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Synthesis of Zinc Oxide (ZnO) Nanoparticles Using Microwave Assistance and Its Application as Photocatalyst in Degrading Methylene Blue

Wahyu F. Nursalam [a], Lidya I. Momuat [a], Henry F. Aritonang [a,*]

[a] Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sam Ratulangi, Jl. Kampus Umsrat, Kleak, Manado 95115 Sulawesi Utara, Indonesia

*Corresponding author: henryaritonang@unsrat.ac.id

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Abstract

The research has been carried out on synthesizing zinc oxide (ZnO) nanoparticles with the help of microwaves. ZnO nanoparticles were synthesized in the microwave at 100°C with heating times of 50, 90, 130, 170, and 210 minutes. The synthesized ZnO nanoparticles were characterized using X-Ray Diffractometry (XRD) and Energy Dispersive Spectroscopy (EDS). The results were analyzed for their ability as a photocatalyst against methylene blue (MB) solution using UV-Vis spectrophotometry. The results revealed that the synthesized product was a combination of ZnO and $Zn(OH)_2$, as supported by XRD ICSD data no. 31052. However, the analysis results with EDS showed that the synthesized product only contained Zn and O elements, indicating that the product had ZnO. ZnO nanoparticles synthesized for 170 minutes of heating showed the highest ability to degrade MB of 85.8247% with a contact time of 150 minutes, while heating times of 50, 90, 130, and 210 minutes had percentage of MB degradation of 84.6065%, 81.0130%, 82.0866%, and 82.9275%, respectively.

1. Introduction

Industrial development is marked by the number of industries that produce various human needs, such as paper, textiles, and leather tanning. As the industry expands, it generates an increasing amount of waste, which can severely harm human health and the environment. Synthetic dyes are included in many industrial wastes [1]. Colored organic compounds that are difficult to decompose are methylene blue, remazol yellow, tartrazine, and others. Discharging colored waste into the environment is a polluting factor that can be hazardous, have toxic effects, and diminish light penetration in contaminated wastewater [2].

The waste becomes a problem for the environment if it is not appropriately managed, primarily synthetic dye waste. Synthetic organic dyes such as methylene blue (MB) are cationic heterocyclic aromatic compounds that have toxic properties, are difficult to decompose, and reduce light penetration in water [3]. Numerous methods, including chlorination, biodegradation, and ozonation, are employed to address the issue of this dye waste. These methods are much less effective in Indonesia due to their relatively costly operational expenses [4]. One method that is relatively inexpensive and easy to implement in Indonesia is photodegradation. The principle uses a photocatalyst derived from semiconductor materials, such as TiO_2, ZnO, Fe_2O_3, and CdS [5]. ZnO semiconductor photocatalysts have been widely used to remove various aqueous pollutants including organic compounds [6, 7].

Various methods have been used to synthesize ZnO nanoparticles, including direct precipitation [8], homogeneous precipitation [9], solvothermal method [10], sonochemical method [11], micelle reverse system [12], sol-gel method [13], biotemplate [14] and coprecipitation method [15].

The usage of microwave heating in synthesizing ZnO nanoparticles is currently quite limited. In general,

synthesizing nanoparticles using microwave heating is more profitable than conventional heating methods because conventional heating methods are prolonged and inefficient [16]. The microwave was chosen for synthesis to make the reaction rapid and environmentally safe (green synthesis) [17].

Based on the description above, this research focused on synthesizing nanoparticle ZnO using an irradiation heating process in a microwave, which can then be used as a photocatalyst in degrading MB synthetic dyes. The resulting ZnO nanoparticles were characterized using X-Ray Diffractometry (XRD) and Energy Dispersive Spectroscopy (EDS), as well as analyzing the optimum time of its ability as a photocatalyst to degrade MB dyes.

2. Experimental

2.1. Materials

The materials used for this study were 70% ethanol, distilled water, $Zn(NO_3)_2.4H_2O$, NH_3, and methylene blue.

2.2. Synthesis of ZnO Nanoparticles

The synthesis of ZnO nanoparticles used in this study followed the procedure by Hasanpoor *et al.* [18] with modifications. All chemical reagents used were of analytical grade. A solution concentration of 0.6 M was obtained by dissolving 78.3 grams of $Zn(NO_3)_2.4H_2O$ in 500 mL of distilled water. Droplets of ammonia solution were then added until the solution's pH reached 11.5. The five beakers were prepared, and 100 mL of the solution was poured into each beaker. The five solutions were heated in the microwave at 100°C with different heating times, 50, 90, 130, 170, and 210 minutes respectively. The synthesized product was sonicated for 30 minutes at a speed of 700 rpm, then centrifuged for 10 minutes. The resulting product was filtered through filter paper and washed four times with distilled water and twice with 70% ethanol. The precipitate was dried in an oven at 100°C for 2 hours. X-Ray Diffractometry (XRD) and Energy Dispersive Spectroscopy (EDS) were employed to analyze the results.

2.3. Photocatalyst Analysis

The activity of the photocatalyst used in this study followed the procedure of Labhane *et al.* [19] with modifications. A 20 mL of 5 ppm methylene blue solution was poured into five glass tubes, followed by 0.01 g of a calcination result sample in each tube. The glass tubes were inserted into the reactor and irradiated with a UV lamp for 30-minute intervals. After 30 minutes, the tubes were removed, filtered, and centrifuged for 30 minutes, then analyzed for the dye remaining in the solution using a UV-Vis spectrophotometer. The same procedure was conducted for 60, 90, 120, and 150 minutes. Percentage degradation was calculated using Equation 1.

$$\% \text{ Degradation} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100\% \quad (1)$$

where C_0 is the initial concentration and C_t is the concentration after irradiation.

3. Results and Discussion

3.1. Synthesis of ZnO Nanoparticles

Synthesis of ZnO nanoparticles using precursors ($Zn(NO_3)_2.4H_2O$) occurred under alkaline conditions by adding ammonia solution to the reaction. According to Wang *et al.* [20], ammonia solution plays an essential role in the formation of hydroxide from zinc ions, as presented in reactions (2) and (3).

$$8Zn(NO)_{3(s)} + 6NH_{3(l)} + 13H_2O_{(l)} \rightarrow 8Zn(OH)_{2(s)} + 7NH_4NO_{3(aq)} \quad (2)$$

$$NH_{3(l)} + H_2O_{(l)} \rightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \quad (3)$$

In this study, $Zn(OH)_2$ to ZnO exchange followed the solubility-precipitation mechanism [21]. Formation of ZnO from $Zn(OH)_2$ through dissolution and re-precipitation mechanisms. $Zn(OH)_2$ dissolves in water and precipitates as ZnO in $Zn(OH)_2$ solution. This can explain the growth of ZnO crystals from a solution of $Zn(OH)_2$ through the help of heating by microwave. Increasing the heating time at higher temperatures can provide sufficient energy to transform the crystallization of $Zn(OH)_2$ to ZnO through dehydration and atomic rearrangement. The reactions that can occur in the formation of ZnO from $Zn(OH)_2$ are shown in reaction (4) [22].

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (4)$$

The ZnO white crystals were obtained and characterized using XRD to determine the phase and crystal size, as well as EDS analysis to identify the composition of the elements using the SEM SU3500.

3.2. XRD Analysis

XRD analysis was performed to determine the formation of ZnO particles from the precursor. On the diffractogram, a diffraction pattern appears with peaks in region 2θ, as shown in Figure 1.

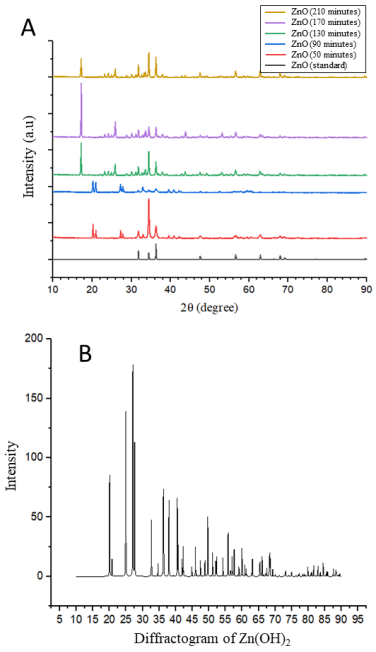


Figure 1. Diffractogram patterns of (a) ZnO standard and synthesized ZnO with different microwave heating times of 50, 90, 130, 170, and 210 minutes (b) $Zn(OH)_2$

Table 1. Comparison of the 2θ (°) area of the synthesized products at different microwave heating times and ZnO and $Zn(OH)_2$ standard

$Zn(OH)_2$ (standard) 2θ (°)	ZnO (*Anatase*) (standard) 2θ (°)	Synthesized products 2θ (°)				
		50 min	90 min	130 min	170 min	210 min
20.056		20.210	20.176	19.203	19.243	19.246
20.780		20.931	20.898			
24.936		25.056	25.044	24.885	24.899	24.905
27.055		27.246	27.224			
27.600		27.828	27.797			
	31.791	31.787	31.733	31.758	31.803	31.770
32.669		32.923	32.897	32.651	32.670	32.653
	34.446	34.429	34.411	34.424	34.454	34.427
36.298	36.278	36.258	36.247	36.239	36.278	36.246
37.958		38.192	38.157	37.895	37.931	37.883
40.488		40.836	40.826			
42.262		42.145	42.136	42.871	42.897	42.858
45.946		45.204	45.150	45.642	45.699	45.667
	47.570	47.555	47.693	47.504	47.546	47.521
51.144				51.042	51.069	51.067
55.795				55.350	55.391	55.349
	56.629	56.589	56.141	56.536	56.585	56.552
57.905		57.964	57.953	58.571	58.570	58.575
59.981		59.539	59.545	59.584	59.571	59.612
	62.894	62.838	62.827	62.791	62.835	62.808
63.449				63.357	63.424	
66.090	66.411	66.532	66.175	66.288	66.407	66.330
	67.985	67.923	67.702	67.884	67.924	67.875
68.381		68.965	68.832			
	69.123			69.029	69.053	69.029
	72.567			72.484	72.238	72.481
	76.959			76.981	76.968	76.875
84.507				84.614		84.770

Table 1 shows that all the products synthesized using microwave have a 2θ region similar to the 2θ region of the JCPDS database for ZnO and $Zn(OH)_2$. The size of the ZnO nanoparticle crystals and the synthesized products were determined using the Scherrer equation based on *Full Width at Half Maximum* (FWHM) data and are shown in Table 2.

Table 2 shows that the microwave heating time for 90 minutes has a relatively smaller particle size than samples with other time variants. Table 2 shows that the crystallite size of the ZnO nanoparticle samples and the results of the synthesized product at different microwave heating times of 50, 130, 170, and 210 minutes have crystallite sizes of more than 30 nm.

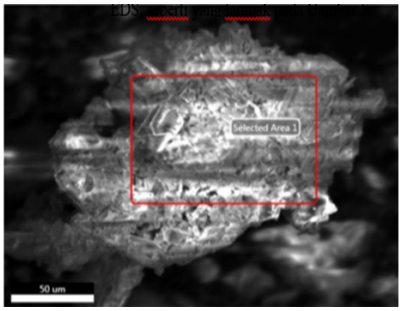
Table 2. The crystal size of ZnO and synthesized nanoparticles at different microwave heating times

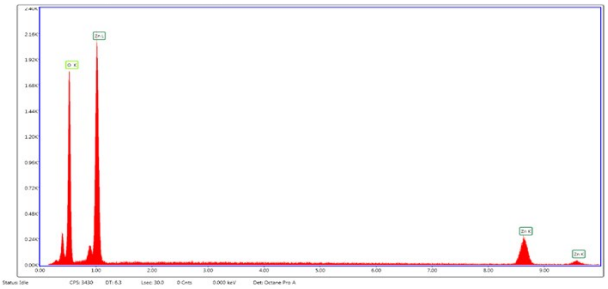
Variation of heating times (minutes)	D (nm) ZnO*	D (nm) Mixed**
50	34.6360	46.8715
90	27.1324	34.1450
130	68.0642	53.7027
170	50.1602	44.8624
210	73.2953	54.8830

*taken from the 2θ ZnO region
**taken from the 2θ region of ZnO and $Zn((OH)_2$

3.3. EDS analysis

The results of the XRD analysis show that the synthesized product was suspected of containing two products, ZnO and $Zn(OH)_2$, and these results were compared with the EDS data, as shown in Figure 2.





eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.
O K	25.74	58.62	668.43
ZnK	74.26	41.38	264.78

Figure 2. EDS data of synthesized product

Figure 2 shows that the elements detected in the synthesized product are Zn and O atoms, with a content of 74.26% and 25.74%, respectively. This result indicates that the synthesized product has been reduced from the precursor ($Zn(NO_3)_2.4H_2O$), and it can be said that the synthesized product is a mixture of ZnO and $Zn(OH)_2$, as well as the results of XRD analysis. According to Stojilovic [22], H atoms are typically undetectable by EDS analysis due to their extreme lightness (only having 1 electron).

3.4. Photocatalyst activity

3.4.1. Analysis of UV-Vis spectroscopy test results

The synthesized nanoparticle product was placed in a tube, and 20 mL MB was added before being analyzed using a UV-Vis spectrophotometer at a wavelength range of 500–700 nm to determine the characteristics of the synthesized nanoparticle formed based on the peak spectrum.

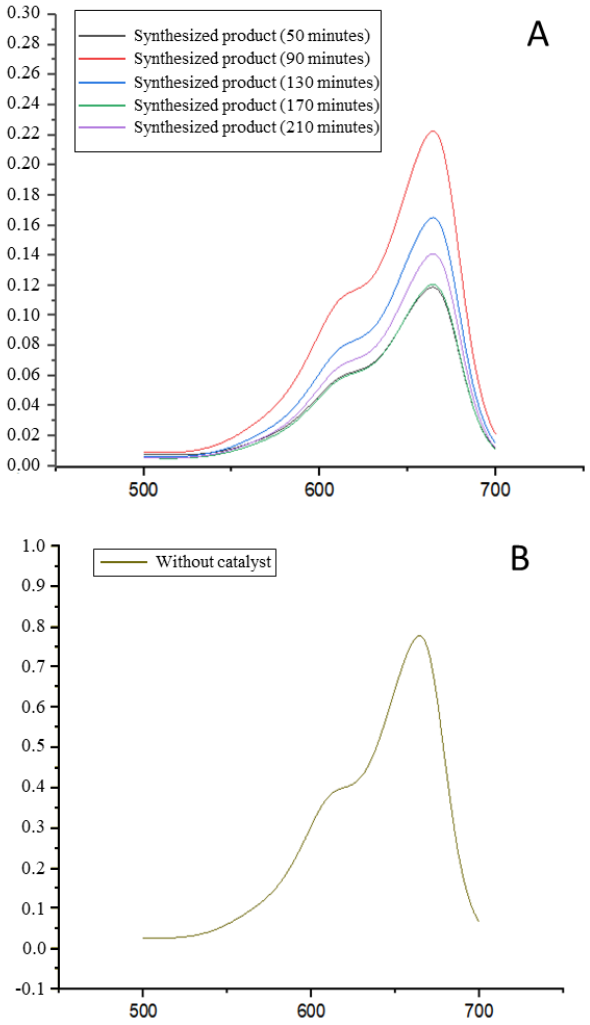


Figure 3. UV-Vis absorption spectra of MB solution (a) synthesized nanoparticles (b) without catalyst

Figure 3 shows that the absorption peak positions of all synthesized products were the same at 664.5 nm for both the synthesized nanoparticle products (50, 90, 130, 170, and 210 minutes) and the MB solution itself. The synthesized nanoparticle products with a microwave heating time of 90 minutes had a relatively higher absorbance than those with other time variants. The synthesized nanoparticles with microwave heating time of 50 minutes had the lowest absorbance, indicating that 50-minute heating had a better ability as a photocatalyst than other time variants in the degradation of MB solution samples relatively.

3.4.2. Photocatalyst activity of synthesized nanoparticle products

Photodegradation activity was carried out on MB dyes using a photocatalyst of synthesized nanoparticle products. The amount of MB dye that was degraded (% degradation) by the nanoparticle photocatalyst at a concentration of 5 ppm MB in 20 mL is presented in Figure 4.

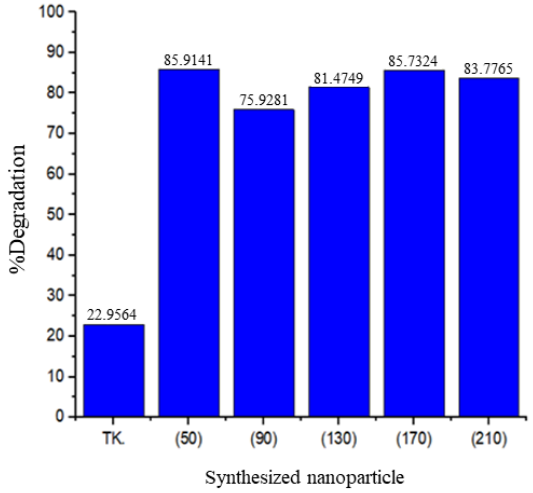


Figure 4. % degradation of MB by synthesized nanoparticles at various microwave heating times

Figure 4 shows that the synthesized nanoparticles at all different microwave heating times can degrade MB solution with a capacity above 70%. The percentage of MB degradation after being degraded without a catalyst and the presence of a catalyst with a time-variant of 50 minutes has a relatively higher ability to degrade than the time variations of 90, 130, 170, and 210 minutes. The synthesized product with 90 minutes of microwave heating had the lowest percentage of MB degradation (75.9281%). This result shows the photocatalyst ability of the synthesized nanoparticles can degrade MB samples.

3.4.3. Photodegradation of methylene blue with the variation of exposure time

The photolysis process begins with UV irradiation of the ZnO photocatalyst, resulting in an electron excitation, an excess energy (excitation) electron from the valence band to the conduction band. The electron excitation creates a hole in the valence band (h_{vb}^{+})) which can react with hydroxy ions (OH^{-}), which can form hydroxyl radicals (·OH) which are strong oxidizing agents. On the other hand, electrons in the conduction band (e_{cb}^{-}) react with the oxygen around them to produce superoxide radical ions (O_2^{-}), which act as reducing agents [23]. Electrons from the valence band are excited to the conduction band due to absorbing energy from UV light. As a result, there will be a vacancy of electrons (holes) in the valence band. Hole (h^{+}) can oxidize water molecules into radical hydroxyl molecules (•OH) [24].

Photodegradation activity was carried out on methylene blue (MB) using nanoparticles samples synthesized with various microwave heating times of 50, 90, 130, 170, and 210 minutes. The amount of MB dye degraded (% degradation) by nanoparticles synthesized as a photocatalyst at a concentration of 5 ppm MB with contact times of 30, 60, 90, 120, and 150 minutes is presented in Figure 5.

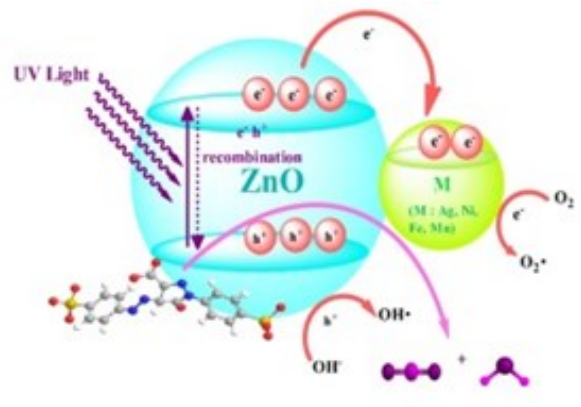


Figure 5. Photodegradation mechanism of MB dye by transition metal-doped ZnO [25]

Figure 6 shows that all synthesized nanoparticle photocatalyst products have the ability to degrade MB solutions based on degradation time. The photocatalyst product (50 minutes) can degrade MB in the 70–90% range, with the highest percentage of MB degradation at 150 minutes of contact time (84.6065%). The photocatalyst product (90 minutes) can degrade MB above 76%, with the highest percentage of MB degradation at 30 minutes (81.013%). The photocatalyst product (130 minutes) can degrade MB above 79%, with the highest percentage of MB degradation at 150 minutes (82.0866%). In addition, the photocatalyst product (170 minutes) has the ability to degrade MB above 76% with the highest percentage of MB degradation at 150 minutes (85.8247%) and the photocatalyst product (210 minutes) has the ability to degrade MB above 75% with the highest percentage of MB degradation was at 150 minutes (82.9275%).

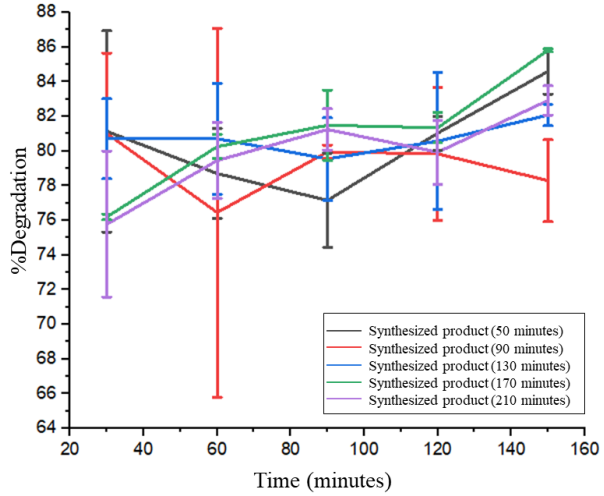


Figure 6. Effect of contact time on photocatalytic degradation of MB dye

4. Conclusion

ZnO nanoparticles can be synthesized using microwave assistance, characterized by the presence of peaks in the 2θ region and matched to ICSD standards based on XRD analysis and EDS analysis. The resulting ZnO nanoparticles are mixed with $Zn(OH)_2$ products. The synthesized product shows its activity as a photocatalyst in degrading methylene blue (MB) dye.

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