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Study of the structural, optical, and morphological properties of ZnO nanoparticle biosynthesis using betel leaf extract as a bioreductant

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ABSTRACT

The biosynthesis of zinc oxide nanoparticles (ZnO) is extensively studied because of its eco-friendly and simple method. Piper ornatum is abundant in Indonesia, and the phytochemical content of Piper ornatum leaves has the potential to be a reductor. The study aims to study the role of Piper ornatum in biosynthesis and the characteristics of the zinc oxide nanoparticles. The sample variations in this study were the volume of Piper ornatum and the precursor solution of zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$ in proportions of 1:1, 1:5, and 1:10. Characterizations performed include UV-Vis spectroscopy, X-ray diffraction (XRD), scanning electron microscopy, energy dispersive X-ray spectroscope and blue methylene degradation test. UV-Vis spectroscopy of all samples showed peak absorption at the interval of 250 – 330 nm, which indicates that ZnO nanoparticles have already formed. The results of characterization using XRD indicated the degree of crystallinity of the ZnO nanoparticles is not perfect because the crystal field (100) or the highest diffraction peak has a very large full width at half maximum value of 0.8187°. Characterization results using SEM indicate an inhomogeneous morphology and the presence of zinc oxide nanoparticle agglomeration where particle size distribution is at an interval of 170 – 758 nm.

Keywords: Bioreductor; biosynthesis; nanoparticle; *Piper ornatum*; ZnO

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INTRODUCTION

Nanotechnology is a recent modern research field that deals with the synthesis, strategy, and manipulation of particle structures in the size range of 1 – 100 nm. This study introduces one of the methods of nanoparticle synthesis, namely the green synthesis of ZnO NPs using *Becium grandiflorum* leaf aqueous extract. The synthesized ZnO NPs were used to remove MB dye from aqueous solutions [1]. ZnO nanoparticles synthesized using plant extracts and their derivatives are more stable compared to the use of other organisms. This is because the content in plant extracts acts as a reducing agent and stabilizer as well as a capping agent in the biosynthesis of ZnO nanoparticles [2]. Research on the synthesis of $Ag/CoFe_2O_4$ nanoparticles using binahong leaf extract has a degradation percentage value of 44.84% with a contact time of 120 minutes [3]. Another study is on the biosynthesis of zinc oxide nanoparticles with *Suaeda japonica* extract. This study succeeded in reducing methylene blue by 54% [4]. Red betel is a plant that is widely used because of its various uses. Red betel contains several compounds, namely phytochemicals from the alkaloid, flavonoid, and tannin groups which are effective as antihyperglycemic and antioxidants [5]. The tannin compound contained in betel leaves is a phenolic compound which is a polymerization of simple polyphenols. The flavonoid and phenolic content obtained from red betel leaf extract is a surface active molecule that can reduce metals in the formation of nanoparticles [6]. Red betel (*Piper crocatum*) is one of the potential medicinal plants that is empirically known to have properties to cure various types of diseases, in addition to also having high spiritual value. This plant is included in the Piperaceae family with the appearance of leaves that are silvery red and shiny when exposed to light.

In 1990, red betel was used as an ornamental plant by hobbyists, because of its attractive appearance. The surface of the leaves is silvery red and shiny (the red betel plant can be seen in Figure 1). In recent years, it has been widely discussed and used as a medicinal plant. From several experiences, it is known that red betel has medicinal properties for several diseases [2].

Figure 1. Red betel plant.

The use of red betel leaves is currently widely used as herbal medicine. Investigations into the benefits contained in red betel leaves are mentioned because several phytochemicals such as phenolics, essential oils, flavonoids, and terpenes provide positive bioactivity effects. These compounds are equipped with functional groups designed to have properties such as inhibiting oxidation in free fatty acids, facing free radical activity or inhibiting the growth of unwanted cells. Therefore, these bioactive compounds have some potential as antioxidants, antiseptics, antimicrobial activity, and antihyperglycemia. In addition, leaf extracts are also indicated to have anticancer activity against human breast cancer cells [7].

Zinc oxide is an inorganic compound with the molecular formula ZnO. This compound is in the form of a white powder and is almost insoluble in water. ZnO powder is widely used as an additive in various materials and products of ointments, adhesives, plastics, sealants, pigments, food (source of Zn nutrition), batteries, ferrites, and flame retardants [3]. Zinc oxide (ZnO) has a band gap width of 3.37 eV at room temperature (RT) and an exciton energy of 60 meV. ZnO has excellent chemical stability because its hexagonal wurtzite structure at normal temperatures causes large Coulomb forces for its positive and negative electron pairs [8]. This study aims to study the structural, optical and morphological properties of ZnO nanoparticle biosynthesis using red betel leaf extract.

MATERIALS AND METHODS

Preparation of Red Betel Leaf Extract

The plants used are fresh leaves. The leaves that have been taken are washed until clean then rinsed using deionized water then the leaves are cut into pieces to facilitate the drying process. The drying process is carried out under sunlight until the red betel leaves are dry. Once dry, the leaves are ground using a blender and sieved. A total of 10 grams of red betel leaf powder is added with 100 ml of deionized water. After that, it is heated on a hot plate for 30 minutes at a temperature of 90ºC while stirring using a magnetic stirrer. Allow the solution to cool, until it reaches room temperature. Furthermore, the boiled water is filtered using Whatman paper no. 1 until the filtrate is obtained as a red betel leaf polyphenol extract. This filtrate will be used as a bioreductor in the ZnO nanoparticle synthesis process.

Preparation of Precursor Solution

Preparation of ZnO precursor solution with a concentration of 0.1 M was carried out by dissolving 2.97 grams of $Zn(NO_3)_2 \cdot 6H_2O$ crystals. The dissolution process was carried out in an Erlenmeyer flask by adding 100 ml of distilled water. Then, the solution was stirred until it was completely mixed evenly.

Synthesis of ZnO Nanoparticles

The synthesis of nanoparticles was carried out using the biosynthesis method by reacting red betel leaf extract with a previously prepared zinc oxide solution. The red betel leaf extract here acts as a bioreductor. Then drip NaOH solution until it reaches pH 7. The addition of NaOH plays a role in regulating the acidity of the solution. Synthesis of ZnO nanoparticles was carried out by comparing the volume of red betel leaf extract with 0.1 M $Zn(NO_3)_2{\cdot}6H_2O$ solution, namely 1:1, 1:5, and 1:10. The solution was continuously stirred until it was homogeneously mixed using a magnetic stirrer. Then, the solution was heated on a hot plate at 90ºC. The solution was sonicated until it turned brownish black and a precipitate appeared. The precipitate was centrifuged and washed several times with distilled water and absolute ethanol before being dried and heated at 150ºC for 30 minutes to obtain a brownish black powder of ZnO nanoparticles ready to be characterized for structural, optical and morphological properties using XRD, UV-Vis, and SEM.

RESULTS AND DISCUSSION

The synthesis process has been carried out by varying the volume of red betel leaf extract with $Zn(NO_3)_2{\cdot}6H_2O$ precursor with a ratio of 1:1, 1:5 and 1:10 to produce nanoparticles. There is a change in the color of the red betel leaf extract to pitch black at the beginning of the synthesis process as shown in Figure 2.

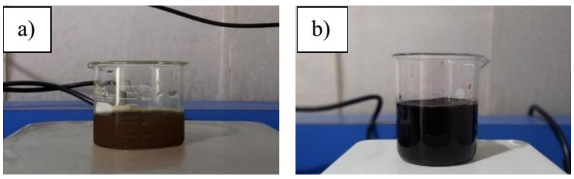

Figure 2. Color change when: (a) before adding NaOH and (b) after adding NaOH.

The color change that occurs during the synthesis process indicates that there is a reaction due to the addition of $Zn(NO_3)_2{\cdot}6H_2O$ and NaOH solutions. The synthesis begins with the formation of $Zn(OH)_2$ which is indicated by the production of a transparent cloudy black solution in the reaction. When Zn^{2+} and OH^- have reached the critical solubility number, a colloid will be produced which is indicated by a change in the color of the solution to pitch black. Zinc cations will then react with hydroxide anions and form a stable $Zn(OH)_4^{2-}$ complex. The presence of H_2O and energy from continuous stirring using a magnetic stirrer, the $Zn(OH)_4^{2-}$ complex can dissociate to form Zn^{2+} and OH- ions which will then form ZnO nanoparticles [2].

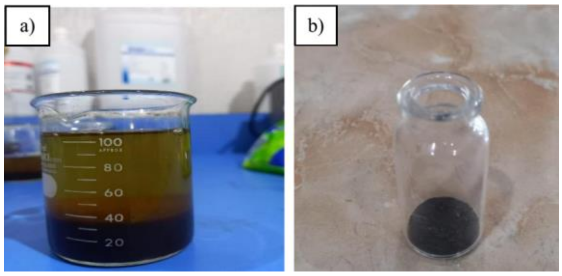

Figure 3. Sample synthesis results: (a) after 1 hour of stirring and (b) powder after drying in the oven.

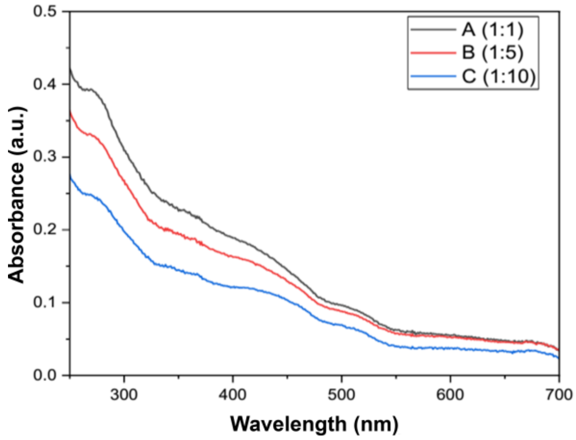

Figure 4. Graph between absorbance and wavelength in sample A (1:1), sample B (1:5) and sample C (1:10).

Continuous stirring using a magnetic stirrer produces a precipitate as shown in Figure 3. The precipitate formed is then dried using an oven for 1 hour at a temperature of 150º to produce powder. In the drying process, this precipitate will cause a dehydration reaction, namely the release of hydrate molecules which are released into the environment in the form of water vapor [9]. The UV-Vis spectrum curve of the ZnO sample with variations in extract and precursor volumes can be seen in Figure 4 showing that this UV-Vis test aims to determine the presence of nanoparticles formed. Analysis of the UV-Vis spectrophotometer test results on samples A (1:1), B (1:5) and C (1:10) with a wavelength range of 250 – 700 nm showed differences in absorbance values. The difference in absorbance and wavelength values indicates the influence of the ratio of the volume of red betel leaf extract to the $Zn(NO_3)_2$ precursor.

Based on the UV-Vis absorbance spectrum curve in Figure 4, the peak absorbance or light absorption of the ZnO sample is in the wavelength range of 250 – 330 nm which indicates that nanoparticles have been formed. These results are in accordance with other studies that recorded the UV-Vis spectrum of ZnO NPs, namely between 250 nm and 300 nm [9]. In another study, the synthesized ZnO NPs showed absorption bands ranging from 308 nm to 330 nm with a maximum peak appearing at 317 nm [10]. Sample A ZnO with a ratio of 1:1 is the sample with the highest absorbance value due to the higher volume of plant extract and sample C with a ratio of 1:10 has the lowest absorbance value. The absorbance values in samples A (1:1), sample B (1:5) and sample C (1:10) were 0.39; 0.33; and 0.24 a.u. Absorbance is directly related to the number of nanoparticles formed. The UV-Vis results show that the absorbance value increases with increasing extract volume. If the absorbance value is higher, the more nanoparticles are formed [11]. Sample A (1:1) was chosen for XRD and SEM characterization because it has the best absorbance intensity. UV-Vis spectrum data is used not only to find out about the absorbance value of the ZnO nanoparticle sample but can also be used to determine the energy gap of the sample. Tauch theory is used to determine the energy gap (E_g) value of sample absorption.

The band gap energy is obtained by transforming the absorbance graph as a function of Wavelength into a graph $(\alpha h\nu)^2$ as a function of the gap energy using the equation $(\alpha h\nu)^2 = B(h\nu - E_g)$, then the gap energy is determined by the extrapolation technique, namely drawing a straight line that intersects the x-axis (energy). The linear transformation graph $(\alpha h\nu)^2$ with energy (eV) of the ZnO sample with a ratio of 1:1 (sample A) has an energy gap of 3.54 eV (see Figure 5). The energy gap results of this study are not much different from the synthesis of ZnO nanoparticles through the wet chemical method with an energy gap value of 3.63 eV [12]. The X-ray diffraction spectrum of the 1:1 sample can be seen in Figure 6 which shows the peak crystallinity of ZnO nanoparticles that were successfully synthesized using red betel leaf extract. The diffraction pattern peaks are located at 4 2θ angles, namely 33.49º, 59.54º, 63.4º, and 70.15º. The resulting Miller indices are (100), (103), (200), and (201). These diffraction peaks correspond to the hexagonal wurtzite structure based on the Joint Committee in Powder Diffraction Standard (JCPDS) No. 36-1451 [13].

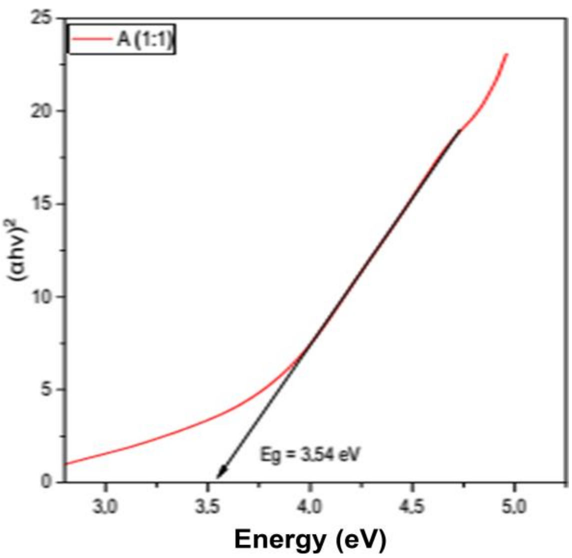

Figure 5. Energy gap graph of ZnO nanoparticles in sample A (1:1).

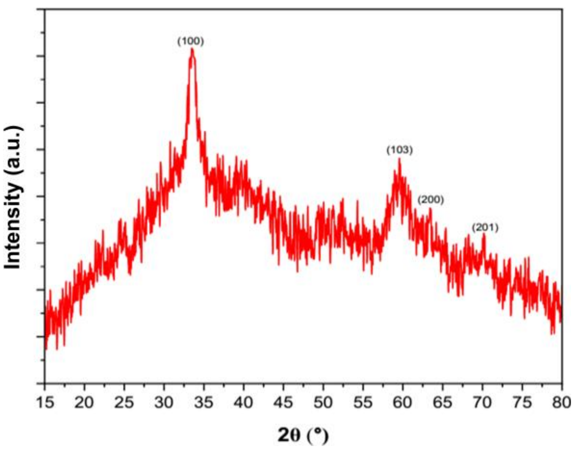

Figure 6. XRD pattern of ZnO nanoparticles in sample A (1:1).

The highest and sharpest diffraction peak based on the XRD pattern as shown in Figure 6 is at position 2θ = 33.49º. Where the diffraction peak is the same as the study on the synthesis of ZnO nanoparticles using trisodium citrate precursors with the Miller index (100) [14].

Scanning electron microscope (SEM) characterization aims to show or demonstrate the surface morphology of ZnO samples synthesized using zinc nitrate hexahydrate precursor solution and red betel leaf extract solution with the best sample ratio in the UV-Vis test, namely a 1:1 sample. SEM results provide information on size and shape based on the surface image of the ZnO sample. Figure 4.6 shows the SEM results with a magnification of 10,000 times and particle size distribution.

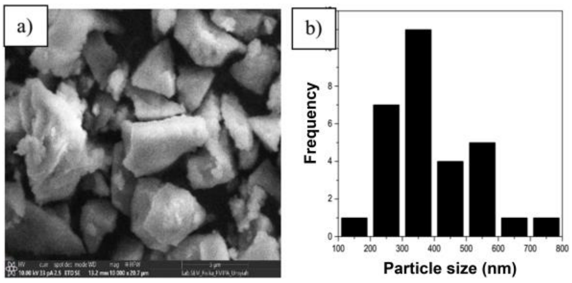

Figure 7. Morphology of ZnO nanoparticle size with (a) 10000x magnification and (b) graph of the results of measuring the diameter of ZnO sample particles.

Based on the SEM results seen in Figure 7 (a) shows the agglomeration (accumulation or collection of nanoparticles) of zinc oxide. Where if a closer look at the agglomerated lumps shows the presence of several nanoparticle aggregates. The surface morphology looks rough and thick, some particles appear elongated and granular like research by [15]. SEM surface morphology analysis can also determine particle size by measuring each particle using ImageJ Software. Figure 7 (b) is a bar chart of measurement results showing the distribution of particle sizes from a scale of 100 – 800 nm. The size of the ZnO nanoparticles obtained varies in the range of 170.4 nm to 758.5 nm with an average nanoparticle size of 402.4 nm. Based on the results, the size of the nanoparticles obtained shows a non-homogeneous particle size distribution. This can be seen from the large standard deviation value obtained, which is 141.63 nm. These results are similar to research where the particle size distribution is between 102 – 733 nm with an average particle size of 607 nm [16].

CONCLUSION

Based on the results of the analysis of the structural, optical and morphological properties of the synthesized ZnO nanoparticles, it can be concluded that red betel leaf extract can act as a reducing agent for zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$ solution. UV-Vis spectrophotometer absorption analysis showed an absorbance peak in the wavelength range of 250-330 nm with the highest absorbance in samples A (1:1), B (1:5), and C (1:10) respectively 0.39, 0.33, and 0.24 a.u. The XRD pattern shows that the nanoparticles have a Hexagonal wurtzite structure with a crystal size of 10.58 nm. SEM analysis shows that the ZnO nanoparticles have an inhomogeneous morphological shape with a non-uniform distribution. The average size of the ZnO nanoparticles is 402.4 nm.

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