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Novel Ni/ZnO Nanocomposites for the Effective Photocatalytic Degradation of Malachite Green Dye

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Abstract

Water scarcity threatens human civilization because of rapid industrialization's damage to freshwater sources. Pollutants like dyes, which are frequently found in the paper, leather, food, plastics, textile, and cosmetics industries, must be removed to preserve water. In the present study, Zinc oxide nanocomposites impregnated with nickel (Ni/ZnO) were prepared using a wet impregnation technique. These novel materials were investigated for their ability to photocatalytically degrade malachite green (MG) under the irradiation of visible. The synthesized nanocomposite catalyst was characterized by various analytical techniques, including SEM, EDX, XRD, and BET methods of surface analysis, and revealed a high surface area of 192.88 m²g⁻¹ with an average size range from 88-354 nm. EDX results showed efficient doping of Ni (28.9%). The composites were then used under the influence of a visible light source to degrade MG dye. The investigation also assessed the degradation of MG using a photo-Fenton reagent. Factors such as catalyst dosage, H₂O₂ levels, pH, and duration were optimized to understand their impact in both degradation studies. The synthesized catalyst showed stunning photocatalytic activities, as 99.4% of the 60 μ g.ml⁻¹ of MG was degraded in 40 min with 100 mg of Ni/ZnO at pH 8. Ni/ZnO had a good application prospect for MG degrading and can be used as a potential photocatalyst.

Keywords: Ni/ZnO; Malachite Green; Water Pollution; Fenton Reagent; Wastewater Treatment; Photodegradation.

1. Introduction

The water quality is impaired by the uncontrolled mixing of industrial effluents, including dyes, pharmaceutical chemicals, pesticides, and organic pollutants, in water bodies [1, 2]. Dyes hold economic value for various industries [3], but their release into the water contaminates the bodies of water, which has been reported with various side effects [4]. Among the synthetic dye pollutants, malachite green (MG) has been reported as one of the highly toxic dyes [5]

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with 275 mg/Kg LD₅₀ in rats (oral use) [6]. MG is carcinogenic, mutagenic, and teratogenic to humans due to its ability to bind DNA [7]. It can cause various diseases, including cancer, and affect the immune system, reproductive system [8], kidneys, tissues, respiratory tract [9], vision, and skin [10]. MG has been reported to decrease the intensity of light from the sun to aquatic plants, which is necessary for photosynthesis. It is toxic for aquatic life due to aromatic rings and chlorine [11]. Many countries have declared against using MG in industries [12]. Biodegradation of MG is very hard even for small concentrations [6] that's why the effective removal of MG from wastewater is very crucial.

Different techniques were used to remove wastewater pollutants like incineration, bio-treatment, ozonation, adsorption on solid phases, etc. [6, 12, 13-16]. These techniques are not sufficient due to some limitations, i.e., the incineration produces volatile poisonous species [6, 17], bio-treatment requires a long time, and it mostly causes a foul smell. Sometimes, it becomes inapplicable due to the resistance of the dye to bio-decomposition [6, 18]. The ozonation technique is limited due to short ozone stability, and sludge formation results from adsorption techniques [19]. Therefore, it is very important to find an alternate technique to remove toxic dyes like MG from industrial wastewater effectively [20]. In the removal of MG, one of the best alternatives is photodegradation, as it degrades toxic contaminants into safe byproducts, thus regarded as one of the most effective methods [21].

A variety of semiconductor metal-based materials like metal oxides have been reported as potential photocatalysts like titania (TiO₂), anatase/titanate nanosheet and nanotubes composite, Cu₂O, Ni₂O₃, Co₃O₄, ZnO, and CdS, etc. [22-26]. However, using these semiconductor materials in a single phase on a wide scale has several drawbacks [27]. Reduced stability, limited surface area, broadband gap, low adsorption capacities, low photon quantum characteristics, inadequate light energy transformation rate, and fast recombination rates of the electron-hole pairs created have all been found to make these materials difficult to recover [28-30]. To address these issues, research was done on doping frequently examined photocatalysts, such as ZnO, with elements metals or doping them into composites of other metal oxides, then loading the resulting materials onto an appropriate substrate as photocatalyst carriers [31].

Recently, a research team of Nayak et. al. [32] prepared $ZnO-TiO_2$ nanoparticles and used them as photocatalysts for the removal of MG. They employed 20 µg.ml⁻¹ dye solutions and reported that 92% MG was degraded using 40 mg ZnO-TiO₂. In another study by Shao et al. [33], 10 µg.ml⁻¹ MG solution was subjected to degradation under UV light, and after 80 minutes of UV light irradiation, an enhanced 95.09% MG degradation was achieved with 30 mg of the Sn/CN-3 combination. Mohanty et. al. [34], prepared BiFeO₃/g-C₃N₄ nanocomposites via simple sonication method. They reported that 86% degradation of 40 µg.ml⁻¹ MG solution was achieved after 50 minutes using 40 mg BiFeO₃/g- C_3N_4 . Sokhansanj et al. [35] achieved 91.6% degradation of 200 µg.ml⁻¹ MG solution, using 1 g of hydrothermally produced macroporous flowerlike Bi₂O₂CO₃-CuBi₂O₄ nano heterojunction photocatalyst under 1.5-hour sunlight irradiation. Madona et al. [36] fabricated carbon-doped $CeO_2/g-C_3N_4$ heterostructure via hydrothermal method. These composites exhibited excellent catalytic performance, achieving 91.9% degradation of 30 µg.ml⁻¹ MG solution using 50 mg CeO₂/g-C₃N₄ under sunlight irradiation for 2.5 hours. The efficacy of most of these methods in photocatalytic degradation is significantly hampered by the utilization of costly and intricate-to-synthesize photocatalysts for the degradation of MG dye. These catalysts exhibit limited capacity in degrading the dye even at low concentrations, declaring them impractical for scenarios involving higher dye concentrations. Furthermore, the prolonged time required for MG removal through conventional methods often results in negligible percentage degradation, thereby underscoring the need for more efficient approaches in this domain.

In the present study, we prepared cost-effective nickel-impregnated zinc oxide (Ni/ZnO) for the effective photocatalytic degradation of MG dye. The degradation of MG via photo-Fenton reagent with the effect of various parameters was also investigated.

2. Experimental

2.1. Materials

During this research work, all the reagents and chemicals used were of analytical grade. Nickel nitrate (Ni(NO₃)₂), zinc oxide (ZnO), hydrogen peroxide (H₂O₂), iron(II) sulfate (FeSO₄), disodium hydrogen phosphate (Na₂HPO₄), citric acid (C₆H₈O₇) and MG (C₂₃H₂₅ClN₂) were purchased from Sigma Aldrich.

A double beam UV-visible spectrophotometer having model AE-S90-2D by A & E Lab, single beam spectrometer (Biotechnology Medical Services (BMS), K. Canada Inc.), visible light lamp (Halonix 500W Halogen Lamp), pH meter (HANNA instruments, Romania, Model No. HI 9811-5F) and magnetic heating stirrer (HPS-340PII) were used.

2.2. Preparation of Ni/ZnO photocatalyst

Nickle impregnated ZnO photocatalyst was synthesized using the wet impregnation technique as shown in Figure 1 [37]. To synthesize Ni/ZnO photocatalyst, 10 grams of dried ZnO was taken and its slurry was made in enough water. In another beaker, 1.640 g Ni(NO₃)₂ was dispersed in 100 ml water. This solution was gradually introduced into the ZnO slurry with continuous stirring for 15 min. The composite solution was kept at room temperature until the water

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evaporated. For complete dehydration, the sample was heated at 120 °C in an oven for 3 hours. The synthesized catalyst was labeled as Ni/ZnO. Then the photocatalyst, Ni/ZnO was calcined at 500 °C for 5 hours, then allowed to cool in a desiccation apparatus. The resulting photocatalyst was then ground into a fine powder and passed through a size filter to achieve uniform particle size.



Figure 1. Flow chart of methodology of catalyst Ni/ZnO synthesis and application for degradation of MG

2.3. Characterization of Ni/ZnO photocatalyst

The surface morphology of Ni/ZnO photocatalyst was examined by scanning electron microscopy (SEM) using JEOL, JSM5910 Japan, instrument, and for determination of the elemental composition of the catalyst a coupled instrument Oxford Inca-200 energy dispersive x-ray (EDX) was used. The phase analysis was carried out with JEOL, JDX-9C, Japan, X-ray diffractometer (XRD) instrument. For XRD monochromatic Cu-K α radiation (λ =1. 5418Å) at a potential 40 kV and current of 30 mA in the 2 θ range of 10-80^o with 1.03^o/min was used. NOVA2200e, Quantachrome, USA, surface area analyzer was used at 77.4 K to analyze the photocatalyst for N₂ desorption/adsorption. The sample was first degassed at 100 °C for an hour and then outgassed.

2.4. Application of Ni/ZnO photocatalyst for the degradation of MG

The synthesized Ni/ZnO photocatalyst was applied for the photocatalytic degradation of MG using visible light irradiation. The lamp was mounted over the solution at a constant distance in such a way that maximum light reached the reaction solution. The degradation experiments were conducted after achieving the equilibrium state of adsorption and desorption. The degradation experiment was conducted with the effect of various parameters on the photocatalytic degradation of MG i.e., pH of the solution, irradiation time, catalyst dose, and addition of H2O2. The concentration of residual MG after each experiment was determined using the double-beam UV–Vis spectrophotometer.

For the degradation, 10 ml of 60 μ g.ml-1 of MG solution was used for all the experiments. The reacting solution after the degradation was centrifuged for 5 minutes at 3 × 103 rpm and analyzed at 615 nm. The concentration of MG was also determined before and after the degradation reaction for the catalytic performance of Ni/ZnO photocatalyst. The % removal of dye was calculated using the given formula:

$$\% Removal = \frac{c_o - c_f}{c_o} \times 100 \tag{1}$$

where, C_o represents the concentration of MG dye before degradation, while C_f denotes the concentration after degradation, respectively.

2.5. Kinetic Studies

To assess the degradation process and explore the mechanism by which the Ni/ZnO photocatalyst degrades MG dye. Two kinetic models could be considered in order: Pseudo-first-order- and pseudo-second-order kinetic models. The linear Lagergren's equation for first-order kinetics is given by Equation 2:

$$\log(qe - qt) = \log qe - k_1/2.303$$

(2)

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where, qt represents the quantity of MG dye degraded (in μ g/mg) at time t, qe denotes the amount of MG dye degraded (in μ g/mg), and k₁ (in 1/min) stands for the rate constant of the pseudo-first-order adsorption process. The plot of ln (qe – qt) versus t was employed to determine the value of k₁.

The Ho and McKay's linear equation of rate for the pseudo-second-order model is given in Equation 3 was used to check the rate of reaction:

$$t/qt = 1/k_2 qe^2 + 1/qe t$$
 (3)

Where, q_e represents the amounts of MG dye degraded (in µg /mg), qt is the amount of dye degraded (in µg /mg) at a time (t) and k_2 (µg/mg.min) is the rate constant of pseudo-second-order kinetics and experimentally, its value can be derived from the intercept and slope of the plot of t/qt against time (t) [38].

3. Results and discussion

3.1. Characterizations

The surface structure of ZnO and synthesized Ni/ZnO photocatalyst was investigated by SEM analysis where Figure 2-a depicts the SEM images of ZnO and Figure 2-b depicts the SEM images of Ni/ZnO photocatalyst. The SEM analysis of ZnO analysis illustrates spherical, uniform particles with average size of 229 to 989 nm and with bright edges. The Ni/ZnO image reveals complete phase-changed morphology indicating the successful impregnation of Ni over the ZnO support. As can be seen, the Ni/ZnO photocatalyst particles are aggregated and disc-like in shape, and their average size ranges from 88 nm to 354 nm. This illustrates that Ni/ZnO photocatalysts have small sizes and highly porous surfaces with much brighter edges compared to ZnO. EDX analysis was used for the elemental composition of both ZnO and Ni/ZnO photocatalysts. Figure 2-c displays the spectrum of ZnO, while Figure 2-d shows the spectrum of the Ni/ZnO catalyst. The EDX spectra investigation showed that the impregnation of Ni was successful on ZnO. Table 1 demonstrates that Zn (35.6%) is the most basic element while Ni (28.9%), Na (27.8%), and C (21.1%) are the major constituents whereas O (6.2 %), and S (0.30%) are the trace elements on the material surface.



Figure 2. (a) SEM image of ZnO (b) SEM image Ni/ZnO (c) EDX of ZnO, (d) EDX of Ni-ZnO (e) XRD patterns of ZnO and Ni/ZnO

| | | L |
|---|---------|----------|
| - | Element | Atomic % |
| | Zn | 35.6 |
| | Ni | 28.9 |
| | Na | 27.8 |
| | С | 21.1 |
| | 0 | 6.2 |
| | S | 0.30 |

Table 1. Elemental composition of Ni/ZnO

XRD diffraction patterns were taken for both ZnO and Ni/ZnO photocatalysts. The relatively sharp and intense peaks show that the prepared catalyst has high crystallinity [39]. All the major peaks for ZnO and Ni/ZnO photocatalyst Figure 2-e are shown in the diffraction patterns of XRD. The ZnO XRD pattern presents different phases with ICDD numbers 11136, 30888, 361451, and 11244 shows peaks at 28°,31°,32°, 34°, 36°, 47°,50°, 56°, 62°, 66°, 67° and 69° [40] and the Ni-ZnO XRD result shows pattern according to ICCD number 30888, 30891, 50664, 211486, 471019 and 11025.

The BET surface areas of the synthesized photocatalyst were measured by N₂ adsorption and desorption studies [40]. It was found that $185.274 \text{ m}^2\text{g}^{-1}$ and $192.88 \text{ m}^2\text{g}^{-1}$ for ZnO and Ni/ZnO photocatalysts, respectively.

3.2. Degradation Studies Using Ni/ZnO Photocatalyst

The dye, MG was degraded under the visible light irradiation of constant intensity and Ni/ZnO photocatalyst. The effects of various conditions were optimized.

3.2.1. Effect of pH

The impact of varying the solution pH on enhancing/reducing the activity of synthesized Ni/ZnO photocatalyst is depicted in Figure 3. The figure concludes that the activity of Ni/ZnO photocatalyst increased by systematically changing the reaction medium from acidic to alkaline (pH 2 to 8). This is because positively charged MG and negatively charged Ni/ZnO photocatalysts are attracted to one other electrostatically. The system exhibits substantial electrostatic interaction with MG molecules due to the majority of negative surficial charges [41]. However, at lower pH, the Ni/ZnO photocatalyst's positive surface charge opposes the absorption of cationic dye, this is due to the electrostatic repulsion, which lowers the rate of degradation [42]. Thus, the best results were achieved at an alkaline medium i.e., at pH 8 with removal percentages of 99.4%.



Figure 3. Effect of pH on the degradation of MG using 10 ml of 60 µg.ml⁻¹ dye and 100 mg of catalyst

3.2.2. Effect of Catalyst Dose and Time

The photocatalytic degradation of MG using different doses of Ni/ZnO composites as a function of the visible light irradiation of different intervals is graphically exemplified in Figure 4.

The degradation percentages of MG increased slowly with increasing the irradiation time from 10 to 40 min as it attained the equilibrium state. The increase in irradiation time above 40 min resulted in no significant degradation [41]. 95.49% degradation of MG was achieved by 100 mg of catalyst and 40 min of irradiation time in an alkaline medium

of pH 8 at room temperature. A further increase in the reaction time was observed with no significant increase in the degradation of MG. This phenomenon could be attributed to the presence of abundant active sites on the catalyst's surface, which at the initial stage of the reaction produce more oxidizing radicals thus enhancing the degradation of MG at faster rates, while as the contact time increases the number of active sites and oxidizing radicals decreased [28].



Figure 4. Effect of catalyst weight and time on the degradation of MG using 10 ml of 60 µg.ml⁻¹ dye

On the other hand, the effect of photocatalyst dose was also investigated. The catalyst dosages used were 25 mg, 50 mg, 100 mg, 200 mg, and 300 mg. The maximum and significant degradation was obtained with 100 mg of the catalyst at room temperature with optimum pH and reaction time. This is due to the increase in the dose of photocatalyst, the overall active surface area experienced a corresponding increase, leading to improved photocatalytic efficiency consequently. Further increasing the dosage of catalyst was not effective for the degradation of MG. This could be attributed to the heightened aggregation of the photocatalyst at higher doses [43]. Hence, the 100 mg is the optimal concentration for Ni/ZnO.

3.2.3. Effect of H₂O₂

The photocatalytic efficiency can be enhanced by the addition of H_2O_2 [44]. The photocatalytic degradation of MG was also carried out with the effect of H_2O_2 from 25 to 500 µmol with optimum catalyst dose, pH, and different time intervals. The degradation data of MG with the effect of time and H_2O_2 concentration is shown in Figure 5. The degradation of the products increased with the increase of H_2O_2 concentration and maximum degradation was achieved using 100 µmol H_2O_2 in 30 min reaction time i.e. 99.12% [45] and beyond this time no significant changes were recorded.



Figure 5. Effect of hydrogen peroxide (H₂O₂) on the degradation process of MG using 10 ml of 60 µg.ml⁻¹ dye and 100 mg of catalyst

3.2.4. Kinetics Study

Kinetics study is the basis for evaluating the reaction process [46]. To evaluate the experimental findings about the MG degradation, the pseudo-first-order model Equation 4 [47] and pseudo-second-order model Equation 5 [48] were used to determine the mechanisms involved in the degradation procedure, the results shown in Table. 2

$$\log(qe - qt) = \log qe - \frac{\kappa_1}{2.303}$$
(4)
$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{\kappa_1 q_e^2}$$
(5)

In the above Equation 4, qt represents the quantity of MG dye degraded at a time (t); qe denotes the amount of MG dye degraded, and k^1 signifies the rate constant of the pseudo-first-order. The value of k^1 was determined by plotting ln (qe - qt) against t.

In this equation, qt represents the quantity of MG dye degraded at a time (t), qe stands for the amount of MG dye degraded overall, and k- represents the rate constant of the pseudo-second-order reaction. The value of this can be calculated experimentally from the plot of the intercept and slope t/qt versus t [38].

Figure 6 in the experimental data displays the plot fitted to the pseudo-first-order model along with the relevant parameters, illustrating the use of the Ni/ZnO catalyst for the photocatalytic degradation of MG. The effectiveness of this model was determined from the coefficient of linear determination (\mathbb{R}^2). The log (qe - qt) versus time (t) i.e., linearity of the model was plotted up to 50 min (0 min to 50 min) of contact time. The \mathbb{R}^2 value was recorded as 0.9064. The theoretical value of qe calculated (5999) was compared with the experimentally determined value (1895.832). The gap between theoretical and experimental values was more and \mathbb{R}^2 value indicated the subpar fit to the model. So, it was necessary to study the data obtained on the pseudo-second-order kinetic model. The resulting straight-line plot is depicted, in Figure 7 is between t/qt versus time (t). In this model the theoretical value of qe calculated (5999) showed closeness with the experimentally determined value (5000), this shows that the model and the experimental data fit each other well. The \mathbb{R}^2 value obtained ($\mathbb{R}^2 = 1$) indicated that the model resulted in better results [38]. These results suggested that the photocatalytic degradation of MG via Ni/ZnO photocatalyst in the presence of visible light follows pseudo-second-order kinetics. The kinetics parameters of pseudo-first and pseudo-second order for the degradation of MG via Ni/ZnO photocatalyst are shown in Table 2.



Figure 6. Kinetic model of pseudo first order for the photocatalytic degradation of MG dye

| Table 2. Kinetics parameters of pseudo-first kinetics and ps | seudo-second-order kinetics for the |
|--|-------------------------------------|
| degradation of MG dye via Ni/ZnO pl | ohotocatalyst |

| Kinetic model | Parameters | Values |
|---------------------|-------------------------------------|--------------------|
| | \mathbb{R}^2 | 0.9064 |
| | С | 3.2778 |
| Pseudo first order | K ₁ (min ⁻¹) | 0.1648948 |
| | Calc. qe (mg/g) | 1895.832 |
| | Exp. qe (mg/g) | 5999 |
| | \mathbb{R}^2 | 1 |
| | С | 2×10^{-5} |
| Pseudo second order | K ² (min ⁻¹) | 500 |
| | Calc. qe (mg/g) | 5000 |
| | Exp. qe (mg/g) | 5999 |



Figure 7. Kinetic model of pseudo-second order for MG degradation

3.2.3. Comparison of Ni/ZnO Photocatalytic Activity with other Catalysts

100 mg of Ni/ZnO photocatalyst showed 99.4% degradation of 10 ml of 60 µg.ml⁻¹ MG with a reaction time of 40 min. As shown in Table 3, this is higher photocatalytic activity compared to other catalysts like PANI/ZnO, Mesoporous ZnO, 5%-N2-8%-Co mesoporous ZnO, ZnO NFs, PAN/ZnO nanofibers, 3% Pt-doped ZnO, ZnO/algae and Co–ZnO/algae because in contrast with these Ni/ZnO photocatalysts act efficiently in low amount with less time for high MG concentration degradation.

| Catalyst | Light Source | Catalyst Weight (mg) | MG Conc. (µg.ml ⁻¹) | Irradiation time | Degradation % | Ref |
|--|-----------------|-------------------------|------------------------------------|---------------------|---------------|-------------------------------|
| PANI/ZnO | Sunlight | 400 | 3.6 | 5 h | 81 | Eskizeybek et al. (2012) [49] |
| ZnO NFs | UV | 200 | 15 | 2 h | 99 | Farhat et al. (2016) [50] |
| 3% Pt-doped ZnO | Vis | 300 | 100 | 1 h | 100 | Mohamed et al. (2016) [51] |
| Mesoporous ZnO | Vis | 500 | 36.4 | 2 h | 10 | Chuhan et al. (2019) [52] |
| 5%-N2-8%-Co mesoporous ZnO | Vis | 500 | 36.4 | 2 h | 78 | Chuhan et al. (2019) [52] |
| PAN/ZnO nanofibers | Vis | - | 36.4 | 3.3 h | 97 | Shah et al. (2019) [53] |
| ZnO/algae | Vis | 300 | 5 | 45 min | 100 | Rabie et al. (2020) [41] |
| Co–ZnO/algae | Vis | 300 | 5 | 30 min | 100 | Rabie et al. (2020) [41] |
| BiFeO ₃ /g-C ₃ N ₄ | Vis | 50 | 40 | 40 min | 86 | Mohanty et al. (2022) [34] |
| Sn/CN-3 | UV | 30 | 10 | 80 min | 95.09 | Shao et al. (2023) [33] |
| Bi ₂ O ₂ CO ₃ -CuBi ₂ O ₄ | Sunlight | 1000 | 200 | 1.5 hr | 91.6 | Sokhansanj et al. (2023) [35] |
| ZnO-TiO ₂ | UV | 40 | 20 | 30 min | 92 | Nayak et al. (2024) [32] |
| CeO ₂ /g-C ₃ N ₄ | Sunlight | 50 | 30 | 2.5 hr | 91.9 | Madona et al. (2024) [36] |
| Ni/ZnO | Vis | 100 | 60 | 40 min | 99.4 | Present Study |

Table 3. MG degradation via various catalysts with the effect of variation in light source, catalyst weight, MG concentration, and time intervals

3.3. Degradation of MG using Photo-Fenton Reagent

The photocatalytic degradation of the MG dye was also investigated with Photo-Fenton reagent (PFR) under visible light irradiation without using any photocatalyst. The effects of various effecting parameters like FeSO₄ concentration, H_2O_2 concentration, and pH were studied on PFR for MG degradation.

3.3.1. Effect of FeSO₄ Concentration

The effect of FeSeO₄ concentration on PFR for the degradation of MG dye was investigated by varying the amount of FeSO₄ concentration (1-9 μ mol) with a constant volume of H₂O₂ solution (500 μ mol) and initial dye concentration of MG (100 μ g.ml⁻¹), the results of the investigation are depicted in Figure 8. The figure shows that with the increase of FeSO₄ concentration in PFR the % degradation of the MG dye increased from 1 to 5 μ mol and the maximum % degradation was 98.04% with 5 μ mol solution of FeSO₄. However further increase in the FeSO₄ conc was not significant for the MG degradation and caused a decrease in the degradation efficiency, this may be due to hindering the absorption of light essential for the Fenton process because of the increase in brown turbidity [54].



Figure 8. Effect of the H₂O₂ conc on PFR for the removal of MG dye using 10 ml of 100 µg.ml-1 solution of MG and 5 µmol of FeSO₄

3.3.2. Effect of H₂O₂ Concentration

The degradation of MG dye using visible PFR was investigated with varying amounts of H_2O_2 (10-90 µmol) with a constant volume of FeSO₄ solution (5 µmol) and MG dye solution (100 µg.ml⁻¹), the degradation data is depicted in Figure 9. The figure indicates that the % degradation of the MG dye increased when the concentration of H_2O_2 increased from 10 to 40 µmol and further increase of H_2O_2 concentration exhibited no significant change in the % removal of the dye. This is most might be due to the self-quenching of OH radicals from H_2O_2 . The excess of H_2O_2 also acted as an OH radical scavenger that directed the generation of the less active per hydroxyl radicals [55]. The maximum % removal was 98.26% with a 40 µmol solution of H_2O_2 .



Figure 9. Effect of the FeSO4 concentration on PFR for the removal of MG dye using 10 ml of 100 µg.ml⁻¹ solution of MG and 500 µmol of H₂O₂ solution

3.3.3. Effect of pH

For MG degradation dye using PFR, the effect of solution pH was also optimized. The pH of the reaction mixture varied from alkaline to acidic (pH 2 to 8) with different irradiation times (10 min to 50 min) using a constant volume of FeSO₄ solution (5 μ mol), H₂O₂ solution (40 μ mol) and MG dye solution (100 μ g.ml⁻¹). The data on the degradation is shown in Figure 10. The figure indicated a decrease in MG degradation with the increase of pH from 2 to 4, then a slight increase was observed up to pH 6, and from 6 to 8 significant and sharp increase was observed for all the time intervals of irradiation time. The maximum degradation i.e., 89.54% of MG was obtained with pH 8 and 50 min of irradiation time.



Figure 10. Effect of the pH on PFR for the removal of MG dye using different time intervals of irradiation of visible light using 10 ml of 100 µg.ml⁻¹ solution of MG, 5 µmol of FeSO₄, and 40 µmol H₂O₂ solution

3.4. MG Degradation Mechanism

The possible proposed mechanism of MG catalysis based on the above experimental analysis is illustrated schematically in Figure 11. Firstly, the MG adsorbs onto the catalyst surface. When a photon of energy (hv) equal to or more than the band gap of the Ni and ZnO interact with Ni/ZnO, an electron residing within the valence band may undergo excitation to transition into the conduction band, thereby concomitantly creating a positively charged vacancy, commonly referred to as a hole, within the valence band. The photogenerated e⁻ and h⁺ can react with O₂ and H₂O to form the reactive superoxide anion ($^{\circ}O_2^{-}$) and hydroxyl radical ($^{\circ}OH^{-}$) The $^{\circ}O_2^{-}$ and $^{\circ}OH^{-}$ are strong oxidative species and can oxidize MG. Research studies have shown that interfacial transfer of charge can be enhanced by doping a metal into a semiconductor, which shifts the Fermi level to a highly negative potential. Hence, it is predicted that the electron within ZnO migrates from the conduction band to the newly formed Fermi level in the Ni/ZnO nanocomposites. The transfer of electrons between the Ni and the photoexcited semiconducting ZnO prevents the recombination of electron-hole pairs. As a result, the production of $^{\circ}OH^{-}$ increased which enhanced the photodegradation of MG. Thus, making the hybrid Ni/ZnO is more efficient photocatalyst in contrast to pure ZnO, this phenomenon has already been reported somewhere else [56-58]. The potential mechanisms of photocatalytic degradation for the Ni/ZnO photocatalysts are suggested as follows:

$$Ni/ZnO + hv \rightarrow Ni/ZnO (e_{CB}^{-} + h_{VB}^{+})$$
(6)

$$Ni/ZnO (e_{CB}) + O_2 \rightarrow O_2^{-1}$$
(7)

 $MG^+ \cdot O_2^- \rightarrow Degradation products$

(9)

(8)

(10)

```
MG + OH^- \rightarrow Degradation products
```

Ni/ZnO (h^+_{VB}) + H₂O \rightarrow 'OH⁻



Figure 11. Degradation mechanism of MG via Ni/ZnO

4. Conclusion

The wet-impregnation method was successfully used in this study to create Ni/ZnO composites, which produced a heterostructure with improved photocatalytic properties. When compared to pristine ZnO, the synthesized Ni/ZnO photocatalyst's surface morphology showed notable alterations. Images captured by scanning electron microscopy (SEM) revealed unique particle morphology with modified sizes and aggregation patterns, suggesting that Ni was successfully impregnated onto the ZnO support. Ni's presence within the composite structure was further authorized by EDX analysis. The high crystallinity of the prepared catalysts, which is necessary for effective photocatalytic activity, was revealed by X-ray diffraction (XRD) analysis. Furthermore, when comparing the synthesized Ni/ZnO photocatalyst to pristine ZnO, nitrogen adsorption measurements showed larger surface areas, indicating better catalytic performance. The synthesized composite photocatalyst exhibited remarkable efficiency in the degradation of MG dye under visible light irradiation. Under various circumstances, the degradation of MG using Ni/ZnO photocatalyst was studied. The effects of pH, catalyst dosage, and reaction time on photocatalytic efficiency were found to be significant by optimization studies. At alkaline (pH 8) conditions, the maximum degradation efficiency of 99.4% was attained with 100 mg of Ni/ZnO catalyst exposed for 40 minutes. Moreover, the effect of the photo-Fenton reagent on the degradation of MG in the absence of any catalyst was methodically investigated. With a constant volume of 5 µmol of FeSO₄ solution and 40 μ mol of H₂O₂, a 100 μ g.ml⁻¹ MG solution was used to achieve the maximum photocatalytic degradation efficiency of 98.26%. Pseudo-first- and pseudo-second-order models were employed to investigate the kinetics of MG photodegradation using the Ni/ZnO photocatalyst. The experimental data was effectively matched by the pseudosecond-order kinetics model, suggesting a chemisorption-related rate-limiting step. This implied that second-order rules applied to the degradation process.

5. Declarations

5.1. Author Contributions

Conceptualization, A.; methodology, N.; software, A.; validation, N. and H.; formal analysis, N. and H.; investigation, S.A.; resources, A. and B.K.; data curation, A.; writing—original draft preparation, N., N.A., N.R., and S.A.; writing—review and editing, A., R.S., F.M.Z., and H.S.; visualization, M.K.; supervision, A.; project administration, A.; funding acquisition, A. and H.S. All authors have read and agreed to the published version of the manuscript.

5.2. Data Availability Statement

The data presented in this study are available in the article.

5.3. Funding and acknowledgements

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5.4. Conflicts of Interest

The authors declare no conflict of interest.

6. References

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