Green synthesis and characterization of silver nanoparticle using natural reducing sugar from cultivated banana peel

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Abstract. Banana is a typical fruit in Southeast Asia which has value in addition to being a food source. Agricultural and plantains processing industries generate enormous amount of waste in the form of banana peel. It is renewed that banana peel has several forms of biomass resources exist (such as starch or sugar crops, weeds, and oils plants, etc.) which can utilize for reducing agent in chemical synthesis. Therefore, this research aims to synthesize silver nanoparticles by a green synthesis using an extract derived from cultivated banana peel waste. To explore optional synthesis condition, characterization of synthesized silver nanoparticles (AgNPs) using UV-visible spectroscopy and Fourier transform infrared spectroscopy (FT-IR) were investigated. Besides, reducing sugar quantities of banana peel extract (BPE) was determined using DNS standard addition method. The results revealed that green synthesis of silver nanoparticles were accomplished using silver nitrate and BPE as the reductant. The optimized conditions for the AgNPs synthesis was a temperature of 60°C, 1.0 mM AgNO\textsubscript{3}, and a reactant ratio of 1: 2 (AgNO\textsubscript{3} to BPE). UV-Visible spectra demonstrated absorbance at 400 nm and 510 nm corresponding to AgNPs with the particle size in the range of 20-30 nm and 90-100 nm, respectively. Moreover, FTIR spectra revealed the role of functional group in BPE as a reducing agent of silver ions.

1. Introduction
Silver nanoparticles (AgNPs) have been widely used during the past few years in various applications, such as optics, antimicrobials, biomedicine, biosensors, catalysis, pharmaceuticals and photonics [1-2]. Synthesis of silver nanoparticles was extensively studied employing chemical and physical methods. In general, the chemical synthesis of AgNPs uses organic solvents and toxic reducing agents which have some disadvantages, including wasteful purifications, environmental defect, economically expensive and high-energy requirements [1-4]. Therefore, the development of green synthesis to produce AgNPs is an important aspect of nanotechnology. The plants or plants extract acting as reducing and capping agents are more advantageous over other biological processes because it is cost-effective, environmentally friendly.

Banana is a typical fruit in agricultural and plantains processing industries generate enormous amount of waste in the form of banana peel. In addition, banana peel has several forms of biomass resources exist (such as starch or sugar crops, weeds, lignin, cellulose, hemicellulose and pectins and oils plants, etc.) which can utilize as reducing agent in chemical synthesis [2-4].
The objective of this research aims to synthesize AgNPs by a green biological route, using an extract reducing sugar derived from banana peel. Influences of extraction temperatures on received content of reducing sugar from banana peel extract (BPE) were investigated by dinitrosalicylic acid (DNS) standard addition method. Besides, the volume ratio of AgNO$_3$ and BPE were varied. The quantity and size of silver nanoparticle was estimated from UV-visible spectroscopy and characterization of the BPE was performed using Fourier transform infrared (FT-IR) spectroscopy.

2. Experiment
2.1. BPE preparation
The banana (Musa paradisiaca) was collected from an agricultural farm, Chanthaburi. Silver nitrate was purchased from Sigma–Aldrich and used as received. Double distilled water was used for the experiments. BPE was used as a reducing agent for the development of silver nanoparticles synthesis. To yield high quantity of reducing sugar, the optimum extraction temperatures were varied including 60, 70 and 80°C. The peels were crushed and boiled in distilled water for 30 min at each extraction temperature, and then diluted in distilled water to receive 0.4% W/V BPE. The BPE was filtered through Whatman No. 1 filter paper twice. Dinitrosalicylic (C$_7$H$_4$N$_2$O$_7$, DNS) solution was employed to determine concentration of reducing sugar via DNS standard addition method. The resultant filtrate was stored at 4°C and used as reducing agent.

2.2. Synthesis of AgNPs using BPE
Silver nitrate was purchased from Sigma–Aldrich and used without feature purification. For all experiments, the reactants using in AgNPs synthesis were 1 mM AgNO$_3$ and 0.4% w/v BPE. To optimize the synthesis condition for producing the AgNPs, volume ratio of AgNO$_3$ and BPE were varied including 1:2, 1:1, and 2:1. The mixtures were incubated at 30 min at room temperature. All experiments were carried out in triplicates.

2.3. Characterization of synthesized AgNPs
The UV-visible spectra of AgNPs were measured as a function of wavelength using Agilent Cary 60 UV-visible spectrophotometer. FT-IR measurements were carried out using Alpha Bruker FT-IR spectrophotometer via the transmission mode (4000-400 cm$^{-1}$). The FT-IR spectra were collected from 64 scans at a resolution of 4 cm$^{-1}$.

3. Results and discussion
3.1. Effect of temperature on BPE extraction
Temperature is one of the principal factors on extraction of reducing sugar due to its effect on conversion of cellulose to simple sugars. DNS method is a rapid and simple estimation of reducing sugars in a sample. By controlling the same extraction time (30 min), different extraction temperatures showed significantly affected on the quantity of obtained reducing sugar (figure 1). The maximum reducing sugar was achieved at 60°C. When the temperature further was increased to 80°C, the obtained reducing sugar content was decreased significantly. It can be implied that reducing sugar content was decreased by increasing extraction temperature. Considering to elevated temperature and a relatively long reaction time (30 min), the reducing sugars can produce may further condensed to disaccharide sugar or decomposed to other products.

3.2. Synthesis of AgNPs
Formation of AgNPs was observed by the color change from pale yellow to dark yellow and violet color due to the reduction of silver ions (Ag$^+$) into silver nanoparticles (Ag$^0$) by reducing sugar in the BPE. Figure 2 showed UV-visible spectra of AgNPs synthesized by BPE which extracted using different temperatures. Figure 3 presented the correlation of absorbance and extraction temperature of BPE. The highest absorbance at 405 nm was observed at 60°C extraction temperature, due to an increase in the silver concentration with particle size about 10-20 nm [3-5]. By increasing the
The effect of volume ratio between AgNO₃ and BPE was investigated at 60°C extraction temperature. The correlation of UV-visible absorbance at 400 nm of AgNPs synthesising with different volume ratio of AgNO₃ : BPE was presented in figure 5. In this study, the results showed that optimal volume ratio of AgNO₃ : BPE is 1:2.

FT-IR measurements were performed to identify the major functional groups of BPE which are possible participating in the synthesis of AgNPs. The spectra of BPE before and after reaction with AgNO₃ are represented in figure 6. The representative spectra of original BPE showed several peaks indicating the complex nature of the biological material in BPE [3,7]. The appearing absorption bands at 3690, 3410, 2935, 1750, 1635, 1386, 1147, 1077, 829 and 640 cm⁻¹ were assigned to stretching vibration of O-H of alcohol or N-H of amines, C-H of alkanes, C=O of carboxylic acid or ester, N-C=O amide I bond of proteins, CH₂ of alkanes, C-O of carboxylic acid, ether, or ester, C-N of aliphatic amines or alcohol/phenol, N-H deformation of amines, and C-C bending, respectively. After reaction with AgNO₃, there was a shift in the peak positions assigned as O-H, N-H, C=O and the peak

extraction temperature from 60°C to 80°C, the absorbance at 405 nm was decreased and shift to high wavelength. It ascribed to aggregation of AgNPs in BPE to obtained larger particle size. Moreover, two absorption bands at 410 and 540 nm appeared when increasing extraction temperature to 70-80°C. Such observations were due to an increase in the particle size of AgNPs rise up to 80-90 nm [3-5]. Figure 4 showed estimate particle size of AgNPs synthesized from different BPE extraction temperatures. It can be concluded that the high extraction temperatures of BPE can produce high diameter of AgNPs.

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**Figure 1.** Effect of temperature on the extraction of BPE with different extraction temperatures.

**Figure 2.** UV-visible spectra of AgNPs synthesised with BPE that extracted from different extraction temperatures.

**Figure 3.** UV-visible absorbance of AgNPs synthesized by BPE that extracted from different temperatures.

**Figure 4.** Estimate particle size of AgNPs synthesized by BPE that extracted from different temperatures.
absorption was decreased. These results indicated that carboxyl, hydroxyl and amide groups on the surface of BPE involved in the process of nanoparticle synthesis. It can be concluded that main components in banana peels such as pectin or cellulose and the functional groups associated with these polymers may thus be participating for reducing the Ag\(^+\) to Ag\(^0\) [2-3,7].

![Figure 5. Absorbance of AgNPs synthesised with different volume ratio of AgNO\(_3\):BPE.](image1)

![Figure 6. Representative FTIR spectra of BPE (blue line) and AgNPs (red line) in BPE.](image2)

4. Conclusion

In this study, the AgNPs were prepared by reducing AgNO\(_3\) with BPE. The effect of extraction temperature to quantity of reducing sugar in BPE was investigated. From DNS standard addition results, the obtained reducing sugar content extracted from banana peel is highest with the extraction temperature at 60°C. According to UV-visible spectra at 405 nm, content of 20 nm AgNPs obtained in BPE reducing agent decreased with increasing of extraction temperatures. Moreover, the results showed the particle size of synthesized AgNPs were in the rage of 20-80 nm depending on the extraction temperature of BPE. In order to explore optimal condition for the synthesis of AgNPs, volume ratio of AgNO\(_3\):BPE were varied. UV-visible showed the optimal volume ratio of AgNO\(_3\):BPE for synthesizing 20 nm AgNPs is 1:2. The structural characterization of the samples was performed using FTIR spectroscopy indicated that carboxyl, hydroxyl and amide groups in BPE may be involved in the process of nanoparticle synthesis.

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