SYNTHESIS OF SILVER NANOPARTICLES USING BIOREDUCTOR OF KETAPANG LEAF EXTRACT (*Terminalia catappa*) AND ITS POTENTIAL AS SUNSCREEN

Irfa Apriliyanti Payapo, M. Zakir[1], Nunuk Hariani Soekamto

Department of Chemistry, Faculty of Science, University of Hasanuddin Jl. Perintis Kemerdekaan 90245,Makassar-Indonesia
Corresponding author: muhammadzakir@gmail.com

Abstrak. Sintesis nanopartikel perak dilakukan dengan metode reduksi kimia menggunakan ekstrak daun ketapang (terminalia catappa) yang berperan sebagai agen pereduksi dengan penggunaan AgNO3 sebagai prekursor. Hasil penelitian berdasarkan perubahan warna, pH, dan serapan UV-Vis menunjukkan perubahan warna dari kuning menjadi kuning kecokelatan dengan pH 4 menandakan terbentuknya nanopartikel perak dengan range panjang gelombang 412,50-404,00 nm untuk penyimpanan hari pertama sampai hari ketujuh dengan ukuran partikel 92,48 nm berdasarkan hasil pengkuran PSA. Analisis gugus fungsi yang berperan dalam sintesis menggunakan FT-IR. Karakterisasi menggunakan XRD menunjukkan bahwa hasil sintesis membentuk kristal kubik dengan ukuran Kristal 53,48 nm. Nanopartikel perak dimanfaatkan sebagai tabir surya dengan paduan senyawa asam hidroksi sinamat. Pengujian aktifitas tabir surya ditentukan dengan nilai SPF yang dianalisis menggunakan spektrofotometer UV-Vis. Hasil pengujian aktivitas tabir surya paduan nanopartikel perak dan asam hidroksi sinamat (AHNP) dengan konsentrasi 16 µg/mL – 20 µg/mL menunjukkan nilai SPF berturut-turut 20,97; 24,71; 26,41; 28,07 dan 31,92. Aktivias tabir surya AHNP meningkat seiring peningkatan konsentrasi AHNP. Berdasarkan hasil penelitian yang dilakukan dapat disimpulkan bahwa paduan AHNP memiliki efek proteksi ultra (SPF $\geq$ 15) terhadap sinar UV-B.

Kata kunci: AHNP, AHS, Ekstrak daun ketapang, Nanopartikel perak, SPF

Abstract. Synthesis of silver nanoparticles is done by the chemical reduction method using the extract of leaves of catappa *(Terminalia catappa)* which acts as a reducing agent with the use of $AgNO_3$ as the precursors. The results, based on changes in color, pH, and UV-Vis absorption shows color changes from yellow to yellow-brown with a pH of 4 indicating the formation of silver nanoparticles with a wavelength range from 412,50- 404,00 nm for the storage of the first day until the seventh day with a particle size 92,48 nm based on the results of taking the measurements of PSA. Analysis of functional groups that play a role in the synthesis using FT-IR. Characterization using XRD showed that the synthesized form a cubic crystal with a crystal size of 53,48 nm. Silver nanoparticles are used as a sunscreen with a blend of hydroxy cinnamic acid compounds. Testing activities determined sunscreen with SPF values were analyzed using a UV-Vis spectrophotometer. Results of testing the activity of sunscreen alloy nanoparticles of silver and hydroxy cinnamic acid (AHNP) with a concentration of 16 µg/mL - 20 µg/ml showed the consecutive SPF value 20,97; 24,71; 26,41; 28,07 and 31,92. Sunscreen AHNP activity increases with the concentration AHNP. Based on the research results can be concluded that the combination of ultra AHNP has a protective effect (SPF $\geq$ 15) against UV-B rays.

Key word : AHNP, AHS, Extract of Catappa Leaf, Silver Nanoparticles, SPF

INTRODUCTION

The development of technology and science at this time, especially in the field of material is growing rapidly (Amiruddin, 2013). In the period of 2010-2020 there will be a tremendous acceleration in the application of nanotechnology in the industrial world and this signifies that the world is now leading to the revolution of nanotechnology (Suwarda and Maarif, 2011). Nanotechnology can generally be defined as the design, manufacture and application of nanometer-dimensional structures/materials (Ariyanta *et al*, 2014).

One of the developing nanotechnology developments is the synthesis of nanoparticles. Synthesis of nanoparticles is growing rapidly because it can be applied widely as in the field of environment, electronics, optics, and biomedical. Nanoparticles are particles that have a one-dimensional size that is less than 100 nanometers (Zakir, 2014).

Nanoparticles can be made using photochemical, electrochemical, radiolytic, sonolytic and bioreduction methods using natural products. The bioreduction method is classified as a new branch of nanotechnology, called nanobiotechnology. Nanobiotechnology combines biological principles with physical and chemical procedures to produce nanometer-sized particles with specific functions (Zakir, 2014).

The synthesis of nanoparticles utilizing living things as biological agents in the synthesis process is known as nanoparticle biosynthesis. The use of biological agents in the synthesis process is to utilize the organic compounds contained in living things. Biological agents act as reducers, stabilizers, or both, in the process of forming nanoparticles. The biosynthesis of nanoparticles are thought to involve organic compounds such as enzymes, proteins, and carbohydrates or groups of secondary metabolite compounds from plants. The principle of biosynthesis of the reduction method in nanoparticle preparation is the use of plants and microorganisms (Bakir, 2011 and Handayani, 2011).

One of the nanoparticles that can be synthesized using a reduction method is a silver nanoparticle. Silver nanoparticles can be synthesized by a reduction method using ketapang leaf extract (Terminalia catappa) (Zakir, 2014). Various extracts of ketapang leaves have been done phytochemical test. Ketapang leaves contain many antioxidant compounds. The compounds contained in ketapang leaf extract that will be utilized in the process of synthesis of silver nanoparticles. Extras n-heksan of ketapan leaves show the compounds contained in them, among others palmitic acid, linolenic acid, and stearic acid (Jaziroh, 2008). Chloroform extract of ketapang leaves contains alkaloid group compounds, triterpenoids, steroids and terpenoids (Restasari , 2008). The identification the class of compounds with phytochemical screening in the ethyl acetate extract of ketapang leaves contained flavonoid, alkaloid, and saponin compounds (Rahayu et al., 2008). Ketapang leaf water cooking extract contains phenolic, flavonoids, and steroids (Lembang, 2013).

According to Lembang, 2013, silver nanoparticles can be synthesized by reduction method using ketapang leaf water cooking extract yielding particle size of 55.77 nm. The resulting compound is a phenolic group estimated to be a type of tannin, as it is well known that the ketapang is rich in tannins. Therefore, tannins also play an important role in the Ag + reduction process.

Silver nanoparticles tend to aggregate to form large sizes. The stability of silver nanoparticles plays a very important role when they are characterized and applied to a product. Prevention of aggregate occurrence among nanoparticles can be done with the addition of stabilizer (Haryono, 2008). The most effective stabilizer used is a polymer that serves to prevent the occurrence of agglomeration. Several polymers have been used as stabilizers, including polyvinyl alcohol (PVA), polyvinyl pyrrolidine (PVP), poly ethylene glycol (PEG), polystyrene sulphonate (PSS), acrylic acid (PAA) and chitosan (Marliyana *et al*, 2006).

The addition of 1% PVA to stabilize the size of the silver nanoparticles is distributed between 40-164 nm with an average size of 96.0 nm. The silver nanoparticles synthesized using PAA 1% were distributed between 23-86 nm with an average size of 71.6 nm. PAA has a relatively good ability to stabilize silver nanoparticles because it has the best affinity (Bakir, 2011., Lembang, 2013., Zakir *et al*, 2014).

The development of silver nanoparticles has now been applied in various fields, one of which is the addition of silver nanoparticles to cosmetic preparations. The size of the silver nanoparticles is very small compared to the body cells so the silver nanoparticles can come out and enter easily into the cell body without disrupting the work of the cell (Abdullah, M, and Khairurijal., 2010). Silver nanoparticles are known to have good capabilities as antimicrobials. Silver nanoparticles have properties that are not toxic to human skin. Nanoparticles are antioxidants and can counteract free radicals. Silver is particularly interesting because it has a unique characteristic and is one of the precious metals that has a fairly good optical quality after gold at a more affordable price (Handayani 2011 and Lembang, 2013).

Cosmetic product development now is sunscreen with nanoparticle alloy. Sunscreen is a compound that can be used to protect the skin from sunburn, especially ultraviolet (UV). The sunscreen activity was determined from the SPF (Sun Protection Factor) value of the samples analyzed using a UV-Vis spectrophotometer. The determination of SPF value through UV-Vis spectrophotometer can be known from the characteristics of sunscreen sample absorption at maximum wavelength (Suryanto, 2013).

Active sunscreen ingredients are classified into two, namely chemical sunbatter (chemical adsorbers) and physical blockers (physical blockers). Chemical sunscreens work on the surface of the skin and absorb UV (making it harmless). The physical sunscreen works by reflecting UV light. Chemical sunscreen compounds known to be either octyl p-methoxy cinnamate (OPMS). OPMS compounds can absorb sunlight significantly in the wavelength range 200-370 nm so it can be used to protect the skin from exposure to sunlight (Bevi *et al*, 2009 and Suryato, 2013)

The characteristic of a chemically absorbing sunscreen compound is to have a substituted benzene nucleus at the ortho position as well as those conjugated with the carbonyl group. The compounds include cinnamic derivatives. One of the cyano-derived compounds other than OPMS is hydroxy cinnamic acid (AHS). The AHS compound is used as an active component of sunscreen because it has a long chain and a conjugated double bond system that will undergo resonance during exposure to UV light. To optimize the ability of sunscreen is usually done a combination of chemical active compounds that contain antioxidants that are able to fight free radicals. Silver nanoparticles are antioxidants and can counteract free radicals. The addition of silver nanoparticles into the AHS was able to optimize the work of sunscreen [17,6].

RESEARCH METHODS

Materials and Devices Research

The material used in this study were ketapang leaf (Terminalia catappa), $AgNO_3$ (pa), Iabides, ethanol, n-hexane, ethyl acetate, chloroform, acrylic acid (PAA), hydroxy cinnamic acid (AHS), filter paper Whatman No. 42, plastic wrap and aluminum foil. The tools used in this research are oven, analytical scales, glassware in laboratory, 30 ml vial bottle, spray bottle, magnetic stirrer, funnel, pH Special indicator (pH range 1-14), centrifugal, UV-spectrophotometer, Vis 2600 series, XRD (Rigaku MiniFlex X-Ray Diffraction), PSA (VASCO DLS), FTIR, Spray Dryer (BUCHI 190), and rotary evaporator.

Time and Place of Research

The research was conducted at Chemical Physics Laboratory Department of Chemistry, Faculty of Science, University of Hasanuddin Makassar, May 2015-April 2016. The sample analysis was conducted at Integrated Chemistry Laboratory Department of Chemistry, Faculty of Science, University of Hasanuddin Makassar, Laboratory of Materials Analysis Department of Physics Faculty of Mathematics and Natural Sciences Bogor Agricultural University, and Animal Feed Laboratory Faculty of Animal Husbandry Hasanuddin University.

Research procedure:
Preparation of 1 mM AgNO3

1 mM $AgNO_3$ solution was prepared by dissolving 0.085 grams of powder with akuabides $AgNO_3$ in 500 mL volumetric flask up to the mark and homogenized.

Preparation PAA solution 1%

PAA 1% solution is made by weighing 1 gram of PAA and dissolved with akuabides in 100 mL volumetric flask up to the mark.

Preparation of Plant Extracts
Sample preparation

Plants used in this study is Ketapang (Terminalia catappa). This plant is obtained in the campus environment FMIPA Hasanuddin University, Makassar, South Sulawesi. Part of the plant used in this study are the leaves in fresh condition. Ketapan fresh leaf is then processed to a dry powder. Dry powder obtained from fresh samples were cleaned first, then dried naturally in air by not subjected to direct sunlight for ± 7 days, then blended and sieved to obtain a powder.

Ketapang Leaf Extraction (Terminalia catappa)

Ketapang leaf powder (Terminalia catappa) of 20 grams is macerated with n-hexane, chloroform and ethyl acetate solvent for 1 x 24 hours several times and filtered. The obtained maserate was then evaporated to obtain n-hexane, chloroform and concentrated ethyl acetate extracts.

A total of 20 grams of dried ketapang leaf powder (Terminalia catappa) was put into a 500 ml chemical glass and 100 ml of Iabides was added and then heated to a boil then cooled. After reaching room temperature, boiling water poured and filtered using filter paper whatman no. 42. The decoction water can then be used directly for the biosynthesis process. Cooking water can be stored in the refrigerator when not in use.

Synthesis of Silver Nanoparticles

Synthesis of silver nanoparticles was done by mixing $AgNO_3$ solution with n-hexane extract, ethyl acetate extract, chloroform extract and ketapang leaf water extract as bioreductors. In this study, as much as 0.5 ml of each extract was mixed into 20 ml of $AgNO_3$ 1 mM. The solution is allowed to react for 2 hours. Next to the solution was added 2 ml PAA 1% and the distirer for 2 hours.

Characterization of Silver Nanoparticles

The characterization of this mixed solution in the form of color, sepktrum UV-Vis and pH at the time of 1 day, 2 days, 3 days and 7 days. Determination of sample size of mixed solution was done with PSA. The solution is then centrifuged to obtain a precipitate of nanoparticles which is then dried in the oven at 100 °C. The dried product is then characterized using FTIR and XRD to identify functional groups, particle shape, elemental composition, and product size.

Preparation of Hydroxyic Acid Solicitation 100 μg/ml

Total of 0.01 grams of hydroxy cinnamic acid were included in a 100 ml measuring flask and ethanol was added until the boundary marks were shaken until evenly mixed.

Preparation of Hydroxy cinnamic acid solution 16 mg/ml, 17 pg/ml, 18 pg/ml, 19 pg/ml and 20 pg/ml

A total of 8 ml; 8.5 ml; 9 ml; 9.5 ml and 10 ml of a 100 μg/ml hydroxy acid solution are pipetted each into a 50 ml measuring flask and deposited until the boundary mark is then homogenized.

Preparation of Hydroxy cinnamic Alloy and Silver Nanoparticles

5 ml solution of hydroxy acid cinnamic 16 ug/ml, 17 pg/ml, 18 pg/ml, 19 p/ml and 20 pg/ml pipette respectively into the flask 10 ml, then in each flask, the Added 2 ml of a silver nanoparticle solution and ethanol added to the boundary mark and shaken until mixed.

Test of Sunscreen Bioactivity

The sunscreen activity was determined from the SPF values of the samples analyzed using a UV-Vis spectrophotometer. The determination of SPF value through UV-Vis spectrophotometer can be known from the characteristic absorption of sunscreen sample at wavelength 290-320 nm with interval 5 nm.

RESULTS AND DISCUSSION

Synthesis of Silver Nanoparticles

Silver nanoparticles synthesized by the method of chemical reduction using a solution of $AgNO_3$ of 1 mM as precursors and extract solution of n-hexane leaf ketapan, chloroform extracts of leaves of Ketapang, ethyl acetate extracts of leaves of Ketapang and water extract of leaves of Ketapang as a bioreduktor as well as the addition of a solution PAA 1% as a solvent stabilizer. The formation of silver nanoparticles is characterized by color, pH, UV-Vis spectra, PSA, FTIR and XRD.

Characterization of Silver Nanoparticles

Color and pH

Characterization color of the solution was conducted to determine the effect of contact time on the formation of silver nanoparticles. Sample A (n-hexane extract), B (chloroform extract), C (ethyl acetate extract) and D (water extract) were characterized by observing the color change from the manufacturing time to 7 days as in Fig. 3.

Sample A, B and C solution after synthesized did not change color from 1 day to 7 days. This shows no silver ion reduction process because the compounds contained in extracts A, B and C that serve as reducers do not react with $AgNO_3$ precursors. Sample D at the beginning of the mixing is clear, then after 4 hours the solution is changed to yellow and after 1 day the color of the solution turns brownish yellow.

Extract name	Early synthesis	Day I	Day II	Day III	Day VII
n- hexane (A)					
chloroform (B)					
ethyl acetate (C)					
water (D)					

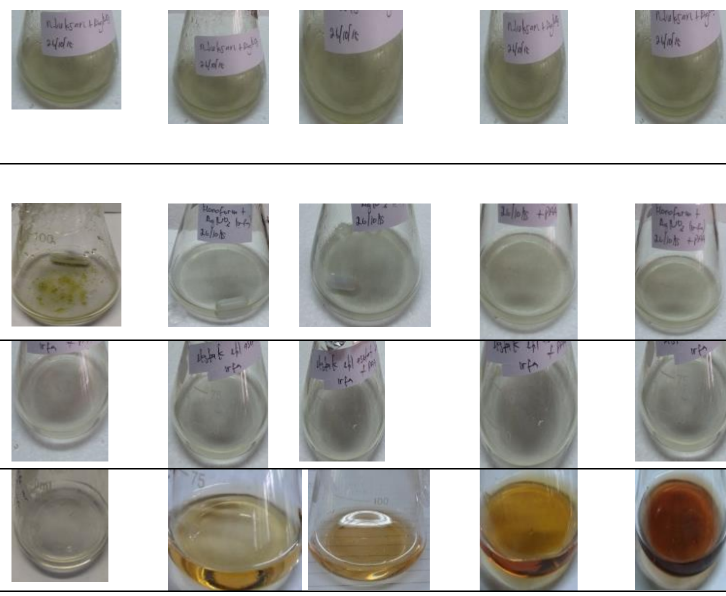


Figure 3. Sample solution A (*n*-hexane extract), B (chloroform extract), C (ethyl acetate extract) and D (water extract) for 7 days

The color of the solution became darker with increasing time. This change indicates the occurrence of silver ion reduction process by the compound contained in extract D to form silver nanoparticles.

The pH value of the sample solution A, B, C and D during the synthesis process is 4 measured when the synthesis of silver nanoparticles to 7 days. The addition of 1% PAA causes the synthesis process in acidic atmosphere. The pH of the solution is unchanged. From 1 day to 7 days synthesis process is because PAA 1% does not reduce Ag^+ but stabilizes the size of the synthesized silver nanoparticle.

Characterization Using UV-Vis Spectrophotometer

One of the instruments that can be used to analyze nanoparticles is the UV-Vis spectrophotometer. In measurements with the UV-Vis spectrophotometer, the Plasmon Resonance Surface (SPR) has a relationship to the color of the silver nanoparticles solution. SPR is an excitation of electrons in the conduction band around the surface of the nanoparticles and vibrations by light over a nanometer-sized structure (Shankar, 2004). When resonance occurs, strong absorption bands appear from surface plasmons.

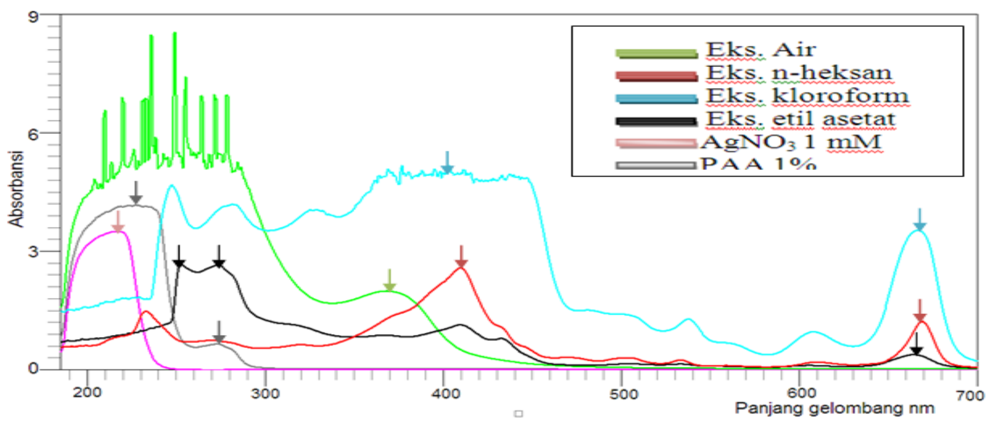


Figure 4. UV-Vis absorption spectra extract *n*-hexane, chloroform, ethyl acetate water, 1% PAA solution and 1 mM AgNO3 solution.

The n-hexane extract of ketapang leaves absorbs energy at λ max 669 nm, chloroform extract absorbs energy at λ max 667 nm, and the ethyl acetate extract absorbs energy at λ max 664,50 nm, and the water extract absorbs energy at λ max 368 nm. 1 mM $AgNO_3$ solution absorbs energy at λ 216,50 nm, while 1% PAA solution absorbs energy at λ max 273 nm.

The peak absorbance spectrum value of a specific silver nanoparticle shows the SPR character of the nano-sized particles. The plasmon resonance that occurs will give uptake in measurements using UV-Vis spectrophotometry. The absorption between 400-500 nm indicates the presence of nano-sized particles (Solomon et al., 2007; Leela and Vivekananda, 2008; Kumar and Yadav, 2008). Characterization begins by measuring the maximum wavelength of various samples (Figure 4).

Maximum absorption and wavelength patterns form the basis for monitoring the formation of silver nanoparticles in which silver colloids provide absorption absorption peaks at wavelengths around 400-500 nm indicating a typical plasmon absorption peak of silver nanoparticles (Wahyudi, 2011).

Table 3. Result of AgNP UV-Vis spectrum analysis from n-hexane extract

Sample	Wavelength (nm)	Absorbant
$AgNO_3$ 1 mM	216,50	3,495
N-hexane extract	669,00	1,217
PAA 1%	273,00	0,647
Silver Nanoparticles		
1 days	419,00	0,544
2 days	421,00	0,241
3 days	419,00	0,123
7 days	419,00	0,055

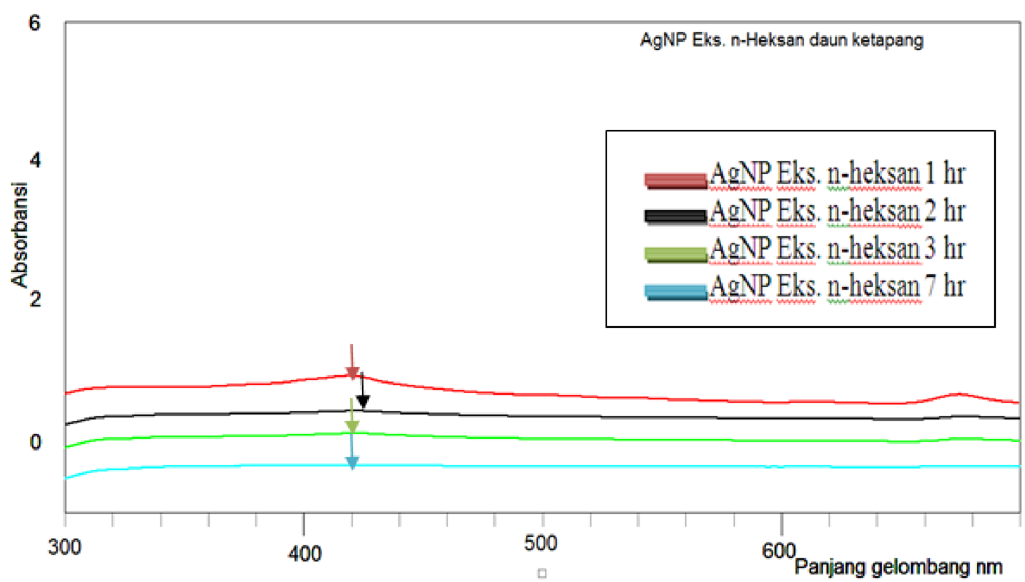


Figure 5. UV-Vis absorption AgNP formation from n-hexane extract for 7 days at wavelength 185-700 nm

The results of the synthesis of silver nanoparticles of n-hexane extract (AgNP.A), silver chloroform extract nanoparticles (AgNP.B), silver nanoparticles of ethyl acetate extract (AgNP.C) and silver extract nanoparticles (AgNP.D) are seen in Fig. And in Table 3-6. When silver nanoparticles are formed, the UV-Vis absorption spectra at wavelengths between 400-500 nm and the absorbance value increase with increasing contact time. The increased absorbance value is an indicator that the silver nanoparticles that are formed are increasing (Handayani et al., 2010).

Figures 5 and Table 3 show the formation of silver nanoparticles from the n-hexane extract of ketapang leaves at λ 419-421 nm and the decreasing absorbance value from day 1 to day 7. A decrease in absorbance indicates that a larger cluster is formed due to the onset of aggregation.

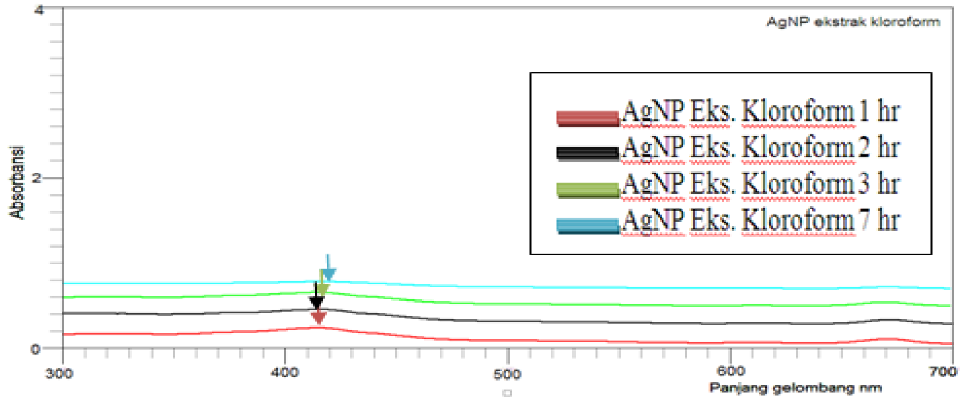


Figure 6. UV-Vis absorption AgNP formation of chloroform extract for 7 days at a wavelength of 185-700 nm.

Table 4. Results of AgNP UV-Vis spectrum analysis from chloroform extract

Sample	Wavelength (nm)	Absorbant
$AgNO_3$ 1 mM	216,50	3,495
chloroform extract	667,00	3,625
PAA 1%	273,00	0,647
Silver Nanoparticles		
1 days	414,50	0,239
2 days	414,00	0,255
3 days	415,00	0,194
7 days	418,00	0,143

Figures 6 and 4 show silver nanoparticles formed from chloroform extract of ketapang leaves at λ 414-418 nm and decreased absorbance value from day 1 to day 7. A decrease in absorbance indicates that a larger cluster is formed due to the onset of aggregate. Figures 7 and Table 5 are seen from the maximum absorption pattern not in the wavelength region of 400-500 nm and the absorbance value from day 1 to 7th day decreases.

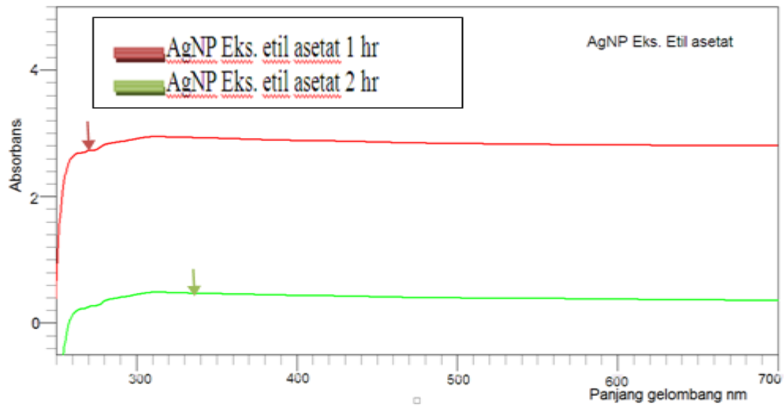


Figure 7. UV-Vis absorption AgNP formation of ethyl acetate extract for 7 days at a wavelength of 185-700 nm.

Table 5. Results of UV-Vis AgNP spectrum analysis of ethyl acetate extract

Sample	Wavelength (nm)	Absorbant
$AgNO_3$ 1 mM	216,50	3,495
ethyl acetate extract	664,50	0,374
PAA 1%	273,00	0,647
Silver Nanoparticles		
1 days	264,00	2,853
2 days	330,50	0,162

This indicates that silver nanoparticles are not formed on the AgNP sample of ethyl acetate extract, this is due to the compounds contained in the extract of ethyl acetate so little that it is unable to reduce Ag^+ to Ag^o. There is a decrease in absorbance over time, indicating the start of a larger cluster due to the onset of aggregation. Figure 8 and Table 6 show the formation of silver nanoparticles from ketapang leaf water extract at λ 404-413 nm and the absorbance value increased from day 1 to day 7. Qualitatively, the higher the absorbance value can be assumed that the more nanoparticles are formed or the concentration of nanoparticles in the solution is higher.

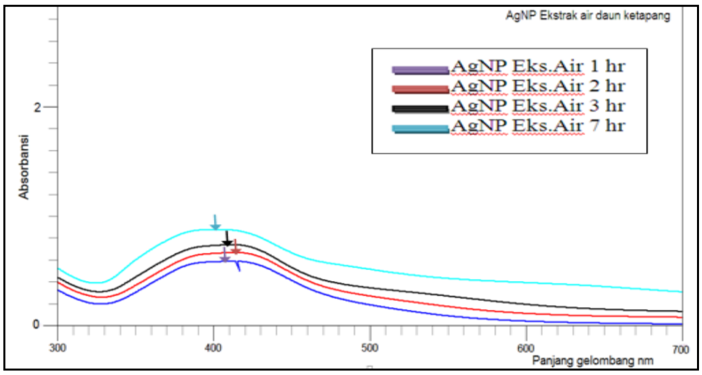


Figure 8. UV-Vis absorption AgNP formation of extract water for 7 days at a wavelength of 185-700 nm

Table 6. Result of AgNP UV-Vis spectrum analysis from water extract

Sample	Wavelength (nm)	Absorbant
$AgNO_3$ 1 mM	216,50	3,495
extract water	368,00	1,986
PAA 1%	273,00	0,647
Silver Nanoparticles:		
1 days	412,50	0,588
2 days	413,00	0,607
3 days	411,50	0,638
7 days	404,00	0,717

The effect of agitation, accelerates the reaction between $AgNO_3$ and Ketapang leaf extract, thus the absorbance value in the biosynthesis of silver nanoparticles by means of stirring becomes higher. Overall, a better water extract in the silver nanoparticle synthesis process so that AgNP from the water extract was continued to analyze PSA, XRD and FTIR data and continued for sunscreen activity test.

Characterization Using FTIR

The analysis using FTIR was performed to determine the functional groups of ketapang leaf extract and silver nanoparticles where before and after the Ag^+ ion ion reduction took place. The spectrum of FTIR results can be used to identify possible functional groups that play a role in reducing silver ions.

Figure 9 shows the FTIR spectrum of the synthesized silver nanoparticles. There is a shift in spectral wavelength from ketapang leaf water extract before and after reducing. The absorption at υ (wavelength) 3446,79 cm^{-1} is seen on the IR spectrum of ketapang leaf water extract, this absorption shows the typical absorption of the -OH group with a widening and strong band. Uptake of C = O groups with a sharp peak at υ 1645.28 cm^{-1} and at υ 1080.85 and 1106.21 cm^{-1} there is a group C-O absorption.While the IR spectrum of silver nanoparticles resulting from reduction using ketapang leaf water extract showed a shift of wave numbers in the -OH group, C = O and CO groups with successive waves of 3437,15 cm^{-1}, 1643,35 cm^{-1}, 1029 , 99 cm^{-1}.

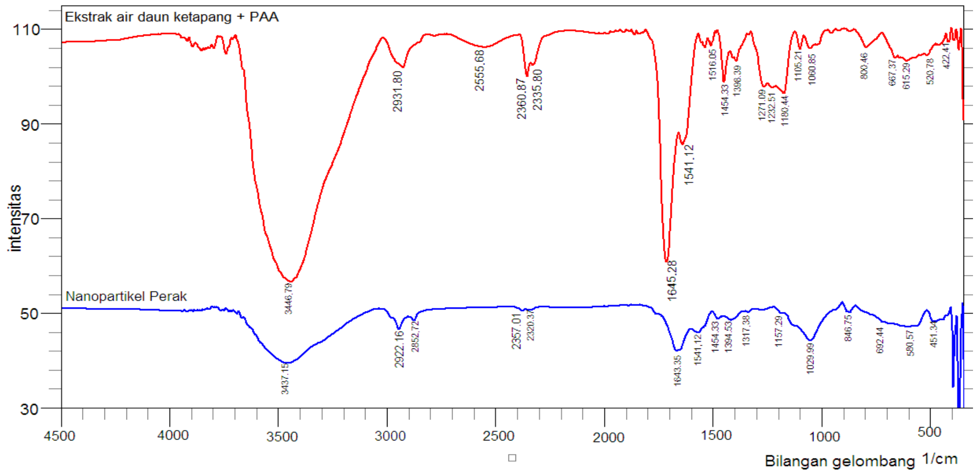


Figure 9. Results of FTIR AgNP water extract

The apparent wavelength shift between ketapang leaf water extract and silver nanoparticles. The shift of wave numbers indicates that there is an interaction between functional groups and silver nanoparticles due to the oxidation process due to the reduction of silver nanoparticles. The presence of absorbent bands is widened and strong at υ 3446,79 cm-1 because of the presence of O-H groups of phenol and O-H from acrylic acid poly groups.

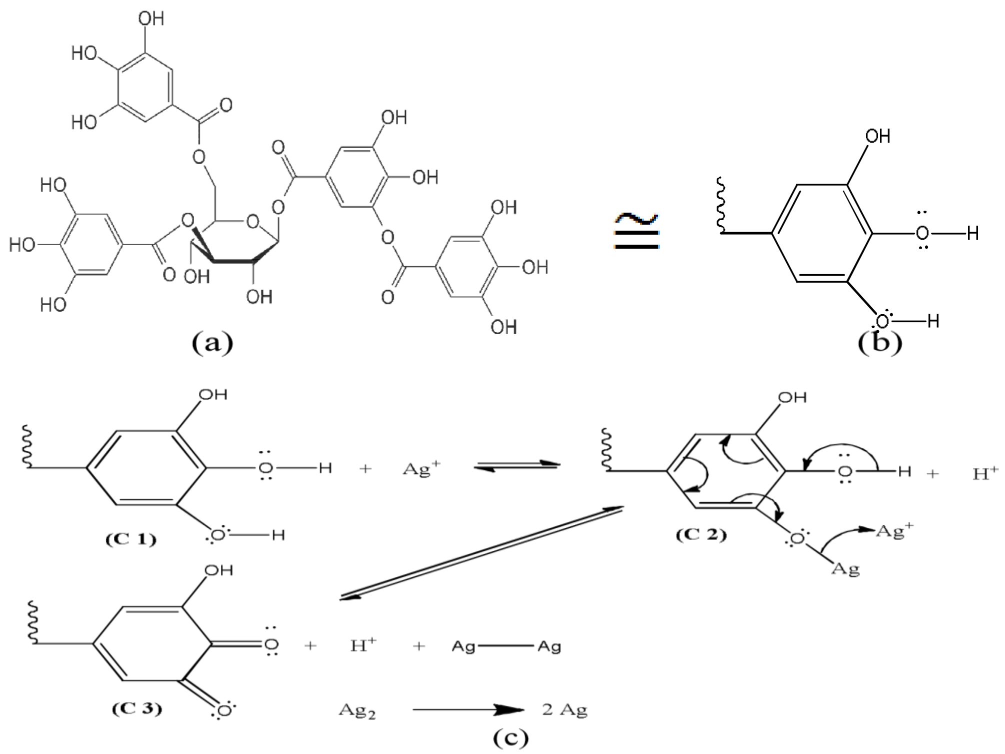


Figure 10. Molecular Structure (a) Tannins, (b) Simple Structures of Tannins,(c) Reaction Mechanisms Possible AgNP Formation

Ketapang leaf water extract contains phenolic, flavonoids, and steroids. The functional group of the tannin compound which plays an active role in reducing Ag^+ to Ag^o is estimated in Fig. 10. The process that may occur in the formation of silver nanoparticles is the formation of Ag polymer and then hydrolyzed to form the core of Ag as in the following scheme:

$$\text{Ag-Ag} \rightarrow \text{Inti Ag} \rightarrow \text{AgNP} \rightarrow \text{Colloid}$$

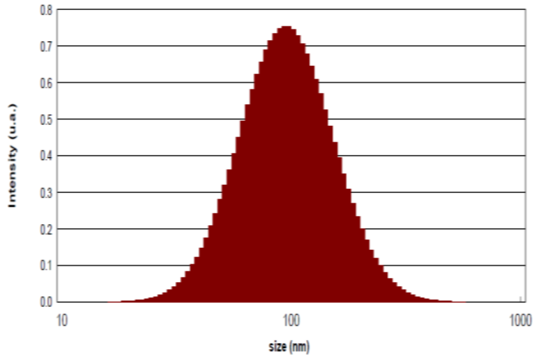
Colloid formation is associated with the emergence of nuclei in saturated conditions. After that formed Ag nanoparticles that will grow into colloids (Zakir, 2005).

Characterization Using PSA

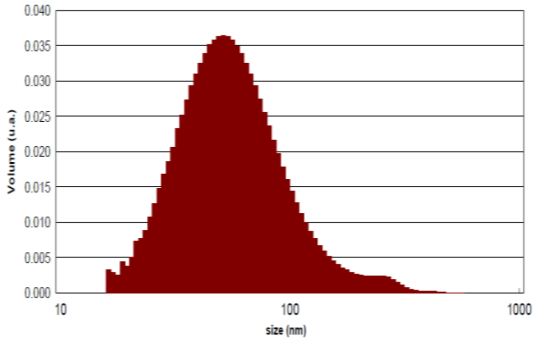
The results of the determination of the size distribution of silver nanoparticles of water extract using PSA are shown in Figure 11.

Figure 11 shows that the sample measured using PSA has a silver nanoparticle size based on an intensity dispersion of 106.16 nm, based on a volume of 65.14 nm, based on a total of 31.14 nm, so the average size obtained is 92.48 nm.

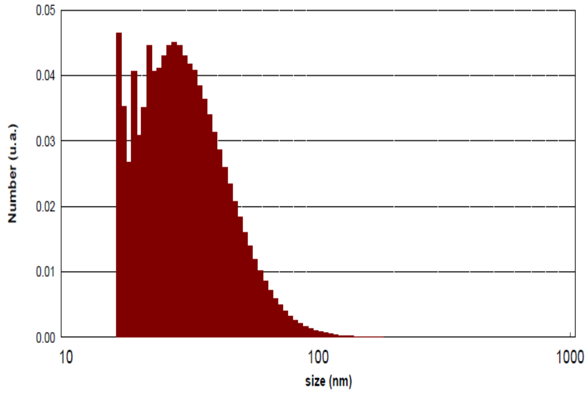
The analysis with the PSA was conducted at the Physics Laboratory of IPB (Bogor Agricultural Institute) with a sample delivery time of about 3-4 days, so it was suspected during the trip to shock that resulted in larger particle size because it may have agglomerated.



Dispersion size with intensity



Dispersion size by volume



Dispersion size by quantity

Figure 11. Analysis of PSA AgNP water extract based on intensity dispersion, Volume and quantity

Characterization Using XRD

According to (Nikmatin et al., 2011) the characterization of XRD aims to obtain information of degree of crystallinity (determination of amorphous-crystal structure) and orientation (hkl). XRD analysis can also determine the size of crystals in nanomaterials through quantitative and qualitative analysis on the identification of diffraction patterns and peak intensity. XRD pattern of silver nanoparticles can be seen in Figure 12.

The peaks of diffraction patterns of silver nanoparticles are clearly shown at values of 2θ 37.85^o, 39.86^o, 44.41^o, 64.70^o and 77.38^o with FWHM (Full Width at Half Maximum) values of 0.3853, 0.2877, 0.3254, 0.6038 and 0.3300 and the miller indexes respectively {111}, {200}, {202} and {311}.

Miller indices are crystal lattice planes {hkl} stating crystal of a material system. The crystalline system of silver nanoparticles is cubic. According to the database in the Joint Committee on Powder Diffraction Standards (JCPDS No. 99-0094), the diffraction patterns of silver nanoparticles are present at the diffraction peaks of 38.11^o, 44.30^o, 64.44^o and 77.40^o as indicated by the Miller index (111) (200), (220), and (311). Based on the JCPDS database, XRD measurements show the presence of silver nanoparticles with cubic crystal systems.

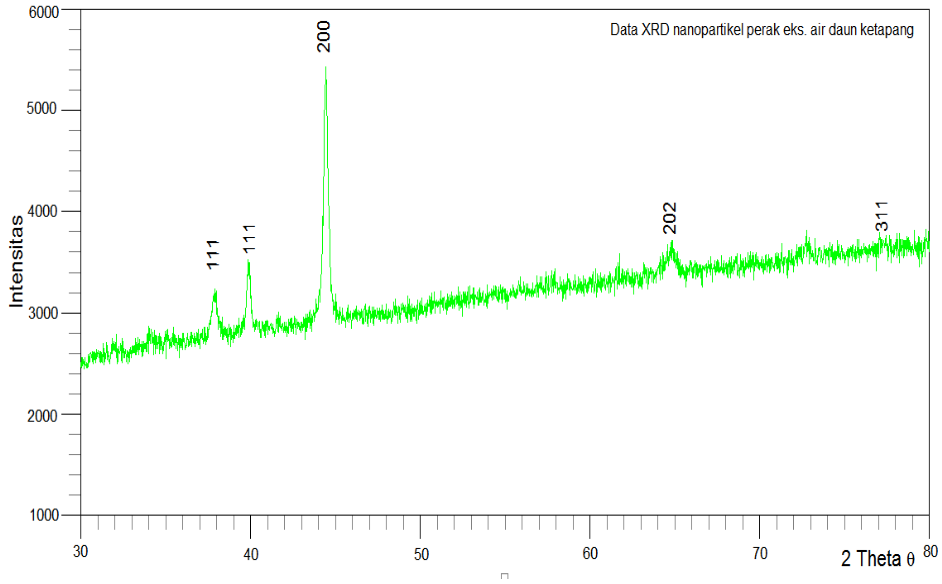


Figure 12. XRD pattern of silver nanoparticles

Table 7. The size of silver nanoparticles based on FWHM and 2θ values

No	2θ (deg)	Height (cps)	FWHM (deg)	Particle size (nm)
1	37,85	286	0,3853	42,47
2	39,86	444	0,2877	59
3	44,41	1642	0,3254	53,48
4	64,70	190	0,6038	31,74
5	77,38	59	0,3300	63,48

The results of XRD analysis other than used to determine the crystal structure in the sample, can also be used to determine the size of the crystalline silver nanoparticles. The Scherrer formula is used to determine the size of a silver nanoparticle crystal. The nanoparticle crystal size can be calculated using the formula as in Appendix 5.

Test Sunscreen Activity

Testing of sunscreen activity is done by making an alloy solution between hydroxy cinnamic acid and silver nanoparticles (AHNP). The sunscreen activity was determined from the SPF values of the samples analyzed using a UV-Vis spectrophotometer. The determination of SPF value through UV-Vis spectrophotometer can be known from the characteristics of absorbance of sunscreen sample at wavelength 290-320 nm with interval 5 nm (Suryanto and Syarief, 2013). The absorbance data of AHNP alloy solutions can be seen in Table 8.

Table 8. Absorbance data of AHNP alloy solution

Wavelength (nm)	**Absorbance**				
	AHNP solution 16 µg / ml	**AHNP solution 17 µg/ml**	**AHNP solution 18 µg/ml**	**AHNP solution 19 µg/ml**	**AHNP solution 20 µg/ml**
290	1,096	1,292	1,370	1,505	1,632
295	1,131	1,339	1,419	1,547	1,693
300	1,157	1,375	1,460	1,573	1,743
305	1,168	1,376	1,466	1,566	1,772
310	1,195	1,411	1,505	1,608	1,819
315	1,139	1,347	1,437	1,535	1,739
320	0,981	1,179	1,254	1,342	1,514

The SPF value can be determined from (Table 8) by using (equation 1). AHNP alloy solution can absorb sunlight so it can be used to protect the skin from exposure to sunlight and can reduce free radicals. This is because the hydroxy cinnamic acid has a long chain and a conjugated double bond system that will undergo resonance during exposure to UV rays (Taufikkurohmah, 2005).

Determination of SPF sunscreen value to know how much radiation can be retained and how long the skin can survive under the hot sun until the skin becomes reddish (Ade et al., 2013).

AHNP alloy solution of concentration variation of 16-29 µg/ml has SPF value of 2,22-3,39 which increase with increasing of concentration of solution. According to the US Food Drug Administration (FDA), the effectiveness of a sunscreen is divided into five groups based on the SPF price, among others:

a.Minimal protection: SPF value 2-<4

b.Protection medium : SPF value 4 -<8

c.Extra protection : SPF value 6-<8

d.Maximum protection: SPF value 8<1514

e.Protection ultra : SPF value or greater

This suggests that the alloy AHNP solution capable of protecting human skin from exposure to UV-B rays are erythema and cancer.

Table 9. SPF values of AHNP alloy solutions

Concentrations (µg/ml)	**SPF Value**
16	2,22
17	2,63
18	2,8
19	2,99
20	3,39

CONCLUSION

Based on the research result, it can be concluded that: The n-hexane, chloroform and ketapang leaf extracts (Terminalia catappa) can be used as bioreductors in the synthesis of silver nanoparticles and silver nanoparticles are not formed using ethyl acetate extracts. The hydroxy cinnamic acid alloy solution and the silver nanoparticles can serve as sunscreens with SPF 2 values, 22; 2.63; 2.8; 2.99 and 3.39 and can protect the skin from UV-B rays Higher concentration of hydroxy cinnamic acid, the greater the activity of the sunscreen

REFERENCES

Abdullah, M, and Khairurijal., 2010, Characterization of Nanomaterial: Theory, Application, and Data Processing, *Journal of Science and Technology*, 2 (1), 1-9.

Amiruddin, M. A, and Taufikurohmah, T., 2013, Synthesis and Characterization of Gold Nanoparticles Using Bentonite Matrices as Antiaging Materials in Cosmetics, *UNESA J. Chem,* 2 (1), 65-71.

Ariyanta, H.A., Wahyuni, S., and Priatmoko, S., 2014, Preparation of Silver Nanoparticles with Reduction Method and Its Application as Antibacterial Cause of Infection, *Indo. J. Chem. Sci*, 3 (1), 1-6.

Bakir, 2011, *Development of Biosynthesis of Silver Nanoparticles Using Water Decocation of Bisbul Leaf (Diospyros blancoi) for the Detection of Copper Ion (II) by Colorimetric Method, Thesis published*, (online) Department of Physics FMIPA Universitas Indonesia, Jakarta.

Bevi, F., Taufikourohmah, T., and Poerwono, H., 2009, *Optimization of Octile Synthesis Time p-Methoxy Sinamat (OPMS) from p-Methoxy Sinamat Acid (APMS) through Direct Esterification Reaction*, Proceedings of National Seminar on Chemistry Unesa , Surabaya.

Handayani, W., 2011, *Tropical Plant Utilization for Silver Nanoparticle Biosynthesis and Its Application as a Colorimetric Indicator of Heavy Metal Presence*, Thesis published, (online), Biology Study Program FMIPA Universitas Indonesia, Jakarta.

Haryono, A., Sondari, D., Harmami, S.B., and Randy, M., 2008, Sitesa Silver Naoparticles and Potential Applications, *Journal of Industrial Research*, 2 (3), 156-163.

Jaziroh, S., 2008, *Isolation and Identification of Active Compounds in Leaf N-Hexane Extract Ketapang (Terminalia catappa L.)*, Seminar on Final Duty of Chemistry FMIPA UNDIP Department, Chemistry Department UNDIP.

Lembang, E.Y., 2013, *Synthesis of Silver Nanoparticles with Reduction Method Using Bioreductor Ketapang Leaf Extract (Terminalia catappa)*, Thesis published, (online), Department of Chemistry FMIPA Universitas Hasanuddin, Makassar.

Marliyana, S.D., Kusumaningsih, T., and Kristinawati, H., 2006, Determination of Total Phenol Level and Antioxidant Activity of Ketapang Seed Skin Extract

(Terminalia catappa L.), *Alchemy Journal*, 5 (1), 39-44.

Rahayu, DS, Kusrini, D., and Fachriyah, E., 2008, *Determination of Antioxidant Activity from Ketapang Leaf Extract (Terminalia catappa L.) by Methods 1.1, Diphenyl-2-picrylhydrazyl (DPPH)*, Chemical Laboratory Organic, chemistry majors Diponegoro University.

Restasari, A., Kusrini, D., Fachriyah, E., 2008, *Isolation and Identification of the Most Active Faction of Chloroform Leaf Extract Ketapang (Terminalia catappa Linn), Thesis published, (online)*, Department of Chemistry Diponegoro University, Semarang.

Saputra, A.H., Haryono, A., Laksmono, J.A., and Anshari, M.H., 2011, Preparation of Colloid Nanosilver with Different Types of Reductor as Anti Bacterial, *Indo. J. Materials. Sci*, 12 (3), 202-208.

Suryanto, B., and Syarief, S.H., 2013, Sunscreen Activity Test of Octoy P-Methoxy Sinamat (OPMS) Gold Nanoparticles As Cosmetic Ingredients, *Journal of Chemistry*, 2 (3), 32-37.

Suwarda, S., and Maarif, M.S., 2011, *Development of PAT-Based Nanoparticle Technology Innovation to Create a Competitive Product*, Department of Industrial Technology of Agriculture, Fateta IPB Bogor.

Taufikkurohmah, T., 2005, Synthesis of p-Methoxycinamate p-Methoxycinnamate from Ethyl p-Methoxycinnamate Isolation of Kencur Rhizome (Kaempferia galanga L) as Candidate of Sunscreen, *Indo. J. Chem*, 5 (3), 193 – 197.

Wahyudi, T., Sugiyana, D., and Helmy, 2011, Sitesis Silver Nanoparticles and Their Activity Test against E.coli and S. Aureus Bacteria, *Textile Arena,* 26 (1), 1-6.

Zakir, M., Maming, Lembang, E. Y., and Lembang, M. S., 2014, *Syntesis of Silver and Gold Nanoparticles through Reduction Method using Boreductor of Leaf of Ketapang (Terminalia catappa)*, Chemistry Department, FMIPA, Makassar.