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Synthesis and Characterization of Silver Nanoparticles from Ethanol Extract of Meniran (Phyllanthus Niruri L.) Using Bioreduction Method

Rizky Abdur Rahman[1], Suyatno Sutoyo[1]

[1]Department of Chemistry, Faculty of Matematics and Natural Sciences, Surabaya State University, Ketintang Street, Surabaya, East Java, Indonesia

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Abstract – The synthesis of silver nanoparticles by the bioreductionmethod has been successfully carried out using the meniran (P. niruri) as bioreductor. The synthesis was started by varying the volume of AgNO3 in the ethanol extract ofmeniran 1:1, 1:2, 1:3, and 1:4, so that the optimal volume was 1:1 based on the results of UV-Visible spectrophotometer analysis with an absorbance of 0.306 at maximum wavelength of 409 nm. Based on the measurement using Zetasizer Nano ZS, the resulting silver nanoparticles has paticle size of 740.4 nm. The FTIR analysis showed that there was an increase in the percentage of transmittance of the hydroxyl group which proved the reduction of Ag+ ions to Ag0 and the formation of silver nanoparticles. The Scanning Electron Microscopy proved that themorphology of silver nanoparticles varies in shape and the surface is smooth due to their tendency to agglomerate.

Keywords – Synthesis, Silver Nanoparticles,Meniran, Bioreduction

I. INTRODUCTION

Indonesia is a country that is rich in natural resources in the form of plants that can be used as traditional medicine. Even plants that are often found around residential areas can be used as medicinal ingredients. Meniran (*P. niruri*) is one of the medicinal plants that can be found in Indonesia. People often use this plant for traditional medicine by adding it to boiled water. This plant can be found in damp and rocky areas such as river slopes, forests, and even in the yard.

[1] states that the substances contained in meniran are essential oils, flavonoids, alkaloids, triterpenoids, glycosides, anthraquinones, phenolic compounds, arbutin, filantin, lignin, saponins and tannins. The content of these secondary metabolites can be efficacious as a diuretic, antioxidant, anti-inflammatory, antidiabetic, antipyretic [2].

In general, people often use this plant as a medicine by boiling or brewing. The use of this method is considered to be less effective and efficient because of its low solubility so that it can reduce its bioavailability and reduce its functional properties due to the length of storage and the manufacturing process.

One way to increase the level of solubility and maintain the functional properties of a material is to make preparations of nanoparticles that can be used for drug delivery. Nanoparticles are nano-sized particles with an average diameter of 1-1000 nm [3]. Silver nanoparticles are one type of metal nanoparticles that have distinctive physical and chemical properties as well as wide applications and have high commercial value [4].

The method used for the synthesis of silver nanoparticles which is relatively cheap, easy, and environmentally friendly is to use plants as reducing agents. The ability to reduce silver ions Ag^+ in $AgNO_3$ to Ag^0 in the synthesis process of silver nanoparticles possessed by antioxidant compounds such as flavonoids, alkaloids, phenolics, tannins and so on can be used as bioreductants and capping agents. These nanoparticles were made from ethanol extract of meniran which was added with 2 mM $AgNO_3$ solution. To

Corresponding Author: Suyatno Sutoyo

get the optimal concentration, the volume ratio variation with the independent variable $AgNO_3$ solution is 1:1; 1:2 ; 1:3 ; and 1:4. The silver nanoparticles obtained then characterized using UV-Vis spectrophotometer, Particle Size Analyzer (PSA), FTIR spectrophotometer, and Scanning Electron Microscopy (SEM).

II. Materials And Methods

2.1. Materials and Equipment

The materials needed in this research are meniran powder (*P.niruri*), technical ethanol (96%), ethanol p.a. (Merck), $AgNO_3$ (Merck), aquabides, aluminum foil, filter paper, and cling wrap.

The equipment used in this research were volumetric flask, measuring cup, stand and clamps, spatula, micropipette, funnel, vial, a set of maceration tools, rotavapor (Buchi R-300), vacuum pump (Gast DOA-P -504-BN), centrifuge, magnetic stirrer (Heidolph), freeze dryer (Martin Christ Alpha 1-2 Ldplus), oven (Heraeus ST-5042), analytical balance (Advanturer Ohaus), UV-Vis spectrophotometer (Shimadzu Pharmaspec UV- 1700), Zetasizer nano ZS (Malvern), infrared spectrophotometer (Shimadzu FTIR-8400S), Scanning Electron Microscope (SEM) (FEI Inspest S50).

2.2. Meniran Sample Preparation

In this study, the research sample in the form of aerial parts of meniran (*P.niruri*) was obtained from the Purwodadi Botanical Gardens, Pasuruan, East Java, Indonesia. The samples that have been obtained are identified first and then cleaned as well as dried and ground into a fine powder so that they are ready for extraction.

2.3. Meniran Sample Extraction

The dry powder of meniran plant (*P. niruri*) as much as 1 gram was macerated exhaustively using 96% ethanol for 24 hours and repeated 3 times at room temperature. The maceration results were filtered using a Buchner funnel and a vacuum pump. The extract obtained was evaporated with a rotary vacuum evaporator. Furthermore, the extract was dried for 20 hours using a freeze dryer.

2.4. Preparation of Sample Solution 25.000 ppm

The dry ethanol extract of the meniran plant (Phyllanthus niruri L.) as much as 1 gram was dissolved in 40 mL of ethanol p.a., then filtered using whatman filter paper no. 42. The ethanol extract solution is blackish green (concentrated) and then stored in the refrigerator.

2.5. Preparation of 2 mM $AgNO_3$ Solution

A total of 0.085 g of $AgNO_3$ powder was dissolved in aquabides using a volumetric flask to a volume of 250 mL and homogenized to make 2 mM $AgNO_3$ solution [5].

2.6. Optimization of Comparison of Amount of Extract Solution with 2 mM $AgNO_3$ Solution

Optimization is done by adding different amounts of $AgNO_3$ solution in each glass with a volume ratio of 1:1 (10 mL: 10 mL), 1:2 (10 mL: 20 mL), 1:3 (10 mL: 30 mL), and 1:4 (10 mL: 40 mL). The mixture was stirred with a magnetic stirrer for 15 minutes. Then tested using a UV-Vis spectrophotometer on each sample. The purpose of this test is to obtain the most optimal comparison shown by λ_{max} and absorbance in the range of 300-700 nm [6].

2.7. Silver Nanoparticle Synthesis

The optimum mixture of meniran ethanol extract (*P.niruri*) and $AgNO_3$ 2 mM was regenerated as much as 40 mL, stirred using a magnetic stirrer for 15 minutes. Next, separate the filtrate and residue in the mixture by centrifugation. The silver nanoparticle solution was analyzed using a Particle Size Analyzer (PSA) while the residue was dried using a freezedryer so that a dry powder of silver nanoparticles was obtained which was ready to be tested for characterization using an FTIR Spectrophotometer and Scanning Electron Microscope (SEM) [6,7].

III. Result And Discussion

3.1. Meniran Sample Extraction

Extraction is the process of withdrawing a chemical compound, principally based on the solubility properties of the chemical compound. Where the compounds that will be used in this study are flavonoids. This flavonoid is polar because it has an unsubstituted hydroxyl group, therefore polar aquabides are used and the method used is infusion [8].

The dried powder of aerial parts of meniran as much as 100 g was macerated using 200 mL technical ethanol 96% solvent for 1 day at room temperature with 3 repetitions. The purpose of using ethanol as a solvent is to extract secondary metabolites of phenolic types contained in meniran plants with their polar nature. Phenolic compounds will dissolve in ethanol contained in meniran plants after the meniran plant cell walls are degraded by ethanol so that it is easier to be pulled out of the meniran plant cells [9]. Then the combined solvent of the macerated extract was evaporated for 3 times using a rotary evaporator to obtain a concentrated ethanol extract of meniran. The extract was dried for 8 hours using a freeze dryer to obtain a solid blackish green ethanol extract of 21.745 g (4.35%).

3.2. Optimization of Comparison of Amount of Extract Solution with 2 mM $AgNO_3$ Solution

Figure 1: Formula for synthesis of silver nanoparticles from meniran extract

Meniran sample solution of 25.000 ppm was added with $AgNO_3$ solution which was manipulated with variations in the composition of 1:1 (10 mL: 10 mL), 1:2 (10 mL: 20 mL), 1:3 (10 mL: 30 mL), and 1: 4 (10 mL: 40 mL)(Figure 1). Each mixture was stirred for 15 minutes with a magnetic stirrer to homogenize the solution with the help of a magnetic stirrer, then the UV-Vis spectrum was measured at a wavelength range of 300-700 nm to determine the plasmon resonance peak typical of silver nanoparticles [10]. The results of the UV-Vis spectrophotometer analysis of the four formulas are presented in Table 1 and Figure 2.

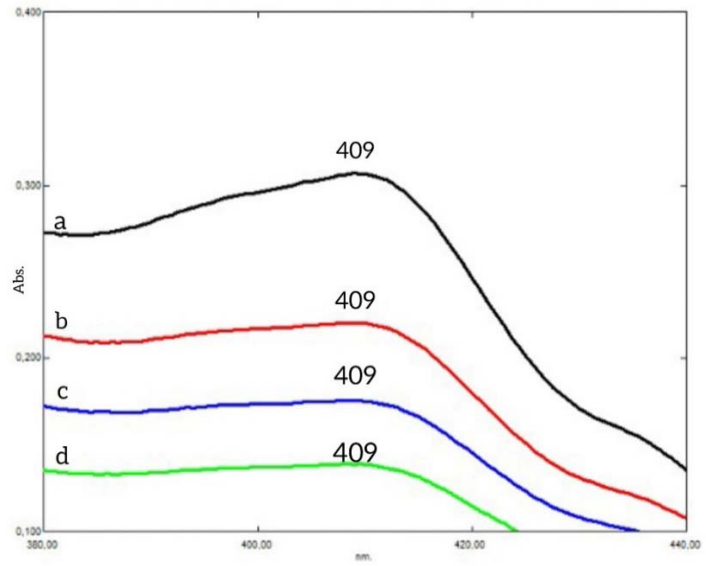


Figure 2: UV-Vis Spectra of Meniran Extract Silver Nanoparticles

Table 1 : Maximum wavelength and absorbance of Meniran extract silver nanoparticles

No.	Composition of ethanol extract solution and $AgNO_3$ solution	λ_{maks} (nm)	Absorbance
1	1:1	409	0.306
2	1:2	409	0.220
3	1:3	409	0.175
4	1:4	409	0.139

Based on Figure 2 and Table 1, in the four combinations of meniran ethanol extract solution with $AgNO_3$ solution, silver nanoparticles have been formed which are indicated by the appearance of a peak at a wavelength of 409 nm, which meets the requirements for the maximum wavelength of UV absorption of silver nanoparticles. According to [11] the absorption band of SPR (Surface Plasmon Resonance) AgNPs occurred at a wavelength of 400-450 nm. A change in color from green to yellow-brown or orange-brown indicates the formation of silver nanoparticles.

The mixture with the volume combination of meniran ethanol extract solution with 1:1 $AgNO_3$ solution has a maximum wavelength of 409 nm with the highest absorbance value of 0.306. Thus the mixture with this combination is the most optimum in producing silver nanoparticles [12,6].

3.3. Silver Nanoparticle Synthesis

Based on the analysis of UV absorption using UV-Vis spectrophotometer, the optimum composition of a mixture of meniran ethanol extract solution and $AgNO_3$ solution was obtained with a volume ratio of 1:1. The optimum composition was made again as much as 40 mL and stirred for 15 minutes using a magnetic stirrer to make it homogeneous, after that is was centrifuged. The particle size of the filtrate was analyzed using Zetasizer Nano ZS and the residue was dried using a freeze dryer to characterize the

functional groups and morphology by FTIR and SEM. From the freeze dryer results obtained solid silver nanoparticles brownish green.

3.4. Silver Nanoparticle Size Characterization

In this research, the Zetasizer Nano ZS (Malvern) instrument was used to determine the particle size of silver synthesized with a bioreductant of meniran ethanol extract. Measurements were made on silver nanoparticles produced from the optimum combination of meniran ethanol extract solution with $AgNO_3$ solution (1:1). Based on the measurement results obtained data that the size of the synthesized silver nanoparticles is 740.4 nm, with a polydispersity index (PdI) of 0.055.

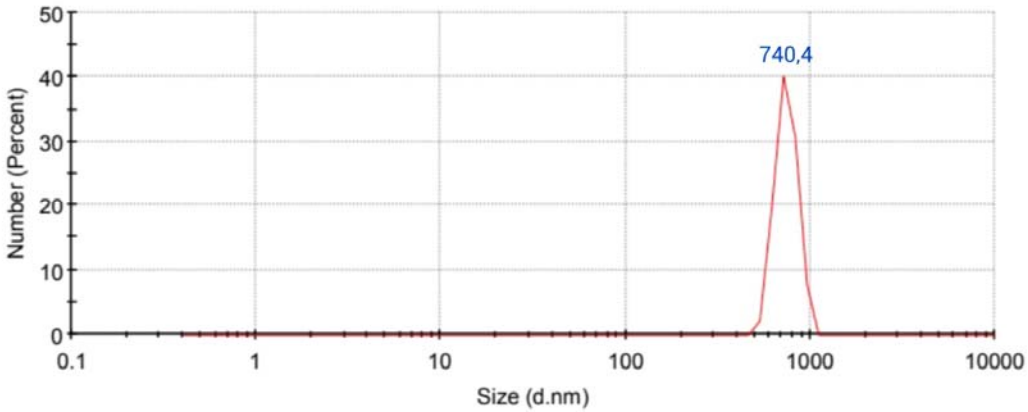


Figure 3: Measurement Results of Synthesized Silver Nanoparticles Using Zetasizer Nano ZS

Based on Figure 3, silver nanoparticles synthesized from meniran ethanol extract have an average particle size of 740.4 nm. According to [3,13] The size obtained from the analysis still meets the requirements for nanoparticle size in the range of 1-1000 nm so that it can be said that the synthesis of silver nanoparticles using a bioreductant of meniran ethanol extract has formed nanoparticles. The size of the silver nanoparticles obtained is still smaller than the results of research by [12] with a green tea leaf extract bioreductant which produces silver nanoparticles with a diameter of up to 740,899 nm, but still larger than the results of [14] with an average diameter of 544.1 nm produced with the help of a bioreductant of shoots of Idat leaf extract. The large size of silver nanoparticles is caused by the tendency of silver nanoparticles to agglomerate so that the particle size is getting bigger. The addition of stabilizers can be done to prevent agglomeration [15].

3.5. Functional Group Characterization of Silver Nanoparticles

FTIR measurements were carried out to identify possible functional groups in the ethanol extract of meniran. Meniran ethanol extract was used not only to stabilize but also to reduce Ag^+ ions in the formation of silver nanoparticles. The hydroxyl group (-OH) of phenolic compounds contained in the active compounds of meniran plants will reduce Ag^+ ions to silver nanoparticles (Ag^0) by donating electrons [16]. This analysis is used to determine what groups are involved in reducing Ag^+ ions to Ag^0. Comparison of the spectra of meniran ethanol extract with synthesized silver nanoparticles is presented in Figure 4 and the wave number and %T values are in Table 2.

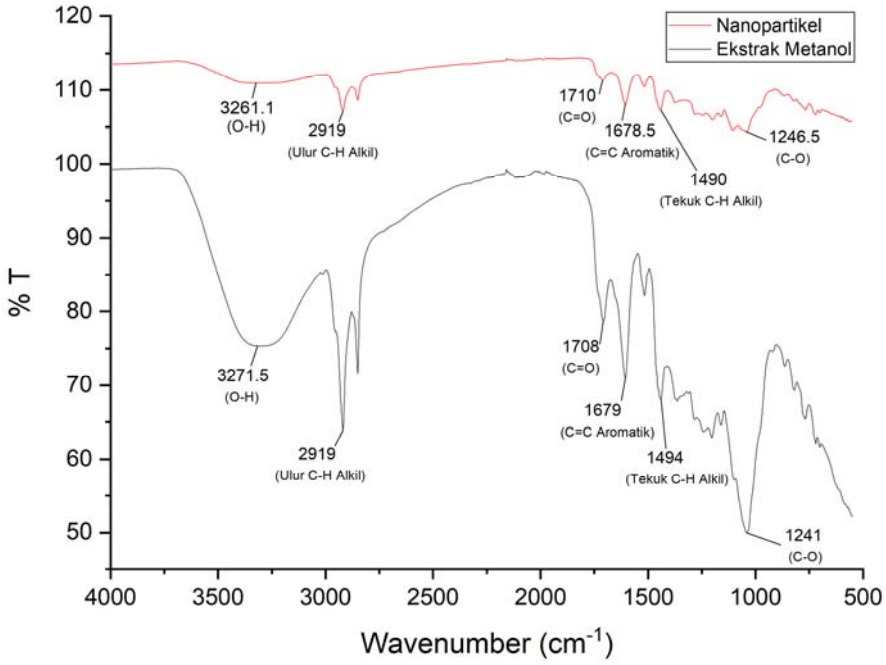


Figure 4: Comparison of the spectrum of Meniran ethanol extract with nanoparticles

The absorption peak that appears at 3271.5 cm^{-1} can be caused by the stretching vibration of the –OH group. The peak that appears at 2919 cm^{-1} is caused by the stretching vibration of –CH. The sharp peak observed at 1679 cm^{-1} and the slightly weak peak at 1708 cm^{-1} were caused by the aromatic C=C and C=O stretching vibrations, respectively. The shift in wave number occurs in the stretching vibration of –OH from 3271,5 cm^{-1} in the ethanol extract of meniran to 3261,1 cm^{-1} in AgNPs and the increasing intensity of absorption of the stretching vibration –C=O in the synthesis results (1708 to 1710 cm^{-1}) gives an indication of the oxidation of the group. –OH becomes the –C=O group. Ag^{+} ions will be reduced simultaneously to silver nanoparticles.

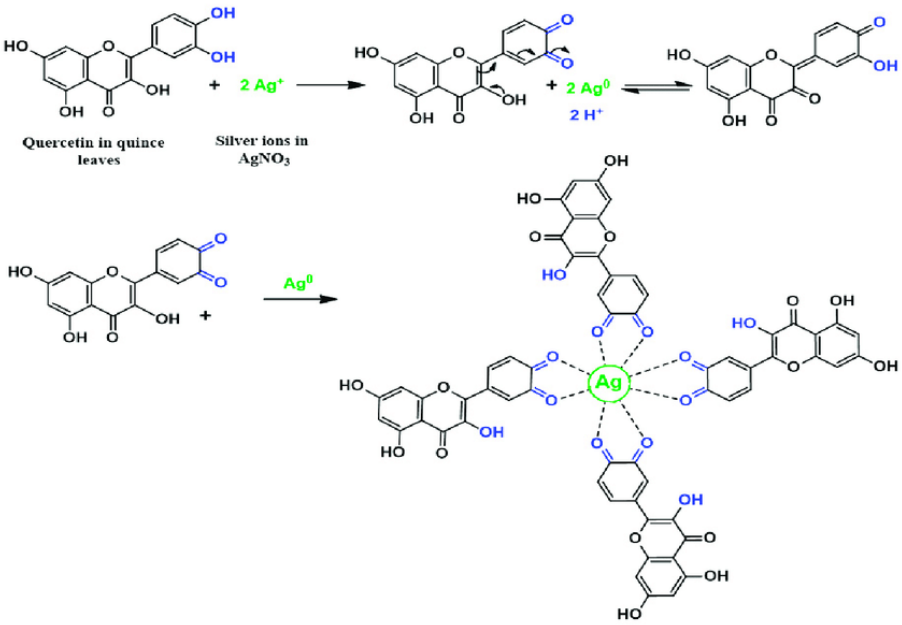
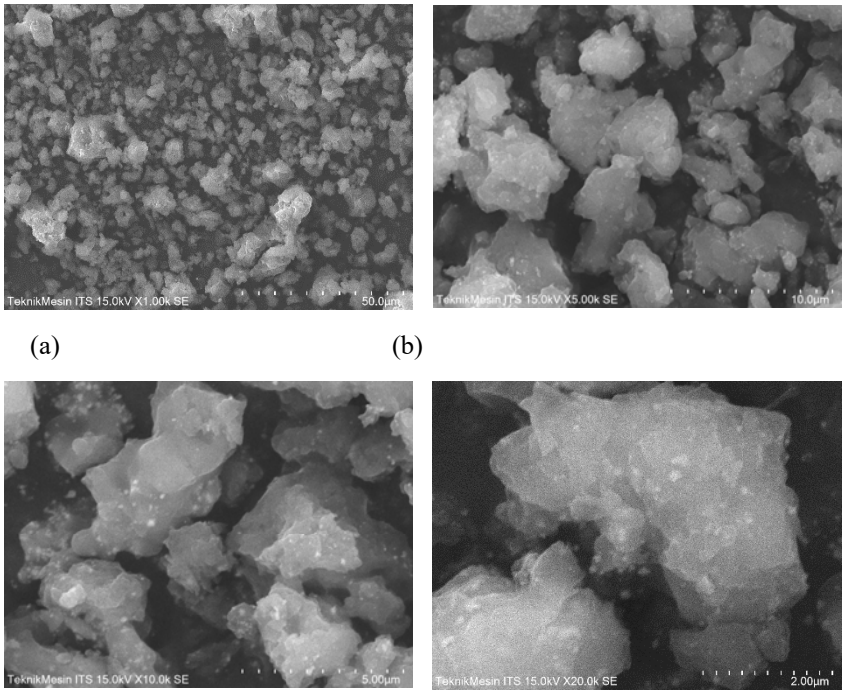


Figure 5: Reaction mechanism for the formation of synthesized silver nanoparticles [17].

Meniran ethanol extract is used as a reducing agent which will convert Ag^{+} to Ag^{0}. The mechanism for the formation of nanoparticles as shown in Figure 5 above according to [18] in the presence of –OH groups in flavonoids, such as in quercetin which will be responsible for reducing silver ions. Quercetin has a hydroxyl group and a ketone, quercetin reacts with Ag^{+} through the most reactive hydroxyl group attached to the carbon atom of the aromatic ring which can reduce silver ions into silver nanoparticles.

3.6. Silver Nanoparticle Morphology

The morphology of the resulting silver nanoparticles was determined with the help of a Scanning Electron Microscopy (SEM) instrument. The morphology of silver nanoparticles using SEM is shown in Figure 6.



(a) (b)

(c) (d)

Figure 6: Morphology of Synthesized Silver Nanoparticles with Magnification:

(a). 1000x (b). 5000x (c). 10.000x (d). 20.000x

Figure 6 shows the morphology of the resulting silver nanoparticles having various shapes and particle sizes with a smooth surface structure. The diversity of shapes and sizes of silver nanoparticles is caused by the aggregation effect of nanoparticles due to the Van der Waals forces of silver nanoparticle molecules in solution [12].

IV. CONCLUSIONS

The conclusion that can be drawn from the results of this study is that the most optimum composition for the synthesis of silver nanoparticles with meniran ethanol extract bioreductor is using meniran ethanol extract solution and 1:1 $AgNO_3$ solution. The synthesized nanoparticles have UV absorption at a maximum wavelength of 409 nm with a particle size of 740.4 nm. The FTIR spectrum of silver nanoparticles showed the presence of absorption bands of OH (hydroxyl), C-H alkyl, C=O (carbonyl), C=C aromatic, and C-O alcohol. The increasing percentage of transmittance of the hydroxyl group of silver nanoparticles compared to the ethanol extract of meniran supports the reduction of Ag^{+} ions to Ag^{0}. The results of SEM measurements show that the surface morphology of silver nanoparticles has a fine structure and various shapes due to the tendency to agglomerate.

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REFERENCES

[1] Septi Santika. "Comparative Analysis of the Effectiveness of Extracts of Roots, Stems and Leaves of Meniran Herbs in Lowering Blood Glucose Levels in Mice". *Journal of Public Health*, 8(1), 53-61, 2012.

[2] Risma M.T., Umm Mastna, Ameria. "Inhibitory Activity of -Glucosidase Enzymes, Cytotoxicity and Content of Phytochemical Compounds from Eight Indonesian Medicinal Plants". National Seminar on Pharmacy 2. Utilization of Pharmaceutical and Clinical Sciences and Regulations in Pharmacy in Indonesia. Graha Pos Indonesia Ballroom Edelweiss 8th floor Jl Banda no 30, 2016.

[3] Mohanraj, V. J. & Chen, Y. *Nanoparticles – A Review, Tropical Journal of Pharmaceutical Research*, 5(1), pp. 561-573, 2006.

[4] Oktavia, I. N., & Sutoyo, S. Article Review: "Synthesis of Silver Nanoparticles Using Bioreductor from Plant Extract as an Antioxidant". *UNESA Journal of Chemistry*, *Vol. 10*, *N*, 9–43, 2021.

[5] Sutoyo, S., Tukiran, & Khodijah, S. "Antioxydant Activity of The Silver Nanoparticles (AgNPs) Synthesized using Nephrolepis radicans extract as bioreductor". *Journal of Physics*; Conference Series, 1747. 012038, 2021

[6] Taba, P., Parmitha, N. Y., & Kasim, S. "Synthesis of Silver Nanoparticles Using Bay Leaf Extract (*Syzygium polyanthum*) as a Bioreductor and Test its Activity as Antioxidant". Indonesian *Journal of Chemical Research*, 7(1), 51–60, 2019.

[7]Amin, R.R. & S. Sutoyo. "Green Synthesis and Characterization of Silver Nanoparticles Derived from Ethanol Extract of Sappan Wood". International Journal of Current Science Research and Review. 5 (7), 2396-2403, 2022.

[8] Rahman, H., Wisnuwardhani, H.A., Rusnadi. "Optimization Of Silver Nanoparticles Synthesis Using Kawista Leaf Extract (*Limonia acidissima Groff*)". *Journal of Clinical Pharmacy and Science*, 31-36, 2022.

[9] Suhendra, C. P., Widarta, I. W. R., & Wiadnyani, A. A. I. S. "Effect of Ethanol Concentration on Antioxidant Activity of Weed (*Imperata cylindrica (L) Beauv.*) Rhizome Extract in Extraction Using Ultrasonic Waves". *Journal of Food Science and Technology*, 8(1), 27–35, 2019.

[10] Maheswari, R. U., Prabha, A. L., Nandagopalan, V., & Anburaja, V. "Green Synthesis of Silver Nanoparticles by Using Rhizome Extract of *Dioscorea oppositifolia L.* and Their Antimicrobial Activity against Human Pathogens". *Journal of Pharmacy and Biological Sciences*, 1(2), 38–42, 2012.

[11] Irwan, R., Muhammad Zakir., Prastawa Budi. "Effect Of $AgNO_3$ Concentration And Synthesis Temperature On Surface Plasmon Resonance (SPR) Of Silver Nanopartikel", Ind. J. Chem. Res, 4(1), 356-361, 2016.

[12] Rahim, D. M., Herawati, N., & Hasri. "Synthesis of Silver Nanoparticles using Green Tea Leaf Extract (*Camellia sinensis*) Bioreductor with Microwave Irradiation". *Chemica Journal*, 21(1), 30–41, 2020.

[13] Buzea, C., Pacheco, I. I., & Robbie, K. "Nanomaterials and Nanoparticles". *Sources and Toxicity. Biointerphases* 2, 2(4), 17–71, 2007.

[14] Fabiani, V. A., Silvia, D., Liyana, D., & Akbar, H. "Synthesis of Silver Nanoparticles Using a Bioreductor of Pucuk Idat Leaf Extract (*Cratoxlum glaucum*) through Microwave Irradiation and Testing its Activity as Antibacterial". *Fullerene Journal of Chemistry*, 4(2), 96–101, 2019.

[15] Haryono, A., Sondari, D., Harmami, S. B., & Randy, M. "Synthesis of Silver Nanoparticles and Potential Applications". *Indonesian Research Journal*, 2(3), 155–163, 2008.

[16] Masakke, Y., Sulfikar, & Rasyid, M. "Biosintesis Partikel-nano Perak Menggunakan Ekstrak Metanol Daun Manggis

(*Garcinia Mangostana* L.)". *Jurnal Sainsmat*, *4*(1), 28–41, 2015.

[17] Kasim, S., Taba, P., Mathematics, F., Alam, P., & Hasanuddin, U. "Synthesis of Silver Nanoparticles Using Water Hyacinth (*Eichornia crassipes*) Leaf Extract as Bioreductant". COVALEN: *Journal of Chemical Research*, 6(2), 126–133, 2020.

[18] Jain, S., Mehata, S.M. "Medicinal Plant Leaf Extract and Pure Flavonoid Mediated Green Synthesis of Silver Nanoparticles and their Enhanced Antibacterial Property". *Scientific Reports*, 1-13, 2017.