Synthesis of ZnO/FA composite for methylene blue decolorization

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Abstract. In this research, a ZnO/FA composite was successfully synthesized for the photocatalytic treatment of methylene blue. ZnO was obtained from Zn-C battery waste by precipitation method. Zinc metal from battery waste was separated, cleaned, and dissolve in hydrochloric acid to get the ZnCl2 solution. After adding some base until pH = 10, white precipitation was formed. This precipitate was filtered out and calcinated at 400 °C for 4 hours to obtained ZnO. Fly Ash (FA) was obtained from coal combustion waste. Fly ash was cleaned and drying at 105 °C for 3 hours. Synthesis of ZnO/FA composite was synthesized by a solid dispersion method using acetone as a medium with a various composition of ZnO: FA = 20:80; 40:60; 60:40; 80:20 in percentage. The XRD data show that the ZnO/FA composite was successfully synthesized. The SEM photo’s show that different morphology where more ZnO in the composite, the FA particles will be increasingly encased with ZnO particles. Photocatalytic performance studies of ZnO/FA composites for decolorization of methylene blue were carried out in various compositions, exposure times, substrate concentrations, and mass composites. The optimum decolorization was found in 40:60 composition, 3 hours irradiation time, 5 ppm concentration of methylene blue, and 150 mg of photocatalyst mass.

1. Introduction
Zink oxide (ZnO) are interesting semiconductor materials with unique chemical and physical properties. These materials were synthesized by a different method with various properties and various applications such as photocatalyst [1], gas sensor [2], and antibacterial [3,4]. Zink oxide with a hexagonal wurtzite structure and n-type semiconductor can be synthesized by precipitation method [5]. Nevertheless, to increase the photocatalyst ability, the other materials can be added to Zink oxide such as fly ash (FA) to form ZnO/FA composite [6]. By adding FA to the ZnO, it is expected to increase the surface adsorption and hydroxyl group in the materials [7].

ZnO/FA composite can be synthesized from waste materials. The 15.79% Zn content in battery waste with high purity is very potential to be the source of Zn [8], and the abundance of coal combustion waste is very potential to be the source of FA [9]. The solid dispersion method is widely used for improving the solubility of two materials in the solid phase. Solvent evaporation with acetone as the solvent has been successfully to synthesize ZnO/FA composite by solid dispersions method. A high surface area was formed by particle size reduction, and resulting in an increased dissolution rate [10].

The purpose of this study was to investigate the photocatalytic activity for the decomposition of methylene blue on the ZnO/FA composite prepared by the solid dispersion method. The photodegradation was carried out using the composite powder in the vial bottle under visible light
irradiation with some various conditions such as various compositions, exposure times, substrate concentrations, and mass composites. The sunlight as an energy source was available for use on a larger scale, including industrial scale [11].

2. **Experimental**

There are four steps in this research, including ZnO preparation, ZnO/FA composite preparation, characterization of samples, and photocatalytic activity.

2.1. **ZnO preparation**

The ZnO was prepared by precipitation method from Zn-C battery waste. Zn plate was separated from the other battery components and dissolved in 36% hydrochloric acid. An appropriate amount of NaOH was added to the solution to control the pH at 10. The precipitate was filtered out and calcinated at 400°C for 4 h.

2.2. **ZnO/FA composite preparation**

Fly Ash from coal combustion waste was cleaned and drying at 105°C for 3 h. The composites were synthesized by solid dispersion method with various compositions of ZnO and FA, there are 20:80; 40:60; 60:40; 80:20 percentage of mass. Acetone was used as the dispersion medium, then the samples were sonicated for 280 s. After the acetone evaporates, each component of the composite was calcined at 400°C for 4 h.

2.3. **Characterization of samples.**

X-ray diffraction patterns of the ZnO/FA composites were measured with PANanalytical-X'Pert High Score instrument using Cu-Kα radiation. The surface morphology of composite was observed with a scanning electron microscope (SEM; JEOL JSM).

2.4. **Photocatalytic activity**

Decolorization of methylene blue was carried out in various compositions, exposure times, substrate concentrations, and mass composites [12]. 1) Various compositions. The effect of composite composition was identified in the vials containing 15 mL of solution and 150 mg of the composite. An aqueous solution of methylene blue was used with a concentration of 10 ppm. After sonicated for 280 s, the samples were irradiated for 3 h under the visible light. This treatment was given to each composite composition. The concentration of methylene blue was monitored by measuring the absorbance of the samples using a UV-Vis spectrometer at the wavelength of 664 nm. 2) Exposure times. The effect of exposure times was examined in the vials containing 15 mL of solution and 150 mg of the 40:60 composite. An aqueous solution of methylene blue was used with a concentration of 10 ppm. After sonicated for 280 s, the samples were irradiated under the visible light with various exposure times such as 60 m, 90 m, 120 m, 150 m, and 180 m. The concentration of methylene blue was monitored by measuring the absorbance of the samples using a UV-Vis spectrometer at the wavelength of 664 nm. 3) Substrates concentration. The effect of substrates concentration was identified in the vials containing 15 mL of solution and 150 mg of the 40:60 composite. The aqueous solution was varied of methylene blue concentrations such as 5 ppm, 10 ppm, 15 ppm, 20 ppm, and 25 ppm. After sonicated for 280 s, the samples were irradiated for 3 h under the visible light. The concentration of methylene blue was monitored by measuring the absorbance of the samples using a UV-Vis spectrometer at the wavelength of 664 nm. 4) Mass composites. The effect of mass composites was examined in the vials containing 15 mL of solution and various mass composites such as 10 mg, 20 mg, 30 mg, 40 mg, and 50 mg. An aqueous solution of methylene blue was used with a concentration of 5 ppm. After sonicated for 280 s, the samples were irradiated for 3 h under the visible light. The concentration of methylene blue was monitored by measuring the absorbance of the samples using a UV-Vis spectrometer at the wavelength of 664 nm.
3. Results and discussion

3.1. Samples and composite preparation

The Zn plates are cut into small pieces to increase the rate of reaction and then added HCl 36%. An exothermic reaction happened when Zn was dissolved in an acid condition. To reduce the release of heat, this process must run slowly. The reaction of Zn dissolution can be represented as:

$$\text{Zn (s)} + 2 \text{HCl (aq)} \rightarrow \text{ZnCl}_2 \text{(aq)} + \text{H}_2 \text{(g)}$$  \hspace{1cm} (1)

To form the Zn(OH)$_2$, an appropriate amount of NaOH was added to the solution to control the pH at 10. In this condition Zn(OH)$_2$ was simultaneously precipitated, as follows:

$$\text{ZnCl}_2 \text{(aq)} + 2\text{NaOH (aq)} \rightarrow \text{Zn(OH)}_2 \text{(s)} + 2 \text{NaCl (aq)}$$  \hspace{1cm} (2)

The precipitate was filtered out and drying at 105°C for 3 h to reduce the water, then calcined at 400°C for 4 h to transform the Zn(OH)$_2$ to be ZnO. The calcination temperature depends heavily on its particle sizes of ZnO. Larger particle sizes with the small surface area produced with increasing annealing temperature [13]. The reaction can be represented as:

$$\text{Zn(OH)}_2 \text{(s)} \rightarrow \text{ZnO (s)} + \text{H}_2\text{O}$$  \hspace{1cm} (3)

Fly Ash from coal combustion waste was cleaned using water to remove the impurities and then drying at 105°C for 3 h. The composites were synthesized by solid dispersion method using acetone as the dispersion medium. To get the optimum composition, the synthesize composite had a percentage mass ratio of ZnO and FA (20:80; 40:60; 60:40; 80:20). Then the samples were sonicated for 280 s to homogenize the composite formed. After the acetone evaporates, each compositions of composite were calcined at 400°C for 4 h.

3.2. Characterization of samples

X-ray diffraction patterns of the ZnO/FA composites were measured with PANanalytical-X’Pert High Score instrument using Cu-Kα radiation. Figure 1 shows the XRD patterns of the prepared FA, ZnO, and ZnO/FA composite at various compositions. X-ray diffraction measurements for ZnO/FA composite showed that they consisted of ZnO in the crystal phase and FA in the amorphous phase. The composite diffraction patterns show typical peaks of ZnO and FA, this means that ZnO/FA composite was successfully synthesized. The increase of ZnO composition in the composite effect to increasing the peak of ZnO, and the increase of FA composition in the composite effect to increasing the peak of FA. This fact shows that the composition of ZnO and FA affects the composite characteristics. FA as the host materials have been used to increase the photodegradation efficiency of ZnO [14].

The surface morphology of composite was observed with a scanning electron microscope (SEM; JEOL JSM-6360). Figure 2 shows the SEM image of FA and ZnO/FA composites of various compositions. The morphology of the composite change with further growth when compared to figure 2(a) which shows the SEM image of pure FA. On the composite, the ZnO particle has enchased the surface of the FA particles. The increased composition of ZnO in Figure 2(d) and Figure 2(e) affect the composite characteristics. The SEM image shows that the ZnO particle was grown on the FA surface [15]. When the composition of ZnO much more than compositions of FA in the composite, ZnO particles was covered the entire surface of FA. The best composition was needed in enhancing the photodecomposition rate of dyes on the ZnO/FA composite in water [16].
3.3. Decolorization of methylene blue

The main reactions of decolorization of methylene blue have been suggested to be schematically represented by the following schemes [12,17]:

\[ \text{ZnO} + h\nu \rightarrow \text{ZnO(h)}^+ + e^- \]  
(4)

\[ \text{ZnO(h)} + \text{H}_2\text{O(ads)} \rightarrow \cdot\text{OH} + \text{H}^+ + \text{ZnO} \]  
(5)

\[ \cdot\text{OH} + \text{methylene blue} \rightarrow \text{intermediate products} \]  
(6)

\[ \text{ZnO(h)}^+ + \text{intermediate products} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{ZnO} \]  
(7)

**Figure 2.** SEM image of FA and ZnO/FA composites of various compositions. (a) FA, (b) 20:80 composite, (c) 40:60 composite, (d) 60:40 composite, and (e) 80:20 composite.
The role of ZnO as a photocatalyst was verified by determining the wavelength transmission of the methylene blue decomposition process using spectrophotometer UV-Vis. To check the degree of the decolorization of methylene blue in solution in different conditions such as various compositions, exposure times, substrate concentrations, and mass composites. The best result in case solutions of methylene blue was obtained using ZnO/FA composite in 40:60 composition. After 3 h of irradiation 79.01% of dye was removed. At the same time, others carried out decolorization achieving 76.77%, 69.31%, and 55.41% of removal for solutions of methylene blue using ZnO/FA composite in 20:80, 60:40, and 80:20 composition. It shows that in 40:60 composition, FA effective to enhance the surface adsorption and increasing surface hydroxyl group in the composite [18]. Based on this result, the ZnO/FA composite in 40:60 composition was used to carry out the effect of exposure times, substrates concentrations, and mass composites to methylene blue decolorization.

The exposure times in the five conducted experiments at different conditions was examined. The best exposure times to removal the methylene blue were obtained at 180 m exposure times. After 3 h of irradiation 75.98% of dye was removed. At the same time, others examined decolorization achieving 53.49%, 64.40%, 68.16%, and 69.96% of removal for solutions of methylene blue at 60 m, 90 m, 120 m, and 150 m exposure times. These measurements demonstrate that the increase of exposure times effect to increasing the percentage of methylene blue decolorization through the formation of free radicals in greater number [4].

An increase of methylene blue concentration in the five conducted experiments at different conditions was carried out to identify the effect of substrate concentration on the percentage of methylene blue decolorization. In the solutions of methylene blue on the degree of dye decolorization in decreasing order is as follows: 5 ppm > 10 ppm > 15 ppm > 20 ppm > 25 ppm. The highest percentage of dye decolorization is 97.45% at 5 ppm of methylene blue. The obtained result shows that the increase of substrate concentration affects to decreasing the percentage of methylene blue decolorization due to reduced numbers of photon absorption [4].

The mass composites in the five conducted experiments at different conditions were carried out to identify the effect of mass composites on the percentage of methylene blue decolorization. In the solutions of methylene blue on the degree of dye decolorization in an increasing order is as follows: 10 mg < 20 mg < 30 mg < 40 mg < 50 mg. The highest percentage of dye decolorization is 94.90% using 50 mg of ZnO/FA composite. These measurements demonstrate that the increase of mass composite effects to increase the percentage of methylene blue decolorization by ensuring the total absorption of solar light photons [4].

4. Conclusion
The ZnO/FA composite was successfully synthesized from waste materials by a solid dispersion method. The crystal phase composition and morphology were characterized by a variety of techniques, including XRD and SEM. The best composition of the ZnO/FA composite for methylene blue decolorization is 40:60 percentage of mass. The increase of exposure times and mass composites effect to increasing the percentage of methylene blue decolorization. While the increase of substrate concentration affects to decreasing the percentage of methylene blue decolorization. The highest percentage of methylene blue decolorization is 97.45% using composite in 40:60 composition, 3 h irradiation time, 5 ppm concentration of methylene blue, and 150 mg of photocatalyst mass.

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