

Article

Visible Light Photocatalytic Degradation of Environmental Pollutants Using Zn-Doped NiO Nanoparticles

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Abstract: The study aims to contribute valuable insights into the potential applications of the photocatalyst, particularly in the realms of sustainable energy and environmental remediation. Here, Zn-doped NiO nanoparticles with different mole percentages of zinc ingredients are produced and analyzed. Synthesized Zn-doped NiO nanoparticles were evaluated structurally, optically, morphologically, elementally, and photocatalytically. According to X-ray diffraction analysis, cubic NiO and hexagonal Zn-doped cubic NiO nanoparticles were formed, and Fourier transform infrared spectroscopy revealed metal dopants and metal-oxygen stretching, as well as Zn substitution and stabilization. A UV analysis revealed that zinc dopants reduced visible light absorption and bandgap. A decrease in bandgap indicates the importance of zinc incorporation and its interface with NiO. Electron scanning microscopy and transmission electron microscopy confirmed that the nanoparticles exhibited quasi-spherical morphologies and contained Ni, Zn, and O elements. Photocatalytic activity of the synthesized Zn-doped NiO nanoparticles increased with increasing Zn content, achieving a maximum at 8% Zn doping into NiO lattices of 92%. Through XPS analysis, the valencies of Zn, Ni, and O elements are demonstrated, as well as electron movements and bonding between the atoms. The zinc dopants on the metal oxide surface led to charge separation and radical reactions, resulting in enhanced degradation of phorate, salbutamol, and rhoda mine B activities. Hence, Zn-doped NiO nanoparticles are proposed as effective photocatalysts for environmental remediation. The findings are expected to have implications for advancing the field of photocatalysis and addressing challenges related to pollution and energy sustainability.

Keywords: nanoparticles; visible light photocatalysts; wastewater treatment; optics; charge separations; phorate and salbutamol; Rh-B



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1. Introduction

There is a significant problem with water scarcity in many regions of the world, and with the growing population, freshwater demand is growing, creating even greater challenges. In order to ensure environmental sustainability and provide safe drinking water, wastewater containing various contaminants must be treated [1–3]. The advancements in agriculture, medicine, energy production, and chemical industries have created a significant

predicament for the modern world: environmental contamination and water scarcity [4,5]. Pollutants discharged into the atmosphere, water bodies, and soil have pernicious effects on human beings, plants, and animals [6,7]. Rhodamine B, a synthetic dye commonly used in the textile, paper, and printing industries, deteriorates water quality, harms aquatic life, and inhibits light transmission [8–10]. Various methods have been explored to eliminate such contaminants, including coagulation, electrochemical oxidation, chemical synthesis, reverse osmosis, adsorption, and photocatalysis [11–13]. However, traditional techniques are insufficient due to the vast volume of effluent that requires treatment. There is a wide range of applications for semiconductive metal oxides such as TiO_2 , ZnO , NiO , and Ag_2CrO_4 , due to their unique properties [14–17]. Their catalytic activity and stability make them suitable candidates for developing sustainable technologies for various industrial uses. There are several methods for synthesizing NiO nanoparticles, a p-type semiconductor with a wide band gap that has shown promise as a photocatalyst [18–20]. The introduction of transition metal ions into metal oxides through doping creates additional energy levels in the band gap, increasing the absorption of visible light and promoting the separation of electron–hole pairs generated by photoexcitation. This leads to an overall enhancement in photocatalytic activity. Researchers are using these innovative techniques to develop sustainable solutions to water scarcity and environmental contamination. The photocatalytic activity of metal oxides can be enhanced by transition metal ion dopants under visible light illumination. The photocatalytic activity of Fe-doped TiO_2 and ZnO has been reported to be greater than that of their undoped counterparts [21,22]. Transition metals, such as copper (Cu), chromium (Cr), and vanadium (V), have been studied for their potential to enhance the photocatalytic performance of metal oxides [23–25]. A photocatalytic system that harnesses visible light is crucial to producing clean energy and restoring the environment. When transition metal ions are included as dopants, they affect the interfacial charge transfer mechanisms and the recombination of electron–hole pairs, which can influence a material's photocatalytic properties [26,27]. These dopants may act as electron or hole traps, thereby facilitating charge transfer. The degree of metal dispersion on the particle surface and the uniformity of the chemical composition within each particle can be significantly influenced by the doping techniques used and the temperature during calcination. These elements contribute to a wide array of structural and crystalline characteristics. As a p-type transition metal, zinc (Zn) holds the potential to enhance the photocurrent in dye-sensitized solar cells (DSSC) when combined with titanium dioxide (TiO_2). As a result of the combination of a p-type semiconductor (Zn) with an n-type semiconductor (TiO_2), the solar cell's overall functionality is enhanced [28]. It enhances the photocatalytic performance of TiO_2 across the visible spectrum by reducing its bandgap. It has been demonstrated that the introduction of zinc ions (Zn) into the anatase structure of TiO_2 can raise the conduction band boundary of the photoanode, resulting in a shift in the Fermi level. As a result of this shift, open-circuit voltage (VOC) and overall photovoltaic performance can be improved [28]. Due to their distinct disadvantages in aquatic systems, salbutamol and phorate pose environmental concerns. In aquatic environments, salbutamol accumulates and is prolonged exposure, potentially harmful to aquatic organisms. The bioaccumulation of the substance at higher trophic levels is of particular concern since it persists and may disrupt organisms' normal behavior, growth, and reproduction. Additionally, salbutamol can form transformation products with potentially different toxicological properties during degradation, necessitating a comprehensive understanding of their environmental fate. However, phorate, which is highly toxic to aquatic life, raises serious ecological concerns. Due to its persistence and bioaccumulation, it gradually moves up the food chain, posing risks to higher trophic levels. Agricultural use of phorate can cause water contamination through runoff, affecting aquatic ecosystems nearby, and its ability to leach into groundwater increases the risk of drinking water contamination for years to come. Salbutamol and phorate emphasize the importance of sustainable practices and careful consideration of their impact on aquatic ecosystems [29,30].

In this study, a simple chemical synthesis technique is used to prepare Zn-doped NiO nanoparticles using a direct solvothermal method. As compared to other synthesis methods, solvothermal stands out for its ease and efficiency in generating nanostructures. Zn^{2+} substitution modifies NiO structure and bandgap, which can reduce the gap between bonds and increase visible light absorption. Furthermore, divalent metal dopants promote reactive oxygen species (ROS) and radical proliferation. The Zn-NiO nanoparticles are synthesized and characterized for their potential applications in the removal of environmental pollutants, namely rhodamine B (Rh-B) dye, phorate, and salbutamol.

2. Materials and Methods

2.1. Materials

The synthesis process involved employing nickel (II) acetate tetrahydrate ($\text{C}_4\text{H}_6\text{NiO}_4 \cdot 4\text{H}_2\text{O}$), 99.9% purity, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), NaOH, ammonia solution, and rhodamine B ($\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$), 99.9% purity. These chemicals were procured from HiMedia in Mumbai, India; phorate and salbutamol chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA), and all of them met the standards of analytical reagent (AR) grade. These compounds were used in their original, unaltered states, and double-distilled water was employed for both the solution preparation and reaction processes.

2.2. Synthesis of Zn-Doped NiO NPs

The 0.3 M nickel acetate and 3 mL ammonia were mixed by continuous stirring using a magnetic stirrer at 750 rpm. Subsequently, varying mole percentages of a solution containing zinc nitrate hexahydrate were systematically introduced, including 2%, 5%, and 8% of Zn concentrations. To attain a solution pH of 12, a 0.3 M NaOH solution was slowly added. The resulting solution was then heated at 80 °C while being stirred for 6 h, leading to the formation of a precipitate with a bluish-green hue. This precipitate underwent several washes using distilled water and ethanol to eliminate any residual by-products. The collected nanoparticle solution was dried at 100 °C for 24 h, and their output powder was stored for further processing. The dried powder was subsequently subjected to a calcination process at 400 °C for 2 h. The application of heat induced a transformation and modification in the lattice structure of NiO through Zn substitutions, influencing the crystal lattice and thereby altering the material's properties. These nanoparticles exhibited a distinct black color, thus yielding a nanopowder with these specific characteristics. The same procedure was duplicated to form the nanostructures of nickel oxide doped with zinc. In this case, zinc nitrate solution was added to the precursor solution at concentrations of 2%, 5%, and 8% of Zn [31,32].

2.3. Characterization of Synthesized NPs

The material phase and crystallinity of the synthesized nanoparticles were examined using the PANalytical X'Pert Pro X-ray diffractometer (Malvern Panalytical, Malvern, UK). To identify chemical interactions and functional groups, FT-IR Perkin Elmer spectroscopy (PerkinElmer Inc., Buckinghamshire, UK) was used. The optical properties of the materials were analyzed with UV-visible spectroscopy, specifically employing the UV-2600 Shimadzu instrument (Shimadzu Corporation, Kyoto, Japan). The surface morphology and elemental composition of the samples were investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) using a Carl Zeiss instrument (Jena, Germany), as well as transmission electron microscopy (FEI-Titan 80-300, TEM, Hillsboro, OR, USA). The valency and binding energy of the synthesized nanoparticles were determined by X-ray photoelectron spectroscopy (XPS) with the PHI 5000 VersaProbe III measurement from the Chanhassen, MN, USA [33–35].

2.4. Pollutants Photocatalytic Degradation Experiment

To evaluate the photocatalytic performance of the Zn-doped NiO nanoparticles in the presence of Rh-B dye, phorate, and salbutamol, an experiment was conducted using visible

light. An initial Rh-B dye solution (40 mg/L) was mixed with 10 mg of nanoparticles in a 100 mL container. The same condition was repeated for phorate and salbutamol contaminants. The mixture was allowed to reach an adsorption-desorption equilibrium in darkness and was then stirred for 30 min. Afterward, the solution was exposed to visible light at a wavelength above 400 nm, generated by a Xenon lamp. The illuminated nanoparticle solution was subjected to absorbance measurements at regular 10-min intervals using UV spectroscopy, with 3 mL of the solution being withdrawn each time. Before measuring absorbance, the samples were centrifuged at a speed of 10,000 revolutions per minute to facilitate the separation of nanoparticles from the polluted solution. The degradation efficiency of the nanoparticles was calculated using the formula provided in reference [36].

$$\text{Dye degradation (\%)} = (C_0 - C_t) / C_0 \times 100 \quad (1)$$

where C_0 represents the initial pollutant absorbance concentration and C_t represents the active pollutant absorbance concentration at 10-min intervals.

3. Results and Discussions

3.1. XRD Analysis

The X-ray diffraction (XRD) analysis of 2%, 5%, and 8% of zinc-doped nickel oxide nanoparticles typically shows characteristic peaks that correspond to the crystalline materials (Figure 1a–c). The most common crystal structure of nickel oxide is cubic with a rock salt lattice, while zinc oxide has a hexagonal wurtzite structure. The doping of nickel oxide with zinc ions can lead to changes in the crystal structure and lattice parameters, as well as changes in the position, intensity, and width of the XRD peaks. The pronounced diffraction peaks of Zn-doped NiO nanoparticles at 2 theta values are 43.8, 62.3, and 76.8 degrees, which correspond to planes of (111), (200), and (220), respectively. These diffraction peaks closely matched the standard values of JCPDS: 78-0643 for nickel oxide [37,38], indicating the formation of crystalline zinc-doped nickel oxide nanoparticles. The strength of the diffraction patterns reduced with the addition of zinc dopants, suggesting that the incorporation of zinc ions may have caused some distortion in the crystal structure of nickel oxide, leading to a decrease in its crystallinity. Specifically, the crystallinity percentages were measured as follows: 52% for 2% Zn-NiO, 60% for 5% Zn-NiO, and 72% for 8% Zn-NiO. Nonetheless, the observed diffraction peaks confirmed the successful synthesis of zinc-doped nickel oxide nanoparticles with a crystalline structure. The presence and position of these peaks can be used to fix the crystal structure and lattice parameters of the Zn-NiO nanoparticles [39,40]. The decrease in the intensity of the XRD peaks for NiO after the addition of zinc dopants can be attributed to the incorporation of zinc ions into the crystal lattice of NiO. Zinc ions are known to have a smaller ionic radius than nickel ions, and therefore, the crystal structure of NiO can be modified because of their lattice distortion and orientation of crystal structure [37–40].

The Scherrer formula helps to calculate the crystallite size of Zn-NiO nanoparticles, and their resulting values were 17, 16, and 15 nm for 2%, 5%, and 8% concentrations of zinc doping, respectively. The addition of zinc dopants to nickel oxide (NiO) leads to a reduction in the crystallite size of the resulting zinc-doped nickel oxide nanoparticles. The incorporation of zinc ions into the NiO can cause lattice alteration and tension in the crystal structure of the material. This strain can result in the formation of defects and vacancies within the crystal structure, which can inhibit the growth of the crystal and lead to a reduction in the crystallite size [41,42]. The decrease in crystallite size of zinc-doped NiO nanoparticles can have significant impacts on the material properties and performance. Smaller crystallite sizes can increase the surface area of the material, leading to higher reactivity and improved catalytic performance. However, smaller crystallite sizes can also result in decreased stability and mechanical strength of the material. Therefore, controlling the crystallite size of zinc-doped NiO nanoparticles is an important consideration in the design and optimization of these materials for various applications.

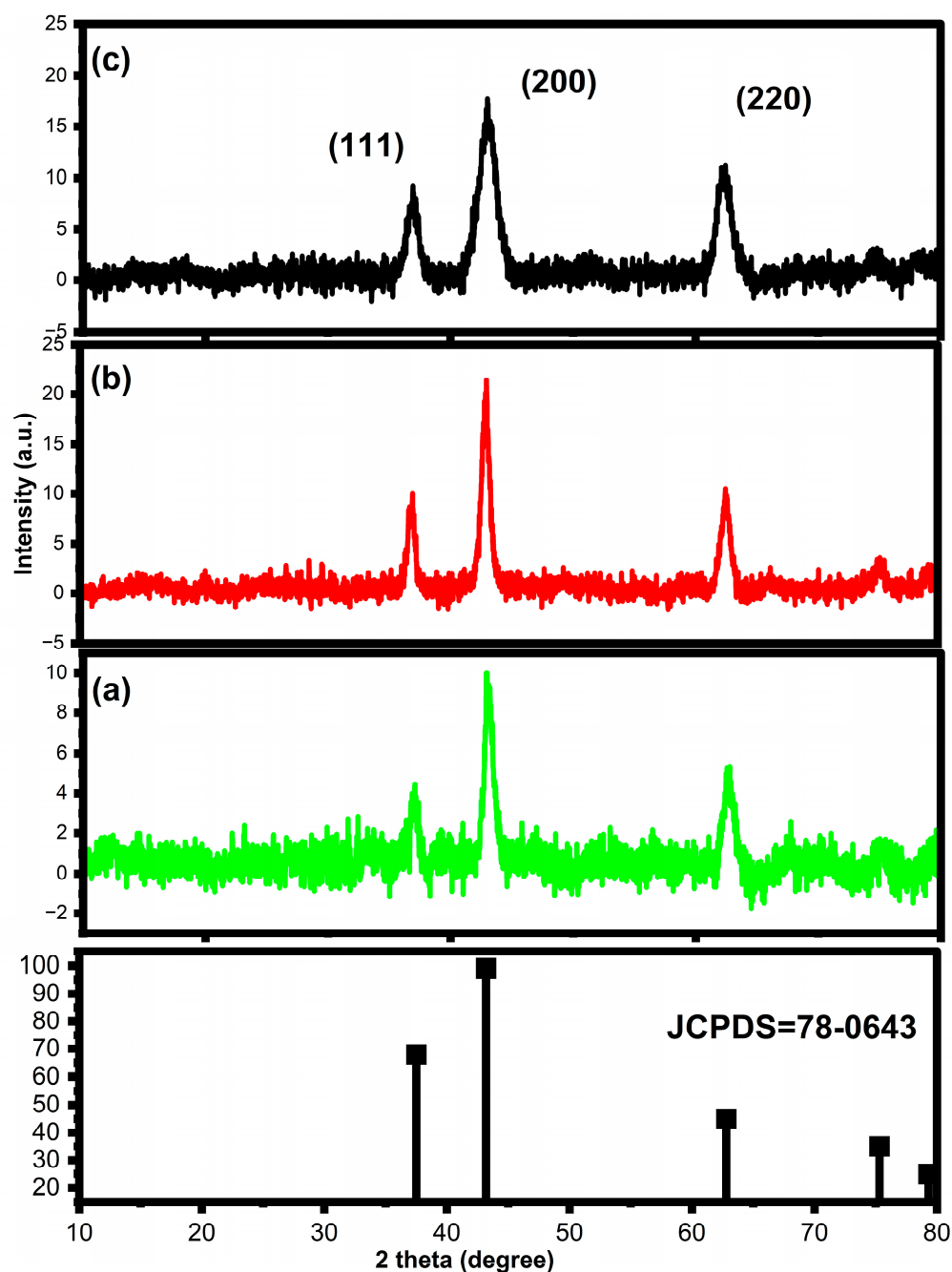


Figure 1. JCPDS spectra of NiO and different mole percentages of (2%, 5%, and 8%) Zn-doped NiO nanoparticles (a,b) X-ray diffraction patterns.

3.2. FTIR Analysis

The FTIR spectra of 2%, 5%, and 8% of Zn-NiO NPs (Figure 2a–c) exhibit the various functional groups and vibrational modes present in the nanoparticles. The broad absorption peak at around $2922\text{--}3436\text{ cm}^{-1}$ corresponds to the stretching vibration of hydroxyl (OH) groups, which are commonly found on the surface of metal oxide nanoparticles [43,44]. The absorption peak at about 1625 cm^{-1} links to the bending vibration of water molecules adsorbed on the nanoparticle surface [45]. The absorption peak at around $1033\text{--}1400\text{ cm}^{-1}$ corresponds to the bending vibration of carbonate (CO_3^{2-}) groups, which can be present as impurities in the nanoparticles [46,47]. The absorption peak at around $600\text{--}775\text{ cm}^{-1}$ corresponds to the stretching vibration of metal-oxygen (Ni-O) bonds in the nanoparticles [48]. The absorption peak at around $420\text{--}600\text{ cm}^{-1}$ corresponds to the bending vibration of

Ni-O-Zn bonds in the nanoparticles, and it can motivate the single phase of the NiO nanostructure [49,50]. FTIR results provide insights into the adsorption and desorption of molecules on the nanoparticle surface. It can be used in corroboration with other techniques, such as XRD and TEM, to understand the material's properties.

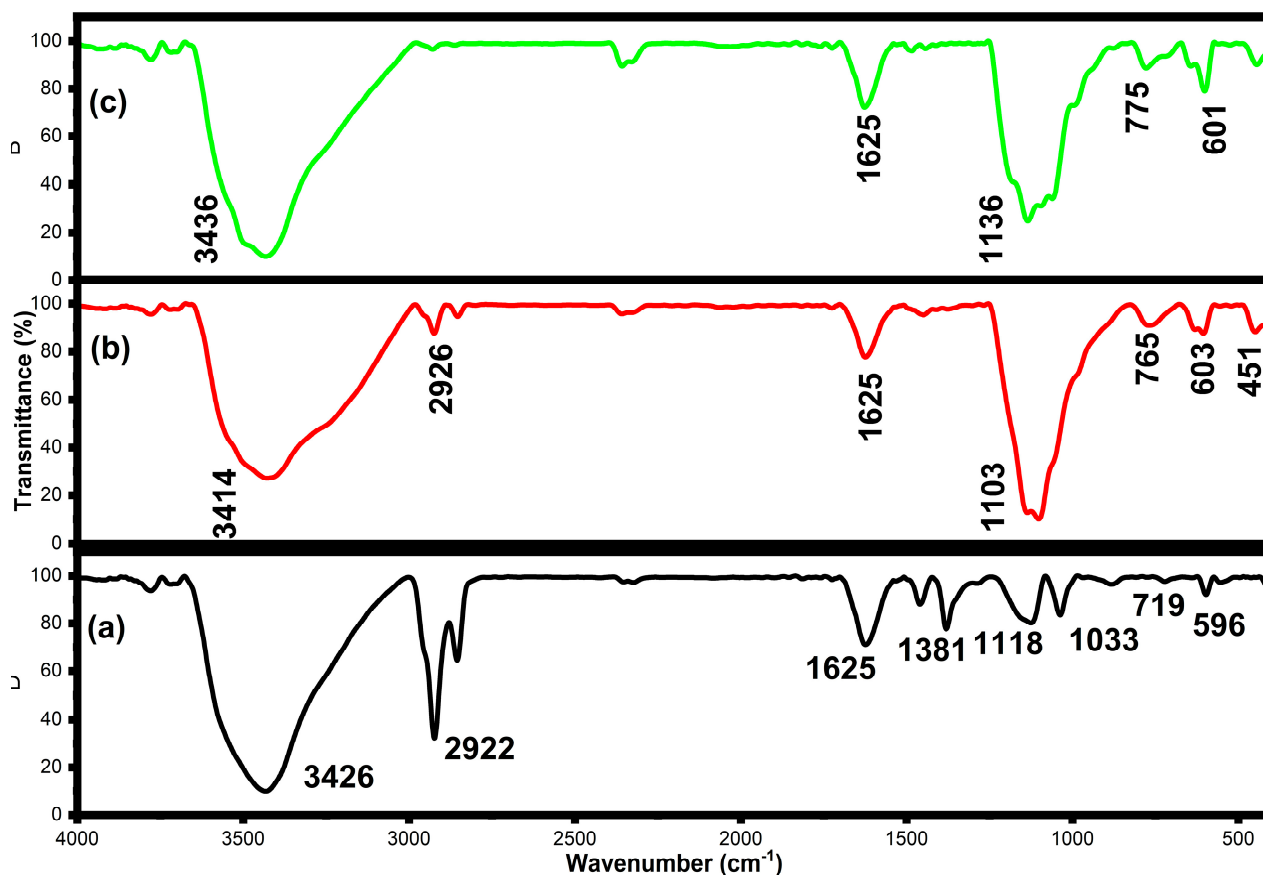


Figure 2. FTIR spectra of NiO NPs doped with 2% (a), 5% (b), and 8% (c) Zn.

3.3. UV-Visible Analysis

Figure 3a,b displays the UV absorbance and Tauc plot bandgap spectra for the synthesized Zn-NiO NPs, with varying dopant concentrations of 2%, 5%, and 8%. An evident decline in absorbance is observed in these spectra, which can be attributed to the accumulation of electrons within the NiO lattice as a consequence of Zn dopant integration. The shift in absorbance toward the visible spectrum implies that the nanoparticles' bandgap decreased after Zn doping. Specifically, the calculated bandgap values were determined to be 3.28 eV, 3.05 eV, and 2.86 eV for nanoparticles doped with 2%, 5%, and 8% of zinc, respectively. The reduction in NiO nanoparticles' bandgap energy due to Zn doping can be ascribed to the adjustments in the band structure induced by doping. This leads to the creation of defect states within the bandgap, resulting in a narrower bandgap [51–55]. Furthermore, the inclusion of Zn dopants into the NiO lattice generates a new impurity energy level near the valence band maximum, reducing the effective bandgap and consequently enhancing the photocatalytic activity of the nanoparticles.

3.4. SEM with EDX Analysis

Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) is a powerful method to examine the morphology and elemental structure of the 2%, 5%, and 8% of Zn-NiO NPs, as shown in Figure 4. In the case of Zn-NiO NPs, SEM images revealed that the synthesized nanoparticles have a flower-like, spherical, and aggregated morphology. This morphology is due to the self-assembling behavior

of nanoparticles during the synthesis process. The flower-like morphology of Zn-NiO NPs is due to the agglomeration of small nanoparticles into a larger flower-like structure. The aggregated morphology is due to the agglomeration of larger nanoparticles into even larger structures.

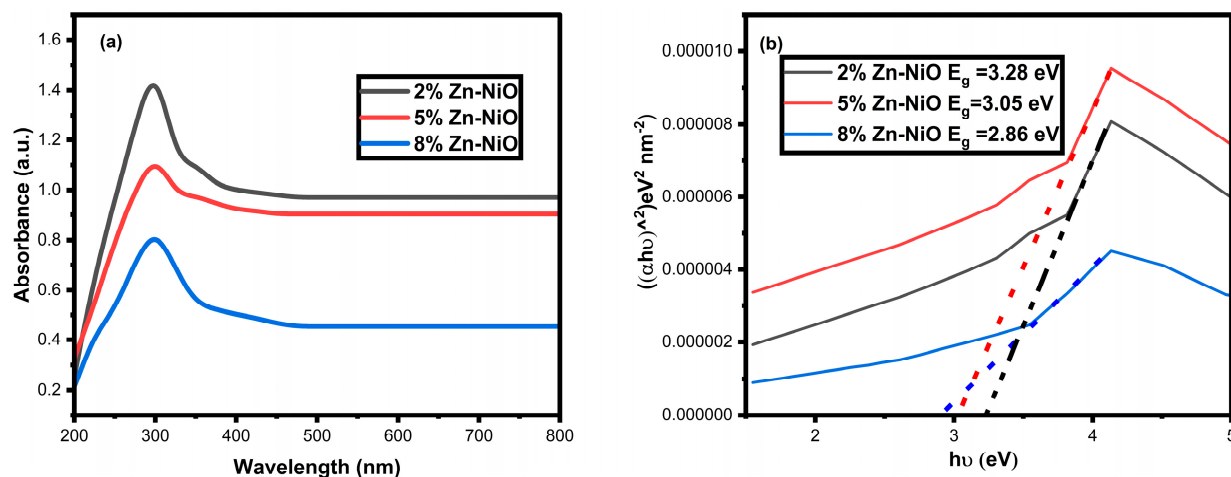


Figure 3. UV absorbance spectra and Tauc plot bandgap graphs of synthesized NiO NPs doped with 2%, 5%, and 8% Zn.

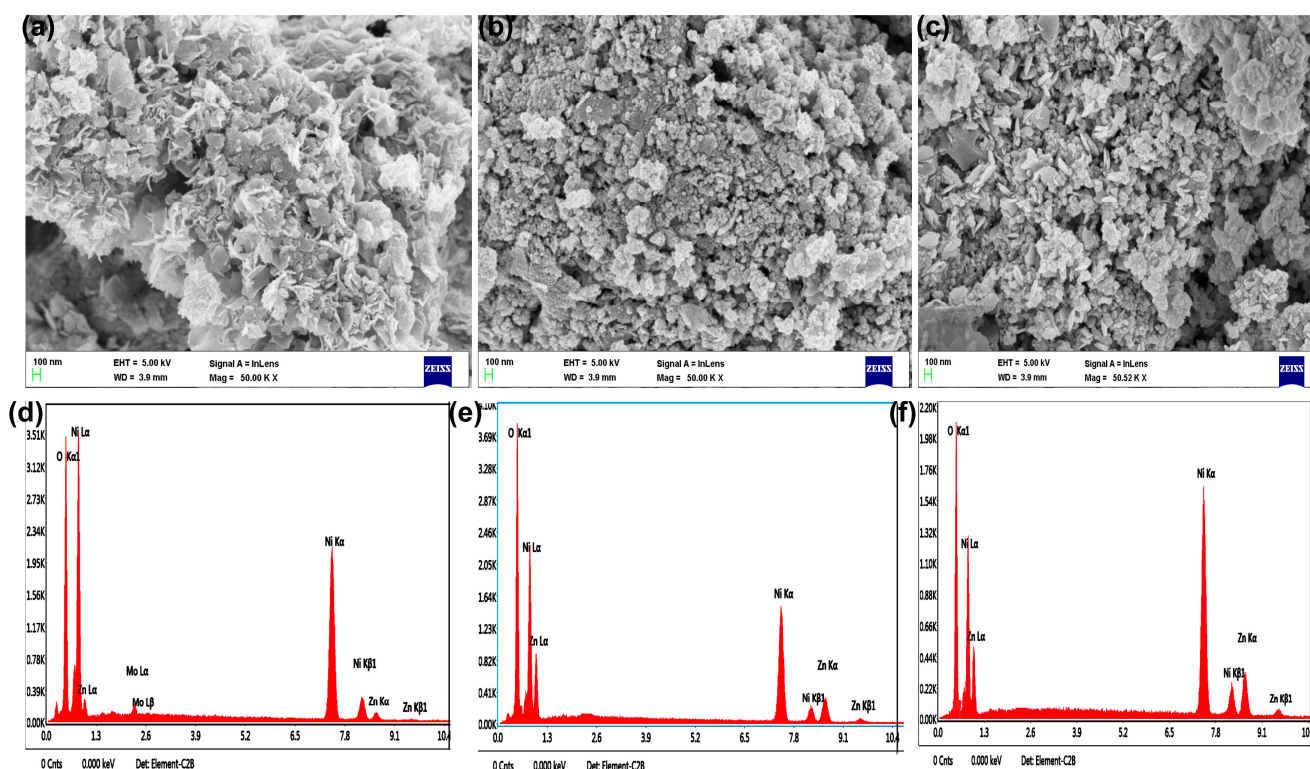


Figure 4. SEM (a–c) with EDX (d–f) images of synthesized NiO NPs doped with 2%, 5%, and 8% Zn.

The aggregated nanoparticles form clusters of individual nanoparticles that are bound together by relatively weak forces, such as van der Waals forces or electrostatic interactions. Aggregation can occur during the synthesis or handling of nanoparticles and can lead to changes in their properties, such as a decrease in specific surface area and an increase in size distribution [55–58]. However, aggregation can also have beneficial effects, such as the formation of porous or hierarchical structures, which can enhance catalytic activity or

light absorption properties. The EDX analysis of the Zn-NiO NPs confirmed the presence of nickel, zinc, and oxygen elements in the synthesized nanoparticles. The presence of zinc in the EDX analysis indicates the successful doping of NiO NPs with zinc.

The SEM morphology images reveal the prime existence of spherical and semi-spherical Zn-NiO nanoparticles. A substantial portion of these nanoparticles exhibit a flower-like, spherical, and semi-spherical morphology, forming bigger grain-sized particles due to reaction derivatives. The excess reactive compounds create a layer on the NiO surface, facilitating their integration with Zn and the agglomeration of particles. Subsequently, the particles exhibit a variety of shapes, including flowers, semi-spheres, and spheres. The distribution of Zn-NiO nanoparticles was quantified using ImageJ software version 6.0, and the corresponding graphs are presented in Figure 5. Zinc doping in NiO NPs enhances the photocatalytic properties of NiO NPs due to the generation of additional defects and oxygen vacancies that promote electron-hole pair separation and the formation of reactive oxygen species.

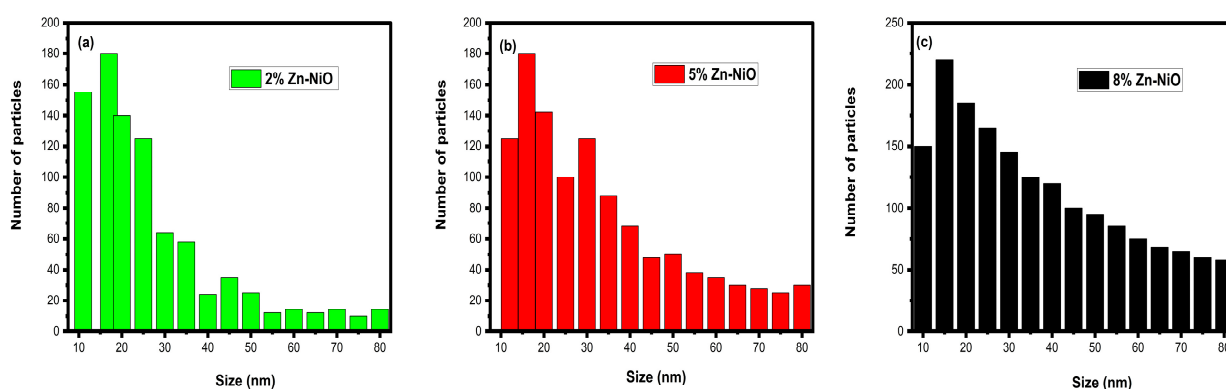


Figure 5. Histogram (a–c) images of synthesized NiO NPs doped with 2%, 5%, and 8% Zn.

3.5. TEM with SAED Pattern Analysis

Transmission electron microscopy (TEM) analysis is used to provide insights into the dimensions, morphology, and spatial arrangement of a subset comprising 8% of zinc-doped nickel oxide nanoparticles. The observation of a spherical morphology is frequently encountered in various materials, such as nanoparticles of zinc-doped nickel oxide (Figure 6a). Spherical nanoparticles exhibit a notable surface area-to-volume ratio, augmenting their reactivity and rendering them valuable in diverse domains, including catalysis, drug administration, and sensing [59,60]. To achieve a spherical morphology in Zn-NiO NPs, it is feasible to control the synthesis parameters in order to facilitate the aggregation of nanoparticles into spherical clusters. The reaction of NaOH and ammonia can facilitate the modification of nanoparticle growth into a spherical configuration, while the regulation of reaction conditions, such as pH and temperature, can effectively hinder the development of other morphologies. The application of selected area electron diffraction (SAED) patterns serves to derive both the crystal structure and the alignment of the nanoparticles. The SAED patterns (Figure 6b) have the ability to unveil the typical crystal structure of nanoparticles, often associated with a spinel structure. These diffraction patterns may display diffraction spots corresponding to the (111), (200), and (220) crystallographic planes, which are indicative of the spinel structure. The presence and intensity of these diffraction spots can provide valuable insights into the crystal alignment, grain size, and imperfections within the nanoparticles. The use of transmission electron microscopy (TEM) and selected area electron diffraction (SAED) techniques in the study of zinc-doped nickel oxide nanoparticles can offer substantial insights into their morphological attributes, crystal structure, and orientation. The structural information is essential for comprehending the characteristics of Zn-doped NiO nanoparticles and enhancing their effectiveness in various applications.

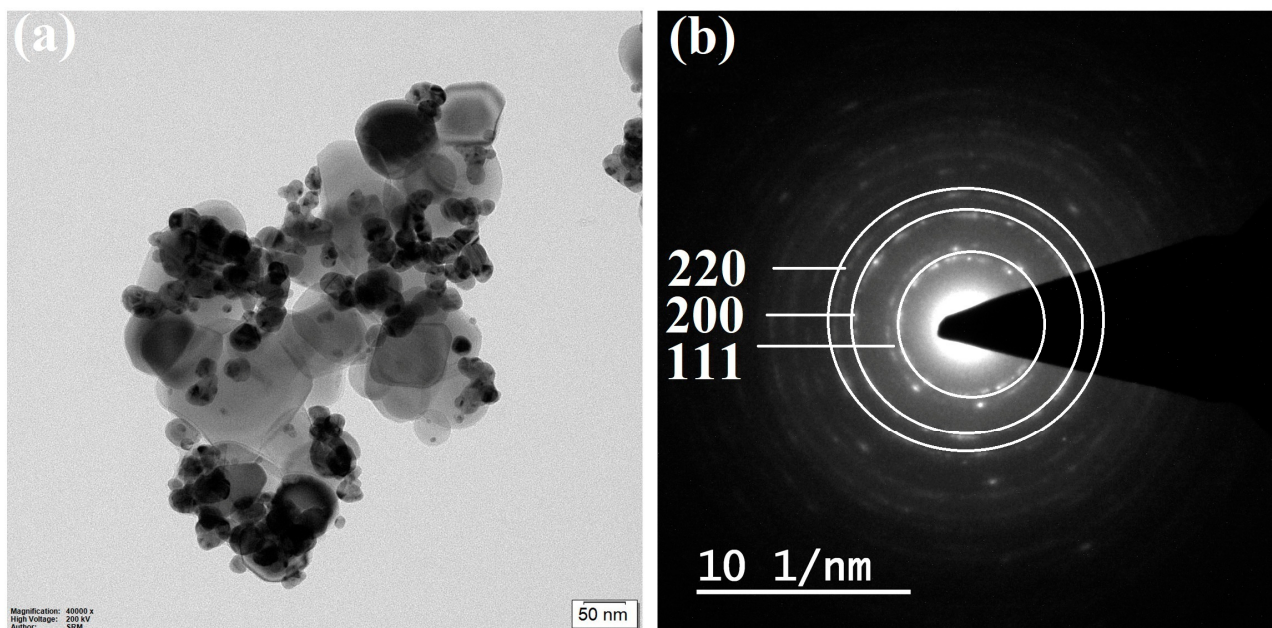


Figure 6. TEM image (a) and SAED pattern (b) of synthesized 8% of Zn-NiO nanoparticles.

3.6. XPS Analysis

The surface material compositions, valency, and binding energy of the 8% Zn-doped NiO nanoparticles were examined by XPS analysis, as shown in Figure 7. The wide spectrum (Figure 7a) confirmed the synthesized Zn-doped NiO nanoparticles with the existence of Zn, Ni, and O elements. The Ni region exhibited peaks at 854.07 eV and 872.71 eV, which indicate the chemical states of Ni-2p_{3/2} and Ni-2p_{1/2}, respectively. The remaining peaks of the Ni-2p region are attributed to the formation of Ni²⁺/Ni³⁺ and Ni(OH)₂. Moreover, additional peaks in the Ni-2p state represent Ni vacancies [61]. The Zn-2p state showed peaks at 1020.84 eV (Zn-2p_{3/2}) and 1043.92 eV (Zn-2p_{1/2}). The spin-orbit coupling of Zn-2p is 23.08 eV, which promotes the bonding between the oxygen [62,63]. In addition, the Zn-2p state modified the electronic structure of the Ni-2p state and ionization energy. The p-type Ni²⁺/Ni³⁺ vacancies are altered by Zn dopants due to their p-type Ni material quasi-localized holes, increasing their density by the substitution of Zn-2p state materials [61]. The O-1s spectrum shows peaks at 529.81 eV, which denote the absorbed oxygen associated with Zn and Ni elements [62,63]. The primary formation of Ni-O bonds was confirmed by the peaks at 531.20 eV. The Ni²⁺ ions were neutralized by O-1s, and Ni and Zn elements shared their localized space with oxygen and established the bond of Zn-Ni-O, which provides the construction of Zn-doped NiO nanoparticles.

3.7. Pollutants Photocatalytic Degradation Analysis

The visible light photocatalytic activity of synthesized 2%, 5%, and 8% Zn-NiO NPs on Rh-B dye, phorate, and salbutamol degradation was evaluated in this work. During this process, the toxic molecules undergo a series of chemical reactions and changes, leading to a shift in their absorption wavelength and a decrease in their absorbance. The shift in the absorption wavelength is due to the formation of intermediate products during the degradation process, which have different chemical structures and optical properties than the parent dye molecule (Figure 8a–c). These intermediates may absorb light at different wavelengths than the original dye, leading to a shift in the absorption spectrum. The decrease in absorbance is a result of the degradation of the dye molecule, which leads to the formation of smaller molecules with lower molar extinction coefficients [64,65]. As the concentration of the dye decreases during the degradation process, the absorbance of the dye solution also decreases.

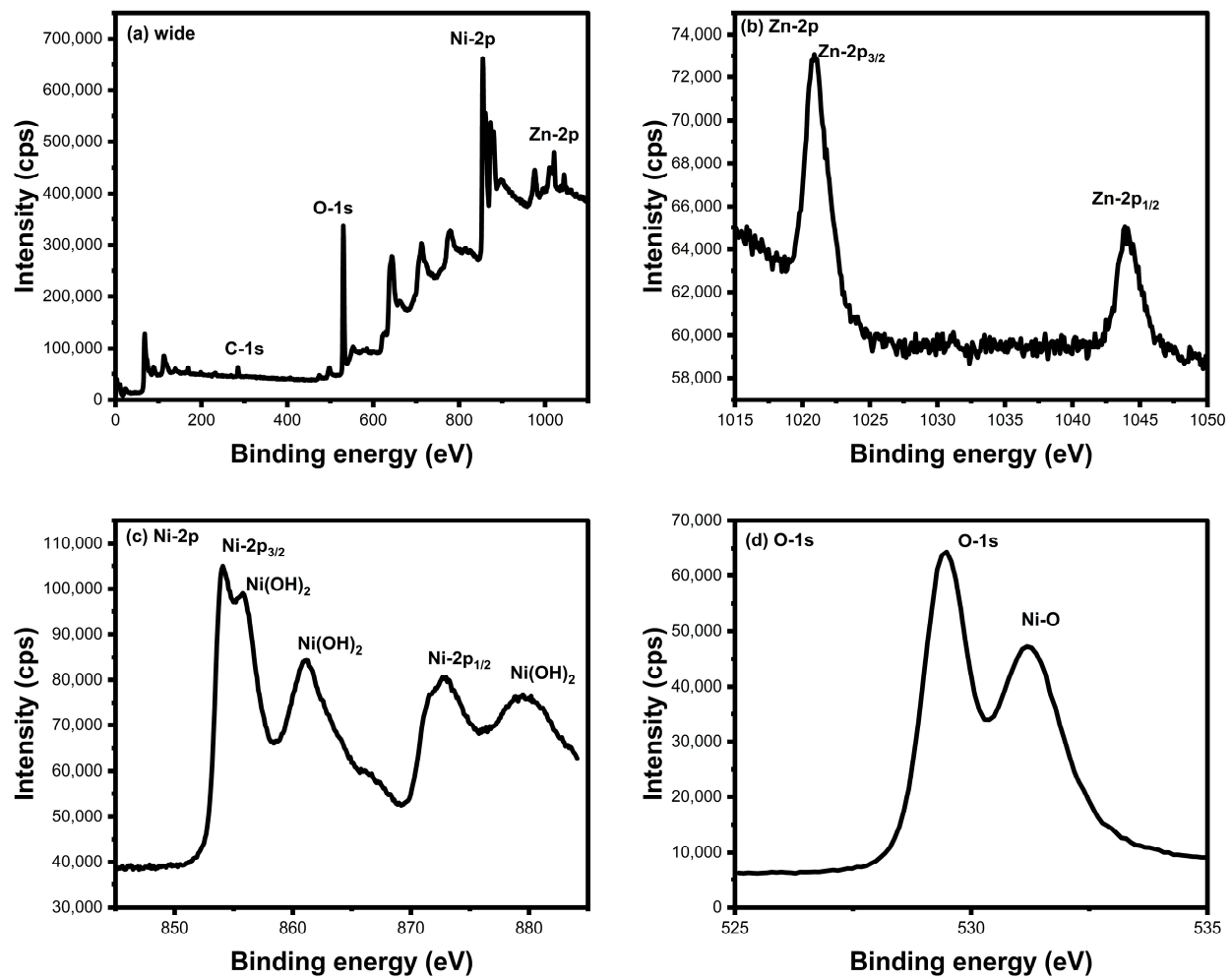


Figure 7. X-ray photoelectron spectroscopy of synthesized 8% Zn-NiO NPs (a) wide, (b) Zn, (c) Ni, and (d) O spectrum.

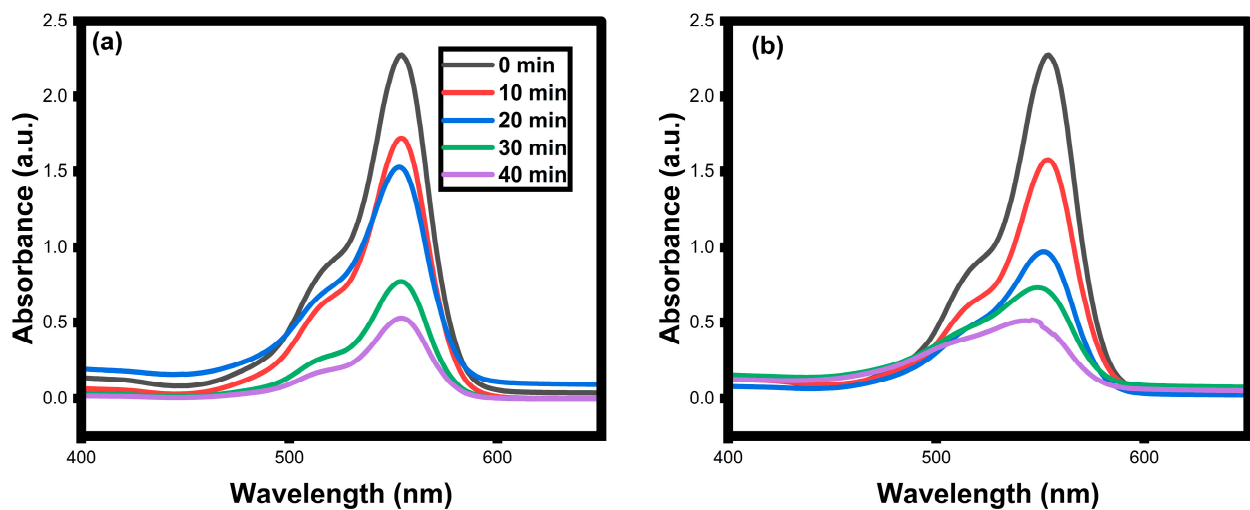


Figure 8. Cont.

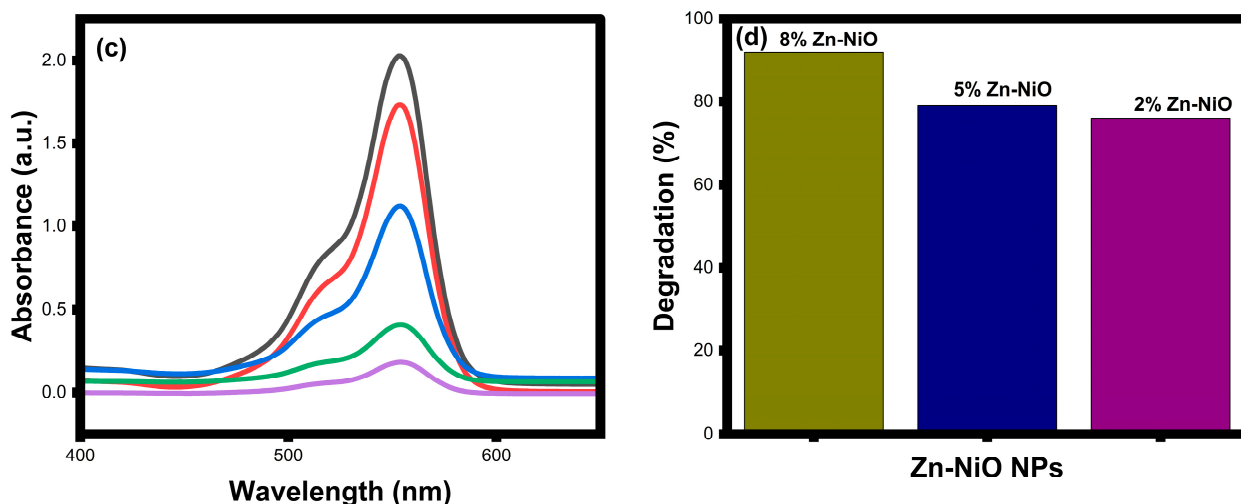
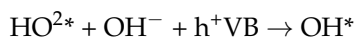
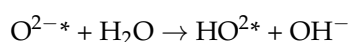
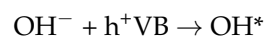
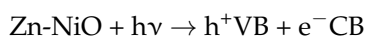


Figure 8. Photocatalytic dye degradation absorbance spectra (a–c) and degradation efficiency (d) of synthesized 2%, 5%, and 8% Zn-NiO NPs.

The results showed that the addition of zinc to the NiO nanoparticles enhanced their photocatalytic activity, with 8% Zn-NiO nanoparticles exhibiting the highest degradation efficiency of 92% after 40 min (Figure 8d). When zinc was used as a dopant for NiO, an enhancement of radical generation and an increase in surface area were obtained. This, in turn, led to a higher degree of oxidation and reduction during the process involving the Rh-B dye and also reduced the occurrence of fast recombination. As a result of this process, a substantial amount of OH radicals and superoxide ions were generated. These highly reactive species effectively attacked the dye molecules, breaking them down into smaller, harmless molecules such as CO₂ and H₂O. Both the small molecules and the original dye molecules are considered environmentally safe compounds.

The degradation mechanism is a multi-step process that involves the generation of charge carriers (electrons and holes) when Zn-NiO is exposed to light. The holes on the valence band (VB) produced hydroxyl radicals (OH^{*}) upon interaction with OH[−], while the electrons on the conduction band (CB) reacted with O₂ to form O₂^{−*}. The O₂^{−*} then reacted with H₂O to produce HO^{2*} and OH[−]. The HO^{2*} and OH^{*} radicals produced by these reactions reacted with Rh-B to form supplementary products, CO₂ and H₂O [66–70]. The pseudo-first-order kinetics and degradation mechanism are presented in Figure 9. The resulting degradation pathway can be summarized as follows:



The photocatalytic performance of Zn-NiO nanoparticles was assessed in comparison to a diverse array of metal oxide and metal-doped metal oxide nanoparticles reported in the literature (Table 1). The approach of enhancing the photocatalytic capabilities of metal oxide nanoparticles through targeted metal incorporation represented a significant breakthrough. This method effectively surmounted the inherent limitations of metal oxide nanoparticles, resulting in enhanced catalytic performance. An innovative approach involved the introduction of metal doping or decoration into metal oxide nanoparticles. This alteration led to a simultaneous reduction in bandgap energy and particle size, augmenting

the nanoparticles' ability to absorb visible light [71–76]. The transformative impacts of noble metal decoration, doping, or coating were pivotal. These adjustments were instrumental in significantly increasing the nanoparticles' surface area, giving rise to the generation of “hot electrons” driven by plasmonic resonance. This intriguing phenomenon, involving the plasmonic resonance-induced excitation of surface electrons, markedly improved catalytic efficiency. Importantly, this phenomenon outperformed other methods of metal decoration, ushering in an era of heightened effectiveness. The research, in particular, spotlighted the exceptional catalytic activity exhibited by Zn-NiO NPs. When compared to both conventional and noble metal embellishments, these nanoparticles demonstrated superior performance when applied to NiO surfaces.

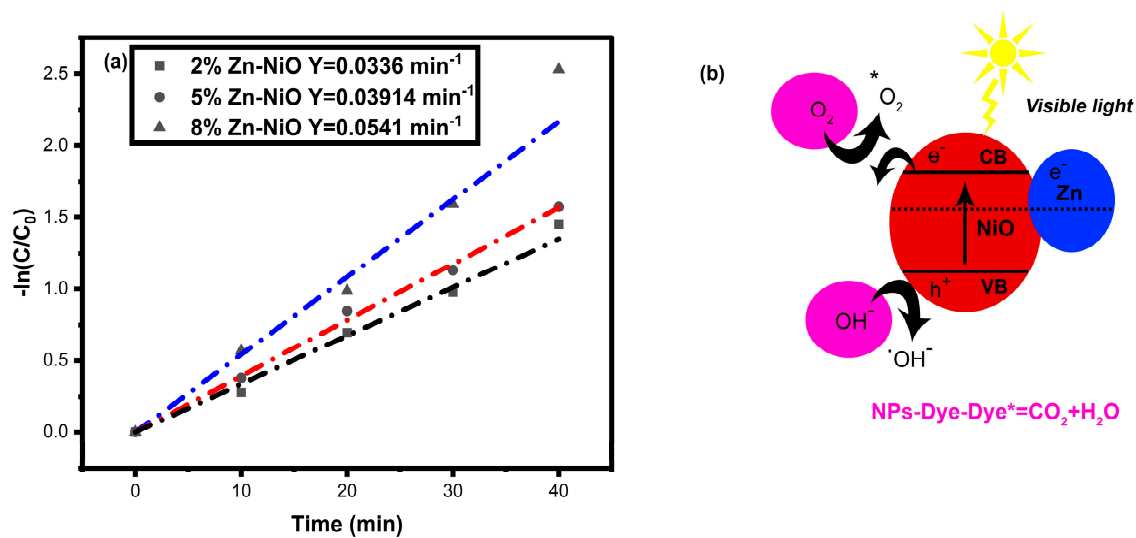


Figure 9. Photocatalytic dye degradation kinetic graph (a) and mechanism (b) of synthesized Zn-NiO NPs.

Table 1. Photocatalytic properties of undoped and metal-doped metal oxides nanoparticles.

S.NO	Nanoparticles	Source	Time (min)	Degradation (%)	References
1	MgO	UV light	120	52	[71]
2	MgO	UV light	180	52	[72]
3	ZnO	Visible light	50	46	[73]
4	Cr/CeO ₂	UV light	100	56	[74]
5	Ag/ZnO	UV light	180	35	[75]
6	Zr-CeO ₂	Visible light	150	75	[76]
7	2%Zn-NiO	Visible light	40	76	Present work
8	5%Zn-NiO	Visible light	40	79	Present work
9	8%Zn-NiO	Visible light	40	92	Present work

The research discoveries expose a positive correlation between the concentration of Zn doping in NiO nanoparticles and the efficiency of degrading both phorate and salbutamol, as shown in Figure 10. Phorate: increasing Zn doping from 2% to 8% results in a steady enhancement of degradation efficiency from 44% to a peak of 72%. This improvement suggests that higher Zn concentrations positively impact catalytic activity, surface area, or electron transfer properties in NiO nanoparticles. Similarly, for salbutamol, the degradation efficiency follows a similar trend, with 2%, 5%, and 8% Zn doping leading to efficiencies of 55%, 62%, and 70%, respectively. The study underscores the tunability of degradation efficiency in Zn-doped NiO nanoparticles by adjusting Zn doping concentrations, offering promising prospects for designing efficient catalysts in environmental remediation and water treatment applications [77–80]. Further exploration into the specific mechanisms and roles of Zn in these processes is warranted for a comprehensive understanding and

targeted development of catalysts for pollutant removal, addressing concerns related to both agricultural and pharmaceutical contaminants in water systems. This remarkable finding underscores the substantial potential of Zn-NiO nanoparticles as a leading photocatalytic material, especially in the degradation of Rhodamine B dye under visible light. Compared to Rh-B, phorate, and salbutamol contaminants, RhB dye exhibited better degradation potential than phorate and salbutamol compounds. The significance of these Zn-doped NiO nanoparticles is underscored by emphasizing the broader implications of these discoveries in the realms of environmental preservation, sustainable energy, and wastewater treatment.

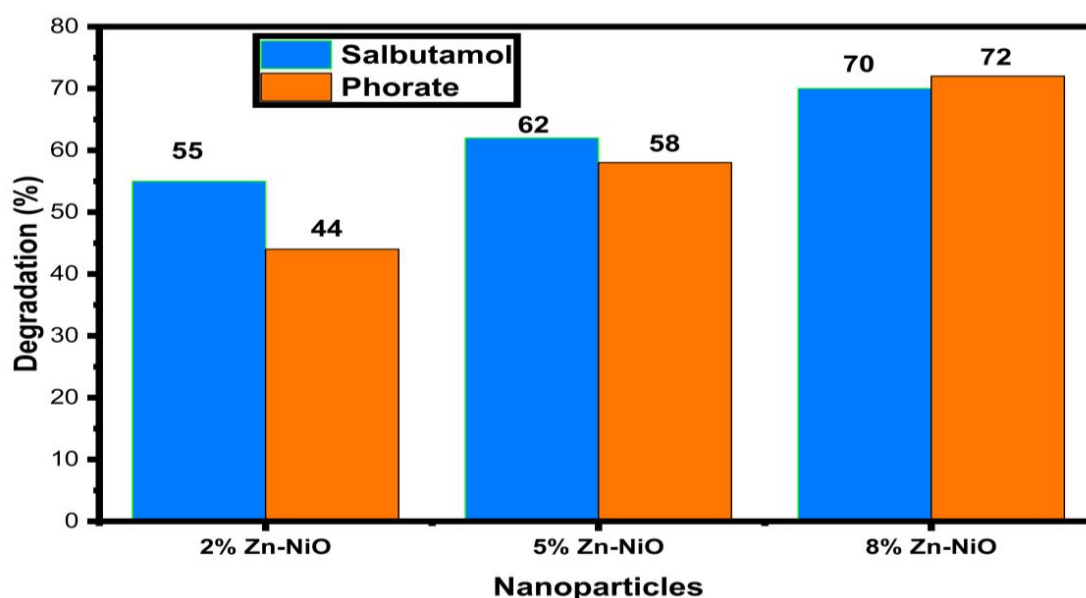


Figure 10. Photocatalytic degradation of synthesized Zn-NiO NPs on Salbutamol and Phorate.

4. Conclusions

The chemically synthesized zinc-doped nickel oxide nanoparticles showed promising results for the production of efficient photocatalysts. Zinc oxide and replaced nickel oxide produced cubic-phase nanoparticles with reduced bandgaps and altered multivalency of nickel lattices. The spherical morphology of the nanoparticles contributed to their high surface area and photocatalytic activity. Under visible light irradiation, 8% Zn-doped NiO nanoparticles demonstrated a remarkable degradation efficiency of 92% in 40 min and enhanced degradation potential for phorate and salbutamol. A thorough examination of metal-oxygen stretching and substitution of zinc for nickel oxide stretching confirmed the successful synthesis of nanoparticles. Chemical synthesis using conventional methods provided a viable route to synthesize nanoparticles. Nickel oxide nanoparticles doped with zinc have enhanced photocatalytic efficiency, making them potentially useful as environmental remediation agents. Based on the results of this research, zinc-doped nickel oxide nanoparticles have the potential to function as efficient photocatalysts for the removal of organic pollutants and toxins.

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