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# A Comparative Photocatalytic Activity of ZnO and $TiO_2$ toward Rhodamine B Degradation under UV Irradiation

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## ABSTRACT

The rapid growth of Indonesia's textile sector has increased waste output. Textile production generally uses synthetic dyes, such as rhodamine B. These manufactured substances typically contain compounds that are harmful to the environment. Photodegradation using photocatalysts is a common dye degradation method. Among various semiconductor materials, $TiO_2$ and ZnO are known to exhibit excellent photocatalytic activity. This study aims to assess the effectiveness of $TiO_2$ and ZnO photocatalysts in the degradation of rhodamine B dye. Several variables, including catalyst dosage (5, 15, 25, 35, 45, 55, 65, 75, and 85 mg), pH (4–8), and degradation time (60–480 min), were used to establish the photocatalytic process's effectiveness and optimum conditions. The properties of $TiO_2$ and ZnO were characterized using scanning electron microscopy, X-ray diffraction, and BET analyses. Each catalyst (65 mg ZnO and 55 mg $TiO_2$) was added to the rhodamine B solution and exposed to a UV lamp to conduct the experiments. The results showed that $TiO_2$ demonstrated better photocatalytic efficiency than ZnO. The optimum degradation occurred after 6 h at pH 5. $TiO_2$ has a smaller crystal size and higher surface area than ZnO, contributing to its superior performance. The degradation efficiency reached 26.50% for ZnO and 48.40% for $TiO_2$. These data indicate that $TiO_2$ is more effective than ZnO for rhodamine B photodegradation under the examined conditions.

**Keywords**: Photocatalyst, Photocatalytic, Rhodamine B, $TiO_2$, ZnO

## 1. Introduction

The rapid growth of the textile industry, particularly in developing countries such as Indonesia, has significantly increased the volume of wastewater containing synthetic dyes. Textile dye effluents are considered one of the most problematic industrial wastes due to their high color intensity, chemical stability, and biodegradation resistance. Dyes can reduce light penetration in water bodies, disrupt photosynthetic activity, and negatively affect aquatic ecosystems even at low concentrations. Among various synthetic dyes, rhodamine B is classified as a hazardous organic pollutant because of its carcinogenic and toxic properties, as well as its high chemical stability, making conventional biological treatment methods ineffective [1], [2].

To address these challenges, advanced oxidation processes (AOPs), particularly photocatalysis, have attracted significant attention as effective methods for the degradation of persistent organic pollutants in wastewater. Photocatalysis employs semiconductor materials that can be activated by ultraviolet (UV) irradiation to generate electron–hole pairs, which subsequently produce highly reactive oxygen species such as hydroxyl radicals (•OH) and superoxide radicals ($O_2^{\bullet-}$). These reactive species can oxidize complex organic dye molecules into simpler, nontoxic end products such as $CO_2$ and $H_2O$ [3], [4]. Among various semiconductor photocatalysts, titanium dioxide ($TiO_2$) and zinc oxide (ZnO) are the most extensively studied because of their strong oxidative ability, chemical stability, non-toxicity, and relatively low cost.

In the last decade, numerous studies have reported significant progress in the application of $TiO_2$- and ZnO-based photocatalysts for rhodamine B degradation. Recent research has shown that ZnO-supported materials and modified $TiO_2$ structures can achieve degradation efficiencies exceeding 90% under UV irradiation, indicating substantial improvements in photocatalytic performance through material optimization [5], [6]. For instance, ZnO-based photocatalysts supported on natural zeolite or modified with noble metals have demonstrated enhanced adsorption capacity and charge separation efficiency, leading to faster degradation rates [7]. Similarly, $TiO_2$-based systems, particularly those with controlled crystal phases and reduced crystallite size, have shown superior stability and reproducibility in repeated photocatalytic cycles [8].

Despite these advances, the photocatalytic efficiency of $TiO_2$ and ZnO remains strongly dependent on physicochemical properties such as crystal structure, crystallite size, surface morphology, and light absorption characteristics. These properties directly influence the generation of charge carriers, recombination rate, and surface reaction kinetics. Therefore, systematic characterization using scanning electron microscopy (SEM) to evaluate surface morphology and particle size, X-ray diffraction (XRD) to determine crystal structure and crystallite size, and ultraviolet–visible spectrophotometry to assess optical absorption behavior is essential for understanding the relationship between material properties and photocatalytic activity [9], [10].

Accordingly, this study aims to perform a comparative analysis of commercial $TiO_2$ and ZnO photocatalysts in the photodegradation of rhodamine B under UV irradiation. This work is expected to provide valuable insights for selecting efficient and practical photocatalysts for textile wastewater treatment applications by correlating structural and optical characteristics with degradation efficiency under optimized conditions.

## 2. Methods

This research will examine various factors influencing the activity of $TiO_2$ and ZnO photocatalysts, including catalyst dosage, solution pH, and UV light exposure duration. Additionally, characterization will be conducted using SEM to assess morphology and particle size, XRD to evaluate phase and crystal size, and BET to measure catalyst surface area. The studies used commercial $TiO_2$ and ZnO catalysts from Merck, employing artificial liquid rhodamine B waste at a concentration of 70 ppm, which was derived from previously measured industrial waste samples in Banten.

### 2.1. Materials

The equipment used in this study included 50 and 500 mL glass beakers, a 500 mL beaker, stirring rods, a magnetic stirrer, test tubes, porcelain crucibles, dropper pipettes, a 10 mL volumetric pipette, filter paper, a 100 mL volumetric flask, a pH indicator, an analytical balance, a tungsten lamp reactor, a 10 W UV lamp reactor (Sankyo Denki), a centrifuge, a UV–Visible spectrophotometer (PerkinElmer), a Scanning Electron Microscope (SEM, Coxem), an X-ray Diffractometer (XRD, PANalytical X'Pert with HighScore Plus software), and a BET surface area analyzer (Quantachrome).

The materials used in this study consisted of titanium dioxide ($TiO_2$) and zinc oxide (ZnO) from Merck, rhodamine B dye from Merck, textile wastewater, demineralized water (aqua DM), distilled water, and 1 M hydrochloric acid (HCl) or sodium hydroxide (NaOH) for pH adjustment.

### 2.2. Method

A rhodamine B stock solution was prepared at a concentration of 1000 ppm by diluting 1 g of rhodamine B dye in distilled water to a volume of 1000 mL. Standard solutions were prepared by pipetting 1 mL of the stock solution into a 100 mL volumetric flask and diluting it to the mark with demineralized water. Calibration solutions with concentrations of 0, 1, 2, 5, 10, and 15 ppm were subsequently prepared. The absorbance of each standard solution was measured over a wavelength range of 400–700 nm using a UV–Vis spectrophotometer to determine the maximum absorption wavelength (λ_max) and construct a calibration curve.

Photocatalytic experiments were conducted by placing 250 mL of textile wastewater into a 500 mL beaker, followed by the addition of $TiO_2$ or ZnO photocatalysts at various masses of 5, 15, 25, 35, 45, 55, 65, 75, and 85 mg. To achieve adsorption–desorption equilibrium, the suspension was stirred in the dark for 30 min before UV irradiation.Then, the photocatalytic reaction was conducted for 8 h with continuous stirring. The samples were withdrawn at 1-h intervals and centrifuged for 5 min to separate the photocatalyst. The supernatant was analyzed at the maximum absorption wavelength using a UV–Vis spectrophotometer.

The photocatalyst mass with the highest rhodamine B degradation percentage was considered the optimum catalyst dosage. After determining the optimum catalyst mass and irradiation time, further experiments were conducted to evaluate the effect of pH on photocatalytic degradation by adjusting the pH of the solution to 4, 5, 6, 7, and 8 using 1 M HCl or NaOH.

## 3. Results and Discussion

### 3.1 Characterization of the catalyst

SEM was used to examine the surface morphology of the photocatalyst (Figure 1).

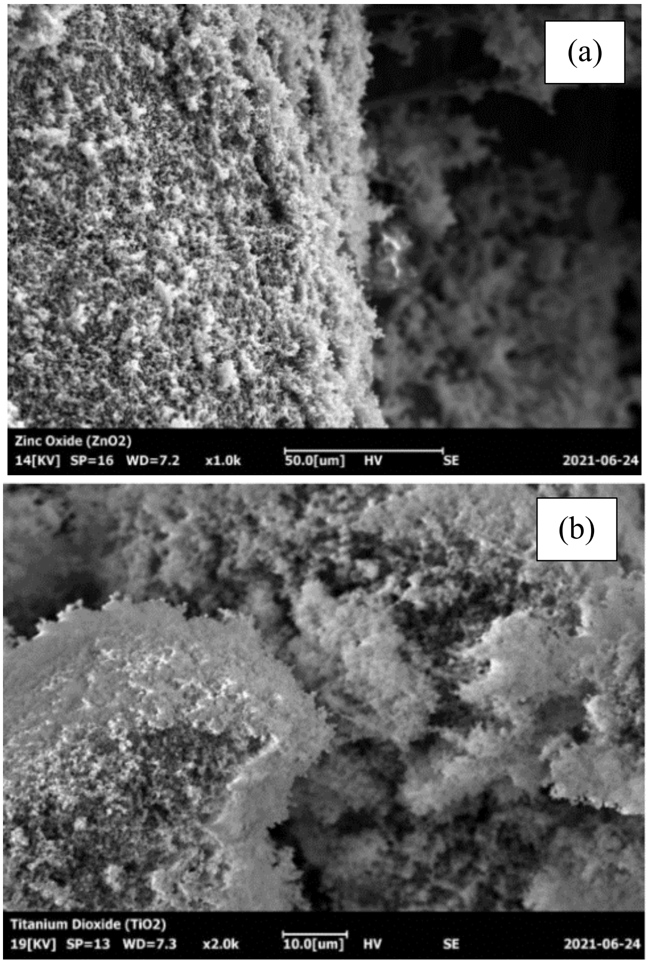

Figure 1. SEM images of the photocatalysts: (a) ZnO and (b) $TiO_2$.

Figure 1a, (magnification 1,000×) exhibit an agglomerated structure characterized by a roughly spherical shape and irregular particle distribution. This shape suggests that the ZnO particles exhibit a propensity to aggregate, hence diminishing the accessible surface area. Conversely, the $TiO_2$ particles (Figure 1b, magnification 2,000×) display a more refined spherical shape, characterized by reduced particle size and enhanced homogeneity relative to ZnO. The increased density of $TiO_2$ particles indicates the possibility of a greater specific surface area, which is crucial for improving photocatalytic activity. The SEM studies indicate that both ZnO and $TiO_2$ exhibit agglomeration; however, $TiO_2$ demonstrates smaller particle characteristics and a more uniform distribution, which is advantageous for photocatalytic applications.

XRD was conducted to obtain information on the crystalline phase and crystallite size of $TiO_2$. The result obtained from the XRD measurements is a diffractogram pattern. The X-ray radiation was recorded over a range of diffraction angles (2θ).

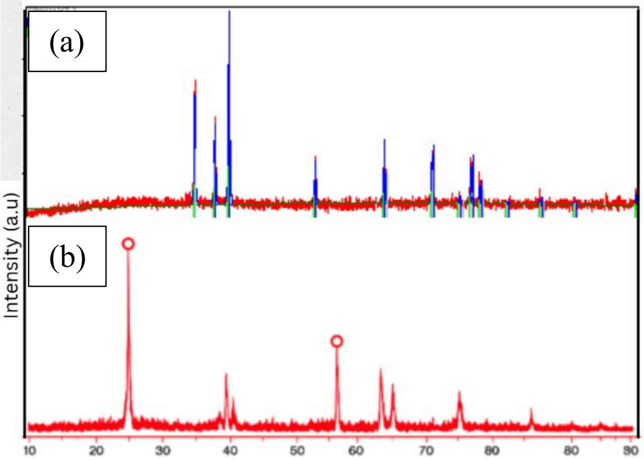

Figure 2. (a) ZnO and (b) $TiO_2$ diffractograms

The XRD pattern (Figure 2) indicates $TiO_2$ nanoparticles. A prominent high-intensity diffraction peak was observed at $2\theta = 25°$. The sharpness of this peak indicates good crystallinity of the sample. The distinct difference between the peaks at approximately 25° and 48° indicates that the $TiO_2$ phase is anatase with a tetragonal crystal structure. The XRD pattern shown in Figure 2, when matched with the Joint Committee on Powder Diffraction Standards (JCPDS) reference data (code 96-101-0943) for $TiO_2$, confirms that the sample has a tetragonal crystal structure and anatase phase. The diffraction angles in the range of 2θ = 25–88° correspond to the characteristic peaks of $TiO_2$, and the calculated crystallite size is 38.7 nm. The ZnO material exhibited eight diffraction peaks, with characteristic peaks observed in the range of 2θ = 36–69°, which are typical of ZnO. Matching the XRD pattern with the JCPDS reference data (code 96-230-0114) confirms that the sample has a hexagonal wurtzite crystal structure with a crystallite size of 51.9 nm (Table 1).

Table 1. Crystallite Size of the Catalysts

| Catalyst | Cristallite size (nm) |
|---|---|
| $TiO_2$ | 38.7 |
| ZnO | 51.9 |

In addition to qualitative information obtained from XRD measurements, semi-quantitative data in the form of crystallite size can be determined. This analysis is considered semi-quantitative because it provides an approximate average crystallite size, which can be calculated using the Debye–Scherrer equation. The crystallite size was calculated using parameters such as X-ray wavelength, diffraction angle (2θ), peak intensity, and full width at half maximum (FWHM) obtained from the XRD results. According to the Debye–Scherrer equation, the crystallite size is inversely proportional to the FWHM value, where the FWHM itself is influenced by the diffraction peak intensity; higher peak intensity corresponds to a smaller FWHM value.

A smaller crystallite size in powdered materials results in a larger total surface area. Consequently, an increased surface area enhances the probability of surface collisions between particles, which can accelerate reaction rates. This condition allows more rhodamine B molecules to interact with and be degraded on the photocatalyst surface.

Based on the BET analysis presented in Table 2, ZnO exhibits a specific surface area of 8.23 $m^2/g$, whereas $TiO_2$ shows a higher value of 12.92 $m^2/g$. The larger surface area of $TiO_2$ suggests a greater availability of active sites, which is beneficial for adsorption processes. This observation is consistent with previous reports indicating that mesoporous structures and well-developed surface properties play a crucial role in enhancing adsorption capacity and facilitating surface reactions in photocatalytic systems. [11], [12], as shown by the BET analysis.

Table 2. Specific Surface Area of Catalysts

| Catalyst | Specific Surface Area ($m^2/g$) |
|---|---|
| ZnO | 8.23 |
| $TiO_2$ | 12.92 |

The difference in the specific surface area between ZnO and $TiO_2$ indicates that $TiO_2$ possesses a greater number of active surface sites compared to ZnO. A larger surface area provides more opportunities for rhodamine B dye molecules to be adsorbed onto the catalyst surface, thereby enhancing the efficiency of the photocatalytic degradation process. Higher BET surface areas correlate with improved photocatalytic adsorption and degradation rates for organic pollutants, supporting the importance of surface area in facilitating photocatalytic reactions [13]. This observation is consistent with the fundamental principle of photocatalysis, where the adsorption of pollutants onto the catalyst surface represents a crucial initial step that determines the success of the degradation reaction.

The BET results correlate well with the crystallite sizes obtained from the previous XRD analysis. $TiO_2$, which exhibits a smaller crystallite size, has a higher specific surface area, whereas ZnO with a larger crystallite size presents a lower surface area. Theoretically, the specific surface area is inversely proportional to the particle size; thus, smaller particle sizes result in a greater total available surface area. This increase in surface area enhances the probability of collisions between reactant molecules and active sites on the catalyst, thereby accelerating the rate of photocatalytic degradation.

Therefore, it can be concluded that $TiO_2$ has an advantage over ZnO in terms of specific surface area, which potentially leads to higher photocatalytic activity in the degradation of rhodamine B. Nevertheless, the overall effectiveness of a photocatalyst is not solely determined by its surface area but is also influenced by other factors, such as crystal structure, optical properties, and the efficiency of electron–hole pair separation.

## 3.2 Optimization of Photocatalytic Conditions for $TiO_2$ and ZnO

Semiconductor photocatalysts such as $TiO_2$ and ZnO, have been extensively studied for the degradation of organic dyes due to their strong oxidative capability under UV irradiation. Photocatalytic performance is highly dependent on operational parameters, particularly catalyst loading and irradiation time, which influence light absorption and charge carrier dynamics. Therefore, UV–Vis spectroscopy is employed to monitor dye degradation by observing absorbance changes at the characteristic maximum wavelength of Rhodamine B.

The UV–Vis spectroscopic results showed that rhodamine B exhibited a maximum absorbance at $\lambda_{max} = 557.4$ nm, which was used to monitor the dye degradation under UV irradiation.

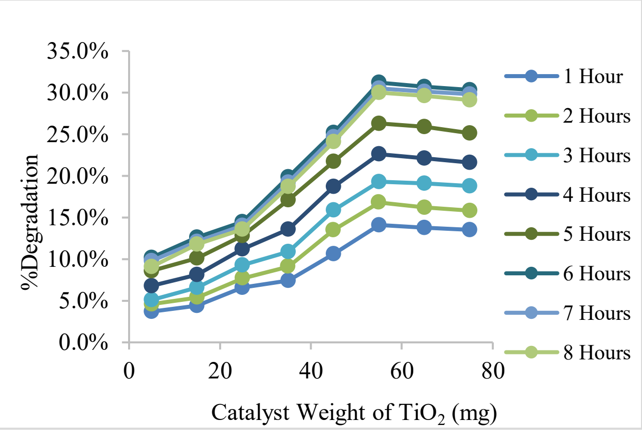

Figure 3. Determination of the Optimum Catalyst Weight of $TiO_2$ in a 250 mL Sample in 8 Hours of UV Radiation Time

According to Figure 3, the optimum $TiO_2$ loading was determined to be 55 mg per 250 mL, yielding the highest degradation efficiency **(**31.2%**)** with a final Rhodamine B concentration of 48.16 ppm after 6 h of irradiation. In contrast, from Figure 4, ZnO achieved a maximum degradation efficiency of 19.1% at an optimum loading of 65 mg per 250 mL**,** resulting in a final concentration of 56.63 ppm after 7 hours of UV exposure. These trends are consistent with recent works reporting that photocatalytic performance first increases with catalyst loading due to the greater number of active sites, followed by a decline at higher loadings due to light scattering and aggregation effects, which limit photon penetration and active surface accessibility [14], [15].

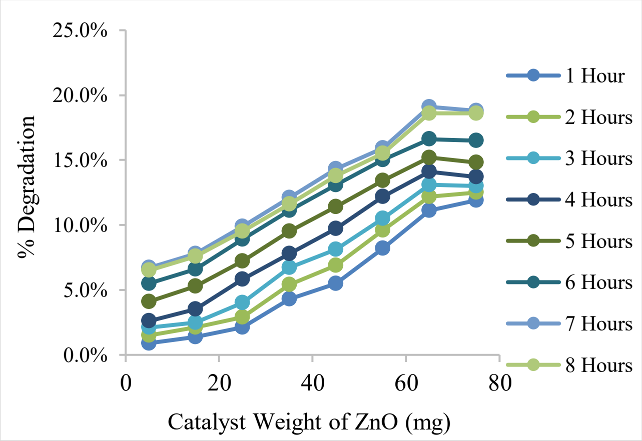

Figure 4. Determination of the Optimum Catalyst Weight of ZnO in a 250 mL Sample in 8 Hours of UV Radiation Time

The photocatalytic process is initiated when ultraviolet (UV) photons excite electrons from the valence band to the conduction band of the semiconductor, generating electron–hole pairs. The photogenerated holes ($h^+$) react with adsorbed hydroxyl ions ($OH^-$) or water molecules to produce hydroxyl radicals (•OH), while conduction band electrons ($e^-$) reduce dissolved oxygen to superoxide radicals ($O_2•^-$). These reactive oxygen species are primarily responsible for the oxidative breakdown of organic dyes in aqueous media, as widely observed in composite and doped photocatalyst systems in recent studies [6], [16]. However, the saturation of active sites can decrease degradation efficiency at elevated catalyst loadings or prolonged irradiation periods.Radical–radical termination reactions, such as the recombination of hydroxyl radicals to form hydrogen peroxide ($•OH + •OH \rightarrow H_2O_2$), also reduce the availability of active radicals and thus diminish photocatalytic activity.

The influence of pH on the photocatalytic degradation of Rhodamine B using ZnO and $TiO_2$ under UV irradiation is illustrated in Figure 5. Both photocatalysts exhibit a similar degradation trend, where the efficiency increases under acidic conditions and reaches a maximum at pH 5, followed by a decline at higher pH values. $TiO_2$ demonstrates superior photocatalytic activity, achieving a maximum degradation efficiency of approximately 48%, whereas ZnO reaches only approximately 26% at the same pH. This behavior is consistent with previous studies reporting that mildly acidic conditions favor photocatalytic reactions on semiconductor surfaces by enhancing dye adsorption and charge transfer efficiency [17], [18].

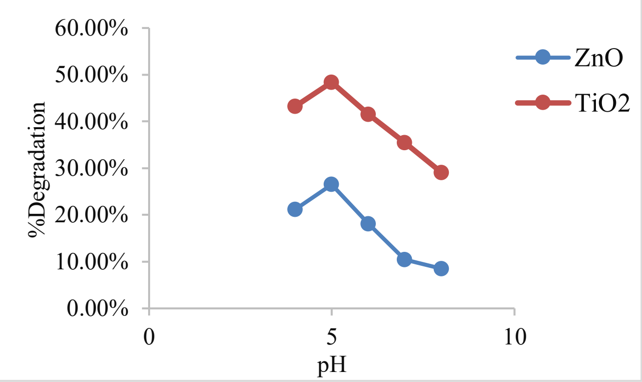

Figure 5. Determination of the Optimum pH

The enhanced degradation performance at pH 5 can be attributed to favorable electrostatic interactions between the positively charged photocatalyst surface and rhodamine B molecules, which promote adsorption and facilitate hydroxyl radical (•OH) formation. At alkaline pH, the photocatalyst surface becomes negatively charged due to excess $OH^-$ ions, resulting in electrostatic repulsion with dye molecules and reduced adsorption efficiency. Moreover, excessive $OH^-$ can act as radical scavengers, limiting the availability of reactive oxygen species, while ZnO exhibits lower chemical stability under alkaline conditions due to surface dissolution and photocorrosion effects. These factors collectively lead to a decrease in photocatalytic efficiency at higher pH values, confirming that weakly acidic conditions are optimal for rhodamine B degradation, particularly when using $TiO_2$-based photocatalysts [19], [20].

## 4. Conclusion

A comparative study between $TiO_2$ and ZnO photocatalysts revealed distinct differences in their physicochemical properties and photocatalytic performances. SEM analysis showed that both materials exhibited spherical morphologies with a tendency toward particle agglomeration; however, XRD analysis demonstrated that $TiO_2$ possessed a smaller crystallite size (38.9 nm) than ZnO (51.9 nm). This finding was consistent with the BET results, where $TiO_2$ exhibited a higher specific surface area (12.92 $m^2/g$) than ZnO (8.23 $m^2/g$), suggesting a greater availability of active sites for photocatalytic reactions. Under identical experimental conditions (rhodamine B concentration of 70 ppm and pH 5), $TiO_2$ required a lower catalyst loading (55 mg/250 mL) and a shorter irradiation time (6 h) than ZnO, which required 65 mg/250 mL and 7 h of irradiation. Consequently, $TiO_2$ achieved a significantly higher photodegradation efficiency of 48.40%, whereas ZnO achieved only 26.50%. These results demonstrate that $TiO_2$ exhibits superior photocatalytic performance compared to ZnO, primarily attributed to its smaller crystallite size and larger surface area, which enhance photon utilization and charge carrier-driven degradation processes.

## CRediT Authorship Contribution Statement

UH: Data Curation, Writing–Original Draft, Formal analysis, Visualization. LJK: Supervision, Conceptualization, Methodology, Writing, Review, And Editing. AI: Review and Editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

## Data availability

Data will be made available upon reasonable request.

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## Declaration of generative AI and AI-assisted technologies in the writing process

The authors utilized the ChatGPT tool to enhance the language and readability of the manuscript.

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