Production of silver nanoparticles via green method using banana raja peel extract as a reducing agent

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Abstract

In this study, biosynthesis of silver nanoparticles using the extract of a local banana peel (variant name: Raja) as bio-reductor was carried out. This study aimed to determine the effect of two different ratios of Banana Peel Extract (BPE)/distilled water on the synthesis of silver nanoparticles. The two of BPE/water ratios were 1\% (v/v) and 5\% (v/v), named as Sample A and Sample B, respectively. Whereas, the concentrations of AgNO\textsubscript{3} solution as the precursor were varied as follows: 0.125; 0.1; 0.075; and 0.05 M. The synthesized colloidal silver nanoparticles were characterized using a UV-Vis spectrometer, while the BPE solution was analyzed using Fourier Transform Infra-Red (FT-IR) to study its functional groups. While, the solid silver nanoparticles was characterized using a Scanning Electron Microscopy (SEM) with an Energy-dispersive X-ray spectroscopy (EDX) analysis. The UV-Vis spectrometer results qualitatively showed that sample A produced better silver nanoparticles than that of sample B. All samples showed absorbance peaks at wavelength of 450 nm. It was found that the highest absorbance value (i.e. 1.59) occurred at sample A with a concentration of AgNO\textsubscript{3} solution 0.1 M. Additionally, FT-IR analysis result showed the presence of a hydroxyl group specifically for alcohols as phenols, which indicated the possibility of polyphenol compounds. The SEM micrograph showed that some of the silver nanoparticles were in the shape of tetrahedron or triangular like particle and spherical. The SEM image analysis results using ImageJ software showed that most of the silver nanoparticles produced had the size of 100-300 nm. Furthermore, the EDX analysis result showed a peak count at 3 keV, which confirmed the formation of silver nanoparticles.

Keywords: Biosynthesis; silver nanoparticles; banana peel extract; reduction reaction.

1. Introduction

Nanotechnology has been growing rapidly in the field of science and technology and nano-biotechnology is considered as an important sub-field of nanotechnology [1]. It is an interconnected field of both biology and nanotechnology in which it can provide a platform for environmentally friendly or "green" development and synthesis of nanoparticles with the help of biological matters such as plants and microorganisms [2,3]. Noble metal nanoparticles have attracted a great interest among researchers due to their wide application in the field of physics, materials science, biology, chemistry, and medicine [1]. One of the noble metal nanoparticles is silver nanoparticles.

Silver nanoparticles have many applications in various fields, such as nonlinear optics, good electrical conductors, catalyst in chemical reaction and chemically stable materials, biolabelling, antibacterial, medicine, medical diagnosis, therapeutics, and development of biosensors [1,4,5]. To maximize the use of silver nanoparticles, various studies have been carried out to control the size and shape of the nanoparticles. Figure 1 typically shows different routes to synthesize silver nanoparticles (i.e. AgNP). As seen in the figure, the synthesis process of silver nanoparticles can be categorized into gas, solid, and liquid-phase routes [6].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{Different routes of silver nanoparticles (AgNP) synthesis. Adopted from literature [6].}
\end{figure}

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The chemical synthesis routes for AgNPs synthesis are the most well-known. Figure 2 shows one of chemical synthesis route using reduction reaction [7]. The most widely used method to synthesize silver nanoparticles using reduction reaction is in the form of colloidal dispersion in organic solvents or water [8]. Recently, environment-friendly synthesis routes, also called “green methods”, have been proposed. One type of these routes is the reduction reaction of Ag⁺ ions into Ag⁰ using living organisms or biomaterial. This method is environmentally friendly for being capable of minimizing the use of inorganic hazardous substances to produce silver nanoparticles. Therefore, this method has emerged as an alternative novel method to the chemical synthetic and physical methods [2,3,5,8,9].

![Fig. 2. Chemical synthesis of silver nanoparticles (AgNPs). Adopted from literature [7]](image)

Additionally, the synthesis process of nanoparticles using living organisms or biomaterial is also known as biosynthesis [10]. Biosynthesis method has been developed by using various biomaterial, such as microorganisms, enzymes, and plant extracts. This method has emerged as an alternative to physical and chemical synthetic methods for producing nanoparticles [2]. Figure 3 shows the schematic diagram of procedure for “green synthesis” of silver nanoparticles using various biological matters. The use of plant extracts as reducing agents for biosynthesis of nanoparticles has been considered more advantageous compared to other biological process methods (i.e. enzymes and microorganism) [11]. It is because, this method eliminates the pre-treatment process of cultivating and maintaining the microorganism, and can be scaled-up for large production of nanoparticles [12]. Moreover, plant extracts based nanoparticles biosynthesis is preferred due to its low cost, eco-friendly, a simple method biosynthesis procedure, and more importantly safe for human therapeutic purposes [10].

There are many types of plants that can be used as agents (i.e. reducing, stabilizing, or both) in the biosynthesis of silver nanoparticles [13]. Biosynthesis of nanoparticles involves secondary metabolites of plants, such as flavonoids and terpenoid [5,14]. Several research studies investigated about biosynthesis of silver nanoparticles using plant extracts, such as sorghum bran extract [15], coffee Arabica seed extract [5], Salvia spinosa extract [16], Azadirachta indica leaf extract [14,17], Aloe vera leaf extract [18], medicinal plant of basil [19], lemon leaf extract [20] and many others.

Banana plant is a plant species belong to the Musaceae family. This plant is a native to the Indonesia-Malaysian region of South-East Asia and one of abundant natural resources in tropical and sub-tropical countries in the world [21–23]. The banana plant can be regarded as one of the most useful plants in the world. Almost all parts of this plant, such as fruit, leaf, stalk, pseudo stem, and inflorescence (flower) can be utilized [23–24]. The banana is one of the most well-known fruits and valuable commodity in the world due to its high nutritional content and important diet. Banana fruit are consumed by people all around the world. Nevertheless, after consuming the banana fruit, the banana peels are just discarded.

Banana peel contains higher antioxidants (such as polyphenols) compared to its fruit, so it can be used as a reducing agent in the synthesis of nanoparticles [5,25]. It is also considered as one of the organic wastes that can be easily found in human life. However, until now the banana peel waste has not been utilized properly to produce friendly products even though banana peel is easily decomposed. Moreover, many varieties of banana are available in Indonesia, and their peel can be utilized to synthesize silver nanoparticles. This study aimed to synthesize silver nanoparticles using a local banana peel extract (BPE) (variant name: Raja) obtained from the food industry wastes with different variables such as banana peel extract/water ratio and precursor (i.e. AgNO₃ solution) concentration. Based on the literatures review, the use of BPE (variant name: Raja) to synthesize silver nanoparticles has not been thoroughly studied yet. Therefore, it is an interesting topic of research.

![Fig. 3. Schematic diagram of procedure for “green synthesis” of silver nanoparticles using biological methods [26]](image)
2. Materials and Methods

2.1. Materials

The main raw materials used in this research were local banana peels (variant name: Banana Raja), obtained from food home industry waste in Sleman city, Yogyakarta. Silver nitrate (AgNO₃) 100%, NaOH 0.1 N, and distilled water were purchased from chemical stores. Figure 4a shows the appearance of the Banana Raja.

2.2. Preparation of Banana Leaf Extract

To prepare the banana peel extract (i.e. BPE), it began by washing the banana Raja peel wastes thoroughly. Then, about 100 gram of the banana peel was weighed (see Fig. 4b), put into a beaker glass, added with 300 ml of distilled water, and heated at 80°C for 30 minutes. The mixture was then manually filtered using a normal cloth to get the extract, then called as the Banana Peel Extract (BPE), as shown in Fig. 4c. The extract can be stored in a refrigerator for further testing or diluted in water at ratio of 1% and 5% (v/v) to be used directly as a reducing and stabilizing agent.

2.3. Synthesis of Silver Nanoparticles

Synthesis of silver nanoparticles was carried out using AgNO₃ as a precursor, which was dissolved in 100 mL of distilled water. The synthesis reaction consisted of 500 ml of aqueous BPE with a ratio of 1% (v/v) (sample A) and 5% (v/v) (sample B) and 100 ml of AgNO₃ solution at a predetermined concentration variation of 0.05; 0.075; 0.1; and 0.125 M. Both of these solutions were poured into a one-neck flask and mixed, heated at 50 °C, and stirred using a hot-magnetic stirrer. The color of the extract changed from colorless to red brownish after couple of minutes, which indicated the formation of silver nanoparticles. The formation of silver nanoparticles can be detected by visually observing the changes of color of the reaction solution [1,2]. The synthesis was stopped when the color of the colloid no longer changed, as shown in Fig. 4d. Figure 5 shows the photographs of silver nanoparticles synthesis steps for Sample A.

2.4. Dry Sample Preparation

To prepare the dry sample of silver nanoparticles used for characterization, the synthesized solution was firstly taken about 100 ml and then added with NaOH 0.1 N solution dropwise until the pH of the solution became basic (i.e. Ph = 8). Afterward, the synthesized solution was filtered using filter paper and then the filtered sample was washed using distilled water. After washing, the sample was dried in an oven at 80°C (about 5 minutes). The sample was dried until reaching a constant weight. Then, the dried samples were scraped to take the solid silver nanoparticles attached to the filter paper.

2.5. Sample Characterization

The synthesized colloidal silver nanoparticles was characterized using a UV-Vis EMC-11-UV spectrophotometer to measure the absorbance of the colloid during the synthesis of silver nanoparticles. Whereas, a Fourier Transform Infrared (FTIR) apparatus, Shimadzu 8201PC (Shimadzu, Japan) was used to identify the functional groups contained in banana peel extract (BPE). Additionally, a Scanning Electron Microscope (SEM) with an Energy-dispersive X-ray spectroscopy (EDX) analysis (SEM-EDX JEOL JSM-6510 LA) was employed to determine the morphology and size of silver nanoparticles.

3. Results and Discussion

3.1. Fourier Transform InfraRed (FT-IR) Analysis

The FT-IR test was used to identify the functional groups existing in the banana peels extract (BPE) based on the intensity of infrared light that was absorbed by the samples. The BPE as a reducing agent can be identified through the functional group of compounds. Figure 6 shows the FT-IR spectrum of the BPE, which was obtained in the wavenumber ranging from 400 to 4,000 cm⁻¹. This range of wavenumber was in accordance with other research studies [2,8].

As seen in the figure, several groups contained in BPE could be determined. The wavelength of 3402 cm⁻¹ indicated the presence of a hydroxyl group specifically for alcohols as phenols. In addition, C-H groups were spread over long waves based on certain types of bonds, e.g. Alkanes C-H at wavelength of 2924 cm⁻¹, alkyl at 1381 cm⁻¹ and 926 cm⁻¹ for alkenes. C-H substituted in benzene was located at wavelengths of 771 and 817 cm⁻¹. C-O alcohol and phenol groups had the wavelengths of 1056 cm⁻¹, C-O-H at 1435 cm⁻¹,
and aromatic C-O at 1250 cm\(^{-1}\). These findings indicated the possibility of polyphenols contained in the BPE. Associated FT-IR test results were also reported by Haytham, et al. [27].

In this work, the mechanism of the synthesis of the silver nanoparticles was mediated by Banana Peel Extract (BPE) as illustrated in Fig. 2 (see introduction section). In this case, the BPE acted as the reducing agents. The silver particles were formed via the so-called bio-reduction reaction of silver ions (Ag\(^+\)) into Ag\(^0\) (in the form of colloidal nanoparticles). Based on the literature, the main phytochemicals contained in the plant extract that are responsible for converting Ag\(^+\) into Ag\(^0\) are alkaloids, glycosides, terpenoid, and phenolic [5,25]. In this research, the bio-reduction reaction was done by the help of polyphenols contained in the BPE through the following process. Initially, the polyphenols in the BPE, mixed with AgNO\(_3\) solutions formed radicals, i.e. compounds that had free electrons. Polyphenols in radical form adsorbed Ag\(^+\) from AgNO\(_3\) solution, and the adsorbed Ag\(^+\) ion continued the reduction reaction by the polyphenols, which caused delocalization, forming Ag\(^0\). The uniqueness of the polyphenol group that has an O-H group and several aromatic rings are characterized by an aromatic C = C group.

![Fig. 6. FT-IR Spectrum from Raja Banana Skin Extract](image)

### 3.2. UV-Vis Spectrometer Analysis

The synthesized colloidal silver nanoparticles were analyzed using UV-Vis spectrometer. The analysis aimed to evaluate the formation of silver nanoparticles. Metal nanoparticles mostly contain free electrons that can generate a surface plasmon resonance (SPR) absorption band because of the vibration of those electrons in resonance with the electromagnetic wave (i.e. light wave). The appearances of absorbance peak during UV-Vis spectrometer analysis showed the SPR characteristic of the silver nanoparticles [1].

The presence of silver nanoparticles in the synthesized colloid were evaluated using UV-Vis spectrometer at the wavelengths in the range of 400-450 nm because of the absorption of light wave in this region by the colloid due to the excitation of SPR [9,15]. Figures 7a-7d show the UV-Vis spectrometer analysis results for sample A (i.e. BPE ratio of 1% (v/v)) and sample B (i.e. BPE ratio of 5% (v/v)) at various concentrations of AgNO\(_3\) solution. Table 1 presents the summary of UV peak absorbance of synthesized colloidal silver nanoparticles.

As shown in the figures, all the absorbance peaks occurred at wavelength of 450 nm, which indicated the presence of silver particles. Additionally, as noticed in the figures, sample A showed higher absorbance peaks compared to the sample B for all level concentrations of AgNO\(_3\) solution. These results qualitatively indicated that the formation of silver particles in the sample A was better in term of number and size. According to the literature, the higher the absorbance value, the more number of silver particles formed [28].

![Fig. 7. UV-Vis analysis results for samples A and B at various concentration of AgNO\(_3\) solution, i.e. a) 0.05 M; b) 0.075 M; c) 0.1 M; d) 0.125 M](image)
Additionally, Fig. 8 shows the comparison of UV-Vis absorbance peak results at wavelength of 450 nm for Sample A (i.e. BPE/water ratio of 1% (v/v)) at various concentrations of AgNO₃ solution (i.e. 0.05 M; 0.075 M; 0.1 M; 0.125 M). As noticed in the figure, all the absorbance peaks occurred at wavelength of 450 nm, which indicated the presence of silver particles. Moreover, the maximum absorbance value (i.e. 1.59) was obtained by sample A and AgNO₃ solution concentration of 0.1 M, and thus it was considered as the optimum condition for the formation of the silver nanoparticles in this current research.

Table 1. UV Spectrometer peak absorbance of synthesized colloidal silver nanoparticles

<table>
<thead>
<tr>
<th>AgNO₃ solution concentration</th>
<th>Peak Absorbance</th>
<th>Sample A</th>
<th>Sample B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>0.57</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>0.075</td>
<td>1.59</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>1.09</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>0.89</td>
<td>0.56</td>
<td></td>
</tr>
</tbody>
</table>

![Graph](image-url)

Fig. 8. Comparison of UV-Vis analysis results for samples A at various concentration of AgNO₃ solution (i.e. 0.05 M; 0.075 M; 0.1 M; 0.125 M)

Furthermore, it is worth to note that the final color of the synthesized colloid for all the synthesized samples were not the same. The color level of the synthesized colloid could be directly related to the UV-Vis absorbance peak. Table 2 shows the correlation between the color of the synthesized colloid with UV-Vis absorbance peak of sample A at various concentrations of AgNO₃ solution (i.e. 0.05 M; 0.075 M; 0.1 M; 0.125 M). As seen in the table, each concentration gave the different level of colloid’s color. When the color of the synthesized colloid became more reddish brown, the absorbance peak also became higher. As mentioned previously, the change in color of the colloid from colorless to reddish brown indicates the formation of silver nanoparticles during the reduction process. The changes of color can be attributed to the excitation of SPR in the silver nanoparticles [1,2]. Furthermore, as seen in the table, the colloid sample with most reddish brown color was obtained by sample A and AgNO₃ solution concentration of 0.1 M. In addition, this sample had the highest absorbance value (i.e. 1.59). Therefore, it can be concluded that the color level of the synthesized colloid could also qualitatively indicate the quality of silver nanoparticles formed.

Table 2. Correlation between the color of synthesized colloid with UV-Vis absorbance peak of sample A at various concentration of AgNO₃ solution (i.e. 0.05 M; 0.075 M; 0.1 M; 0.125 M)

<table>
<thead>
<tr>
<th>AgNO₃ solution concentration</th>
<th>0.05</th>
<th>0.075</th>
<th>0.1</th>
<th>0.125</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesized colloidal silver nanoparticles</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absorbance peak</td>
<td>0.8851</td>
<td>1.0953</td>
<td>1.5898</td>
<td>0.5722</td>
</tr>
</tbody>
</table>

3.3. Scanning Electron Microscopy (SEM) Analysis

Figure 9 shows SEM micrographs of sample A at concentration of AgNO₃ solution 0.1 M. The morphology of the silver nanoparticles produced was analyzed by the SEM at magnification of 5,000X. As seen in the figure, there was a difference in the shape of silver nanoparticles produced. Some of the particles were in the form of tetrahedron or triangular like particle (shown by yellow-dashed line) and spherical (shown by blue-dashed line). It has been reported that the silver nanoparticles could have several morphologies. A.L. Gonzales, et al. [29] studied about the size, shape, and color of plasmonic silver nanoparticles. They reported several morphologies that silver nanoparticles may have tetrahedron, octahedron, cube, rhombic dodecahedron, triangular prism, or spherical.

![SEM micrographs and EDX analysis](image-url)

Fig. 9. a) SEM micrographs and b) EDX analysis of silver nanoparticles produced at concentration of AgNO₃ solution 0.1 M for sample A.
The shapes of the silver nanoparticles greatly depend on the processing conditions during the synthesis of the silver nanoparticles. Additionally, X-Ray Powder Diffraction (XRD) analysis can be used to confirm the crystal structure of the silver nanoparticles. However, in this study, we did not perform an XRD analysis and analyze why the resulting silver nanoparticles are octahedron and spherical. This will be a good recommendation for the future work. Furthermore, an Energy-dispersive X-ray spectroscopy (EDX) analysis was also done together with the SEM analysis. The EDX analysis could qualitatively confirm the elements of the nanoparticles produced. Figure 9b shows the EDX analysis of sample A at concentration of AgNO₃ solution 0.1 M. As seen in the figure, there was a peak count at 3 keV, which confirmed the formation of silver nanoparticles [27].

Additionally, the size of the silver nanoparticles particles were not uniform. Some of them had a large size so that they could be categorized as micro particles. As seen in the figure, the ones with tetrahedron or triangular-like particles had larger size compared to the ones with spherical shape. Figure 10 shows the particles size distribution of the silver nano/micro particles produced at concentration of AgNO₃ solution 0.1 M of sample A. The data were extracted from the SEM micrograph in Fig. 9a. About 50 silver nano/micro particles were counted and their sizes were measured digitally with the help of Free Software called ImageJ, developed by the collaboration of National Institutes of Health and Laboratory for Optical and Computational Instrumentation (LOCI), University of Wisconsin. As seen in the figure, most of the silver nanoparticles produced had the size of 100-300 nm.

4. Conclusion

The silver micro/nano particles has been successfully produced via reduction reaction using Banana Peel Extract (BPE) with precursor of AgNO₃ solution. The morphology of the silver micro/nano particles were characterized using a Scanning Electron Microscopy (SEM). The SEM micrograph showed that some of the particles were in the shape of tetrahedron or triangular like particle and spherical. Additionally, the SEM micrograph was analyzed using a free software called ImageJ to study the particle size distribution of the silver micro/nanoparticles produced. The image analysis result showed that most of the silver nanoparticles produced had the size of 100-300 nm. Furthermore, the Energy-dispersive X-ray spectroscopy (EDX) analysis result also showed a peak count at 3 keV, which confirmed the formation of silver nanoparticles. Additionally, from the UV-Vis spectrometer analysis results, it was found that sample A showed higher absorbance peaks compared to sample B for all level concentrations of AgNO₃ solution. This result qualitatively indicated that the formation of silver particles in sample A was better in term of number and size. The maximum absorbance value (i.e. 1.59) was obtained by sample A and AgNO₃ solution concentration of 0.1 M, and thus considered as the optimum condition for the formation of the silver nanoparticles. Furthermore, Fourier Transform Infra-Red (FT-IR) analysis results indicated the possibility of polyphenols contained in Banana Peel Extract (BPE).

Acknowledgements

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