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<https://doi.org/10.5109/4372261>

出版情報 : Evergreen. 8 (1), pp.63-68, 2021-03. Transdisciplinary Research and Education Center
for Green Technologies, Kyushu University

バージョン :

権利関係 :

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(Received August 26, 2020; Revised December 18, 2020; accepted January 23, 2021).

Abstract: Synthesis of silver nanoparticles, as potential mercury metal detection, using Lamtoro Pods extracts has been successfully carried out by the green reduction method. The peak spectrum of plasmon resonance (SPR) at 415 nm confirmed the formation of silver nanoparticles. The Fourier transform infrared (FTIR) test obtained a characteristic functional group vibration spectrum in Lamtoro Pods. A shift of wavenumber was distinguished by comparing the FTIR spectrum between Lamtoro pods extract and silver nanoparticles. This indicated the involvement of phenol and flavonoid compounds found in the Lamtoro act as a reducing agent of Ag^+ to Ag^0 (silver nanoparticles). The X-ray diffractometer (XRD) pattern showed that the material synthesized as silver nanoparticles. The transmission electron microscopy (TEM) characterization showed that the nanoparticles have an average size 15.70 nm. The color intensity of silver nanoparticles decreased to be colorless after being contacted with mercury ion, indicating its potential for mercury metal ions detection.

Keywords: Silver Nanoparticles; Green Synthesis; Monitoring of Mercury

1. Introduction

Recently, nanomaterials have become a major interest for many researchers. Nanomaterials have been used in wide applications in various fields because of their size, shape, and composition associated with their chemical, physical and optical properties. For instance, nanomaterials have been widely applied in human life, such as medicine, chemistry, and technology^(1,2). The synthesis of silver nanoparticles is generally carried out through the thermal decomposition method, electrochemistry approach, or microwave-assisted method³⁻⁵⁾. Economically, those methods are quite expensive because they require high energy, use hazardous chemical compounds, and produce toxic waste to humans. Therefore, they are not under the Green Chemistry principle, aiming to design chemical synthesis products by minimizing toxic waste by-products. The green chemistry approach can reduce environmental degradation effects with green culture and green lifestyle in science society⁶⁾.

Currently, the biosynthesis method, which employs plant extracts as reducing and stabilizer agents, has been developed as an alternative method to synthesize silver nanoparticles without using toxic chemical compounds. This method has several advantages, such as relatively low cost, easy to process and purification, and classified as green synthesis. Various plant extracts were reported as reducing agents to synthesize silver nanoparticles such as dragon fruit peel⁷⁾, pomegranate skin⁸⁾, jicama⁹⁾, salvia Spinosa¹⁰⁾, and so forth.

Lamtoro (*Leucaena leucocephala*) is a shrub or evergreen tree. It can grow to 7-20 m tall with bipinnate leaf anatomy, 4-7 pairs of pinnae less than 4-10 cm long, each with 10 to 20 pairs of Lanceolate leaflets. Lanceolate leaves are less than 45 mm long. The flowers are white, with a round head about 2 cm in diameter. The pods are flat with a length of 10-15 cm¹¹⁾. Lamtoro is a local plant in Indonesia whose fruit is currently used as additional food. The Lamtoro pods become household waste and can be processed to have benefits.

Mercury has a density of $13,546 \text{ gm cm}^{-3}$, which is classified as a group of heavy metal. This heavy metal is one of the most toxic elements for human health when exposed directly or enters the human body through environmental pollution. The mercury Hg^{2+} metal ions are the most stable and widespread pollutants. According to the WHO *Guidelines for Drinking-water Quality*, mercury levels may not exceed 0.001 ppm in drinking water¹²⁾. Mercury and other heavy metal can release into the water environment by human activity such as the mining industry¹³⁾. Methods, such as desalination¹⁴⁾, membrane¹⁵⁾, and bioremediation technology for sustainable wastewater treatment¹⁶⁾, have been developed by researchers to obtain clean water. Other researchers also focus on wastewater monitoring, especially detecting mercury levels in the water, which is vital for daily life.

The methods commonly used to detect the presence of mercury with accuracy and precision are atomic absorption spectrometry (AAS)¹⁷⁾, electrochemical analysis¹⁸⁾, cold vapor atomic fluorescence spectrometry¹⁹⁾, and inductively coupled plasma mass spectrometry (ICP-MS)²⁰⁾. Unfortunately, these methods require expensive equipment, expensive maintenance, elaborate sample preparation, and difficult to be applied in the analytical field. This research detects mercury metal ions using a simple, facile, and inexpensive colorimetric method, utilizing the redox reaction between mercury metal ions and silver nanoparticles. This method measures the compound color concentration by determining the specific wavelength absorbance value using a spectrophotometer²¹⁾. Nowadays, silver and gold nanoparticles have been used widely in colorimetric analysis for biosensors of many substances (such as viruses, cancer cells, toxic substances, pesticides, heavy metals, inorganic and organic pollutants in water)²²⁾.

In this research, Lamtoro pods waste was utilized as a reducing agent in the synthesis of silver nanoparticles. Exploring the use of Lamtoro pods as reducing agents in synthesizing silver nanoparticles has never been reported before.

2. Materials and methods

2.1 Materials

All reagents were analytical grade and used directly without any further purification. The reagents were AgNO_3 , HgCl_2 purchased from Merck Indonesia. The 1000 ppm of Pb (II) solution was prepared from HgCl_2 salt dissolved in distilled water.

2.2 Method of qualitative analysis

The characterization of Silver Nanoparticles (AgNPs) was carried out by using UV-Vis spectrophotometer (Agilent Spectrophotometer Cary 50, America) using a quartz cuvette. The Fourier Transform Infrared (FTIR) (Agilent FTIR Cary 630, America) instrument was used

to record the functional group vibration in material, operated at 1 cm^{-1} in resolution using KBr plate, and range $650\text{--}4000 \text{ cm}^{-1}$. Transmission Electron Microscopy (TEM) (Hitachi H-7100, Japan) instrument was carried out to obtain the nanoparticles size and structure observed in 120 kV and zooming 150K-200Kx. X-ray Diffractometer (XRD) (Rigaku Smartlab, Japan) instrument was carried out to determine the nanoparticles crystal structure. The software ImageJ 1.46r was used to process the average particle size data from TEM images.

2.3 Synthesis of silver nanoparticles (AgNPs)

The Lamtoro pods extract was freshly prepared by removing impurities, cutting into small pieces, and drying at room temperature. Afterward, it was mashed using a blender to be a fine Lamtoro pods powder. 10 grams of powder boiled in 100 mL of distilled water at 80°C for 15 minutes to get the extracts. The extract was filtered through Whatman paper. The filtrate was stored in a refrigerator at 4°C for further use.

AgNO_3 1 mM solution was prepared from a 10 mM stock solution. 10 mL of AgNO_3 solution was put into the chemical glass 25 mL. It was then slowly dropped the Lamtoro pods extract with various volumes (0.1; 0.5; 1 and 2 mL). The mixture was shaken by hands and let stand for 15 minutes in sunlight radiation until the color was observed changes.

The AgNPs solution was centrifuged at 4500 rpm, then dried in the oven at 80°C to obtain silver nanoparticle powder. Then the AgNPs powder was further characterized.

2.4 Colorimetry detection of Hg(II) ions using silver nanoparticles solution

Hg (II) ion solutions of various concentrations were prepared from stock solutions. 3 mL of silver nanoparticles (AgNPs) solution was added into each variation of the Hg (II) ions concentration while shaken by hand. The change of solution color was determined using a UV-Vis spectrophotometer.

3. Results and discussion

3.1 Synthesis of silver nanoparticles (AgNPs)

Fig. 1: The color change of AgNO_3 solution after adding Lamtoro pods extract

The synthesis of silver nanoparticles was done by slowly adding Lamtoro pods extract into 1 mM silver

nitrate (AgNO_3) solution. The synthesis process was carried out under sunlight irradiation for 15 minutes to elevate the reaction rate. The nanoparticles solution was characterized by a change in the silver nitrate solution color from colorless to reddish-brown. Over time the reddish-brown color was getting thicker. It showed that the synthesis process with the bottom-up method has occurred. Over time, the reddish-brown color becomes more intense, as shown in **Fig. 1**.

Fig. 2: The absorption spectrum of silver nanoparticles (AgNPs)

Fig. 2 shows the plasmon resonance spectrum (SPR) of silver nanoparticles. It can be seen that the maximum absorbance value was elevated by increasing the Lamtoro pods extract volume. This indicates that the more extract used in this research, the more species that act as reducing agents to produce nanoparticles. The SPR peak at 415 nm confirms the formation of silver nanoparticles.

Fig. 3: Effect of time on absorbance value at 415 nm.

Fig 3 shows that silver nanoparticles formation increased over time, revealed by an increase in absorption value. Green synthesis of silver nanoparticles under optimal sunlight radiation for 15 minutes has been

performed. This result was much better than previous research conducted by Lutfi et al., synthesizing silver nanoparticles without treatment under sunlight requires an optimum time of 7 days⁹.

3.2 Characterization of silver nanoparticles (AgNPs)

FTIR analysis

Fig 4 depicts a functional group vibrational spectrum in a sample of Lamtoro pods extract, showing a typical vibration at a wavenumber of 3257.7 cm^{-1} corresponding to a hydroxyl group (O-H), which is likely to originate from alcohol and phenol. Wavenumbers at 1610.2 cm^{-1} and 1437.3 cm^{-1} are typical vibrations of the C=O asymmetry and C=O symmetry functional groups found in Lamtoro pods extracts. A peak at 1028.7 cm^{-1} is vibrational of the C-OH functional group. A shift in wavenumber was observed by comparing the FTIR spectrum of Lamtoro pods extract and silver nanoparticles. This indicates the involvement of phenol, ascorbic acid, and flavonoid compounds found in the Lamtoro pods used as a reducing agent of Ag^+ to Ag^0 (silver nanoparticles)^{23,24}.

Fig. 4: FTIR Spectrum for Lamtoro pods extract and silver nanoparticles.

XRD analysis

A diffractogram of silver nanoparticles is shown in **Fig 5**. The peaks were in accordance with JCPDS No. 01-1167. The crystal of silver nanoparticles was confirmed by X-ray diffraction (XRD) patterns. The diffractogram pattern shown in **Fig 5** revealed the silver nanoparticle crystal.

Fig. 5: Diffraction pattern of silver nanoparticle (AgNPs)

The Crystal size can be calculated using the Debye Scherrer equation. The following are Debye Scherrer's equations:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where k is Scherrer constant (0.89), β the peak width of half-maximum (FWHM), λ the X-ray wavelength (0.15405 nm), and θ is the Bragg diffraction angle. The average crystal size is 15.25 nm, which is not much different from the transmission electron microscopy measurement results.

Fig. 6: TEM image analysis of silver nanoparticles in (a) 150 Kx and (b) 200Kx

Fig. 7: The synthesis illustration of AgNPs using Lamtoro Pods extract and redox reaction of Hg (II) colorimetric

TEM analysis

The transmission electron microscopic (TEM) image from Fig. 6 shows the morphology and size of the silver nanoparticles. The size of spherical silver nanoparticles showed from the TEM image was calculated by using ImageJ software, which was found around 15.70 nm. This result was in good agreement with the XRD diffractogram data. The spherical shape has been reported in many previous studies using another reduction agent include extracts of pumpkin ²⁵⁾, Reetha and Shikakai ²⁶⁾, and Azadirachta indica leaf extract ²⁷⁾. The nanosize makes AgNPs have many benefits in many fields. Such as antimicrobial activities, catalysis, plasmonics, optoelectronics, DNA sequencing, contamination monitoring and climate change, water purification technology, energy generation, information storage, biomedical and biological applications ^{28,29)}.

The potential of silver nanoparticles to detect mercury metal ions.

Fig 7 reveals an illustration synthesis of AgNPS and its potential for Hg(II) detection. The reaction potential cell is positive, indicating a spontaneous reaction due to the negative value of Gibbs free energy. The presence of Hg(II) ions in a solution of silver nanoparticles (AgNPs) will oxidize Ag^0 to Ag^+ , which is marked by a decrease in color intensity to be more clear ⁹⁾. The absorbance value of Surface Plasmon Resonance (SPR) decreases with increasing Hg ions concentration added to the silver nanoparticle solution (AgNPs) shown in Fig 8. The calibration curve of silver nanoparticles (AgNPs) solution after incorporating Hg(II) ion with various concentrations showed the correlation coefficient (r^2) = 0.9917. It indicated that silver nanoparticles have the potential to be a colorimetric method of determining Hg

ion levels in solutions with redox reactions:

Fig. 8: UV- Visible spectra of AgNPs. a) After the addition of various concentrations of Hg(II) ions. b) Calibration curve of AgNPs after re-oxidation by various concentration of Hg(II) ions

4. Conclusion

Green synthesis of silver nanoparticles with an inexpensive and efficient potential to detect mercury metal ions has been successfully reported. The optimal treatment of this green synthesis was under the sunlight for 15 minutes. The compounds such as phenols, flavonoids, and vitamin C contained in the Lamtoro pods extract act as a green reductor to form silver nanoparticles. The silver nanoparticles have the potential to be a method of determining Hg ion levels in solutions. It confirms from the calibration curve of silver nanoparticles (AgNPs) solution after the presence of Hg(II) ion with various concentrations showed the correlation coefficient (r^2) = 0.9917.

Acknowledgment

This experiment was supported by HIBAH SMART FRIENDLY INSTITUT TEKNOLOGI SUMATERA 2019 (contract number: B/298/IT9.C1/PT.01.03/2019).

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