SYNTHESIS OF SILVER NANOPARTICLES USING BIOREDUCTOR OF CATAPPA LEAF EXTRACT (*Terminalia catappa*)

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Abstrak. Penelitian tentang biosintesis nanopartikel perak (AgNPs) menggunakan ekstrak daun ketapang telah dilakukan. Hasil karakterisasi spectrum UV-Vis, XRD, PSA, TEM, dan FTIR menunjukkan peningkatan konsentrasi $AgNO_3$ meningkatkan panjang gelombang (λ), konsentrasi $AgNO_3$ yang terbaik adalah 1 mM dengan SPR pada λ 430-432 nm. Peningkatan suhu sintesis cenderung menurunkan intensitas serapan, suhu sintesis yang terbaik adalah 30^{o}C dengan intensitas serapan 3.492. Menunjukkan kristal perak dengan distribusi ukuran rata-rata 47.1 nm. Ukuran AgNPs yang diperoleh berdasarkan TEM yaitu 36 nm dengan bentuk menyerupai bola. Gugus –OH berperan dalam reduksi $AgNO_3$ menjadi AgNPs.

Kata kunci : Bioreduksi, Nanopartikel Perak, Ketapang

Abstract. It had been done research about biosynthesis of nanoparticle silver (AgNPs) by using extract of ketapang leaf. The characterization result spectrum UV-Vis, XRD,PSA, TEM, dan FTIR show that increasing concentration $AgNO_3$ increase wavelength (λ), the best concentration $AgNO_3$ is 1 mM with SPR at λ 430-432 nm. The increasing temperature tend to decrease intensity of absorption, the best temperature of synthesis is 30^{o}C with intensity absorption 3.492 show the obtained crystal of silver with average size distribution about 47.1 nm. Based on TEM measurement, size of obtained AgNPs is 36 nm with ball shape. The –OH group responsible in reduction of $AgNO_3$ to become AgNPs.

Keyword : Bioreduction, Silver nanoparticle, Extract of Catappa

INTRODUCTION

Development of nanotechnology had opened a new foundation for application of science and engineering materials in recently decade. The most important part of nanotechnology material is nanostructure in various of composition, shape, and size which had been synthesized through various method. The conventional physic and chemical methods needed intensive amount of energy and didnot friendly environmental during usage of dangerous solvent and additive materials. Bioreduction method (based on plant) had been done as cheaper and environmental friendly method (Huang *et al*, 2011).

Silver had high electricity, catalytic, and thermal conductivity properties. The effect of surface area and quantum in nanometer (1-100 nm) scale was increased, therefore it would increase the properties of silver such as its mechanic, electricity, optical, magnetic and other properties (Ajitha *et al*, 2015). AgNPs is potential to be applied in several field such as: electro-catalysts (Edison *et al*, 2013), semiconductor materials (Nuryeti *et al*, 2012), and as sensor (Nuryeti *et al*, 2012 and Song *et al*, 2014)

Ketapang is a plant which had potential to be used as reductor in synthesis of AgNPs. The dominant compound in extract of ketapang leaf is phenolic (tannin) (Zakir *et al*, 2014). The phenolic compound tend to reduce the metals strongly, this one caused by the higher nucleofilicity in aromatic ring (Michalak, 2006). The recently researcher had synthesized AgNPs by using extract of plant as reductor, such as: extract *Ziziphora tenuior* with amine, carbonyl, and hydroxyl as reduction group, (Sadeghi and Gholamhoseinpoor, 2015), extract of *Eucalyptus oleosa* with carbonyl and hydroxyl as reduction groups (Pourmortazavi *et al*, 2015), extract *Piper longum* with Tannin as reductor compound (Reddy, 2013), extract *Annona squamosal* leaf with tannin as reductor compound (Vivek *et al*, 2012). The research that had been used extract of ketapang leaf as bioreductor in synthesis of AgNPs (Zakir *et al*, 2014), but optimum concentration of $AgNO_3$ and temperature had not been reported.

MATERIAL AND METHOD

Tools

The used tools in this research are: general laboratory glass equipment, oven (Gen Lab), analytical balance (OHAUS), spectrofotometer UV-Vis (UV-2600), *X-ray diffraction* (Shimadzu 7000), *Particle Size Analyzer* (PSA) HORIBA, SZ100, *Transmission Electron Microscopy* (TEM) TECNAI G2 STWIN 200 kV, pH meter, washing bottle and spatula.

Materials

The used materials in this research are: extract of ketapang leaf (*Terminalia ketapang*), AgNO3 (Merck, 99,8%), *p*-coumaric (Merck, 99%), methanol, dan aquabidest.

Procedure

1. Preparation of extract

The fresh ketapang leaf was washed with aquabidest and dried out. 10 g of ketapang leaf was cut off and added 40 mL of aquabidest and heated for 15 minutes. The extract (0.25 g/mL) was filtered and store at freezer when it was not used (Ankamwar, 2010).

2. Synthesis of Nanoparticle Silver

0,2 mL of extract sample (0,25 g/mL) was added into each 50 mL solution of $AgNO_3$ 1, 3, dan 5 mM respectively at temperature 30^oC. The synthesis of AgNPs was also done at temperature 60 dan 90 °C (Ankamwar, 2010).

3. Analysis UV-vis

Analysis UV-Vis was done to reaction solution at room temperature with spectrofotometer UV-2600.

4. Analisis XRD

Colloid AgNPs was sentrifuged at 10.000 rpm for 30 minutes. The obtained precipitate was dried and measure by spectrofotometer XRD.

5. Analisis PSA

Measurement PSA was conducted at colloid AgNPs at room temperature by using spectrofotometer PSA (HORIBA, SZ100).

6. Analysis FTIR

The extract solution was before and after reaction was dried at temperature 60 °C, then it was analyzed with spectrofotometer FTIR.

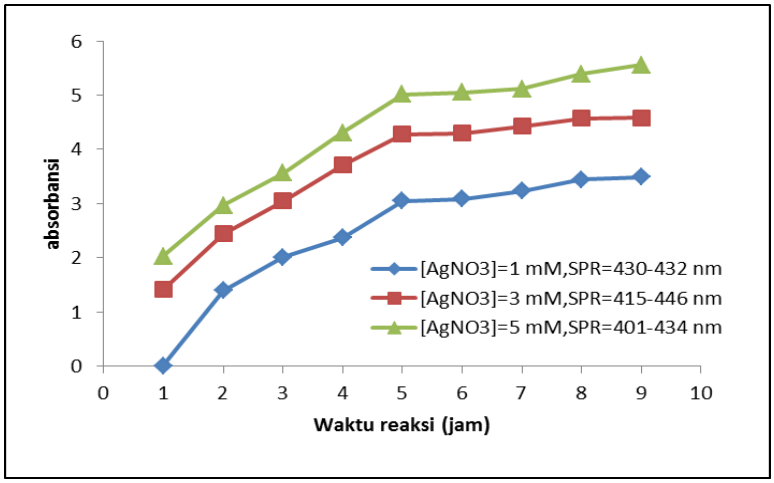

Figure 1. The changing of absorption intensity SPR of AgNPs as reduction product from $AgNO_3$ 1, 3 and 5 mM by using extract of catappa leaf 0.25 g/mL at temp 30 °C, for 54 hours

RESULT AND DISCUSSION

Biosynthesis of Nanopaticle Silver.

1.Absorption UV-Vis.

Various concentration and temperature was done to know the influence of concentration of $AgNO_3$ and temperature of reaction at SPR AgNPs that show the growth and distribution size of AgNPs, by using same extract. Figure 1 (a-c) show the absorption spectrum of UV-Vis as the function of concentration AgNPs against time reaction which was formed from reduction of solution $AgNO_3$ 1, 3, dan 5 mM with extract ketapang leaf at temperature 30 ^oC. The frequency and width of absorption *Surface Plasmon Resonance* (SPR) depend on size of AgNPs. Figure 1 show the peak SPR AgNPs in each concentration at 430-432, 414–446 and 401–434 nm, it indicate the presence of growth of AgNPs (Mittal *et al*, 2014) and spectrum dan spektra SPR become wide as the increasing concentration of $AgNO_3$. The changing of absorption intensity SPR as the function of time reaction was shown in figure 1d, it indicate the absorption intensity increase during reaction until it reach its stability. beside that, at the same reaction time the intensity increase as the increasing of concentration of $AgNO_3$. Based on collision theory, she increasing of concentration means that a lot amount of particle contained therefore the interparticle collision is intensive due to closer distance interparticles, this one cause effective collisions increase and it impact to the increasing of absorption intensity.

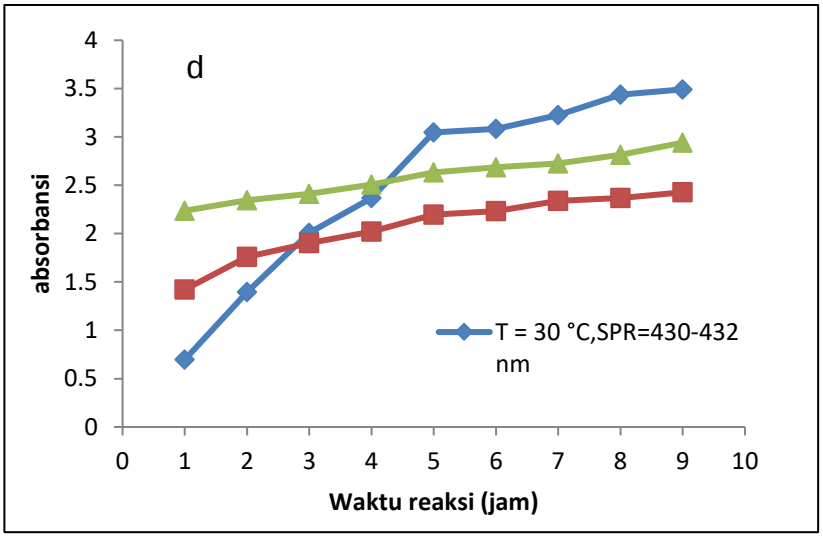

Figure 2. The changing of absorption intensity SPR of AgNPs as reduction product from $AgNO_3$ 1 mM by using extract of catappa leaf 0.25 g/mL at temp. 30, 60 and 90°C for 54 hours

Figure 2 (a-c) show the absorption spectrum UV-Vis pattern at temperature 30,60, and 90^oC with same reaction time and reducing agent.At concentration of $AgNO_3$ 1 mM, the measurement result show the peak SPR at 430-432, 428 - 429,

and 429 nm. Figure 2d show the changing of absorption intensity SPR during time reaction. comparing the absorption spectrum SPR at different temperature reaction (30, 60 and 90 ^{o}C), the peak at temperature 30 ^{o}C is sharpest and occur blue shift significantly (λ<) from 30 to 60 and 90 ^{o}C (Huang *et al*, 2011). Absorption intensity SPR of synthesized AgNPs at temperature 30 ^{o}C is higher than 60 and 90^{o}C. The shift λ SPR of AgNPs to the smaller(blue shift) indicate that the increasing of temperature make the kinetic energy of particle increase and form much bigger effective collision which cause bioreduction process occur faster, therefore the remaining time give chance to particle form bigger cluster. and possible to the growth of nanoparticle AgNPs is still ovvur after time 54 hours at temperature 30 °C than 60 and 90 °C. beside that, the effective collision could produce smaller size of AgNPs. It could be concluded that the increasing of temperature, λ and absorption intensity SPR of AgNPs tend to decrease.

2. Analysis XRD

Analysis XRD was conducted to confirm the presence of crystal AgNPs. The characteristic which was observed in pattern of XRD confirm the presence of crystal AgNPs (Figure 3). The diffraction pattern at angle 37.82°, 44.06°, 64.40° was match with miller index (111), (200), and (202), it indicate presence of crystal AgNPs (Rusnaenah, 2017). This data almost same which had been reported by Mitttal, et al., (2014), peak XRD at the angle 38.2^{o}, 44.4^{o}, and 64,6^{o} could be corresponded with (111), (200), and (220) which proved of crystal AgNPs.

3. Size Distribution

Characterization result by PSA inform that overall average distribution size at the initial, 24th and 54th hour are: 109.8, 55.1, and 47.1 nm respectively (Figure 4a-c). Average distribution size at 54th hour is smaller than initial and 24th hour, this one caused by, in the initial time, the AgNPs was not formed, but it was the beginning process of nucleations formation.

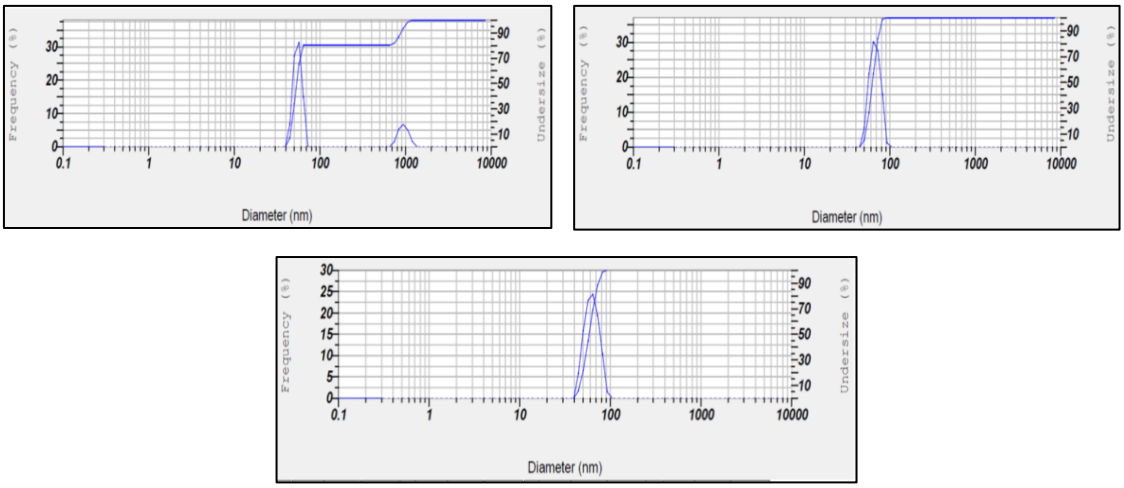

Figure 3. PSA Result of synthesized AgNPs at initial time (a), 24 (b), and 54 h (c)

At time 24th, the AgNPs had been formed, but average distribution size is bigger than at time 54th, this one caused by shorter duration for bioreduction process than 54th hour, therefore the small possibilities to form smaller size of AgNPs. The increasing of absorbance as indicator that the size of AgNPs is smaller. The longer time would possible more amount of Ag^{+} was reduced to be Ag^{0} and the reaction is continous could form the smaller size of AgNPs, impact to the absorbance become higher.

4. Analysis TEM

Figure 5 was measurement result TEM of synthesized AgNPs from $AgNO_3$ 1 mM at temperature 30 ^{o}C. The result show that obtained AgNPs with ball shape and diameter 36 nm (Figure 4).

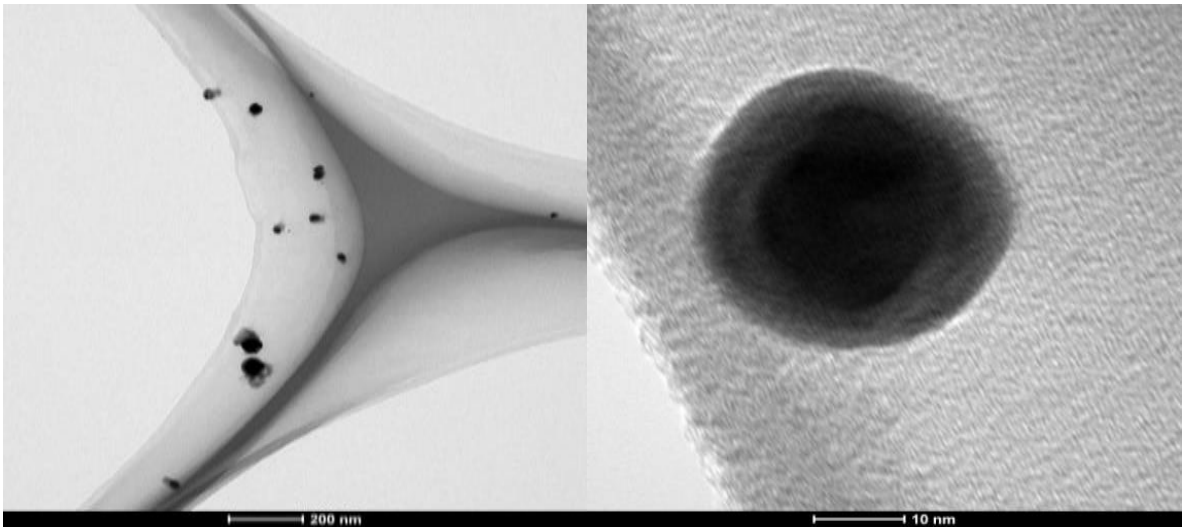

Figure 4. TEM measurement in scale 200 nm (a) and 10 nm (b)

5. Mechanism formation of Nanoparticles

Biosythesis of nanoparticle silver (AgNPs) correspond with biomolecules component in extract sample (Huang *et al*, 2011). Based on data SPR of AgNPs, suspension of nanoparticle indicate the stability during time reaction. This one show that AgNPs was stabilized by biomolecules in extract solution (Mittal *et*

responsible in bioreduction of Ag^{+} become Ag^{0}, it was done measurement of absorptionn *infrared* (IR). The measurement was conducted at resolution 4 cm^{-1}. The measurement of absorption IR was done to extract sample before and after reaction. Spectrum IR of extract sample (Figure 5a) and AgNPs (Figure 5b) show significant different. The wide peak at wavenumber 3417 cm^{-1} indicate presence of vibration of O-H groups.

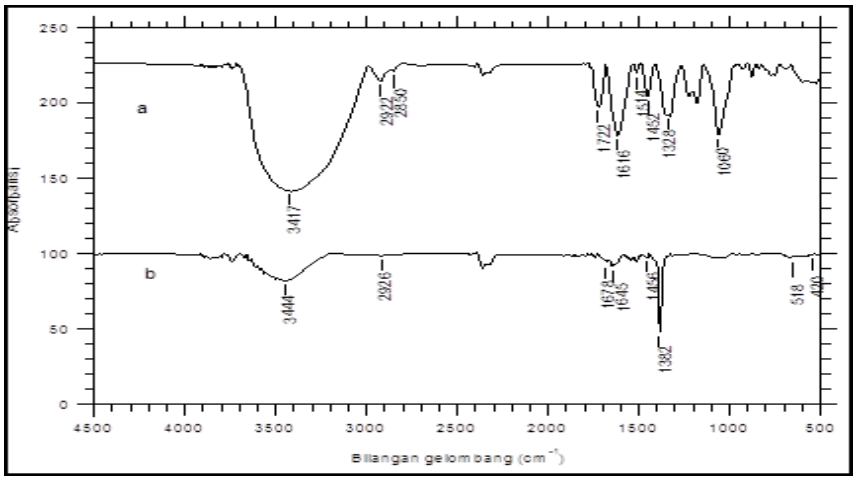

Figure 5. Spectrum IR extract of catappa leaf (a), and AgNPs (b)

The absorption at wavenumber 2922 and 2850 cm^{-1} correspond to C-H aliphatic groups. This one supported by the presence of methylen (CH_2) and methyl (CH_3) groups respectively at 1452 cm^{-1} and 1328 cm^{-1}. The peak at 1722 cm^{-1} indicate vibration of C=O ester group and supported by absorption of C–O ester at 1060 cm^{-1}. The C=C aromatic absorption was shown at wavenumber 1616 cm^{-1} dan 1514 cm^{-1}. while, in spectrum of AgNPs which had been reduced with extract ketapang leaf show the changing intensity, shift of wavenumber and the disappearance of decreasing intensity and shift of wavenumber at 3444 cm^{-1}, and shift of wavenumber C=O ester to be C=O ketone at 1678 cm^{-1}, it was supposed that O-H groups was oxidized to be C=O ketone. The disapperance of C=C aromatic and the appearance of absorption Ag at wavenumber 518 and 420 cm^{-1} and also Ag^0 at wavenumber 3700 cm^{-1} (Zamiri *et al*, 2011 and Ifa, 2013), indicate that Ag^+ had been reduced to be Ag^0. This one was match with the reduction mechanism of $AgNO_3$ by tannin which was proposed by zakir et al., 2014 (Figure 6).

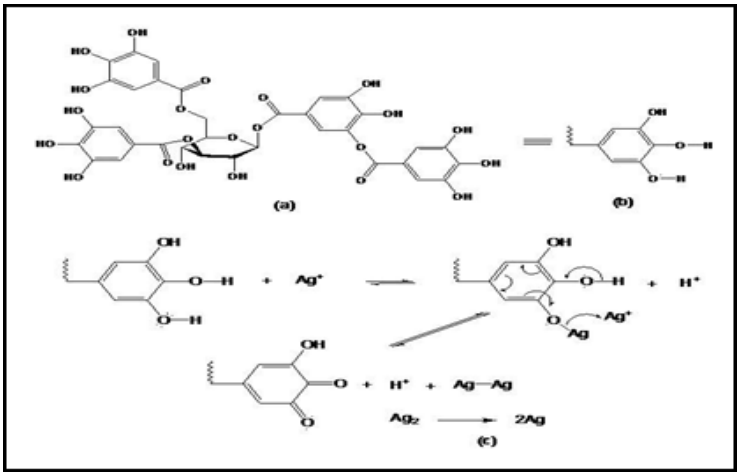

Figure 6. Estimation reaction in bioreduction process of Ag^+ to become AgNPs by tannin

CONCLUSION

The best concentration of $AgNO_3$ and temperature are: 1 mM and 30^oC respectively, with SPR at λ 430-432 nm. The average size distribution is 47.1 nm. Size of obtained AgNPs which had been measured by TEM istu 36 nm and it was ball shape. The -OH group –OH responsible in reduction of $AgNO_3$ to become AgNPs.

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