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# Optimization of $TiO_2$ Photocatalyst Through The Variation of Zinc Ratio for Degradation Organic Dye Methylene Blue

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## *Abstracts*

The synthesis of $ZnTiO_2$ photocatalyst materials using the sol-gel method has been successfully carried out, which will be used to degrade organic dyes in water solvent. Several conventional methods have been implemented to address organic pollutant water contamination. $ZnTiO_2$ is a semiconductor material and could be used as a photocatalyst material. In this study, $ZnTiO_2$ was successfully synthesized with variations of Zinc (Zn) at 8%, 13%, and 26%. Analysis of the band gap energy shows that the addition of Zn to the photocatalyst material decreases the bandgap values to 2.90, 2.87, and 2.79 eV, respectively. Furthermore, the acidity test of the photocatalyst material using the IR method confirms the presence of Zn with vibration spectra between Zn and Nitrogen atoms originating from ammonia. The interaction between the two can be seen in the vibration spectrum in the area between 1100 $cm^{-1}$ and 1200 $cm^{-1}$. From the measurement of the specific surface area density of the photocatalyst material, values of 0.015, 0.018, and 0.010 mol/g were obtained for variations of Zn at 8%, 13%, and 26% wt., respectively. Finally, a photocatalytic test was performed on $ZnTiO_2$ material against methylene blue (MB) dye for 1 hour using UV light and visible light. The results showed MB degradation values of 56%, 63%, and 68% under visible light and 80%, 87%, and 91% using UV light for each increased Zn variation. These results indicate the effectiveness of $ZnTiO_2$ in degrading methylene blue increases as the Zn metal ratio increases.

**Keywords:** Photocatalyst, $ZnTiO_2$, organic dyes, Zn doping, sol-gel method, acidity test, photocatalytic activity, methylene blue

## Introduction

Over the past decade, the pollution of freshwater by organic dyes has become a significant concern for governments worldwide. The wastewater from industries containing organic dyes poses a challenge due to its high toxicity, complex degradation process, intense coloration, and difficulty in colour removal [1]. Various methods, such as adsorption, coagulation, and filtration, have been utilized to remove organic dyes, but they are costly, inefficient, and generate large amounts of sludge [2]. Therefore, alternative technologies must be developed for the effective removal of toxic organic dyes from wastewater. Advanced oxidation processes (AOPs) have emerged as a highly efficient method for converting organic substances into simpler mineral products [3]. Among these processes, photocatalysis is considered the most promising solution due to its non-selectivity, efficiency in pollutant removal, and toxicity reduction [4]. However, complete degradation of organic dyes through photocatalysis has been found to be time-consuming and less effective in some studies, necessitating the development of improved photocatalysts.

Semiconductors have shown promise as materials for photocatalysts in degrading liquid organic waste [5]. They offer advantages such as low energy consumption, mild reaction conditions, and reduced secondary pollution, attracting widespread attention domestically and internationally [6]. However, some semiconductor materials have drawbacks like limited responsiveness to visible light and rapid recombination of electrons and holes [7]. To address these issues, the development of new photocatalysts with high efficiency, long-term stability, and the ability to utilize visible light is essential.

Titanium dioxide ($TiO_2$) is a semiconductor compound with photocatalytic properties that has three main crystal forms: anatase, rutile, and brookite, with anatase being the most used due to its high photocatalytic activity [8]. As a photocatalyst, $TiO_2$ absorbs ultraviolet photons, generating electron-hole pairs that can react with water and oxygen molecules to produce hydroxyl radicals that destroy organic pollutants. Rutile and anatase are the most stable and commonly used forms, with anatase having a more open tetragonal structure and a larger specific surface area compared to rutile [9]. The band gap of anatase is about 3.2 eV and rutile is about 3.0 eV, making $TiO_2$ ideal for photocatalytic and photovoltaic applications due to its inert, non-toxic, chemically stable, and photostable properties [10].

When exposed to ultraviolet light, $TiO_2$ produces highly reactive hydroxyl and superoxide radicals that can oxidize organic compounds on its surface, making it an ideal white pigment for various products [11]. To improve the performance of $TiO_2$ as a photocatalyst, doping with transition metals and non-metals is carried out to extend the light absorption range, reduce the electron-hole recombination rate, and enhance charge separation [12]. Modification with zinc (Zn) produces $ZnTiO_2$, which has better photocatalytic activity compared to pure $TiO_2$, with a reduced band gap energy allowing for more effective visible light absorption. $ZnTiO_2$ is used in photodegradation of pollutants, wastewater treatment, and air purification [11].

In this study, we will perform and report the degradation process of organic dyes, methylene blue (MB), contaminating water using $ZnTiO_2$ The photocatalyst synthesis method uses sol gel techniques, Measurement of $ZnTiO_2$ bandgap with different Zn ratio shows great potential in photocatalysis because all variation has band gap less than 3 eV. The presence of Zn doping in $TiO_2$ material is expected to delay the electron-hole recombination process in this semiconductor material.

**Material and Methods**

The chemicals used in this research are Zinc Acetate Dihydrate 99.5% ($Zn(CH_3.COO)_2.2H_2O$, Merck KGaA), Titanium (IV) Oxide ($TiO_2$, Sigma-Aldrich), Acetic acid 99.8% anhydrous (Merck KGaA), Ethanol (≥ 99.9% Sigma-Aldrich), Ammonium Hydroxide pro analysis (Sigma-Aldrich). Furthermore, Methylene Blue solution 10000 ppm was supplied by ROFA. All chemicals were gained commercially and used without any additional purification. In addition, to support the synthesis process of photocatalyst materials, we use various glassware from different brands such as IWAKI, Gratech, and Duran, as well as a range of volumetric sizes.

**Synthesis of $ZnTiO_2$**

The photocatalyst materials, $ZnTiO_2$, are synthesized using sol-gel method. The details are defined as follows. We have prepared three photocatalyst material compositions. These compositions are based on the weight percentage of Zinc Acetate dihydrate (% wt.) relative to the total weight of the raw materials, namely 8%, 13%, and 26% wt. Zn. The details of the mass of each photocatalyst raw material are presented in Table 1. The precursor of Titanium Oxide and Zinc Acetate dihydrate are dissolved in 100mL Ethanol and 2 mL Acetic Acid anhydrous. After the mixing process, the material was stirred (400 rpm) for 3 hours at 60°C. Subsequently, the mixture was dried and was calcined at 500°C for 3 hours to form the $ZnTiO_2$ phase.

**Characterization of $ZnTiO_2$**

The bandgap size of the photocatalytic material, $ZnTiO_2$, was characterized using a JASCO V 750 UV-Visible Spectrophotometer, while Infrared spectra were recorded in transmission mode within the range of 500 – 4000 $cm^{-1}$ using a NICOLET iS5 FT-IR Spectrophotometer, employing the KBr pellet method.

### Acidity Test

An ammonia solution is prepared in a closed 20 mL vial with a concentration of 10-20% v/v in a suitable organic solvent such as ethanol. $ZnTiO_2$ powder weighing between 20 and 50 mg is weighed, and the prepared ammonia solution is added to the same vial using magnetic stirring. To facilitate ammonia binding on the $ZnTiO_2$ surface, the mixture is heated to a temperature of 50-80°C and allowed to react for 12 hours. After the reaction is complete, the modified $ZnTiO_2$ solid is separated using filter paper. To remove unbound residual ammonia, the solid is dried in a vacuum oven for several hours at a temperature of 60-80°C. The obtained solid is then analyzed using FTIR in transmittance mode with KBr pellets.

### Photocatalytic Activity Test

The photocatalyst testing of $ZnTiO_2$ was conducted by mixing 12 mg of the photocatalyst material with 40 mL of Methylene Blue (MB) at a concentration of 20 ppm in a reactor vessel. Using a magnetic stirrer, the mixture was stirred at a speed of 400 rpm for 60 minutes. The experimental setup for testing the photocatalyst material uses a glass reactor with the equipment arrangement as shown in Figure 1. The photocatalyst performance tests were conducted under two types of light: UV light and sunlight. For UV light, the test was performed using a UV-A lamp with a wavelength range of 320-400 nm. For sunlight testing, the reactor containing the test solution was placed near a window to expose it to sunlight throughout the testing period. Additionally, the cooling jacket was filled with water, and the temperature was maintained at 30°C. This temperature was chosen as it is a moderate temperature typical for Jakarta and its surroundings.

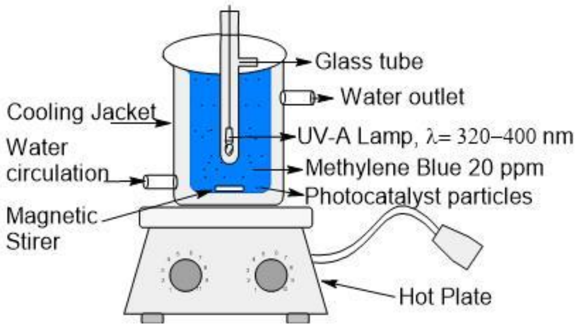


**Figure 1**. Experimental setup for fotocatalyst materials performance.

## Results and Discussion

### Synthesis of $ZnTiO_2$

This research involved the synthesis of $ZnTiO_2$ photocatalysts with four different Zn concentrations: 8%, 13%, and 26%. These variations in Zn concentration affect the energy and impact on the degradation of organic pollutants. The $ZnTiO_2$ samples were synthesized using zinc acetate ($(CH_3COO)_2Zn$) and titanium (IV) oxide ($TiO_2$) as the main precursors via the sol-gel method, with ethanol as the solvent due to its effective dissolution properties and low boiling point, which facilitates the solvent evaporation and gel formation processes [13].

Acetate ions acted as chelating agents, forming complexes with $Zn^{2+}$ ions and enhancing the dispersion of $TiO_2$ [14]. The resulting gel consisted of a polymeric network with ethanol trapped in its pores. The calcination process removed residual solvents and induced crystallization, improving the material's catalytic properties, thermal stability, and electrical or ionic conductivity [15].

**Table 1.** Mass of Synthesis $ZnTiO_2$

| Concentration Zn in $ZnTiO_2$, % wt. | Mass of Zn (gram) | Mass of $TiO_2$ | Volume Ethanol | Volume $CH_3COOH$ | Final Mass $ZnTiO_2$ | % Yield |
|---|---|---|---|---|---|---|
| **$ZnTiO_2$ 8%** | 0,65 gram | 7,19 gram | 100 mL | 2 mL | 4,387 gram | 55,9 |
| **$ZnTiO_2$ 13%** | 0,98 gram | 6,79 gram | 100 mL | 2 mL | 4,714 gram | 60,6 |
| **$ZnTiO_2$ 26%** | 1,96 gram | 5,59 gram | 100 mL | 2 mL | 4,147 gram | 54,9 |

From Table 1, the yield values or % yield from the synthesis of $ZnTiO_2$ photocatalysts were obtained. The yields for $ZnTiO_2$ with 8%, 13%, and 26% Zn content were 55.9%, 60.6%, and 54.9%, respectively. Factors influencing the yield of the synthesis include the different molar ratios of each precursor, the duration and speed of stirring the mixture, and the temperature used during the synthesis process [16].

**Band Gap Energy of Photocatalyst Materials**

Band gap energy analysis is a crucial step in the characterization of photocatalyst materials. Band gap energy defines the energy required for the excitation of electrons from the valence band to the conduction band, allowing these electrons to participate in photocatalytic reactions [17]. The band gap energy determines the wavelength of light that can be absorbed by the photocatalyst compound. $TiO_2$ has a large band gap energy, which induces- electron excitation and creates electron-hole pairs that are essential for photocatalytic reactions in pollutant degradation. To enhance photocatalytic efficiency, doping is performed by incorporating Zn into $TiO_2$, resulting in the $ZnTiO_2$ product [18].

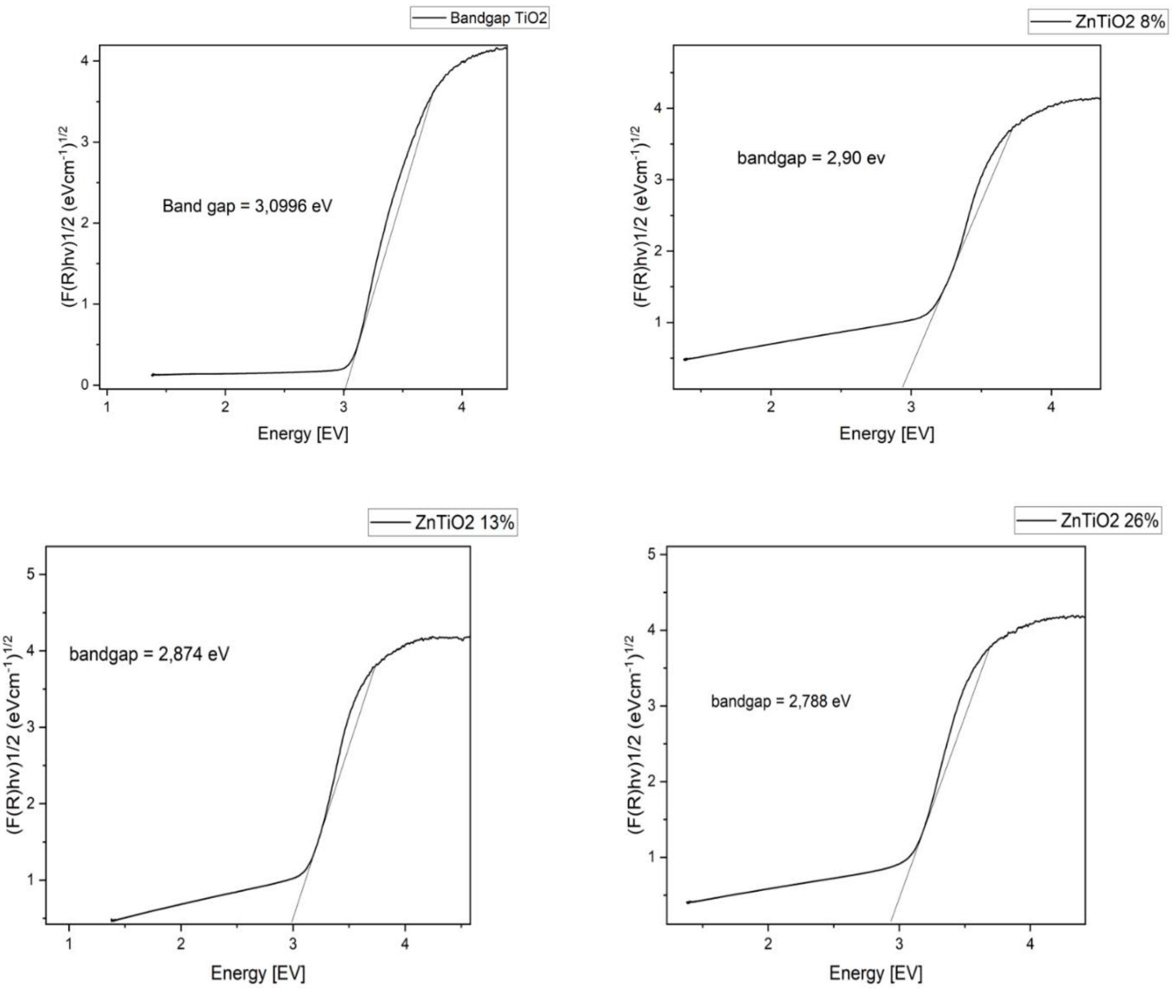


**Figure 2.** Band Gap Energy Graphic of $ZnTiO_2$ (0%;8%; 13%; & 26% of Zn ratio)

The band gap value of the mixture of $TiO_2$ and Zn is smaller due to the difference in electronegativity (EN) between Zn and Ti. According to the Pauling scale, the EN value of Zn is higher than that of Ti. Because of this difference, the energy level of Zn orbitals is lower than that of Ti orbitals for the same type of orbital. As a result, when their orbitals mix, the band gap energy of the $ZnTiO_2$ material decreases [18].

From the graph of (F(R)hv) $^{(1/2)}$ versus energy in Figure 1, the effect of Zn doping on $TiO_2$ in changing the band gap can be analysed. (F(R)hv) $^{(1/2)}$ is used in the band gap energy-analysis of $ZnTiO_2$ because this equation is specifically for semiconductors with direct electron-hole transitions from the valence band to the conduction band without any change in momentum [19]. Figure 1 shows the band gap energy of pure $TiO_2$ samples and band gap energy of $ZnTiO_2$ with different concentrations of Zn (8%, 13%, and 26%). The band gap energy values are explained in the following table:

**Table 2.** Band Gap Energy Values of $ZnTiO_2$

| Name of Sample | Bandgap Energy (eV) |
|---|---|
| **$TiO_2$** | 3,0996 |
| **$ZnTiO_2$ 8%** | 2,90 |
| **$ZnTiO_2$ 13%** | 2,874 |
| **$ZnTiO_2$ 26%** | 2,788 |

From the data in Table 2 above, the Zn doping process on $TiO_2$ can reduce the band gap energy value of the $TiO_2$ material. The presence of Zn atoms replacing Ti atoms in the $TiO_2$ structure (substitutional alloy mechanism) will decrease the band gap between the valence band and the conduction band of the synthesized material [20].

**Acidity Test**

The acidity test is a quantitative analysis method used to determine the acidic properties of a material, whether in solid, liquid, or gas form. This test aims to measure surface acidity, total acidity, or the acid-base properties of a material. In the context of material analysis such as photocatalysts, acidity testing is useful for estimating the number of active sites on a photocatalyst material. The acidity measured in this test includes Bronsted-Lowry acidity and Lewis's acidity. Since the synthesized material does not contain protons ($H^+$), the acidity test was only calculating Lewis's acid sites. In this acidity test, ammonia was used as the Lewis base because it has one pair of free electrons (lone pair), while the Lewis acids being measured are metal/ion Zn and ion Ti in the form of $TiO_2$ [21].

The acidity test is conducted using both qualitative and quantitative methods. Qualitative analysis involves IR spectroscopy, measuring absorbance between 500-4000 $cm^{-1}$ using a high-intensity NIR diode source with an In GaAs detector and a $CaF_2$ light reflector. IR spectra for acidity tests are shown in figure 3 and the specific information regarding to wavenumbers are presented in table 3. Quantitative analysis involves calculating the density of active sites on $ZnTiO_2$ are presented in table 4.

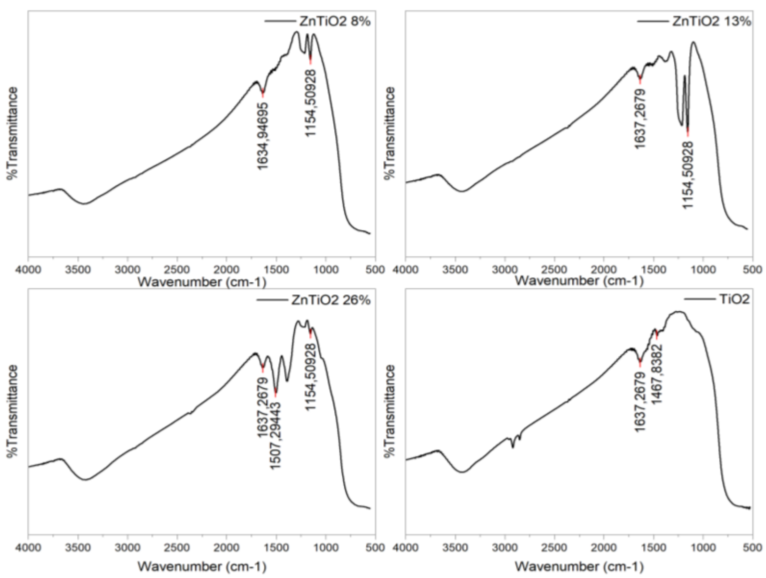


**Figure 3.** IR Spectra of $TiO_2$ and $ZnTiO_2$ Variants (8%; 13%; & 26% wt.) after Acidity Test

**Table 3**. Acidity Test Analysis Spectrum Data Using FTIR Instrument

| Vibration Spectrum ($cm^{-1}$) | | | | Bonding Interaction |
|---|---|---|---|---|
| $TiO_2$ | $ZnTiO_2$ 8% | $ZnTiO_2$ 13% | $ZnTiO_2$ 26% | |
| 1637 | 1634 | 1637 | 1637 | N-H*Stretching* |
| 1467 | - | - | 1507 | N-O *Bending* |
| - | 1154 | 1154 | 1154 | Triple coordination bond interaction between Zn-NH and increased Lewis's acid sites |

The presence of $NH_3$ as a Lewis base forms amine ($NH_2$) and amide (NH) groups on the photocatalyst surface, affecting acidity and reactivity. The acidity test measures how many ammonias molecules form covalent coordination bonds with metal ion active sites. FTIR spectra focus on wave numbers 1600-1700 $cm^{-1}$, 1400-1500 $cm^{-1}$, and 1100-1200 $cm^{-1}$ to estimate active site density [22].

**Table 4.** Active Sites Density Values of $ZnTiO_2$

| Sample | Area *peak* 1600-1700 ($m^{-1}$) | Area *peak* 1400-1500 ($m^{-1}$) | Area *peak* 1100-1200 ($m^{-1}$) | *Molar Extinction Coefficient* (mol/m) | Cross-sectional area IR ($m^2$) | Catalyst Mass (g) | Density of Active Sites (mol/g) |
|---|---|---|---|---|---|---|---|
| $TiO_2$ | - | 3,42863 | 3,32754 | 0,5 | 0,0000785 | 0,008 | 0,03314 |
| $ZnTiO_2$ 8% | 4,64897 | - | 3,54615 | 0,5 | 0,0000785 | 0,008 | 0,04020 |
| $ZnTiO_2$ 13% | 4,48175 | - | 3,84937 | 0,5 | 0,0000785 | 0,008 | 0,04061 |
| $ZnTiO_2$ 26% | 4,28816 | 3,77586 | 3,56330 | 0,5 | 0,0000785 | 0,009 | 0,05038 |

The results show that $Zn^{2+}$ ions on the $ZnTiO_2$ crystal surface form bonds with NH, and the density of active sites varies with Zn content [22]. Higher Zn concentrations (26%) result in more active sites and effective light absorption. This data correlates with photocatalytic testing results for methylene blue degradation.

**Photocatalytic Test Analysis**

The photocatalytic test was performed using $ZnTiO_2$ samples and the organic dye methylene blue. Photocatalytic testing is a method used to degrade organic pollutants. $TiO_2$ is commonly used for degrading organic pollutants due to its chemical and physical properties, and its semiconductor nature is suitable for photocatalytic processes [20]. However, $TiO_2$ has limitations in visible light absorption because of its large band gap energy. To address this, doping $TiO_2$ with metals like Zn reduces the band gap and improves light absorption.

In this study, photocatalytic tests were conducted using both visible light and UV light with a UV chamber box to compare the effectiveness of $ZnTiO_2$ with pure $TiO_2$. Methylene blue, an organic pollutant with conjugated double bonds and π-electrons, was used. The conjugated π-electron- pairs are easily excited to higher orbitals, leading to π-bonding transitions that absorb light at longer wavelengths [11].

The first analysis involved photocatalytic testing with visible light on methylene blue at a concentration of 20 ppm for 1 hour. The results are depicted in figure 4.

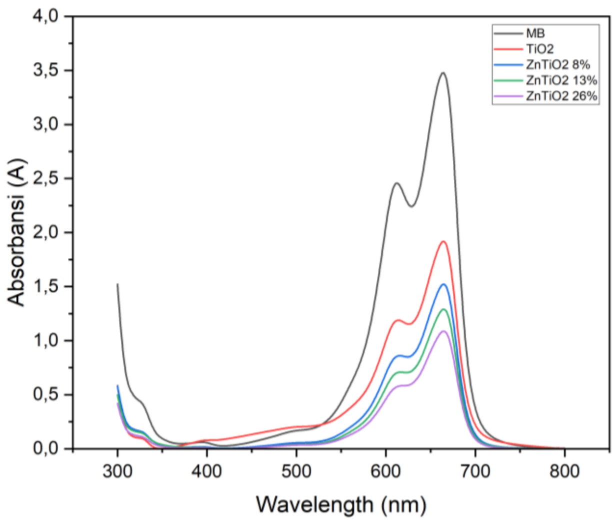


**Figure 4.** Absorbance Values of Methylene Blue after Testing Various Photocatalysts with Visible Light

In this photocatalytic test, a decrease in absorbance was obtained with the effectiveness values in table 5.

**Table 5.** Data Analysis of Effectiveness with Visible Light

| Sample | Absorbance $ZnTiO_2$ | MB 20 ppm decomposition (%) |
|---|---|---|
| Methylene Blue | 3,5 | 0 |
| $TiO_2$ | 1,9121 | 45 |
| $ZnTiO_2$ 8% | 1,5166 | 56 |
| $ZnTiO_2$ 13% | 1,2818 | 63 |
| $ZnTiO_2$ 26% | 1,0887 | 68 |

Next, a photocatalytic test was also conducted using UV light inside a UV chamber box on methylene blue with a concentration of 20 ppm for 1 hour. The results are presented in figure 5.

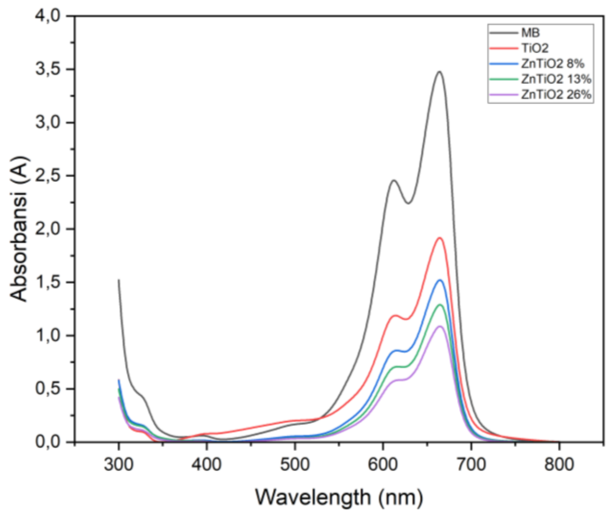


**Figure 5.** Absorbance Values of Methylene Blue after Testing Various Photocatalysts with UV Light

In this photocatalytic test, a decrease in absorbance was obtained with the effectiveness values in table 6.

**Table 6.** Data Analysis of Effectiveness with Ultraviolet Light

| Sample | Absorbance $ZnTiO_2$ | MB 20 ppm decomposition (%) |
|---|---|---|
| Methylene Blue | 3,5 | 0 |
| $TiO_2$ | 1,6811 | 52 |
| $ZnTiO_2$ 8% | 0,6801 | 80 |
| $ZnTiO_2$ 13% | 0,4489 | 87 |
| $ZnTiO_2$ 26% | 0,3172 | 91 |

In this context, photocatalytic activity is marked when solar energy absorption occurs by the photocatalyst, which is produced from both visible light and UV light. The absorbed solar energy has energy levels like or even greater than the bandgap energy of the photocatalyst. This process results in the excitation of electrons ($e^-$) from the valence band to the conduction band, creating positively charged holes ($h^+$) in the valence band [20].

Next, the electrons in the conduction band react with oxygen ($O_2$), forming superoxide anion radicals ($\bullet O^{2-}$). Meanwhile, the holes ($h^+$) in the valence band react with water molecules ($H_2O$) in the solution, producing hydroxyl radicals (•OH). Both the (•$O^{2-}$) and (•OH) radicals are highly reactive species capable of degrading methylene blue molecules into simple end products like water, $CO_2$, sulfate ions ($SO_4^{2-}$), and nitrate ions ($NO_3^-$) [20].

From the two tests conducted, the doping of Zn in $TiO_2$, shown in tables 5 and 6, can reduce the absorbance value absorbed by the material. This is crucial for enhancing photocatalytic activity. $ZnTiO_2$ with 8% Zn shows significant results in reducing absorbance compared to pure $TiO_2$. The 26% Zn doping also shows better results in reducing absorbance and increasing photocatalytic activity. The higher the Zn content added, the smaller the bandgap used in the photocatalytic process. More and faster-excited electrons in the conduction band result in the degradation of methylene blue. This increases the reduction and oxidation processes of electrons in large quantities, enhancing the effectiveness of the photocatalyst in the degradation process. The tests using visible light and UV light are based on comparing the absorbance values of methylene blue as a baseline and the absorbance after degradation with the photocatalyst [19].

In optimizing the doping variation to reduce bandgap energy and enhance the photocatalytic process of $TiO_2$, electron-hole recombination remains a limiting factor. Zn can only reduce the bandgap energy of $TiO_2$ without slowing down the electron-hole recombination occurring during the photocatalytic test. Electron-hole recombination is a process where electrons in the conduction band rejoin holes in the valence band, releasing energy in the form of light bias. This process occurs because electrons in the conduction band move quickly, or the energy gap is very close. This allows them to interact and easily rejoin the holes in the valence band. The fast recombination process reduces the number of electrons and holes needed for the photocatalytic reaction, decreasing the effectiveness of methylene blue degradation due to the reduced formation of reactive species like hydroxyl radicals and superoxide radicals [20].

**Conclusion**

The synthesis of the $ZnTiO_2$ photocatalyst material and its characterization, as well as the photocatalytic testing with this photocatalyst, were conducted in this study. The conclusions that can be drawn from the results of this research are as follows:

1. The synthesis of $ZnTiO_2$ photocatalysts using the sol-gel method resulted in yields of 55.9% ($ZnTiO_2$ 8%), 60.6% ($ZnTiO_2$ 13%), and 54.9% ($ZnTiO_2$ 26%). Among these, the synthesis process of $ZnTiO_2$ 13% yielded the best result. The synthesized photocatalysts were then tested using several characterization methods. The band gap energy analysis using UV-RDS spectrophotometry showed a reduction in the band gap energy due to the doping of Zn into $TiO_2$, with respective values of 2.90 eV ($ZnTiO_2$ 8%), 2.874 eV ($ZnTiO_2$13%), and 2.788 eV ($ZnTiO_2$ 26%). The acidity test using FTIR analysis on the reaction between $ZnTiO_2$ and $NH_3$ focused on three wavenumbers: 1600-1700 $cm^{-1}$, 1400-1500 $cm^{-1}$, and 1100-1200 $cm^{-1}$. These vibration values indicate the presence of Lewis acid-base reactions on the surface of $ZnTiO_2$, with active site density values of Zn being 0.04020 mol/g ($ZnTiO_2$ 8%), 0.04061 mol/g ($ZnTiO_2$ 13%), and 0.05038 mol/g ($ZnTiO_2$ 26%).
2. The photocatalytic degradation of methylene blue was analyzed using two methods: visible light photocatalytic testing and UV light photocatalytic testing. In the visible light photocatalytic testing, the effectiveness values were 56% ($ZnTiO_2$ 8%), 63% ($ZnTiO_2$ 13%), and 68% ($ZnTiO_2$ 26%). In the UV light photocatalytic testing, the effectiveness values were 80% ($ZnTiO_2$ 8%), 87% ($ZnTiO_2$13%), and 91% ($ZnTiO_2$ 26%). These effectiveness values indicate the comparison of photocatalytic test results between the absorbance of methylene blue and the photocatalytic test results of $ZnTiO_2$ variants

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