Synthesis and Application of Zinc Oxide Nanoparticles as Efficient Photocatalysts for Organic Pollutant Degradation: Bromothymol Blue as a Model System

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Abstract
The release of synthetic dyes and organic contaminants into water bodies from industrial effluents poses significant environmental threats. Photocatalysis using semiconductor nanoparticles, such as zinc oxide (ZnO), offers a sustainable solution due to its high photocatalytic activity and eco-friendliness. This study examined the synthesis of ZnO nanoparticles via a chemical precipitation reaction using zinc nitrate and sodium hydroxide at 80°C. It further evaluated their photocatalytic efficiency in degrading bromothymol blue (BTB) as a model organic pollutant. BTB's degradation was monitored by measuring absorbance at 616 nm, corresponding to its deprotonated form (pH ~7.6). A linear decrease in absorbance over time was reported (R^2 = 0.9997), indicating efficient degradation, with ANOVA confirming statistical significance (R^2 = 0.9996, SE = 0.310). These findings highlight the efficiency of ZnO nanoparticles in photocatalytically degrading BTB under UV light irradiation, affirming their potential application in wastewater treatment. This efficiency is likely due to the generation of reactive oxygen species by ZnO under visible light. Notably, the ZnO nanoparticles exhibited superior performance compared to TiO_2 under identical conditions, as documented in previous related studies. While these results highlight ZnO's potential for wastewater treatment, future studies should characterize the nanoparticles to correlate structure with activity. Overall, this study demonstrates the promising application of ZnO nanoparticles as an effective, cost-effective, and reliable photocatalytic solution for degrading organic pollutants in environmental cleanup processes.

Keywords: Bromothymol blue, photocatalysis, organic contaminants, wastewater, ZnO nanoparticles

Introduction

Water pollution caused by synthetic dyes has become a serious environmental concern as they are widely used in the manufacture of textiles, paper, plastics, and medicines (Yusuf, 2019). These dyes are predominantly chemically stable, resistant to natural degradation, and represent significant health and environmental concerns when introduced into aquatic systems (Chavan, 2013). Conventional treatment methods, such as coagulation, filtration, and chemical oxidation, often fail to adequately eliminate persistent dye pollution, emphasizing the need for more advanced and long-term remediation strategies (Slama et al., 2021).

Global industrial, scientific, and technological advancements have led to a growing demand for new chemicals in industrial production activities (Vasanthi et al., 2024). Organic dyes are among the newly developed compounds of significant industrial importance, particularly in the paper, textile, cosmetics, and food processing industries. However, studies on surfaces and wastewater have reported these dyes as potentially toxic (Danwittayakul et al., 2015). Consequently, effective degradation strategies for these pollutants have garnered global

attention. Moreover, dyes and their associated intermediates can undergo reductive transformations, forming carcinogenic compounds that pose serious risks to humans, microorganisms, and aquatic ecosystems (Vasanthi et al., 2024). This underscores the urgent need to remove them from environmental compartments and matrices.

Among other new approaches, photocatalysis employing semiconductor nanoparticles stands out as a particularly promising method for addressing environmental pollutants (Albarakaty et al., 2023). Notably, zinc oxide (ZnO) nanoparticles have drawn interest due to their high photocatalytic activity, low cost, and UV-resistant photochemistry (Chemingui et al., 2024). Although the ability of ZnO to degrade organic dyes has been extensively studied, focused tests against specific contaminants, such as bromothymol blue (BTB), remain useful for improving wastewater treatment techniques.

ZnO is unique among metal oxides because of its wide band gap, strong oxidative properties, and capacity to create reactive oxygen species under illumination, which can degrade complicated dye molecules into less damaging byproducts (Albarakaty et al., 2023). The photocatalytic efficacy of ZnO is heavily impacted by parameters such as particle size, shape, crystallinity, and surface area, all of which are controlled by the synthesis procedure. Sol-gel, hydrothermal, and chemical precipitation techniques have allowed for control of these properties (Uribe-López et al., 2021) with the chemical precipitation method being used in this investigation. Tailoring synthesis conditions remains critical to improving ZnO performance in environmental applications (Chemingui et al., 2024).

This study examines the photocatalytic breakdown of bromothymol blue, a model organic pollutant widely used in laboratories and industries. The study uses ZnO nanoparticles under UV radiation to analyse the dye's degradation and discoloration behaviour under controlled laboratory conditions, but does not include kinetic analysis or morphological characterization, which were extensively evaluated elsewhere in related studies (Arora et al., 2014; Salim et al., 2022). The goal is to demonstrate ZnO's practical effectiveness in pollutant breakdown and contribute to environmental remediation. Despite the lack of extensive material characterization, the findings support the viability of ZnO-based photocatalysis for long-term water treatment solutions. Figure 1 shows the schematic structure of bromothymol blue.

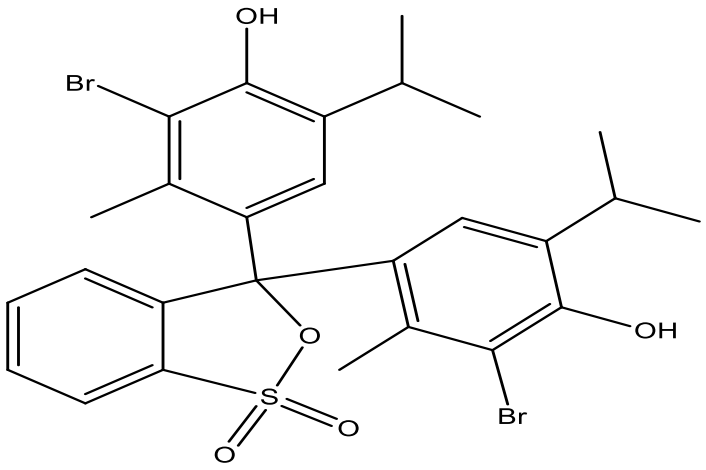

Fig. 1: Chemical Structure of Bromothymol Blue

Materials and Methods

Materials and Experimental Procedure

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), sodium hydroxide, and bromothymol blue used in this investigation were purchased from reputable suppliers and were of high purity (> 99 %). A 10-ppm solution of bromothymol blue was prepared by dissolving 10 mg of the indicator in distilled water, corresponding to 10 mg/L of solution. Zinc oxide nanoparticles were fabricated

by the precipitation method. A 0.1 M solution of zinc nitrate hexahydrate, used as the ZnO precursor, was prepared by dissolving the appropriate mass in deionized water, as described by Ghorbani and his group (Ghorbani et al., 2015). The solution was heated to approximately 60 °C with continuous stirring. A 0.2 M sodium hydroxide solution, serving as the precipitating agent, was added dropwise under constant stirring until the pH reached 8, allowing the precipitation of $Zn(OH)_2$.

To ensure complete reaction, the mixture was stirred for an additional 2 hours. To remove residual ions, the precipitate was allowed to settle, then repeatedly rinsed with distilled water and ethanol. The rinsed precipitate was subsequently dried overnight at 80°C. The obtained powder was then calcined in a muffle furnace at 400°C for 2 hours to produce crystalline ZnO nanoparticles.

Evaluation of Photocatalytic Performance

The photocatalytic performance of the synthesized ZnO nanoparticles was assessed by measuring bromothymol blue degradation under UV irradiation. A mixture of 100 mL of BTB solution and 0.05 g of ZnO nanoparticles in a 250 mL conical flask was magnetically stirred for 30 minutes in the dark to achieve adsorption-desorption equilibrium (Uribe-López et al., 2021). The resulting suspension was then subjected to UV radiation using a mercury vapor lamp (365 nm) while constantly swirling. After every 15 minutes, 5 mL aliquots were removed and centrifuged to remove ZnO particles. The absorbance of the clear solution was then measured using a UV-Vis spectrophotometer at 616 nm, λ_{max} for bromothymol blue.

The degradation efficiency (% degradation) was computed using Equation1, based on the change in absorbance values over time. The extent of dye degradation was assessed from the relative decrease in absorbance. All experiments were carried out in triplicate, and the values were averaged. Characterization, kinetic modelling and adsorption studies were not considered in this work.

$$\%\ Degredation = \left(\frac{A_0 - A_t}{A_0}\right) \times 100 \quad (1)$$

Where A_0 denotes the absorbance at t = 0, and A_t the absorbance at a given time t

Results and Discussion

The photocatalytic activity of the ZnO nanoparticles was evaluated by monitoring changes in absorbance of the dye solution over time, corresponding to the contact duration between the nanoparticles and the model contaminant. A consistent decrease in absorbance with longer contact time indicated a corresponding decrease in bromothymol blue concentration, confirming successful degradation under UV illumination. The photodegradation process involves the breakdown of BTB's chromophoric structure (Mehta et al., 2021). Table 1 displays the changes in the absorbance of BTB with increasing contact time with ZnO NP and the corresponding % degradation.

Table 1: **% Degradation and Change in Absorbance with Increase in Contact Time**

Time (min)	0	15	30	45	60	75
Absorbance(nm)	1.98	1.79	1.58	1.37	1.18	0.97
% Degradation	0.0	10.4	20.0	30.8	40.4	51.0

The data show the trend of change in the absorbance of the model organic pollutant solution over time. This change occurred as photodegradation and discoloration took place in the presence of ZnO nanoparticles. The decreasing absorbance trend with increasing contact time with ZnO nanoparticles suggests a highly effective photocatalytic-driven activity of the nanomaterial. The attractive photocatalytic performance is linked to their large surface area

and strong oxidative capabilities. According to Zhang et al. (2021), these features facilitate the generation of reactive oxygen species (ROS) under ultraviolet (UV) light exposure. The mechanism involves the absorption of UV light by ZnO, which excites electrons from the valence band to the conduction band, leaving behind holes in the valence band, as discussed under the photocatalytic degradation mechanism below.

The initial concentration of bromothymol blue solution was indicated by an absorbance of 1.98 at t = 0, and a gradual decrease in concentration was observed throughout the 75-minute contact time with the nano-ZnO. The substantial ~51 percent degradation confirms that ZnO nanoparticles enhance photocatalytic reaction processes, consistent with findings from previous studies on ZnO-based photocatalysts (Bhandari et al., 2023). Further research could delve into how mixed metal doping or joint semiconductor implementation with ZnO materials will optimize visible light performance (Zhang et al., 2021).

Figure 2 illustrates the variation in percentage degradation of bromothymol blue by ZnO nanoparticles with time under UV irradiation. The degradation increased steadily over time, with a strong linear correlation ($R^2 = 0.9997$) described by the equation $y = 0.6773x + 0.04$. This linear trend suggests a zero-order or pseudo-first-order kinetic behaviour, consistent with findings by Mehta et al. (2021). ZnO nanoparticles achieved 10.4 percent degradation at 15 minutes and 51 percent at 75 minutes, indicating high photocatalytic efficiency. Future studies could evaluate the potential influence of enhanced particle size, surface properties, and improved visible light responsiveness on the photodegradation efficiency of nano-ZnO.

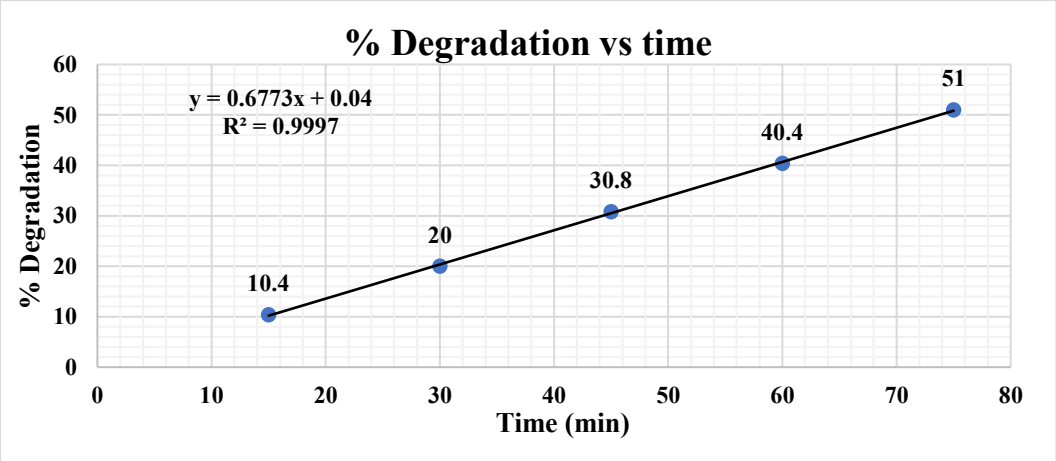

Fig. 2: % Degradation of BTB Over Contact Time with ZnO Nanoparticles

Evidently, there is a linear relationship between percentage degradation and contact time, with an R^2 value of 0.9997 indicating a strong correlation between the variables.

An analysis of variance (ANOVA) was used to assess the effect of contact time on bromothymol blue (BTB) degradation by ZnO nanoparticles. The ANOVA table illustrates variability in observed degradation percentages over time and indicates whether the changes in degradation are statistically significant. The F-statistic and p-value indicate the effect of contact time on the photocatalytic effectiveness of ZnO nanoparticles. The ANOVA results assume normal distribution of residuals. Table 2 summarizes the statistical findings based on this assumption.

Table 2: ANOVA Summary Table

	df	SS	MS	F	Significance F
Regression	1	1065.024	1065.024	11094	1.887×10^{-6}
Residual	2	0.288	0.096		
Total	3	1065.312			

Legend: df-Degrees of freedom, **SS** Sum of squares, **MS** Mean squares, **F** is F-factor

Regression analysis was used to investigate the relationship between contact time and percentage degradation of bromothymol blue (BTB) by ZnO nanoparticles. Significant statistical indicators such as the correlation coefficient and coefficient of determination were used to assess the strength of the linear relationship between these variables. These indicators show how well the contact period predicts the extent of photocatalytic degradation.

Table 3: Regression Statistics Table

Multiple R	0.999864819
R Square	0.999729657
Adjusted R Square	0.999639542
Standard Error	0.309838668
Observations	5

The independent and dependent variables show an extremely powerful link through the Multiple R value of 0.9999, which shows a nearly perfect positive linear correlation. The independent variable successfully explains 99.97 percent of the dependent variable variations since the R^2 value reaches 0.9997. The Adjusted R^2 value of 0.9996 persists at a nearly perfect level even after accounting for adjustment factors and predictor variables, which confirms the model's reliability and accurate data match. The model's precision is clear from the Standard Error of 0.310, as observed values are only 0.31 units apart from predicted values, given the scale of the variables. The research data contains only five observations. Table 4 shows regression coefficients for the correlation between % degradation and contact time.

Table 4: Regression Coefficients for the Relationship Between Contact Time and Percentage Degradation of Bromothymol Blue

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-0.6	0.3249	-1.8464	0.1620	-1.6342	0.4342	-1.6342	0.4342
X Variable 1	0.688	0.006532	105.33	1.887E-06	0.6672	0.7088	0.6672	0.7088

The model includes an intercept value of -0.6, but its p-value (0.162) shows its statistical insignificance at a 5 percent significance level, thus demonstrating minimal influence on the change in the dependent variable. In contrast, Variable 1 Coefficient (0.688) exhibits high significance (p-value = 1.8878E-06), which indicates a 0.688 unit increase in the dependent variable for each unit increase in X Variable 1. The interval between Lower 95% = 0.667 and Upper 95% = 0.709 does not include zero, thus validating its significance.

A normal probability plot, displayed in Figure 3, was generated to determine whether the regression residuals followed a normal distribution. This visual diagnostic aids in assessing the suitability of the linear regression model by correlating the observed residual patterns to those

expected under a normal distribution. The plot shows a near-linear trend, suggesting the residuals are nearly normally distributed.

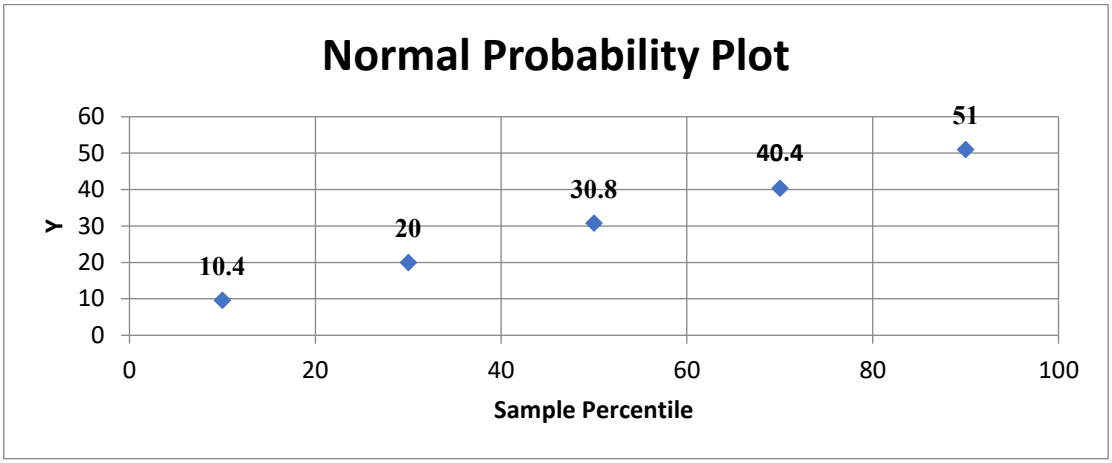

Fig. 3: Normal Probability Plot of % Degradation Data

Photocatalytic Degradation Mechanism of ZnO (Involving •OH and h^+ action)

Photocatalytic dye degradation has been studied worldwide, regardless of a country's level of scientific development. Typical variables considered for degradation research include the type and concentration of the dye, the desired level of degradation, the catalyst used, and the intensity and source of photons used (Singh et al., 2022). In photocatalytic degradation, the pollutants are degraded under UV-visible light irradiation in the presence of catalysts. Due to their susceptibility to UV and visible light radiation, various semiconductor metal oxide nanomaterials, including Fe_2O_3, TiO_2, WO_3, and Cu_2O are used as photocatalysts (Motamedi et al., 2022). ZnO nanoparticles present a huge promise in photocatalytic performance, especially in a variety of applications, including wastewater treatment, environmental pollution reduction, and water splitting for hydrogen production (Ragupathy et al., 2022).

Dye degradation by engineered nanomaterials occurs in the presence of UV light (Singh et al., 2022). The mechanism is a four-step reaction (Tomar et al., 2020): (a) the photocatalyst absorbs light and excites the electrons of the semiconductor photocatalyst to move from the valence band to the conduction band; (b) potential e-/h+ pair recombination as a result of the photogenerated electrons and holes' low stability; (c) generation of active species (radicals) on the surface due to the trapping of electron-hole pairs initiates redox reactions; and (d) finally, pollutant degradation occurs, as depicted in Figure 3.

The photocatalytic properties of nanomaterials result from the formation of an excited electron/hole pair when the material is subjected to UV light (Tomar et al., 2020). UV radiation causes charge separation by exciting an electron (e-) from the valence band to the conduction band of the nanomaterial, generating a hole (h+, a region of positive charge density) in the valence band.

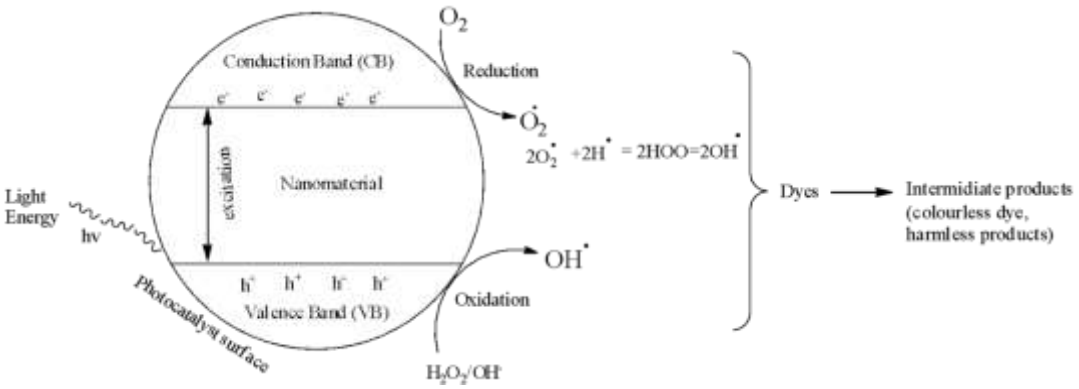

Fig. 4: Photocatalytic Degradation Phenomenon of Nanomaterials

As illustrated in Figure 4, the photocatalytic process generates two species: a photoexcited electron and a hole, represented in Equation 2

$$TiO_2 + h\upsilon \rightarrow e^- + h^+ \quad (2)$$

Redox reactions of photogenerated electron-hole pairs may produce oxidant radical species such as superoxide (O_{2^-}), hydroxyl ($OH^{\cdot}$), or peroxide ($OOH^{\cdot}$) (Jeyaraj et al., 2021). On the nanomaterial surface, these radical species produce heterogeneous photodegradation of organic substrates such as dyes (Anjali et al., 2022). The very presence of the hydroxyl radical, which is a highly strong oxidizing agent, causes the majority of these degradation processes (Tomar et al., 2020) as depicted in Equation 2.

$$\text{Dye} + OH^{\cdot} \rightarrow \text{Degradation products} \quad (3)$$

As described in Equations 4 and 5, dyes that do not react with the hydroxyl radical can proceed via either the oxidation or reduction route (Jeyaraj et al., 2021).

$$\text{Dye} + {h_{VB}}^+ \rightarrow \text{Degradation products} \quad (4)$$

$$\text{Dye} + {e_{CB}}^- \rightarrow \text{Degradation products} \quad (5)$$

Conclusion

This study demonstrated that ZnO nanoparticles have effective photocatalytic activity for photodegrading bromothymol blue dye under UV radiation. Within 75 minutes, a degradation efficiency of approximately 51 percent was achieved, with a strong linear relationship between contact time and % degradation. Statistical analyses, including regression and ANOVA, confirmed the data's significance and reliability, and the normal probability plot validated the normality assumption. The efficiency of nano-ZnO is attributable to its large surface area and capacity to produce reactive oxygen species upon UV activation. These findings suggest ZnO nanoparticles' potential as low-cost, environmentally friendly photocatalysts for dye removal in wastewater. Future investigations could examine how particle size, surface properties, and doping affect visible-light absorption and the photocatalytic efficiency of nano-ZnO.

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