Green route of silver nanoparticles synthesis using watermelon *(Citrullus lanatus)* fruit extract for mercury ions detection

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**Abstract.** In this paper, we report the green synthesis of silver nanoparticles using a reductant of fruit extract of watermelon *(Citrullus lanatus)*, and its application for mercury ions detection. Silver nanoparticles were made from small amount of silver nitrate, assisted with sunlight irradiation. After 30 minutes of irradiation, the yellowish-brown silver nanoparticles were formed with peak absorbance at 420 nm wavelength. The formed silver nanoparticles were then tested to various alkaline, alkaline earth and transition metals. Most of the metals has no effect to the silver nanoparticles except for mercury ions that change the color of silver nanoparticles to colorless. Therefore, silver nanoparticles are selective to detect mercury ions in aqueous solution. Compared to the reference method, the developed colorimetry method for mercury ions detection was accurate up to 99.38%.

1. **Introduction**

Mercury is one of the top chemicals that possess major public health concern [1]. Exposure to small amounts of mercury cause serious health problems, threatening the development of the baby and children [2]. Mercury have toxic effects on the nervous, kidneys, skin, eyes, digestive and immune systems, and on lungs. Poisoning can result from mercury vapor inhalation, ingestion, injection, and absorption through the skin [3]. Mercury occurs naturally in air, water and soil. It is released into the environment from volcanic activity, weathering of rocks and as a result of human activity. Human activity is the main cause of mercury releases, particularly coal-fired power stations, industrial processes, waste incinerators and as a result of mining for mercury, gold and other metals. Mercury has 3 forms, namely elemental mercury, inorganic salts, and organic compounds [4]. The deadliest form of mercury is organic compounds of methylmercury. People are exposed to methylmercury when they eat fish and shellfish contaminated by mercury compounds. Mercury can be transformed by bacteria into methylmercury, in the environment. Methylmercury then bioaccumulates and biomagnifies. Large predatory fish will have higher concentration of mercury as a result of eating smaller fish that have acquired mercury through ingestion of plankton [5].

The growth of science and technology has been giving opportunities for scientists to synthesize nanomaterials which have many advantages compared to the properties of its corresponding bulk materials. The unique properties of nanomaterials are mostly due to its higher surface area compared to those of bulk materials. One of example, silver nanoparticles (AgNPs) have a localized surface plasmon
resonance that make it colorful and can be used for many purposes [6]. In analytical chemistry, the colorful AgNPs can be utilized as a probe for mercury ions detection based on colorimetry [7–9]. These properties have improved the way of analytical chemists to do a more environmentally benign procedure in detecting analytes of interest by using silver nanoparticles. In addition, the use of sunlight as an energy source and biomaterials (i.e. fruit extract) as reductant will further reduce the need of electric energy and chemicals reagent. In this research, we utilize watermelon fruit extract as bio reductant with the assistance of sunlight irradiation to synthesize silver nanoparticles. The prepared AgNPs were then used as a probe for toxic mercury quantification.

2. Methods

2.1. Materials and instruments
Precursor of nanoparticles, silver nitrate, and other chemicals were obtained from Merck (Germany). Watermelon was obtained from local market in Bengkulu. All glassware was washed to remove organic contaminants with detergent (5%), and then rinsed with water. Diluted HCl (4M) was used to remove inorganic contaminants. Finally, deionized water was used for the final step. Double-distilled deionized water was used throughout the experiments. A more detail washing procedure were published elsewhere [10]. Absorption spectra of AgNPs formation were monitored UV–visible BioSpectrometer (Eppendorf, Germany) in 270–700 nm wavelength. A Canon 30D digital camera (Tokyo, Japan) was used to record the digital images.

2.2. Green synthesis of silver nanoparticles
Fresh watermelon was cleaned and washed with water to remove dust. Fifty grams of fine-cut watermelon were boiled with 50 mL of water at 80°C for 15 min. After the mixture was cooled at room temperature, the extract was then separated from the remaining small solids by filtration through Whatman filter paper. The fresh extract was prepared daily to obtain consistent and accurate results.

A small amount of aqueous solution of silver nitrate (1 mM) was put into Erlenmeyer flask and the appropriate volume of watermelon extract was added to reduce Ag(I) ions to colloidal metallic Ag(0) nanoparticles under natural sunlight irradiation. Additionally, the mixture of silver nitrate and watermelon extract as control was kept without sunlight irradiation, at room temperature.

Green synthesis of silver nanoparticles was optimized by testing different ratios of watermelon extracts and silver nitrate solution. The ratios of fruit extract to silver nitrate were 1:5, 1:1, 2:1, and 5:1. An aliquot of the solution was sampled at given time to monitor the formation of silver nanoparticles by UV-Vis spectrophotometer. The pH of the reaction was kept at 4.5 ± 0.2.

2.3. Colorimetric quantification of mercury ions
For colorimetric quantification of mercury ions in the samples, an aliquot (i.e. 5 mL) of freshly prepared silver nanoparticles was transferred to transparent glass vials, and then a known concentration of mercury ions and other metal ions (Al, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb and Zn) were mixed into the vials. The spectra of absorption were recorded using UV-Vis spectrophotometer and digital image was recorded with a camera. For real water analysis, tap and lake water samples were collected in the nearby area of UNIB campus and filtered prior to use. All experiments were conducted three times as replicates.

3. Results and discussion
Sunlight irradiation was used as an alternative energy to the conventional ones, to fasten the silver nanoparticles formation. Figure 1 shows that the assistance of sunlight irradiation improved the time of synthesis of AgNPs compared to the control without sunlight irradiation. After 15 minutes, the yellowish brown AgNPs were formed with maximum absorbance. Therefore, we chose 15 minutes of irradiation for further experiments. However, after 7 days, the peak absorbance was decreased and thus we recommend to use a freshly-prepared AgNPs for accurate Hg (II) ions detection.
Selectivity test was conducted to evaluate the effect of other metals on the quantitative analysis. The results show that silver nanoparticles only selective to mercury ions that is appropriate for the analysis. Other metals ions do not change the yellowish-brown color of silver nanoparticles to colorless, as did by the mercury ions. Further experiments were sensitivity test, to know how low the concentration of analyte can be detected by the proposed method.

Figure 1. Time-dependent formation of AgNPs with sunlight irradiation. The peak of SPR wavelength was at 425 nm.

Figure 2. The test of sensitivity of AgNPs toward different Hg ions concentration. Addition of Hg (II) ions fading the color of AgNPs, and after addition 100 ppm Hg (II) the color of AgNPs become colorless.

Figure 2 shows that concentration of mercury ions of 50, 250 and 500 ppm remove the color of silver nanoparticles, visually, due to re-oxidation of Ag (0) to Ag (I) by mercury ions. By using the calibration curve method, we can achieve the limit of detection (LOD) of 0.1 ppm for the developed colorimetry method. The sensitivity of the method can be improved using digital image colorimetric method with samples placed in a flat-surface container such as cuvettes. Figure 3 shows that the addition of mercury
ions of 50, 250 and 500 ppm change the absorption spectra with no peak absorbance at visible region. Compared to the spectrometry as reference method, the developed colorimetry method for mercury ions detection was accurate up to 99.38%.

Table 1 shows the data of plant extract that were already used as bio-reductant as an alternative to those of chemicals reductants such as NaBH₄. Almost all parts of plant such as fruit, leaf, stem, root, etc. can be used as reductant to reduce Ag (I) to Ag (0) as silver nanoparticles. Most of those plant have a bioactive compounds such as flavonoid, etc. that is responsible for the reduction process [8].

Table 1. Various plant extract (i.e. fruit, leaf, stem, root, etc.) as reductant for AgNPs synthesis that is used as probe of Hg (II) detection.

| Plant name   | Latin name             | Reference |
|--------------|------------------------|-----------|
| Water apple  | Syzygium aqueum        | [8]       |
| Jicama root  | Pachyrhizus erosus     | [9]       |
| Spinach      | Spinacia oleracea      | [11]      |
| Watermelon   | Citrullus lanatus      | [12]      |
| Mannapant    | Alhagi maurorum        | [13]      |
| Babunah      | Matricaria recutita    | [14]      |
| Papaya       | Carica papaya          | [15]      |
| Grape        | Vitis vinifera         | Submitted |
| Watermelon   | Citrullus lanatus      | This work |

4. Conclusion
To conclude, we have successfully green-synthesized silver nanoparticles using watermelon fruit extract and sunlight irradiation as source of energy to fasten the synthesis. After 15 minutes, a yellowish-brown AgNPs were formed with surface plasmon resonance peak at 420 nm. The prepared AgNPs were then used as a probe to detect heavy metal ions in aqueous samples. AgNPs were selective only to Hg (II) ions, thus it can be used as an alternative route to commonly employed colorimetric method that use a lot of chemicals. The sensitivity of the method can be improved using a flat-surface samples container coupled with digital image colorimetric analysis.
Acknowledgments
Authors wishing to acknowledge the Indonesia Ministry of Research, Technology and Higher Education (Kemenristek-Dikti) for financially supporting this research.

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