

Research Article

Synthesis and Characterization of *Parthenium hysterophorus*-Mediated ZnO Nanoparticles for Methylene Blue Dye Degradation

Dennis Nzilu ¹, Edwin Madivoli ¹, David Makhanu ², Sammy Wanakai ¹,
Gideon Kirui ¹, Vincent Mwangi ¹, and Patrick Kareru ¹

¹Chemistry Department, Jomo Kenyatta University of Agriculture and Technology, P.O. Box 62000-00200, Nairobi, Kenya

²Department of Biological & Physical Sciences, Karatina University, P.O. Box 1957-10101, Karatina, Kenya

Correspondence should be addressed to Dennis Nzilu; dennisym21@gmail.com

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Herein, zinc oxide nanoparticles (ZnO NPs) were synthesized using *Parthenium hysterophorus* whole plant aqueous extract as reducing and capping agents. The synthesized ZnO NPs were characterized via UV-Vis spectroscopy, Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and dynamic light scattering (DLS). An intrinsic optical absorbance of ZnO NPs occurred at 337 nm in the UV-Vis spectrum. The FTIR analysis revealed the presence of secondary metabolites responsible for reducing and stabilizing the nanoparticles. Furthermore, SEM and TEM images revealed that ZnO NPs were spherical with an average particle size of 38 nm. The XRD analysis revealed that ZnO NPs had a hexagonal wurtzite crystal structure with a crystallite size of 42.6 nm. The synthesized nanoparticles were investigated for degradation ability against methylene blue dye at varying conditions of ZnO NPs' dosage, methylene blue concentrations, pH, temperature, and interaction time. Degradation efficiency of 55.69% was obtained at optimal conditions using 50 mg of ZnO NPs, 5 mg/L of MB dye concentration, and pH 12 and at 65°C within 32 minutes. Due to their novel green synthesis route, *Parthenium hysterophorus*-mediated ZnO NPs are promising candidates for removing persistent organic dyes from aquatic environments.

1. Introduction

Aquatic pollution by industrial effluents and emissions from wastewater treatment plants is a serious threat facing humanity and the ecosystem [1, 2]. Among the industrial wastewater contaminating our water systems are organic dyes from textile, cosmetic, paper, plastic, and pharmaceutical factories [3–5]. These organic dyes endanger water quality, and some, such as methylene blue, are non-biodegradable and toxic because of their mutagenic and carcinogenic properties, threatening human health [6].

Chemical, physical, and biological methods are conventional methods employed in wastewater treatment to remove contaminants, including dyes [5]. However, these methods have drawbacks in removing the contaminants at low concentrations. Recently, researchers have embraced green nanotechnology to develop materials in nanoscale size

that can effectively remediate the pollutants before being discharged into the water system [7–11]. Chemical, biological, and physical methods are the primary methods employed in the synthesis of nanoparticles [11, 12]. Chemical and physical processes of synthesizing nanoparticles include coprecipitation, pyrolysis, thermal decomposition, sol-gel, solvothermal, laser ablation, and ball milling [13, 14]. However, both chemical and physical processes of synthesizing nanomaterials have drawbacks of using toxic chemicals and being time-consuming, energy inefficient, and cost-ineffective [14–16]. Researchers find biological methods for synthesizing nanomaterials more attractive because they are environmentally friendly and cost-effective [16, 17]. Biological methods involve the use of microorganisms and plants. However, the use of microorganisms is characterized to be labor-intensive and involves delicate procedures in microbe isolation, growth,

maintenance, longer synthesis time, and the possibility of forming toxic byproducts [18, 19]. To promote environmentally friendly chemistry, using aqueous plant extracts in synthesizing metallic nanoparticles is preferred because of their cost-effectiveness, simplicity, little or no toxicity in products, and ease in large-scale production of nanoparticles [15, 18–21].

Zinc oxide nanoparticles (ZnO NPs) find wide application in cosmetic, photocatalysis, plasmonic, sensors, pure water technologies, and optoelectronics, among others [14, 22]. The ZnO NPs possess improved chemical and physical properties which make them suitable for removing pollutants from the environmental compartments [14, 22]. The use of plant extracts for synthesizing ZnO NPs makes the process cost-effective and nontoxic to carry out [23].

Therefore, this study reports a simple, cost-effective, environmentally friendly, and easy approach to decontaminating a highly toxic MB dye from our wastewater system using readily available plant materials, *Parthenium hysterophorus*, as raw materials, which are renewable and biodegradable, for preparing the ZnO NPs. *Parthenium hysterophorus* plant is an invasive weed that abundantly grows in cultivated and agricultural lands and along the roadsides [24]. Previous studies report that *Parthenium hysterophorus* possesses medicinal and bioherbicidal properties [25, 26]. The phytochemical profiling of the *Parthenium hysterophorus* shows the presence of tannins, flavonoids, phenols, saponins, and terpenoids, essential for reducing, capping, and stabilizing metal ions from high oxidation state to zero-valent species [25]. The synthesized ZnO NPs were characterized via UV-Vis spectroscopy, FTIR, SEM, TEM, XRD, and DLS techniques and investigated on their ability to degrade methylene blue (MB) dye. The catalytic properties of ZnO NPs against MB dye were also explored at varying conditions of pH, ZnO NP dosage, MB dye concentration, interaction time, and temperature. The study places ZnO NPs obtained in *Parthenium hysterophorus*-mediated synthesis as powerful plant-based nanoparticles that aim to reduce increasing aquatic pollution from dyes, a significant issue currently pressing humanity. In this light, a comparative overview of the efficiency of *Parthenium hysterophorus*-mediated ZnO NPs in the removal of MB dye with other nanomaterials that have previously been studied for the removal of MB dye in aquatic systems is provided in this study.

2. Experimental Methods

2.1. Materials. Zinc nitrate hexahydrate (96%), hydrogen peroxide (30% w/w), and methylene blue dye (82%) were procured from Legacy Lab Africa Limited, Kenya. The materials were used as procured without any form of purification.

2.2. Sample Collection and Preparation. The *Parthenium hysterophorus* plant sample was collected from Kalimoni, Juja, Kiambu County, Kenya. Mr. John Kamau authenticated the plant sample, and a voucher specimen was

deposited at Jomo Kenyatta University of Agriculture and Technology (JKUAT) Botany Herbarium and assigned accession number DMN-JKUATBH/001/2023A-C as described in our previous study [24]. The sample was washed with running tap water, rinsed with distilled water, and shed-dried for two weeks at room temperature [26]. We followed the methods of Datta et al. in which the dry sample was ground to a fine powder by using a milling machine, after which the phytochemicals were extracted by dissolving 20 g of the plant sample in 200 mL of distilled water [26]. The extraction was carried out at 45°C for 45 minutes and stored at 4°C in a freeze drier before further being used to synthesize zinc oxide nanoparticles [26].

2.3. Preparation of Zn Ions Solution and Synthesis of ZnO NPs. 0.01 M zinc solution of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was prepared by using distilled water. The nanoparticles were synthesized by modification of a previously established protocol of Iqbal et al. and Naseer et al. in which the zinc ions solution was mixed with plant extract in a ratio of 1:4 and heated in a hot plate at 60°C for 1 hour with constant stirring [27, 28]. The formation of ZnO NPs was monitored by color change and UV-Vis spectrophotometric measurement [28–30].

2.4. Characterization of ZnO Nanoparticles

2.4.1. UV-Vis Analysis. The UV-Vis absorption analysis of ZnO NPs was performed by scanning a double beam UV 1800 UV-Vis spectrophotometer (Shimadzu, Japan) to confirm their surface plasmonic resonance at 200–800 nm wavelength range [24].

2.4.2. FTIR Analysis. The functional groups present on the surface of the ZnO NPs were acquired by Bruker Tensor II FT-IR spectrophotometer (Bruker, Ettlingen, Germany). The samples were directly placed on the sample holder, pressed, and scanned in the frequency range of 4000–400 cm^{-1} [31, 32].

2.4.3. XRD Analysis. The crystallinity nature of the nanoparticles was determined by using X-ray diffraction, and the diffractograms were obtained by using a Bruker D8 Advance Diffractometer (Bruker, Ettlingen, Germany) with a copper tube operating under a voltage and current of 40 kV and 40 mA. The samples were irradiated with a monochromatic $\text{CuK}\alpha$ radiation of 0.1542 nm, and the diffractograms were acquired between 2θ values of 5°–90° at 0.05° intervals with a measurement time of 1 second per 2θ intervals. The nanoparticles' crystalline size was calculated by using the Debye Scherrer's equation as follows:

$$D = \left(\frac{K\lambda}{\beta \cos \theta} \right), \quad (1)$$

where D is the average particle size (nm), K is a constant equal to 0.94, λ is the wavelength of X-ray radiation, β is

full-width at half maximum of the peak in radians, and theta is the diffraction angle (degree) [24, 29, 33].

2.4.4. SEM Analysis. The surface morphology analysis of the nanoparticles was visualized by using the Tescan Mira3 LM FE scanning electron microscope (Tescan, Brno-Kohoutovice, Czech Republic), operating under an accelerating voltage of 3 kV. Before analysis, the samples were sputter coated with 4 nm gold to avoid charging effects by using a AGB7340 Agar Sputter Coater (Agar Scientific, Essex, United Kingdom) [32, 34].

2.4.5. TEM Analysis. Surface morphology and shape of the nanoparticles were observed using TEM and was performed on a Tecnai G2 Spirit (Thermo Fischer Scientific, Oregon USA) under an operating voltage of 120 kV equipped with Veleta 2048 × 2048 wide angle and Eagle 4096 × 4096 bottom mount detectors. The dry samples were suspended in ultrapure water (Barnstead GenPure, Thermo Scientific, Germany) and ultrasonicated to obtain a solution that was drop casted on 300 mesh carbon films before analysis [32, 34].

2.4.6. DLS Analysis. To determine the particle size distribution and polydispersity index of the suspended nanoparticles, the metallic nanoparticles were resuspended in ultrapure water (18 MΩ·cm Barnstead GenPure UV-TOC, Thermo Scientific, Germany) and ultrasonicated to obtain a solution of suspended nanoparticles. The solutions were filtered through 0.25 μM PTFE syringes into glass vials, and 45 μL of each solution was transferred onto quartz cuvettes before analysis. The particle size distribution and polydispersity index were then measured by using a Beckman Coulter DelsaMax PRO dynamic light scattering analyzer (Beckman Coulter, Indianapolis, United States) [35, 36].

2.5. Degradation Studies. Methylene blue (MB) dye was used as a model organic dye in the degradation studies using ZnO NPs. The degradation of MB dye was monitored by using a UV-Vis spectrophotometer by measuring the change in absorbance of the dye alone; the dye spiked with hydrogen peroxide and the dye spiked with hydrogen peroxide and ZnO NPs at a constant time of 150 minutes. The degradation studies of MB dye by ZnO NPs were also conducted at varying reaction conditions, including the concentration of the MB dye solution, the dosage of ZnO NPs, interaction time, pH, and temperature [37–39]. The recyclability capability of ZnO NPs in the degradation of MB dye was also investigated in this study [17, 39–42]. For this study, 5 mg/L of the MB dye solution was prepared as the standard MB concentration except where the variation of MB concentration was studied. The degradation efficiency was calculated by using the following equation, where A_o is the absorbance of MB at time = 0, and A_t is the absorbance after a particular time, t [24]:

$$\% D (\text{Degradation}) = \frac{(A_o - A_t)}{A_o} \times 100. \quad (2)$$

The kinetics of degradation of MB dye was determined by assuming a pseudo-first-order kinetic model (equation (3)) and a pseudo-second-order kinetic model (equation (4)) [38, 40, 41].

$$\ln[A]t = -k \cdot t + \ln[A]_o, \quad (3)$$

$$\frac{1}{[A]t} = -k \cdot t + \frac{1}{[A]_o}, \quad (4)$$

where A_o = is the absorbance of MB at time = 0, A_t = is the absorbance after a particular time, and t = is the time in minutes.

The thermodynamics of the degradation reaction was determined by using the linear form of Van't Hoff 's equation to obtain the change in heat and enthalpy of the reaction as follows:

$$\ln K_{eq} = \frac{\Delta H}{RT} + \frac{\Delta S}{R}, \quad (5)$$

where ΔH and ΔS are the change in heat and entropy of the degradation reaction, respectively. The T is the temperature in Kelvin, and R is the universal gas constant [38, 43].

3. Results and Discussion

3.1. Biosynthesis of ZnO NPs. *Parthenium hysterophorus* aqueous extract contains phytochemicals such as saponins, flavonoids, terpenoids, and phenols [25]. These phytochemicals contain functional groups, which, upon reaction with zinc metal solution, reduce Zn^{2+} to Zn^0 , as previously described in the biosynthesis mechanism of metallic nanoparticles [44–46]. Figure 1 illustrates a generalized mechanism for the synthesis of *Parthenium hysterophorus*-mediated ZnO NPs.

3.2. Visual and UV-Vis Spectral Analysis of ZnO NPs. Figure 2 depicts the formation of ZnO NPs by color change and observation of the intrinsic optical absorbance band by UV-Vis spectrum.

As can be seen in Figure 2, the color changed from brown to dark brown after the zinc ion solution was mixed with *Parthenium hysterophorus* aqueous extract. This color change can be attributed to secondary metabolites in the aqueous extract that reduces zinc ions (Zn^{2+}) into Zn^0 species [47]. Furthermore, the formation of ZnO NPs was confirmed by its intrinsic optical absorbance band by UV-Vis spectrophotometer centered at 337 nm. Our synthesis of ZnO NPs agreed with UV-Vis results from previous studies [27, 28, 47, 48].

3.3. FTIR Analysis. Figure 3 compares the IR spectra of *Parthenium hysterophorus* aqueous extract and ZnO NPs identified by infrared spectrometry.

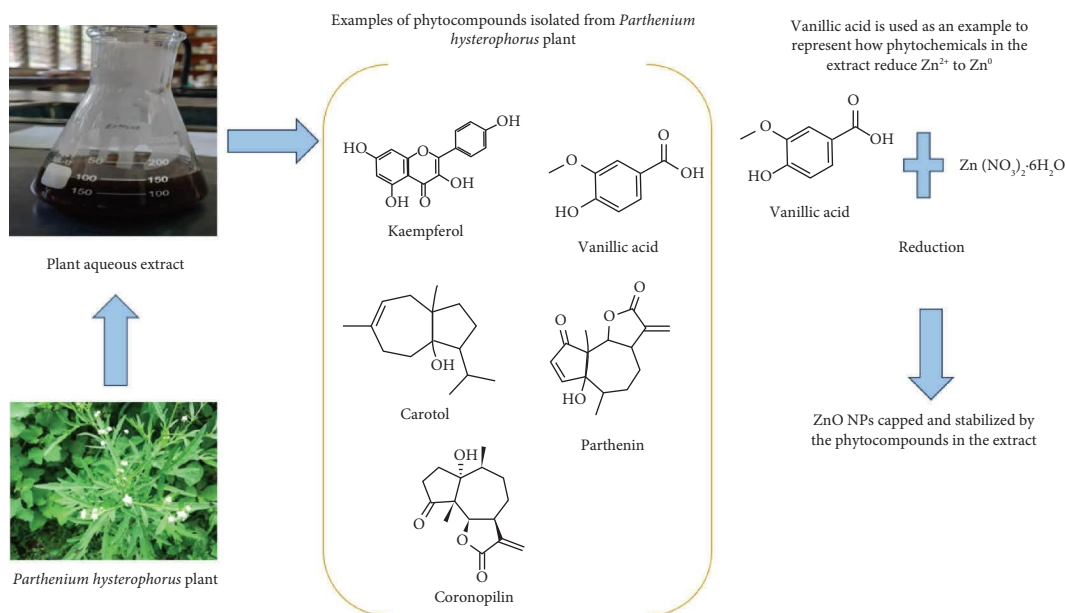


FIGURE 1: Schematic representation of the plausible mechanism of biosynthesis of ZnO NPs using aqueous extracts of *Parthenium hysterophorus* plant.

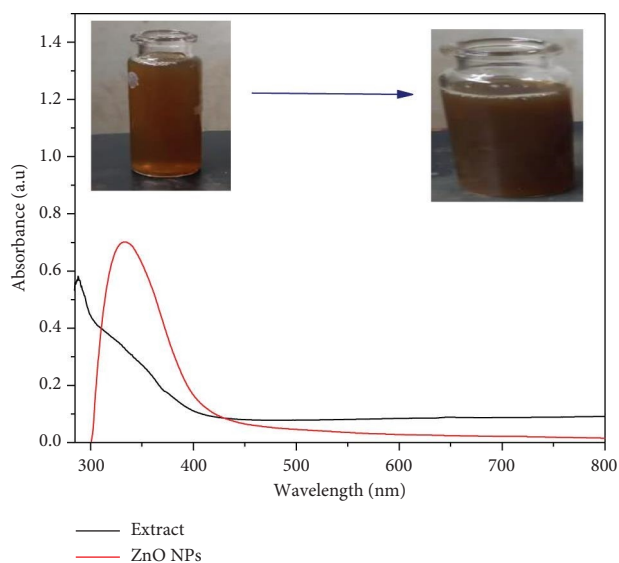


FIGURE 2: Visual observation and UV-Vis spectrum of synthesized ZnO NPs.

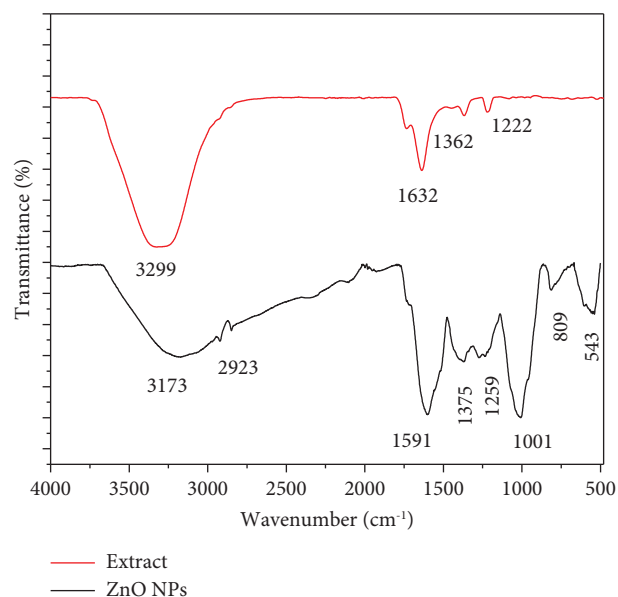


FIGURE 3: IR spectra of *Parthenium hysterophorus* aqueous extract and ZnO NPs.

As can be seen in Figure 3, the plant extract has peaks at 3299 cm^{-1} , 1632 cm^{-1} , 1362 cm^{-1} , and 1222 cm^{-1} . These peaks are attributable to broad O-H, C=O, and C-N stretching bands characterized by phenols, flavonoids, and amine metabolites in the plant extract [26]. A slight shift in the functional groups present in the extract was evident in the IR spectra of the ZnO NPs, indicating that some metabolites bonded or capped ZnO during its formation [49]. Observable vibration bands in ZnO NPs spectra were at 3173 cm^{-1} , 2923 cm^{-1} , 1591 cm^{-1} , 1375 cm^{-1} , 1259 cm^{-1} , 1001 cm^{-1} , 809 cm^{-1} , and 543 cm^{-1} . Three new peaks appeared in the IR spectra of ZnO NPs at 1001 cm^{-1} , 809 cm^{-1} , and 543 cm^{-1} . The peak at 1001 cm^{-1} showed that

ZnO NPs underwent C-H bending. The peak at 543 cm^{-1} was characteristic of the Zn-O stretching vibration band. The FTIR analysis showed the role of functional groups in the plant metabolites as reducing and capping agents in forming ZnO NPs, which were consistent with previous studies using plant extracts as sources of reducing and capping agents in the formation of ZnO NPs [28, 40, 47, 49].

3.4. SEM Analysis. Figure 4 shows the SEM micrograph of ZnO NPs and the histogram used to determine particle size distribution using ImageJ software.

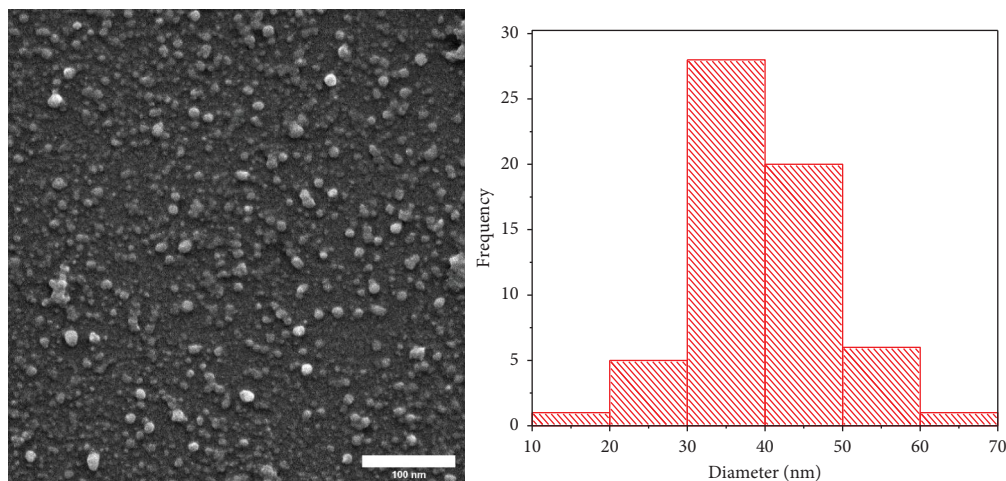


FIGURE 4: SEM micrograph and particle size distribution histogram of ZnO NPs.

The surface morphology from the SEM micrograph revealed that the ZnO NPs were nearly spherical. These findings agreed with previous studies, which showed that ZnO NPs synthesized using the coffee leaf extract and *Elaeagnus angustifolia* leaf extracts were spherical [27, 48]. The micrograph revealed less evidence of agglomeration of the nanoparticles, which indicates that the synthesis method was effective in obtaining highly homogenous nanoparticles with desired catalytic properties [26, 49, 50]. The particle diameter size ranged from 10 to 70 nm, with the average particle size diameter of the ZnO NPs calculated using ImageJ software being 38.47 nm. The particle diameter size was in the range of previously prepared ZnO NPs [12, 51].

3.5. TEM Analysis. Figure 5 depicts the TEM images and particle diameter size distribution histogram of the synthesized ZnO NPs.

As shown in Figure 5, the TEM images were spherical with little agglomeration evidence, which agrees with SEM image results. The average particle size of the nanoparticles was calculated from ImageJ data to be 7.54 nm. These results agree with previous studies that synthesized ZnO NPs using coffee leaf extract [48].

3.6. XRD Analysis. Figure 6 illustrates the XRD diffractogram patterns of ZnO NPs obtained from a powder diffractometer.

The XRD diffractogram reveals 11 peaks at 31.74° , 34.40° , 36.4° , 47.56° , 56.73° , 62.88° , 66.55° , 68.05° , 69.22° , 72.54° , and 77.05° obtained between 20 and 80 2θ degrees. The 2θ values correspond to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) crystallographic planes, respectively, which correspond to the International Center for Diffraction Data (ICDD) database for ZnO NPs [27, 48, 49]. These crystallographic planes reveal that the ZnO NPs had a hexagonal wurtzite structure [12, 48, 49]. The crystallite size was calculated by using the Debye Scherrer equation and was found to be of 42.6 nm. In a previous study, the particle

size of ZnO NPs was 66.43 nm [52]. In another study, the crystalline particle size of ZnO NPs was calculated to be 52.23 nm [47]. Therefore, we confirm the formation of ZnO NPs from the XRD pattern.

3.7. DLS Analysis. Figure 7 depicts the size distribution of ZnO NPs as observed by using the dynamic light scattering (DLS) technique.

The particle size distribution revealed that the particles were polydisperse, with most of the particles below 500 nm. The polydispersity index (PDI) obtained in the DLS determination was ≤ 0.3 , which proved that the particles were polydisperse. In contrast, individual groups of particles were monodisperse, supporting possible particle agglomeration [49, 53]. The monodispersity of the particles shows that the particles were homogenous, which is desired in the catalytic activity of the nanoparticles.

4. Degradation Studies of Methylene Blue Dye

Figure 8(a) shows the UV-Vis spectrum of MB alone observed after 150 min, Figure 8(b) shows the changes in absorbance intensity of MB after it is reacted with 1 mL of H_2O_2 , and Figure 8(c) shows the changes in absorbance intensity of MB after it is reacted with 1 mL of H_2O_2 and 10 mg of ZnO NPs.

As shown in Figure 8(a), there was no observable change in absorption intensity for the MB dye after 150 minutes. However, spiking the same amount of MB dye with 1 mL hydrogen peroxide, there was a slight decrease in the absorbance intensity of the dye as shown in Figure 8(b). A significant change in the absorbance intensity of the MB dye was obtained when the same amount of the MB dye was reacted with 1 mL of H_2O_2 and 10 mg of ZnO NPs as shown in Figure 8(c). This indicated that the ZnO NPs have the catalytic properties to degrade the MB dye [39, 54]. The degradation studies were then investigated by varying MB dye concentration, pH, ZnO NP dosage, temperature, and interaction time [37–39].

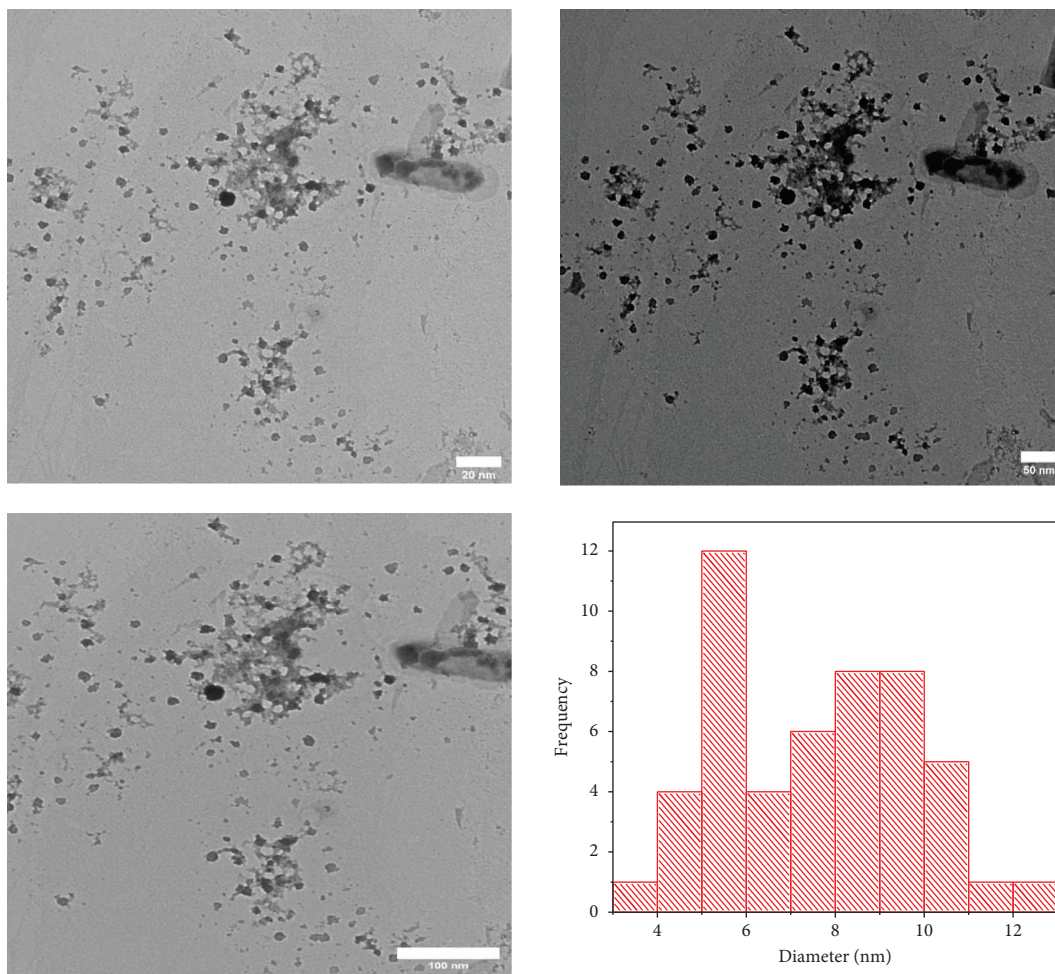


FIGURE 5: TEM micrographs and particle size distribution histogram of ZnO NPs.

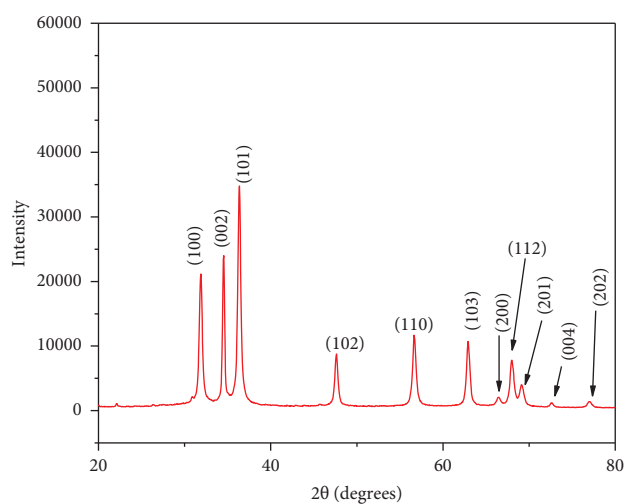


FIGURE 6: XRD diffractogram pattern of ZnO NPs.

4.1. Effect of MB Dye Concentration on Degradation Efficiency of ZnO NPs. To study the influence of dye concentration on the degradation efficiency of ZnO NPs, the study was

conducted using 2.5 mg/L, 5 mg/L, 7.5 mg/L, 10 mg/L, and 12.5 mg/L concentrations, and their effect on degradation efficiency is depicted in Figure 9.

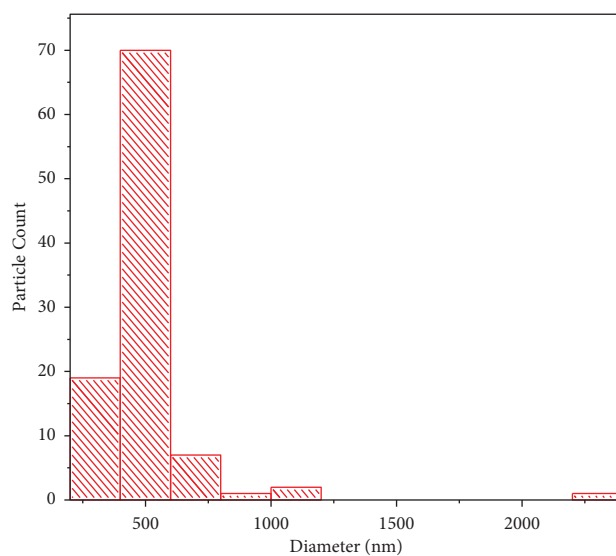
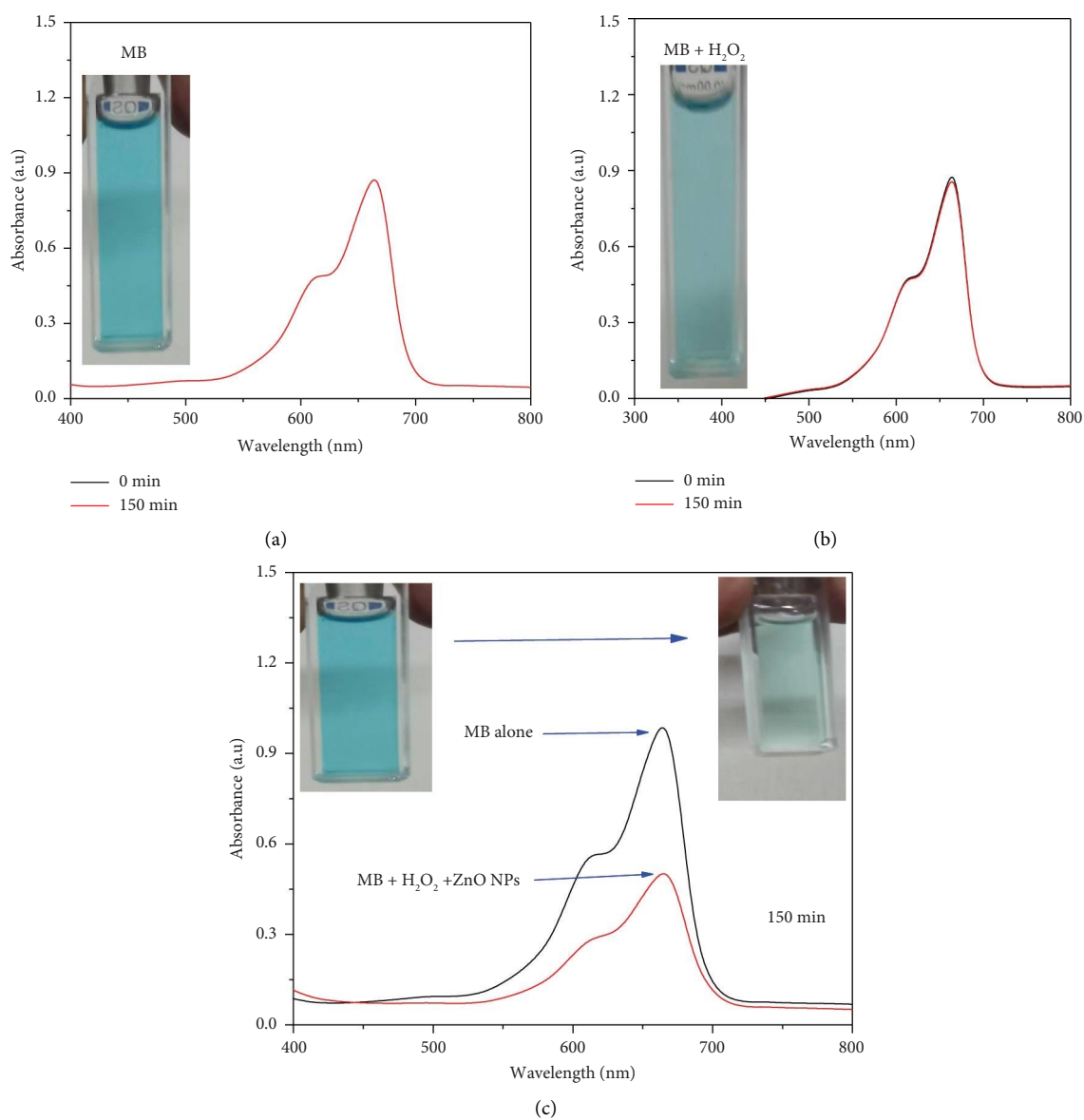


FIGURE 7: Size distribution of ZnO NPs obtained by DLS.

FIGURE 8: (a) UV-Vis spectrum of MB dye alone after 150 minutes, (b) UV-Vis spectrum of MB dye reacted with 1 mL of H₂O₂ after 150 minutes, and (c) UV-Vis spectrum of MB dye reacted with 1 mL of H₂O₂ and ZnO NPs after 150 minutes.

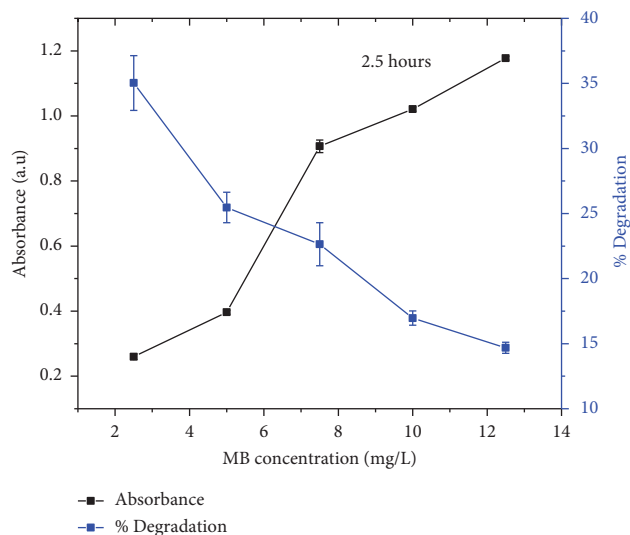


FIGURE 9: Effect of concentration of MB dye on degradation efficiency of ZnO NPs.

The concentration of dyes affects the activity of the nanoparticles because of the saturation of active sites at higher dye concentrations. It was observed that the percentage of degradation of MB dye decreased as the dye concentration increased. At 2.5 mg/L of MB dye, the degradation percentage was 35.03%, while at 12.5 mg/L (the highest concentration of MB dye used for this study), the degradation percentage was 14.68%. The decrease in the efficiency of ZnO NPs in MB degradation studies can be attributed to the saturation of the nanoparticles' active sites by more MB dye molecules [40, 55]. Simultaneously, more molecules of MB dye were available with insufficient active sites on the surface of the nanoparticles because the ZnO NPs were saturated [55]. The MB solution's absorbance increased as the MB dye concentration increased. This means that the nanoparticles become highly saturated at higher concentrations of MB dye, and little dye breakdown occurs.

4.2. Effect of Nanoparticle Dosage on Degradation Efficiency of ZnO NPs. In this study, the dosage of ZnO NPs was conducted at 10 mg, 20 mg, 30 mg, 40 mg, and 50 mg, and their degradation efficiency was determined within 2.5 hours, and the results are illustrated in Figure 10.

It was observed that the percentage of degradation of MB dye increased proportionally to the dosage of the ZnO NPs. The degradation percentage increased from 22.32% at 10 mg to 44.52% at 50 mg within 2.5 hours. The increase in degradation percentage of MB upon increasing the amount of ZnO NPs was probable because, at higher ZnO NPs dosage, the total surface area of the nanoparticles was higher, making more active sites available to bind the MB dye molecules [3, 56]. The decrease in absorbance at a higher nanoparticle dose (50 mg) revealed that the MB dye molecules were degrading towards completion because more active sites were present on the surface of the nanoparticles to bind, interact, and result in the

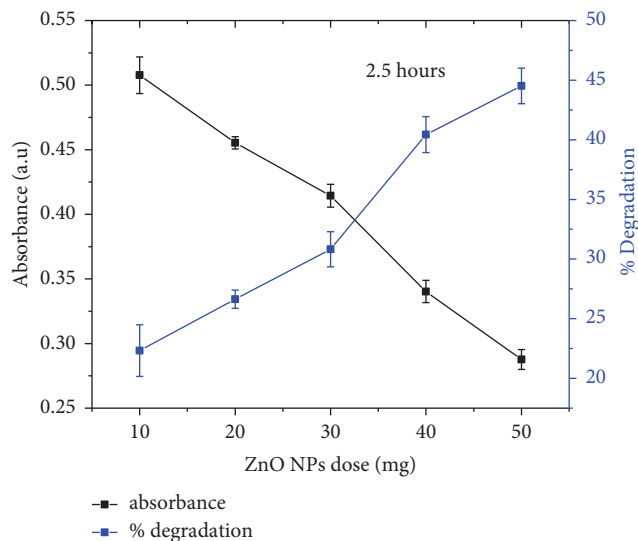


FIGURE 10: Effect of nanoparticle dosage on the degradation efficiency of ZnO NPs against MB dye.

degradation of MB dye [40]. Our results agreed with previous studies which reported that the degradation efficiency increased as the amount of the nanoparticles was increased against the same amount of the pollutant [3, 24, 40, 50, 55, 56].

4.3. Effect of Interaction Time on Degradation Efficiency of ZnO NPs. Figure 11 illustrates the effect of interaction time on the percentage of degradation of MB dye by ZnO NPs.

It was observed that as the interaction time of MB dye with ZnO NPs was increased, the degradation percentage increased from 18.09% at 30 min to 56.87% within 360 minutes. The corresponding absorbance of MB decreased as the reaction time increased, implying that molecules were allowed enough time to interact with the surface of ZnO NPs and break down. The increase in the degradation percentage of MB dye was also supported in previous studies employing ZnO NPs [12, 50].

4.4. Effect of pH on Degradation Efficiency of ZnO NPs. To monitor the optimal pH that results in the higher degradation of MB using ZnO NPs, the solution pH was adjusted to pH 2, 4, 8, and 12, and their effect on the degradation efficiency is depicted in Figure 12.

The acidic conditions of the MB dye solution were adjusted using 0.1 M of HCl, while the basic conditions of the MB dye were adjusted using 0.1 M of NaOH. At pH 2 and 4, the degradation efficiency was 26.00% and 29.91%, respectively. At pH 8 and 12, the degradation efficiency was 45.34% and 114.72%, respectively. The interaction of the acid and the base resulted in the generation of free radicals from the hydrogen peroxide used as a catalyst and radical generator for this reaction. In acidic pH 2 and 4, the degradation efficiency could be attributed to the increase in hydrogen radicals generated from H_2O_2 and the positive

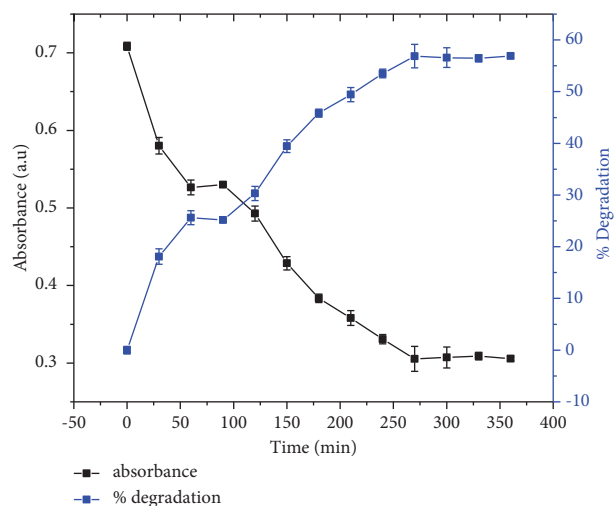


FIGURE 11: Effect of interaction time on degradation efficiency of ZnO NPs against MB dye.

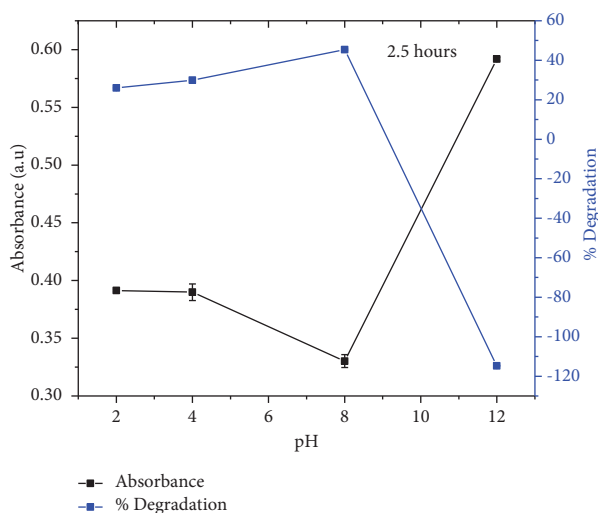


FIGURE 12: Effect of pH on degradation efficiency of ZnO NPs against MB dye.

charge imparted on the surface of nanoparticles, which activates the active sites to improve reaction with the dye molecules [55]. In basic pH 8 and 12, degradation efficiency was attributed to the generation of hydroxyl radicals, which increased the degradation ability of the nanoparticles towards the MB molecules [3]. Uniquely, at pH 12, a negative percentage of degradation was observed within the 2.5 hours used for this study. At pH 12, it implies that MB dye molecules were destroyed to yield probable degradation products with higher absorbance than those obtained in other pH values.

4.5. Effect of Temperature on Degradation Efficiency of ZnO NPs. The temperature of the MB dyes was varied at 25°C, 35°C, 45°C, 55°C, and 65°C, and the highest degradation efficiency was observed at higher temperatures, as illustrated in Figure 13.

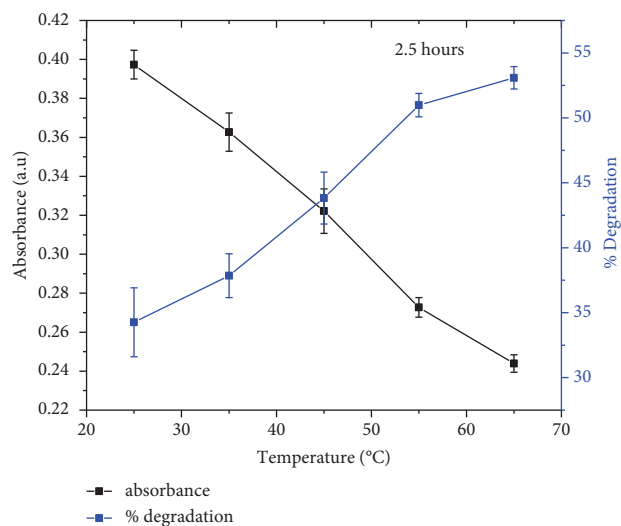


FIGURE 13: Effect of temperature on degradation efficiency ZnO NPs against MB dye.

The temperature significantly influences the activation of the surface of nanoparticles and, therefore, improves the degradation efficiency of ZnO NPs on the degradation of MB dye. The increase in temperature was observed to increase the percentage of degradation of MB dye to 53.08% at 65°C, which is attributed to the Brownian motion, which increases the kinetic energy of MB dye molecules [38]. Another probable reason for the increase in degradation efficiency at higher temperatures is that the MB dye molecules have enough energy to react and undergo degradation [53].

The change in heat and entropy of the reaction was obtained by Van't Hoff's plot of $\ln K_v(1/T)$, as shown in Figure 14.

Figure 14 shows that the degradation of MB dye using ZnO NPs was an endothermic reaction, demonstrating that the MB degradation rate increases as the temperature increases. The change in the heat of the degradation reaction was determined experimentally and calculated from the slope of Van't Hoff's plot to be $14.199 \text{ kJ} \cdot \text{mol}^{-1}$, and the change in entropy was calculated from the intercept value to be $1.37264 \text{ J} \cdot \text{K}^{-1}$. The entropy indicated enhanced system disorder due to the increase in temperature resulting from the breakdown of the MB dye molecules [57].

4.6. Degradation of MB Dye Using ZnO NPs at Optimal Conditions. The degradation of MB dye by ZnO NPs was also investigated by combining all the conditions that resulted in the highest degradation efficiency of MB dye, as described in the previous section. Figure 15 depicts the change in absorption intensity of MB dye obtained using 5 mg/L concentration of MB dye, temperature maintained at 65°C, 50 mg of ZnO NPs, and solution at pH 12.

As shown in Figure 15, a significant change in the absorption intensity of MB dye was observed to occur within 32 minutes in optimal conditions described in this study. Degradation efficiency of 55.69% was obtained under the combined optimal conditions.

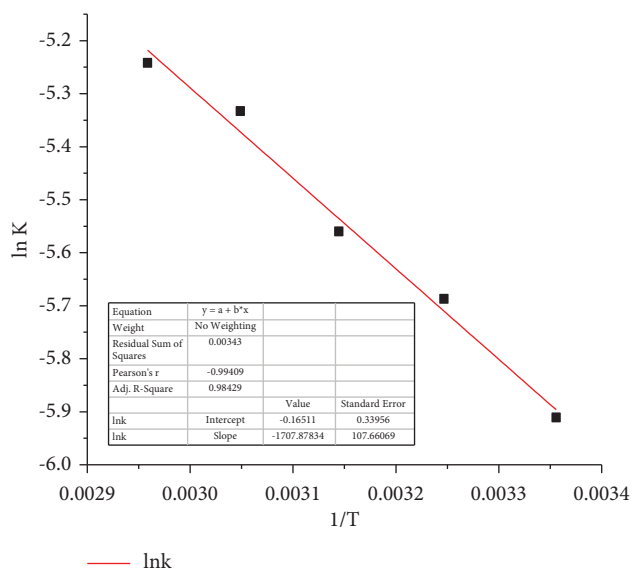


FIGURE 14: Van't Hoff's plot of the degradation of MB dye used to obtain the change in heat and entropy of the degradation process.

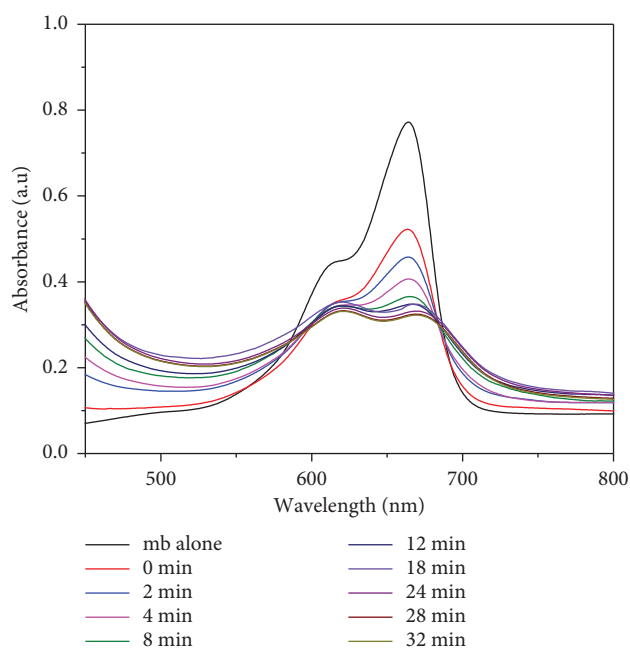


FIGURE 15: A plot showing the change in absorption intensity of MB dye by ZnO NPs at optimal conditions of temperature, pH, ZnO NPs dosage, and dye concentration.

5. Kinetics of Degradation of Methylene Blue Dye

The kinetics of degradation of MB dye using ZnO NPs was determined by fitting the pseudo-first-order and pseudo-second-order kinetics at 298, 308, 318 328, and 338 K, and the results are depicted in Table 1 and Figures 16 and 17.

The kinetic data were analyzed to fit the pseudo-first-order other than the pseudo-second-order because most R^2 (correlation coefficient) values were higher compared to the

R^2 of the pseudo-second-order kinetic model. From this determination, it can be concluded that the degradation of MB was highly dependent on temperature. The increase in temperature increases the reacting molecules' Brownian motion, resulting in the highest degradation efficiency [58, 59]. Figure 16 shows the first-order kinetic plots of $\ln (At/Ao) \nu T$, and Figure 17 shows the second-order kinetic plots of $(1/At) \nu T$.

6. Functional Group Analysis of ZnO NPs after Degradation Studies

The analysis of changes in the frequencies of functional groups present in ZnO NPs after degradation studies with MB dye was investigated. The IR spectra in Figure 18 show changes in the peaks before and after degradation studies.

The frequencies of functional groups in the IR spectrum of ZnO NPs before degradation were observed at 3173 cm^{-1} , 2923 cm^{-1} , 1591 cm^{-1} , 1375 cm^{-1} , 1259 cm^{-1} , 1001 cm^{-1} , 809 cm^{-1} , and 543 cm^{-1} . The peak at 3173 cm^{-1} was attributed to the O-H group of phenols and 2923 cm^{-1} was due to the C-H band, while the bands at 1375 cm^{-1} and 1259 cm^{-1} were characteristic of C-N. The peak at 1001 cm^{-1} and 809 cm^{-1} was attributed to C=C bending vibration. The peak at 543 cm^{-1} was characteristic of Zn-O stretching vibration [3, 49]. The shifts in the IR spectrum of ZnO NPs after degradation studies with MB dye were observed at 3023 cm^{-1} , 2958 cm^{-1} , 1734 cm^{-1} , 1447 cm^{-1} , 1364 cm^{-1} , 1215 cm^{-1} , 1095 cm^{-1} , 891 cm^{-1} , and 521 cm^{-1} . The peaks at 3023 cm^{-1} were due to O-H of phenols, the band at 2958 cm^{-1} was due to C-H band, 1734 cm^{-1} was attributable to C=O, 1445 cm^{-1} band was attributable to C-H bending, and the bands at 1364 cm^{-1} and 1215 cm^{-1} were attributable to C-N stretching band. The 1095 cm^{-1} and 891 cm^{-1} peaks were due to C-O and C=C bending bands, respectively. The characteristic peak at 521 cm^{-1} was associated with Zn-O vibration bands. The slight changes in the frequencies of the functional groups after reaction with MB dye indicated that a molecule of MB was adsorbed onto the surface of the ZnO NPs, which resulted in a slight shift in the functional group frequencies and their intensities after degradation [60].

7. Recyclability of ZnO NPs

The recyclability ability of ZnO NPs was investigated experimentally in four cycles for MB dye degradation. The recyclability studies were conducted under the same conditions (20 mg of ZnO NPs and 5 mg/L of MB concentration). The degradation cycle was determined at constant time (2.5 hours), after which the solution was decanted and washed with water, and the nanoparticles were dried at 80°C in an oven for 6 hours [48]. The degradation of MB was observed by the change in intensity of the absorbance monitored using a UV-Vis spectrophotometer, and the results are plotted as shown in Figure 19. After each cycle, fresh 5 mg/L of MB solution was spiked with 1 mL of H_2O_2 . As observed in Figure 19, the percentage of degradation of MB decreased after each cycle of using the ZnO NPs.

TABLE 1: Experimental data fitted assuming pseudo-first-order kinetics and pseudo-second-order kinetic models at different temperatures.

Temperature (K)	Pseudo-first-order kinetics		Pseudo-second-order kinetics	
	Rate constant (min^{-1})	R^2	Rate constant (min^{-1})	R^2
298	-0.00271	-0.98203	0.00552	0.97305
308	-0.00339	-0.97307	0.0074	0.95715
318	-0.00385	-0.99156	0.00886	0.98896
328	-0.00483	-0.99318	0.01238	0.98201
338	-0.00529	-0.99532	0.0154	0.99618

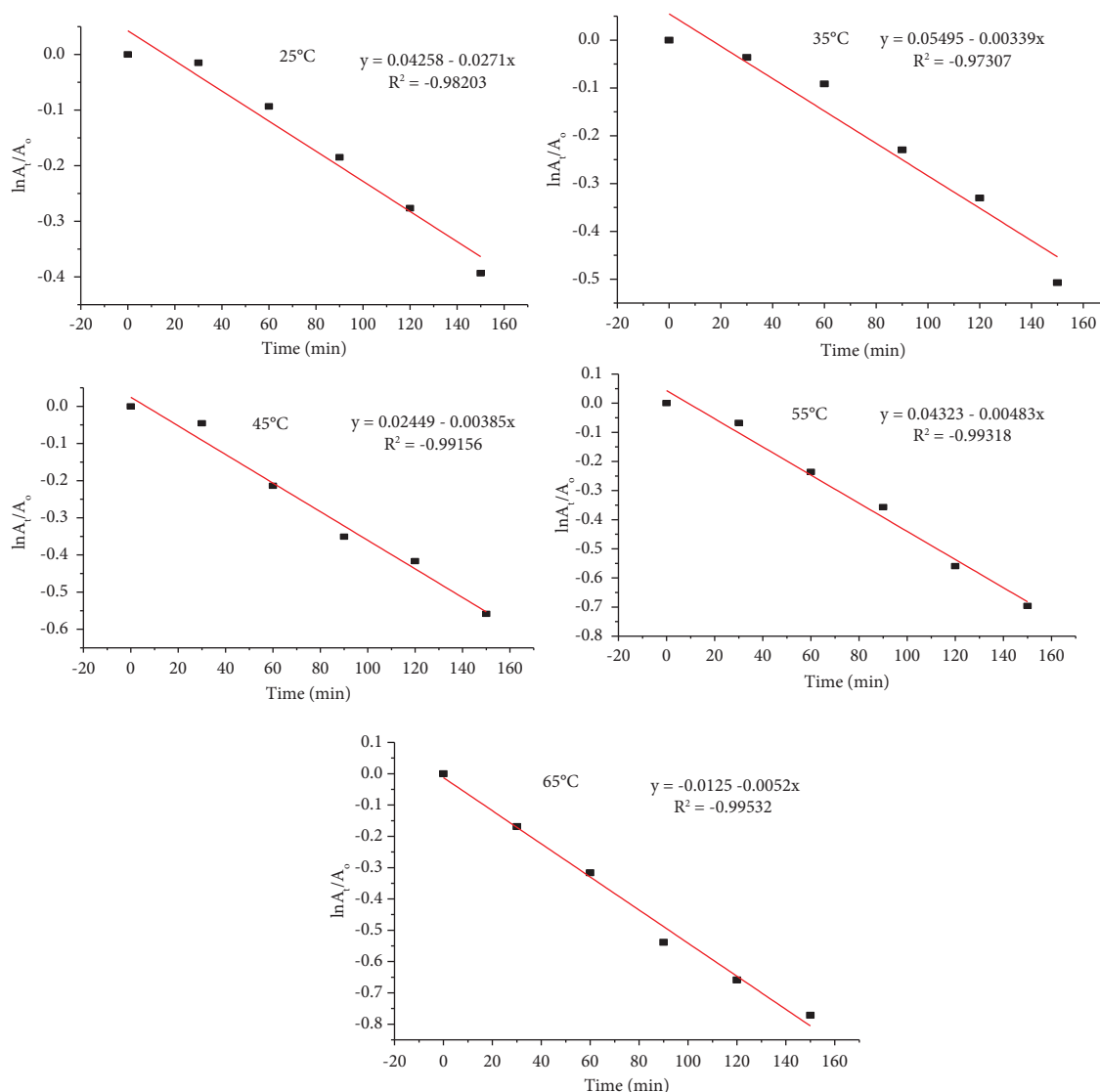


FIGURE 16: Pseudo-first-order kinetics for degradation of MB dye and ZnO NPs at varying temperatures.

The decrease in the degradation efficiency of ZnO NPs with multiple uses in the recyclability process indicates a loss in the catalytic potential of the nanoparticles [17]. The reduction in degradation efficiency of ZnO NPs can be attributed to the loss of nanoparticle catalytic ability during the separation, washing, and drying procedures after each application cycle [45, 61]. These procedures result in a decrease in the number of active sites available on the

surface of ZnO NPs to interact with the fresh MB dye molecules. We also performed FTIR analysis to get insights into the stability of the nanoparticles by observing structural changes of ZnO NPs after their use in the first cycle and after their fourth cycle, and the results are depicted in Figure 20.

The structure of ZnO NPs from the IR spectrum revealed that no remarkable changes in the functional groups were

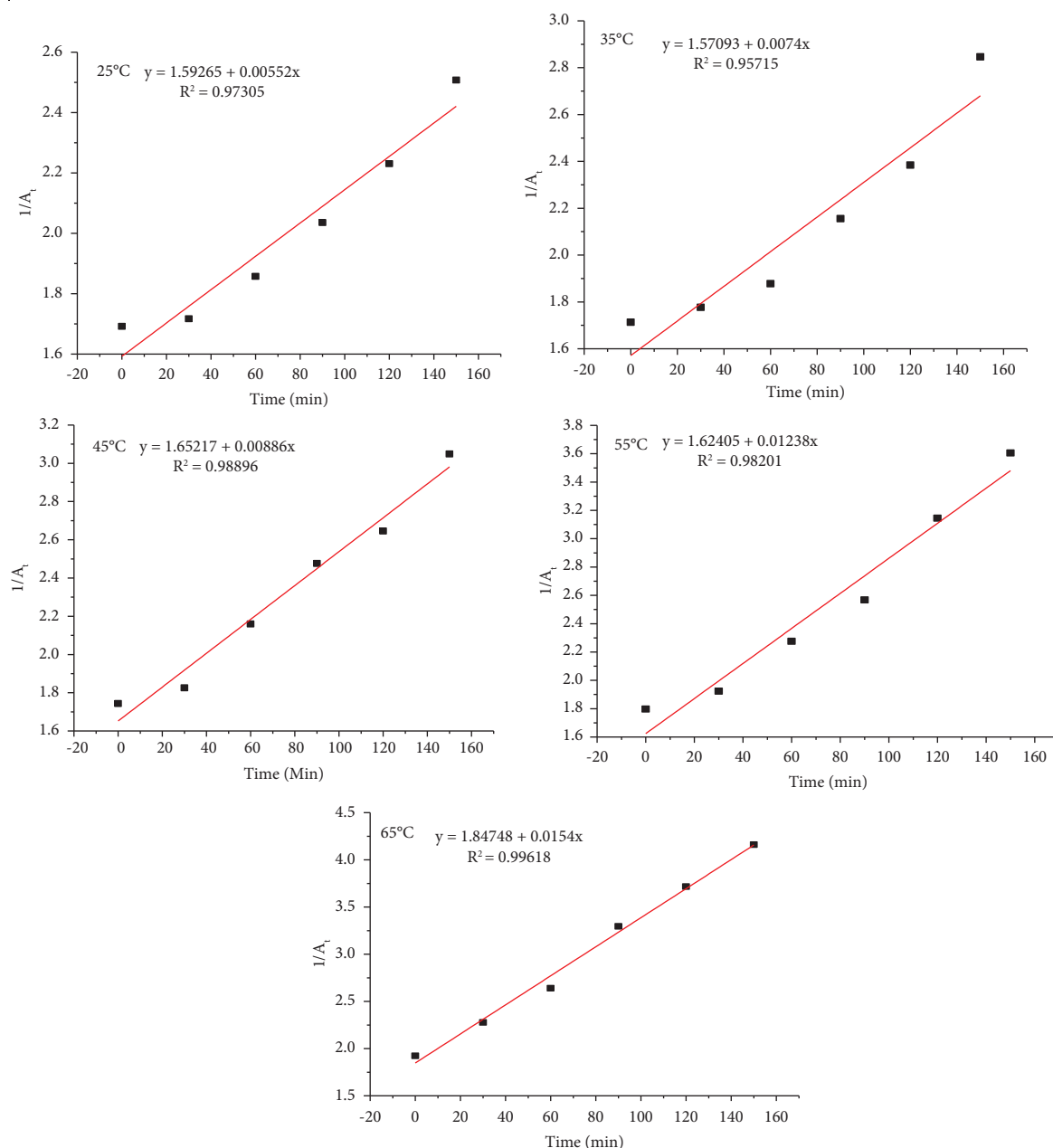


FIGURE 17: Pseudo-second-order kinetics for degradation of MB dye using ZnO NPs at varying temperatures.

observed for a single cycle and when four recyclability processes were used during the degradation of MB dye. This can support that the ZnO NPs exhibited strong stability and were not altered after several uses, a valuable characteristic of nanoparticles [13, 62].

8. Mechanism of Degradation of Methylene Blue Dye Using ZnO NPs

The mechanism of degradation of MB dye by ZnO NPs has been explained in previous studies [11, 50, 63–66]. The incident light leads to the excitation of an electron from the valence band (VB) to the conduction band (CB) on the ZnO

NPs surface, leading to the creation of a positive hole in the VB (h_{VB}^+) [50, 63, 64]. The electron on the CB (e_{CB}^-) is taken up by oxygen adsorbed onto the surface of ZnO NPs, generating a superoxide anion radical ($O_2^{\bullet-}$). The ($O_2^{\bullet-}$) anion radical is then involved in the degradation of MB dye [64, 67]. The positive holes in the valence band react with H_2O_2 used as a radical generator on the surface of ZnO NPs to produce OH radical which reacts with the dye, leading to the generation of degradation products. The positive hole in the VB then moves onto the surface of ZnO NPs, releasing more oxygen that produces ($O_2^{\bullet-}$). A similar process repeats itself to produce OH radicals, which are involved in the degradation of MB dye. Consequently, the (h_{VB}^+) acts as the

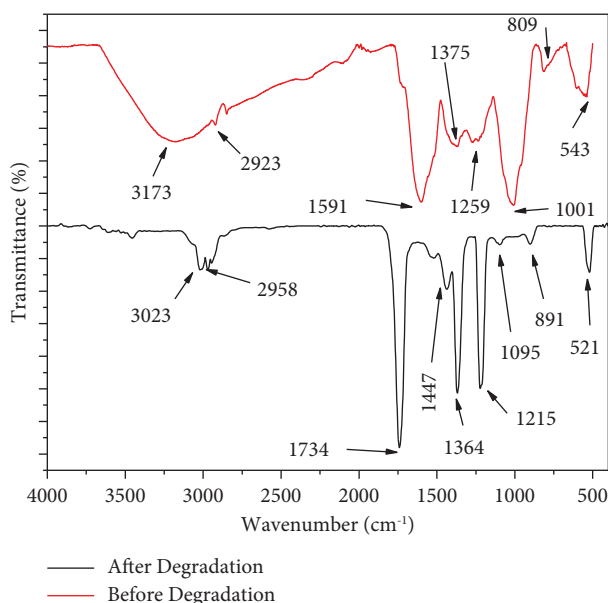


FIGURE 18: IR spectra showing ZnO NPs before and after the degradation process.

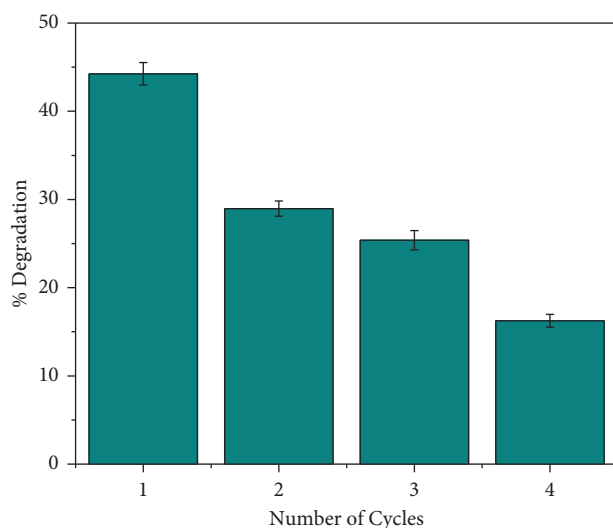
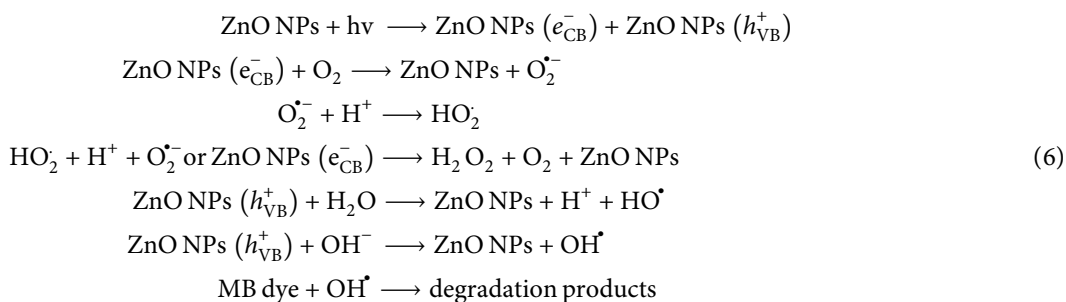


FIGURE 19: Recyclability of ZnO NPs in degradation of MB dye.

oxidizing agent and interacts with the OH^- , leading to the significant generation of OH radicals that react with MB dye adsorbed onto the surface of the ZnO NPs, enhancing the

oxidation of MB dye [65]. The mechanisms of degradation of MB dye by ZnO NPs can be illustrated using the steps shown in the following equations:



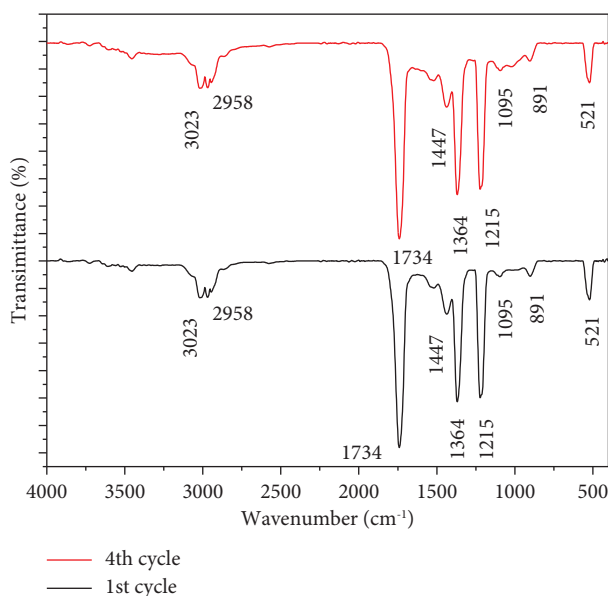


FIGURE 20: IR spectra of ZnO NPs after a single and four recycling cycles.

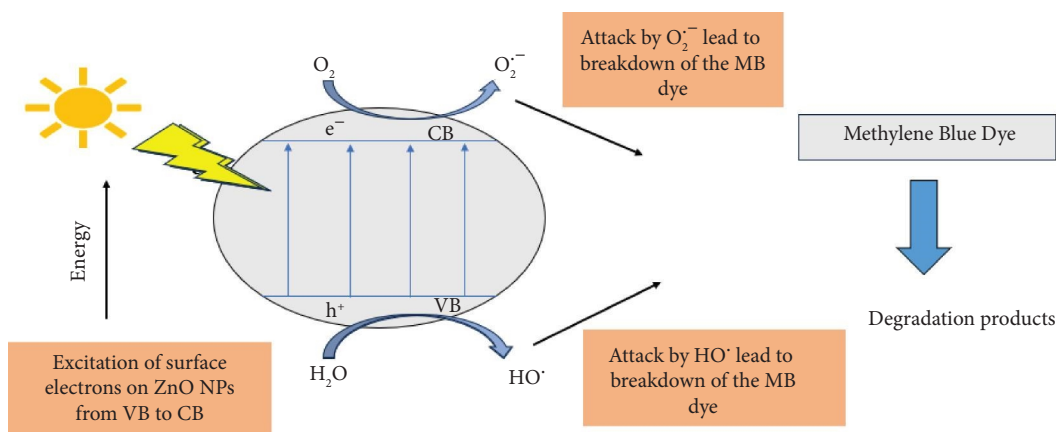


FIGURE 21: Probable mechanism of degradation of MB dye by using ZnO NPs.

Figure 21 further provides an illustration of the probable mechanism of degradation of MB by ZnO NPs.

The ZnO NPs prepared using plant extracts have been reported to be less toxic than chemically prepared ZnO NPs [68, 69]. The reducing agents such as hydroxyl radicals and superoxide radical anions reduce the methylene blue dye to less toxic degradation products such as carbon dioxide and water which are less harmful and environmentally friendly [33, 50, 68–71].

9. Comparative Overview of Degradation Efficiency of MB Dye Using Other Nanomaterials

Table 2 provides an overview of previously utilized nanomaterials in removing MB dye from aquatic systems and their performance efficiency. From Table 2, it can be concluded that ZnO NPs prepared from *Parthenium hysterophorus* aqueous extract are attractive in the degradation of

TABLE 2: Comparative overview of nanomaterials previously utilized in the removal of MB dye.

Nanomaterials	Pollutant	Reaction conditions	Removal efficiency (%)	References
MnTiO ₃ /TiO ₂	MB dye	Visible light irradiation, 0.005 g of MnTiO ₃ /TiO ₂ , pH 6.4, 1 × 10 ⁻⁵ M of MB dye, 240 min	75	[40]
Iron titanate (Fe ₂ TiO ₅)	MB dye	Natural sunlight, 50 mg of Fe ₂ TiO ₅ , 10 mg/L of MB dye, 250 min	>50	[56]
Zirconium oxide nanoparticles (ZrO ₂ NPs)	MB dye	Solar irradiation, within 5 h	89.11	[72]
Doped zinc oxide nanoparticles	MB dye	Solar irradiation, pH 9, 10 ppm of MB dye, 100 mg/L of nanoparticle dose 2 hours	80	[73]
Tungsten trioxide (WO ₃)	MB dye	Xenon light, 2.5 hours		[58]
ZnO	MB dye	UV irradiation, ZnO dosage of 250 mg/L, pH 10, 20 mg/L of MB, 2 hours	85	[41]
CeO ₂ NPs/graphene oxide/polyacrylamide composite	MB dye	UV light, 2.5 mg of CeO ₂ , pH 12, 5 mg/L of MB, 90 min	90	[74]
ZnO-NPs	MB dye	UV irradiation, 10 mg/L of MB, pH 2, 1.8 g/L of ZnO NPs 140 min	86	[59]
2% Fe-ZnO	MB dye	UV irradiation, 10 mg/L of MB dye, 1.8 g/L of 2% Fe-ZnO, irradiation time 140 min, pH 2	92	[59]
CuO-NPs	MB dye	Visible light, 0.1 g of CuO, 10 ppm of MB, pH 9, 120 minutes	63.44	[54]
Iron oxide nanoparticles (Fe ₃ O ₄)	MB dye	UV light, pH 7, 60 min	25	[75]
		pH 12, 60 min	99	
		pH 3, 60 min	18	
<i>Parthenium hysterophorus</i> -mediated ZnO NPs	MB dye	50 mg of ZnO NPs, 5 mg/L of MB, 1 mL of H ₂ O ₂ , 150 min	44.52	This study
		2.5 mg/L of MB, 10 mg of ZnO NPs, 1 mL of H ₂ O ₂ , 150 min	35.03	
		5 mg/L of MB, 10 mg of ZnO NPs, pH 4, 1 mL of H ₂ O ₂ , 150 min	29.91	
		5 mg/L of MB, 10 mg of ZnO NPs, pH 8, 1 mL of H ₂ O ₂ , 150 min	45.34	
		5 mg/L of MB, 10 mg of ZnO NPs, 65°C, 150 min	53.08	
		50 mg of ZnO NPs, 5 mg/L of MB, pH 12, 65°C, 1 mL of H ₂ O ₂ , 32 min	55.69	

MB dye and thus are promising in future exploitation of biosynthesized nanoparticles in environmental remediation of dyes.

Our study confirms that aqueous extract from the *Parthenium hysterophorus* plant can act as reducing, capping, and stabilizing agents in the formation of ZnO nanoparticles. The presence of secondary metabolites makes *Parthenium hysterophorus* a potential universal candidate in the formation of other nanoparticles in an eco-friendly and cost-effective manner.

10. Conclusion

ZnO NPs were successfully synthesized using an aqueous extract of the *Parthenium hysterophorus* plant as a reducing, capping, and stabilizing agent. The ZnO NPs were analyzed via UV-Vis spectroscopy, which revealed an intrinsic optical absorbance band associated with ZnO NPs that occurred at 337 nm. The functional group analysis by FTIR confirmed the presence of secondary metabolites in the extract, which were responsible for reducing Zn^{2+} to Zn^0 , with a characteristic Zn-O vibration band being observed at 543 cm^{-1} . SEM and TEM analyses revealed that the ZnO NPs were spherical with an average particle size of 38 nm. The XRD analysis confirmed the hexagonal wurtzite structure of ZnO NPs, and the crystallite size calculated using the Debye Scherrer equation was 42 nm. The pH, temperature, dosage of ZnO NPs, concentration of MB solution, and interaction time influenced the degradation ability of ZnO NPs against MB dye. Under optimal conditions set at 65°C , pH 12, 50 mg of ZnO NPs, and 5 mg/L of MB dye concentration, a degradation efficiency of 55.69% was obtained within 32 minutes. The stability of ZnO NPs after multiple uses was confirmed by running an FTIR analysis in which there were no observable changes in the position of the functional groups. Therefore, *Parthenium hysterophorus*-mediated ZnO NPs demonstrated to be fruitful in degrading MB dye making the nanoparticles suitable for addressing aquatic pollution by dyes. However, future prospects should consider understanding the toxicity profile of the degradation products on the environment and encapsulation of the ZnO NPs with polymeric adsorbents to enhance their degradation efficiency, recyclability, and large-scale application. The green synthesis of ZnO NPs is still in its early stages and should be exploited by using other plant materials and studied in the degradation of other organic dyes before they are deployed in large-scale waste water treatment.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Dennis M. Nzilu conceptualised the study, developed the methodology, curated the data, and wrote the original draft. Edwin S. Madivoli conceptualised the study and collected the resources. David S. Makhanu supervised the study. Sammy I. Wanakai curated the data and visualised the study. Gideon K. Kiprono investigated the study. Vincent N. Mwangi visualised the study. Patrick K. Gachoki supervised the study. All authors have read and agreed on the final version of the manuscript.

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