

Biosynthesis of Silver Nanoparticles using Jicama Extract and Its Application for Colorimetric Sensing of Mercury Ions

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Abstract

We present a report on the extracellular synthesis, characterization and application of silver nanoparticles (AgNPs) as a sensor for mercury (II) ions detection. AgNPs were synthesized using an aqueous extract of jicama root (*Pachyrhizus erosus* L.) that acts as a bioreductant. By using sunlight irradiation, synthesis of AgNPs was completed within 60 minutes. The formation of AgNPs was characterized using UV-visible spectrophotometry that gives a surface plasmon resonance (SPR) peak at 427 nm.

From the FTIR spectra, we inferred that phenolic compounds with hydroxyl functional groups in jicama root are those who are responsible for the reduction processes. The synthesized AgNPs were selective and sensitive to Hg(II) ions. The yellowish-brown color of AgNPs changed into colorless in the presence of Hg (II) ions due to reoxidation of Ag (0) nanoparticles to Ag(I) ions. These findings give a new alternative to the conventional method that usually uses a toxic chemical complexant for mercury ions colorimetric detection such as dithizone, rhodamine B, xylenol orange etc.

Keywords: Silver nanoparticles, jicama, *Pachyrhizus erosus*, mercury, colorimetry.

Introduction

Analysis of mercury in the aquatic environment is an area of concern and active research till now due to toxic properties of mercury for human health. Various food originated from the aquatic environment including drinking water, is the dominant route of human exposure to mercury. Both inorganic and especially organic mercury compounds (i.e. methylmercury chloride and dimethylmercury chloride) are toxic substances. Mercury in different speciation is introduced to the environment from a variety of sources and converted into a more toxic form by aquatic organisms and accumulated in the tissue of fish and birds^{1,2}.

The mercury content of various samples has been measured by various techniques including cold vapor atomic absorption, cold vapor atomic fluorescence spectroscopy, atomic absorption spectrometry, inductively coupled plasma

atomic emission spectrometry, electrothermal atomic absorption spectrometry, atomic fluorescence spectrometry and electrochemical detection^{3,4}. However, the total mercury content provided insufficient information to evaluate its potential toxicity, because the toxicity of mercury not only depends on its concentration but also on its chemical speciation⁵.

In analytical chemistry, colorimetry is a technique used to determine the concentration of colored compounds in a mixture by measuring its absorbance of a specific wavelength of light using colorimeter or spectrophotometer as a device. In digital imaging, a colorimeter is tristimulus device used for color calibration. Accurate color profiles ensure consistency throughout the imaging workflow from acquisition to output. Reflected color from the samples can be measured using a spectrophotometer which takes measurements in the visible region of a given color sample^{6,7}. If the custom of taking readings at 10 nm increments is followed, the visible light range of 400-700 nm will yield 31 readings. These readings are used to draw the sample's spectral curve (how much it reflects, as a function of wavelength), the most accurate data that can be provided regarding its characteristics. The readings are typically not as useful as their tristimulus values, which can be converted into chromaticity coordinates and manipulated through color space transformations.

The main advantages of colorimetry are low-cost, robust and capable of qualitative and quantitative analysis. Furthermore, the combination of colorimetry with the digital image from a camera will enhance its portability for remote and in-situ analysis⁸⁻¹². So far, the colorimetric method to analyze heavy metals from environmental samples often uses toxic organic and inorganic colorants. Here we report and discuss a green method of mercury ion colorimetric detection as an alternative procedure that can be used to substitute the conventional method. Silver nanoparticles (AgNPs) were used as a probe to detect the analyte Hg ions. In this report, we propose a green route to synthesize AgNPs using a jicama extract instead of traditional chemical reductants such as sodium borohydride (NaBH₄).

Material and Methods

Materials: Silver nanoparticles were synthesized from a small amount of silver nitrate as a precursor. Silver nitrate and other chemicals were purchased from Merck (Germany). Jicama root was purchased from a local market in Indonesia.

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All glassware was washed with detergent 5%, diluted HCl (4M) and water before use. Double-distilled deionized water was used throughout the experiments. More detail washings and other procedures were published elsewhere^{8,9}.

Instruments: UV-visible absorption spectra of the synthesized AgNPs were monitored using a BioSpectrometer (Eppendorf, Germany) in 270 – 700 nm range. FTIR measurements were obtained on a Prestige 21 (Shimadzu, Japan). The X-Ray Diffraction (XRD) patterns were obtained using Philips Analytical X-Ray diffractometer (PANalytical, Netherlands). A Canon 30D digital camera (Tokyo, Japan) was employed to record the pictures.

Biosynthesis of silver nanoparticles with an air of Jicama extract: Fresh jicama roots or fruits were washed with water to remove the dust. Twenty-five grams of fine-cut fruits was boiled with 50 ml of water at 80°C for 15 minutes. The extract was separated from the remaining small solids by filtration through Whatmann filter paper. Silver nitrate with concentration 1 mM was prepared in Erlenmeyer flasks and the appropriate volume of fruit extract was added to the mixture under sunlight radiation for 60 minutes. The volume ratio of fruit extract to silver nitrate was 2:1. An aliquot of the mixture was taken periodically to monitor the progress of AgNPs biosynthesis by using UV-vis spectrophotometer. UV-visible spectra were recorded at a resolution of 1 nm. The pH of the reaction was kept at 4.5.

Results and Discussion

The UV-visible spectra of AgNPs synthesized by using jicama extract at room temperature and with sunlight radiation are shown in fig. 1. From these time-dependent results, we concluded that the formation of AgNPs was completed within 60 minutes much faster than without sunlight irradiation (~7 days). The synthesized AgNPs have a yellowish-brown color with a peak absorbance at 420 nm which indicates a good dispersity of 35 – 50 nm size of AgNPs in water.

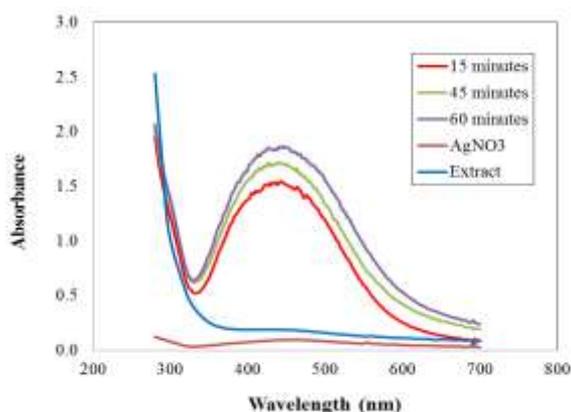


Figure 1: Time-dependent UV-visible spectra of AgNPs synthesized by using jicama extract at room temperature and with sunlight radiation. AgNPs were completed synthesized after 60 minutes with a peak absorbance observed at 420 nm.

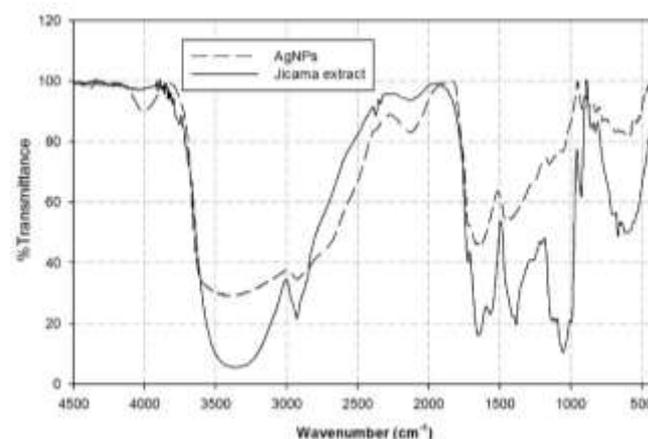


Figure 2: FTIR spectra of dried powder of jicama root extract and silver nanoparticles.

Characterizations of synthesized AgNPs was conducted by using FTIR and XRD methods. Figure 2 shows FTIR spectra of dried powder of jicama root extract and silver nanoparticles. For both samples, intense absorption bands at 3400 cm^{-1} indicate absorption bands of O-H stretching of alcohols and phenols. Absorption bands at 2900 cm^{-1} are characteristic of C-H stretching vibration. Adsorption bands at 1750, 1675, 1110 and 690 cm^{-1} may result from the C=O stretching, C=C ring stretching, C-OH bending and C-C ring stretching vibration respectively. Comparison of FTIR spectra of the jicama extract and AgNPs indicated the shift of wavenumbers coupled with the decrease and disappearance of the bands at 3400 and 1100 cm^{-1} . These results suggest that polyol and phenolic compounds are mainly responsible for the reduction of Ag(I) to form Ag(0) of AgNPs⁸.

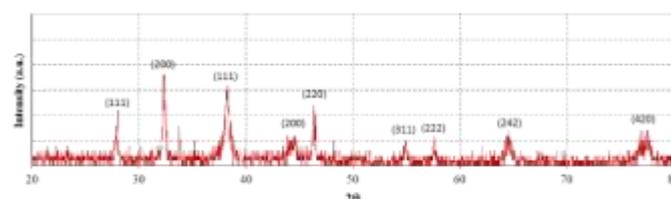


Figure 3: XRD pattern of synthesized silver nanoparticles.

The crystalline nature of AgNPs was confirmed by the analysis of the X-ray diffraction (XRD) pattern. XRD patterns shown in figure 3 indicate that the sample has well crystallized AgNPs. The diffraction pattern shows sharp and well-defined diffraction lines at several 2θ which can be assigned to (111), (200), (220) and (311) reflections of the face-centered cubic (fcc) structure of metallic silver.

Figure 4 shows the digital photograph of synthesized silver nanoparticles after addition of various metals at a concentration of 250 ppm (upper scheme), with its corresponding UV-visible spectra (lower scheme). These results show that the biosynthesized AgNPs are selective to mercury ions. The peak absorbance of AgNPs at 420 nm vanished after addition of Hg ions. It is assumed that the

mercury ions re-oxidized Ag (0) to Ag(I) that eventually removes the nanoparticle and the yellowish-brown color simultaneously. Hg (II) has a higher reduction potential than Ag(I), thus spontaneous redox reaction occurs⁹.

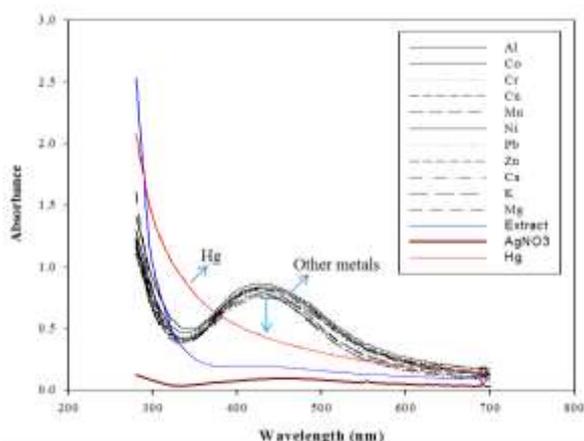
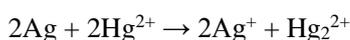


Figure 4: Digital image of synthesized silver nanoparticles after addition of various metals at a concentration of 250 ppm (upper scheme), with its corresponding UV-visible spectra (lower scheme).

Conclusion

A novel economic, rapid and green method for colorimetric detection of mercury ion using silver nanoparticles (AgNPs) was reported. The synthesis of AgNPs can be completed within 60 min at room temperature with assistance from sunlight irradiation. The water-soluble bioactive compounds from jicama root extract that act as bio-reductants to form AgNPs were determined as most likely be ascorbic acid and phenolic compounds. The presence of Hg(II) ions in the mixture will oxidize Ag(0) of AgNPs to Ag(I) ions and change the yellowish-brown color of AgNPs that has a 420 nm wavelength to colorless, linearly with the increase of Hg(II) ion concentration.

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