Research Article

Green Synthesized Unmodified Silver Nanoparticles as Colorimetric Sensors for the Selective Detection of Hg(II) Ions

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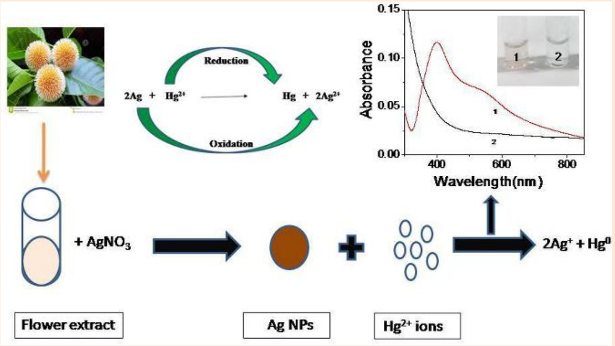
Abstract

The cost effectively of nanoparticles as colorimetric sensors has attracted much attention in recent years. They can be exploited in various environmental and biological analyses over a varied range of targets such as heavy metal anions, cations, proteins etc. Herein, we reported the colorimetric sensing of mercury ions using silver nanoparticles (Ag NPs) synthesized from flower extract of *Neolamarckia cadamba* in aqueous medium. After addition of Hg^{2+} ions to the Ag NPs solution, its color changed instantly from yellowish brown to colorless, even for a very small concentration of Hg^{2+} ions (0.000005 to 0.00004 M). The sensitivity and selectivity of these biosynthesized Ag NPs towards other cations such as Pb^{2+}, Ni^{2+}, Fe^{3+}, Cu^{2+}, Cd^{2+}, Zn^{2+} and Co^{2+} was also studied, which reveals that it has more selectivity for Hg^{2+} ions rather than other ions. The plausible mechanism of the reaction is also discussed here.



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Introduction

Heavy metal cations are commonly encountered toxic substances in environment which may be hazardous beyond certain limit. Among them inorganic form of mercury is highly water soluble and can cause major health problems such as brain damage, nervous breakdown, kidney malfunction, skin irritation, DNA damage and allergic reactions [1-3]. Hence it is essential to detect level of Hg^{2+} in natural analytes with high selectivity, high sensitivity and without obstruction of extra metal ions. Now a day, gold and silver nanoparticles based colorimetric sensors are used extensively due to their potential to detect heavy metal ions, toxic compounds, organic and inorganic pollutants in biological samples quickly. Thus they play important role in ecological monitoring. [4]. An array of detection techniques such as flame photometry [5], atomic fluorescence spectrometry [6], electrochemical sensors [7], cation-specific functionalized sensor [8] and inductively coupled mass spectrometry [9] have been developed for detection of Hg^{2+} ions. Literature also reports detection techniques associated with surface modification of nanoparticles with specific functional groups that can easily bind with the target ions which may be due to ligand formation, chelation or redox reactions. Stanly et al reported β-cyclodextrin functionalized silver nanoparticles based sensing of Hg^{2+}ions [10]. Tan et al reported adenosine monophosphate functionalized silver nanoprobes for the detection of Hg^{2+} ions in water [11]. Nidya et al reported structural, morphological and optical studies of L-cysteine modified silver nanoparticles and its application as a probe for the selective colorimetric detection of Hg^{2+} [12]. Chen et al reported highly sensitive and selective colorimetric detection of Hg^{2+} based on the morphology transition of silver nanoprisms [13]. Khorshidi et al reported, anisotropic silver nanoparticles deposited on zeolite A for selective Hg^{2+} colorimetric sensing and antibacterial studies [14]. Duan et al reported facile colorimetric detection of Hg^{2+}ions based on anti-aggregation of silver nanoparticles [15]. Wang et al reported ultrasensitive and dual functional colorimetric sensors for detection of Hg^{2+}ions and hydrogen peroxide, based on the catalytic reduction property of silver nanoparticles

[16]. These techniques are associated with certain limitations such as variation in functional groups with variation in targets, expensive separation processes and loss of reactivity of nanoparticles. Unmodified and biosynthesized nanoparticles may provide better solutions to these problems as they allow economical and easy to use solutions. Further their surfactant may allow easy and flexible binding with specific targets. Metal nanoparticles especially gold and silver nanoparticles are paying more attention as colorimetric probes due to their distinctive surface, size, shape and distance dependant properties associated with color change [17, 18]. They can easily be used as colorimetric probes as we can control their size and shape merely with changing concentrations of precursors. Among these silver nanoparticles are proved to be best colorimetric sensors due to their high extinction coefficient as compared to that of gold nanoprobes. There are very few reports available for the use of biosynthesized and unmodified silver nanoparticles in colorimetric detection of Hg^{2+} ions. Farhadi et al reported biosynthesized unmodified silver nanoparticles for the detection of mercury ions but there method needed addition of freshly prepared soap root extract as a stabilizing agent [19]. Bhattacharjee et al reported cysteamine capped silver nanoparticles for the detection of Hg^{2+} in water. The addition of H_2O_2 increases the sensitivity of method [20]. Wang et al reported colorimetric detection of Hg^{2+}ions using unmodified silver nanoparticles and mercury-specific oligonucleotides which involve harsh process of nanoparticle synthesis and modification [21].

In our study we use simple, economical**,** rapid and selective techniques for the sensing of mercury ions in aqueous media based on green synthesized and unmodified silver nanoparticles at room temperature and with a fast detection time of 1 min that are previously reported by Ankamwar and co-workers [22].

Experimental

Chemicals and reagents

All chemicals used were of AR grade and having highest purity available. All solutions were prepared with MiliQ water. Silver nitrate ($AgNO_3$, 99.8%) was obtained from Merck. $Ni(N0_3)_2.6H_2O$, $(CH_3COOH)_2$ $Zn.2H_2O$, $C_4H_6CdO_4.2H_2O$, $CuCl_2.2H_2O$, $CoCl_2.6H_2O$, $Pb(NO_3)_2$, $FeCl_3$, $HgCl_2$were purchased from Merck or Himedia chemical companies and used as it without further purification. A stock solution of metal salts was prepared by dissolving a known amount of them in 100 ml MiliQ water and was further diluted as required.

Instruments and apparatus

A double beam UV-Visible spectrophotometer [UV-1800 (Shimadzu)] with 3.5cm quartz cuvette was used to study the changes in UV-Visible spectra. In addition, Field Emission Scanning Electron Microscopic (FESEM) analysis of Ag nanoparticles sample was done in order to explore morphology change of the nanoparticles before and after the reaction. A drop of nanoparticle colloidal solution was loaded on carbon standard FESEM grids and allowed to dry inside a vacuum dryer. The grid containing silver nanoparticles was scanned by a Scanning Electron Microscope (NOVA NANOSEM 450) (BRUKER) operated at an accelerating voltage of 200 kV.

Synthesis of Silver Nanoparticles

Silver nanoparticles were green synthesized from the flower extract of *Neolamarckiacadamba*. For this purpose15µl of flower broth was added to 2 ml $AgNO_3$ (1×10^{-3} M) solution followed by the addition of15 µl ammonia solution in a beaker. After complete reaction the silver nanoparticles were separated by centrifugation at 12000 rpm for 15 min. The pellet formed was further purified by washing it repeatedly with de-ionized water and stored for further characterization and its possible applications.

Colorimetric detection of Hg^{2+}

The colorimetric detection of mercury ions was performed by adding (20 µl -120 µl) of 0.001mol $L^{-1}$of Hg^{2+} in 3ml of AgNPs solution and absorbance was recorded instantly. The interference of other ions was studied by adding 120 µl of 0.001mol $L^{-1}$of various cation solutions (Ni^{2+}, Co^{2+},Pb^{2+}, Cd^{2+}, Fe^{3+},Zn^{2+}, Cu^{2+}) in 3ml Ag NPs solution.

Results and discussion

Interaction of silver nanoparticles with metal ions

It is known that color of bio-synthesized silver nanoparticles is yellowish brown due to the presence of specific surface plasmon resonance peaks in the UV- visible spectrum [23]. The UV-Visible spectrum of AgNPs prepared via biosynthesis is shown in **Figure 1**. The UV visible spectrum reveals two absorbance bands at 399nm which is sharp followed by a broad spectrum around 505nm indicating synthesis of monodispersed AgNPs.

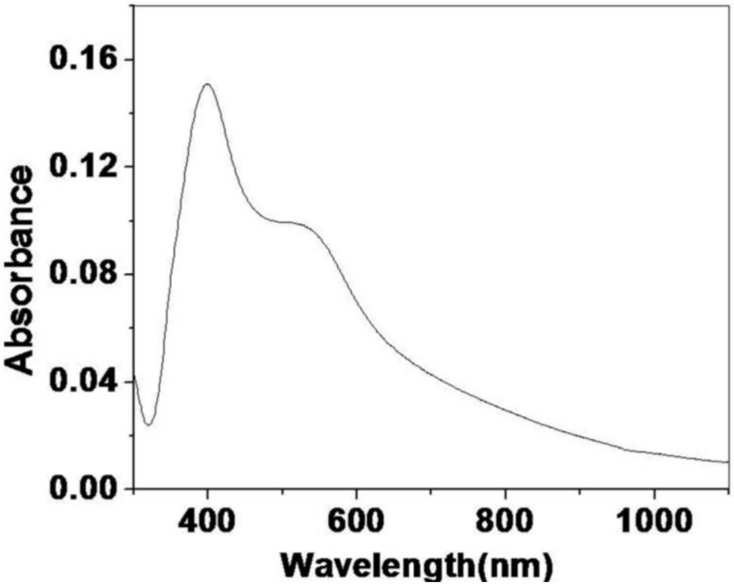

Figure 1UV-Visible absorption spectrum of as synthesized silver nanoparticles.

After addition of Hg^{2+} solution to AgNPs solution the color of the nanoparticles solution became colorless at about 120 µl concentration of Hg^{2+}. SPR peak was modified indicating that there specific binding between Hg^{2+} and AgNPs. UV-visible spectrum of AgNPs with varied concentrations of Hg^{2+} is depicted in **Figure 2** (left). The colorimetric response of the assay at various concentrations of Hg^{2+} ions shows that the reduction in the intensity of SPR band is proportional to Hg^{2+} concentration. This high linear response is shown in Figure 2 (right) with linear regression coefficient 0.9859 and lowest detection limit of 0.62 ppm above the range of 10 µM to 40 µM.

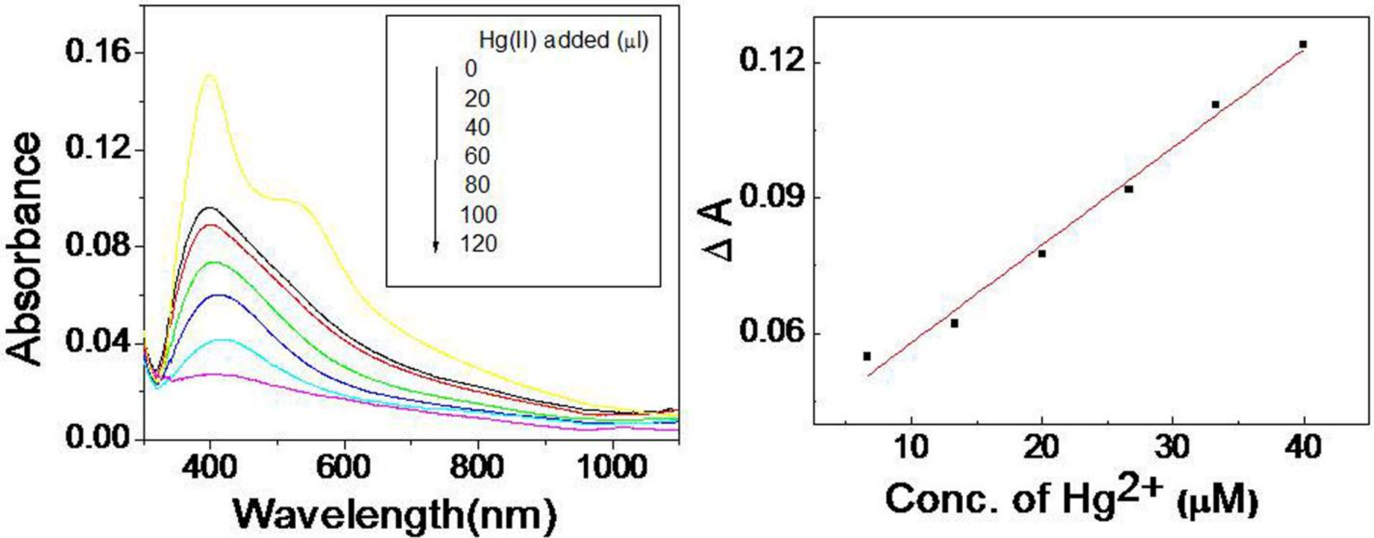

Figure 2 Changes in UV-Visible absorption intensities of AgNPs after addition 0-120µl of Hg^{2+}ions [Left]; Plot of ΔA versus Hg^{2+}concentration [Right].

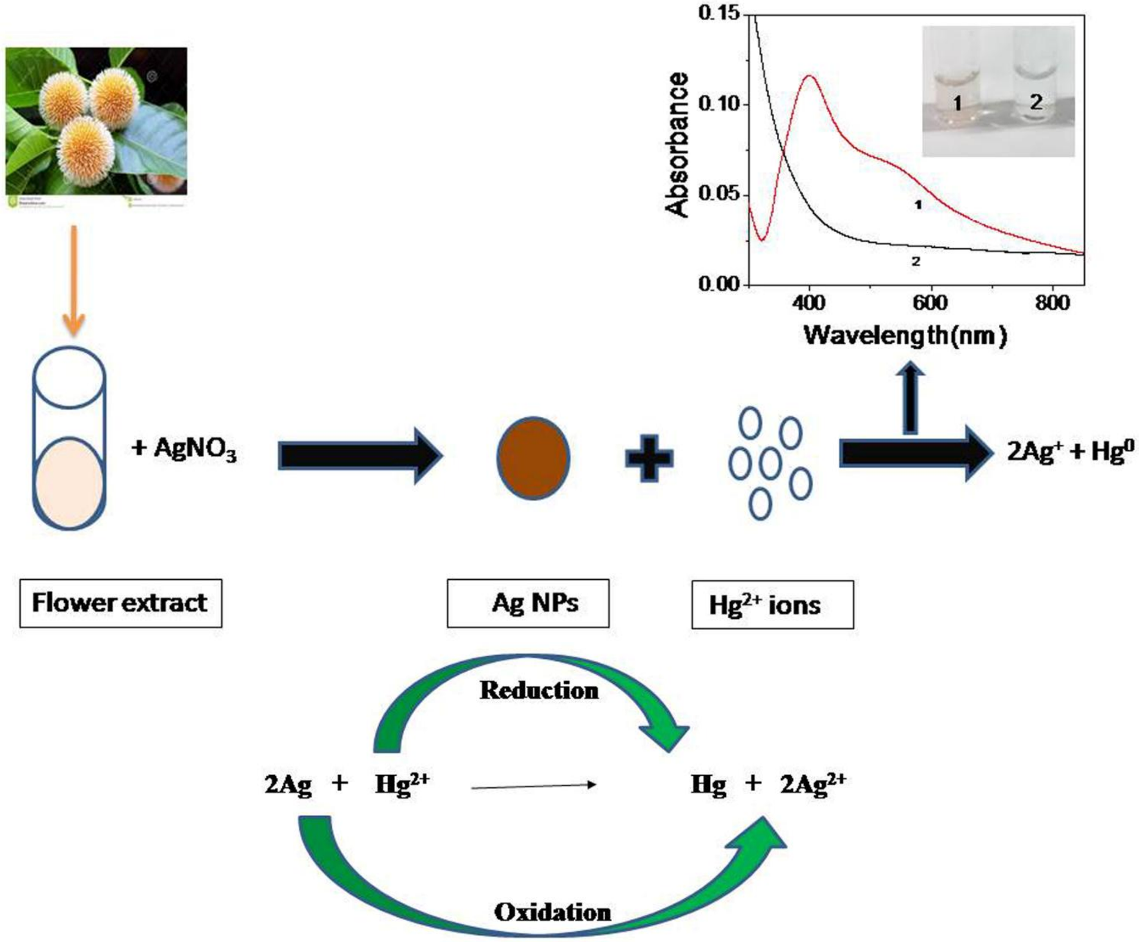

Figure 3 Plausible mechanism and schematics of mercury (II) detection technique.

The mechanism of interaction betweenHg^{2+} and AgNPs can be described on the basis of electrochemical variances of Ag^+ and Hg^{2+}ions [24]. As explained in electrochemical series, metal with higher standard reduction potential acts as an oxidising agent. In this case standard reduction potential for Ag (+0.80V) is higher than that of Hg^{2+} (+0.92V). Hence Ag will act as an oxidising agent and oxidises from Ag 0) to Ag (I).This oxidation of Ag is also supported from the reduction in absorption intensity of SPR band for AgNPs after addition of Hg^{2+} ions [25]. Thus proposed mechanism is bonding between AgNPs and Hg^{2+} ions through the formation of a redox couple in which there is oxidation of AgNPs followed by the reduction of Hg(II) to elemental Hg. In this reaction there is formation of Ag-Hg complex which may alter the optical (SPR band) and physical properties (colour) of the AgNPs. Using this interaction mercury formed may penetrate through the surfactant and remove it so as to permit this reaction to materialise.

FESEM studies

The changes in the morphology of nanoparticles have been verified by FESEM analysis of Ag NPs before and after reaction with Hg (**Figure 4**). From the figure it is clear that pure AgNPs are well dispersed. However particle diameter gradually becomes larger after addition of Hg (II) ion due to wrapping of Ag surface by metallic Hg and formation of Ag-Hg complex.

Selectivity studies

To study reaction of biosynthesized AgNPs to other cations, several common cations such as Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Cd^{2+}, Pb^{2+} and Zn^{2+} were tried. For this purpose, 120µl of 0.001 mol L^{-1} of each ion was added to 3ml Ag NPs solution and corresponding absorbance were recorded. The SPR band and plot of ΔA (A_0-A) where A_0 and A are absorbance in absence and presence of Hg^{2+} ions vs. concentrations of Hg^{2+} ions are shown in **Figure 5** (left) and (right) respectively. From the graph it can be inferred that the response of these cations towards AgNPs solution is low as we observe there is slight color change which corresponds to the change in SPR peak after addition of these ions in AgNPs solution. This indicates that the assay approach is highly selective and specific towards Hg^{2+} ions.

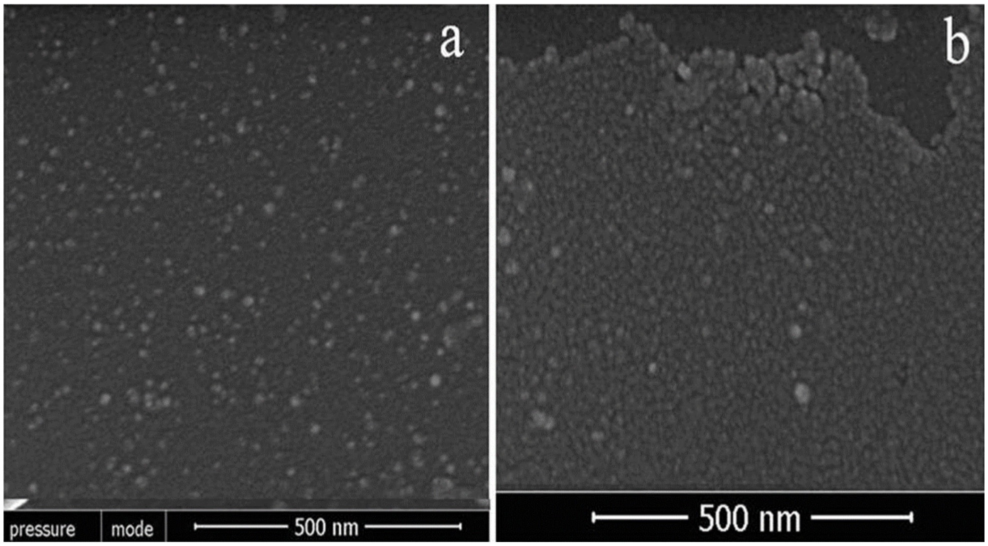

Figure 4 The FESEM images of AgNPs (a) in the absence and (b) in the presence of 40µMHg (II) ions.

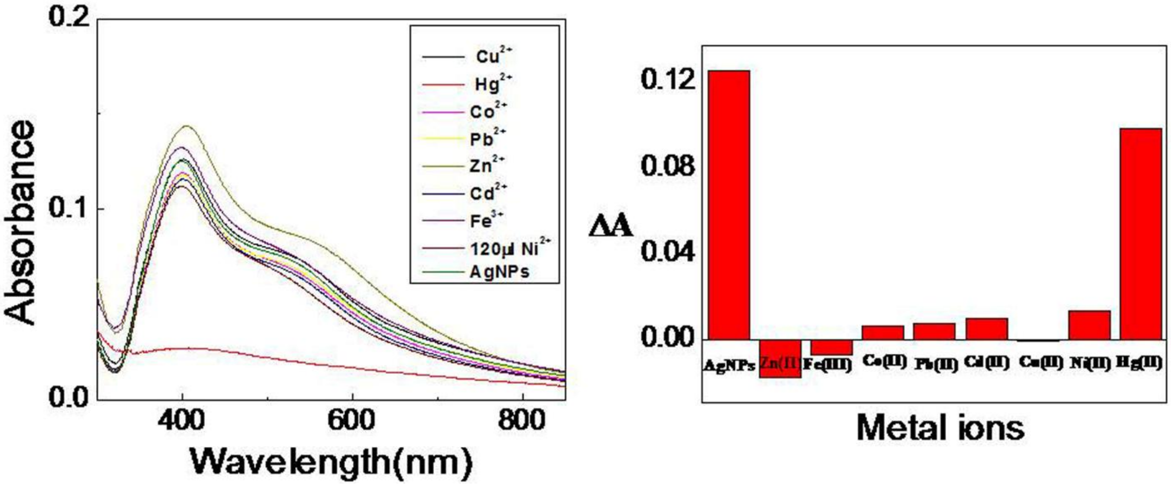

Figure 5 Changes in UV-Visible intensities of 3ml of AgNPs containing 40µM of various cations [Left] and colorimetric sensing of various cations to AgNPs [Right].

Real sample analysis

The above method was applied successfully for the quantitative detection of Hg^{2+} ions in water sample from Pune university campus. After addition of 120µl of water sample to 3ml AgNPs solution there was no any drastic color and absorbance change in nanoparticles solution was observed confirming that the reaction system contains minuteHg^{2+} ions, lower than the detection limit.

Conclusions

Here we reported cost-effective, rapid, sensitive and selective colorimetric technique for the detection of Hg^{2+} ions using biosynthesized AgNPs in biological sample. No complex instrumentation and solvents are involved in this study. Furthermore these studies can be extended further for the estimation of amount minute quantities of mercury ions.

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