Of ZnO Nanoparticle using Sandoricum Koetjape Peel Extract as Bio-stabilizer under Microwave Irradiation

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Abstract. The use of sentul (Sandoricum koetjape) peel extract as a biostabilizer in the synthesis of zinc oxide (ZnO) nanoparticles has been carried out as an environmentally friendly production. This research was conducted by reacting a 0.2 M of Zn precursor (zinc nitrate hexahydrate) solution with Sentul peel extract (10g/l). The samples were varied based on the ratio of the volume of the Zn solution to the Sentul peel extract, i.e., 1:4, 2:3, 1:1, 3:2, and 4:1 where each sample was assigned a ZSk initial code. The ZnO synthesis used a microwave technique with a power of 360 Watt. Morphological, structural, optical absorption, and functional groups were analyzed based on the results of the characterization of SEM, XRD, UV-Vis, and FTIR Spectroscopy. SEM images show the morphology of ZnO particles in the form of semi-hollow spheres and macaron-like shapes. The particle size decreases with the addition of the volume of the Zn solution. The XRD diffraction pattern shows the diffraction peaks that correspond to the hkl plane of the wurtzite hexagonal structure of ZnO. The highest optical absorption of the UV-Vis spectrum occurred in the wavelength range of 300-360 nm. The FTIR spectrum represents the involvement of the O-H functional groups derived from the polyphenolic compound of sentul peel extract.

1. Introduction
Zinc oxide (ZnO) is a powdered metal oxide material that is difficult to dissolve in water and has excellent properties with a wide bandgap energy of 3.37 eV and a high exciton binding energy of 60 meV[1]. The existence of a wide bandgap energy value in ZnO compounds makes this metal oxide widely synthesized, modified, and applied by researchers in various applications such as sensors, energy generation, and photocatalysts in hydrogen production[2]. In addition, ZnO is easy to manufacture and more economical.

The methods developed by researchers to synthesize ZnO nanoparticles have been widely used, including dip coating, chemical vapor deposition (CVD), hydrothermal, and electrochemical deposition methods. Although this method produces high purity and crystallinity, it requires high operating temperatures[3]. Additionally, these methods are very difficult to apply on an industrial scale and extremely expensive. Synthesis of ZnO by utilizing plant extracts is recently developed. This step can reduce the use of hazardous chemicals and is low-cost, environmentally friendly, and does not use high temperatures. Secondary metabolite compounds found in plant extracts such as phenols, flavonoids, tannins, and terpenoids will act as biostabilizer and bioreduction in the growth of nanoparticles[4]. The production of ZnO nanoparticles that have been carried out by utilizing plant
extracts includes moringa leaf[5], pomegranate[6], and rambutan[4]. It resulted in various morphology, shape, and size[4-6].

High-speed synthesis by microwaves has attracted considerable attention because microwave heating results in higher reaction rates, faster volumetric heating, and shorter reaction times[7]. One of the main characteristics of this technique is to ensure uniform heating of the precursor and results in a very fast reaction rate where the process changes from several hours to several minutes[8]. In other words, microwave synthesis is considered an important approach towards a green chemical synthesis because this microwave technique is more environmentally friendly. Its ability to pair directly with reaction molecules and bypassing thermal conductivity causes a rapid temperature rise. Microwave irradiation has been widely used to improve many organic syntheses[9].

In this research, ZnO nanoparticles were synthesized using sentul (Sandoricum koetjape) peel extract as a biostabilisator incorporating microwave irradiation technique. Sentul fruit trees are grown in the Faculty of Mathematics and Natural Sciences, Riau University. However, every part of this fruit, especially the peels, contains secondary metabolites such as flavonoids, terpenoids, saponins, and polyphenols[10]. The use of the microwave technique was chosen because it is easier, faster, and economical[11]. This study analyzed the effect of volume ratio of Zn solution (zinc nitrate hexahydrate) with Sentul peel extract in the formation of ZnO nanoparticles on their physical properties, namely particle morphology, crystal structure, optical absorption, and functional groups.

2. Methodology

2.1. Preparation of sentul peel extract

The fresh fruit peel was selected to be extracted. Sentul peel was dried in direct sunlight and then crushed into powder. The purpose of drying was to remove the moisture content of the Sentul peel. Sentul peel extract was made by heating 100 mL of distilled water and add 2 grams of Sentul peel powder to a constant temperature of 80°C[12]. Finally, the extract was filtered with Whatman filter paper and stored in a dark glass bottle. The extract results are shown in Figure 1.

![Figure 1. (a) Dried sentul peel (b) Sentul peel extract](image)

2.2. Synthesis of ZnO Nanoparticle

ZnO nanoparticles were prepared by reacting 0.2 M zinc nitrate hexahydrate solution with Sentul peel extract into 100 mL Erlenmeyer. The solution was stirred using a magnetic stirrer until homogeneous. Microwave irradiation was using a microwave oven model Kris at 360 W (until a white precipitate appears). After the synthesis is completed, the white colloidal solution is precipitated and collected by centrifugation at 4000 rpm. The ZnO nanoparticles were dried in an oven at 110°C overnight.
3. Results and discussion

The morphological properties of ZnO samples were evaluated using the SEM technique (figure 2). Micrographs of the ZnO samples exhibit the shape of a semi-hollow, macaron-like sphere and quasi-spherical particles. ZSk-1:4 sample has a semi-hollow spherical shape with a diameter of 608.7 nm. ZSk-2:3, ZSk-3:2, and ZSk-1:1 samples show a macaron-like shape with diameters ranging from 540.9-581.6 nm, while the ZSk-4:1 sample shows a spherical shape with fine holes on the surface which has a diameter of 236.5 nm. ZSk-1:4 sample with the highest Zn precursors volume has the smallest particle size compared to other samples. The particle size of ZnO decreases with increasing Zn solution volume. The difference in the shape of the ZnO particles was influenced by the volume ratio of the Zn solution and the Sentul peel extract. In addition, it appears that the formed ZnO particles undergo agglomeration between particles so that they have a non-uniform particle shape[13].

![Figure 2](image_url)

Figure 2. SEM morphology of ZnO sample (a) ZSk-1:4, (b) ZSk-2:3, (c) ZSk-1:1, (d) ZSk-3:2 and (e) ZSk-4:1.

The XRD diffraction pattern of the ZnO sample is shown in Figure 3. The diffraction peaks of the ZnO crystal phase are at 2θ = 31.76°; 34.42°; 36.24°; 47.52°; 56.58°; 62.82°; 66.34°; 67.96°; 69.04°; 72.78° and 76.94° with hkl plane of (100), (002), (101), (012), (110), (013), (200), (112), (201), (004) and (202), respectively. These diffraction peaks correspond to Crystallography Open Database No. 9004179 wherein the ZnO sample has a characteristic hexagonal wurtzite crystal structure. The peaks of the above hkl plane are similar to the results of research conducted by Raysa et al[14].
The diffraction pattern shows a sharp peak of the synthesized ZnO phase without any impurities or other phases found. The crystal size of the ZnO sample obtained from the Scherrer equation is 21.31 nm and the lattice parameters of ZnO are \( a = 3.25 \) Å and \( c = 5.20 \) Å. These results are in agreement with previously reported studies using pomegranate peel extract (Punica granatum)[15].

The optical absorption spectra of ZnO samples are shown in Figure 4. The maximum absorption of ZSk-1:4, ZSk-2:3, ZSk-1:1, ZSk-3:2, and ZSk-4:1 samples occurred at different wavelength ranges namely, 300-357 nm, 300-358 nm, 300-360 nm, 300-357 nm, and 300-359 nm, respectively. The absorption peak of the ZnO sample at ~360 nm is a characteristic of ZnO absorption which indicates that ZnO nanoparticles have been formed[16]. The absorption peaks are shifted most likely due to slight agglomeration[15].

![Figure 3. X-ray diffraction pattern of ZnO sample](image1)

![Figure 4. Optical absorption spectrum of ZnO sample with various of volume ratio of Zn solution and sentul peel extract](image2)
The optical absorption spectrum can also determine the band gap energy of the ZnO sample. The determination of the band gap energy is obtained using the following equation:

\[ E_g = \frac{hc}{\lambda_c} \]  

(1)

Where \( E_g \), \( h \), \( c \), and \( \lambda_c \) are band gap energy (eV), Planck’s constant (6.626x10^{-34} \text{ Js}) , the speed of light in a vacuum (2.997x10^8 \text{ m/s}) and the cut off wavelength (nm). The band gap energy of ZSk-1:4, ZSk-2:3, ZSk-1:1, ZSk-3:2, and ZSk-4:1 samples are 3.38 eV, 3.05 eV, 3.03 eV, 3.04 eV, and 3.18 eV, respectively. Based on this value, the smaller the band gap energy obtained, the narrower the band gap between the valence band and the conduction band. Therefore, if the band gap energy is small, the optical absorption will be greater. This small band gap energy has the potential to be applied as a photocatalyst[17].

4. Functional Group
The FTIR spectrum of the sentul peel extract and the ZnO sample, namely ZSk-1:1, is shown in Figure 5. ZSk-1:1 sample was chosen because it has the highest optical absorption.

![FTIR Spectrum](image)

Figure 5. Spectrum of FTIR (a) Sentul Peel Extract (b) ZnO.

According to FTIR results, sentul peel extract contains (O-H) functional groups from the phenolic compound represented by wide and strong IR absorption at a wavenumber of 3316 cm^{-1}. This wide spectrum shifted from wavenumber 3316.74 cm^{-1} to wavenumber 3368.82 cm^{-1} caused by the reduction of this functional group from the sentul shell extract and the formation of absorption indicating the presence of a hydroxyl functional group in ZnO. In the ZnO sample, there are alkane compounds (C-H) at wavenumbers 2897.21 cm^{-1} and 2795.94 cm^{-1}. At wavenumber 1411.95 cm^{-1} there are carboxylic acid compounds (O-H) which show the presence of a hydroxyl functional group in the ZnO sample. This is also reinforced by the compound (C-H) which shows the presence of a hydroxyl functional group because (C-H) is an overlap of (O-H). This hydroxyl functional group is obtained from the group of alcohol compounds (O-H) found in the sentul peel extract[18]. This is also confirmed by the presence of a peak at a wavenumber of 467.52 cm^{-1} which indicates the formation of a ZnO crystalline structure[19]. The functional group detected by FTIR spectroscopy is listed in Table 1.
Table 1. Functional groups and wavenumber of Sentul peel extract and ZnO sample.

| Sentul peel extract | ZnO Sample |
|---------------------|------------|
|                     |            |
| Wave number (cm\(^{-1}\)) | Functional groups | Wave number (cm\(^{-1}\)) | Functional groups |
| 3316.74            | O-H        | 3368.82 | O-H        |
| 2110.22            | C≡C        | 2897.21 | C-H        |
| 1639.56            | N-O        | 2795.94 | C-H        |
| 655.83             | C=C        | 2079.2  | C≡C        |
|                    |            | 1583.63 | N-O        |
|                    |            | 1411.95 | O-H        |
|                    |            | 1120.69 | C-O        |
|                    |            | 847.75  | C≡C        |
|                    |            | 467.52  | Crystalline ZnO |

5. Conclusion
In summary, the synthesis of ZnO nanoparticles using sentul peel extract with microwave techniques has succeeded in producing ZnO nanoparticles with a various morphological shapes such as a semi-hollow ball and macaron-shaped. The particle size obtained is influenced by the volume ratio of Zn solution and sentul peel extract. The greater the extracted content, the greater the particle size obtained. The XRD pattern shows that the resulting ZnO has a hexagonal wurtzite crystal structure with a crystal size of 21.31 nm. The UV-Vis spectrum shows that the maximum optical absorption of ZnO samples is at ~360 nm. The FTIR spectrum shows the involvement of the dominant O-H functional group in the ZnO synthesis process using sentul peel extract as a biostabiliser.

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