Synthesis of Silver Nanoparticles from Silver Nitrate Solution Using Green Tea Extract (Camelia sinensis) as Bioreductor

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Synthesis of Silver Nanoparticles from Silver Nitrate Solution Using Green Tea Extract (*Camelia sinensis*) as Bioreductor

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Abstract

The synthesis of silver nanoparticles with micro size is highly required in antibacterial fields. The biorefinery material is highly potential as a bioreductor which is applied in the synthesis of nanoparticles. The bioreductor is made from green tea leaves extraction using aquadest to extract its active substance, the catechin which is derived from polyphenol. The polyphenol can reduce the synthesis of silver nanoparticles naturally. The result of FTIR analysis from green tea leaves extract containing polyphenol shown in the uptake functional groups is -OH group located in 3425 cm^{-1}, C=O group located in 1635 cm^{-1}, C=C group located in 1527, and 1442 cm^{-1} , and C-O group located in 1234 cm^{-1}. The precursors of $AgNO_3$ was used as the main synthetic material. The synthetic condition was resulted from the reaction between the extraction of green tea extract and $AgNO_3$ as the precursors in the variation of synthetizing time. The heating process during synthesizing is done in 50 °C along with stirring to foster the creation of silver nanoparticles. The analysis result of XRD shows that silver nanoparticles has the diffraction peaks in the angle of 2 theta that are 44.08, 64.40, and 77.51. The types of silver nanoparticles is Ag^0 nanoparticles with face-centered cubic crystal structure. Based on TEM analysis, the size and particle size distribution can be determined using image J. The distribution shows that the longer synthesizing time, the bigger nanoparticles produced. With synthesizing times at 24 hours, 6 hours, 3 hours, and 2 hours produce average particle size of 26.4 nm; 9.2 nm; 8.4 nm; and 7.4 nm respectively.

INTRODUCTION

Nanotechnology is an interesting innovation of technology in research area which is related to production, size, and form in industry (Amiruddin et al., 2013). Researches in nanotechnology produces numerous invention of products with better performance. It motivates the research of chemistry to synthesize nano size particle from precious metal. One of the metal which is mostly investigated is silver which is commonly used in the application as antibacterial and antifungal. (Dwandaru et al., 2016; Rengga et al., 2017).

The colloid of silver has been known as an antimicrobial. The antimicrobial ability of silver can kill all pathogenic microorganism and there has not been any report of microbes which is resistant to silver (Ariyanta et al., 2014). Silver nanoparticles have wider surface allowing it improving its contact to bacterial or fungus and able to improve the effectiveness as bactericides and fungicides (Montazer et al., 2012). The silver nanoparticle is slowly able to release silver ion which can break the RNA and DNA of bacterial making them unable to replicate (Blaker et al., 2004).

Several methods used in producing nanoparticles are chemical reduction, photo-

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chemistry and sonochemistry. Nevertheless, the most used method is chemical reduction method. The reduction method is mostly chosen since it is simple and easy. The synthesis of silver nano-particles with eco-friendly chemical reduction method is using the extract of plants as the reductor agents (Sathishkumar et al., 2009). Several plants containing these chemical compounds can be used as reducing agents. The antioxidant compounds contained inside plant have been known to be metal ion reducing agents in the biosynthetic process (Vidhu et al., 2011).

The use of plants in the biosynthesis of nanoparticle is related to the composition of secondary metabolite compounds with antioxidant activities. The antioxidant is the alternative to produce green chemistry nanoparticles, because it is able to deduce the use of dangerous chemical substance along with its waste (Dyduch-Sieminska et al., 2015).

Tea can be used as a bioreductor for reducing silver to become nanoparticle. It is because tea possess many antioxidant material which can be a reductor of metal in the process of biosynthesis (Begum et al., 2009). One of the plants with high antioxidants is green tea. The composition of chemical substance in green tea leaves are including caffeine, catechin, flavonol, theanin, glutamate acid, aspartate acid, arginine, glucose, and potassium. The biggest composition in the bud of green tea leaf is catechin or epigallocatechin-3-gallate (EGCG) in the level of 20-29%. The activity of antioxidant from catechin is 200 times stronger in fighting free radicals comparing to vitamin E (Widyaningrum, 2013).

RESEARCH METHODOLOGY

The material used in this research were green tea leaves, $AgNO_3$ (Merck), aquadest, and NaOH (Merck). The tools used in this research were chemical glasses, measuring pipette, glass stirrer, watch glass, hot plate, spatula, analytical balance, oven, whatman filter paper number 42, Fourier Transform InfraRed (FTIR), Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), and Image-J application.

Preparation of Green Tea Extract Solution

Green tea of 2 g and water of 1000 mL are placed into 2000 mL of beaker. It is stirred and heated using hot plate at 60 ° C for 20 minutes. After that, the heated green tea solution is filtered using whatman filter paper number 1 in chemical glass. The extract of green tea is cooled to room temperature. The extract of green tea was then analyzed using FTIR to find the catechin composition in the green tea.

Preparation of 0,1 N $AgNO_3$ SOLUTION

Solid $AgNO_3$ solution is weighed as 1.7 grams and taken into the 100 mL chemical glass. $AgNO_3$ is dissolved with 100 mL aquadest. First, $AgNO_3$ was dissolved with 50 mL aquadest in the chemical glass. The mixtures then was stirred until it was perfectly dissolved perfectly. $AgNO_3$ solution was then moved into a 100mL volumetric flask and added with aquadest to the size of 100mL. The mixtures were shaken until they were blended perfectly.

The Synthesis of Nanoparticles Using Reduction Method

The solution of green tea leaves was taken in 1000 mL. The solution of 100 mL AgNO3 and 1000 mL the extract of green tea leaves is mixed in 2000 mL chemical glass. The mixture of green tea leaves and $AgNO_3$ solution is stirred at 50°C for 1 hour. Then, bit by bit, it was added with 0.1 N NaOH solution until the pH surpass the level of 8. The mixture was respectively heated for an hour until the Ag nanoparticles were deposited. The deposition of Ag nanoparticles was separated from the filtrate using a filtration. The deposition of Ag nanoparticles which had been separated then was consequently roasted to dispel the existing water. This deposition was then analyzed using XRD and TEM. The variation of samples used in different time allocations, which were 24 hours, 6 hours, 3 hours, and 2 hours.

RESULTS AND DISCUSSIONS

Results of Green Tea Characterization Using FTIR

Figure 1 shows the comparison between FT-IR spectra analysis result for catechin compounds from the extraction of green tea leaves. The absorbance peak at 3425 cm^{-1} shows OH bond indicating the existence of hydroxyl groups. The absorbance peak at 1635 cm-1 shows C=C bond in a aromatic compounds. The absorbance peak at 1527 cm-1 and 1447 cm-1 show the C=O bond indicating presence of a carbonyl group. The

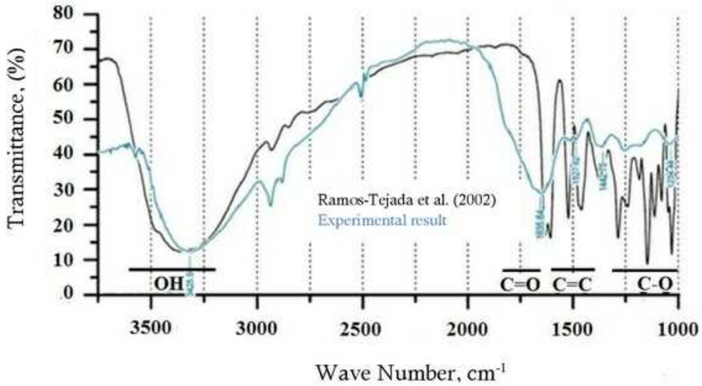

Figure 1. The comparison of spectra result from FTIR analysis to catechin compounds.

Table 1. The Comparison of Functional Group in Catechin Compounds based on FTIR Analysis Results.

Absorption Area (cm^{-1})		Types of Bond
Researches	(Ramos-Tejada *et al.*, 2002)	
3425	3400	–OH (hydroxyl group)
1635	1628	C=O (carbonyl group)
1527, 1442	1519, 1464	C=C (aromatic)
1234	1240	C-O (polyol group)

absorbance peak at 1234 cm^{-1} shows the C-O bonds indicating the existence of ether and polyol groups. The bonds of several functional groups were the functional group found in catechin compounds. The researches of Ramos-Tejada et al. (2002), explain that the result of analysis from catechin compound analysis with the existence of –OH, C=C, C=O, and C-O groups. Thus, the result of green tea extract supporting the research of Begum et al. (2009) that specifically, the absorbance peak at 1226 cm^{-1} containing C-O group indicating polyol, like hydroxy flavonoid or catechin. This result is shown in Table 1. In summary, the samples of green tea extract is proven containing catechin.

Silver Nanoparticles Synthesis

Catechin compounds contained in green tea extracts can be used to reduce $AgNO_3$ become Ag nanoparticles, or reducing Ag+ into Ag^0. The color of extraction is light brown and the color of 0,1 N $AgNO_3$ solution is turbid white, when both of them is mixed, it resulted light white color mixture as shown in Figure 2.

The reduction reaction occurs between the bioreductor solution and $AgNO_3$ 0.1 N which undergoes rapid color change. This color change indicates a reduction reaction. After 5 minutes of mixing, the mixture will change from light white to

Figure 2. The extract of green tea after mixed with AgNO3 solution.

light brown. In the 10^{th} minutes, the color will change again to be darker brown, and after 60 minutes, the solution will be darker as shown in Figure 3. The changes of color will show the reaction of reduction from the mixtures. The changes of color from white turbid into dark brown is caused by the oxidation of catechin to create another compound of theaflavin and theaburigin. After the washing process, the result of the synthesis became dark grey in color and shone like crystal indicating that the deposition is a silver nanoparticle, as can be seen in Figure 4.

Synthesis of nanoparticles was treated with heating at 50 °C for 1 hour aimed at accelerating oxidation of catechin and reduction of Ag^+ become Ag^0. During the process, the pH was set until pH = 8 with the addition of 0.1 N NaOH. The function of

Figure 3. The change of color after mixing bioreductor and $AgNO_3$ solution in (a) 5 minutes, (b) 10 minutes, and (c) 60 minutes.

Figure 4. Silver Nanoparticles from the reaction of reduction.

NaOH addition was to speed up silver nanoparticle formation. The increment of pH can increase the concentration of OH^- , so that OH^- will be more effective in producing negative surface charge in the base pH environment (El Badawy et al., 2010). The electron in bioreductor reduce the Ag^+ become Ag^0, so, it became nanoparticle, whilst bioreductor experiences the oxidation process where this antioxidant is the compound which produces electron (Silalahi, 2000).

Result of Silver Nanoparticles Analysis Using XRD

Based on Figure 5, it can be inferred that the sample of deposition reached its peak position and intensity. In details, the peak of diffraction appears at 2θ angle of 44.08, 64.40, and 77.51 each in the reflection area of (2 0 0), (3 0 0), (3 1 1) with crystal structure of face centered cubic (FCC) for silver nanoparticle. Meanwhile, based on the research of Raghavendra et al., (2016), the peak positions are in the angles of 38.06, 44.14, 64.38, and 77.26 where each of them is in the reflection area of (1 1 1), (2 0 0), (3 0 0), and (3 1 1). The comparison between XRD results of silver nanoparticles from the research conducted by Raghavendra, et al., (2016) can be seen in Table 2.

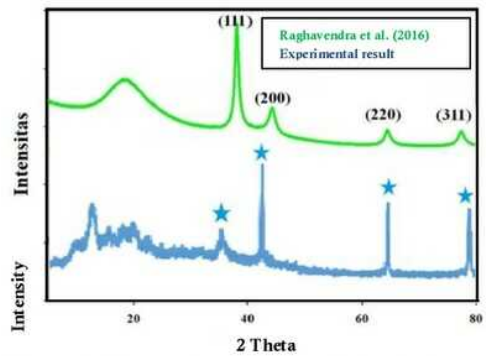

Figure 5. The result of XRD analysis of silver nanoparticles

Table 2. The Comparison of Peak Diffraction in the Research and Reference.

Research	Raghavendra *et al.* (2016)
37.83°	38.06°
44.08°	44.14°
64.40°	64.38°
77.51°	77.26°

Results of Silver Nanoparticles Analysis Using Transmission Electron Microscopy (TEM)

The deposition of nanoparticles were analyzed using TEM to predict the size of the nanoparticles. The TEM results presented are a form of nanoparticles based on their synthesis reaction time of 24 hours, 6 hours, 3 hours, and 2 hours. Based on these figures, the nanoparticles were shown in the figure with black color. The time of synthesis between precursor and bioreductor influence the formed nanoparticles. The longer the time of synthesis contact results the bigger size of nanoparticle size, since there is an aggregation of particle formation which is shown in Figure 6 (a)

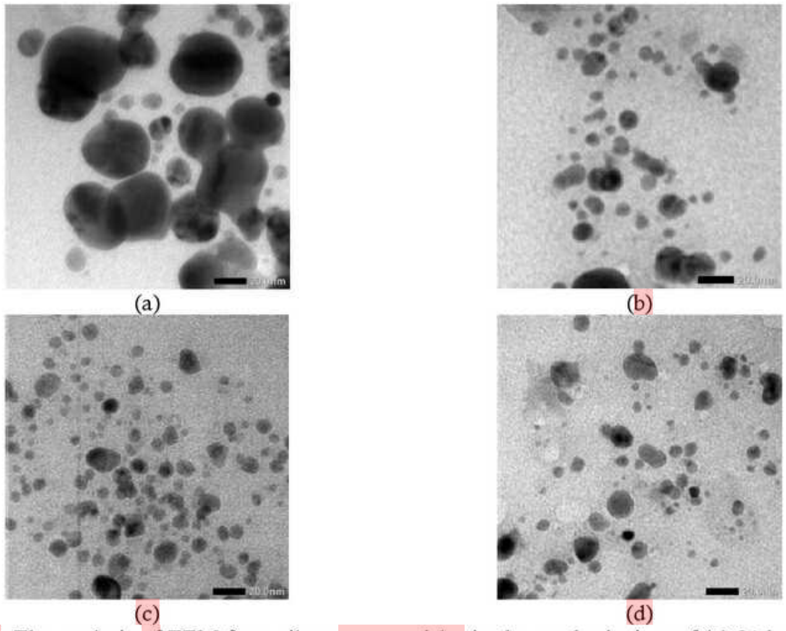

Figure 6. The analysis of TEM from silver nanoparticles in the synthesis time of (a) 24 hours; (b) 6 hours; (c) 3 hours (d) 2 hours

where the size of the nanoparticles is bigger than the other figures. The aggregation is resulted from the force between particles, thus the particles will approach to each other and gather creating a cluster of particle which gets bigger each time. The analysis of TEM in the nanoparticle synthesis in 6 hours can be seen in Figure 6 (b) where the particle is smaller in size and not similar to particle which is synthesized in 24 and 2 hours. The particles in synthesis time of 3 hours in Figure 6 (c) and 2 hours in Figure 6 (d) has smaller size than the synthesis of 6 hours. The particle size during the reduction process appears on the TEM results of varying size indicating the collision process between the reactants has not been maximized. Nonetheless, many crystals seeds have slowly appeared though it have not reached in the process where the crystal seed can become bigger crystal.

The analysis of TEM can determine the distribution of particles size as pictured in Figure 7 (a) where the results of synthesis of 24 hours were still bigger comparing to other figures with the biggest size about 80 nm. In the figure it appears that the dominant diameter of nanoparticles were 20 and 40 whereas the particle with a size of 10 nm was only 18%. The average size of silver nanoparticles in 24 hours synthesis was 26.4 nm. Figure 7 (b) showed the TEM analysis results in synthesis time of 6 hour with smaller nanoparticle size than nanoparticle size for 24 hours synthesis. The distribution of nanoparticle diameter size for 6 hours synthesis was mostly in the diameter size of 10 nm (64.2%), followed by 20 nm (32.1%), and 30 nm (3.8%). The nanoparticle with 10 nm size is increasing in number comparing to the 24 hours synthesizing process. The whole nanoparticle average size was 9.2 nm. According to Figure 7(c), silver nanoparticles was distributed in the diameter size of 10-60 nm. The distribution of silver nanoparticles for 3 hours synthesizing process was more variative than the 6 hours process of synthesizing, but the size of 10 nm nanoparticles is increasing until become 71.3% than the 60 nm particles in 1.2%, the other size were 20-40 nm. The average size of silver nanoparticles was 8.4 nm. The distribution of nanoparticle size in 2 hours synthesizing process can be seen in Figure 7(d) shown that the diameter of nanoparticles was about 10 nm in the highest proportion (79.4%) comparing to 20 nm nanoparticles and the lowest diameter (30 nm (5.56%). The size of silver nanoparticle in the synthesis time of 2 hours resulting a narrower size of particle, 10-30 nm, with the average diameter of 7.4 nm. The synthesis time of 2 hours resulting smallest nanoparticles. The process of synthesizing of silver nanoparticles with reaction of reduction will result less nanoparticles until the limit where the nanoparticles is formed. Natural bioreductor,

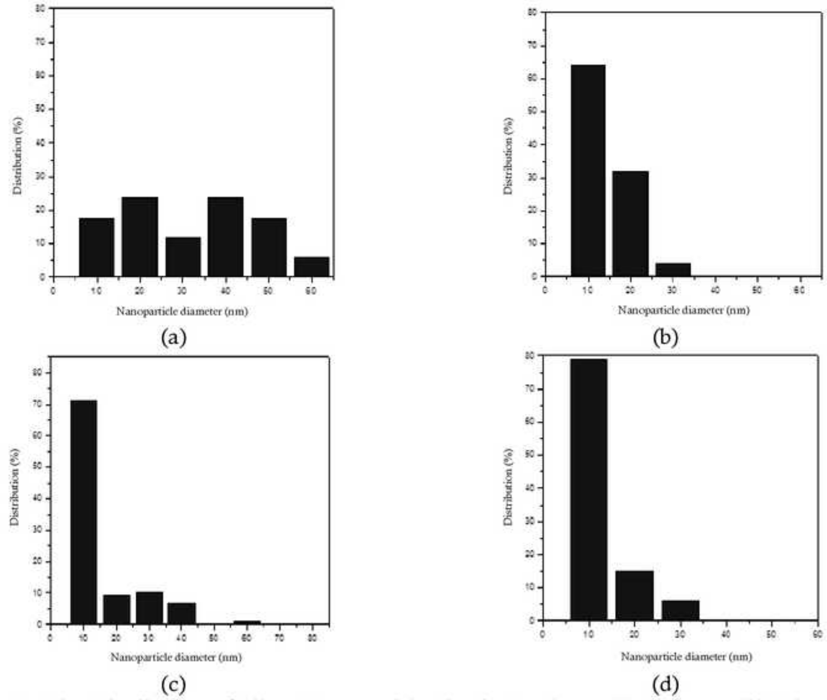

Figure 7. The Distribution of Silver Nanoparticle Size in Syntheses (a) 24 hours; (b) 6 hours; (c) 3 hours; (d) 2 hours

the extract of green tea is impossibly possessing catechin, so, even when the size of nanoparticles is less than 10 nm, the research of Rengga et al. (2017) was proven able to produce silver nanoparticle with the average size of 5.44 nm which is attached to active carbon because the used bioreductor is a pure starch. The results of the research was better than the extraction of tea by Nestor et al. (2008) *Camiellia sinensis* can result silver nanoparticles in the size of 40 nm. The extract of other leaves is *Cytrus sinensis* which results silver nanoparticles of 22.3 nm (Logeswari et al., 2015).

CONCLUSION

Bioreductor of green tea extract can reduce $AgNO_3$ precursor to become silver nanoparticles. It can be proven from the FTIR analysis results where the variable of green tea extract contains catechin compounds as the reductor agent for silver. The result of XRD also proves that the formation of silver nanoparticles has Face Centered Cubic (FCC) crystal structure. Based on the TEM analysis results, the smallest nanoparticle size was when the synthesizing time between $AgNO_3$ and bioreductor was 2 hours with 7.4 nm average diameter of nanoparticles. Based on TEM analysis, the time of synthesizing process influences the formed silver nanoparticles. The longer the synthesizing time, the bigger size of nanoparticles formed, since there is a particle aggregation, so the creation of initial crystal and crystal formation should be concerned more.

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