Melastoma malabathricum Fruit Extract-Mediated Synthesis of Silver Nanoparticles with Sensing Ability for High Concentrations of Mercury (II) Nitrate

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ABSTRACT

A strategic approach was developed to synthesize silver nanoparticles from AgNO3 using Melastoma malabathricum fruits extract. The reaction of silver ions with the organic compounds in the fruits extract proceeded smoothly at room temperature without any additional capping agent. The appearance of an absorption peak around 427 nm provided evidence for the presence of silver nanoparticles in the reaction mixture. A diluted solution of the silver nanoparticles was treated with various concentrations of mercury (II) nitrate solutions and the resulting reaction was monitored using UV-Vis spectrophotometry.

Keywords: Melastoma malabathricum, silver nanoparticles, mercury nitrate, surface plasmon resonance, sensor

INTRODUCTION

Because of their unique properties, nanomaterials have attracted widespread research, not only into their various uses but also their synthetic techniques [1]. There are some general approach for synthesis of nanoparticles such as chemical reduction techniques using sodium borohydride (NaBH4) [2] and trisodium citrate (C6H5O7Na) [3]. Besides that, other techniques are sonochemical [4], sunlight radiation [5], hydrothermal [6] and microwave irradiation [7]. In some cases, the mentioned techniques need longer time and higher temperature condition for nanoparticles synthesis. Methods for the “green” synthesis of nanoparticles, which do not use toxic chemicals or expensive materials, are currently of particular interest [8-9]. The last decade has seen the development of numerous synthetic methods using biological materials such as plants [1,8], bacteria, fungi, and yeast [1]. The use of plant extracts is expected to widen the applicability of nanomaterials in industry while meeting the demand for green synthesis methods [10-11].

Silver nanoparticles are among the most important nanomaterials, being used as antibacterial agents [8] as well as components of cosmetics, electronics, biosensors, food additives, industry, paints, and medicines [12]. Biological materials that have proven useful for synthesis of metal nanoparticles include Hibiscus rosasinensis [8] and Foeniculum vulgare [13]. Another area of current interest in the nanoparticles field is the use of nanomaterials as sensors [11, 14]. Metal nanoparticles are known to be capable of detecting various toxic metal ions. In particular, many reports have described the utility of silver...
nanoparticles as sensors for detection of heavy metal ions. For example, silver nanoparticles were recently reported to function as a colorimetric sensor of mercury ions [14-16].

In this report, we describe a method for the synthesis of silver nanoparticles using *Melastoma malabathricum* fruits extract [17]. This plant, which belongs to the Melastomataceae family, is found to live in a wide range of environments [18]. The fruits extract of *M. malabathricum* is known to contain several phenolic compounds, with a total phenol content of approximately 0.90 ± 0.19% (mg/100 mg) [19].

**EXPERIMENT**

**Chemicals and instrumentation**

Silver nitrate (Merck) was used as received. Demineralized water was used as the main solvent in most of the experiments. *M. malabathricum* fruits were obtained from naturally growing plants around the University of Bengkulu, Indonesia. Their UV-Vis absorption spectra were recorded using an Agilent Cary 60 UV-Vis spectrophotometer (in the range of 400 – 800 nm). A particle size analyzer (Beckman Coulter - DelsaNano) was used to measure the size and size distribution of the metallic silver particles produced in the reaction mixture. Their characterization was also supported by transmission electron microscopy (TEM) (Jeol JEM 1400) analysis to determine the nanoparticles morphology.

**Procedure**

The fresh *M. malabathricum* fruits were cut open and sliced into small pieces. The material (1 gram) was added to an Erlenmeyer flask containing 25 mL of hot demineralized water (70 °C). The mixture was kept at this temperature for 15 minutes. Then, the undissolved solids and the filtrate were separated through a Whatman No. 1 filter paper. The filtrate was retained for further experiments. The synthesis of silver nanoparticles was carried out following our previous result in the synthesis of gold nanoparticles with slight modification [20] by direct addition of 2 mL of silver nitrate (0.01 M) to the *M. malabathricum* fruits extract (4 mL) in a reaction tube under constant stirring for 1 hour using a magnetic stirrer at room temperature. UV-Visible spectrophotometry (400 nm – 800 nm) was used to monitor the progress of the reaction at various intervals. The UV-Visible spectra were also recorded to study the interaction between diluted solutions of the silver nanoparticles and various concentrations of mercury (II) nitrate (20; 40; 60; 80; 100 ppm) according to modified reported procedure [14].

**RESULT AND DISCUSSION**

The treatment of the *M. malabathricum* fruits using demineralized water yielded a purple extract, as shown in Fig. 1a. The *pH* value of the extract was 6, as determined using a *pH* paper universal indicator. The untreated extract was analyzed using UV-Vis spectrophotometry and the spectrum showed a clear peak around 540 nm, as shown in Fig. 1b. The fruit pulp of *M. malabathricum* is known to contain anthocyanin [18].
Fig. 2a. shows a photograph of the reaction product of silver nitrate and the *M. malabathricum* fruits extract. The color changed from the original color, as shown in Fig. 1, to that shown in Fig. 2a, indicating that a reaction had occurred in the reaction vessel. It has long been known that plant extracts are able to reduce metal ions, yielding nanoparticles [21]. The pH of the reaction mixture was 4, as determined using the universal indicator. This result indicated the formation of acid from the nitrate and hydrogen ions present in the reaction mixture. The UV-Vis absorption spectrum of the reaction mixture is shown in Fig. 2b. The presence of silver was indicated by the clear peaks at 426–427 nm, which correspond to the surface plasmon resonance (SPR) of silver nanoparticles. The progressive formation of silver nanoparticles with reaction time was monitored by measuring the continuing increase of their absorption intensity. Two secondary metabolite compounds of this plant are predicted to be able to reduce metal ions to metal nanoparticles [21].

**Figure 1.** (a) Photographs and (b) UV-Visible spectrum of *M. malabathricum* fruit extract

**Figure 2.** Photographs (a) and UV-Visible spectra showing the growth (b) of silver nanoparticles in *M. malabathricum* fruit extract
The size distribution of the silver nanoparticles, as determined using a particle size analyzer, is shown in Fig. 3. The current synthetic conditions produced metallic silver particles with an average size of 48 nm.

![Figure 3](image1.png)

**Figure 3.** Particle size distribution of silver nanoparticles in *M. malabathricum* fruit extract

The TEM image in Fig. 4 illustrates that the silver nanoparticles were spherical in shape. This result clearly suggested that some of the compounds present in the *M. malabathricum* fruits extract could be used as reducing agents for silver ions as well as capping agents and stabilizers for the formed silver nanoparticles.

![Figure 4](image2.png)

**Figure 4.** TEM pattern of silver nanoparticles in *M. malabathricum* fruit extract

The interaction between the silver nanoparticles and mercury (II) nitrate was studied using a diluted solution of the silver nanoparticles. The diluted solution was prepared by adding 3 mL demineralized water to 0.1 mL of the original solution. The addition of various concentrations of mercury (II) nitrate solution (1 mL) to the diluted silver nanoparticles induced a range of color changes, as shown in Fig. 5.
Fig. 5 shows the decreasing color intensities of the silver nanoparticles upon the addition of increasing concentrations of mercury (II) nitrate. Eventually, when 100 ppm of mercury (II) nitrate was added to the silver nanoparticles, total decolorization occurred. To supplement these visual observations, all the homogeneous mixtures were subjected to spectrophotometry analysis, and the results are shown in Fig. 6. The absorbances of the silver nanoparticles decreased as the concentration of mercury (II) nitrate solutions increased. These results show that the SPR of the silver nanoparticles at 427 nm was suppressed by the presence of mercury (II) nitrate. This clearly indicates an interaction between the two species. The color-change phenomenon suggests that the silver nanoparticles could be used as a visual sensor for high concentrations of mercury (II) nitrate.

![Figure 5](image)

**Figure 5.** Photographs of diluted silver nanoparticles in the presence of various concentrations of mercury (II) nitrate solutions

![Figure 6](image)

**Figure 6.** UV-Visible spectra of solutions of silver nanoparticles (obtained from *M. malabathricum* fruits extract) in the presence of various concentrations of mercury (II) nitrate solutions

Although there is no conclusive evidence, one possible mechanism of this interaction is the detachment of the organic compounds that capped the silver nanoparticles, leading to the aggregation of the nanoparticles. Another possibility, based on a suggestion by other researchers, is that the solution of silver nanoparticles reacted with mercury (II) to form
metallic mercury in the solution, and this reaction suppressed the surface plasmon resonance of the corresponding silver nanoparticles [14, 22].

CONCLUSION
Silver nanoparticles were successfully synthesized by a facile process using *M. malabathricum* fruit extract at room temperature. The silver nanoparticles visibly reacted with various concentrations of mercury (II) nitrate solutions. Further research into other properties of these nanoparticles is ongoing in our laboratory.

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REFERENCES
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[22] During the preparation of this manuscript, we learned that similar study on the utility of silver nanoparticles for colorimetric detection of mercury. The nanoparticles was synthesized using aqueous fruits extract of water apple (*Syzygium aqueum*), see: Firdaus, M.L., Fitriani, I., Wyantuti, S., Hartati, Y.W., Khaydarov, R., Mchalister, J.A., Obata, H., Gamo, T., *Analytical Sci.* 2017, 3, 831–837.