Critical Parameters of Silver Nanoparticles (AgNPs) synthesized by Sodium Borohydride Reduction

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Abstract

Nanoparticle technology has rapidly developed during the past few years. The Center for Radioisotope and Radiopharmaceutical Technology (PTRR), National Nuclear Energy Agency (BATAN) developed silver nanoparticles (AgNPs) that can be applied in the medical field through Iodine-125 labeling. There are numerous methods for AgNPs synthesis, but details of important parameters in the synthesis are not available. This study aims to learn the simplest approach to AgNPs synthesis and to determine the critical parameters of stable AgNPs. The synthesis of AgNPs was performed by the reduction method. Silver nitrate was reduced using sodium borohydride and stabilized by using polyvinylpyrrolidone (PVP) and NaCl.

The critical parameters observed in this study were reducing agent, stabilizer effect and pH. Analysis of AgNPs was performed using a UV-Vis Spectrophotometer, Transmission Electron Microscopy (TEM), Particle Size Analyzer (PSA) and Zeta Potential. The stable AgNPs formation demonstrated a clear yellow solution at a pH of 8 without any sediment. The Surface Plasmon Resonance peaked at around 400 nm by UV-Vis Spectrophotometer analysis. The AgNPs size was measured using TEM which was found to be 20 nm. The analysis using PSA showed that the polydispersity index was 0.369 whereas for Zeta Potential it was -15.93 mV. The presence of reductor and stabilizer had an impact on the product stability. In the simplest approach of stable AgNPs, synthesis must be in exact composition of silver nitrate (1mL, 0.001 N), reductor $NaBH_4$ (1 mL, 0.002N), 40 mL PVP 0.3% (w/v) and 20 mL NaCl 1.5 N, without stirring and temperature setting.

Keywords: Stable, Zeta Potential, Surface Plasmon Resonance, Transmission Electron Microscopy.

Introduction

The development of nanotechnology research in the medical field has developed toward imaging[1,2], therapeutic[3] and theranostic[4]. This is supported by the availability of instruments for imaging systems and anatomical markers, merging by PET (Positron Emission Tomography) as a metabolic function detection. Currently, the generation of nanotechnology devices using PET was developed and utilized for pre-clinical trials, since it increases diagnostic accuracy.

Radionuclide-labelled Ag nanoparticles (AgNPs) have double values. The first successful synthesis of Ag nanoparticles can be utilized in various fields including the development of catalysts[5], batteries[6] and colon cancer therapy or drug conductors[7]. Nanoparticles have multivalent interactions effect between the conjugate biomolecules on the surface of the nanoparticles to biomolecules and specific receptors on the cell surface[8]. Yezhelyev et al[9] suggested that Ag nanoparticles with a size of 1-1000 nm are useful for cancer diagnosis and treatments in nano oncology. Silver Nanoparticles have unique properties such as optical, electrical, and thermal. For example, AgNPs were used as chemical sensors, conductive inks, fillers which utilize their high electrical conductivity, stability and low sintering temperatures.

In addition, AgNPs were applied in molecular diagnostics and photonic devices[10]. The application of silver nanoparticles in medicine is relatively increasing, but their distribution in tissues in vivo has not been fully investigated. It can be labelled with Iodine-125 or Iodine-131. The use of internal radiation delivered through a particular target molecule labelled with radionuclides at safe doses gives low pharmacological side effects. The utilization of nanotechnology is useful because it absorbs directly into the target. The treatment cost for cancer patients can be reduced and one does not require to travel abroad to receive good treatment. This will increase domestic revenues.

There are several methods of AgNPs synthesis including the photochemical method[11], chemical reduction with a reducing agent (citrate[12], sodium borohydride[13], glucose[14]) and radiolysis[15]. A key element in AgNPs synthesis is stable in nano size. Polymer compounds such as poly (vinyl alcohol), poly (vinylpyrrolidone), poly (ethylene glycol), poly (methacrylic acid), and polymethacrylate all serve as protective agents that are effective to stabilize the nanoparticles[16]. According to Chrastina et al[17], AgNPs demonstrated a Surface Plasmon Resonance (SPR) at a wavelength of around 390-400 nm for analysis results using Spectrophotometer UV-Vis. Surface Plasmon Resonance depends on the size, shape, dielectric properties of the particle as well as the surrounding environment.

Several methods for AgNPs synthesis have been reported, but the critical parameters to synthesis stable AgNPs are not available. We investigated the easiest approach in the synthesis of stable AgNPs, and the effects of each material as critical parameters. The synthesis method was conducted by Umi et al[18] previously. The result was evaluated using a UV-Vis Spectrophotometer, Transmission Electron Microscopy (TEM), Particle Size Analyzer (PSA) and Zeta Potential.

Material and Methods

Materials: Silver Nitrate ($AgNO_3$), Sodium Chloride (NaCl) and a pH Universal indicator were purchased from Merck. Sodium Borohydride ($NaBH_4$), Nitrite Acid (HNO_3) and Polyvinylpyrrolidone (PVP) 360.000 (wt) were purchased from Sigma-Aldrich. Demineralized water was processed at the Center for Radioisotope and Radiopharmaceutical Technology. Aluminum foil was used to seal the vials.

Instrumentation: The tools employed in this investigation included glassware, micropipette, disposable cuvette, and vials. This experiment used an analytical scale Acculab, UV-Vis Spectrophotometer Jasco32, TEM JEOL JEM 1400 at the Chemistry Department, Faculty of Mathematics and Natural Sciences, Gadjah Mada University, Particle Size Analyzer and Zeta Potential at PT. Nanotech Herbal Indonesia.

Determination of Critical Parameters in Silver Nanopartile Synthesis: Silver nanoparticles synthesis was performed using a simple method. The reductor effect was investigated by reacting 1 mL $AgNO_3$ 0.001 N with various volumes of $NaBH_4$ 0.002 N (0.25, 0.50, 0.75 and 1 mL), 40 mL PVP 0.3% (w/v) and 20 mL NaCl 1.5 N. The synthesis was conducted without stirring and temperature setting. The optimized parameters of AgNPs synthesis were reductor, stabilizer and pH effect. The polymer stabilizer effect was investigated both with and without PVP addition. The NaCl effect on the addition of NaCl 1.5 N (0, 10, 20, 30, 40 and 50 mL) and pH effect (pH value 4-10) were also studied. The pH setting used HNO_3 0.1 N, pH 3. Every trial process was characterized using the UV-Vis Spectrophotometer. This study also involved raw materials ($AgNO_3$ 0.001 N, $NaBH_4$ 0.002 N, PVP 0.3% (w/v) and NaCl 1.5 N) analysis. The results were generated using a UV-Vis Spectrophotometer.

Optimum Parameters in Silver Nanoparticles Synthesis: After an investigation of critical parameters, the optimum parameters were used for further synthesis. Silver nanoparticles characterization of the samples was performed using a UV-Vis Spectrophotometer, TEM, PSA and Zeta Potential. The stability of the optimum parameters was also investigated in-depth.

Results and Discussion

The determination of critical parameters in AgNPs synthesis was studied from the SPR peaks. Figure 1a shows the raw materials analysis using the UV-Vis Spectrophotometer. They are clear, so there are no SPR peaks. The reductor effect was studied by reacting various volumes of $NaBH_4$. Reducing agents were needed in sufficient quantities to reduce $AgNO_3$. According to figure 1b, various $NaBH_4$ volumes added results in similar SPR peak at about 399±2 nm wavelength. The similar UV-Vis spectrum shows that the AgNP size is similar. The fourth broad peak, which resulted from the SPR at a wavelength of about 400 nm, shows the formation of AgNPs. The optimum quantity in this study was 1 mL $NaBH_4$ 0.002 N.

The stabilizer effect of PVP was studied. After adding $NaBH_4$, a color change from clear white to clear yellow was noticed. This means Ag^+ is reduced to Ag^0, but after 30 minutes, it turned into a blackish brown color. Ag nanoparticles underwent aggregation because there was no further stabilizer. After 30 minutes of observation using the UV-Vis Spectrophotometer, there was no SPR in the AgNPs sample without PVP addition. The solution color also changed from clear yellow to clear white with black deposits. This represents unstable AgNPs without PVP stabilizer. The AgNPs with PVP showed SPR peak at a wavelength of about 400 nm (Figure 1c).

The broad peak indicates the formation of polydisperse nanoparticles. The absorbance and width of the surface plasmon absorption depends on the size, shape and the dielectric constant of AgNPs. The color of AgNPs with PVP addition is clear yellow without sedimentation. The experiment using PVP demonstrated more stability compared to without PVP, but in less than 24 hours, the yellow color of the solution became clear. Polyvinylpyrrolidone is an additive polymer which can inhibit coagulation through a steric stabilization mechanism[19]. Steric stabilization by polymers adsorbed on the surface of inorganic materials becomes important, attributable to its role in stabilizing colloidal dispersions. The inhabited are functional groups such as carboxyl, hydroxyl, amine and ester groups.

In this research, PVP is a polymer which has amine functional groups. The steric effect is because of the coordination between N atoms and Ag^+. Although electronegativity of atom N is smaller than atom O, the donating electron ability of atom N is larger than atom O, so it can coordinate with silver ions[16]. It is crucial to protect unstable silver nanoparticles, since those which are smaller than 50 nm will interact with the nitrogen atom from PVP and form a protective surface[20]. The same result was demonstrated by Salvador et al[21] who showed that PVP can enhance AgNPs stability.

Silver nanoparticles tend to undergo kinetic aggregation which is influenced by its environmental conditions such as pH and NaCl. NaCl is needed in a precise amount. Deviation from this amount of NaCl makes the AgNPs easy to agglomerate. Sodium chloride is an electrostatic

stabilization which is cheap and easy to stabilize nanoparticles[22]. In this experiment, the addition of 20 mL NaCl 1.5 N yielded the best stability. The ionic strength can be controlled through pH setting[23]. The optimum pH is between 6 and 10. The AgNPs at a pH of 6-10 is more stable without aggregation. Steric stabilizer, electrostatic stabilizer, and ionic strength play an important role in AgNPs synthesis and stability.

The exact parameters derived from the critical parameter determination were also used for Ag nanoparticles synthesis. Well-dispersed and stable suspension of AgNPs can be synthesized by the reduction method using sodium borohydride, without heating and stirring at room temperature. The presence of $NaBH_4$ to reduce Ag^+ to Ag^0 was marked with a clear color solution, changes to yellow, and a pH of 8, as in figure 2(a). The presence of a negative charge from BH_4^- ion can stabilize AgNPs electrostatically[24]. The samples were analysed using TEM for size and morphology, PSA for the average particle size and Zeta Potential for the zeta value.

The results of analysis using TEM are shown in figure 2(b). According to the figure, it produces a spherical shape with several sizes including 20 nm. Further analysis using spectrophotometer UV-Vis spectra is shown in figure 2(c). The formation of Ag NPs shows SPR at a specific wavelength (400 nm), depending on nanoparticle size. The results of this study show that SPR peak is at a wavelength of 398 nm. Zeta Potential (Figure 2d) shows a peak at -15.58 mV which indicates generally stable nanoparticles because of the influence of high-enough charge rejection to prevent aggregation[25].

The measurement of the zeta potential is to investigate the silver nanoparticles stability. The zeta potential results were similar to those by Baca et al.[26] Their results have a value in the range of -15 to -35 mV. Based on the analysis results by using PSA (Figure 2e), the average size was 21.2 ± 5.6 nm and polydispersity value index was 0.369. The zeta potential analysis was conducted to obtain information about the surface properties of the nanoparticles. Zeta potential is an important parameter for predicting the overall stability of the nanoparticles[27]. The value of the zeta potential measurement results shows that the nanoparticle spacing between the particles is near. The negative value shows the OH^- ion absorption. The increasing OH^- ion adsorption on silver nanoparticles increases the zeta value. The electrostatic repulsion can enhance the stability of the nanoparticles while the OH^- ions help in preventing the formation of aggregates and maintaining the size of silver nanoparticles.

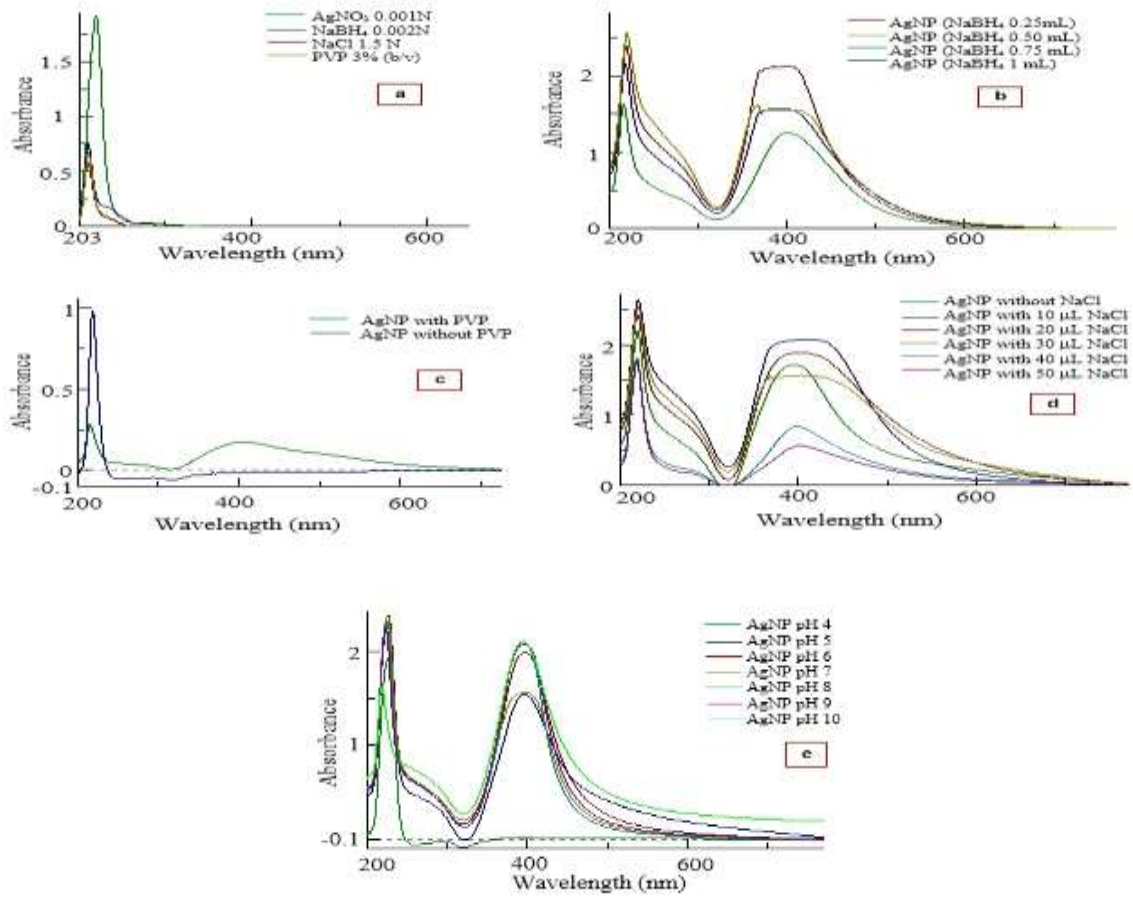

Figure 1: The Overlay UV spectra of samples of (a) raw materials of AgNPs, (b) various $NaBH_4$ 0.002 N, (c) with and without PVP, (d) various NaCl 1.5 N and (e) various pH

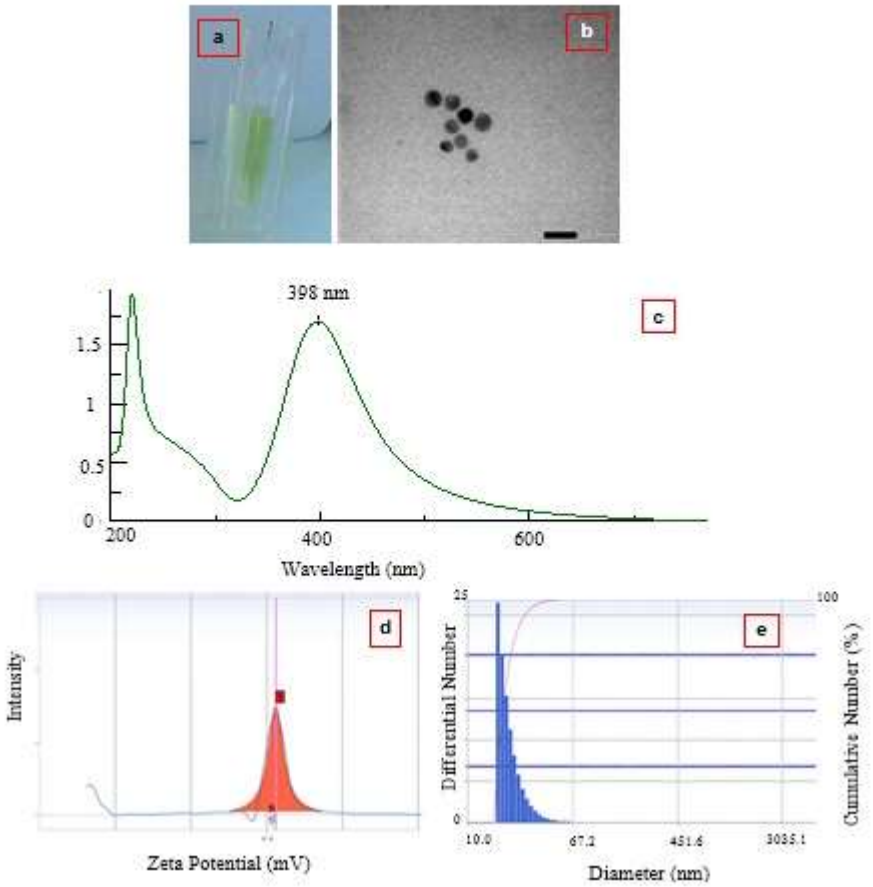

Figure 2: (a) Ag NPs Solution, (b) TEM image, (c) UV-Vis spectra, (d) zeta value and (e) size distribution

Conclusion

Stable silver nanoparticles can be simply synthesized by silver nitrate reduction with sodium borohydride at room temperature without stirring. The SPR of Ag nanoparticles is found at a wavelength of about 400 nm. We can achieve nanoparticles size below 100 nm by TEM. The results of PSA measurement are 21.2 ± 5.6 nm and zeta potential is -15.58 mV. The optimum pH is between 6 and 10. Critical parameters in Ag NPs synthesis are steric stabilizer, electrostatic stabilizer and pH.

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