The effect of catalyst weight on the photocatalytic performance of ZnO-Ag nanocomposites prepared by flame pyrolysis method

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Abstract. ZnO is the most widely used as a catalyst material for photocatalytic application due to the suitable band gap energy and the chemical stability. It was reported by our previous study that the photocatalytic performance was significantly affected by the Ag content. In this study, ZnO-Ag nanocomposite materials have been successfully fabricated by flame pyrolysis and the effects of catalyst weight ranging from 2 to 10 mg on the photocatalytic performance were also investigated. Zinc acetate and silver nitrate were used as precursors for producing ZnO-Ag nanocomposites. The catalyst products, ZnO-Ag nanocomposite, were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). While, UV Vis spectrometry was used to measure the concentration of methylene blue (MB) before and after irradiations. Photocatalytic performances of nanocomposites were performed by evaluating the degradation of MB under UV and sunlight irradiations. The photocatalytic tests showed that the best performance was attained when the Ag content was 5 wt% and the weight of catalyst was as much as 10 mg after irradiation with sunlight, where the degradation rate of MB was 98% and the rate constant was 0.09/min.

1. Introduction
The rapid development of the textile industry causes environmental problems due to the toxic dye waste. Disposal of waste into the environment is a source of pollution that may cause hazards, toxic effects and reduction of light penetration in the water [1]. Many methods have been developed to overcome these problems. Photodegradation is the most promising method to degrade organic waste because it only requires fairly low operational costs and fast processing [2]. The principle of the photodegradation method is the usage of catalyst derived from nano semiconductor materials such as TiO₂, ZnO, Fe₂O₃, etc under light irradiation [3]. Generally, the semiconductor used for photocatalyst is ZnO because it is able to absorb the sun spectrum and more quantum light. The band gap of ZnO is also greater than that of TiO₂ [4]. However, the use of ZnO as photocatalysts has disadvantage; where electron pairs can become unstable and cause electron hole recombination. To overcome this issue, addition of doping to the photocatalyst material can make a balance of the charges. Moreover, the electrical properties and optical properties of semiconductor materials can be altered by the addition of...
dopants. When semiconductor materials are doped, the conduction can be enhanced. Several studies have been conducted to improve the efficiency of the photocatalyst, such as by adding Ag metal. Kusdianto et al reported that the addition of Ag enhanced the photocatalytic performance up to 35% [5].

ZnO-Ag nanocomposites can be synthesized by liquid and gas phase methods [6]. Gas phase method has some advantages compared to liquid phase, such as it requires a less number of processing step and no further treatments are needed. In this study, flame pyrolysis is selected to fabricate ZnO-Ag nanocomposites among other gas-phase methods because of the one step process. In addition, the flame pyrolysis produces particles with high crystallinity [7]. In our previous study, we have successfully fabricated ZnO-Ag nanocomposites through flame pyrolysis [5]. It was known that Ag content at 5 %wt showed the best photocatalytic performance. Height et al. (2006) also used ZnO-Ag nanocomposite with various concentrations of Ag and reported that the best photocatalytic performance was attained when Ag concentration was as much as 3 % [8].

Generally, the photocatalytic activity is affected by many parameters, such as: surface area, particle diameter, crystallinity, crystal phase, and so on. In our hypothesis, the photocatalytic activity may also be affected by weight of ZnO-Ag. The effect of catalyst dosage for the degradation of the organic pollutant have been reported by Mohammadi et al. using TiO$_2$-ZnO [9] and MnIn$_2$S$_2$/Ag-C$_3$N$_4$ [10]. The previous researchers only used UV or visible lights as irradiation source and the catalyst materials were synthesized by liquid phase methods, which has some disadvantages as reported in the previous paragraph. Inspired by this limitation, the objective of this study is to investigate the effect of Ag concentration as well as catalyst weight on the photocatalytic performance of ZnO-Ag nanocomposite fabricated by the gas-phase method using one-step process via flame pyrolysis. Methylene blue (MB) was used as a model of organic pollutant. We believe that this result will give valuable information in the future especially for nanotechnology field.

2. Research Methodology

2.1 Sample preparation and experimental set up

Silver nitrate (AgNO$_3$, Merck), zinc acetate dehydrate (Zn(CH$_3$COO)$_2$•2H$_2$O), p.a. 99.5 %, Merck), methylene blue (C$_{16}$H$_{18}$C$_4$N$_3$S, Merck), and deionized water were used as precursors. The precursors were used as received without purification. The precursor solution was prepared by dissolving crystal zinc acetate dehydrate with deionized water under homogenization to obtain a solution of 0.1 M. The various concentrations of silver nitrate at 1, 5 and 10 % wt based on the weight % of zinc acetate were prepared by dissolving silver nitrate with deionized water under sonication for 10 min. The prepared silver nitrate with different concentration was mixed with zinc acetate under homogenization process using a sonicator for 10 minutes. The precursor solution was then subjected into an ultrasonic nebulizer (Omron). The concentration inside the nebulizer was kept constant by adding the precursor continuously using a peristaltic pump.

The experimental setup used for fabrication ZnO-Ag nanocomposite is shown in Figure 1. Details of the experiment can be found in our previous study [5]. Briefly, the droplets were generated by the ultrasonic nebulizer and carried to the flame reactor by compressed air. The combustion occurred in the flame reactor by flowing the liquefied petroleum gas (LPG, commercial grade, PT. Pertamina) and the compressed air as the oxidizer. The parameter setup of the operating conditions in this study were: LPG flow rate at 0.3 LPM, carrier gas flow rate at 3 LPM, and oxidizer flow rate at 2.8 LPM. The ZnO-Ag nanocomposites were synthesized inside the flame reactor by the decomposition of zinc acetate and silver nitrate. Electrostatic precipitator set at temperature of 120 °C was used to collect the nanoparticles. Vacuum pump was used to attract non-condensable gas, while the uncollected particles in the electrostatic precipitator was captured in the water trap.
2.2 Characterizations

X-ray diffraction (XRD, Xpert Philips) was used to analyze the crystalline phase and crystallite size of the nanocomposite produced from the flame pyrolysis. XRD was operated at 30 mA with an accelerating voltage of 40 kV. CuKα with $\lambda = 0.15418$ nm was used as radiation source. Scanning electron microscopy (SEM, S-5200, Hitachi High Technologies) was used to observe the morphology of the produced ZnO-Ag nanocomposites. Measurement of the photocatalytic performance was conducted by measuring the degradation of MB solution under UV and sunlight irradiations. The weight of ZnO-Ag nanocomposites at 2, 4, 6, 8 and 10 mg was used as variable of the catalyst weight. The specific weight of ZnO-Ag nanocomposites was dispersed in 60 ml of MB solution. Before irradiation with UV or sunlight, the prepared samples were stirred for 30 min in a dark chamber to reach the adsorption-desorption equilibrium. After that, the prepared samples were exposed to the UV or sunlight irradiations under stirring. Every 15 min, the sample was taken and then centrifuged. The supernatant was analyzed using UV-Vis spectrophotometry (Thermo Scientific Genesys 10s) to determine the absorbance of MB before and after the irradiation at wavelength of 664 nm, originating from the MB solution. To obtain the concentration of MB, the absorbance of the measured samples was then converted to the concentration using the calibration curve of MB.

3. Results and discussion

Figure 2 shows the XRD patterns of ZnO-Ag nanocomposites with various contents of Ag at 1, 5 and 10 %wt. Based on the XRD patterns shown in Figure 2, the appearance peaks at 31.77°, 34.42°, 36.25°, 47.54°, 56.60°, 62.87° and 78.0° are matched with the peaks from the JCPDS 36-1451 of ZnO. It can be simply concluded that the flame pyrolysis synthesis method was able to synthesize the ZnO nanoparticles. Moreover, the ZnO nanoparticles formed are hexagonal Wurtzite structures ($w$-ZnO) with various crystal diameters. It is stated that $w$-ZnO is the most stable structure and also thermodynamically stable [9]. Figure 2 also shows that the existence of Ag can be detected by XRD when the concentration of Ag is greater than or equal to 5 %wt. The existence of Ag can be shown in the XRD peaks at 38.12°, 44.28°, 64.34°, 77.48°. These peaks are matched with the JCPDS 04-0783 of Ag. The absence of Ag peaks at concentration of Ag at 1 %wt may be due to the possibility of small concentration of Ag in the nanocomposites which makes it undetectable by XRD. Increasing the Ag
content up to 10 % wt increased the intensity of Ag peak at 38.12°. It indicates that the flame pyrolysis method can be used to fabricate Ag-ZnO nanocomposites. The crystallite size of the nanocomposites was estimated using Scherrer equation, where the crystallite size did not change significantly with increasing Ag content as reported in our previous study [5].

Figure 2. XRD patterns of ZnO-Ag nanocomposites with various Ag contents.

Figure 3 shows SEM images of the produced nanocomposites with various concentrations of Ag at 1, 5, and 10 % wt.

Figure 3. SEM images of the ZnO-Ag nanocomposites prepared by flame pyrolysis with various Ag contents at (a) 1 % wt, (b) 5 % wt and (c) 10 % wt.
Based on the SEM results as depicted in Figure 3, it can be obviously observed that the morphology of the primary particles of the nanocomposite is a spherical shape. It may be caused by nucleation process and the growth of particles inside the flame reactor to form bigger particles with spherical shape [12]. Figure 3 also shows that there is no significant differences in the morphology between nanocomposites with various Ag loadings. It seems that the primary particle size increased slightly with increasing Ag content. This result is a good agreement with previous results which mentioned that the addition of Ag did not alter the morphology of the nanocomposites [13]. SEM observation also indicated that the agglomeration of primary particles occurred with increasing of Ag content. The possibility of agglomeration can be attributed due to the high concentration of particles in the gas stream when passing through the flame reactor in resulting the collisions between particles [14].

After characterizations of the produced ZnO-Ag nanocomposites in the previous section, we evaluated the performance of those materials with photocatalytic test. MB degradation efficiency (MDE) was used to identify the photocatalytic performance of ZnO-Ag nanocomposites under UV and sunlight irradiations using the following equation [15]:

\[ MDE = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\% \]

Where \( C_0 \) is the initial concentration of MB and \( C_t \) is concentration of MB after irradiation at a certain time (t).

![Figure 4](image-url)

**Figure 4.** Methylene blue (MB) degradation efficiency of ZnO-Ag nanocomposites with various catalyst weights under UV light irradiation at the Ag contents of (a) 1 %wt, (b) 5 %wt and (c) 10 %wt.
Figure 4 shows the normalized curve of the MB degradation efficiency of ZnO-Ag with different catalyst weight ranging from 2 to 10 mg at various Ag contents at 1, 5, and 10 %wt under UV light irradiation. In this case, the data for adsorption-desorption equilibrium carried out in the dark condition under agitation for 30 min before UV light irradiation did not include in the figures, because the degradation efficiency is very small and can be neglected. It means that the photocatalytic activity is the most dominant in comparison with adsorption of ZnO as an adsorbent. Generally, the degradation efficiency increased with increasing the catalyst weight (see Figure 4). Sahoo et al. reported that the degradation increased with an increase of catalyst weight [16]. It can be seen that the MB can be degraded up to 76 % when the ZnO-Ag nanocomposite was 10 mg (1 %wt) after irradiation with UV light for 75 min (see Figure 4(a)). However, the MB degradation efficiency decreased and reached only about 47 % when the concentration of Ag was increased to 5 and 10 %wt. This can be ascribed due to too much of the catalyst weight added to the MB. The excessive catalyst weight will block the penetration of UV light to the samples [17]. Based on these results depicted in Figure 4, it can be simply concluded that the best degradation efficiency was obtained when the Ag content was as much as 1 % and the weight of catalyst at 10 mg.

Moreover, the photocatalytic activity of ZnO-Ag can also be expressed by plotting $\ln (C_t/C_0)$ versus irradiation time ($t$) based on the equation of $\ln (C_t/C_0) = kt$. It assumes that the degradation rate follows the pseudo first order kinetic.

![Figure 5](image_url)

**Figure 5.** Plot $\ln(C_t/C_0)$ vs irradiation time of ZnO-Ag nanocomposite at different catalyst weight under UV light irradiation with various Ag contents at (a) 1 %wt, (b) 5 wt% and (c) 10 %wt.

It can be seen in Figure 5, the degradation rate of MB increased with the increase of catalyst weight in exception for 10 %wt with 8 mg of catalyst. Furthermore, the photocatalytic performance was
estimated by measuring the slope based on the fitting curve of Figure 5. These slopes are corresponded to the rate constant \( k \) indicating the performance of the photocatalyst as depicted in Figure 6.

**Figure 6.** Rate constant \( k \) of ZnO-Ag nanocomposite at different catalyst weight under UV light irradiation with various Ag contents.

Figure 6 shows the highest rate constant, value of \( k = 0.018 \) /min, obtained when the Ag content at 1 %wt with the catalyst weight at 10 mg. It is clear that increasing the catalyst weight will enhance the rate constant, except for 2 mg at 5 %wt. We cannot explain why this phenomenon happen, the additional experiments will be conducted later for explaining this mechanism. As can be seen in Figure 6, the best rate constant was attained with the usage of 10 mg of catalyst for 1 and 5 %wt of Ag content, while at 6 or 8 mg for 10 %wt. The increase of catalyst weight (for 10 %wt) decreased the rate constant. Increasing of rate constant with increasing catalyst weight can be explained by the total active surface area. The surface area increases with increasing catalyst weight resulting the enhancement of the contact area between catalyst surface and MB. However, the increase catalyst weight above optimum loading will decrease the UV light penetration due to screening effect of excess catalyst particle in the solution. Therefore, the rate constant decreased at the higher catalyst loading [16].

In addition of UV light irradiation, we also conducted the photocatalytic test under sunlight irradiation. Photocatalytic measurement was carried out at sunny condition. The intensity of sunlight during the photocatalytic test was monitored by intensity meter with average intensity around 60,000 lux. The all measured intensities were calibrated using the same baseline to avoid error due to different intensity measurement for each experiment. It was done to make the results more comparable. The methylene blue degradation efficiency with sunlight irradiation can be seen in Figure 7. The same tendency can be obtained with UV irradiation, where the degradation efficiency increased with increasing catalyst weight. MB can be degraded up to 98 % for all experiment with various Ag contents. By comparing the results under sunlight irradiation (Figure 7) and UV irradiation (Figure 4), it can be concluded that degradation efficiency under sunlight irradiation is twice greater than that of UV irradiation. This is because the intensity of the sunlight is much higher than UV light. On the other hand, the existence of Ag nanoparticles may play an important role during the photocatalytic activity under sunlight irradiation, because Ag nanoparticles can work not only in the UV area but also in visible light [4]. Furthermore, the photocatalytic activity of ZnO-Ag under sunlight irradiation was then expressed by plotting \( \ln \left( C_t / C_0 \right) \) versus irradiation time \( t \) as mentioned previously as depicted in Figure 8.
Figure 7. MB degradation efficiency of ZnO-Ag nanocomposites with various catalyst weights under sunlight irradiation at the Ag contents of (a) 1 %wt, (b) 5 %wt and (c) 10 %wt.

Figure 8. Plot $\ln(C/C_0)$ vs irradiation time of ZnO-Ag nanocomposite at different catalyst weight under sunlight irradiation with various Ag contents at (a) 1 %wt, (b) 5 wt% and (c) 10 %wt.

Figure 9 shows the rate constant of ZnO-Ag nanocomposites with various catalyst weights and Ag loadings after irradiation with sunlight. The highest rate constant was found when the catalyst weight as much as 10 mg with Ag content at 5 %wt, where the rate constant is about 0.1/min. Similar tendency can be observed from Figure 9 that increasing the catalyst weight increased the rate constant. In the case of Ag content, the rate constant can be enhanced with the increase of Ag content from 1 to...
5 %wt. Unfortunately, the rate constant then decreased after increasing the Ag content at 10 %wt. This may be attributed due to the agglomeration of Ag particles, which blocked the penetration of light resulting in the decreased of the photocatalytic performance [5]. This result is a good agreement with the result reported by Mohammadi et al., which mentioned that the dosage of the catalyst influenced the photocatalytic performance.

**Figure 9.** Rate constant ($k$) of ZnO-Ag nanocomposite at different catalyst weight under UV light irradiation with various Ag contents.

4. Conclusion
Ag-ZnO nanocomposites have been successfully synthesized by gas-phase method via flame pyrolysis. The existence of Ag nanoparticles was detected by XRD analysis after the concentration of Ag was greater or equal to 5 %wt. SEM images indicated that the produced ZnO-Ag nanocomposites had a spherical shape. The methylene blue degradation efficiency under sunlight irradiation was twice greater than that of under UV light irradiation. The best photocatalytic performance under UV light irradiation indicated by the rate constant showed that the best photocatalytic activity was obtained at 1 %wt of Ag with the catalyst weight as much as 10 mg. While, the best photocatalytic activity under sunlight irradiation was found at 5 %wt Ag with the weight catalyst at 10 mg. The maximum rate constant after irradiation under UV and sunlight were 0.018 and 0.09 /min, respectively. It indicates that the photocatalytic activity under sunlight was much better than that of under UV light irradiation.

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