“Green Synthesis of Zinc Oxide Nanoparticles Using Banana Peel Extract for Efficient Dye Removal from Water”

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I, **VANSHIKA, 24/BIO/11**, student of **M.Tech (Bioinformatics)**, hereby declare that the project dissertation titled **"Green Synthesis of Zinc Oxide Nanoparticles Using Banana Peel Extract for Efficient Dye removal from Water"** is submitted to Department of Biotechnology, Delhi Technological University, Delhi, by me in partial fulfillment for the award of degree of **Master of Technology (Bioinformatics)**. This thesis is original work done by me and contains information with proper citation. This project work has not formed the basis for award of any degree, fellowship or other similar title or recognition.

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CERTIFICATE

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ABSTRACT

The industry of textiles is one of the most water-intensive, using almost 200 gallons per kilogram of fabric during dyeing and washing procedures. Inadequate dye fixation to fabrics causes the discharge of dye-contaminated effluents with high pH, biological oxygen demand (BOD), chemical oxygen demand (COD), lignins, tannins, and heavy metals, resulting in severe environmental contamination. This study focuses on the green production of zinc oxide (ZnO) nanoparticles with banana peel extract (BPE) as a reducing and stabilizing agent for long-term wastewater treatment applications. Banana peel extract contains biomolecules such as polyphenols, flavonoids, and pectin, which aid in the conversion of zinc sulfate into ZnO nanoparticles under alkaline circumstances. The produced nanoparticles were analyzed by XRD, SEM/TEM, FTIR and UV-Vis spectroscopy which confirmed the presence of crystalline wurtzite ZnO nanoparticles ranging in size from 30 to 60 nm. The ZnO/BPE nanoparticles were tested for adsorption and photocatalytic degradation of dyes such as methyl red and methylene blue. Batch experiments demonstrated quick dye adsorption and over 80% dye clearance. The improved performance was attributed to the adsorption-photocatalysis mechanism and surface functional groups provided by banana peel extract. Overall, this work offers a cost-effective, environmentally benign, and long-term way to producing functional nanomaterials for wastewater cleanup.

Keywords : Textile industry, dyes, nanoparticle, remediation, sustainability

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LIST OF ABBREVIATIONS AND SYMBOLS

º - Degree Celsius

%- Percentage

ZnONPs- Zinc Oxide Nanoparticles

NPs- Nanoparticles

ZnO- Zinc Oxide

UV- Ultraviolet

Zn- Zinc

SEM- Scanning Electron Microscope

FTIR- Fourier-transform infrared specrtoscopy

XRD- X-ray diffraction

BPE- Banana peel extract

MB- Methylene Blue

MR- Methylene Red

CHAPTER 1 - INTRODUCTION

Dyes are employed in many different industries, even though they were originally natural extracts from things like roots, flowers, berries, leaves, etc [1]. Today's world has completely supplanted natural dyes with synthetic dyes because of their low cost, wide range of color possibilities, ease of manufacture and application, and, most crucially, affordability [2]. One such synthetic dye is the azo dye, which has the unique azo linkage (-N=N-) [3]. Because the dye is refractory, it frequently doesn't break down when released into the environment as part of the effluent from the dying process. Due to their ability to reduce oxygen concentration and light penetrance, these dyes have an instant impact on aquatic life [1]. Globally, the dying process effluent output is estimated to be between 60×10^7 and 90×10^9 kg yearly; of that, 1/10th ends up in the environment as industrial wastewater, depending on the size of the dye-using firms [3]. Although most of these methods have shortcomings, a number of physical and chemical dye cleanup initiatives have been launched recently. To resolve this problem, a practical and ecologically friendly solution must be found. One strategy that might work is nano remediation.

Nanotechnology has managed to make a name for itself in a variety of areas, including food, agriculture, medicine, cosmetics, etc. This allows for the utilization of a whole new range of properties that nanoparticles have to offer, including a high surface area to ratio of volume, on already existing bulk materials. Metal oxide nanoparticles have gained attention recently for dye cleanup due to their catalytic activity [19]. Furthermore, compared to chemically synthesized ones, biologically synthesized nanoparticles have been shown to be less dangerous, use less energy, and harm the environment. Additionally, a nanoparticle's basic properties, such its catalytic activity, are determined by its size and structure [1]. Because it offers more control over the formation of the nanoparticles, the green synthesis strategy is an eco-friendly approach for the formation of nanoparticles [1],[16]. Due to their low cost, environmental friendliness, and powerful dye degradation capabilities, green synthesized NPs have also attracted a lot of attention [21].

In this experiment, our model dye has been Methylene blue (MB) and Methyl Red (MR). MR, a monoazo dye, has a 4-[(dimethylamino) phenyl] diazenyl group at position 2 in place of benzoic acid. It goes by the name Acid Red 2 and has a C.I. of 13020. The zinc oxide nanoparticles were first formed by green synthesis approach, characterized and used for their efficiency in remediation of methylene blue and methyl red. The experimental study could provide a starting point for the remediation of MR and future prospects for the sustainable environment [2], [4].

Banana peel waste is an ideal material for green synthesis. Bananas (Musa spp.) are one of the world's most popular fruits, with yearly output in the hundreds of millions of tons. Banana peel accounts for over 40% of the fruit's weight, resulting in approximately 46 million tons of garbage annually worldwide. These peels are rich in polysaccharides and phytochemicals: cellulose (18-59%), hemicellulose (17-20%), pectin (10-20%), lignin, and tannin. Biomolecules like polyphenols, flavonoids, and pectin can serve as natural reducers and capping agents in nanoparticle formation [17]. Banana peels have been investigated for NP production as well as low-cost pollutant adsorbents, utilized pectin from unripe banana peels to create ZnO NPs that degraded methylene blue by around 78% in 30 minutes [18]. Another work utilized banana peel extract-derived ZnO for photocatalytic destruction of water contaminants, displaying effective performance and stability [15].

Considering these advancements, the combination of waste valorisation and pollution remediation remains an active field. This thesis focuses on a waste-to-nanomaterials strategy: synthesizing ZnO NPs from banana peel extract and using them to remove dyes by adsorption and photocatalysis. The problem is that standard ZnO synthesis is neither sustainable nor cost-effective, whereas untreated banana peels are an underutilized feedstock. Using banana waste, we hope to build a green ZnO material that solves waste management and water purification at the same time.

Chemical reduction methods are thought to be safely replaced by the Green Method. For example, plant extracts containing reducing agents can reduce zinc ions and convert them into nanoparticles [20]. These days, nanotechnology is having a big impact on physics, chemistry, biology, medicine, and electronics. Nanotechnology has numerous applications, including waste management, agriculture, medical, pollution control, antibacterial and anticancer drugs, and catalysis.. Nanoparticles can have any size, shape, morphology, or geometry. The physical and chemical processes used to produce nanoparticles have an adverse effect on both human health and the environment. Chemical manufacturing of nanoparticles emits toxic and dangerous substances including sodium borohydride and hydrazine, which have an adverse effect on human health and the environment. Exposure to hydrazine irritates the eyes, nose, and throat [16], [21]. In severe cases, it may also cause seizures, coma, and damage to the liver and kidneys. Chemical procedures like microemulsion and evaporation/condensation have comparable prices. Physical methods, such as microwave-assisted, require more energy and are expensive, time-consuming, and resource-intensive. As a result, using green technology to create nanoparticles seems more sensible, secure, cost-effective, and environmental friendly. Copper, silver, gold, zinc, iron, and other nanoparticles are produced by medicinal herbs. These plants are commonly used as reducing agents in environmentally friendly nanoparticle manufacturing. Among other uses, biologically generated metal nanoparticles can be employed as antioxidant powder, antibacterial, anticoagulant, and cytotoxic agents against cancerous cells. Alkaloids and flavonoids are among the many secondary metabolites that make up NPs. Among other metal nanoparticles, copper nanoparticles have a variety of important applications, especially in the biological field. The nanoparticles of are used in sensors, catalysts, optical, electrical, gas, and superconductors to create organic-inorganic nanostructure composites, transform solar energy, and create massive magnetic resistant materials. They have potent antifungal, anticancer, and antibacterial properties.

1.1 Objective of the study

Consequently, the goal of this project is to investigate the environmentally friendly manufacturing of zinc oxide nanoparticles utilizing extract from banana peels. The zinc oxide nanoparticles were further used to study their potential for remediation of methyl blue and methylene red dye. To study the characteristic attributes of formed nanoparticles and their efficiency for MB and MR remediation could facilitate research on future use of such nanoparticles for sustainable environment.

Firstly, the synthesis of ZnO nanoparticles was initiated using banana peel extract and their characterization was done. To determine the extent of nanoparticle production, a number of analytical methods were applied.

a. UV-Vis spectrophotometry
b. Scanning electron microscope,
c. Fourier-transform infrared (FTIR) spectroscopy,

The formed nanoparticles were further studied to check their efficacy in methylene blue and methyl red remediation by decolorization [18], [36].

The current study is limited to bench-scale laboratory synthesis and experimental evaluation, while practical wastewater treatment and large-scale industrial applications are beyond the scope of this research. This thesis is unique in that it combines green chemistry with waste valorisation by using banana peel, an agricultural waste material employing a combined adsorption-photocatalysis approach to improve dye degradation efficiency, and providing a detailed comparison with previously reported greensynthesized ZnO nanoparticle systems. Overall, this study improves sustainable nanotechnology by proposing a low-cost, eco-friendly technique for creating functional nanomaterials for environmental remediation applications.

CHAPTER 2 – REVIEW OF LITERATURE

Synthetic dyes are used in a wide range of sectors, including food, textiles, cosmetics, and leather [1]. Dyes are classified into five broad kinds based on the chromophore groups they contain: azo, trimethyl methane, nitro/nitroso, indigo, and anthraquinone. The chromophoric, auxochromic, or conjugated aromatic structures give dyes their characteristic color [2]. Chromogenic groups transform white light into colored light by selectively absorbing energy [2]. Of the several groups, azo dye is the most significant because it accounts for 70% of all dyes used in industry. These dyes have an azo linkage (N=N-).A wide variety of dyes have been produced as a result of further dye modifications that have improved yields and color characteristics even more. However, because textile dyes include a high concentration of pigments and chemicals, their release into the environment is a global concern [1], [3]. Ten to fifteen percent of the color used is discharged untreated into neighboring waterways [10].

Water pollution is a significant environmental issue that affects many countries, including India. A rapidly rising population, industrial expansion, and insufficient waste management pose substantial difficulties to the country's water supply management. Industrial water pollution in India is a complex problem that affects a variety of rivers, lakes, and groundwater resources. The UN Secretary General's press release for World Water Day 2002 underlines the importance of having access to safe drinking water. Every year, about 5 million people die as a result of illnesses brought on by contaminated drinking water [1]. According to current research, water bodies contain large proportions of manufactured and newly discovered organic pollutants[12]. Pesticides, pharmaceuticals, drugs, colors, and other chemicals are examples of persistent and harmful pollutants [12].

Textile dyeing is the world's second-largest source of water pollution, and it is well recognized as having a substantial impact on water contamination. In India, a sizable component of the textile sector employs synthetic colors, which are primarily derived from petroleum. Heavy metals, formaldehyde, and aromatic compounds are examples of dangerous ingredients that may be present in these dyes [26]. Toxic contaminants are being poured into bodies of water, causing fish populations to decline, marine

animals to die, and biodiversity to be lost [26]. The biological oxygen demand (BOD) in aquatic environments may be raised by certain colors. The amount of dissolved oxygen needed by microbes to decompose organic molecules is measured by BOD [11]. When colors are released into water, microorganisms take significantly more oxygen while breaking them down, causing the water to become depleted of oxygen [11]. Water bodies can become visibly stained as a result of dye leakage. This discoloration not only reduces sunlight penetration and affects photosynthesis in aquatic plants, but it also has a negative impact on the aesthetic appeal of the water, further disrupting the ecology [3]. Some colors include toxic substances that can be swallowed or absorbed via the skin, resulting in allergies, skin irritations, and other major health issues [1], [3].

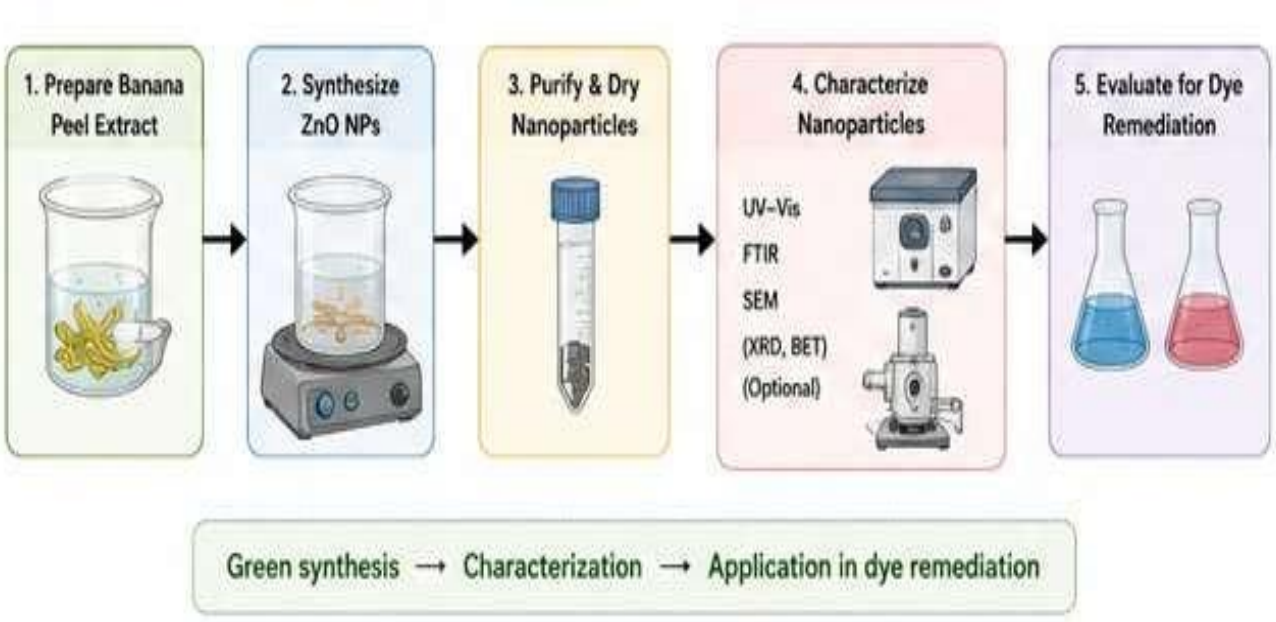


Figure 2.1: Experimental workflow for green synthesis and application of ZnO nanoparticles using banana peel extract.

2.1. Toxic effects of synthetic dyes

Synthetic colors are harmful to all living things, either directly or indirectly [3]. The dyeing procedure is the most risky part of the textile business. This is because many dyes and chemicals are released as dye effluent rather than sticking to the fabric [10]. The main issue is that this effluent enters waterbodies untreated. First and foremost, this effluent damages the aesthetic aspects of water bodies, impeding photosynthesis by producing an unpleasant odor, an untidy appearance, and even preventing sunlight from penetrating. BOD and COD, or biochemical and chemical oxygen demand, are growing [11]. They continue for a long time and can escalate because of their resistant conduct.

Auxiliary substances and heavy metals like Sulphur, acetic acid, chromium, cobalt, nickel, etc. are also present in these synthetic colors. These all increase the effluent's toxicity [26]. Furthermore, the productivity of the soil is lost if these effluents are used to water the fields [1]. Additionally, these effluents have the potential to directly affect drinking water supplies if they seep into subterranean water reservoirs or flow into river. These colors are non-biodegradable, teratogenic, allergic, and mutagenic. Therefore, before the dye effluents are released into the water bodies, they must be remedied [2], [26].

2.2 Wastewater and emerging pollutants

Pollution and water scarcity are getting worse. The bioaccumulation of these persistent contaminants poses a threat to human health and ecosystems. For instance, agricultural runoff containing phosphates and nitrates can encourage eutrophication and textile dye wastewater contains harmful metals and chemicals. Conventional treatments can remove many contaminants, but they often have high energy and capital costs, require chemicals, and may cause secondary pollution (e.g. concentrated sludge). Adsorption techniques have attracted attention for removing low-concentration or resistant contaminants because they can achieve high clearance without creating chemical byproducts.

2.3. Remediation of Textile Dyes by Nanoparticles

While the energy of photons exceeds the threshold in the existence of light, excitation causes an electron to shift from the valence band to conduction band, creating a hole in the VB. [21]. While the hole in the VB mixes with the adsorbed H2O to form the hydroxyl free radical, a strong oxidizing agent, the electron in the CB reacts with O2 to make superoxide 02, a powerful reducing agent [23]. When the dye is adsorbed to the nanoparticle's surface, it reacts with the oxidizing and reducing chemicals, causing the dye to break down into smaller molecules [19].

2.3.1 Adsorption vs Photocatalysis for Dye Removal

Adsorption: ZnO NPs have the ability to adsorb dyes through surface interactions such as hydrogen bonding, π–π stacking, and electrostatic attraction [25]. Surface area, pore structure, and pH (which influences dye speciation and ZnO surface charge) all influence adsorption capacity [29]. Models are used in kinetic and equilibrium research; generally, adsorption fits Freundlich or Langmuir isotherms and follows pseudo-second-order kinetics, which indicates chemisorption [1], [3]. For instance, Acid Red 88 was eliminated by a ZnO-based adsorbent; pseudo-second-order kinetics explained the rate, and Freundlich was the best-fit isotherm [3]. $\Delta G°$, $\Delta H°$, and $\Delta S°$ showed spontaneous, exothermic adsorption in that investigation. The adsorption of methylene blue (MB) on ZnO can be treated similarly. Although high-affinity sites might resemble Langmuir monolayers, we anticipate that the Freundlich model would frequently prevail (heterogeneous adsorption).

Photocatalysis: ZnO produces –OH and $\cdot O_2^-$ radicals under UV (or visible, if doped), which oxidize dyes into CO_2 and H_2O [19]. Pseudo-first-order kinetics is a common model for photocatalytic dye removal. There is an optimum since high ZnO loadings can impede light penetration and result in recombination [19]. Reusability is a problem: ZnO is tested for 2–5 cycles in numerous research (loss

~5–10%) [21]. Strong photocatalytic activity has been demonstrated by banana-peel ZnO produced ~78.5% degradation of MB in 30 minutes under UV [18]. Interestingly, banana extract alone can remove some pigment through dark adsorption and self-absorbance, but photocatalysis speeds up and finishes the process [35]. In contrast to photocatalysis, which irreversibly breaks down the dye, adsorption just concentrates the pigment on the ZnO surface (reversible). To measure the actual photocatalytic impact, pre-adsorption equilibrium (dark stirring) is often established prior to illumination [19].

2.4 Banana Peel Phytochemistry

Starch, cellulose (~10–20%), hemicellulose, lignin, pectin, and other phytochemicals are among the numerous biomolecules found in banana peels [17]. For every 100 g of dry peel, there may be 0.5–0.9 g of total phenolic content. Flavanols (like gallocatechin), catechins, and phenolic acids are examples of major polyphenols [17]. Notably, banana peels are high in neurotransmitters including serotonin precursors and dopamine, a catecholamine, at up to 0.5 g per 100 g [17]. Heat causes the polysaccharide pectin (5–8% by weight) to dissolve in water [17]. Banana peel is a useful reducing media because of these chemicals' high hydroxyl content [17]. These polyols and phenolics provide electrons to lower metal ions during biosynthesis. FTIR analyses of ZnO NPs derived from banana peels verify the presence of -OH, -COOH, and C–O–C functional groups from cellulose/pectin on the NP surface, suggesting that these biomolecules serve as capping agents to stabilize NPs. Because banana peels make up around 40% of fruit weight but are frequently thrown away, waste valorization also supports sustainability and the circular economy [15], [17].

PHYTOCHEMICAL	FUNCTION IN NANOPARTICLE SYNTHESIS

POLYPHENOLS	Reduction of Zn^{2+} ions
FLAVONOIDS	Stabilization and capping
PECTIN	Surface coating and stabilization
TANNINS	Antioxidant activity
CELLULOSE	Structural support
HEMICELLULOSE	Binding and stabilization

Table 2.1: Important phytochemicals present in banana peel and their role in green synthesis of nanoparticles.

2.5 Nanoparticles Classification

Nanoparticles can be categorized based on the number of dimensions they display [39]. The classification includes zero-dimensional, one-dimensional, two-dimensional and three-dimensional, nanoparticles [39]. Zero-dimensional nanoparticles are particle-like structures without an additional dimension as shown in Figure 2.2. They may have non-spherical or spherical forms [45]. One dimension of a one-dimensional nanoparticle is significantly larger than the other two. These are often long structures such as nanotubes, nanowires, or nanorods. One of the two dimensions of two-dimensional nanoparticles is notably larger bigger than the others. Usually, they take the form of incredibly thin layers or sheets known as graphene or nanoplates. They can have a variety of shapes, including cubes, polyhedrons, and spheres [40].

Scientists can better grasp the unique characteristics of nanoparticles and tailor their application for specific purposes by using dimension-based classification [39], [42].

2.6 Properties of Nanoparticles

Despite their bulk counterparts, nanoparticles possess special properties [40]. The nanoparticles significant surface-to-volume ratio and nanoscale size give them these distinctive properties [45]. Sizedependent behaviors, improved responsiveness [39]. The characteristics mentioned above set nanoparticles apart from their bulk counterparts and allow for their extensive use in a variety of sectors. [42].

2.6.1 Optical Properties

In earlier times, it was generally acknowledged that when a material's size changed, so did its color [40]. For example, gold particles turn black and lose their shine when their size is reduced to a level below the wavelength of light. The color intensity darkens as particle size decreases [41]. The phenomenon can be explained by the fact that ultrafine metal particles, which are usually smaller than 1%, reflect less light [42]. Light absorption rises and particle size decreases to a few micrometers or less. As a result, solar energy is converted into power and heat, and infrared-sensitive electronics are developed [45].

2.6.2 Thermal Properties

A solid material's melting point dramatically drops when its size of particle is reduced to ultrafine levels [40]. When the particles are smaller than ten nanometers, this impact is very apparent [39].

2.6.3 Electrical Properties

The restriction of electrical mobility within nanoparticles causes the electron energy in nanomaterials to be quantized [39]. This phenomenon enables the formation of unique metal particles that are nonconductive at certain voltages but show significant conductivity at others. For example, when they get smaller than a few nanometers, metals like zinc, which are commonly employed as conductors, lose part of their conductivity [45]. However, insulators used for insulation, like silicon dioxide, lose their insulating qualities as they start to conduct at the nanoscale. Because of the intriguing phenomena known

as the Coulomb blockade effect, scientists are exploring the development of single-electron devices. These devices can create silicon chips as we know them today because they rely on the manipulation of individual electrons [42].

2.6.4 Mechanical Properties

The magnetic characteristics of minuscule particles with strong coercivity can be advantageous for highdensity storage devices, including magnetic discs and cards [45].

2.6.5 Chemical Properties

The sol-gel, co-precipitation, hydrothermal, and polyol procedures are among the chemical methods frequently employed in the production of nanoparticles [40]. It is important to keep in mind that these chemical processes have limitations and challenges [39]. One of the primary problems is that stabilizers and surfactants are frequently dangerous and detrimental to the environment [41]. These substances may be hazardous to ecosystems and human health even if they are employed to control the size and characteristics of nanoparticles [42]. Hazardous effects of chemical synthesis may potentially exacerbate environmental degradation [41].

2.6.6 Physical Properties

Nanomaterials are produced by a variety of physical processes, including microwave-assisted synthesis, pulsed laser deposition, spray pyrolysis, and evaporation. Nevertheless, these strategies have some serious problems that need to be resolved. To solve these issues, scientists are always looking for more affordable, sustainable, and effective synthesis methods [39]. Because of their benefits—such as reduced energy consumption, softer reaction conditions, and the potential for scalable and sustainable manufacturing—green synthesis methods are increasingly employing biological agents or ecologically friendly solvents [21], [22].

2.7 Green Chemistry

With the goal of improving both the environment and human well-being, it combines a variety of elements, including as raw materials, reagents, solvents, finished goods, and wastes. Another facet of green chemistry is the use of eco-friendly resources and fuels during production [43]. Twelve principles serve as the foundation for green chemistry techniques in this discipline. The application of these ideas to the production of nanoparticles is one relatively recent sustainability issue [22]. Green chemistry concepts must be incorporated into nanotechnology in order to accomplish this [39], [42].

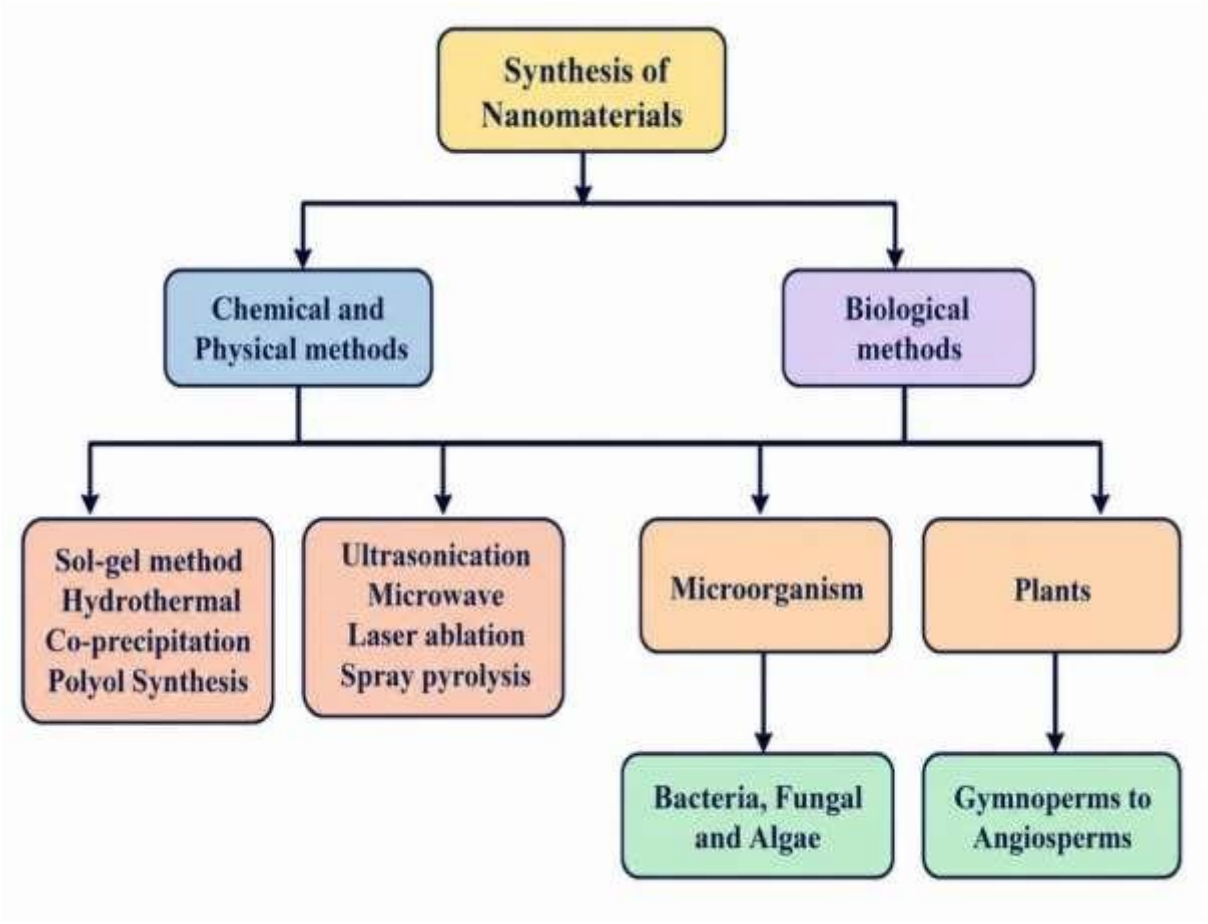


Figure 2.2: Classification of nanomaterial synthesis methods.

2.8 Nanoparticle Synthesis

Nanoparticles are used by definition and literal translation, incredibly small materials ranging in size from one to one hundred nanometers [21]. Nanomaterials have enhanced the properties of previously available bulk materials. One such example is the greater surface area to volume ratio, which results in a surface with a large number of atoms and provides the nanoparticles with catalytic activity [19], [33]. Physical vapour deposition, sol-gel, optical lithography, and biological synthesis are some of the approaches that have lately acquired popularity in nanomaterial fabrication [16], [22]. Dimensionality (at least one dimension in nanosize), chemical composition, and porosity are the three criteria used to classify nanomaterials [21].

Physical and chemical synthesis techniques are the most popular since they are often inexpensive and yield large quantities of nanoparticles. Unfortunately, these techniques frequently require hazardous chemicals to complete the process, which contaminates the NPs that are produced and may be bad for the environment [16], [20]. Nonetheless, due to their wide range of uses, metallic nanoparticles have gained significant importance. Therefore, to synthesise these nanoparticles, non-toxic, affordable, and environmentally acceptable methods are required. Using bacteria, fungi, and plants to synthesise these metallic nanoparticles is one method known as biological synthesis. Nanoparticles produced biologically are more resistant to oxidation and are more stable. Reduction, stabilisation, nucleation, aggregation, and capping are typically involved in the synthesis of nanoparticles .

Fungal Synthesis: Additionally, there are two mechanisms for this: extracellular and intracellular. Metabolites such as cyclosporine and mevastatin are present in the fungal culture filtrate/fungal mycelia culture, and the metal ions are reduced to nanoparticles by enzymes such as peroxidases [16].

Bacterial Synthesis: In the presence of reducing enzymes, microorganisms produce metal nanoparticles. Extracellular or intracellular synthesis could be involved. The benefits of bacterial synthesis are numerous. Bacteria grow quickly, are simple to keep healthy, and most importantly, their

development conditions are controllable. This modification enables the nanoparticle's size and shape to be altered, which directly affects the function and, consequently, its applications [21].

Plant-mediated Synthesis: Utilising plants is an additional eco-friendly strategy as shown in Figure 2.1. In addition to enzymes that break down the metal precursor into nanoparticles, the plant extracts contain active phytochemicals such as terpenoids, alkaloids, and phenols [17], [21].

2.9 ZnO nanoparticles

ZnO NPs are less than 100 nm in size. They can be made in a variety of ways, including solid, liquid (chemical), and gaseous. Numerous chemical techniques exist, such as mechanochemical, precipitation, precipitation with surfactant, hydrothermal, emulsion and micro-emulsion techniques. The chemical approach offers versatility in managing the size and shape of produced nanoparticles and is the most economical, dependable, and ecologically friendly. Stabilizing the nanoparticles is crucial to producing these kinds. Because nanoparticles can readily clump together to form macro-sized particles, the creation of nanoparticles alone is not productive. As a result, surfactants, polymer molecules, or any organic molecules attached to the surface of nanoparticles—such as PEG or TritonX 100—are used to stabilize them. The primary relevance of nanoparticles is that their size reduction to the nanoscale may result in the creation of novel, distinctive physicochemical, structural, electrical, and magnetic features that are absent from their larger or macro counterpart [21]. The unique and extensive use of nanoparticles in the biological and medical fields is mostly due to these innovative features. These days, ZnO NPs used in many different fields, including cancer treatment, biosensing, drug and gene delivery etc. A ZnO nanoparticle may easily absorb UV light since it is a large bandgap semiconductor. Because of this characteristic, ZnO nanoparticles are used in a variety of fields, including biomedicine, electronics, cosmetics, and face goods. The anticancer effects of ZnO NPs are currently the subject of extensive research. The following describes some of the traits of ZnO NPs that

have contributed to their rise in anticancer therapy. Increased surface contact, enhanced reactivity and solubility, and a variety of additional applications are made possible by this characteristic of nanoparticles. One key component of medication delivery by nanoparticles is the conjugation of different ligand and targeting molecules on their surface. The mechanism of ZnO nanoparticles formation shown in Figure 2.3.

A nanoparticle's fate is also significantly influenced by its surface charge. High surface charges accelerate the removal of nanoparticles from blood arteries by increasing macrophage scavenging activity. In a similar vein, surface charge should be preserved so that it exhibits selectivity towards tumor cells with little self-self and self-nonself interaction. ZnO NPs can be synthesized using a wide range of techniques, making the procedure very simple. Their size and size distribution are easily regulated because of these various synthesis techniques. Studies have demonstrated that the toxicity of nanoparticles is closely correlated with their size; additionally, size manipulation is important for generating a stronger EPR effect to raise the intra-tumor concentration of nanoparticles.

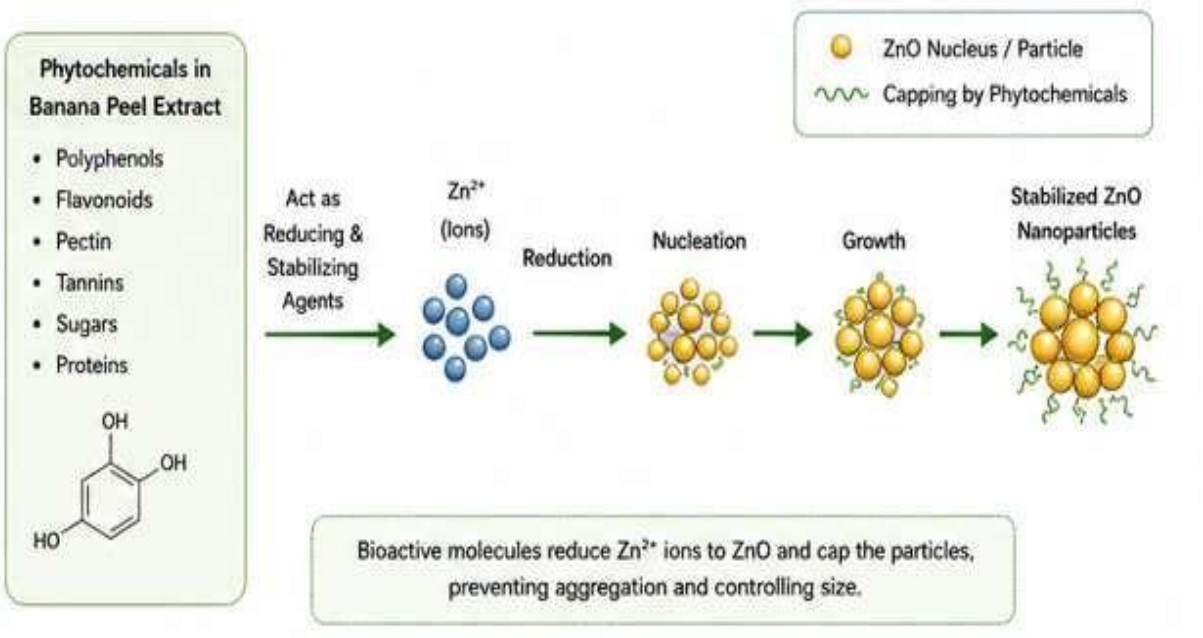


Figure 2.3: Mechanism of ZnO nanoparticles formation

2.10 Impact of synthetic azo dyes on environment

Since the textile sector releases vast volumes of contaminated wastewater into aquatic systems, it contributes significantly to environmental contamination, which is regarded as one of the most important global concerns. Aquatic ecosystems and environmental quality are adversely affected by the high biological oxygen demand (BOD) and strong coloring of textile effluents. Because of their intricate synthetic structures, which make them extremely resistant to biodegradation, azo dyes are among the most hazardous of these contaminants. Numerous azo dyes also have harmful properties, such as cytotoxic, carcinogenic, and mutagenic effects. One of the biggest long-term threats to human health is its genotoxic nature, which can harm DNA and chromosomes.

Significant volumes of untreated effluents are directly discharged into many water bodies, posing serious ecotoxicological threats as well as toxic effects on living organisms.

2.11 Gaps and Challenges

Even yet, there are still a number of gaps. In order to maximize ZnO yield and characteristics, few research systematically change all synthesis parameters (extract concentration, pH, precursor type). Because banana chemistry varies, reproducibility between labs is dubious. The majority of studies concentrate on antimicrobial or simple dyes (MB); thorough comparisons (e.g., other dye classes, actual wastewater) are uncommon. Scale-up viability (batch vs. continuous) and long-term stability (UV usage, storage) are not well studied. Lastly, there are still unresolved mechanistic issues (such as which phytochemical is the major reductant). By offering a thorough technique and contrasting performance to previous research, this effort will try to fill up certain gaps.

Parameter	Green Synthesis	Chemical Synthesis	Physical Synthesis
Cost	Low	Moderate	High
Toxic Chemicals	Not required	Required	Not required
Environmental Impact	Eco-friendly	Harmful by-products	High energy consumption
Energy Requirement	Low	Moderate	Very high
Stability of Nanoparticles	High due to biomolecules	Moderate	High
Safety	Biocompatible	Toxic reagents involved	Requires specialized equipment
Reducing Agent	Plant phytochemicals	Chemical reducing agents	Heat/physical force

Table 2.2: Comparison between green, chemical, and physical synthesis methods for nanoparticle production.

CHAPTER 3 – MATERIALS AND METHODS

3.1 Aim The aim of this project was to produce and characterize zinc oxide nanoparticles utilizing a green synthesis technique with banana peel extract.

3.2 Chemicals and Reagents

This experiment included analytical-grade chemicals and reagents that were acquired from SigmaAldrich, including zinc chloride [$ZnCl_2$], methylene blue, methyl red [C.I. 13020], Sodium hydroxide (NaOH), hydrochloric acid (HCl), ethanol and all other materials.

3.2. Collection of plant sample

The banana peels were obtained from the fruit shop of Delhi Technological University. Following a thorough cleaning with distilled water, the peels were dried on blotting paper. A fine powder was obtained by grinding them with a mortar and pestle, following a day of sun drying to remove any residual moisture. This powder was boiled in five to ten minutes using MilliQ water. With the extract that was left over after dissolving, zinc oxide nanoparticles were created.



Figure 3.1: Banana peels

3.3. Preparation of Banana Peel Extract

Banana peels were cleaned multiple times with tap water to eliminate dust and other pollutants before being sliced into little pieces. To completely remove surface moisture, the cleaned peels were air-dried before being oven-dried for 3-4 hours at 80°C. In a beaker, approximately 24 g of dried peel pieces were mixed with 240 mL of deionized water and heated for 20 minutes at 80 °C with constant stirring on heating mantle. After the peel extract solution was brought to a boil and allowed to cool, it was allowed to cool at room temperature. Filtration was done using Whatman filter paper to create filtrate once the solution had cooled to room temperature. While the completed extract was stored at 4°C, the remainder was disposed.

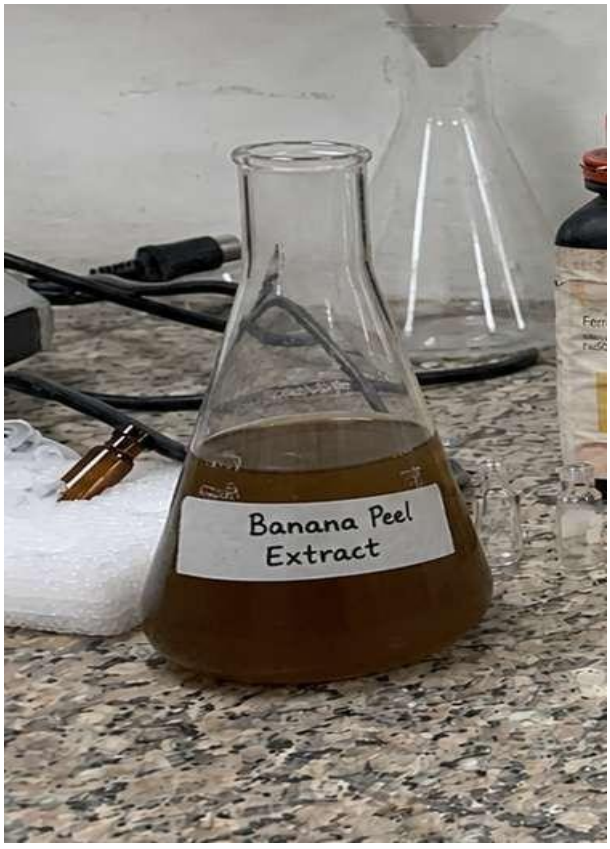


Figure 3.2: Banana peel extract for formation of NPs

3.4. Green Synthesis of ZnO nanoparticles

All of the chemicals came from reputable suppliers and were of AR Grade. An eco-friendly method was used to create ZnO nanoparticles. To a 90 ml stirring solution containing 10 mM zinc chloride, filtrated peel extract was added drop by drop until the colour changed from pale yellow to yellowish brown. The liquid was centrifuged at 6000 rpm for 10 minutes. For an hour, the resulting mixture was stirred. Before being evaluated using a variety of spectrophotometer methods, it was covered in aluminium foil and allowed to stand at room temperature for the entire night.



Figure 3.3: Synthesis of ZnO nanoparticles

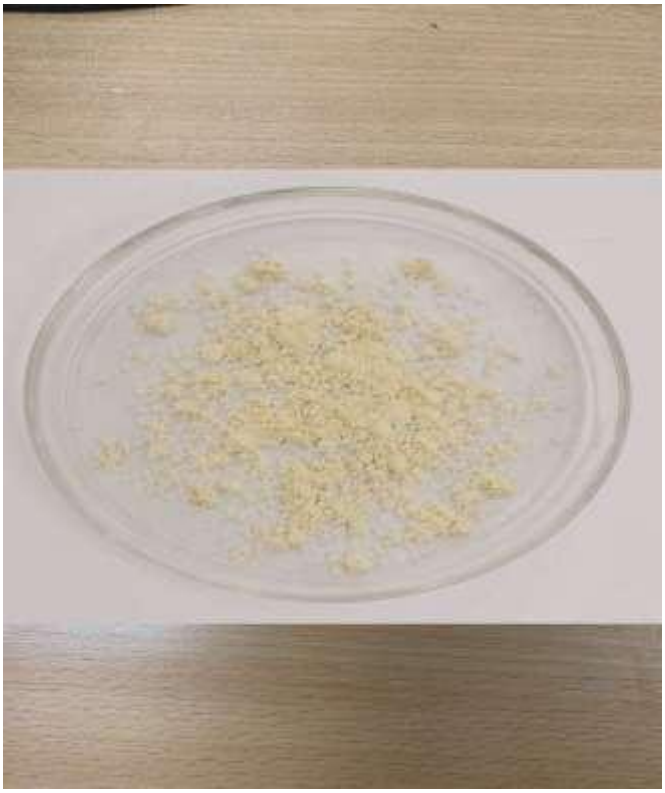


Figure 3.4: Powdered ZnO nanoparticles

3.5. Characterization of ZnO Nanoparticles

Fisher Scientific Chemicals was the source of all the reagents. By using an Eppendorf spectrometer to record the absorption spectra of the nanoparticles, the special characteristics of the particles were examined. The resultant nanoparticles were subsequently examined by SEM, FTIR, following the UV examination. To ensure the remediation of methyl red, formed nanoparticles were further studied for decolourization of the dye.

3.6. Scanning Electron Microscope (SEM)

The formed nanoparticles were tested and morphologically examined using scanning electron microscopy to ascertain their structural.



Figure 3.5: Zeiss Sigma VP Scanning Electron Microscope

3.7.Fourier-transform infrared (FTIR) spectroscopy

Changes observed in the structure of nanoparticles were analyzed by FTIR spectroscopy at around 4000-450 cm^{-1} range of frequency.



Figure 3.6: Perkin Elmer Spectrum 2 FTIR system

3.8.Remediation of Methyl Red

A concentration of 100 mg/L was used to make the dye solution. The dye degradation investigation was conducted over four days at 35°C and 120 rpm in a shaker incubator. In a control group, the dye sample was treated under conditions identical to those of the experimental samples, but without the addition of the nanoparticles. Using a UV-Vis spectrophotometer, the decolorization efficiency (DE) was determined by tracking the variation in absorbance at 425 nm.

CHAPTER 4 – RESULTS AND DICUSSION

With biological agents like plant extracts, nanoparticles can be produced with significant advantages over traditional methods. Plus, it makes large-scale manufacturing unnecessary when it comes to keeping an eye on cell cultures. Nucleating nanoparticles is most economically accomplished using an banana peel extract. As a dissolvable rather than natural solvent, ZnO NPs were used in the current investigation in conjunction with an extricated arrangement of Banana Peel extract. The manufacture of zinc oxide nanoparticles can be verified by an array of analytical methods that offer accurate details.

4.1.UV–Visible Analysis

Using an Eppendorf Biospectrometer, UV-Vis absorption spectroscopy was used to characterize the nanoparticles. The UV-visible spectrum of MgO NPs produced by Banana Peel Extract is shown in Figure 4.1. There was a noticeable absorption band seen in the 350–390 nm range, which suggests the presence of MgONPs. ZnO nanoparticles are produced when the extract composition rises, as shown by changes in the absorption spectra. As a result, the absorption spectrum expands along with the plant extract content, reaching its maximum absorption at about 370 nm. The generation of ZnO NPs is responsible for the observed spectra. The absorption spectra held true even after prolonged storage. The synthesized nanoparticles were symmetrical and spherical in shape, as shown by the spectra that were gathered.

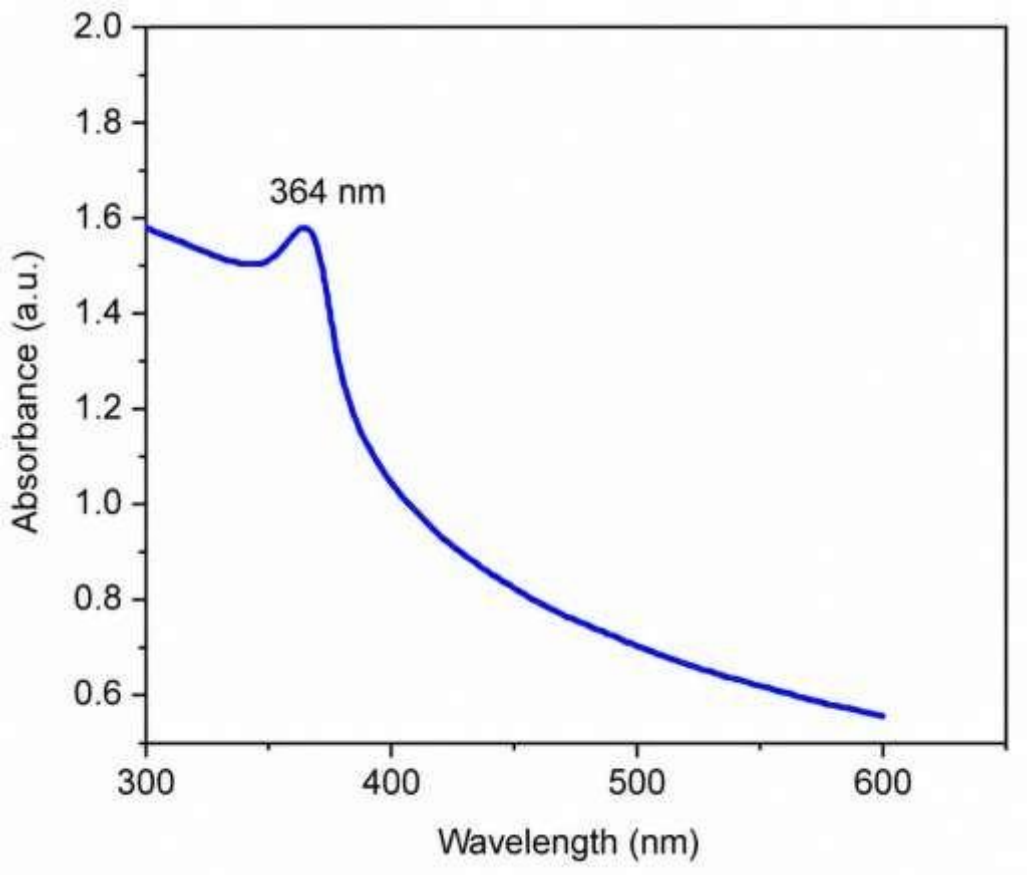


Figure 4.1: UV-Vis Spectra of ZnO nanoparticles

4.2.FTIR Analysis

Figure 4.2 displays the FTIR spectra calculated for ZnO NPs. As per S and Kavitha's (2023) findings, the existence of ZnO at the nanoscale is indicated by peaks that arise between wavenumber 400 and 700 cm^{-1}. We have detected a peak at 597.93 cm^{-1}. Indicating the existence of the -OH functional group was the broad peak at 3313 cm^{-1}. Because of the amide group (O=C–NH), there is a band at 1641 cm^{-1}. The peak at 1112 cm^{-1} corresponds to the Amide group (C-N stretching).

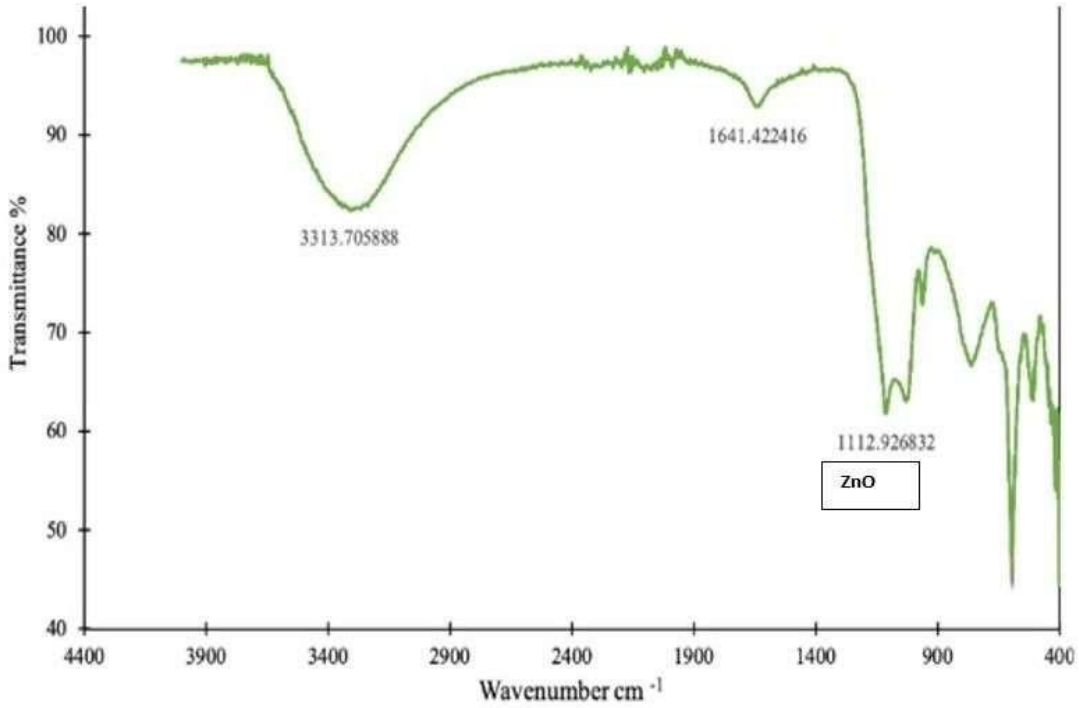


Figure 4.2: FTIR analysis of ZnO nanoparticles

4.3. SEM analysis

Analyzing the size and shape of the produced zinc nanoparticles is essential to understanding their morphological characteristics. The morphological shape and structure of the produced ZnO nanoparticles were examined using scanning electron microscopy .The picture created for the SEM analysis of ZnO nanoparticles as shown in Figure 4.3. Typically, the resulting nanoparticles have a spherical or rod form.

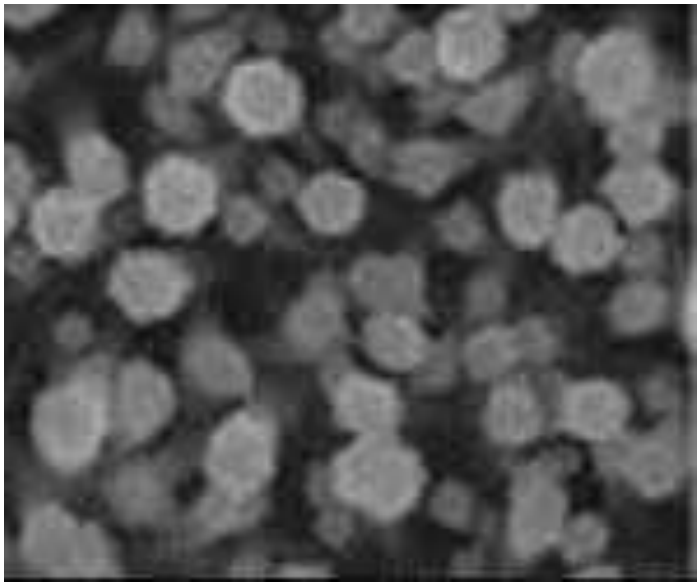


Figure 4.3: SEM image of ZnO nanoparticle

4.4 Degradation of Methylene blue dye

For the production of a 10 ppm methylene blue dye solution, a 1000 ppm stock solution was diluted . To prepare the solution, 0.3 mL of 1000 ppm methylene blue dye was added to 29.7 mL of distilled water in a measuring cylinder and vigorously mixed to create 30 mL of 10 ppm dye solution. The solution that was created was shaken gently for 2 minutes to achieve uniform mixing before being transferred to a 100 mL conical flask. The dye solution was treated with approximately 10 mg of magnetized naturally produced adsorbent material. To enhance dye adsorption onto the adsorbent surface, the conical flask was wrapped in aluminum foil and shaken for 3 hours. Following the completion of the adsorption procedure as shown in Fig 4.4, a visible reduction in the blue color intensity of the solution was detected, suggesting that the methylene blue dye was successfully removed from water. Due to its magnetic properties, the adsorbent material was removed from the solution by an external magnet.

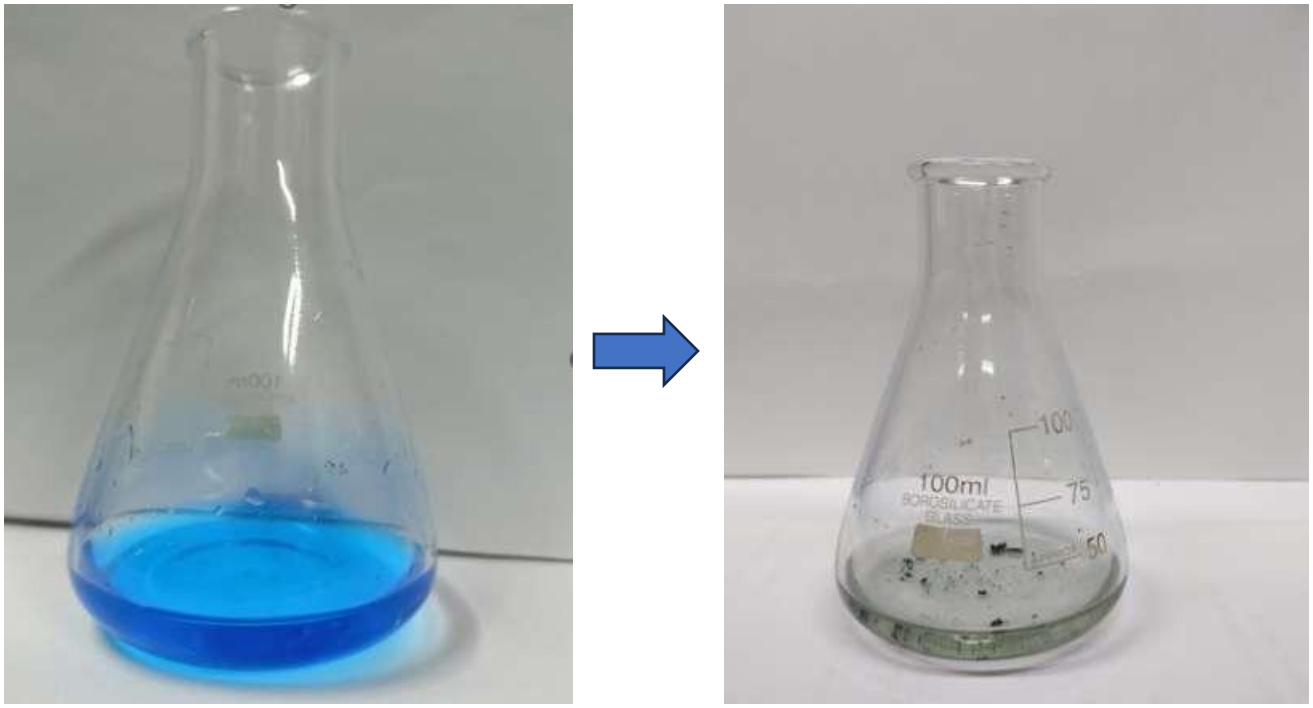


Figure 4.4: Degradation of Methylene blue dye

4.5 Remediation of Methyl Red

ZnO nanoparticles were employed in this work to break down MR. We configured two distinct experimental setups: one with just methyl red, and the one with simply ZnO nanoparticles. A 72-hour measurement was made of the decolorization efficiency. The position and kind of substituents on the dye's aromatic rings are known to affect how biodegradable the dye. Compared to its meta-position analogue, the dye having the sulfonic group at para position to the azo link had a higher degree of decolorization. Additionally, a dye's redox potential and decolorization are directly correlated, however further research is required to fully comprehend this link.

It has been demonstrated in earlier research that ZnO NPs have strong antibacterial qualities because, when exposed to oxygen, they readily create superoxide, which rapidly breaks down bacterial cell walls. Additionally, ZnO NPs have been shown to repair organic dyes due to their high reactivity, specificity, and surface area to volume ratio. Our findings indicate that ZnO can impair MR by 23.3%.

Fig 4.5 confirms the decolorization of methyl red in the presence of ZnO nanoparticles.



Figure 4.5: Decolorization of methyl red by ZnO nanoparticle

CHAPTER 5 – CONCLUSION

Textile dye effluents are known to pose a serious risk to both human health and the environment. Over the years, many physical and chemical methods have been used, including membrane separation, aggregation, flocculation, and more. However, one method is insufficient and not always practical. Aside from this, environmental damage is frequently caused by physical and chemical procedures. Thus, the hunt for a less expensive, more sustainable, and environmentally friendly method had begun. One such method is nano remediation, which cleans up pollution by using nanoparticles. But once more, a single strategy is frequently ineffective. Further, researchers have tried various combinations of using nanomaterials with physical, chemical and biological means to remediate pollutants.

In the current work, the degradation of Methylene blue and Methyl Red dye was investigated using the combination of ZnO nanoparticles synthesized by banana peel extract. The characterization of ZnO nanoparticles by SEM, FTIR and UV-Vis spectrophotometry confirms the formation of ZnO nanoparticles. Further the nano remediation of methylene blue and methyl red by synthesized ZnO nanoparticles was studies. The decolorization of methylene blue and methyl red in the presence of ZnO nanoparticles confirms its remediation. Following a 72-hour period, we observed MB and MR degradation in each setup of 85% and 23.3% respectively. As predicted, using ZnO NPs increased the decolorization efficiency of MB and MR. This is explained by the synergistic action of ZnO nanoparticles in the presence of methyl red and could represent as a viable source for sustainable environment in future.

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