green synthesized zinc ferrite nanoparticles

3.5. UV-Vis Spectroscopy Analysis of Nanoparticles

3.5.1 NiO nanoparticles

When the solution's once-bright green tint became brown, NiO NPs were formed. UV-visible spectroscopy was used to confirm the synthesis of nickel oxide nanoparticles. Its hue changed as the valency of the nickel particles changed from +2 to 0, confirming reduction. These alterations are caused by the active metabolites in the plant extract.

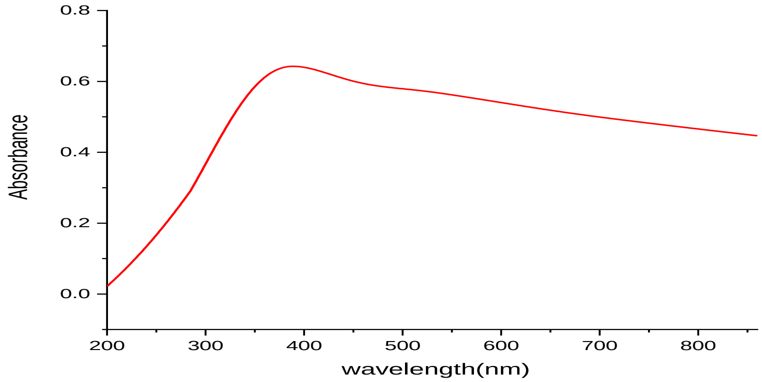


Figure 3.5: UV-Visible spectra of NiO nanoparticles

The presence of zinc ferrite nanoparticles is confirmed by the UV-visible spectrum, which shows two distinct peaks at 372 nm and 460 nm (figure 3.6). The peak at 372 nm is caused by Fe3+ ion absorption, which is in line with the typical range of Fe3+ ion absorption in zinc ferrite nanoparticles (350–400 nm). The signal at 372 nm indicates that the Calotropis procera leaf extract effectively reduced the iron ions to create zinc ferrite nanoparticles.
The peak at 460 nm is caused by the Zn2+ ion, which is in line with zinc ferrite nanoparticles' 450–500 nm Zn2+ ion absorption ranges. This peak indicates that the nanoparticles contain Zn2+ ions, which are necessary for the production of zinc ferrite.
According to research, the absorbance peaks seen in the 350–400 nm and 450–500 nm ranges of zinc ferrite nanoparticles are caused by Fe3+ and Zn2+ ions, respectively. The wider peak at 500 nm is believed to be caused by light absorption by the spine structure of zinc ferrite since zinc ferrite nanoparticles normally absorb light between 500 and 600 nm.

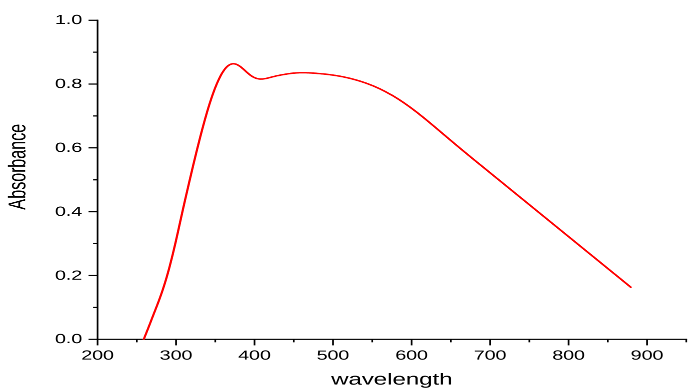


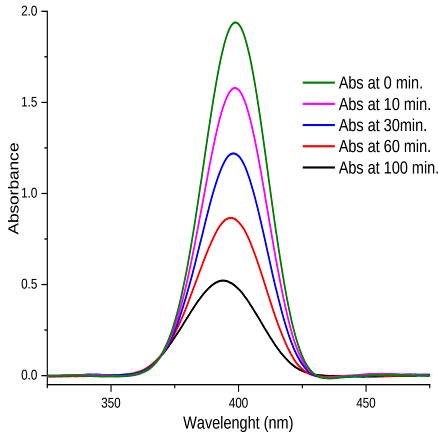
Figure 3.6: UV-Visible spectra of zinc ferrite nanoparticles

3.6. Catalytic reduction of 4-nitrophenol

The catalytic reduction of 4-nitrophenol was investigated using zinc ferrite nanoparticles as the catalyst and sodium borohydride as the reducing agent. Without a particular catalyst, reducing 4-nitrophenol is extremely challenging since sodium borohydride is a poor reducing agent and there is a significant kinetic barrier between the two reactants. Therefore, a powerful catalyst such as $ZnFe_2O_4$ nanoparticle is needed to overcome the barrier and finish that reduction.

3.7.1. Kinetics of 4-nitrophenol Reduction

A UV/visible spectrophotometer may be used to examine the kinetics of 4-nitrophenol reduction by green produced $ZnFe_2O_4$ and NiO nanoparticles. Since both the reactants and the products displayed UV sensitivity and a UV-Vis absorption peak, this approach was employed for analysis. Therefore, the experiment's degradation of 4-nitrophenol (0.064 mM) in the presence of NaBH4 (6.08 mM) and 2.7 mg/mL of green $ZnFe_2O_4$ nanoparticles and NiO nanoparticles, which act as a catalyst, was monitored using a UV visible spectrophotometer at a predetermined scanning interval of time. The results are displayed in figures 4.7 and 4.8, respectively. The production of 4-aminophenol is shown by peaks at 300 nm in the catalytic reduction of 4-nitrophenol by $ZnFe_2O_4$ nanoparticles [122].



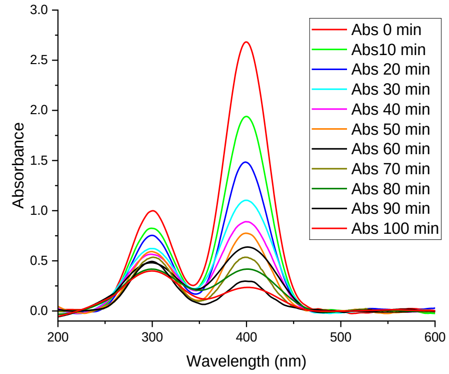


Figure 4.7: UV-visible spectra of 4-nitrophenol catalytic reduction by NiO nanoparticles

Figure 4.8: UV-visible spectra of 4-nitrophenol catalytic reduction by ZnFe2O4 nanoparticles

The following formula was used to determine the catalytic efficiency of ZnFe2O4 and NiO nanoparticles. Catalytic percentage degradation is equal to (A0-At / A0) × 100, where A0 is the absorbance at time 0 and At is the corresponding absorbance at time t.

Over the course of 100 minutes, zinc ferrite nanoparticles degraded 4-nitrophenol by 90%. Figure 4.9 below illustrates the proportion of 4-nitrophenol that zinc ferrite nanoparticles degrade over time. 4-nitrophenol was broken down in a single beam spectrophotometer using NiO nanoparticles and a little amount of sodium borohydride as a reducing agent. The absorbance against time was thought to

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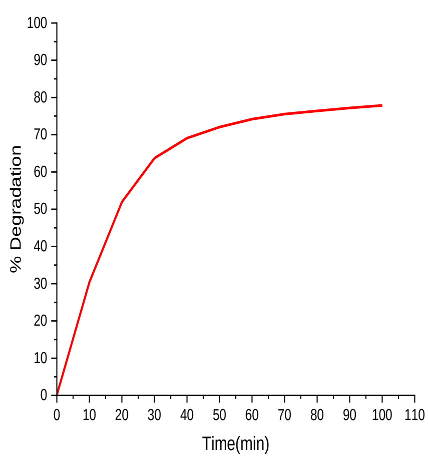


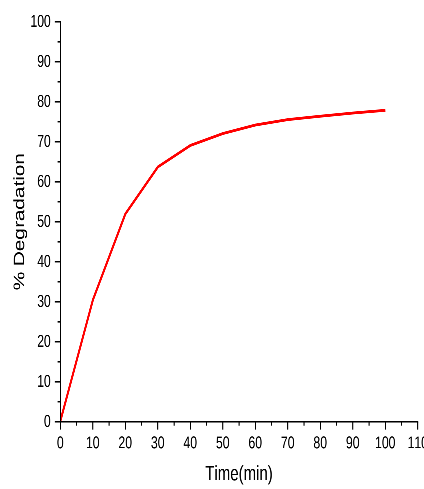


Figure 3.9: % degradation of 4-nitrophenol by zinc ferrite nanoparticles

Figure 3.10: % degradation of 4-nitrophenol by NiO nanoparticles

Figures 3.11 and 3.12 illustrate the temporal variations in a substance's concentration. The Beer-Lambert equation allows us to calculate the pace of the chemical reaction and get more insight into how the reactants are transformed into products. The Beer-Lambert law helps us understand how rapidly a chemical reaction happens. This is achieved by comparing the mixture's initial absorption of light to the quantity it absorbs at a given moment in time. The quantity of reactant that is still present at that time (Ct/C0) is shown by the ratio (At/A0) that arises from this comparison. This helps track the evolution of the response and pinpoint the underlying ideas that guide its functioning. The effective elimination of 4-nitrophenol is shown by a linear reduction in ln At/A0 values.

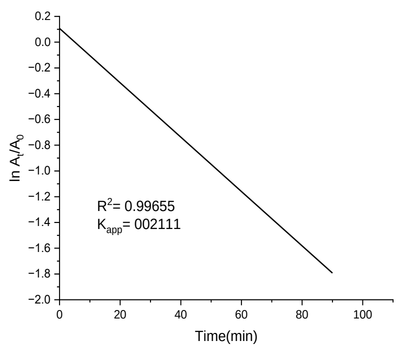
This finding suggests the catalytic reduction of 4-nitrophenol usually obeys the pseudo first order kinetics, which is mostly shown by the aromatic contaminants. Equation for first order kinetics is

Kapp (dye) -------------------------------- Eq. (1)

Kapp = pseudo 1st order constant

After integrating the equation 1 we got

ln (At/Ao) = $-kapp$ t ----------------------------------Eq. (2



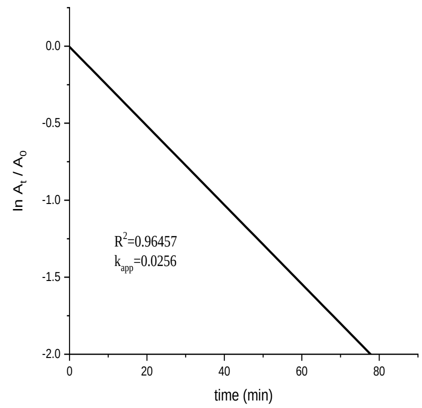


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Figure 3.11: Plot of ln At/A0 vs time when NiO nanoparticles were utilized as a catalyst

Figure 3.12: Plot of ln At/A0 vs time when ZnFe2O4 nanoparticles were utilized as a catalyst

3.7.2. Catalytic reduction mechanism of 4-nitrophenol

The catalytic reduction of 4-nitrophenol (4-NP) with nickel oxide and zinc ferrite nanoparticles involves the following processes.

Adsorption of BH4- and 4-nitrophenol: Both the 4-NP and the reducing agent sodium borohydride (NaBH4) are absorbed on the surface of ZnFe2O4 nanoparticles. The ZnFe2O4 nanoparticles' electron-relayed capability allows borohydride ions to carry out an extra electron. Hydrogen is released by BH4-ions as hydride ions (H-), which come into contact with the surface of the 4-NP. Reduction of the electron transfer process produces the intermediate from 4-NP to 4-hydroxylaminophenol.

4-Nitrophenol + 3NaBH4 → 4-Aminophenol + 3NaBO2+3H2

NiO nanoparticles follow the same mechanism for 4-nitrophenol degradation by lower the activation energy for conversion of 4-nitrophrnol into 4-aminophenol as ZnFe2O4 nanoparticles provide double active site for reaction than NiO nanoparticles thus ZnFe2O4 nanoparticles are more efficient than NiO nanoparticles.

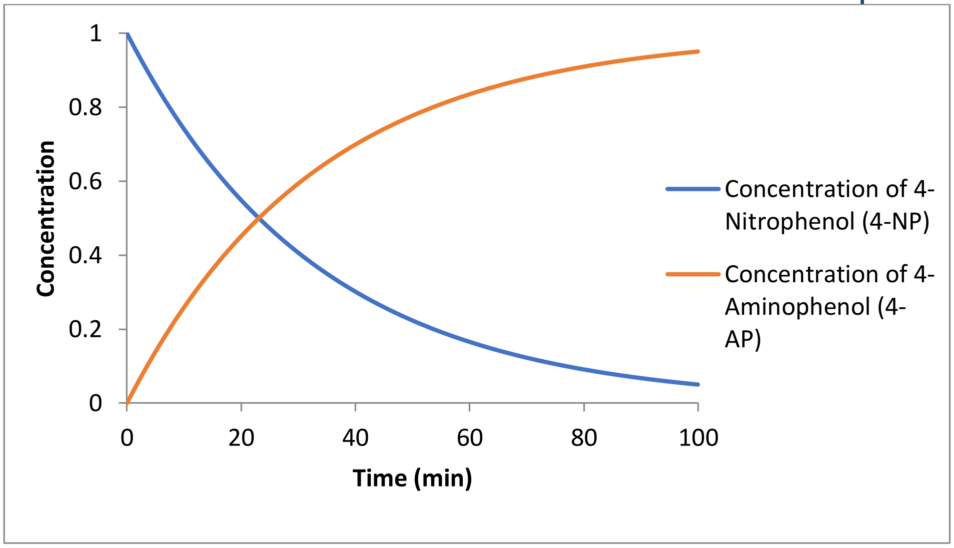

Figure 3.13: Catalytic reduction of 4-nitrophenol by ZnFe2O4 nanoparticles over time and conversion of 4nitrophenol into 4-aminophenol

The graph represents process of reduction of 4-nitrophenol by ZnFe2O4 nanoparticles, which act as a catalyst. The decrease of 4-nitrophenol concentration was exponentially represented by the blue line with the elapse of time and red color show the appearance 4-AP which increase by time. This graph shows how the reduction process is being helped by the ZnFe2O4 nanoparticles over time, for the production of 4-AP by the usage of 4NP.

5. Conclusion and Future work

5.1. Conclusion

The potential of the extract from *Calotropis procera* leaves as a reducing and capping agent in the green production of $ZnFe_2O_4$ and NiO nanoparticles has been successfully demonstrated in this work. NiO and $ZnFe_2O_4$ nanoparticles was successfully synthesized by microwave assisted method using *Calotropis procera* leave extract and precursor's salt related to nanoparticles. For NiO NPs the precursor salt was Ni $(NO_3)_2.6H_2O$ and for $ZnFe_2O_4$ nanoparticles Zn $(NO_3)_2.6H_2O$ and Fe $(NO_3)_2.9H_2O$ 1:2 respectively was used. The findings of this study demonstrate the potential of plant-based extracts in nanoparticle fabrication and provide a substantial contribution to the growing collection of knowledge on green nanotechnology. The use of extract from *Calotropis procera* leaves provides an economical, environmentally sustainable and readily scalable approach to the production of high-performing nanoparticles. The confirmation of NiO and $ZnFe_2O_4$ nanoparticles was done by two characterizing techniques UV-Visible and FT-IR spectroscopy. The results show that these nanoparticles are effective at degrading the dangerous pollutant 4-nitrophenol; they are appealing catalysts for use in environmental applications. The synthesized nanoparticles percentage degradation was computed and explained. This study highlights how important it is to look into eco-friendly methods of producing nanoparticles in order to reduce our reliance on hazardous chemicals and mitigate the negative environmental consequences of such compounds.

5.2. Future Work

Over the past 50 years, nanotechnology has been the cornerstone of remarkable commercial processes, industries and fast development. Through the use of Calotropis procera leaf extract, green synthesis of NiO and ZnFe2O4 nanoparticles has created new opportunities for sustainable catalytic applications. Researchers are becoming more interested in the catalytic reduction approach as a means of breaking down harmful aromatic pollutants, such as dyes that are not biodegradable and can cause cancer. Researchers are now very interested in creating affordable, straightforward and effective efficient nanoparticles.

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