

Chitosan-stabilized Silver Nanoparticles for Colorimetric Assay of Mercury (II) Ions in aqueous system

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Abstract. Mercury is considered as dangerous pollutant. Among the many form of mercury, the most stable and soluble in water is mercury (II) ions which it cause threat to human health and surroundings. Silver nanoparticles (AgNPs) used in this method were prepared by chitosan (chi) which act as stabilizing agent. The Chi-AgNPs has good dispersity with size ranging from 2.50 to 6.00 nm as shown by transmission electron microscopy (TEM) analysis and it is stable for 3 months. Color of Chi-AgNPs fades from brownish-yellow to colorless only with Hg^{2+} ions, but it shows no significant changes upon addition of other metal ions such as Al^{3+} , Ba^{2+} , Ca^{2+} , Cd^{2+} , Cr^{3+} , Co^{2+} , Cu^{2+} , Fe^{2+} , K^{+} , Mg^{2+} , Mn^{2+} , Na^{+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} . The detection limit for Hg^{2+} ions by bare-eye is estimated to be $\sim 1\mu\text{M}$. This method can be used for sensing mercury(II) ions in numerous water samples.

1. Introduction

Nobel metal nanoparticles such as silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs) have attracted researchers' attention because of their unique chemical and optical properties, which are very much dependent on particle shape and size. [1,2]. Noble metal nanoparticles commonly synthesized through chemical reduction method because of its convenient procedure, easy in controlling, and use simple equipment [3]. However, nanoparticles are generally unstable and tend to aggregate. One way to solve this problem is to disperse them into natural or synthetic polymer matrices such as chitosan, cellulose, and PVA. Chitosan is one of the most abundant natural, renewable, biocompatible, biodegradable, non-toxic, having ability to form film, has high mechanical strength, and highly adsorptive polymer. It can be used as stabilizing agent and immobilization matrix due to the existence of hydroxyl and amino functional groups [4,5].

The prepared metal nanoparticles have been reported to be applied for catalysis, sensors, antibacterial, and numerous other areas [4,6,7,8]. Nobel metal nanoparticles can be used as colorimetric assay because of their high absorption coefficient, light stability, functionality, extent of surface-to-volume ratio, changing optical properties [9] and absorbing colors in visible light areas [10].

Mercury is considered as dangerous pollutant. Among the many form of mercury, the most stable and soluble in water is mercury (II) ions, which it cause threat to human health and surroundings through food chain [11]; hence, the development of methods for its detection at very low concentration



is important. Detection of mercury(II) ions can be done using instrument like *Atomic Absorption/Emission Spectrometry* (AAS/AES), Inductive Coupled Plasma-Mass Spectrometry (ICP-MS), and Fluorescence Spectrometry AFS) [12]. Nevertheless, these methods rather complicated, expensive, and take a long time to analysis. An alternative method such as colorimetric sensing offers advantages over other methods due to its simplicity, low cost, and bare eye application [13,14].

In present work, focus of study was to prepare and characterize a material comprised of chitosan-stabilized nanoparticle (Chi-AgNPs) and use it for colorimetric assay of mercury (II) ion. As commented earlier, AgNPs are used as catalysts for many reactions and chitosan is used to stabilize metallic nanoparticles. However, there has been very limited use of materials comprised of chitosan-stabilized silver nanoparticles for the fabrication of sensor to detect mercury (II) ions.

2. Materials and Methods

All chemicals used in the present study were of the highest purity (p.a). Chitosan of medium molecular weight and sodium borohydride purchased from Aldrich (USA). Silver nitrate, acetic acid, methanol, salt of additional cation tested and all other chemicals bought from Merck (Germany). Characterization of size and shape of the synthesized silver nanoparticles was carried out using Transmission electron micrograph (TEM) recorded on JEOL JEM-1400 operating at 100 kV.

2.1. Synthesis of Silver Nanoparticles

A colloidal silver was prepared by reduction of AgNO_3 using sodium borohydride as our reported method with slight modification [15]. All glassware was washed with a mixture of nitric acid and hydrochloric acid (1:3) before use. Distilled water was used throughout the experiment. Silver (I) stock solution was prepared 10^{-4} mol/mL from silver nitrate as a precursor. In typical experiment, 5.6×10^{-4} mol (0.0900) was dissolved in 88.8 ml acetic acid (1.5%) and the mixture was stirred overnight to obtain homogeneous solution. Next, 90 ml of methanol slowly added with vigorous stirring. Afterwards, 1.12 ml (1.12×10^{-4} mol) of silver stock solution was added little by little to the mixture. Then 0.0265 g of sodium borohydride was added slowly while kept stirring vigorously to reduce the silver ions to silver particles to yield brown yellowish colloid. This silver nanoparticles were characterize with TEM.

2.2. Colorimetric assay of mercury (II) ions using Chi-AgNP as a probe

For colorimetric assay of mercury (II) ions, 3.0 mL of Hg^{2+} ions with various concentration were mixed with 0.5 mL of the prepared chi-AgNPs. The mixture were shaken and settled at room temperature for 15 minutes and then UV-vis absorption spectra were recorded. Colorimetric color change of the sensor after addition with mercury (II) ion were also observed by bare eye and the photograph was taken by camera. In the experiment of selectivity, all samples containing metallic ions were tested in same way. This method was also applied in similar manner for detection of mercury ions using tap, river, and bottle water from nearby Syiah Kuala University campus.

3. Result and Discussion

The chi-AgNPs based chemical sensors are synthesized by reduction of silver nitrate as precursor with sodium borohydride. Silver nitrate is added to a solution of chitosan kept under continuous stirring, dispersion of Ag^+ ions is enabled by the action of chitosan as a stabilizing agent/surfactant. The Ag^+ ions is reduced to Ag^0 (metallic silver) after addition of sodium borohydride and remnants embedded in the chitosan matrix [16]. The presence of $-\text{NH}_2$ and $-\text{OH}$ groups in the chitosan can assist in possible adsorption interaction between chitosan and heavy metal ions including Ag^+ [17]. Besides as stabilizing or capping agent, chitosan also acts as a reducing agent [15]. Figure 1(a) shows TEM image of silver nanoparticle stabilized with chitosan. It is revealed that chi-AgNPs had good dispersity with size ranging from 2.50 to 6.00 nm. After addition of mercury(II) ions to the chi-AgNP shows its aggregated nature as exhibited in Figure 1(b). The interaction between Hg^{2+} ions with chitosan as stabilizing agent to form the larger size of nanoparticles that lead to agglomeration.

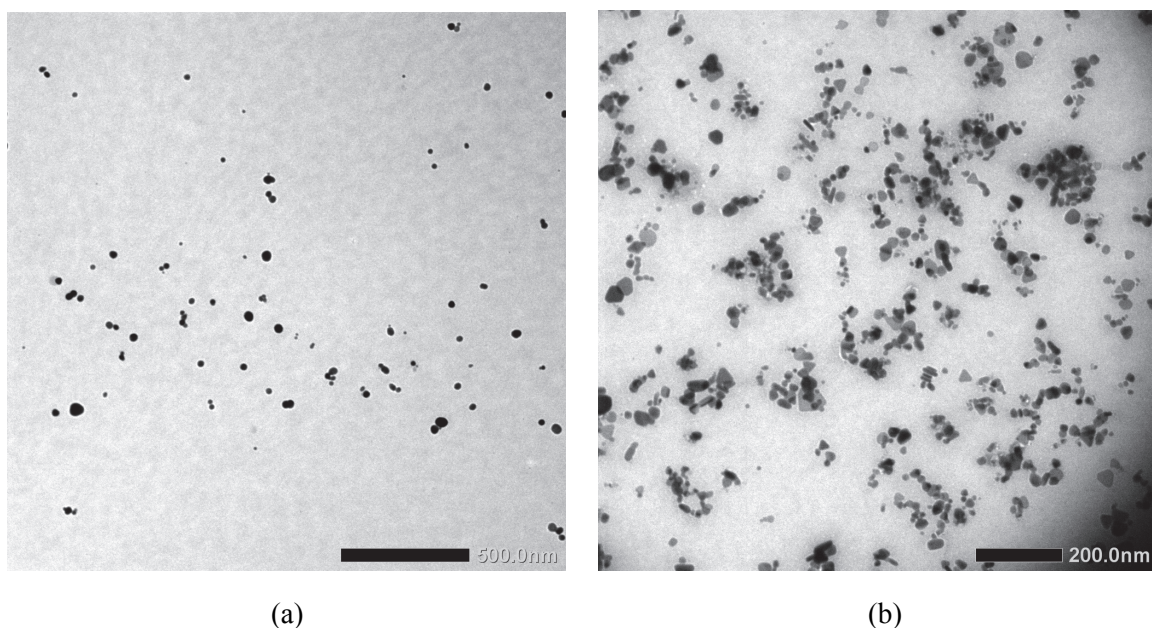


Figure 1. (a) TEM image of non-aggregated AgNPs stabilized by chitosan and (b) TEM image of the aggregated AgNPs after addition of Hg^{2+} ions.

3.1. Selectivity and sensitivity of assay

The selectivity of this probe for Hg^{2+} ions has been evaluated through testing the response of the assay to different metal ions Al^{3+} , Ba^{2+} , Ca^{2+} , Cd^{2+} , Cr^{3+} , Co^{2+} , Cu^{2+} , Fe^{2+} , K^{+} , Mg^{2+} , Mn^{2+} , Na^{+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} at concentration of 100 μM after 10 minutes of mixing. As depicted in Figure 2, only the Hg^{2+} sample shows a significant color change to colorless relative to that of the blank whereas all others remain brownish-yellow color without any eye-distinguishable change. It means that the probe highly selective to detect mercury(II) ions.

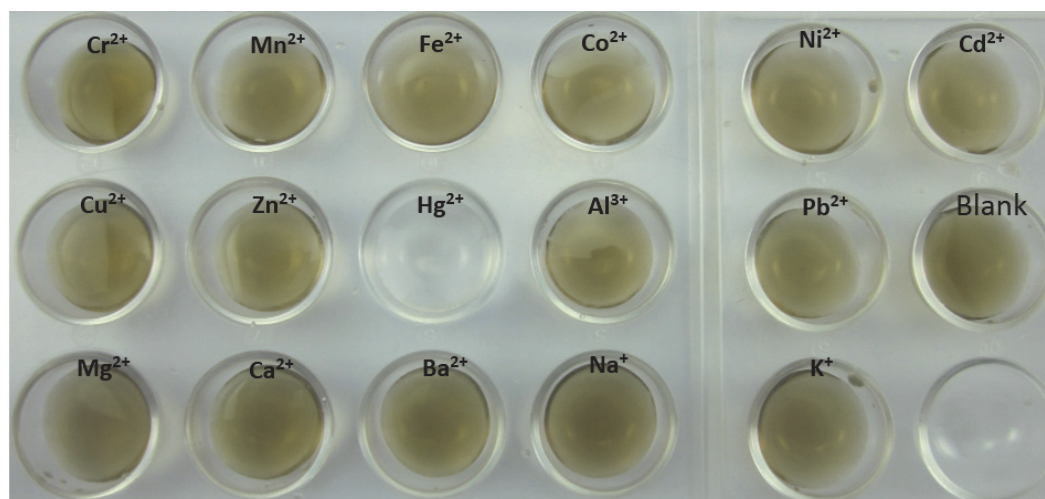


Figure 2. Color change of Chi-AgNPs in the existence of various metal ions

To estimate sensitivity of chi-AgNPs for detecting Hg^{2+} ions, a series of various concentration of Hg^{2+} ions were mixing with the probe. Figure 3 demonstrated the digital image of the AgNPs after addition with various concentraion of Hg^{2+} ions and the limit detection is estimated to be $\sim 1\mu\text{M}$.

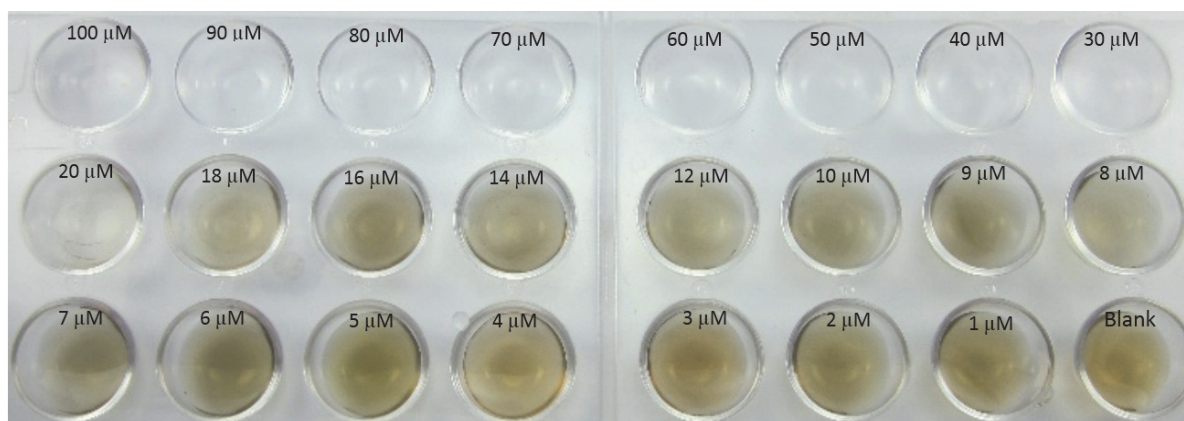


Figure 3. Sensitivity of Chi-AgNPs toward different concentration of Hg^{2+} ions.

3.2. Detection of Hg^{2+} ions in real water samples

Practicability of this colorimetric method is evaluated for various water sample application. It is found that none of the water samples caused visible color change in chi-AgNPs probe (Figure 4a), indicating that concentration of Hg^{2+} ions of these water samples are below $1 \mu\text{M}$. On the contrary, when the water samples spiked with Hg^{2+} $100 \mu\text{M}$, the color of the water change to colorless (Figure 4b). These results confirm that the detection method established here can be used for the detection of Hg^{2+} ions in real water samples.

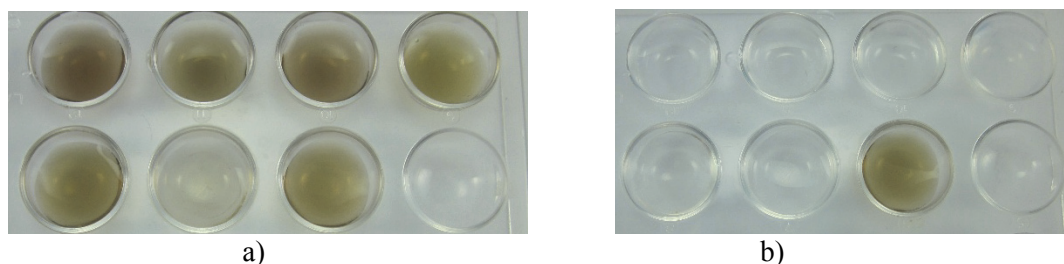


Figure 4. a) Color of water samples after addition of the AgNPs
b) Color of water samples that spiked with Hg^{2+} after addition of the sensor. (Top line from left to right: local water refills, well water, tap water, Lamnyong river water. Bottom line, from left to right: bottled water (Cleo)), mercury (II) ions solution and blank.

4. Conclusions

In summary, AgNPs stabilized by chitosan can be used as a colorimetric assay for mercury (II) ion with limit of detection $1 \mu\text{M}$. Several other commonly encountered metal ions present in the environment does not affect detection of Hg^{2+} ions. The practical applicability of AgNPs stabilized by chitosan exhibits selective sensing of Hg^{2+} ions in various water samples such as bottled, well, tap, and river water.

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