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Synthesis of Modified Polyvinyl Pyrrolidone (PVP) Silver Nanoparticles Using Soursop (Annona muricata Linn) Leaf Extract and Its Application as a Heavy Metal Colorimetric Sensor

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Abstract

This study aims to analyze the characteristics and performance of silver nanoparticles (AgNP) synthesized using soursop leaf extract bioreductor modified with the addition of polyvinyl pyrrolidone (PVP) stabilizer as a colorimetric sensor for heavy metal ions. The synthesis of silver nanoparticles was carried out by reducing $AgNO_3$ using soursop leaf extract (Annona muricata Linn) bioreductor modified with the addition of PVP as stabilizer. The results showed that the optimum synthesis volume ratio of AgNP synthesis was 0.7 mL of soursop leaf extract: 10 mL $AgNO_3$ with the addition of 3% PVP stabilizer. The formation of AgNP was characterized by a change in the color of the solution from yellow to brownish with a surface plasmon resonance peak at a maximum wavelength of 438 nm. Fourier-transform infrared spectroscopy studies showed hydroxyl groups (-OH) and carbonyl groups (C=O) play a role in the reduction process of silver ions. Particle size analysis results demonstrated an average particle size of 71.5 nm with a polydispersity index value of 0.364. The results of the colorimetric analysis showed that the synthesized AgNPs proved to be highly selective towards Cu metal ions.

Keywords: AgNP, biosynthesis, sourshop leaf extract, PVP, colorimetry.

1. Introduction

Increasing cases of heavy metal pollution in air, water, and soil pose a serious threat to humans and the environment. This is because heavy metals are persistent, toxic, and easily accumulated in the human body, which can cause various diseases [1]. Therefore, there is a need to develop a quick and easy analytical method to detect the presence of heavy metals in the environment.

In recent years, nanotechnology has shown tremendous potential in various fields of application, one of which is as a sensor for hazardous chemical compounds in the environment. Nanotechnology involves the fabrication of nanoparticles with better physical and chemical properties than large-sized materials. One type of nanoparticle widely developed today is nanoparticles of silver metal (AgNP).

Methods to synthesize silver nanoparticles can use top-down methods by converting large materials into nano-sized particles involving mechanical, electrical, and thermal energy. These include physical methods such as mechanical/ball milling, sputtering, and thermal/laser ablation. Physical and chemical methods provide good yields, but require high energy consumption and expensive equipment, and produce residues as by-products during synthesis [2].

Biosynthesis is an alternative method to synthesize nanoparticles with several advantages including fast and easy synthesis procedures and being more environmentally friendly. The biosynthesis of silver nanoparticles utilizes the content of secondary metabolite compounds in plant extracts as bio-reduction. The hydroxyl and carboxyl functional groups in these compounds help the reduction process of Ag^+ to Ag^0 [3]. Commonly used plant parts in the synthesis of silver nanoparticles include bark, leaves, flowers, fruits, seeds, and rhizomes.

Silver nanoparticles are also known to have superior optical properties compared to other metal nanoparticles, so they can be applied as colorimetric sensors to detect various pollutants in the environment such as heavy metals. Silver nanoparticles from plant extracts can detect the presence of heavy metals but colorimetrically are not yet selective and sensitive enough to certain metals [4]. This is due to the tendency of nanoparticles to agglomerate easily, resulting in a decrease in nanoparticle size stability and sensory response-ability. Therefore, the addition of stabilizers is needed in the modification of silver nanoparticle synthesis to increase their selectivity and sensitivity as colorimetric sensors for heavy metals.

In this study, silver nanoparticles were synthesized using soursop leaf extract with the modification of adding polyvinyl pyrrolidone (PVP) stabilizer. The soursop plant (*Annona muricata L.*) was chosen as a bioreduction because the leaves have many secondary metabolite compounds that play a role in the silver ion reduction process, while the addition of PVP serves to control the size and morphology of nanoparticles by reducing surface energy and providing steric effects for nanoparticle dispersion in suspension [5]. The use of PVP makes the surface of silver nanoparticles more organized and controlled to provide a more specific interaction between silver nanoparticles and the intended target analyte. It is expected that silver nanoparticle-based sensors modified by the addition of a PVP stabilizer can be more sensitive and selective in detecting certain compounds in the sample.

2. Materials and Method

The materials used in this study were soursop leaf extract (*Annona muricata Linn*) were air-dried in sunlight for ten days, $AgNO_3$ (Merck), $Pb(NO_3)_2$ (Merck), $3CdSO_4.8H_2O$ (Merck), $ZnCl_2$ (Merck), $CuCl_2.2H_2O$ (Merck), $MnSO_4.H_2O$ (Merck), PVP K-30, aquabides, magnesium metal, $FeCl_3$ solids (Merck), HCl p.a., H_2SO_4 p.a., chloroform, anhydrous acetic acid, Dragendroff reagent, and Mayer reagent.

The process of making soursop leaf extract was carried out as done by Pedroza *et al*. [4]. Soursop leaves were washed and then dried. After that, the leaves were pulverized using a blender until a homogeneous powder was obtained and filtered using a 60 mesh sieve. Then as much as 3 grams of soursop leaves that have been mashed are boiled in an Erlenmeyer flask containing 200 mL of aquabides. The extract was filtered using Whatman No. 1 filter paper to take the filtrate. The second filtration was done with a centrifugation at 3000 rpm for 15 minutes. The extract can be used immediately or stored at 4-8˚C. Furthermore, phytochemical tests were carried out to determine the class of compounds contained in soursop leaf extract. Phytochemical tests on soursop leaf extract include alkaloid, flavonoid, terpenoid, steroid, and tannin tests.

Optimization of silver nanoparticle synthesis was carried out using the bottom-up method as done by Pedroza *et al*. [4]. Soursop leaf extract was mixed with 1 mM $AgNO_3$ solution with variations in the ratio of soursop leaf extract: $AgNO_3$ (v/v), namely 0.5:10 (A), 0.7:10 (B), and 1:10 (C). Then the mixture was stirred until homogeneous using a magnetic stirrer and placed on a hot plate with a temperature of 60-85˚C for 10 minutes. After that, 2 mL of PVP solution (1%, 2%, and 3%) was added drop by drop until a brownish-yellow color was obtained without heating. Then, the colloidal silver nanoparticles formed until the 30th day after synthesis were observed and measured with a UV-Vis spectrophotometer. Furthermore, the synthesis process was repeated without using a PVP stabilizer solution as a comparison. The sample code of silver nanoparticle synthesis can be seen in Table 1.

Table 1. Code of the sample synthesis AgNP

Volume ratio (mL)	Concentration PVP (%)		
Extract: $AgNO_3$	1%	2%	3%
0,5 : 10	SA1	SA2	SA3
0,7 : 10	SB1	SB2	SB3
1: 10	SC1	SC2	SC3

The resulting silver nanoparticles were then characterized with a UV-Vis spectrophotometer at a wavelength of 300-600 nm, characterized with FTIR to identify the functional groups involved in the silver ion reduction process, and characterized with PSA to obtain the average particle size distribution. Colorimetric analysis based on silver nanoparticles was carried out by mixing each analyte solution containing Cd^{2+}, Cu^{2+}, Pb^{2+}, Mn^{2+}, and Zn^{2+} ions was pipetted as much as 1 mL with a concentration of 1000 ppm with 2 mL of silver nanoparticles. Then observed visually and recorded the time of each solution color change that occurred. The analyte solution that experienced a visual color change was further analyzed by making the analyte solution with a concentration variation of 0.1; 1; 10; 100; 500; and 1000 ppm. Furthermore, it was characterized by a UV-Vis spectrophotometer at a wavelength of 200-600 nm.

3. Results and Discussion

Extraction of soursop leaf and phytochemical testing, based on this study, the soursop leaf filtrate obtained was brownish yellow with an average volume of 130 mL. Furthermore, phytochemical tests were carried out on soursop leaves and the test results can be seen in Table 2. This phytochemical test is carried out by adding specific reagents to provide typical color changes that indicate the presence of certain groups of secondary metabolite compounds in the sample.

Table 2. Photochemical testing results of soursop leaf

Class of Secondary Metabolites	Result	Remarks
Alkaloid (Dragendroff)	+	Brownish red precipitate
Alkaloid (Meyer)	+	Brownish white precipitate
Flavonoid	+	Yellow solution with lots of brownish-yellow foam
Terpenoid	+	Brownish ring
Steroid	-	No change
Tanin	+	Blackish green color

Based on Table 2, the results of the secondary metabolite test show that soursop leaves contain secondary metabolite compounds of alkaloid, flavonoid, terpenoid, and tannin groups but negatively contain steroids. Other studies have also revealed that leaves are one part of the soursop plant that has the highest levels of secondary metabolites compared to other parts [5].

In general, the formation of colloidal silver nanoparticles is characterized by a change in the color of the solution from colorless to yellow to brownish over time [4, 6]. At the beginning of mixing the $AgNO_3$ solution with soursop leaf extract, the solution showed a pale yellow color. After stirring for 30 minutes, the color of the solution changed to bright yellow and slowly became brownish (Fig.1). The color change also proves the change in the optical properties of the nanoparticles.

Figure 1. Silver nanoparticles from Soursop Leaf Extract

The Surface Plasmon Resonance (SPR) value of AgNPs has a peak in the range of λ_{max} 400-500 nm. Based on the UV-Vis spectra, the results show a new absorption in the 435-452 nm region which proves that this biosynthesis process produced AgNPs. In addition to the wavelength, the absorbance value also increased and formed a characteristic peak width that became sharper as the storage time progressed. This indicates that the quantity of AgNPs formed is more and more homogeneous.

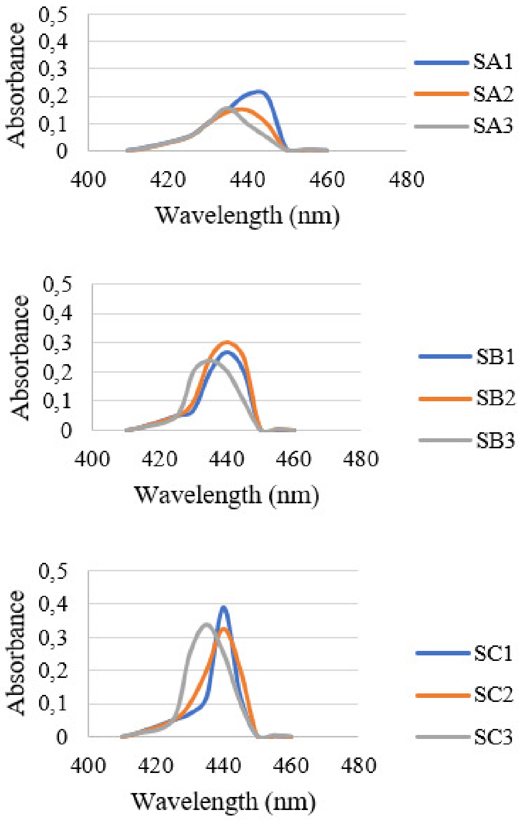

Figure 2. AgNP-DS with code SA, SB, and SC

The results showed that the variations of 0.5:10 (SA), 0.7:10 (SB), and 1:10 (SC) have absorbance peaks after 24 hours at wavelengths of 442, 441, and 445 nm, respectively, so it can be concluded that AgNP-DS has been formed because its maximum absorption is in the wavelength range of 400-500 nm [7]. However, when viewed from the absorbance, the 1:10 (SC) variation showed the highest value than the absorbance value shown by the 0.5:10 (SA) and 0.7:10 (SB) variations, so more AgNP-DS quantity was produced in the SC variation. After 24 hours (Fig. 2), the AgNPs modified with 1%, 2%, and 3% PVP showed a wavelength shift towards smaller wavelengths with decreasing absorbance. When viewed from the three PVP variations, it shows that the AgNP-DS sample with the addition of 3% PVP experienced a much smaller wavelength shift compared to the addition of 1% and 2% PVP concentrations. This indicates that the use of a PVP stabilizer with increasing concentration can restrain the agglomeration rate of nanoparticles significantly by shifting the wavelength to a smaller direction due to changes in particle size.

PVP in low concentration will form short PVP chains that result in less steric effect and a good combination of PVP with AgNP-DS in colloids, although the protection of AgNP-DS from agglomeration is less perfect. However, if the concentration of PVP used increases, the PVP chains formed become longer to protect AgNP from agglomeration [8]. Other interactions between PVP molecules and metal atoms on the nanocrystal surface also occur through the affinity of oxygen and nitrogen donor atoms contained in the carbonyl amide groups of the PVP molecules. These interactions are responsible for reducing surface energy and preventing grain growth and particle agglomeration.

The spectrum of AgNPs biosynthesized using soursop leaf extract continues to shift its maximum wavelength, but it is still in the range of the maximum wavelength of AgNPs between 435-452 nm and increases in absorbance until measurement at 30 days. These results show similarities with previous research from Pedroza *et al*. [4] who successfully synthesized AgNPs using soursop leaf extract without stabilizers with an absorbance peak at a wavelength of 447 nm. This is related to the shift in wavelength to be larger which indicates the particle size is increasing so this phenomenon can show that the particle size tends to increase with storage time due to the merging of nanoparticles that form larger particles [9-10]. In addition, this is due to the bathochromic effect produced by the presence of certain substituents or auxochromes on the chromophore contained in the secondary metabolite compounds of soursop leaf extract. The increase in absorbance is thought to be due to the ongoing process of AgNP-DS formation and the phenomenon is referred to as the hyperchromic effect [11-12].

When viewed from the maximum absorption of all sample variations (Fig. 3), the results show that the particle size distribution value in the SB3 sample is increasingly homogeneous so it can be concluded that the synthesized AgNPs can still be used as colorimetric sensors up to 30 days of storage age because they still provide good stability. However, further characterization using PSA is needed to confirm the particle size distribution accurately. These results also indicate that the SB3 sample with a formulation of 0.7 mL of soursop leaf extract and a modification of 3% PVP addition has the best stability among all sample variations used up to 30 days of storage. Thus, the synthesis ratio has provided optimal results and can be used in the next stage of nanoparticle synthesis.

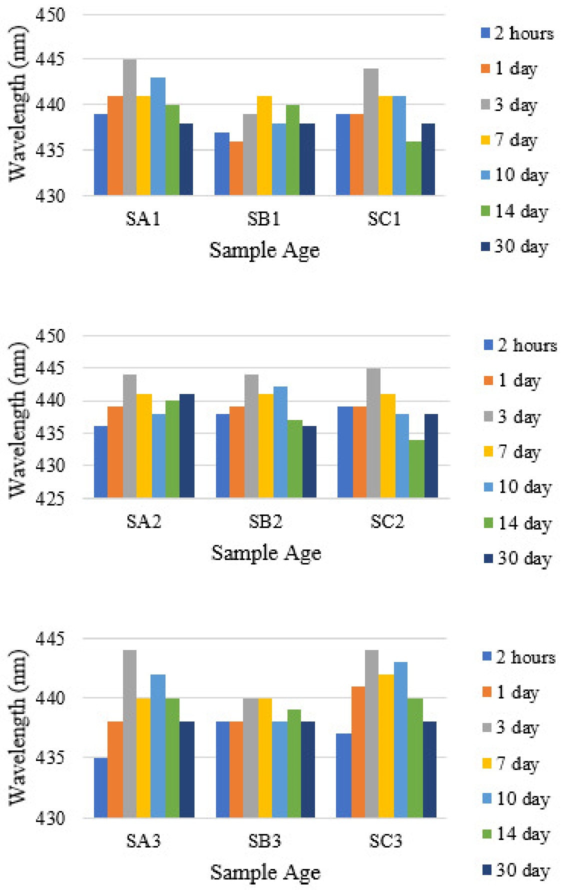

Figure 3. Comparison of λ_{max} to age of 3% AgNP-PVP sample

Characterization of silver nanoparticles, the FTIR spectra of the synthesized nanoparticle samples can be seen in Fig. 4. The resulting FTIR spectra show an absorption band at wave number 3332.59 cm^{-1} corresponding to O-H stretching which indicates the presence of hydroxyl groups in alcoholic, phenolic, and flavonoid compounds. This number can also indicate the presence of amine groups ($-NH_2$) which are thought to come from PVP molecules in the synthesized silver nanoparticles. In addition, there is also an absorption band at wave number 1639.13 cm^{-1} corresponding to C=O stretching which is characteristic of carbonyl groups, and an absorption band at wave number 608.71 cm^{-1} which is a C=C ring stretching vibration or AgNP stretching vibration. The formation of silver nanoparticles with plant extract bioreduction can occur due to the reduction reaction of Ag^+ ions to Ag^0 (Fig. 5). Functional groups contained in plant extracts will undergo oxidation reactions so that changes such as hydroxyl groups (-OH) become ketone [13-15].

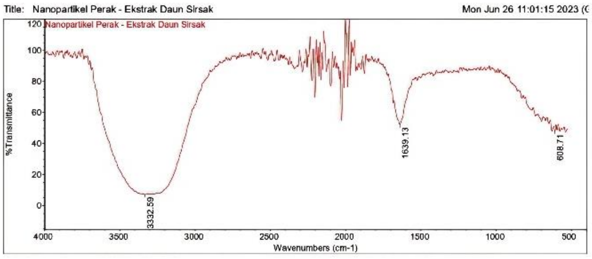

Figure 4. FTIR spectra of AgNP-DS

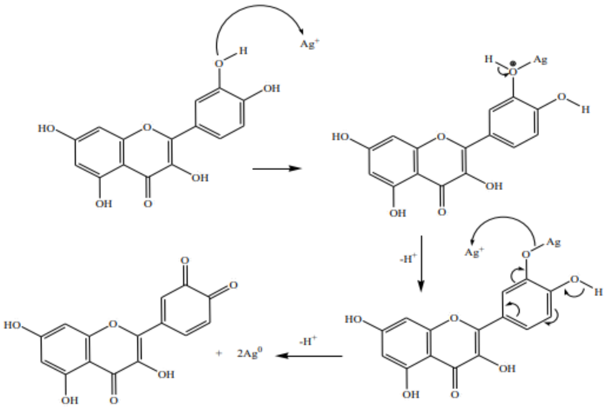

Figure 5. Reaction mechanism of AgNP formation

Particle size data and polydispersity index from PSA testing can be seen in Table 3 and Figure 6. The optimum formula of soursop leaf aquabides extract nanoparticles modified with PVP stabilizer at the age of 7 days produces physical characteristics with an average particle size of 71.5 nm, with a polydispersity index value of 0.364. This proves that there is a relationship between λ_{max} and the size of silver nanoparticles as revealed by Solomon *et al*.[7] that AgNPs with a maximum wavelength of 438 nm have a size in the range of 60-80 nm, so it can be concluded that the AgNP-DS produced under these optimum conditions is already included in the class of nanoparticles. The size obtained is smaller than other AgNP biosynthesis studies using soursop leaf extract without stabilizers such as the research of Badmus *et al*. [16] which produced silver nanoparticles with a size of 86.8 nm. It can also be seen that the use of a PVP stabilizer in this study is able to maintain the size of AgNP-DS to be below 80 nm until the age of 7 days which indicates that the sample has good stability.

Based on the polydispersity index value obtained in the measurement of AgNP-DS, the selected optimum formula has a polydispersity index in the monodispersion category because its PDI value is below 0.7 which indicates that the sample is completely dissolved or well dispersed. The low PDI value indicates that the PVP stabilizer can prevent agglomeration between particles [17]. Where values close to 0 indicate homogeneous dispersion, while values greater than 0.7 indicate high heterogeneity.

Table 3. Particle size analyzer test result

Sample	Particle Size	PDI Value	Count Rate
AgNP-DS	71,5 nm	0,364	1720 kCPS

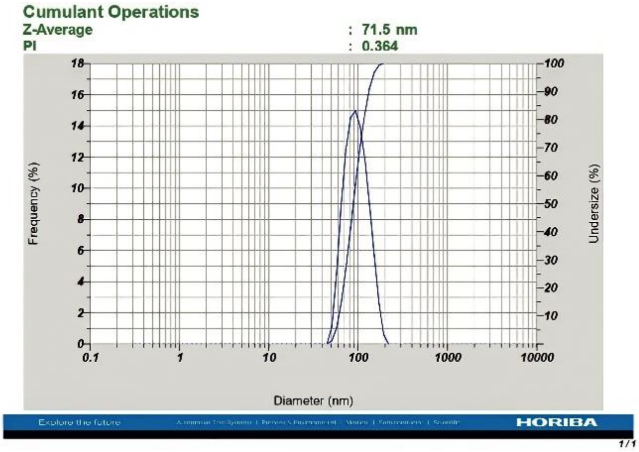

Figure 6. Particle size analyzer test result

The graph (Figure 6) also only forms a single peak indicating that the sample has good uniformity and there is no significant increase in particle size [18]. These results indicate that aggregation does not occur in the sample which results in an enlarged particle size with the color getting darker as the nanoparticles are stored for longer. Thus, this study proves that the use of PVP stabilizer can help control the microstructure and LSPR properties of biosynthesized AgNP-DS and potentially optimize its performance as an LSPR-based sensor in the future.

Table 4. Colorimetric test results

Metal Ions	Result
Cd^{2+}	Brown → Light brown (-)
Mn^{2+}	Brown → Light brown (-)
Pb^{2+}	Brown → Light brown (-)
Zn^{2+}	Brown → Orange (-)
Cu^{2+}	Brown → light green(+)

Remarks:

(+): no absorbance peak at 400-500 nm wavelength, aggregation of silver nanoparticles causing LSPR shift towards larger wavelength.

(-): there is a peak at a wavelength of 400-500 nm but the absorbance is lower than the silver nanoparticle solution alone, there is little aggregation, and visually there is only a fading of the nanoparticle color.

The colorimetric principle is based on the aggregation of metal nanoparticles when in contact with the target analyte causing LSPR (Localized Surface Plasmon Resonance) to shift towards larger wavelengths [11]. This aggregation shows an increase in particle size with a characteristic color change so that AgNPs can be used as sensors to detect various analytes such as heavy metal ions. The colorimetric test results can be seen in Table 4 and Fig. 7.

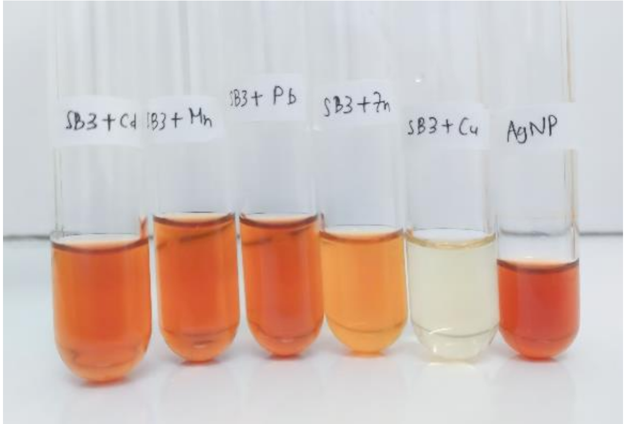

Figure 7. Colorimetric test results

Based on qualitative tests, the most reactive metal ion to AgNP-DS is Cu^{2+} . The results showed a color change in AgNP-DS from brownish to clear white (clear) when added with Cu^{2+} analyte and only took less than 1 minute, while testing of other metal ions such as Cd^{2+} Mn^{2+}, Zn^{2+}, and Pb^{2+} did not give significant color changes. This indicates that the AgNP-DS produced is more sensitive to Cu^{2+} ions.

This change occurs due to AgNP aggregation when in contact with the analyte which will disrupt the interaction of the Ag^0 dipole-ion with oxygen/nitrogen in the PVP molecule so that the stability of AgNP is reduced and tends to experience aggregation [19]. In addition, Cu^{2+} ions have a cell potential price E^0 greater than Cd^{2+}, Mn^{2+}, Zn^{2+}, and Pb^{2+} metals, causing Cu^{2+} ions to be more easily reduced by Ag^0 than other metal ions.

The interaction between PVP and Cu^{2+} not only causes AgNP-DS aggregation but also affects the electronic structure of PVP causing the LSPR effect to be observed. PVP not only acts as a stabilizer but also as an ion coordination reagent. The nitrogen and oxygen atoms of PVP can form specific coordination complexes with Cu^{2+} ions [20, 21].

The UV-Vis spectra obtained showed that no more AgNP absorbance peaks were detected in the AgNP sample with Cu^{2+}. This result indicates a change in the characteristics of AgNP-DS, while the spectra of the Cd^{2+}, Mn^{2+}, Zn^{2+}, and Pb^{2+} metal ion tests still showed a peak at a wavelength of 400-500 nm. However, the absorbance decreased compared to the silver nanoparticle solution alone, so that visually there was only a fading of the nanoparticle color because there was little aggregation. Therefore, further tests were carried out on Cu^{2+} ions using lower concentration variations to determine changes in the characteristics of the absorbance peak of AgNP-DS.

The next test was carried out on Cu^{2+} ions with concentration variations ranging from 1000 ppm to 0.1 ppm (Fig. 8). Qualitatively, there is a significant change in colloidal color in the test against Cu^{2+} ions 1000 ppm-100 ppm, while in the test against Cu^{2+} ions, 10 ppm-0.1 ppm does not give too significant changes. When viewed from the resulting UV-Vis spectrum, the absorbance value in all additions of Cu^{2+} ion concentration decreased, while the wavelength shift tended to shift towards a larger direction. This indicates a decrease in electrostatic repulsion and faster agglomeration. This agglomeration causes the distance between AgNP-DS to become closer, thus weakening the ion-dipole interaction of AgNP-DS with PVP [11, 22].

Figure 8. Colorimetric test of various concentrations of Cu^{2+}

Table 5. Colorimetric test results

Concentration Metal Ions	λmax (nm)	Abs
Cu 1000 ppm	537	0,021
Cu 500 ppm	518	0,065
Cu 100 ppm	448	0,132
Cu 10 ppm	449	0,376
Cu 1 ppm	445	0,445
Cu 0,1 ppm	443	0,453
AgNP	440	0,492

Based on the resulting spectrum in Table 5, there is a decrease in absorbance at all Cu^{2+} concentrations. This result is related to the color change of the solution in both concentration tests, which indicates that AgNP-DS has undergone physical changes in both particle size and particle distribution. When viewed from the wavelength shift curve, the data obtained from concentrations of 0.1 to 100 ppm shifted significantly towards larger wavelengths ranging from 443-449 nm, indicating a decrease in electrostatic repulsion and faster agglomeration.

This agglomeration causes the distance between AgNP-DS to become closer thus weakening the dipole-ion interaction of AgNP-DS with PVP. Therefore, the effect of low analyte concentration is relatively less destabilizing for

AgNP-DS and less agglomeration occurs. The results of this test conclude that as the concentration of Cu^{2+} used increases, the smaller the absorbance value obtained.

4. Conclusion

The optimum characteristics of soursop leaf extract nanoparticles (AgNP-DS) resulted in an average particle size of 71.5 nm and a maximum absorption peak at a wavelength of 438 nm and showed homogeneous dispersion. Silver nanoparticles proved to be highly selective to Cu metal as indicated by the color change from brownish to clear white and the change in spectrum towards a larger wavelength due to aggregation. However, further research is still needed with the addition of other parameters in the optimization of silver nanoparticle synthesis and characterization using XRD and SEM.

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