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Synthesis of ZnO Nanoparticles from Zink Acetate using Red Betel and Bay Leaves Extract and It's Application as Sunscreen

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ABSTRACT

The ZnO nanoparticles have been synthesized using red betel and bay leaves extract and characterized to analyze the maximum wavelength, crystallinity, particle size, composition, and its activity as sunscreen. The synthesis of ZnO nanoparticles was carried out through reflux method using $Zn(CH_3COO)_2$. $2H_2O$ red betel leaf as bioreductor. The same procedure was also applied by changing the betel leaf extract with bay leaf extract. The resulted materials were characterized by UV-Vis spectrophotometry, FTIR, PSA, XRD, and SEM EDX. The ZnO nanoparticles synthesized with red betel leaf have a maximum wavelength of 374.5 nm, wave number of 462.92 cm^{-1}, particle size of 23.309 nm, 74.1% of Zn and 16% of O, SPF value of 8.047942. ZnO nanoparticles synthesized using bay leaf extract have a maximum wavelength of 374 nm, high crystallinity properties with a hexagonal crystal structure, an average particle size of 2.463 nm, 64.21% of Zn and 22.85%, and an SPF value of 2.886969. The activity test of ZnO nanoparticles as sunscreen showed that synthesis both using red betel and by leaves extract resulted in a good sunscreen activity test comparing with ZnO synthesized using ethanol as a control. Thus the synthesis of ZnO nanoparticles using natural extract is being a better way to use as a green synthesis that environmentally friendly.

Keyword: *ZnO nanoparticles, bay leaf extract, red betel leaf extract, sunscreen, SPF*

1. INTRODUCTION

High sun exposure can cause skin redness (erythema), dark spots (pigmentation), premature aging and even skin cancer. This is because sunlight emits a certain amount of energy at a wavelength of 200-400 nm, which is known as ultraviolet (UV) light. Therefore, sunscreen is needed to reduce the negative impact of UV rays (Dale Wilson, Moon, & Armstrong, 2012). One of the raw materials used to make sunscreen is ZnO nanoparticles. Based on research by Smijs & Pavel (2011) the use of ZnO nanoparticles as an additional ingredient in sunscreen shows protection from UV A rays. In addition,

ZnO nanoparticles are a GRAS material by the USA Food and Drug Administration so they are safe to use as food, cosmetics, personal care and medicine

ZnO nanoparticles can be synthesized using chemical methods. In the process of synthesizing ZnO nanoparticles, conditions that can affect the character of the particles are temperature, reaction time, solvent, pH, and concentration used (Bandeira et al, 2020). In previous studies, ZnO nanoparticles have been synthesized using ethanol and have the best characteristics compared to acetone and water (Khoza et al, 2012). However, to reduce the impact of the use of solvents on environmental safety, it is necessary to conduct research using biosynthetic methods using plant extracts.

The plant extracts used in the synthesis process are plant extracts containing flavonoids. Flavonoids contained in plant extracts play a role in forming nano-sized particles in the process of synthesizing nanoparticles by reacting with metal salts (Makarov et al, 2014). According to Makarov, Love, Sinitsyna, Makarova, Yaminsky, et al. (2014) terpenoids, tannins and flavonoids play a role in forming nano-sized particles. One of the natural ingredients that contain flavonoids is red betel leaf and bay leaf. . Based on research by Prayitno, Kusnadi, & Murtini (2018), the total flavonoid content of red betel leaf is 155.27-168.33 mg QE/g. While research by Harrizul et al (2019), bay leaf extract contains flavonoids 0.486%.

This article reported the synthesis of ZnO nanoparticles using red betel and bat leaves as an alternative green synthesis to result a same ZnO material that synthesized using 20% ethanol.

2. RESEARCH METHOD

The study began with the extraction of red betel leaves and bay leaves using the Fakhari, Jamzad, & Kabiri Fard (2019), namely red betel leaves and bay leaves washed with water and then cut to a size of about 3 mm. A total of 10 grams of red betel leaf was heated with 100 mL of distilled water for 10 minutes at a temperature of 85^{o}C. After that, the red betel leaf extract was cooled and filtered using filter paper. To make bay leaf extract, 10 g of bay leaf was heated with 100 mL of distilled water for 25 minutes at a temperature of 80^{o}C. The heating results are filtered. After obtaining red betel leaf extract and bay leaf extract, they were used for the synthesis of ZnO nanoparticles.

Synthesis of ZnO nanoparticles using red betel leaf extract was done with a mixture of red betel leaf extract and 0.15 M zinc acetate with a ratio of 1:9 was refluxed and stirred for 1 hour at a temperature of 80^{o}C-85^{o}C. Then 0.1 M NaOH was added until the pH became 8. The mixture was continuously stirred for 1 hour and allowed to stand for 12 hours. The solid formed was centrifuged at 4000 rpm for 10 minutes and washed with deionized water. The solids were dried at a temperature of 100^{o}C for 6 hours and then the calcination process was carried out with a furnace at a temperature of 450^{o}C for 4 hours. The same procedure was done by substituting the red betel leaf extract with bay leaf extract.

In the synthesis of ZnO nanoparticles using 20% ethanol extract, 10 mL of 20% ethanol was added 90 mL of 0.15 M $Zn(CH_3COO)_2.2H_2O$ solution. The mixture was stirred and heated at 80oC for 1 hour, then the pH of the solution was conditioned to 8 with addition of 0.1 M NaOH solution. The mixture was stirred for 1 hour. The solids formed were centrifuged at 4000 rpm for 10 minutes and washed with deionized water, then dried at 100oC for 6 hours, then the solids were put into the furnace at 450oC for 4 hours.

The resulted materials were characterized using UV-Vis Spectrophotometer, XRD, PSA, dan SEM-EDX. Sunscreen activity test were done using spectrophotometer method.

3. RESULTS AND DISCUSSION

Synthesis of ZnO nanoparticles with red betel leaf extract resulted in 0.9148 grams of gray ZnO nanoparticle powder. The reaction between zinc acetate and red betel leaf extract at the beginning of the reaction was brownish red after the reflux process, the color changed to brownish green and there was a gray green precipitate. The color change occurs due to the interaction between the OH

group at the 4' position of the flavonoid compound with Zn^{2+} which forms a Zn-flavonoid complex. The reaction mechanism between zinc acetate and flavonoids is as shown in Figure 1. Furthermore, the Zn(OH)2 that occurs reacts with NaOH to form ZnO nanoparticles (Khan et al, 2014).

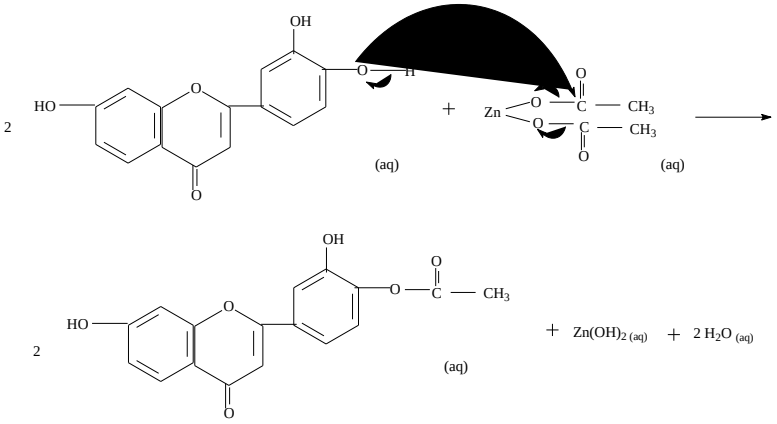

Figure 1. Mechanism of ZnO nanoparticle synthesis using red betel leaf extract

The results of the UV-Vis spectrophotometer test of ZnO nanoparticles of red betel leaf extract had absorption at a wavelength of 374.5 nm (Figure 2), while the results of the synthesis with bay leaf had a maximum wavelength of 374 nm (Figure 3). The test results were in the typical range of ZnO nanoparticles absorption wavelength which is 360-380 nm (Chieng et al, 2012), this shows that the synthesis results may contain ZnO nanoparticles.

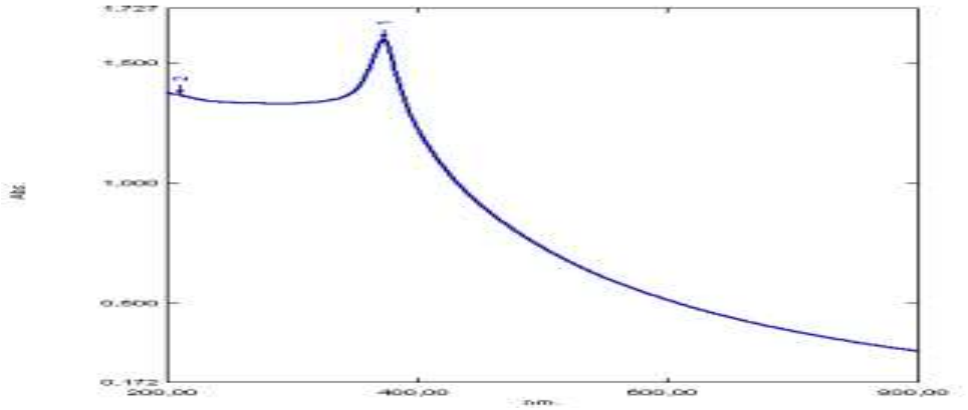

Figure 2. UV Vis Spectrum of ZnO synthesized using red betel leaf extract

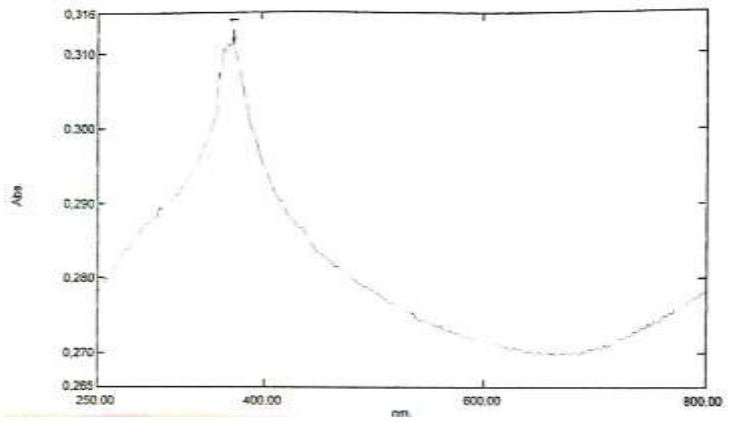

Figure 3. UV Vis Spectrum of ZnO synthesized using bay leaf extract

In order to strengthen the evidence that ZnO (zinc oxide) compounds have been formed, the FTIR test showed that ZnO nanoparticles synthesized using red betel leaf extract had a strong absorption peak at a wave number of 462.92 cm^{-1} (Figure 4). The FTIR results of ZnO nanoparticles with betel leaf showed absorption peaks at the same wave number except for the wave number of 1473 cm^{-1}. The aromatic C=C bond comes from the flavonoid component contained in red betel leaf extract.

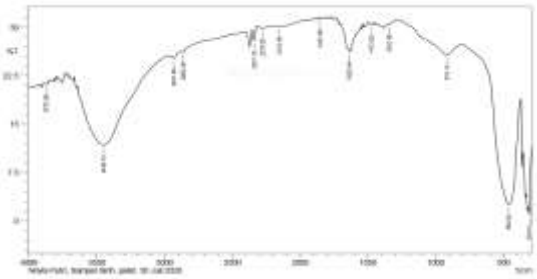

Figure 4. FTIR result of ZnO synthesized using red betel leaf extract

XRD analysis obtained 2 theta data, the results of 2θ ZnO nanoparticles of raw betel leaf have similarities with the results of 2θ COD (Crystallography Open Database), the Match application where this data is a diffactrogram of ZnO compounds. The data show that the resulting ZnO nanoparticles have high crystallinity and purity. This can be seen from the graph which has a sharp intensity and there are no peaks that do not match the database (Figure 5). Based on crystal size determination using Debye Scherer formula, the average size of ZnO is about 23.30898092 nm. The

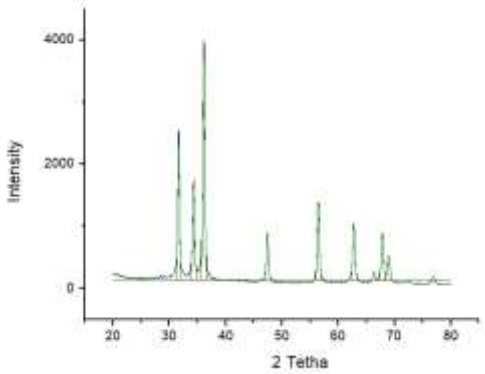

Figure 5. XRD result of ZnO synthesized using red betel leaf extract

The XRD analysis result of ZnO nanoparticles synthesized using bay leaf extract and 20% ethanol were shown in Figure 6. Based on the diffractogram XRD analysis results that have been adjusted to COD (Crystallography Open Database) in the Match! with entry number 96-230-0451, the two synthesized compounds are zinc oxide or ZnO compounds which have high crystallinity properties, which are indicated by sharp peaks, and a hexagonal crystal system.

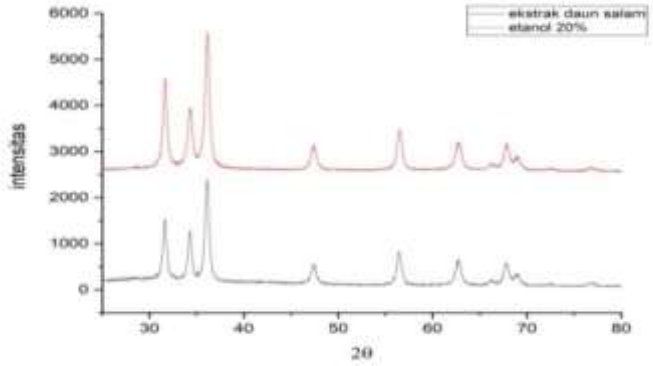

Figure 6. Difractogram of ZnO nanoparticles synthesized using bay leaf extract and 20% ethanol

ZnO nanoparticles synthesized using red betel leaf undergo agglomeration which is clearly shown on the surface. Agglomeration is thought to occur due to the lack of volume of red betel leaf extract which acts to reduce Zn^{2+} ions to Zno and bind ZnO clusters so that the particle surface is covered with negatively charged ions so as to prevent agglomeration between particles and form stable particles. The lack of betel leaf extract causes excess Zn^{2+} ions during synthesis. Excess Zn^{2+} ions cause interactions with ZnO particles which are covered with negatively charged ions, resulting in particle attachment or better known as agglomeration. This is in accordance with research reported by Soto-Robles et al. (2019) that the particle agglomeration occurred at low concentration. The EDX spectra (Figure 7) showed that the composition of ZnO nanoparticles synthesized with red betel leaf contained 74.1% Zn, 16% O and 9.9% Au.

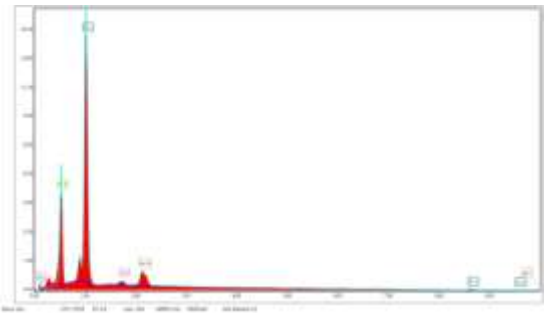

Figure 7. EDX Result of ZnO nanoparticle synthesized using red betel leaf extract

The results of data analysis using SEM-EDX can be used to determine the shape of the formed ZnO particles and the composition of the ZnO particles. Based on micrographs of the synthesis of ZnO bay leaf extract and ZnO ethanol 20%, it was seen that there was an uneven distribution of particles. However, bay leaf extract ZnO was more agglomerated than 20% ethanol ZnO which was indicated by a larger particle size. This is supported by PSA data, namely 20% ethanol ZnO nanoparticles have an average particle size of 1012 nm while the bay leaf extract ZnO nanoparticles have an average particle size of 2463 nm. Based on the EDX results, the % mass composition of Zn and O which is close to the theoretical Zn composition is owned by ZnO synthesized with bay leaf extract (Table 1).

Table 1. EDX result of ZnO nanoparticles synthesized using bay leaf extract

Nama Sampel	Komposisi	
	%Massa Zn	%Massa O
ZnO 20 % ethanol	80.34	19.66
ZnO bay leaf extract	64.21	22.85

The sunscreen activity test was carried out using a UV-Vis spectrophotometer. The synthesized ZnO sample with a concentration of 1000 ppm was searched for its absorbance value with a UV-Vis spectrophotometer at a wavelength of 290-320 nm with an interval of 5 nm. The SPF value was calculated using Mansur's (1986) formula. The sunscreen activity test was carried out using a UV-Vis spectrophotometer. The synthesized ZnO sample with a concentration of 1000 ppm was searched for its absorbance value with a UV-Vis spectrophotometer at a wavelength of 290-320 nm with an interval of 5 nm. The SPF value was calculated using Mansur's (1986) formula.

$$SPF_{spectrophotometric} = CF \times \sum_{290}^{320} EE\ (\lambda) \times I\ (\lambda) \times Abs(\lambda)$$

EE is *erythemal effect spectrum*, I is light intensity, Abs is material absorbance, and CF is correction factor (=10).

SPF value analysis is used to determine how long sunscreen can protect the skin from sun radiation (UV) without sunburn. Based on the SPF calculation results, the Sayre formula ZnO nanoparticles synthesized with red betel leaf extract had an SPF of 8.047942, ZnO with bay leaf extract is 2.886969, ZnO synthesized using 20% ethanol is 4.845393. According to SPF value of *Food and Drug Administration* (FDA) (Table 2), ZnO synthesized using bay leaf extract has a minimal protection, ZnO synthesized using 20% ethanol has a medium sun protection, while ZnO synthesized using red betel leaf extract has a maximal protection.

Tabel 2. SPF value according to FDA

Protection type	SPF value
minimal	1-4
medium	4-6
extra	6-8
maximal	8-15
ultra	>15

4. CONCLUSION

The results of the analysis of ZnO nanoparticles synthesized with red betel leaf have a wavelength of 374.5 nm, wave number 462.92 cm^{-1}, size 23.309 nm, mass percentages of Zn and O elements are 74.1% and 16% and SPF value of 8.047942. ZnO nanoparticles of bay leaf extract have a maximum wavelength of 374 nm, high crystallinity properties with a hexagonal crystal structure, an average particle size of 2463 nm, mass percentages of Zn and O elements are 64.21% and 22.85%, and SPF 2 values, 886969. ZnO nanoparticles of ethanol extract have a maximum wavelength of 369.5 nm, high crystallinity properties with a hexagonal crystal structure, an average particle size of 1012 nm, mass percentages of Zn and O elements are 28.23% and 35.57%, and an SPF value of 4.845393. The results of the synthesis of ZnO nanoparticles using red betel leaf extract and bay leaf extract were not different from the synthesis of ZnO nanoparticles using ethanol. Thus the synthesis of ZnO nanoparticles is better to use natural extracts that are environmentally friendly.

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