Effect of Reaction Time and Stability Properties of Gold Nanoparticles Synthesized by *p*-Aminobenzoic Acid and *p*-Aminosalicylic Acid

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Abstract: *In this work, we determined the influence of reaction time in the synthesis of gold nanoparticles (AuNPs) by* p-*aminosalicylic acid and* p-*aminobenzoic acid as reducing agents. Besides working as a reducing agent, the* p-*aminobenzoic acid and* p-*aminosalicylic acid also simultaneously played a role as a capping agent/stabilizing agent. Gold ions were first mixed with the pH adjusted* p-*aminobenzoic acid and* p-*aminosalicylic acid. The mixture was then heated in boiling water at 86 °C. The formation of AuNPs was indicated by the appearance of red color and analyzed with UV/Vis spectrophotometry to evaluate their surface plasmon resonance (SPR) absorption in the wavelength range of 400–800 nm. The reducing ability of the reducing agents was affected by its structure. Gold nanoparticles that were synthesized with* p-*aminosalicylic acid were more stable, formed faster and had a smaller size than its counterpart that were synthesized with* p-*aminobenzoic acid. The stability test over a period of 5 months showed that the AuNPs were relatively stable.*

Keywords: *gold nanoparticles;* p-*aminosalicylic acid;* p-*aminobenzoic acid*

■ INTRODUCTION

Metal nanoparticles have become an incessant part of the current research in nanotechnology. They exhibit unusual physical and chemical properties which are quite different from their bulk counterparts [1]. When particles are reduced to their nano level, their physical and chemical properties (e.g., melting point, fluorescence, electrical conductivity, magnetic permeability, and chemical reactivity) can drastically change. The changes in these properties are highly influenced by their size, shape, and nature of the surrounding environment [2]. Application of nanomaterial follows its unique properties including high surface to volume ratio, high surface energy, and unique mechanical, thermal, electrical, magnetic and optical behaviors [3].

Gold nanoparticles are the most compatible nanomaterial for preparation of engineered nanoplatforms in smart sensing devices. Surface plasmon resonance property of gold nanoparticles makes them most suitable engineered nanomaterial for bioimaging, biomedical therapeutics, and biodiagnostic tools. Gold nanoparticles colloids have attracted increasing attention due to their unique properties in multi-disciplinary research fields [4].

A gold nanoparticle is generally synthesized through the reduction of the $HAuCl_4$ solution with $NaBH_4$ in high temperature [5]. However, the synthesized AuNPs tend to aggregate as soon as it is formed. The use of other reducing agents, such as citric acid, polyols, sugars, hydrazine, formaldehyde, hydrogen peroxide, and ascorbic acid still could not solve the aggregation problem of gold nanoparticles. To protect the particles from aggregation and reduce the collision possibility between particles of gold, in order to make AuNPs become stable, the researchers use stabilizers [6]. The most common capping agents used in previous studies were SDS [7], PVA [8], cysteamine [9], and surfactant [10]. The stabilizing agent was added after the reduction process to maintain the size of gold nanoparticles. The formation of AuNPs are indicated by the colloid formation with red or purple color and has strong adsorption of visible light at the wavelengths between 520–550 nm [11]. Nguyen et al. synthesized AuNPs by capping Au^{3+} ion using a CTAB

and then reducing with $NaBH_4$ [12]. $NaBH_4$ was also used as a reducing agent for gold nanoparticles. Wu et al. [13] added trisodium citrate as a stabilizing agent and used it for pesticides detection. However, the use of two different compounds was less effective.

Previous studies have been conducted by using the same chemicals as reducing agent and stabilizer. In 2004, Aslam et al. synthesized gold nanoparticles using oleylamine as both a reducing agent and stabilizing agent. The particle size of the gold nanoparticles that were synthesized with this method was 8–12 nm [14]. In 2016, Gusrizal et al. had synthesized AgNPs using *p*-hydroxy benzoic acid and *m*-hydroxybenzoic acid as both a reducing agent and capping agent [15]. The reduction process occurs by the presence of hydroxyl group (–OH) and the amino group that can reduce Au^{3+} to Au^0 and the presence of the carboxylic group (–COOH) that can facilitate electrostatic interactions with Au^{3+} ions in solution. This interaction can prevent the aggregation of Au^{3+} ions so it will not precipitate.

In previous work, we reported the optimalization condition of gold nanoparticles that were synthesized with the double function of *p*-aminobenzoic acid and *p*-aminosalicylic acid as reducing and capping agents in the formation of AuNPs. Several parameters, such as pH, the concentration of reducing agent and precursor concentration have been reported [16]. In this work, we studied the effect of reaction time in the synthesis of gold nanoparticles using *p*-aminobenzoic acid and *p*-aminosalicylic acid as a reducing agent and stabilizing agent. In addition, we reported the advanced study of the stability properties of gold nanoparticles that were formed. Effect of reaction time in the formation of gold nanoparticles was studied using UV-visible spectroscopy to monitor the appearance of surface plasmon resonance absorption. Stability properties of the gold nanoparticles were determined by UV-visible spectroscopy, transmission electron microscopy (TEM), zeta potential data and dynamic light scattering (DLS).

■ EXPERIMENTAL SECTION

Materials

The materials that were used in this research were gold(III) chloride acid solution ($HAuCl_4$ 100 ppm), *p*-aminobenzoic acid ($C_7H_7NO_2$, Merck), *p*-aminosalicylic acid ($C_7H_7NO_3$, Merck), and sodium hydroxide (NaOH, Merck). For the preparation of the mixture solution, double distilled water was used in all experiments.

Instrumentation

SPR spectra of gold nanoparticles were obtained by measurement using a UV-visible spectrophotometer (Shimadzu UV-1700 PharmaSpec instrument). Transmission electron microscope (JEOL JEM-1400) was used to determine the size and morphology of gold nanoparticles. Fourier transmission infrared spectrophotometer (Shimadzu FTIR Prestige-21) was used to identify functional groups present in the gold nanoparticles and to investigate the interaction of the AuNPs surface with the reducing agents. Zeta potential data was determined using Horiba SZ-100.

Procedure

Sample preparation

AuNPs were synthesized by reducing $HAuCl_4$ solution with *p*-aminobenzoic acid and *p*-aminosalicylic acid as reducing agents at pH 12 and 13, respectively, by adding a solution of NaOH. Ten mL of 20 mM reducing agents were put into a beaker glass and added with 10 mL of 100 ppm $HAuCl_4$ solution. The mixture was stirred vigorously and heated at temperature of 86 °C. The reaction time was varied from 0–100 min to obtain the optimum reaction time. Formation of gold nanoparticles was visually identified by observing the color change of the reaction from light yellow to pink or light red. All solutions were also monitored by UV/Vis Spectrophotometer at a wavelength of 300–800 nm. The presence of maximum absorption at the wavelength range of 520–550 nm showed that AuNPs are formed [16].

Characterization of gold nanoparticles

The UV-visible spectra of the samples were recorded in the wavelength range of 300–800 nm at room temperature. All UV-Visible measurements were performed using 1 cm optical path length quartz cuvette. To obtain the stability of gold nanoparticles, UV-visible measurements were performed periodically for a period of 5 months.

The solid sample for FTIR analysis was prepared using gold nanoparticles recovered from colloidal via centrifugation at 12000 rpm and then were dried at 60 °C in an oven. Approximately, a sample of 5 mg was mixed with KBr and condensed into pellet using a hydraulic press. This method was used for all FTIR spectra analysis.

The sample for TEM analysis was prepared by dropping the samples and depositing them in TEM carbon covered copper grids, and letting it evaporate at room temperature. The TEM image was recorded with a 120 kV acceleration voltage. The size of the particles was calculated using ImageJ software.

■ RESULTS AND DISCUSSION

Synthesis of Gold Nanoparticles

Several synthesis parameters of gold nanoparticles using *p*-aminobenzoic acid and *p*-aminosalicylic acids, such as pH condition, precursor concentration, and reducing agent concentration were reported in previous work [16]. Based on previous work, in this study, the formation of gold nanoparticles was performed by mixing $HAuCl_4$ solution with *p*-aminobenzoic acid and *p*-aminosalicylic acid as reducing agents at pH 12 and 13, respectively, by adding a solution of NaOH. When *p*-aminobenzoic acid and *p*-aminosalicylic acid reduced the gold ions, the color of the solution changed to pink or red color indicating the formation of gold nanoparticles. The change in color of the reaction medium indicated the formation of gold nanoparticles due to surface plasmon resonance phenomenon. To prove the formation of gold nanoparticles, the solutions were analyzed by UV-Vis spectrophotometer at the wavelength range of 300–800 nm. The formation of gold nanoparticles was indicated by the maximum absorbance which happened in the wavelength range of 520–550 nm [17]. The result in Fig. 1 showed that the gold nanoparticles were formed. The narrow SPR peak of the gold nanoparticles that were synthesized by *p*-aminosalicylic acid indicated that the size of the AuNPs were uniform. On the other hand, the broadening SPR peak of the gold nanoparticles that were synthesized by *p*-aminobenzoic acid indicated that the size of the AuNPs were non-uniform. The SPR peak showed only one plasmon band centered at about 520 nm, indicating that

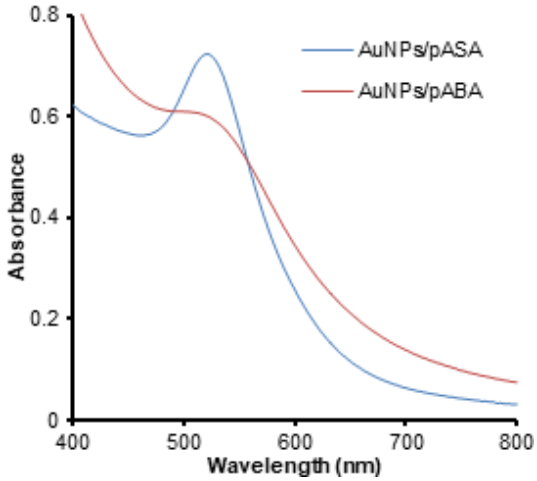

Fig 1. UV-visible spectra of gold nanoparticles made from 100 ppm $HAuCl_4$ and 20 mM reducing agent

the shape of the AuNPs were spherical with the size of 2–50 nm. Meanwhile, two SPR bands usually appear when the symmetry is reduced from spherical to cylindrical, i.e., in gold nanorods [18]. Fig. 1 showed that *p*-aminosalicylic acid as a reducing agent produced more gold nanoparticles than *p*-aminobenzoic acid on equal synthesis conditions. This data indicated that the structure of the reducing agents influenced the reducing ability.

Effect of Reaction Time on the Formation of Gold Nanoparticles

Another factor that is very important in the synthesis of gold nanoparticles using *p*-aminobenzoic acid and *p*-aminosalicylic acid is reaction time. Kumari et al. demonstrated in their study the evolution of the morphology of gold nanoparticles from nanospheres to triangular nanoprisms with an increase in time in *T. asperellum* [19]. The difference in reaction time using the same method could induce different sizes of gold nanoparticles that could be synthesized. The spherical nanoparticles can be produced in a relatively short reaction time. The reduction of Au^{3+} ions to Au^0 mediated by *p*-aminobenzoic acid and *p*-aminosalicylic acid at optimum conditions was examined spectroscopically at different reaction times and the stacked spectra are displayed in Fig. 2. All reactions showed the formation of gold nanoparticles. Although the intensity of peaks was different at different reaction times, all peaks were centered at 520–530 nm.

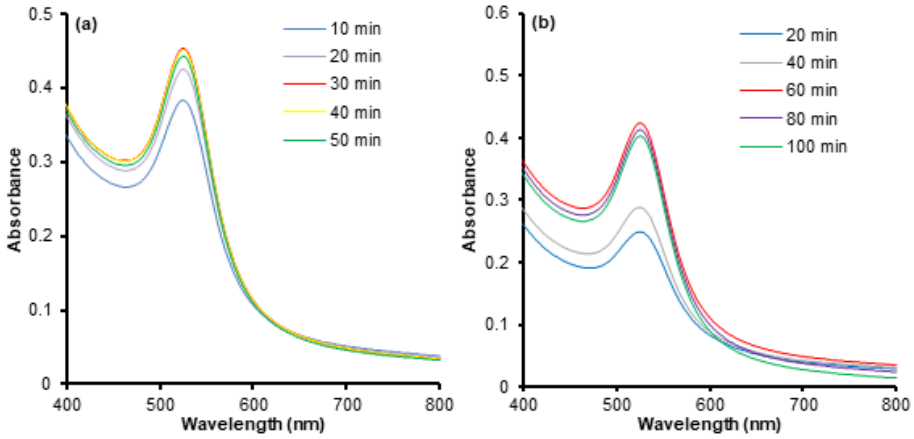

Fig 2. UV/Vis spectra of gold nanoparticles with various reaction times with (a) *p*-aminosalicylic acid at pH 12 and (b) *p*-aminobenzoic acid at pH 13

Fig. 2 shows that the formation of gold nanoparticles with *p*-aminosalicylic acid as the reducing agent was faster than with *p*-aminobenzoic acid. Using 20 mM *p*-amino salicylic acid and 100 ppm $HAuCl_4$ solution, the optimum reaction time was 30 min. Increase in absorbance during 10 min to 30 min of reaction time was attributed to the reduction of gold precursors and an increase in the population of AuNPs. The absorbance value became constant and slightly decreased after 30 min of reaction time due to the complete reduction of available gold ions. The synthesis was found to be completed within 30 min because no further rise in the intensity of the SPR band was detected. In addition, the optimum reaction time using 20 mM *p*-aminobenzoic acid and 100 ppm $HAuCl_4$ solution took 60 min. As the reaction continues, the intensity of this band increased together with a little blue shift attributed to the creation of small sized spherical nanoparticles. The synthesis was found to be completed within 60 min and no further rise in the intensity of the SPR band was detected.

After the reaction, the colloidal gold nanoparticles was stored for 7 days and its absorbance was re-measured. This is done to evaluate the influence of heating time on the stabilization performance of AuNPs that was synthesized by *p*-aminobenzoic acid and *p*-aminosalicylic acid. Based on the data in Fig. 3, it can be explained that the gold nanoparticles that were formed by *p*-amino salicylic acid at less than 30 min of heating time were not stable because its absorbance still increased after 7 days. This data showed that the formation of gold nanoparticles still continued when the reaction was stopped. The gold nanoparticles formed by *p*-aminosalicylic acid at 30 min

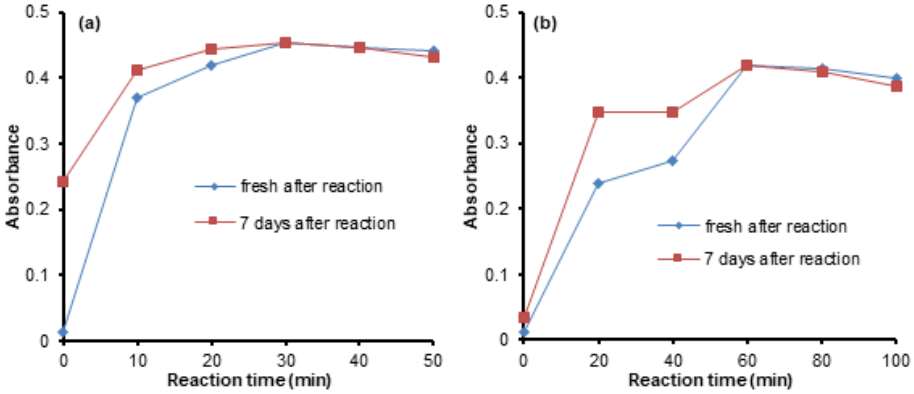

Fig 3. UV/Vis absorbance of fresh-synthesized and 7 days-stored of AuNPs with various reaction times with (a) *p*-aminosalicylic acid at pH 12 and (b) *p*-aminobenzoic acid at pH 13

reaction time was most stable, shown by the unchanged value of absorbance after 7 days. Meanwhile, the gold nanoparticles formed by *p*-aminosalicylic acid at more than 30 min reaction time was less stable because its absorbance slightly decreased after 7 days. The gold nanoparticles formed by *p*-aminobenzoic acid at 60 min reaction time was most stable shown by the unchanged value of absorbance after 7 days. After 7 days stored, the gold nanoparticles formed by *p*-aminobenzoic acid had the same pattern with the gold nanoparticles formed by *p*-aminosalicylic acid. The gold nanoparticles that were formed by *p*-aminobenzoic acid at less than 60 min reaction time was not stable because its absorbance still increased after 7 days. On the other hand, the gold nanoparticles formed by *p*-aminobenzoic acid at more than 60 min reaction time was less stable because its absorbance slightly decreased after 7 days. It is predicted that the longer the solution is heated, the molecules in the solution would still be active, even when the heating process has stopped. The active molecules will react further so the reduction process would still occur even when the heating has been stopped [20].

The best reducing and stabilizing performance of *p*-aminosalicylic was obtained at the reaction time of 30 min. This optimum reaction time was faster than using *p*-aminobenzoic acid as a reducing and stabilizing agent, which needed 60 min to reach the optimum reaction time. In *p*-aminosalicylic, the hydrogen atom at the hydroxyl group and the oxygen atom at the carboxyl group could produce intramolecular hydrogen bonding. Intramolecular hydrogen bonding in the *p*-aminosalicylic acid structure causes the reduction reaction to be more effective [21]. Therefore, the performance of *p*-aminosalicylic acid as a reducing agent and capping agent was better than *p*-aminobenzoic acid.

p-Aminobenzoic Acid and *p*-Aminosalicylic Acid as a Capping Agent

The stability test was performed to gold nanoparticles produced by the reaction of 100 ppm $HAuCl_4$ solution with 20 mM reducing agent to describe the role of *p*-aminobenzoic acid and *p*-aminosalicylic acid as a capping agent. The gold nanoparticles were stored in a capped bottle at room temperature condition for 5 months. After 5 months of observation, all gold nanoparticles that was resulted did not give significant decrease in absorbance value (Fig. 4), only 0.126 (15.47%) for *p*-aminosalicylic acid and 0.210 (29.13%) for *p*-aminobenzoic acid. This data described that all resulted gold nanoparticles were relatively stable until 5 months.

Other than the absorbance decrease, the stability of gold nanoparticles can also be studied from the maximum wavelength shift. The maximum wavelength shift happened after 5 months as far as 3 nm for *p*-aminosalicylic acid and 6.5 nm for *p*-aminobenzoic acid. The longer storage will decrease the gold nanoparticles stability because the particles are suspended by agglomeration (Fig. 5). However, after the shift, the maximum wavelength was still located around 520 nm. It means that the gold nanoparticles were relatively stable over a period of 5 months.

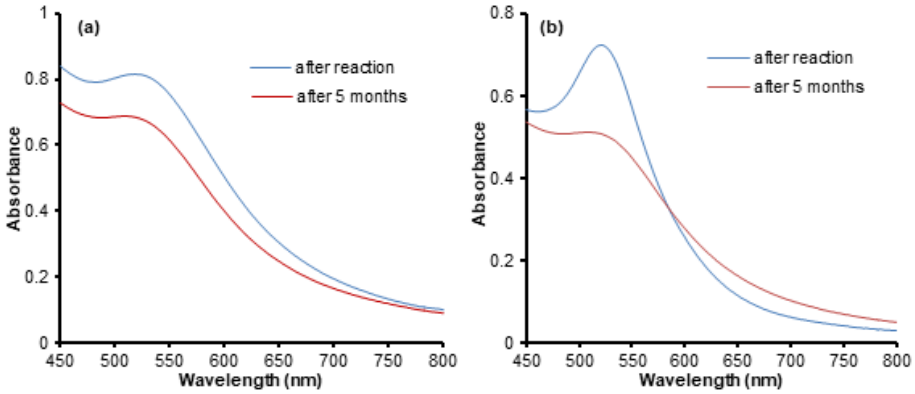

Fig 4. UV/Vis spectra of fresh and after 5 months stored of AuNPs at room temperature (a) AuNPs produced from *p*-aminosalicylic acid (b) AuNPs produced from *p*-aminobenzoic acid

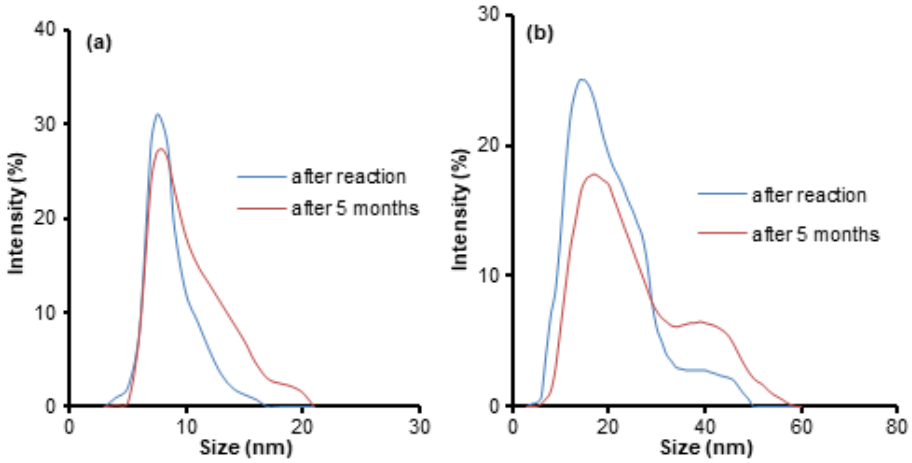

Fig 5. DLS spectra of fresh and after 5 months stored of AuNPs at room temperature (a) AuNPs produced from *p*-aminosalicylic acid (b) AuNPs produced from *p*-aminobenzoic acid

For comparison, the gold nanoparticles that were synthesized by *p*-aminosalicylic acid was more stable than the gold nanoparticles that resulted from *p*-aminobenzoic acid. This fact may indicate that the existence of the hydroxyl group in *p*-aminosalicylic acid can increase the stability of gold nanoparticles. In *p*-aminosalicylic, the hydrogen atom at the hydroxyl group and the oxygen atom at the carboxyl group could produce intramolecular hydrogen bonding. Intramolecular hydrogen bonding in the *p*-aminosalicylic acid structure can cause the reduction reaction to be more effective and increase the stability of the AuNPs.

The size and morphology of the resulted gold nanoparticles were observed using DLS data and TEM, shown in Fig. 6. The TEM results showed that both reducing agents gave the same shape but different size of gold nanoparticles. The *p*-aminosalicylic acid reducing agent (Fig. 5(a)) gave a round shape and smaller particle size than gold nanoparticles that were reduced by *p*-aminobenzoic acid. The *p*-aminobenzoic acid reducing agent (Fig. 6(b)) gave a round shape and less uniform size of gold nanoparticles. The aggregation did not happen with both *p*-aminobenzoic acid and *p*-aminosalicylic acid reducing agent, which showed that the reducing agents can also act as stabilizers.

The stability of the colloidal gold nanoparticles is often described by their zeta potential value [22]. The higher zeta potential value indicates the smaller size and higher stability of gold nanoparticles. In this work, gold nanoparticles that were synthesized by *p*-aminosalicylic acid had a higher zeta potential value than gold nanoparticles that were synthesized by *p*-aminobenzoic acid. The zeta potential value of the AuNPs that were synthesized by *p*-aminosalicylic acid and by *p*-aminobenzoic acid was -42.8 mV and -32.4 mV, respectively. Particles with zeta potentials of more than +30 mV and more negative than -30 mV are normally considered stable. The greater the zeta potential value causes higher repulsion between the particles, so aggregation could be prevented [23]. Therefore, the size of gold nanoparticles that were synthesized by *p*-aminosalicylic acid was smaller and more stable than the ones synthesized by *p*-aminobenzoic acid. The negative value in this data indicates the presence of negative charge at the surface of the gold nanoparticles [24]. This zeta potential value is in agreement with the size data from the TEM image and the stability data that was determined from the UV/Vis spectra of the gold nanoparticles.

The presence of *p*-aminosalicylic acid and *p*-aminobenzoic acid as a capping agent should be a result from the interaction of gold nanoparticles with the functional groups of the reducing agent. FTIR analysis was performed to characterize any chemical changes that occurred during the synthesis of gold nanoparticles with *p*-aminosalicylic acid and *p*-aminobenzoic acid as a

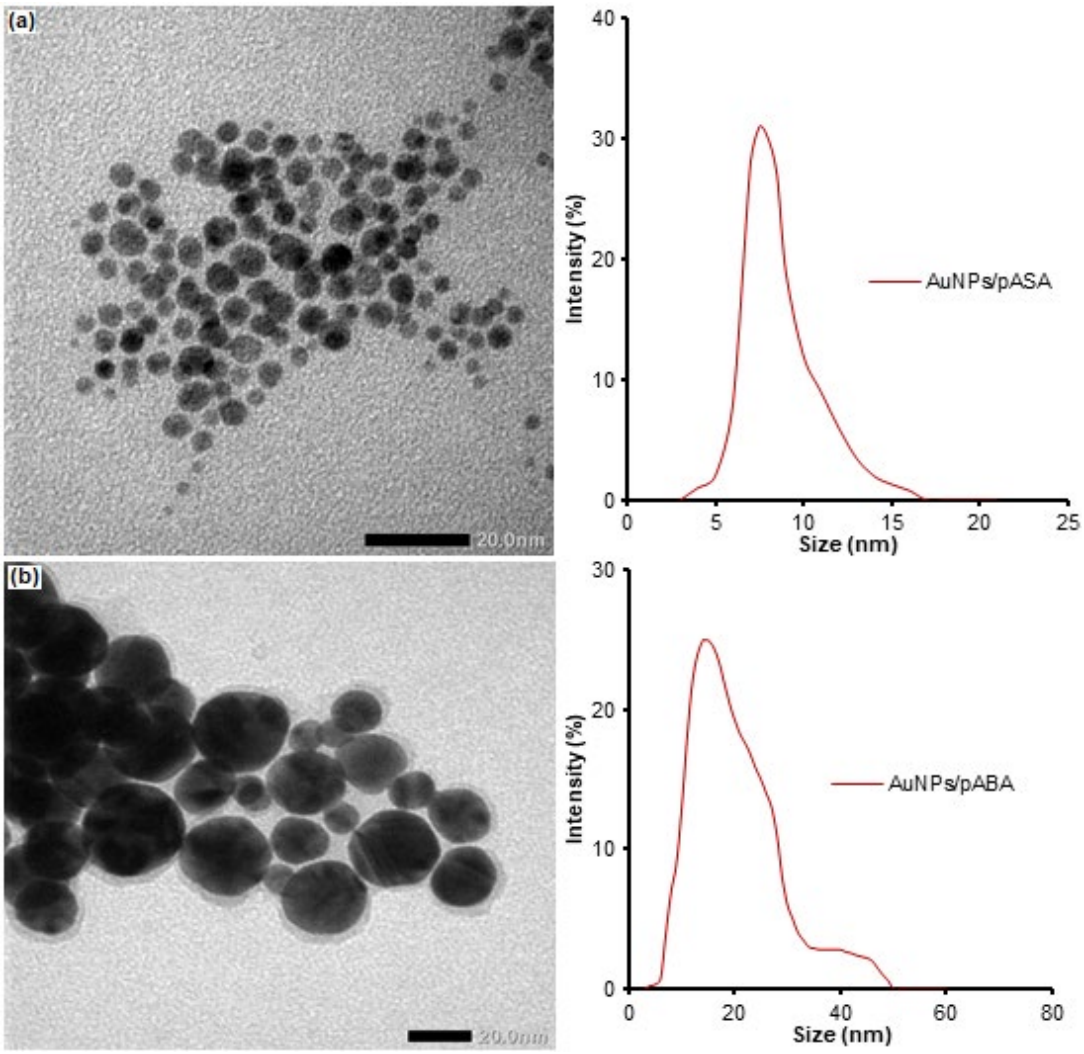

Fig 6. The TEM image and particle size distribution of gold nanoparticles synthesized by a reducing agent (a) *p*-aminosalicylic acid at pH 12 (b) *p*-aminobenzoic acid at pH 13

capping agent (Fig. 7). Because no additional capping agent was used in this experiment, it is clear that the reducing agents not only acted as a reducing agent but also as a capping agent.

FTIR spectra of p-aminobenzoic acid showed two strong absorption bands at 3476 and 3383 cm^{-1}, while *p*-aminosalicylic acid showed two strong absorption bands at 3490 and 3381 cm^{-1} which are due to the asymmetric and symmetric N–H stretching vibrations of the $–NH_2$ group. The band of valence vibrations of the C=O group in the carboxyl acid was observed at 1638 cm^{-1} for *p*-aminobenzoic acid and 1609 cm^{-1} for *p*-aminosalicylic acid. The absorption bands at 1604, 1575 and 1524 cm^{-1} correspond to the valence vibrations of C=C bonds in the benzene ring. The absorption band of the valence vibrations of the C–N bond in the amino group connected with the benzene ring was observed at 1314 cm^{-1} for *p*-aminobenzoic acid and 1317 cm^{-1} for *p*-aminosalicylic acid. It can be observed that the characteristic spectral bands of *p*-aminobenzoic acid and *p*-aminosalicylic were completely shifted or changed by the functionalization of the AuNPs. Additionally, the characteristic features of stretching modes of benzene were observed at 1597, 1512 and 1442 cm^{-1} and –COOH and $–NH_2$ stretching modes were observed at 1635 and 3425 cm^{-1}, respectively. The results indicate that *p*-aminobenzoic acid and *p*-aminosalicylic molecules were successfully assembled on the surfaces of the AuNPs.

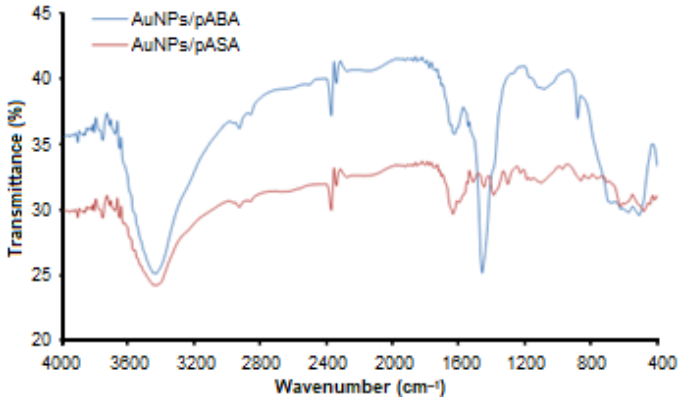

Fig 7. FTIR spectra of gold nanoparticle that synthesized by *p*-aminosalicylic acid at pH 12 (AuNPs/pASA) and *p*-aminobenzoic acid at pH 13 (AuNPs/pABA)

Furthermore, the spectral changes give clear evidence of amine groups interactions on the surfaces of the AuNPs, which was well agreed with the reported methods on the functionalization of metal NPs with two organic molecules including amino group containing ligand [25].

■ CONCLUSION

p-Aminosalicylic acid and *p*-aminobenzoic acid have been successfully used as reducing agents and also stabilizing agents in the synthesis process of gold nanoparticles. This reaction process was highly influenced by reaction time. AuNPs that were synthesized by *p*-aminosalicylic acid was produced faster than the AuNPs that were synthesized by *p*-aminobenzoic acid. The stability of the AuNPs that were synthesized by *p*-aminosalicylic acid was better than the AuNPs that were synthesized by *p*-aminobenzoic acid until 5 months of observation. In addition, the *p*-aminosalicylic acid reducing agent can produce smaller gold nanoparticles than the ones by *p*-aminobenzoic acid. Results from UV/vis spectra, TEM, Zeta potential and FTIR proved that *p*-aminosalicylic acid as a reducing agent and also a stabilizing agent had better performance than *p*-aminobenzoic acid.

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