Preparation of ZnO nanoparticles in n-hexane-water system using Moringa oleifera leaf extract and its photodegradation activity

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Abstract. In this study, ZnO nanoparticles were successfully synthesized using Moringa oleifera leaf extract in two phases system of n-hexane-water. The presence of secondary metabolites in n-hexane acts as a weak base source and precursor of Zn(NO₃), in water were needed for the formation of ZnO nanoparticles. ZnO nanoparticles were further characterized using UV-Vis Diffuse Reflectance Spectroscopy (DRS), Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX), and Tunneling Electron Microscopy (TEM). Based on TEM characterization, the particles size of ZnO nanoparticles was approximately 67 nm. The band gap energy of ZnO was 3.2 eV. The photocatalytic activities of ZnO nanoparticles were observed through the methylene blue (MB) degradation under UV-light irradiation. The percentage of MB degradation was 99 % for 2 h.

Keywords: ZnO nanoparticles, Moringa oleifera, n-hexane-water system, photodegradation, methylene blue

1. Introduction

The preparation method of metal oxide nanoparticle has been done by green synthesis. One of them is green synthesis with liquid-liquid extraction [1]. Green synthesis method using plant extract is more environmentally friendly and harmless. The shape and size of nanoparticles can be controlled [2]. Green synthesis of nanoparticle has been mostly reported for metal oxide like zinc oxide (ZnO). ZnO is a semiconductor with a wide band gap (3.37 eV) and has good photocatalytic properties in the UV-Visible region [3]. ZnO can absorb ultraviolet (UV) radiation from sunlight or fluorescent lamps. Moreover, it will produce oxidation reactions where electrons are released and captured. The photocatalytic reaction is activated by photon absorption with the same or higher energy levels of the band gap energy in catalyst [4]. Various types of photocatalysts from metal oxide nanoparticles have been reported to degrade some organic compounds [5–7].

On the other hand, some of Indonesian plants for green synthesis of metal and metal oxides nanoparticles are Oldenlandia corymbosa L., Graptophyllum pictum, Terminalia catappa, Physalis angulata, Theobroma cacao and Polyscias fruticosa [8–12]. One of the plants used for green synthesis of ZnO nanoparticles is Theobroma cacao [11]. Moringa oleifera is a plant species of moringaceae that has many functions due to the presence of secondary metabolites. The secondary metabolites of Moringa oleifera consist of alkaloids, flavonoids, tannins, saponins, and steroids [13].

To the best of our knowledges, we reported the synthesis of ZnO nanoparticles using moringa leaf extract on n-hexane-water system and the test of its photocatalytic activity for the degradation of methylene blue.

2. Experimental
2.1. Apparatus and chemicals
*Moringa oleifera* was obtained from Study Center of Tropical Biopharmaca, Bogor, Indonesia. Zn(NO₃)₂·4H₂O as precursor and methylene blue as a model of dyes was purchased from Merck, Germany. All reagents and solvents were in analytical grade.

2.2. Preparation of Moringa leaf extract
Moringa leaves were washed, dried and ground to form powders. Moringa leaves powders were macerated in hexane for 7 x 24 h. The results were partitioned in aquabidest to separate the polar and non-polar metabolites compounds. The hexane fraction contains non-polar secondary metabolite and the aqueous fraction contains polar secondary metabolite. The hexane fraction was used as Moringa leaf extract for ZnO nanoparticles synthesis.

2.3. Synthesis of ZnO Nanoparticles
2.0 x 10⁻² M Zn(NO₃)₂ solutions was reacted with the hexane fraction of moringa leaf extract. The mixture was extracted for 1.5 h to get the hexane phase and water phase of Zn(OH)₂ sol. The water phase of Zn(OH)₂ sol was heated at 80 °C for 4 h to get the gel system. The result was calcined at 500 °C for 4 h.

2.4. Characterization of ZnO nanoparticles
UV-Vis Diffuse Reflectance Spectroscopy (DRS), Shimadzu 2400 was used to calculate the band gap energy. Fourier Transform Infrared (FT-IR) spectrophotometry, IR Prestige-21 Shimadzu, was used to determine the functional group. Scanning electron microscopy (SEM), Zeiss Evo MA10, was used to analyze the surface morphology. Transmission electron microscopy (TEM), JEOL JEM 1400, was used to know the particle size. Energy dispersive x-ray spectroscopy (EDX), Zeiss Evo MA10, was used to determine the elemental composition. X-Ray Diffraction (XRD), Shimadzu 610 was used to determine the crystallinity. The methylene blue photodegradation was studied by UV-Vis spectrophotometer (Shimadzu 2600).

2.5. Photodegradation activity test
ZnO powder was added into methylene blue 2.0 x 10⁻² M. The mixture was stirred under UV irradiation every 30 min for 2 h. The photodegradation activity was performed by observing the absorbance of methylene blue by UV-Vis spectrophotometer.

3. Results and discussion
ZnO nanoparticles were characterized by UV-Vis DRS at the wavelength of 200–800 nm. The band gap energy value was determined by the Tauc Plot method as shown in figure 1. The result shows a linear regression equation of straight line as the band gap energy value. The band gap energy of ZnO nanoparticles was 3.2 eV.

**Figure 1.** The band gap energy of ZnO nanoparticles

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The FT-IR spectrum of ZnO nanoparticles is shown in figure 2a. The absorption band at 474 cm\(^{-1}\) is assigned to the presence of a Zn-O vibration bond, indicating that ZnO has been successfully formed. The C-C vibration bond at 1407 cm\(^{-1}\) assumes that there are still organic compounds due to the remain of secondary metabolites compounds on the ZnO surface.

XRD characterization was performed to find the typical peak, diffraction pattern, and crystallinity of ZnO nanoparticles. As can be seen in figure 2b, ZnO nanoparticles have the diffraction pattern of \(2\theta\) at 31.37\(^{\circ}\); 34.41\(^{\circ}\); 36.24\(^{\circ}\); 47.53\(^{\circ}\); 56.57\(^{\circ}\); 56.90\(^{\circ}\); 59.72\(^{\circ}\); 63.03\(^{\circ}\) and 66.75\(^{\circ}\). According to this pattern, the crystal phase of ZnO was theoretically in accordance with hexagonal wurtzite. This result conforms with the data of ZnO from AMCSD No. 96-900-4181.

SEM results describe that the morphology of ZnO nanoparticles synthesized using moringa leaf extract on the n-hexane-water system have the aggregate form and small spheres as shown in figure 3a. EDX result clearly indicates that ZnO nanoparticles contain the atoms of zinc and oxygen as shown in figure 3b.

TEM characterization was conducted to determine the shape and particle size of ZnO nanoparticles. As can be seen in figure 4a, the particle sizes of ZnO nanoparticles were approximately 67 nm in agglomerated form. The photocatalytic activity showed that ZnO nanoparticles have a role as photocatalyst for MB degradation at 99 % for 2 h as shown in figure 4b. The results also showed that the longer of irradiation time can cause much light absorption and a greater decrease of methylene
Blue concentration. This is due to the increasing number of electrons (e⁻) from the valence band to the conduction band on catalyst, which produces a hole (h⁺) in the valence band. The resulting electrons are capable to reduce the color by reacting with electron acceptor from O₂ adsorbed on the catalyst surface to form superoxide radical anions (O₂•⁻). The result hole is able to oxidize the organic molecules by reacting with OH⁻ or H₂O to produce OH•. O₂•⁻, OH• is a very strong species, which is capable to degrade almost all azo dyes in the simpler products [14].

4. Conclusions
ZnO nanoparticles were successfully synthesized in n-hexane-water system using Moringa oleifera leaf extract. The formation of ZnO nanoparticles can be described by the presence of secondary metabolites in n-hexane phase that acts as a weak base source and Zn(NO₃)₂ in water phase. Based on TEM characterization, the particles size of ZnO nanoparticles was approximately 67 nm. The band gap energy of ZnO was 3.2 eV. The photocatalytic activity of ZnO nanoparticles were observed for the MB degradation under UV light irradiation. The percentage of MB degradation was 99% for 2 h.

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