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SYNTHESIS, CHARACTERIZATION, AND PHOTOCATALYTIC ACTIVITY OF ZnO/NI COMPOSITE FOR METHYL ORANGE DYE DEGRADATION UNDER UV LIGHT IRRADIATION

(Penyediaan, Perincian dan Aktiviti Fotomangkin Komposit ZnO/Ni untuk Penyingkiran Metil Jingga Di Bawah Sinaran Lampu UV)

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Abstract

ZnO/Nickel (ZnO/Ni) heterostructures have been studied extensively as potential hybrid materials for photocatalysis applications due to their unique properties and potential applications. The photocatalytic efficiency of ZnO alone is compromised by its wide bandgap energy and high exciton binding energy. To enhance the effectiveness and photostability of ZnO nanoparticles, they can be doped with other elements such as transition metals, non-metals, and noble metals. Herein, we report a facile ultrasonic-assisted chemical mixing technique to prepare ZnO/Ni composite photocatalyst at various weight percentage (10 – 50%). Photocatalytic ability of as synthesized samples was examined for the degradation of methyl orange dye. The ZnO/Ni composite has been characterized by X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM) and Energy-dispersive X-ray (EDX) spectroscopy. It is found that the 10 wt.% ZnO/Ni composite produce the highest photocatalytic efficiency with percentage degradation of 89.17% and photodegradation rate constant of 0.0285 min^{-1} compared to other samples. These results suggest that the introduction of Ni acts as an electron sink, promoting charge separation in ZnO results in efficient light absorption and enhanced the photocatalytic activity The enhanced photocatalytic ability of ZnO/Ni composite make it a potential candidate for removal of organic pollutants from wastewater.

Keywords: composite, methyl orange, nickel, photocatalytic, UV light

Abstrak

Heterostruktur ZnO/Nikel (ZnO/Ni) telah dikaji secara meluas sebagai bahan hibrid berpotensi untuk aplikasi fotokatalisis disebabkan oleh sifat unik dan potensi dalam banyak aplikasi. Kecekapan fotokatalisis ZnO secara tunggal terjejas oleh tenaga jalur lebar dan tenaga ikatan eksiton yang tinggi. Untuk meningkatkan keberkesanan dan kestabilan ZnO nanopartikel, ia boleh didop dengan unsur-unsur lain seperti logam peralihan, bukan logam, dan logam adi. Di sini, kami melaporkan teknik campuran kimia dengan bantuan ultrasonik yang mudah untuk menyediakan fotomangkin ZnO/Ni komposit pada pelbagai peratus berat (10 – 50%). Keupayaan fotokatalisis sampel yang disintesis diuji untuk penguraian pewarna metil jingga. Komposit ZnO/Ni telah dicirikan oleh spektroskopi pembelauan sinar-X (XRD), mikroskopi imbasan tenaga medan elektron (FESEM), dan spektroskopi tenaga penyerakan sinar-X (EDX). Didapati bahawa komposit ZnO/Ni 10 wt.% menghasilkan kecekapan fotokatalisis tertinggi dengan peratus penguraian 89.17% dan pemalar kadar degradasi sebanyak 0.0285 min^{-1} berbanding dengan sampel lain. Hasil ini menunjukkan bahawa pengenalan Ni bertindak sebagai penyerap elektron dan menggalakkan pemisahan cas kepada ZnO dapat menyerap cahaya dengan cekap dan meningkatkan aktiviti fotokatalisis. Keupayaan fotokatalisis yang dipertingkatkan bagi komposit ZnO/Ni menjadikannya calon berpotensi untuk penyingkiran pencemar organik dari air yang tercemar.

Kata kunci: komposit, metil jingga, nikel, fotomangkin, sinar lembayung

Introduction

The batik industry in Malaysia, particularly in the states of Kelantan, Terengganu, Pahang, Sabah, and Sarawak, is primarily composed of small businesses and cottage industries [1]. These enterprises play a significant role in the craft-based economy of Malaysia. However, the production of batik generates wastewater that is highly contaminated, making it a major concern. The pollutants found in batik wastewater pose a significant threat to both human health and the environment [2]. Consequently, researchers have focused their efforts on wastewater treatment as a crucial issue to address and establish a sustainable treatment system [3]. Extensive research has been conducted to explore the utilization of photocatalysts for the removal of dyes in wastewater.

Various semiconductor materials which act as photocatalysts have been utilized as a solution to address water contamination. Among these semiconductor materials, zinc oxide (ZnO) was extensively used in water treatment applications due to its advantages such as direct band gap, high electron mobility, cost-effectiveness, ease of synthesis, and relatively low toxicity [4, 5]. Nevertheless, ZnO nanostructures face limitations in efficiently absorbing and utilizing light in the visible region of the spectrum due to their large band gap [6]. Additionally, the recombination rate of the generated electron-hole pairs is relatively high, further impacting the optical performance of ZnO, particularly its photocatalytic activity [7]. To overcome such limitations the photocatalysts (e.g., ZnO) are usually doped with other constituents such as Ag, Ni, Cd, Al, Cu and Mg [8, 9, 10]. In addition, the light harvesting properties of ZnO can be adjusted by incorporating metal accumulation on its surface, introducing metal ion impurities, or creating composites of ZnO with other semiconducting materials.

The introduction of Ni as dopant to ZnO photocatalysts has garnered significant attention due to its enhanced photocatalytic properties compared to ZnO alone. Ni doping can reduce the recombination rate of electron-hole pairs in ZnO, thus enhancing the photocatalytic activity. The concentration of Ni affects the availability of these charge carriers. Previous studies by Vignesh et al. have shown that incorporating Ni into ZnO can effectively reduce charge carrier recombination [11]. Furthermore, the addition of Ni to the ZnO lattice can induce changes in the crystal structure and morphology of ZnO nanoparticles. These structural modifications can influence the surface area and active sites, which are crucial factors for photocatalytic efficiency. Alternately, Iqbal et al. reported that by optimizing the Ni content, the material's bandgap energy, crystallite size, as well as lattice parameters, the photocatalytic performance can be enhanced [12]. They attributed the improved photocatalytic degradation efficiency of Ni-doped ZnO to the Ni substitution in ZnO, which is associated with the tuning of the material's bandgap.

Herein, we report ZnO/Ni composites as photocatalysts prepared via facile ultrasonic-assisted chemical mixing technique. For this purpose, a various of ZnO/Ni composites at different weight percentage (wt.%) has been prepared and their photocatalytic activities have been assessed employing methyl orange (MO) as a model organic pollutant. While numerous studies have explored the photocatalytic properties of ZnO/Ni composites at different weight percentages, there is a notable lack of research specifically examining the photocatalytic degradation of methyl orange (MO) dye using these combinations. In addition, employing field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDX) and X-ray diffraction (XRD), the structural, morphological, surface compositions, and functional groups of the ZnO/Ni composite photocatalysts are examined. To evaluate the photocatalytic efficacy of ZnO/Ni composite photocatalyst under UV light irradiation, MO dye has been used as the probe molecule. Integrating Ni into the ZnO photocatalyst presents an alternative approach for creating a stable and effective photocatalyst for water remediation processes.

Materials and Methods

Materials

Commercial zinc oxide powder and nickel nanopowder were obtained from Sigma Aldrich and used for synthesis of ZnO/Ni composites. Deionized water was used throughout the synthesis process. Methyl orange dye as pollutant representative was obtained from R&M Chemical.

Synthesis and characterization of ZnO/Ni composites

In this work, ZnO/Ni composites were synthesized via facile ultrasonic-assisted chemical mixing technique. To synthesize ZnO/Ni composites, about 0.5869 g of Ni nanopowder was mixed with 8.139 g of ZnO nanopowder which was dissolved in deionized water (DI). The mixture underwent ultrasonic for several minutes to form a stock solution, then the stock solution was kept stirred for 24 h at 120 °C and collected by centrifugation. Following that, the obtained powder was washed with DI water and then dried at 300 °C for 1h. The final products were noted as ZnO/Ni10, ZnO/Ni20, ZnO/Ni30, ZnO/Ni40 and ZnO/Ni50, corresponding to the different weight percentage of Ni (10, 20, 30, 40 and 50 wt.%), respectively. X-ray diffraction (XRD) results were obtained with a PAN analytical powder X-ray diffractometer with CuKα radiation probe of 1.54056 Å wavelength (2θ scale from 25-70°) with a scanning speed of 2°/min. Morphological and elemental composition studies were determined by Field emission scanning electron microscopy (JEOL JSM-7600F) equipped with energy dispersive X-ray analyzer. The photocatalytic analysis was employed by UV–Visible spectroscopy.

Photocatalytic degradation activity of ZnO/Ni composites

The photocatalytic degradation performance of the ZnO/Ni composites was studied at room under UV lamp irradiation that predominantly emitted at 365 nm with the definite power of 6 W, 230 Volts and 50 Hz frequency. It was employed as a UV source and positioned parallel to the beaker, as depicted in Figure 1. The reaction was carried out with 50 mg of catalyst dispersed in 100 mL of 10 mg/L methyl orange (MO) aqueous solution. Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 minutes to establish the adsorption-desorption equilibrium of MO. Subsequently, the UV light was turned on to commence the photocatalytic reaction. At first, 5 mL of pure MO without the catalyst was withdrawn after every 30 minutes for 90 minutes interval. Following that, 5 mL of samples with the presence of catalyst also went through the same procedure. The degradation of MO solution in each sample was monitored by a UV- visible spectrophotometer by measuring the absorption of MO dye at 464 nm. The percentage of degradation of MO was calculated using Equation (1) below [13]:

$$\text{Percentage of degradation } (\%) = (C_o - C_t)/C_o * 100 \quad (1)$$

where C_0 is the concentration of MO before irradiation, while C_t is the concentration of MO at time ‘t’.

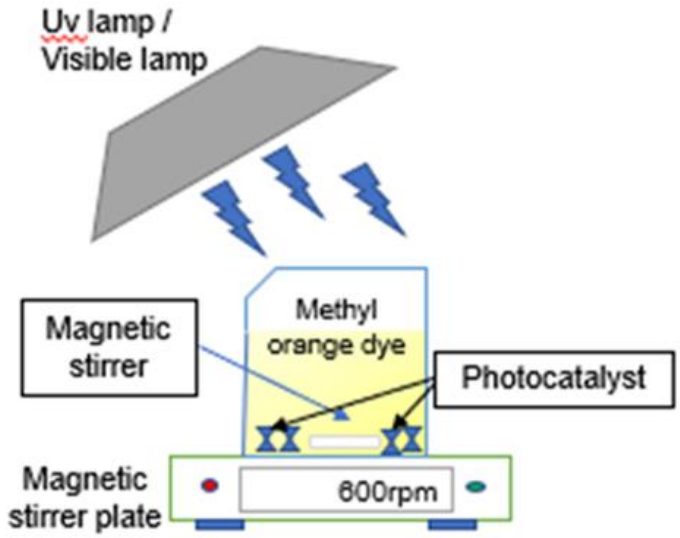

Figure 1. Illustration of the degradation process of ZnO/Ni composites against MO under UV light irradiation (initial dye concentration: 10 mg/L, 10 mg catalyst, 90 min irradiation time, UV light irradiation (6 W, λ: 254 nm))

Results and Discussion

Surface morphological and structural analysis

Field emission scanning electron microscopy (FESEM) was utilized to investigate the morphology and microstructure of the synthesized composites and distribution of particle size. Figure 2 (a)-(f) shows the micrographs of ZnO/Ni composites sample along with analysis of EDX results. According to the FESEM images, pure ZnO exhibit a long rod-like structure. However, the structure of ZnO/Ni is clearly altering when Ni is integrated into the ZnO. The nanorod dimension has been shaped into short rod-like pentagon shapes and composed of particles that do not have a specific morphology. Agglomerates are also seen in the samples due to the high surface energy of the particles during synthesis process, thus particles tend to reduce the surface energy by agglomeration. Other than that, the morphology of ZnO/Ni becomes denser and more homogeneous as the amount of Ni added increases. The elemental compositions of pure ZnO and ZnO/Ni composites were identified using EDX. The EDX study was conducted to support the results from the FESEM examination and to further confirm the presence of nickel, zinc and oxygen elements, which are the components of composites. The existence of composition and distribution structure of ZnO/Ni are shown in the inset of Figure 2 (b)-(f). Furthermore, based on the quantified data from EDX analysis, it is evident that the atomic percentage of Ni progressively rising (16.68, 22.56, 28.74, 31.30, and 35.49 at. %) corresponding to the increased weight percentage of Ni (10, 20, 30, 40, and 50 wt.%) throughout the synthesis process.

X-ray diffraction pattern analysis

Figure 3 illustrates the crystallinity and validation of ZnO/Ni composites samples that were carried out using X-ray diffraction (XRD). It can be observed that all the pure and ZnO/Ni composites have polycrystalline nature. The diffraction peaks of ZnO in ZnO/Ni composites can be indexed to the pure hexagonal phase of wurtzite-type ZnO (ICDD reference number 96-230-0291). The XRD patterns exhibit 8 major peaks which reveal the presence of hexagonal wurtzite structure of ZnO for all samples that are corresponding to (100), (002), (101), (102), (110), (103), (112) and (201) lattice planes [13, 14]. In addition, an additional low- intensity peak assigned to the (111), (200) plane of Ni and (200) plane of NiO is also exhibited [15, 16]. The weak peak of NiO, a common oxidation product of Ni might be formed during the synthesis process, where some of the nickel could oxidize to form NiO, especially if exposed to air. As the amount of Ni incorporated to ZnO increases, more NiO can be formed, making this peak more pronounced (Figure 3 (d-f)), respectively. These peaks clearly show that a segregation phase occurs in ZnO/Ni composites. The formation of NiO in a segregated phase make possible for a p-n heterojunction between NiO and ZnO oxides when the Ni incorporate to ZnO. This is expected to enhance the electron/hole separation and promote the photocatalytic activity. Other than that, when NiO is dispersed on the surface of ZnO, it provides additional active sites for the adsorption and oxidation of MO molecules. This increases the accessibility of MO molecules to the photocatalytic surface, leading to improved degradation efficiency [17].

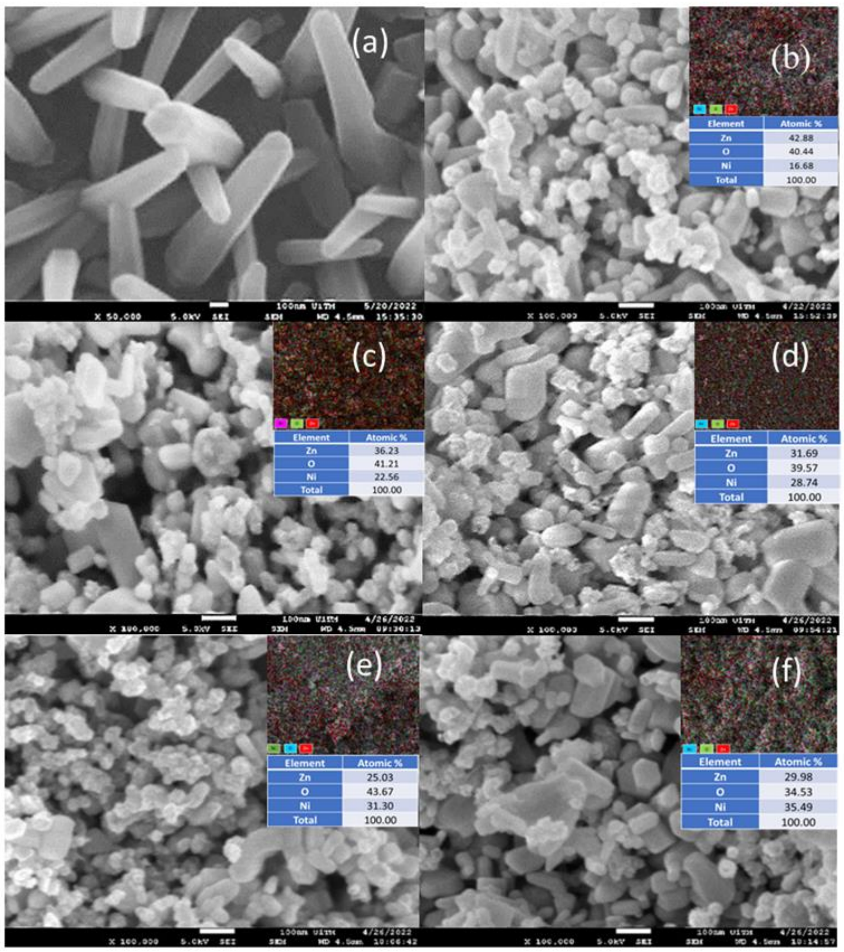

Figure 2. FESEM images of (a) pure ZnO, (b) ZnO/Ni10, (c) ZnO/Ni20, (d) ZnO/Ni30, (e) ZnO/Ni40 and (f) ZnO/Ni50 at 10,000 x magnification

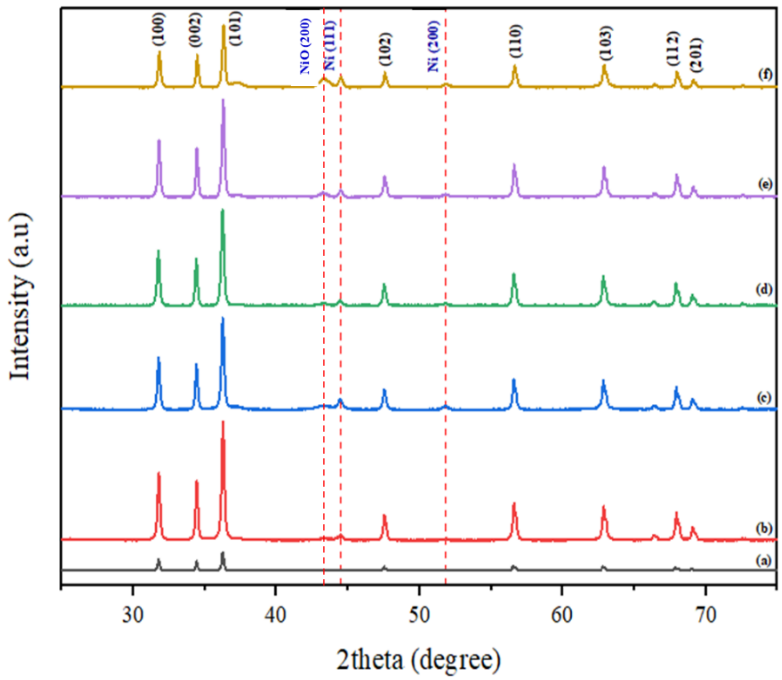

Figure 3. XRD Pattern (a) Pure ZnO, (b) ZnO/Ni10, (c) ZnO/Ni20, (d) ZnO/Ni30, (e) ZnO/Ni40 and (f) ZnO/Ni50

The estimated average crystallite size of pure ZnO and ZnO/Ni composites at various wt.% has been obtained and calculated using Scherrer's equation as in Equation (2) below [3, 14]:

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

where the estimated average crystallite size is denoted by D, k is the Scherrer constant (k = 0.89), λ represents the incident Xray wavelength, θ is the Bragg diffraction angle and β refers to the peak full width at half maximum (FWHM) of the samples. The estimated average crystallite size for pure ZnO is 46.49 nm and ZnO/Ni composites at various wt.% are found to be in the range of 52.20 – 65.28 nm respectively. The increase in the average crystallite size with the Ni content might be due to the Ni segregation over the grain boundarie, suggesting that Ni^{2+} ion with a slightly smaller ionic radius (0.70 Å) was substituted at a Zn^{2+} (0.74 Å) site inside the ZnO lattice [18, 19, 20].

Evaluation of photocatalytic activity

The photodegradation of MO by prepared photocatalyst was measured using UV-vis spectrophotometer and the results are presented in Figure 4. According to preliminary investigations, no degradation of MO is found throughout the photolysis process, indicating that MO is stable against UV light irradiation, with a negligible effect. In the control experiment, the removal of MO was carried out in the dark for 30 min initially and subsequently for 60 min in the presence of photocatalysts and UV light. No photodegradation of MO is observed when experiments are conducted under dark conditions (Figure 4 (a) and (c)). The photolysis of MO is also negligible, indicating its stability under UV light. In 90 minutes, pure ZnO photocatalyst shows 74.78% degradation as shown in Figure 4 (a), and the percentage degradation is increased once 10 and 20 wt.% of Ni incorporated to ZnO, which yielded a slightly similar percentage degradation of 89.17 and 89.15 % (Figure 4 (c)), respectively. As higher amount of Ni (30 and 40 wt.%) is added into the ZnO, the percentages of MO dye degradation is observed to decreased to 83.96% and 81.34%. The decrease of photocatalytic activity and degradation rate might be due to the presence of aggregated particles, which lowers the surface area and light absorption capacity of the composite photocatalysts. Nevertheless, a sudden improvement is observed for ZnO/Ni50 with percentage degradation of 86.06% which might be due to re-establishment of optimal structure of the photocatalyst. As can be seen from the FESEM image, when ZnO is incorporated with 50 wt.% of Ni, a different structural arrangement is formed, where Ni and ZnO create a more effective composite structure. This can lead to the re-establishment of efficient charge separation and transfer mechanisms. In addition, at this concentration, there might be an enhancement in light absorption, which contributes to a higher generation of electron-hole pairs and better photocatalytic performance. The findings indicate that the quantity of nickel has a substantial impact on photocatalytic performance, and there exists a threshold for Ni that can be incorporated onto the ZnO surface without adversely affecting the degradation percentage and degradation rate. Consequently, ZnO/Ni10 possesses the optimal ratio for the degradation of MO dye under low-intensity UV light exposure. Considering the robust synergistic interactions between ZnO and Ni, it becomes evident that both elements play a vital role in augmenting photocatalytic activity.

The Langmuir-Hinshelwood (L-H) kinetic model was used to examine the rate of MO degradation (Fig. 4(b) and (d)), as expressed in the following equation [21].

$$r = \left(\frac{dC}{dt}\right) = k_{obs} \tag{3}$$

which can be rewritten as

$$ln\left(\frac{C_0}{C_t}\right) = k_{obs}t \tag{4}$$

where k_{obs} is the apparent pseudo-first-order rate constant determined by the slope of the plot ln (C/C_o) vs. irradiation time. C_o is the initial concentration, and C_t the concentration at a specified time interval, t.

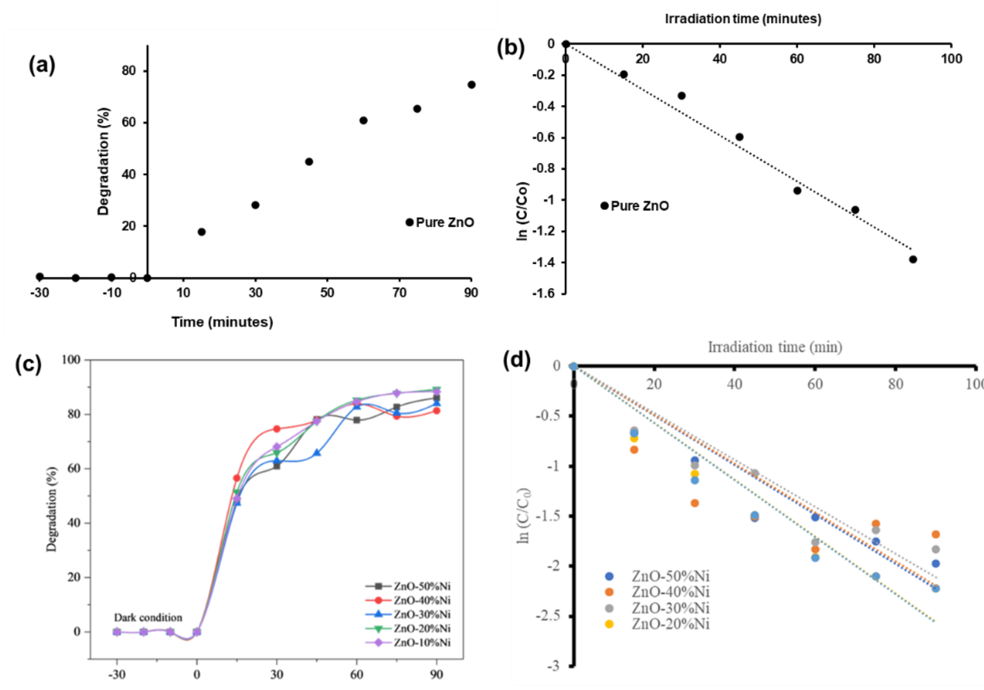

Figure 4. (a) The percentage degradation curve, (b) plots of -ln (C/Co) versus irradiation time for the kinetic of disappearance of MO in the presence of pure ZnO, (c) the percentage degradation curve and (d) plots of -ln (C/Co) versus irradiation time for ZnO/Ni10, ZnO/Ni20, ZnO/Ni30, ZnO/Ni40 and ZnO/Ni50 photocatalyst

Referring to Figure 4 (b) and (d), it is evident that linear plots are observed, with R2 values exceeding 0.9, indicating that the photodegradation of MO follows pseudo-first order kinetics. Furthermore, the photodegradation rate constant for ZnO/Ni10 displays the highest value of 0.0285 min-1 compared to others. It is well known that doping semiconductor particles with transition metal is an efficient way to increase photocatalytic activity because the metal can have an impact on charge transfer processes such as band gap narrowing, band gap splitting into multiple sub-gaps, and suppressing recombination of photoinduced charge carriers [22]. The kinetic parameters calculated using L–H model and the apparent first-order rate constants of pure ZnO and Ni/ZnO composites photocatalysts are summarized in Table 1.

Table 1. Photodegradation activities of MO using pure ZnO and ZnO/Ni composites with different wt.% under UV light irradiation

Sample	Percentage Degradation (%)	Photodegradation Rate Constant, k_{obs} (min^{-1})	Correlation Factor, R^2 Value
Pure ZnO	74.78	0.0146	0.9944
ZnO/Ni10	89.17	0.0285	0.9797
ZnO/Ni20	89.15	0.0284	0.9799
ZnO/Ni30	83.96	0.0247	0.9799
ZnO/Ni40	81.34	0.0244	0.9068
ZnO/Ni50	86.06	0.0235	0.9671

R^2: The square of correlation coefficient of kinetic energy

As depicted in Table 1, the incorporation of Ni into the ZnO/Ni composite influences the photocatalytic performance as ZnO/Ni10 composite exhibits the highest percentage degradation and photodegradation rate constant of MO under direct UV light irradiation. It can be suggested that ZnO/Ni10 composite should be regarded as the best photocatalyst as compared to pure ZnO and other samples. Nevertheless, incorporating an excessive quantity of Ni into ZnO (between 20 to 40 wt. %) leads to a decline in photodegradation efficiency. This decline is linked to the obstruction of active sites by excess Ni atoms, which in turn hinders light penetration and optimal absorption on the surface of the photocatalyst. This scenario suggests that light scattering and restricted light penetration towards the catalyst's surface diminish effective irradiation, impeding the reaction's advancement.

Table 2 lists previous reports on the photocatalytic reaction that employ ZnO/Ni composites under UV light irradiation. This current study reports that the synthesized composites with the optimum amount of nickel (ZnO/Ni10) photocatalyst exhibited comparable photocatalytic degradation activity in comparison with previous research.

Table 2. Previous studies on photocatalytic degradation using ZnO/Ni

Composites	Light Source	Dye Molecule	Percentage Degradation (%)	Reaction Time (Minutes)	References
Ni-doped ZnO	Visible	Methylene Blue	98.00	60	[12]
Ni-ZnO	Visible	Indigo Carmine	89.17	60	[20]
Ni/ZnO	UV	Methyl Orange	89.30	180	[23]
ZnO/Ni10	UV	Methyl Orange	89.17	90	present study

Conclusion

ZnO/Ni composites containing 10-50 wt.% Ni were fabricated using a facile ultrasonic-assisted chemical mixing technique and employed as photocatalysts for the degradation of methyl orange (MO) under UV irradiation. The incorporation of Ni to ZnO significantly influenced the morphology, while the crystal structure remained largely unchanged. Among the samples tested, the 10 wt.% ZnO/Ni composite photocatalyst exhibited the highest photocatalytic efficiency, achieving a degradation percentage of 89.17% and a photodegradation rate constant of 0.0285 min^{-1}. These findings suggest that the introduction of Ni serves as an electron sink, facilitating charge separation in ZnO, thereby enhancing light absorption and charge separation efficiency, leading to improved photocatalytic activity. Overall, this study proposes a feasible approach for enhancing the photocatalytic performance of ZnO-based photocatalysts, with promising implications for addressing environmental concern.

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