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SYNTHESIS OF POLY ACRYLIC ACID (PAA) MODIFIED SILVER NANOPARTICLES USING TRISODIUM CITRATE FOR HEAVY METAL DETECTION

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ABSTRACT

Therefore, this project was to prepare and characterize silver nanoparticles (AgNPs) and study their application for colorimetric detection of heavy metal ions. AgNPs are synthesized by a bottom-up method in which AgNO3 serves as the precursor, which is then reduced using trisodium citrate and stabilized by 1 vol.% polyacrylic acid (PAA). Trisodium citrate facilitates the reduction of Ag^+ ions due to its negatively charged carboxylic groups, whereas PAA enhances stability and selectivity. Under the best reaction parameters, AgNPs produced brown-yellow colloids with a Surface Plasmon Resonance (SPR) peak of 403 nm. A particle size analysis showed an average particle diameter of 29.9 nm, with a standard deviation σ of 0.482. Fourier Transform Infrared Spectroscopy (FTIR) analysis confirmed that hydroxyl groups -OH and carbonyl groups C=O play a role in reducing Ag+ ions. Because they are highly active, AgNPs can respond to Hg^{2+} in tests, marking the color change from brown-yellow to transparent white within about one minute. Methods testing for validation of linearity revealed an R^2 = 0.9985, and a LOD and LOQ are 0.074 ppm and 0.224 ppm, respectively. At 700 ppm $Hg^{2+,}$ the selectivity was good. These results demonstrate that AgNPs are sensitive and efficient sensors of Hg^{2+} ions and indicate how to find promising new ways to detect heavy metals in environmental monitoring.

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INTRODUCTION

Heavy metal contaminants cause environmental pollution in aquatic ecosystems, affecting human health, the animals living around them, and the plants on them. Toxic heavy metals are pollutants that are very hazardous to both the environment and the health of human beings. Humans can use these compounds in food and drinking water and breathe them into their lungs from air pollution. The larger they are in size, too, this could lead to a more severe amount of injuriousness for any given metal poisoning route [1]. Common heavy metal contamination includes mercury (Hg), copper (Cu), cadmium (Cd), lead (Pb), and chromium (Cr) [2]. Heavy metals are typically present in water at very low levels of no more than 1 µg, but when the concentration exceeds the standard limit, it can pose a risk to human health when it enters the pro chain [2]. Nanoparticle-based inexpensive chemosensors are used to detect the presence of heavy metal ions in water. One common kind of nanoparticle synthesized is silver nanoparticles. Silver nanoparticles (AgNPs) differ in properties from other metals: they have anti-inflammatory and antibacterial actions and can act as sensors to detect various heavy metals [3].

Due to these effects, silver nanoparticles have become an option of choice in heavy metal qualitative analyses of every kind. Nanoparticles can then be used for heavy metal colorimetric sensors. They make it easy to do testing in the field (Sometimes literally) and are inexpensive. They have quite limited life spans, but because of SPR's extraordinary sensitivity, they are 80 times more sensitive than conventional methods such as spectroscopy [4]. AgNPs have shown unique properties in detecting the presence of heavy metal ions. The most important of these properties is their ability to use the SPR (Surface Plasmon Resonance) effect, which results in large selectivity and high sensitivity [5]. The mechanism of heavy metal detection using colorimetry is to observe the change in color of nanoparticles when they react with heavy metals. This is due to reduction-oxidation reactions and other processes, such as hydrogen bonding or Van der Waals force. Cooperation between the heavy metal molecules and nanoparticles happens [5].

There are two ways to synthesize AgNPs: physical methods (top-down) and chemical methods (bottom-up). Since this method is relatively easy, inexpensive, and can be scaled up quickly, the reducing agents (organic or inorganic substances) are usually used to reduce silver nitrate solution as a precursor 6. The chemical reduction method of synthesis of AgNPs uses organic and inorganic reductants. Selecting a suitable reductant is an important factor. This is because the size, shape, and particle distribution greatly depend on the properties of the reductant [7]. In this case, trisodium citrate was used as the reductant. Trisodium citrate contains negatively charged carboxylic groups, which can attract positively charged silver ions and then reduce them to atoms. Using the reduction groups that already exist in the [8].

Silver nanoparticles can absorb and scatter light in the visible region of the light spectrum, giving rise to related plasma resonance (SPR) peaks at wavelengths in or under ultra-violet or violet light. Silver nanoparticles can have sizes, shapes, and other characteristics that are more in line with light at different wavelengths in their various interactions. The actual display of color occurs when these different interactions come about through irradiation by visible light. So, silver nanoparticles become the preferred material for various researchers; one can make it into a heavy metal ion sensor [10]. To prevent agglomeration and change in color, the synthesis of silver nanoparticles by rhubarb root will be changed with a stabilizer whose task is to aid both in controlling the size and morphology of nanoparticles [11].

Silver nanoparticles prepared using trisodium citrate were characterized. They were checked for their size using methods such as the UV-Vis Spectrophotometer, Particle Size Analyzer (PSA), and Fourier Transform Infrared (FT-IR) spectroscopy; experiments were undertaken to ascertain whether a normal atomic absorption wavelength would be within 400-500 nm and it was necessary to determine functional groups in organic compounds responsible for the reduction of metal in nanoparticle synthesis. These nanoparticles were then employed for colorimetric sensing of metal ions, and then standard validation took place. The methods to verify whether or not a particular method meets its intended use. It can be used for the intended purpose. Validation involves analyzing parameters during laboratory testing that allow a given method to fulfill its intended use. Some key parameters examined in method validation include specificity, linearity, sensitivity, LOD (Limit of Detection), and LOQ (Limit of Quantification).

Based on the above description, the research is conducted in this paper to synthesize AgNPs using trisodium citrate and $AgNO_3$, modified with Polyacrylic Acid (PAA) as a stabilizer. Up to now, no research has been done into AgNP synthesis with trisodium citrate modified by polyacrylic acid (PAA) that includes reaction optimization conditions such as reductant pH, reaction when $AgNO_3$ concentration, reduce when ant concentration and stability moment as a heavy metal ion sensor. So, Its author is interested in using trisodium citrate to prepare AgNPs and then using it as a heavy metal colorimetric sensor.

METHODS

1. Chemicals and Materials

Trisodium citrate (Merck) 99%, $AgNO_3$ (Merck) 99.98%, Polyacrylic Acid (PAA) 99%, NaOH (Merck), $Pb(NO_3)_2$ (Merck) 99%, $CdSO_4.8H_2O$ (Merck) 99%, $CuCl_2.2H_2O$ (Merck) 99%, ZnCl (Merck) 99%, $HgCl_2$ (Merck) 99%, $Cr(NO_3)_3$ (Merck) 99%, KI (Merck) 99%, $MgCl_2.2H_2O$ (Merck) 99% dan $MnSO_4.H_2O$ (Merck) 99%.

2. Optimization of pH trisodium citrate

The formation of silver nanoparticles following various pH optimization experiments under appropriate reductants adjusted to different values: pH 9, 10, 11, 12, and 13, using 1.25 M NaOH. This work takes silver nitrate as a single-phase precursor. We chose a pH range of 9-13 as prior studies have shown this range not only promotes Ag^+ ions. As shown above, the pH range works for both, with well-polished nanospheres as a compromise. 1×10^{-3} M $AgNO_3$ was taken in 50.0 mL and heated at 85-90°C on a hotplate. Add 5.0 mL of 1% trisodium citrate solution, adjusted for pH. With a magnetic stirrer, stir the mixture for 2 minutes during heating. Then, stop the heating process, add 2.0 mL of 1% PAA to the solution, and keep it homogenized for 20 minutes. After that, all solutions were measured using a UV-VIS spectrophotometer with a wavelength of 300-600 nm.

3. Optimization of Reaction Time

The optimization of reaction time was realized by trying the reaction time with several variations, 1, 2, 3, 4, and 5 minutes, to be exact reaction times measured in minutes. Based on previous studies, the reaction interval of 1–5 minutes was chosen because it was known that small particles start forming at various locations within those first few minutes, with enough trial and error work to show this holds generally. So, a silver nanoparticle is formed within seconds, and so on in this range. For the $AgNO_3$ solution of 1 x 10^{-3} Moles per liter, 50.0 mL were taken and heated in a thermostatically controlled bath at about 85-90°C. Add 5 mL of 1% trisodium citrate. Additionally, the mixture was stirred constantly during heating for 1-5 min. Finally, the heating stops; as soon as it does, 2 mL of 1% PAA is poured over where the $AgNO_3$ is now, and the solution has 20 minutes to be kept constantly homogenized everywhere in all directions. Then, UV-VIS spectroscopy measured the solutions at a wavelength ranging from 300 to 600 nm.

4. Optimization of AgNO3 Concentration

Different concentrations of $AgNO_3$ solution were prepared (0.5 x 10^{-3} M; 0.75 x 10^{-3} M; 1 x 10^{-3} M; 1.25 x 10^{-3} M; 1.5 x 10^{-3} M), the concentrations range of $AgNO_3$ was selected in connection with previous studies, were used to reduce the effective range of $AgNO_3$ concentration, at this level, these concentrations could always provide an adequate amount of Ag ions for nucleation and growth of the particles but did not lead to aggregation or precipitation. A 50.0 mL $AgNO_3$ solution of various concentrations was placed on a hotplate at 85-90°C. Add 5 mL of 1% trisodium citrate in optimum pH to the solution. In the heating stage, the mixture is agitated with a magnetic stirrer depending on the optimal reaction time. After that, the heating procedure was terminated, and 2.0 mL of 1% PAA was dropped into the solution and allowed to stir up for 20 minutes. Next, all solutions were measured by UV-VIS spectrophotometry at the wavelength 300-600 nm.

5. Optimization of Trisodium Citrate Concentration

Trisodium citrate solution was prepared in concentrations of 0.5%, 0.75%, 1%, 1.25%, and 1.5%. The concentration of trisodium citrate influences the reduction of Ag^+ ions and the stabilization of the resulting nanoparticles. The higher the concentration, the stronger the stabilizing effect. Fewer, less powerful stabilizers tend to aggregate into groups of larger particles. This is why a larger stabilizer is necessary for lower concentrations. $AgNO_3$ solution of 50.0 mL with optimum concentration was heated on a hotplate at 85-90°C. Then, the heating process was stopped, and 2.0 mL of 1% PAA was added to the solution and kept homogenized for 20 minutes. As with the rest of the process, measurements for all solutions can be obtained by UV-VIS spectrophotometer at a wavelength of 300-600 nm.

6. Characterization of Silver Nanoparticles.

The UV-Vis spectrophotometer was used to characterize the resulting silver nanoparticles by measuring absorbance (Fig. 1) and their wavelength to test whether the synthesized nanoparticles had reached the nanoparticle size range. The production of AgNPs is characterized by high absorbance in the wavelength range of 400-500 nm [12]. Then, FTIR characterization was performed to discover functional groups bonding in synthesizing AgNPs. It was characterized with PSA to get an average particle size distribution [13].

7. Colorimetric Analysis Based on Silver Nanoparticle

The colorimetric analysis was conducted to evaluate the potential of the synthesized silver nanoparticles in detecting heavy metal ions. This method is based on the change in color of the nanoparticle solution in the presence of specific metal ions, providing a simple and rapid detection technique.

Solutions for heavy metal ions and single other tested cations were made using the following methods. They were made from high pure analytical grade chemicals (99% pure): Hg^{2+} from $HgCl_2$, Cu^{2+} from $CuCl_2 \cdot 2H_2O$, Pb^{2+} from $Pb(NO_3)_2$, Cd^{2+} from $CdSO_4 \cdot 8H_2O$, Zn^{2+} from $ZnCl_2$, Cr^{3+} from $Cr(NO_3)_3$, K^+ from KI, Mg^{2+} from $MgCl_2 \cdot 2H_2O$, and Mn^{4+} from $MnSO_4 \cdot H_2O$. These reagent materials ensured uniformity and trustworthiness in the colorimetric experiments. A standard solution has a predetermined and accurate concentration of heavy metal ions. Knowledge of the signals given out by standard solutions is used as a reference in an experiment to determine the concentration or strength of other substances involved in the reaction. In this experiment, 1.0 mL of the standard solution with a concentration of 1000 ppm was added to 2.0 mL of AgNPs (silver nanoparticles) to test the detectability of heavy metal ions. It was then compared with a standard solution whose concentration of the other substance was already known to give it suitable units. The solution color change and the time each change occurred were recorded visually with a stopwatch. The solution was then analyzed using a UV-vis Spectrophotometer in the 200-800 nm wavelength range. The combination of silver nanoparticles (AgNPs) and heavy metal ions was characterized by a UV-Vis Spectrophotometer over the wavelength range of 200-800 nm to determine the absorbance of light by the sample at different wavelengths. When light is incident on the sample, the spectrophotometer measures how much of it is absorbed at each wavelength, and the generator can catch a reading for specific absorption peaks. In this experiment, the absorbance spectrum in the region 400-500 nm is characteristic of a surface plasmon resonance (SPR) peak due to AgNPs.

8. Performance in Detecting Metal Ions

Detecting performance for some designated metal ions was then checked. This is done using complete linearity, sensitivity, specificity, LoD, and LoQ study. The absorbance of the silver nanoparticles at the wavelength appropriate to the surface plasmon resonance (SPR) of the AgNP. Using NP-LSPR at this wavelength, as seen in Fig. 1, a characteristic absorption peak appears in AgNPs that can change in intensity or wavelength according to the presence and concentration of metal ions one has in its sample. The selectivity of silver nanoparticles (AgNPs) was tested by detecting the change in absorbance at a particular wavelength of a solution system consisting of two metal ions--one that causes color changes and another metal. In the end, a selectivity test was conducted by taking 2.0 mL samples of AgNPs and sequentially adding them into mixed solutions containing different amounts of certain metals. The wavelength in the range of 200-800 nm is determined by using a spectrophotometer to determine the absorbance of the resultant mixture. Sensitivity and linearity tests were conducted by reacting the prepared silver nanoparticles in a vial with varying metal concentrations. A volume of 2.0 mL of the nanoparticle solution was added, followed by 1.0 mL of metal solutions at concentrations of 0.2, 0.4, 0.6, 0.8, and 1 ppm, respectively. The nanoparticle samples were first tested for their wavelength in the range of 300-600 nm. Under observation, the color turned yellow; absorbance was recorded using a UV-Vis spectrophotometer at 411 nm (Fig. 1). Linear regression analyses were performed to determine the relationship between the concentration of added metal ions and the absorbance response generated by AgNPs. This was used to calculate linearity, molar absorptivity (the slope of a linearized chart plot), the Limit of Detection (LOD), and the Limit of Quantification (LOQ).

The synthesis was successful, as shown by the characteristic plasmon resonance peak for silver nanoparticles at around 400-500 nm, marking their formation. A narrow and symmetrical peak means uniform size of particles, whereas a broader distribution noted on the chart indicates nonuniform sizing. A higher wavelength means a larger particle, redshift in the peak; a lower wavelength means a smaller particle, blueshift in the peak. These spectral features of AgNPs help to judge their ability to detect heavy metals since a shift occurs in the peak (plasmon resonance frequency) that stems from interaction with metal ions and causes changes in NP size structure.

UV-Vis spectra were then determined at wavelengths of 200-800 nm. The 0.2-1 ppm range was selected for sensing and linearity calibration, corresponding to the average concentration of metal ions in actual samples. The above concentration values are chosen so that the method has reasonable linearity and is sensitive. Also, minor changes in metal ion concentrations can be detected.

Sensitivity uses the linearity equation to calculate the molar absorptivity. LOD or LoQ values are calculated from the slope's standard deviation (σ) in the linearity plot: LoD is 3.3 σ/slope, while LoQ is 10 σ/slope.

RESULTS AND DISCUSSION

1. pH Optimization of trisodium citrate

First, the pH variation of trisodium citrate should be optimized to determine a more stable AgNP manufacturer with the best-suited reaction conditions. In this study, we varied pH from 9 to 13 by adding NaOH. No solutions are prepared at acidic pH because high concentrations of H^+ ions at those conditions will reduce the ability of different groups to reduce. However, when pH is increased, the ability of various functional groups as reducers increases, and as a lad, it will end up much more stable. This prevents agglomeration together with growth in OH^- ions [14].

As Fig. 1 shows, at pH 11, conditions bring about maximum absorption and a redshift. The wavelength acquired fits within this range from 400-500 nm of nanoparticle wavelengths [12]. The UV-Vis spectrum of the synthesized AgNPs showed peaks at different wavelengths depending on the pH of the solution. At pH 9, the peak appears at 411 nm with an absorbance of 0.099, indicating very weak nanoparticle formation. At pH 10, the peak is detected at 406 nm with an absorbance of 0.215, showing nanoparticle formation but at a lower intensity.

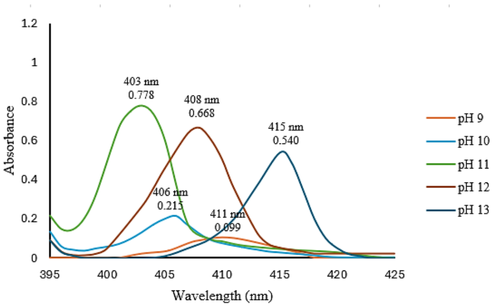


Figure 1. UV-VIS spectra of Optimization of pH Trisodium Citrate

Figure 2. Trisodium Citrate pH Optimization Results

At pH 11, the peak appears at 403 nm with an absorbance of 0.778, indicating stronger silver nanoparticle formation. The peak is at pH 11 and is the most optimal. As a result of this, the nanoparticle size also is the smallest, 32.00±1.55 nm, which is supported by corresponding research by [15] reduced $AgNO_3$ with $NaBH_4$ finding that at pH 11, there is a hypsochromic maximum wavelength shift. This suggests a balance between nucleation and growth as well as an increase in the reduction rate of the silver (Ag^+) precursor.

In contrast, pH values below 11 result in larger nanoparticle sizes of 43.00 ± 1.87 nm due to a slower reduction rate of the precursor and an imbalance between nucleation and growth. This explains that the optimum pH of the trisodium citrate solution is pH 11 due to the repulsion between the negative charges of COO- which is greater as evidenced by the maximum absorbance and maximum wavelength that is hypsochromic.

At pH 12, the peak shifts to 408 nm with an absorbance of 0.668, and at pH 13, the peak appears at 415 nm with an absorbance of 0.540, indicating changes in particle size or aggregation. Peak position shifts and absorbance varies reveal the influence of pH on the formation, size, and distribution of silver nanoparticles. The color produced at pH 11 in Fig. 2 is yellow. This signifies that silver nanoparticles are being produced. This result is backed up by the work of [16], who used trisodium citrate to synthesize AgNPs that have a yellow color.

2. Optimization of Reaction Time

A time optimization investigation was performed to find a suitable reaction time for trisodium citrate to reduce silver ions and thus produce silver nanoparticles. Fig. 3 shows that the best reaction time is three minutes because, at this moment, total absorption reaches its maximum value, and the redshift is as significant. Longer reaction times result in more particles, yielding a greater absorbance intensity. This observation is consistent with Lambert-Beer's law, which states that absorbance is directly proportional to the quantity of nanoparticles in the solution.

This study synthesis reaction time is faster than that of previous reports. The reaction time for synthesis in this study is faster than the study conducted by [17], which produced AgNPs using trisodium citrate as a reductant with a reaction time of 9 minutes. This difference is because pH optimization was not performed in their study, whereas this study produced AgNPs in a reaction time of 3 minutes under pH 11 conditions. As the pH becomes more basic, the rate of nanoparticle formation increases [18].

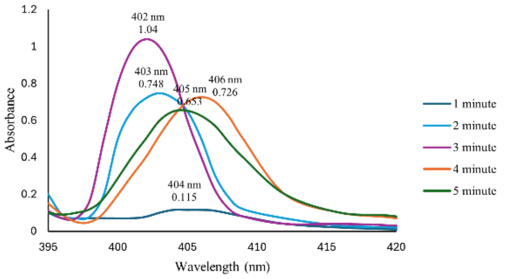


Figure 3. UV-VIS spectra of Optimization of Reaction Time

Figure 4. Reaction Time Optimization Results

With a longer reaction time, as Fig. 4 depicts, the solution becomes darker, with more silver nanoparticle content. From the appearance of a more concentrated solution, it can be seen that what is happening may gradually form into a nanoparticle, so conditions have been successfully optimized for this process.

3. Optimization of $AgNO_3$ Concentration

The experiment to optimize the concentration of $AgNO_3$ was designed to find the proper concentration of $AgNO_3$ for making silver nanoparticles.

As is seen from Fig. 5, the maximum absorbance of a one mM $AgNO_3$ solution occurs at a lower wavelength. The wavelength corresponds to the size of particles (400-500 nm), indicating that silver particles have formed. Now, if we change from 1 mM, the concentration of $AgNO_3$, to another concentration, the absorbance value will increase at almost the same maximum absorption wavelength. This is according to Lambert Beer's law, where concentration and absorbance are directly proportional.

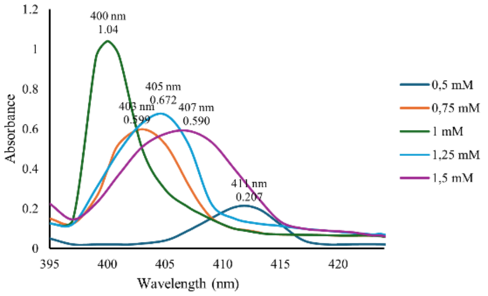


Figure 5. UV-VIS spectra of Optimization of $AgNO_3$ Concentration

Figure 6. $AgNO_3$ Concentration Optimization Results

In this context, the best concentration of $AgNO_3$, according to the study methods in this paper, can be computed as 1 mM. This finding coincides with [6] observation that trisodium citrate acted as a reductant and that as the concentration of $AgNO_3$ was increased, more particles were made. In other words, it's just a question of making the most.

The figure also increases the resulting color in an increasing concentration of $AgNO_3$. This means more reductant is oxidated and more Ag^+ electrode is reduced to Ag^0 [20], [21].

4. Optimization of Trisodium Citrate Concentration

We optimized the concentration of citrate for nanoparticles was carried out. Nanoparticle aggregation tends to intensify as the concentration of trisodium citrate rises. Citrate ions are anions from anionic species that attach to the AgNP surface. These citrates introduce a negative charge on the nanoparticle surface. These negatively charged AgNPs must seek each other out and provide electrostatic stability for the AgNP colloids against the electrolyte [21].

As shown in Fig. 7, the trisodium citrate concentration was 1%, and there are hypsochromic maximum wavelengths; hence, the formational threshold for silver nano-particles has been reached. Therefore, we have chosen 1% as the optimum concentration of trisodium citrate since when the concentration is too low; there will not be any stabilizing effect; particles grow bigger and finally combine to form large clusters again in the solution. According to research from [6], the best concentration of trisodium citrate is 1%. This results in better stability and smaller size of silver nanoparticles than any concentrations at either 0.5 % or 1.5 %.

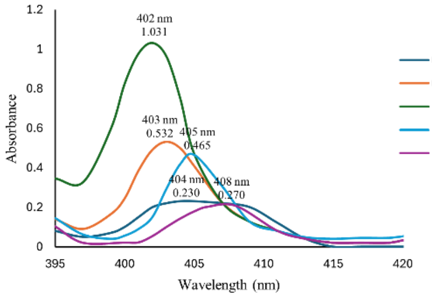


Figure 7. UV-VIS spectra of Optimization of Trisodium Citrate Concentration

Figure 8. Trisodium Citrate Concentration Optimization Results

5. Stability of Silver Nanoparticles

The AgNPs stability test was carried out to determine whether or not trisodium citrate with 1% PAA added could maintain the stability of AgNPs over thirty days. Silver nanoparticles are considered stable if they keep a similar peak shape and wavelength maximum. A wide peak may suggest that the sample has a wide particle size distribution. Meanwhile, a shift in maximum wavelength can show a broadened particle size distribution. Bathochromic (to larger wavelengths) or hypsochromic (to smaller wavelengths) shifts of maximum wavelengths can occur.

The results of the wavelength measurements from 1 hour after synthesis until day 30th are shown in Fig. 9. The maximum wavelength shift of AgNPs tends to be stable until day 30 and is 402-404 nm. The presence of a maximum wavelength shift reflects a variation in particle size [11]. However, while there is a change in maximum wavelength, it could be said that the maximum wavelength shift is relatively constant. This shows that AgNPs characterized by trisodium citrate reductant and the addition of 1% PAA stabilizer have a high level of stability.

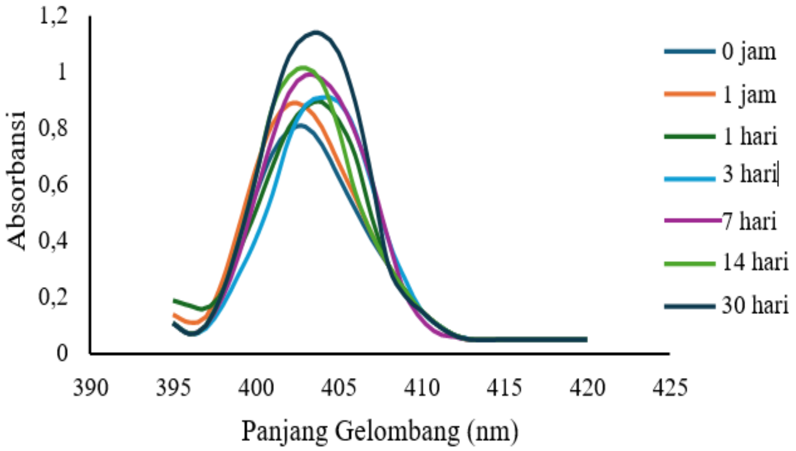


Figure 9. UV-VIS Spectra Stability of AgNPs

The 1% PAA stabilizer successfully stabilizes AgNPs: it has carboxylic groups that can bond to the silver nanoparticle surface more strongly. This makes it better for PAA to protect the nanoparticles and helps manage their size. The other carboxylate groups on an uncoordinated polymer chain are dispersed into the aqueous solution surrounding the nanoparticles to help Ag nanoparticles remain homogeneously dispersed in a very dilute solution of aqueous media. This effectively keeps the silver nanoparticles separated from one another [22].

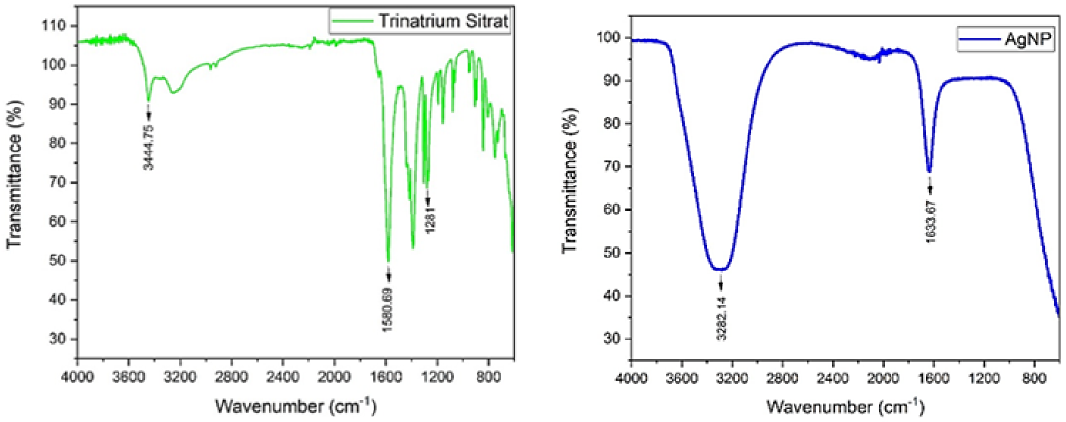
The stability of AgNPs is also seen from the increase in absorbance. Based on Fig. 9, absorbance measurement results show virtually no significant increase in absorbance from 0 hours after synthesis until the 30th day. The rising absorbance intensity is derived from the increasing amount of AgNPs produced. This is due to the reduction process of Ag^+ to Ag^0 during storage time, although the heating process has been no longer carried out. Prolonged reduction, the larger the AgNP size and the poorer stability it later has [11], [23]. However, the AgNPs produced in this research can hold their own until the 30th day. This is shown by their absorbance not increasing significantly due to possessing a 1% PAA stabilizer.

6. Characterization of Silver Nanoparticles

a. Characterization of FTIR

Absorption bands with weak or strong intensity, stretching vibrations of the OH bond, are present at wave numbers 3444.75 cm^{-1}, respectively, in the synthesis of AgNPs by $AgNO_3$ and trisodium citrate shown above.

These bands are difficult to interpret. The size of AgNPs in an aqueous solution appeared unique to a distinct spectra region. If the size was in the nanoscale range, then FTIR was used to characterize it. The FTIR analysis included the reducing agent trisodium citrate and AgNPs synthesized under optimal conditions: pH 11, 3 minutes reaction time, 1 mM $AgNO_3$ and 1% trisodium citrate, 1% PAA. It must be pointed out that nanoparticles trapped in sodium citrate being unablelized result from residual water. Water contained residual silver ions, too, which can confirm silver nanoparticles presence in AgNPs.



(a) (b)

Figure 10. FTIR Spectra of (a) Trisodium Citrate and (b) AgNPs

Table 1. Table of Trisodium Citrate

Wavenumber (cm-1)	**Functional Groups**
3444.75 cm^{-1}	Stretching OH
1580.69 cm^{-1}	Stretching carbonyl
1281 cm^{-1}	Stretching C-O

Table 2. Table of AgNPs

Wavenumber (cm-1)	**Functional Groups**
3282.14 cm^{-1}	Stretching OH
1633.67 cm^{-1}	Stretching carbonyl

According to the FTIR spectra analysis of trisodium citrate reductant in Fig. 10, molecular absorption bands at wave numbers weak intensity its 3444.75 cm^{-1} between 3000 and weakly 3600 $cm^{-1.}$ These correspond to OH group vibrational stretching vibrations. At wave number 1580.69 cm^{-1} is the stretching band of a carbonyl group. In addition, wave number 1281 cm^{-1} indicates that C=O bond stretching vibrations are present. The FTIR spectra in Fig. 10 show molecular absorption bands with strong and broad intensity at wave number 3282.14 cm^{-1}, which indicates OH group stretching vibrations. At bending waves of a trisodium citrate OH group of bands trin sodium citrate successfully reduced Ag^+ ions to Ag^0, as is seen in the formation of a new absorption site at wave number 3282.14 cm^{-1} The disappearance of the citrate band at wave number 3446 cm^{-1} and the presence of new ones between 3000 cm^{-1} indicate that silver nanoparticles are present. These wavelengths also indicate the presence of PAA in AgNPs during a surface coating procedure depending on carboxyl OH groups on poly acrylic acid. Then, at 1633.67 cm^{-1}, a faint peak emerges, indicating the presence of carbonyl groups. No peak wave number

1281 cm^{-1} shows the absence of COO^{-} groups on trisodium citrate and the creation of carboxyl groups into AgNPs derived from secondary sources. As shown in Fig. 11, this can be deduced from the reaction mechanism.

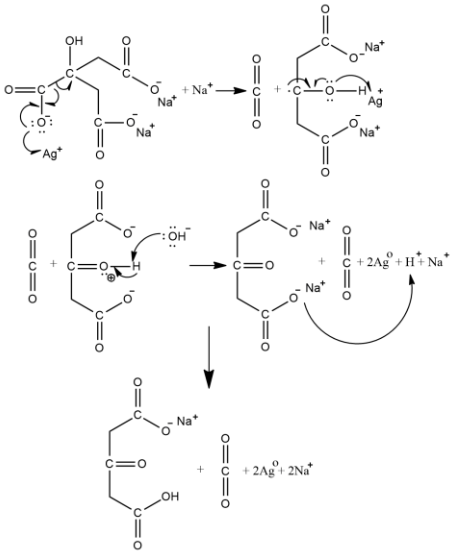


Figure 11. Reaction mechanism of AgNP Formation

Since they form hydrogen bonds and provide a protective layer that stops aggregation, OH at 3444.75 cm^{-1} (trisodium citrate) and 3282.14 cm^{-1} (AgNPs) is crucial to steric stabilization. The interaction between the carbonyl group (C=O) at 1580.69 cm^{-1} and 1633.67 cm^{-1} through coordination bonds and the particle's surface causes repression in reactivity, indeed obstructing lumping together. The carboxylate group (COO^{-}), which disappears at 1281 cm^{-1} after AgNP formation, serves as a reductant, transforming Ag^{+} ions to Ag^{0} before it finally turns into a carboxyl group (COOH) and helps disperse the nanoparticle's electrostatic stabilization. Therefore, these functional groups interact synergistically, ensuring the silver nanoparticles remain stable and well-dispersed.

These results were similar to those mentioned in the [24], in which authors synthesized nanoparticles with trisodium citrate as the reducing agent with no other stabilizers. A broad and strong band at 3000–3500 cm^{-1} found in the FTIR spectrum allows the detection of stretching vibrations of OH groups that are broader due to binding on the surface of AgNPs. Absorption at a wavenumber of 1644 cm^{-1} indicates carbonyl groups that arise from the interaction of sodium citrate molecules with the surface of silver nanoparticles, leading to the formation of Ag/trisodium citrate complex.

b. Characterization with PSA

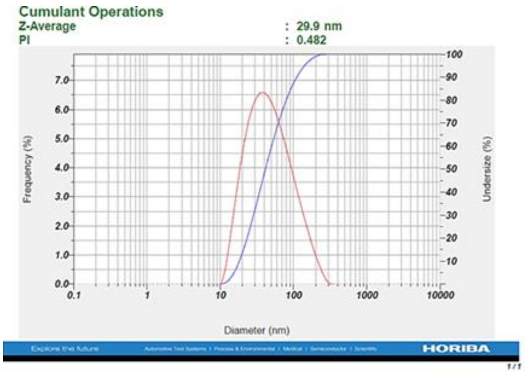


Figure 12. PSA test result

The synthesized nanoparticles were characterized by a Particle Size Analyzer (PSA) to measure the size distribution of the synthesized nanoparticles [13]. The analyses were done in optimal conditions: pH 11, 3 min of reaction, 1 mM AgNO$_3$, and 1% trisodium citrate.

As shown in Fig. 12, the synthesized AgNPs had a particle size of 29.9 nm, well below the threshold of 100 nm for classification as a nanoparticle. Such small sizes are smaller than those previously reported in the literature using trisodium citrate without a stabilizer, where the achieved particle size was 38.47 nm. A 1% PAA stabilizer used in this study helped produce smaller particle sizes. The interaction between carboxylic groups in PAA and the nanoparticle surface leads to its effective stabilization. This interaction keeps them from agglomerating and allows for better nanoparticle size control, causing a narrower size distribution and more stable colloidal solutions. The results indicate that these optimized synthesis conditions and the stabilizer can generate AgNPs with excellent size attributes categorized under the nanoparticle specification.

7. Colorimetric Analysis

Preparation of spectroscopic colorimetric for qualitative determination of heavy metal ions and determination of selectivity initiated through synthesized silver nanoparticles. Upon contact with the target analyte, metal nanoparticulate will aggregate as indicated by a shift of SPR peak to a longer wavelength or bathochromic effect [26]. Such aggregation results in a size increase of the particles accompanied by a typical color change [27], performed in sensors where AgNPs would be used to detect different analytes like heavy-metal ions.

According to the qualitative test of Fig. 13 and Table 3, the metal ion having the highest reactivity toward AgNPs is Hg^{2+}. Results of visual color change indicate that agNPs before the introduction of Hg^{2+} ions, whose initial color was brownish yellow, yielded a clear color (transparent); in addition, this conversion occurs in a very short time (less than 1 minute). The color change is caused by the aggregation of AgNPs due to the analyte [27], as AgNPs lessen instability and aggregation occurs.

Figure 13. AgNP-based Metal Ion Colorimetric Test Results

Table 3. Colorimetric Test Results

Metal Ion	Result
Hg^{2+}	Brownish-yellow → Colourless
Mg^{2+}	Brownish-yellow → Yellow
K^{+}	Brownish-yellow → Yellow solid
Zn^{2+}	Brownish-yellow → Yellow
Cd^{2+}	Brownish-yellow → Yellow
Pb^{2+}	Brownish-yellow → Yellow
Cu^{2+}	Brownish-yellow → Yellow
Al^{3+}	Brownish-yellow → Yellow
Mn^{2+}	Brownish yellow → Yellow

The other heavy metal ions (Cd^{2+}, Pb^{2+}, Mn^{2+}, Zn^{2+}, $Al3^{+}$, Cu^{2+}, Mg^{2+}, and K^{+}) were tested, and no significant color changes were observed. This is because the reduction potential (vs. standard hydrogen electrode) of Hg^{2+} (+0.852 V) is greater than that of Ag^{+} (+0.799 V). This would result in Ag^{0} turning into Ag^{+}, which leads to losing the LSPR absorption and the yellow color of AgNP colloids. Furthermore, they may also aggregate, forming agglomerates (larger size AgNPs), which move the localized surface plasmon resonance (LSPR) to longer wavelengths. Other metal ions such as Cd^{2+}, Pb^{2+}, Mn^{2+}, Zn^{2+}, Al^{3+}, Cu^{2+}, Mg^{2+}, and K+ do not show LSPR-shift or color change due to lower reduction potentials [28]. This means that the AgNPs synthesized are more selective to the Hg^{2+} ions.

Based on Fig. 13, as can be seen in Fig. 14, The AgNP reaction with Hg^{2+} is associated with high-intensity loss of absorbance, which is due to the strong coordination of covalent bonds and the formation of a more stable complex between Hg^{2+} ions and carboxylate groups on nanoparticles than analyzers containing other metal ions. Moreover, the bathochromic shift of 642 nm also indicates the total removal of nanoparticles in the AgNP solution. This decrease in absorbance is also caused when Hg^{2+} ions oxidize the AgNPs formed in the reaction such that the AgNPs can lose their electrons and re-form Ag+ ions, which have a transparent color.

8. Selectivity Test

Selectivity tests were performed with different concentration levels of Hg^{2+} ions ranging from 100-700 ppm; metal ions were mixed with AgNPs. The UV-VIS spectrophotometer test results of different concentrations of Hg2+ ions are shown in Fig. 14 and Fig. 15.

From the visual observation of Fig. 14, AgNP with 1% PAA is brownish yellow. The solution becomes clear (colorless) after adding Hg^{2+} ions with different concentrations from 100 ppm to 700 ppm. The more Hg^{2+} metal at the highest concentration added, the more decrease of AgNP absorbance, and the AgNP color becomes clearer [29]. The 1% PAA-modified silver nanoparticle solution becomes clear (colorless), indicating that it is sensitive to adding Hg^{2+} ions. This happens due to the addition of Hg^{2+} ions, which results in the formation aggregation of 1% PAA-modified silver nanoparticles. In this assay, the appearance of a certain color is due to the SPR (Surface Plasmon Resonance) phenomenon resulting from the interaction of AgNP with Hg^{2+} ions that alters the optical properties of the nanoparticles.

Figure 14. Hg^{2+} Ion Testing Results Various Concentrations

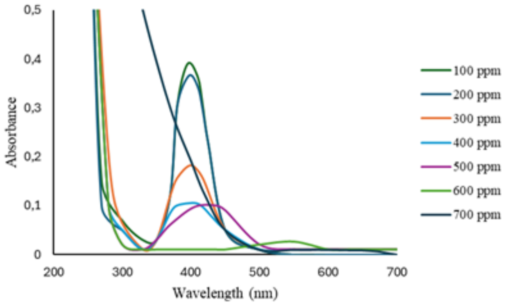


Figure 15. UV-VIS Spectrophotometer Testing Results of Hg^{2+} Ion Various Concentrations

The addition of different concentrations of Hg^{2+} ions observed the redshift. At the same time, the hypochromic effect (decrease of absorbance) of 1% PAA-modified silver nanoparticles was noted as the concentration of Hg^{2+} ions was increased, using a UV-VIS spectrophotometer for further analysis. It shows that the free silver nanoparticles in the solution agglomerate in the presence of Hg^{2+} ions, so the absorbance on the SPR nanoparticles or 400–500 nm will decrease with the amount of each added concentration of Hg^{2+} ions.

The oxidation of AgNPs into Ag^{+} ions led to the loss of SPR absorption and the change of brownish yellow color of AgNPs because the nanoparticles agglomerated thoroughly in the coordination and redox covalent bond reactions caused by the AgNPs with mercury metal ions. Consequently, the nanoparticles grow and gain a size no longer in the nanoparticle realm such that the SPR shifts to longer wavelengths (bathochromic). These results are consistent with the study by [28] as a reductant and a selective stabilizer against Hg^{2+} ions abstracted from chitosan, respectively.

9. Sensitivity and Linearity

Linearity describes the response of the analytical technique available to the concentration of the analyte sample. Fig. 16 shows the measurement data of the linearity of AgNPs toward mercury metal.

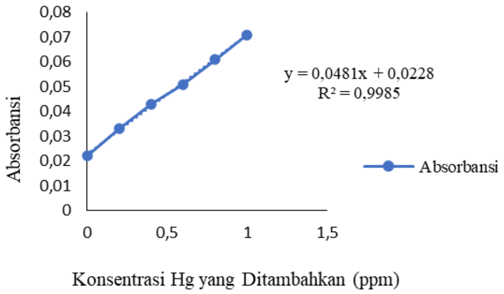


Figure 16. Linearity Curve

A calibration curve was obtained with the line equation y = 0.0481x + 0.0228 with coefficient of determination (R^2) = 0.9985 in the 0.2 ppm–1 ppm concentration range. Suppose any linear regression analysis's coefficient of determination (R^2) is at least 0.999. The calibration curve is classified as linear based on the CDER (Centre for Drug Evaluation and Research) recommendations [30].

These findings offer greater linearity than other research, including those by M. Avissa et al. [28] by a coefficient of determination (R^2) = 0.9556 with a line equation y = 0.0267x + 0.21 using trisodium citrate as a reductant and selective chitosan stabilizer against Hg^{2+} ions.

Sensitivity quantifies how the corresponding instrument response (absorbance) varies with the analyte concentration. According to Lambert Beer's law, a = ƐbC, where absorbance (A) increases with concentration. Fig. 16 demonstrates the linearity value, represented by the line equation y = 0.0481x + 0.0228. The slope value of the equation was found to be 0.0481, confirming a quantitative detection of Hg^{2+} metal ions by AgNPs with a molar absorptivity value of 9.648 x 103 L $mol^{-1}cm^{-1}$.

10. LOD and LOQ

LOD (Limit of Detection) is the minimum concentration or amount of analyte in a sample that yields an absorbance value on the instrument (without considering accuracy and precision). The Limit of Quantification (LOQ) is the lowest concentration of analyte present in the sample, at which the instrument/tool can accurately produce data [31]. The method determined the blank solution for this study; LOD and LOQ values were determined at 0.074 ppm and 0.224 ppm for the developed method, respectively. A device with lower limits of detection (LOD) and limit of quantitation (LOQ) values shows better detection capability in providing an appropriate analysis of the analytes [32].

Compared to the reported results [28], those who used trisodium citrate with chitosan as a stabilizer were LOD: 1.3 ppm and LOQ: 4.03 ppm, much higher than the nanoparticles produced in this work. The improvement was due to using the polyacrylic acid (PAA) as a stabilizer.

Compared to chitosan, PAA has polymer chains with larger carboxyl (-COOH) groups. The electrostatic interactions between target metal ions and functional groups further improve the adsorption of metal ions on the surface of nanoparticles, which greatly enhances the sensitivity. However, chitosan holds only amine ($-NH_2$) groups, active under particular conditions (usually acidic pH). Still, it can rarely interact with the same metal ions in a neutral or basic medium, thus making it less stable than the stabilizer under such conditions. This shows that PAA can be beneficial in enhancing the charging capability of AgNPs for metal ion detection when compared with chitosan.

Table 4. Comparison of Detection Limits with WHO Standards

Heavy Metal	LOD (ppm)	LOQ (ppm)	Standard WHO (ppm)
Hg^{2+}	0.074	0.224	0.002

Table 4 shows the WHO (2005) [33] drinking water standard obtained a mercury value of 0.002 ppm as the maximum allowable limit. Hence, detection at lower concentrations is imperative to preserve drinking water quality. The limit of detection (LOD) of 0.074 ppm obtained in this study shows that mercury at higher concentrations is still detectable yet cannot meet the WHO guidelines. So, this study requires more optimization by the WHO standards to detect mercury at lower concentrations. However, this technique is actively employed for detecting mercury at higher concentrations because there is a need to develop new and rapid techniques for efficiently detecting mercury. After all, it is the most toxic and dangerous to humans and living organisms.

In this work, AgNPs were used in a colloidal synthesis, and creating a portable detection system isn't easy. To overcome this problem, chitosan and starch will be incorporated into a film as a plasticizing agent to develop AgNPs and enhance their stability.

The synthesis method for AgNPs using trisodium citrate as a reducing agent was selected due to its economic feasibility compared with other synthesis methods. Sodium borohydride reduction methods are less cost-effective due to a more expensive reducing agent and longer processing duration. On the contrary, trisodium citrate serves as a cost-effective agent with a quicker reaction time and readily available components. Moreover, physical synthesis methods usually have a longer processing time, leading to higher overall cost. So we can say that this way is not just an inexpensive but also a cheap way along with balancing out cost, time, and efficiency, which is fruitful for big projects and real-world applications.

The AgNPs-based colorimetric devices developed in this study exhibit great potential for testing water quality and food safety, especially in remote regions or industries that demand rapid and straightforward detection methods. These colorimetric biosensors work by recognizing that heavy metal ions like Hg^{2+} interact with silver nanoparticles to produce a color change, allowing for on-site water testing in rural areas. Similar devices can also be used in the food industry to control heavy metal content (raw materials or final products, such as water used in food processing and the food itself).

Nonetheless, AgNP-based colorimetric devices have limitations, including interferences from complex sample matrices and difficulties retaining AgNP stability in the field, e.g., harsh temperature or light. However, these issues will be addressed with the development of films incorporating chitosan and starch, allowing the devices to remain accurate and consistent in detection over time.

CONCLUSION

After the data analysis, including the effect of trisodium citrate addition, Polyacrylic acid, storage time stability, and visual characteristics of colloidal AgNPs, samples under optimum conditions were selected for colorimetric testing and method validation. The sample optimum conditions included pH 11, a reaction time of 3 minutes, an AgNO3 concentration of 1 mM, and a trisodium citrate reductant concentration of 1%. The AgNP has a brownish yellow with a wavelength of 403 nm and a size of 29.9 nm, and it can be maintained up to day 30. The method validation shows that synthesized silver nanoparticles are selective to Hg^{2+} metal ions where it changes color from yellow to clear, the selectivity value of Hg^{2+} metal ion is 700 ppm, the molar absorbivity value is 9.648 x 103 L $mol^{-1}cm^{-1}$, linearity existing at the value with the line equation $y = 0.0481x + 0.0228$ with the $R^2 = 0.9985$, the LOD value is 0.074 ppm, and the LOQ is 0.224 ppm respectively. The PAA-modified trisodium citrate reductant nanoparticles have high selectivity, low detection limit, and high sensitivity, making them an efficient sensor product for detecting heavy metals in environmental elements. Further characterization of the AgNPs is needed using Scanning Electron Microscopy to determine a more accurate size distribution. Moreover, it is recommended that future research develop the modification of the synthesis process to produce high amounts of AgNPs with high uniformity. Separate lab experiments will follow the use of AgNP's performance in detecting Hg2+, and AgNP will also be tested in field applications using real wastewater or river samples. Lastly, testing for the AgNPs will produce accurate results because the color will change systematically.

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