The study of structural properties and photocatalytic activity of ZnO prepared by ultrasonic assisted precipitation method

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Abstract. ZnO is a semiconductor that has excellent activity as photocatalyst under UV light region. ZnO is precipitated by adding oxalate acid onto zinc acetate dehydrate solution with ultrasonic assisted at various times and flattened at 500 °C. The structural properties of the ZnO samples are characterized by X-Ray Diffraction (XRD) and Brunauer-Emmett-Teller (BET). XRD result has confirmed the ZnO structure as hexagonal phase. Rietveld refinement of XRD pattern by La Beil method is employed to analyze the lattice parameters of ZnO. It provides that ZnO as wurtzite with accurate values. Debye-scherrer equation examines the crystallite size. It is confirmed that the crystallite size of ZnO is decreased by ultrasonic assisted at precipitation. BET result shows that ultrasonic assisted could increase the surface area of ZnO, which are 45.64 m²/g of ZnO without ultrasonic assisted and 143.487 m²/g of ZnO with ultrasonic assisted along 2 hours. The photocatalyst experiment is set up to analyze the photocatalytic activity of ZnO for degradation of methylene blue under UV light irradiation. By significantly that decolorization of methylene blue occurred at pH 10 for 30 minutes irradiation. The photocatalytic activity for ZnO samples with an hour and 2 hours ultrasonic assisted are 79.54 % and 86.50 % respectively, whereas ZnO sample without ultrasonic assisted is 70.90 %, and almost all of methylene blue contaminant have done degraded successfully after 120 minutes irradiation. According to the results, the structural properties and photocatalytic activity of ZnO are increased as consequence to the presence of ultrasonic assisted on precipitation.

1. Introduction

Environmental problems are still a topic that is widely discussed. There are many pollutions which can damage the environment, such in water, soil and air needs more attention and must be solved. One of the pollutant is the contamination of organic compounds such as dyes in the wastewater. These organic compounds are mostly produced by industries, especially in the textile sector. Waste treatment in some textile industries are not meeting the standards as it is costly. The content of organic chemicals in wastes that are difficult to degrade naturally [1].

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In order to reduce the levels of organic waste contamination, various biological, physical and chemical methods have been carried out. Bioremediation systems could degrade organic pollutants by microbe activity, but it requires a large area and limitations in degrading complex organic substances [2]. Chemical method such as coagulation is often used to solve the problem. But in this process, it produces a sludge that must be removed [3]. Physical methods with membrane filtration and adsorption are such a simple method, but either the membrane or adsorbent must be replaced periodically and it requires more costs [4,5-10]. Chlorination and ozonation methods are also effective method, but they require high operational costs [11,12].

Photocatalyst is one of the effective ways to decrease the organic waste contamination such as textile dyes. It can degrade organic compounds into compounds that have simpler structure and smaller toxicity level [13]. Photocatalyst use photon as a source of emission for activation the surface of the catalyst. When a photon is absorbed by semiconductor, it occurs photoexcitation. Electron from valence band transferred to the conduction band and form electron-hole pairs. Both holes and electrons on the surface of the catalyst will react with H$_2$O and oxygen around it. The result of these reactions are reducing agents namely radical hydroxyl compounds and radical superoxide anion which are active in degrading organic compounds [14].

Semiconductor materials such as TiO$_2$ [15], ZnO [16], Fe$_2$O$_3$ [17] and SnO$_2$ [18] can be used as Photocatalyst. ZnO is widely studied because of being environmentally friendly and relatively lower cost. It has interesting physical and chemical properties like: thermal stability, non-toxic and wide-bandgap. ZnO has a slightly wider bandgap (3.07 eV) compared to TiO$_2$ (3.00 eV), that makes ZnO have better performance to absorb the spectrum of sunlight than TiO$_2$ [5].

In this study, ZnO prepared by precipitation method. Precipitation method is a simple method for forming a metal oxide using a metal salt or metal hydroxy as the precursor. During precipitation process, ultrasonic vibration was given to the solution to obtain better ZnO in its physical properties. Ultrasonic vibrations caused the formed precipitate particles will be dispersed in solution and could prevent the agglomeration. The obtained particles would have smaller size due to the vibration motion of the ZnO particles caused by ultrasonic assisted [19]. As it is known, when a material has smaller particle size, the surface area as active side of its material will be wider. It will have a significant impact to the reaction rate when the material applied as photocatalyst. In the presence of ultrasonic assisted during precipitation, the obtained ZnO could have good physical properties and better performance to degrade methylene blue as dye contaminant.

2. Materials and methods

Chemicals used in this research was Zn(OAc)$_2$.2H$_2$O (Merck®), oxalic acid (Merck®), HCl (37%, Merck®), NaOH (Merck®), methylene blue (Merck®), and aqua DM.

2.1. Preparation of ZnO

10.79 g Zn(OAc)$_2$.2H$_2$O was dissolved in 50 mL distilled water. Oxalic acid solution (9.29 g on 50 mL distilled water) was slowly poured into the solution and stirred for 15 minutes. The mixed solution is made into three different variations. Two variations were given ultrasonic vibration for an hour and 2 hours, and one other variation without the treatment. The obtained precipitate is filtered, dried at 110 °C for 12 hours, and flattened at 500 °C for 2 hours. The obtained materials (ZnO powder) were characterized by X-Ray Diffraction (XRD) and Brunauer-Emmett-Teller (BET).

2.2. Photocatalyst activity

2.2.1. Determination of pH optimum. 20 mL of 10 g/L methylene blue solution in 100 ml beaker is set up to the various pH, 4, 6, 8 and 10 by adding NaOH solution and HCl solution. ZnO powder (0.02 g) was added to the solution and gave ultrasonic vibration for a minute. The suspension was irradiated with UV light (353 nm) in various irradiation times for 30 minutes. The samples were separated by centrifuge
at a speed of 3000 rpm for 10 minutes. The concentration of methylene blue solution after irradiation was measured by UV-Vis spectrophotometer at a wavelength of 664 nm.

2.2.2. Photodegradation efficiency in various time irradiation. ZnO powder (0.02 g) was added to 20 ml of 10 g/L methylene blue solution in 100 ml beaker and gave ultrasonic vibration for a minute. The suspension was irradiated with UV light (353 nm) in various irradiation times for 15.30, 45, 60, 75, 90, 105 and 120 minutes. The samples were separated by centrifuge at a speed of 3000 rpm for 10 minutes. The concentration of methylene blue solution after irradiation was measured by UV-Vis spectrophotometer at a wavelength of 664 nm.

3. Results and discussion

3.1. Characterization of ZnO
The XRD pattern of the prepared ZnO with various time ultrasonic assisted shown in Figure 1. XRD pattern recorded pure ZnO as wurtzite phase for those synthesized compared to standard ZnO (PDF number #96-900-4182).

![XRD pattern of ZnO various ultrasonic assisted time.](image)

Rietveld refinement is performed to determine the lattice parameters of ZnO. By using the Le Bail method in Rietica program, changes in the crystal lattice parameters caused by ultrasonic assisted can be detected. In general, the success of matching with the Le Bail method is determined by some criteria. The difference plot between the diffraction pattern (black line) and the calculation pattern (red line) has a low fluctuation value (green line) and tends to approach a straight line. A goodness-of-fit (GoF) value approaching 1 or no more than 4%, the results of the profile factor (Rp) and the weighted profile factor (Rwp) <20% [20].

Figure 2 showed the results of refinement has a match between standard ZnO and all of ZnO synthesized. The ZnO diffraction pattern is shown with black dots reached by the diffraction pattern in the form of a red line. The lattice parameter measured by rietveld refinement in Table 1 showed that all of the prepared ZnO reach accurate value compared to standard. The value of cell parameters (a, b and c) became shorter along with the increase in the time of ultrasonic vibrations given during precipitation process. This can be interpreted that the crystal lattice size was decreased.
Based on XRD result, the value of particle size of ZnO without ultrasonic assisted is 17.69 nm obtained by very conventional Debye Scherrer method followed by this equation: \(D = \frac{k \lambda}{\beta \cos \theta}\). The particle size decreased by the time of ultrasonic assisted given during precipitation, 16.10 nm for an hour and 14.64 nm for 2 hours treatment. Based on this data, ZnO prepared by ultrasonic assisted can give better physical properties of ZnO.

### Table 1. Lattice parameter of ZnO.

| Lattice parameter | ZnO standard | ZnO-0 | ZnO-1 | ZnO-2 |
|-------------------|--------------|-------|-------|-------|
| Phase             | hexagonal    | hexagonal | Hexagonal | hexagonal |
| Space group       | P63mc        | P63mc | P63mc | P63mc |
| a (Å)             | 3.25330      | 3.25543 | 3.24922 | 3.24922 |
| b (Å)             | 3.25330      | 3.25543 | 3.24922 | 3.24922 |
| c (Å)             | 5.20730      | 5.21658 | 5.20843 | 5.20775 |
| α (°)             | 90.0         | 90.0   | 90.0   | 90.0   |
| β (°)             | 90.0         | 90.0   | 90.0   | 90.0   |
| γ (°)             | 120.0        | 120.0  | 120.0  | 120.0  |
| V (Å³)            | -            | 47.87802 | 47.62068 | 47.61434 |
| Rp (%)            | -            | 12.53  | 10.42  | 10.32  |
| Rwp (%)           | -            | 8.44   | 7.43   | 7.68   |
| GoF (χ²)          | -            | 0.2087 | 0.1424 | 0.1400 |

### Table 2. BET analysis result.

| Sample       | ZnO-0 | ZnO-1 | ZnO-2 |
|--------------|-------|-------|-------|
| Surface area (m²) | 45.639 | 66.733 | 143.49 |
| Particle size (nm)  | 23.434 | 16.026 | 7.4537 |

Brunner-Emmett-Teller (BET) theory is used to analyze the surface area of prepared ZnO using surface area analyzer (SAA). The measurement is based on nitrogen absorption to saturation conditions at a relative pressure (P/Po) in range 0.05 - 0.30 Pa. The result is presented in Table 2. The surface area of ZnO is increased in the presence of ultrasonic assisted given during precipitation. With increasing the surface area, the particle size of ZnO is decreased. There is a difference in particle size due to the calculation of Scherrer and BET. ZnO is considered a solid ball in the Scherrer approach, whereas BET can calculate the presence of pores contained in ZnO powder. Ultrasonic assisted during precipitation can obtain wide pores on the surface of ZnO particles. With the wide pores on the surface, the active side of ZnO particles will increase. It will be very beneficial for application as a photocatalyst.

### 3.2. Photocatalytic activity

Due to the photocatalytic activity, pH of the solution has an important role in the reaction rate and dye adsorption on the surface of semiconductor. The effect of the pH of the methylene blue solution on the photocatalyst activity is shown in Figure 3 (a). Based on the curve, the photocatalyst activity of three
prepared ZnO showed better under alkaline conditions. The highest photocatalytic activity occurs at pH 10 causing the methylene blue degraded more quickly. The surface of the ZnO catalyst will be negatively charged under alkaline conditions. Whereas in acidic conditions, the surface will be positively charged. This happens according to the reaction equation below:

\[
\text{ZnO-OH + H}^+ \rightarrow \text{ZnO-OH}_2^+ \tag{1}
\]

\[
\text{ZnO-OH + OH}^- \rightarrow \text{ZnO-O}^- + \text{H}_2\text{O} \tag{2}
\]

When ZnO is added to the methylene blue solution, it will spontaneously absorb water and form ZnO-OH. If the solution is in acidic pH condition, the OH\(^-\) group will bind to the H\(^+\) ion and form ZnO-OH\(_2^+\). Whereas if the solution is in an alkaline condition, the OH\(^-\) group on the surface of ZnO will bind OH\(^-\) ions and form ZnO-O\(^-\). This reaction causes the surface of ZnO to become negatively charged \[21\].

Figure 3 (b) shows the experiment results of photodegradation efficiency in various UV light irradiation times. It is proven that the longer the irradiation time given, degradation has better performance as the number of radical hydroxy anions (•OH) formed is increasing. The highest activity is shown by ZnO with 2 hours ultrasonic assisted, as mentioned above, ZnO prepared by ultrasonic assisted has better physical properties.

Based on the result, the optimum irradiation time occurs at 60 minutes under UV light, when all of ZnO are at the most significant change point. ZnO without ultrasonic assisted has a slow degradation rate, 94.51 % of methylene blue can be eliminated after 60 minutes irradiation. When ultrasonic assisted given to the ZnO, the degradation rate is increased, it is given 97.58 % for ZnO with an hour ultrasonic assisted and 98.52 % for 2 hours ultrasonic assisted under the same UV irradiation time.

![Figure 3. (a) Photodegradation efficiency of ZnO Photodegradation efficiency of ZnO due to the various pH solution of methylene blue, (b) Photodegradation efficiency of ZnO in various time of UV light irradiation and (c) Adsorption activity of ZnO in various time.](image)

In addition to determine the adsorption activity of ZnO, the same experiment is carried out without UV light irradiation. The condition for adsorption reaction is set up in the dark condition. In this condition, the adsorption reaction takes over, and it is expected that decreasing of methylene blue is not influenced by photocatalytic activity of ZnO. The test results can be seen in Figure 3 (c). Based on the curve, the adsorption of methylene blue by ZnO is very low. The highest activity is showed only 10.55 % by ZnO without ultrasonic assisted after an hour reaction. It is proven that the adsorption activity of ZnO is weak. Before the photodegradation reaction carried out, the presence of UV light irradiation as an energy source in the photocatalyst reaction is very important. The process of decreasing the concentration of methylene blue in the previous test mostly took place by photodegradation reaction.

4. Conclusion

Ultrasonic assisted during precipitation gives better physical properties of ZnO. Wurtzite phase with accurate lattice properties prepared well by this method. ZnO with ultrasonic assisted has a better performance in the photodegradation of methylene blue. The highest photocatalytic activity showed by
ZnO with 2 hours ultrasonic assisted after 120 minutes irradiation under UV light, it can eliminate 98.52% of methylene blue.

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