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Gum kondagogu reduced/stabilized silver nanoparticles as direct colorimetric sensor for the sensitive detection of Hg^{2+} in aqueous system

Lori Rastogi [a], R.B. Sashidhar [b,*], D. Karunasagar [a], J. Arunachalam [a]

[a] National Centre for Compositional Characterization of Materials, Bhabha Atomic Research Centre, ECIL-Post, Hyderabad 500062, A.P., India
[b] Department of Biochemistry, University College of Science, Osmania University, Hyderabad 500007, A.P., India

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ABSTRACT

A highly sensitive and selective method is reported for the colorimetric detection of Hg^{2+} in aqueous system by using label free silver nanoparticles (Ag NPs). Ag NPs used in this method were synthesized by gum kondagogu (GK) which acted as both reducing and stabilizing agent. The average size of the GK–Ag NPs was found to be 5.0 ± 2.8 nm as revealed by transmission electron microscope (TEM) analysis and the nanoparticles were stable at various pH conditions (pH 4–11) and salt concentrations (5–100 mM). The GK reduced/stabilized Ag NPs (GK–Ag NPs) were directly used for the selective colorimetric reaction with Hg^{2+} without any further modification. The bright yellow colour of Ag NPs was found to fade in a concentration dependent manner with the added Hg^{+} ions. The fading response was directly correlated with increasing concentration of Hg^{2+}. More importantly, this response was found to be highly selective for Hg^{2+} as the absorption spectra were found to be unaffected by the presence of other ions like; Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, As^{3+}, Fe^{2+}, Cd^{2+}, etc. The metal sensing mechanism is explained based on the turbidometric and X-ray diffraction (XRD) analysis of GK–Ag NPs with Hg^{2+}. The proposed method was successfully applied for the determination of Hg^{2+} in various ground water samples. The reported method can be effectively used for the quantification of total Hg^{2+} in samples, wherein the organic mercury is first oxidized to inorganic form by ultraviolet (UV) irradiation. The limit of quantification for Hg^{2+} using the proposed method was as low as 4.9×10^{-8} mol L^{-1} (50 nM). The proposed method has potential application for on-field qualitative detection of Hg^{2+} in aqueous environmental samples.

1. Introduction

Mercury is a naturally occurring element that is found in air, water and soil. It exists in several forms: elemental or metallic mercury, inorganic mercury compounds, and organic mercury compounds [1]. Major source of mercury emissions are thermal power plant emissions, which are of great environmental hazard because their exposure can affect the human nervous system and harm the brain, heart, kidneys, lungs, and immune system [2]. Mercury is treated as an occupational hazard by World Health Organization (WHO). Environmental releases and disposal of mercury are strictly regulated in the U.S. primarily by the United States Environmental Protection Agency (US EPA) [3]. Mercury is known to pose high risk to human health and environment; therefore the development of methods for its detection at very low level is crucial. Current approaches for analysing Hg^{2+} include: inductively coupled plasma mass spectrometry (ICP-MS) [4], cold vapour atomic absorption spectrometry (CVAAS) [5], inductively coupled plasma optical emission spectrometry (ICP-OES) [6], atomic fluorescence spectrometry (AFS) [7,8], and stripping voltammetry [9]. Though these methods provide excellent selectivity and sensitivity for the detection of Hg^{2+}, they are rather costly, time-consuming, complex and non-portable. As compared to these methods, colorimetric probes are of great advantage because it is possible to obtain real time detection either by naked eye or using a simple spectrophotometer [10].

Nanoparticles based colorimetric probes have attracted lots of attention in the recent past because of their high extinction

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Abbreviations: AFS, atomic fluorescence spectrometry; Ag NPs, silver nanoparticles; Au NPs, gold nanoparticles; CVAAS, cold vapour atomic absorption spectrometry; GK, gum kondagogu; ICP-MS, inductively coupled plasma mass spectrometry; ICP-OES, inductively coupled plasma optical emission spectrometry; LOQ, limit of quantification; SEM–EDAX, scanning electron microscope–energy dispersive X-ray spectroscopy; TEM, transmission electron microscope; USEPA, United States Environmental Protection Agency; UV–Vis, ultraviolet–visible; WHO, World Health Organization; XRD, X-ray diffraction

* Corresponding author. Tel./fax: +91 40 27097044.
E-mail address: sashi_rao@yahoo.com (R.B. Sashidhar).

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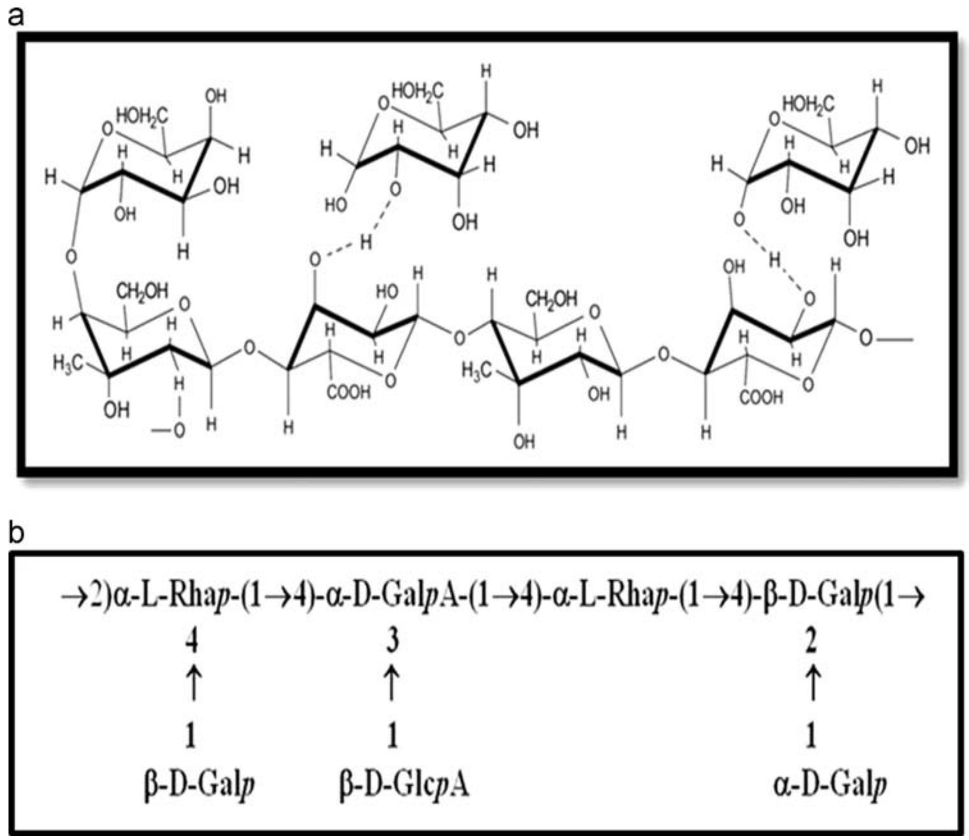

Fig. 1. (a) The assigned structure of the gum kondagogu based on ^{1}H, ^{13}C, 2-D NMR and GC–MS analysis. (b) Nature of biopolymer linkage [24].

coefficients (10^8–10^{10} M^{-1} cm^{-1}) often several orders of higher magnitude than those of organic dyes [11]. Most of the nanoparticles based colorimetric probes were designed by rational modification of nanoparticles surfaces with specific ligands which upon interaction with analyte can change the dispersion/aggregation state of nanoparticles accompanied by colour change [12–15]. Various colorimetric sensors based on functionalized gold nanoparticles have been developed in the recent past for the selective and sensitive detection of Hg^{2+} [16–21]. Although these methods have led to successful development of mercury ion sensors, they suffer from the drawback of high cost of ligands (oligonucleotide probes/fluorescent dyes/selective organic molecule) used and long detection times. Apart from this Ag NPs are preferred over Au NPs due to their higher extinction coefficient as compared to Au NPs of same size [22]. Hence, there is a need for the development of simple ligand free colorimetric protocols for the facile detection of Hg^{2+}. The main aim of this study is to demonstrate the use of silver nanoparticles (synthesized by a green method) as efficient colorimetric probe for the Hg^{2+} in aqueous media. The present study reports Gum kondagogu (GK) reduced/stabilized unmodified Ag NPs based colorimetric approach for the sensitive detection of Hg^{2+} in aqueous system. Gum kondagogu is an Indian tree gum derived as an exudate and belongs to the family *Bixaceae*. In the recent past, gum kondagogu has been established as a matrix to remove toxic metals like lead, cadmium, nickel and total chromium from aqueous solutions and as a reductant for the synthesis of metal nanoparticles [23,24]. The morphological, physico-chemical, structural and rheological properties of gum kondagogu have been comprehensively studied. The primary structure of this biopolymer contains sugars, such as arabinose, rhamnose, glucose, galactose, mannose, glucuronic acid and galacturonic acid. Based on the spectroscopic categorization, the probable structural feature assigned to gum kondagogu is (1→2) β-D-Gal *p*, (1→6) β-D-Gal *p*,(1→4) β-D-Glc *p* A, 4-0-Me-α-D-Glc *p* A, (1→2) α-L-Rha and (1→ 4) α-D-Gal *p* A (Fig. 1) [25]. The developed gum kondagogu reduced/stabilized unmodified Ag NP-sensor was found to be highly sensitive (4.9×10^{-8} mol L^{-1}) and selective towards Hg^{2+} without any interference from alkali and alkaline earth metals. The Ag NPs show no reaction with CH_3Hg^+; however, it was possible to determine this form of mercury after subjecting it to UV radiation at pH 4.0. The treatment with UV is known to convert CH_3Hg^+ to Hg^{2+}, which was successfully detected by the proposed Ag NPs sensors. Thus the developed method provides a highly selective and sensitive method for the detection of Hg^{2+} and it can also be used for the determination/speciation of total mercury forms with the assistance of UV irradiation to the samples.

2. Materials and methods

2.1. Instrumentation

2.1.1. UV–visible spectrophotometer

Synergy H1 Hybrid Reader Model, BioTek Instruments, Germany, with 1 nm resolution to record absorption spectra.

2.1.2. X-ray diffraction

XRD patterns of the lyophilized powders were recorded with a Rigaku DMAX 2200 diffractometer (Japan) using monochromatic Cu Kα radiation (λ=0.154056 nm) running at 40 kV and 30 mA by placing the powder on a clean glass slide.

2.1.3. Transmission electron microscope analysis

The synthesized GK–AgNPs were subjected to TEM (TEM Model: Philips CM200, The Netherlands) analysis so as to know their size and morphology. The sample for the TEM analysis was prepared by placing a drop of GK–Ag NPs on carbon coated TEM grid followed by air drying the sample.

2.1.4. Scanning electron microscopy–energy dispersive X-ray spectroscopy

SEM–EDAX analysis of the GK–AgNPs before and after treatment with Hg^{2+} was recorded with a Zeiss EV018 special edition model (Germany). Sample for the analysis was prepared by placing a drop of colloidal solution on carbon tape and air drying it at room temperature followed by gold coating.

2.1.5. Cold vapour atomic absorption spectrometry

A mercury analyser (Model MA 5800E, Electronics Corporation of India Ltd., India) was used for analysing mercury by cold vapour atomic absorption spectrometry (CV-AAS) at 253.7 nm.

2.2. Reagents

Gum kondagogu Grade 1, [26] was purchased from Girijan Cooperative Corporation-Government of Andhra Pradesh Undertaking, Hyderabad, India. Silver nitrate, mercury (II) chloride and other metal salts were purchased from E. Merck (Mumbai, India). All the chemicals used are of analytical grade or of highest purity available and used as supplied without any purification. Standard stock solutions of Na^{+}, K^{+}, Mg^{2+}, Ba^{2+}, Ca^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Cr^{6+}· Pb^{2+}, As^{3+}, Hg^{2+} Fe^{2+}, and Mo^{2+} were prepared by dissolving appropriate amount of their corresponding nitrate and chloride salts in de-ionized (Milli Q) water with resistivity of 18 MΩ cm.

2.3. Preparation of silver nanoparticles and stability

Silver nanoparticles were prepared by the reported method [23]. Briefly, “gum kondagogu (KG)” was dried at 60 °C for 8 h, powdered in a high-speed mechanical blender (Prestige, Bangalore, India) and sieved to obtain a mean particle size of 38 μm. Then 1.0% (w/v) of homogenous gum stock solution was prepared by adding this powder to a reagent bottle containing ultra-pure water and stirring overnight at room temperature. The silver nanoparticles were synthesized by autoclaving the 1 mM silver nitrate solutions containing 0.5% of KG at 121 °C and 15 psi for 60 min. The stability of synthesized gum capped Ag NPs was tested at different conditions of pH and salt concentrations.

2.4. Detection and determination of Hg^{2+} ions

The as synthesized silver nanoparticle preparation was first diluted 5 times using ultra-pure water for further use in the colorimetric determination of Hg^{2+}. In order to demonstrate the detection of Hg^{2+}, 200 μL of the diluted Ag NPs (1:5 times) was added to a solution containing Hg^{2+} ions (at different concentrations) in polystyrene microtiter plate wells and mixed immediately by re-pipetting the solution. The UV–visible spectrum was recorded in order to quantify the Hg^{2+} ion concentration using a calibration graph. The calibration graph was obtained by plotting known concentrations (50–1000 nM) of Hg^{2+} ions against absorbance at 400 nm. The selectivity of the proposed Ag NPs preparation for Hg^{2+} was confirmed adding various alkalis (Na^{+}, K^{+}), alkaline earths (Mg^{2+}, Ba^{2+}, Ca^{2+}) and transition metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Cr^{6+}, Pb^{2+}, As^{3+}, Hg^{2+} Fe^{2+}, and Mo^{2+}) followed by analysis using the UV–visible spectrophotometer.

2.5. Determination of monomethyl mercury (CH$_3$Hg^{+})

In order to determine CH$_3$Hg^{+}, which does not decolorize the silver nanoparticles, the samples were initially irradiated with a UV lamp (8 W, peak λ=360 nm) based on the method reported earlier [27]. The irradiated samples were then used to determine mercury concentration using the developed method. The results obtained by the proposed Ag NPs method were verified using cold vapour atomic absorption spectroscopy (CVAAS) [28].

2.6. Analysis of ground water samples

Ground water samples were collected from in and around Hyderabad city zones exposed to polluted waste water. The water samples were filtered through 0.22 μm syringe filters so as to remove any particulate matter and used for determination of mercury content using the method described herein. The ground water samples were also analysed by CVAAS which provided independent data for comparison.

3. Results and discussion

3.1. Colorimetric detection of Hg^{2+} and sensing mechanism

As shown in Fig. 2 (inset), the bright yellow colour of gum synthesized Ag NPs (GK–Ag NPs) disappeared immediately after addition of 1.2 × 10^{-6} mol L^{-1} of Hg^{2+}. This was also demonstrated by UV–visible spectra analysis which shows complete absence of absorption peak at 400 nm (signature of Ag NPs) in the presence of Hg^{2+} (Fig. 2). Such a rapid reaction is difficult to explain on the basis of only difference in their standard electrode potential of Ag^{+}/Ag (E^0=0.79 V) and Hg^{2+}/Hg (E^0=0.85 V), which is very small. Further, this process is not expected to favour a fast redox reaction between zero valent Ag^{0} and divalent Hg^{2+}. However, it is well established that physical and chemical properties of nanoscale metal particles differ from those of bulk metal due to size quantization [29,30][]. It has been reported that the redox potential of M^{x+}/M^{0} couple is very different from that of corresponding M^{x+}/M$_{\text{metal}}$ couple. The reduction potential value becomes progressively negative as the size of the metal particle goes to the finely divided state particularly to a nanodomain [31]. Thus the effective difference between Ag^{+}/Ag$_{\text{nano}}$ and Hg^{2+}/Hg will be much higher and would favour reduction of Hg^{2+} to Hg^{0} with partial oxidation of Ag^{0}. Because of the high affinity between Ag^{0} and Hg^{0}, the reduced Hg^{0} gets deposited onto the Ag surfaces leading to the formation of Hg–Ag alloys [32] which in turn lead to decreased SPR intensity and shift in absorption maxima. The changes in the morphology of nanoparticles have been demonstrated by

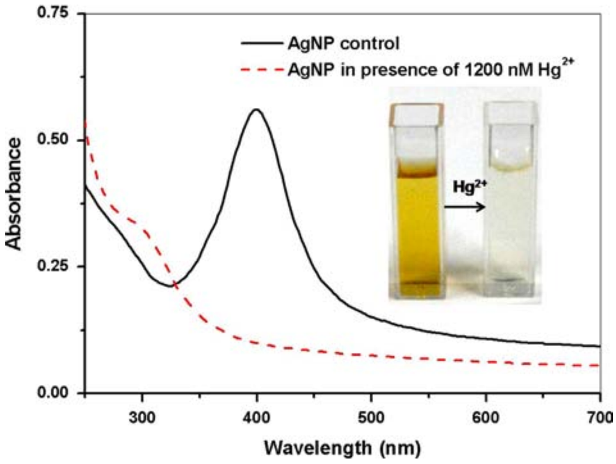

Fig. 2. UV–visible spectra of as synthesized GK–Ag NPs and Ag NPs in the presence of 1200 nM of Hg^{2+} ions. **Inset**: Photograph showing colour change of Ag NPs from yellow to colourless after Hg^{2+} addition.

SEM–EDAX analysis of Ag NPs before and after reaction with Hg^{2+}, (Fig. 3). The formation of Ag–Hg alloy in the above explained reaction was established by lyophilizing the Ag NPs colloidal solution before and after reaction with Hg^{2+} and XRD spectra were recorded. The typical XRD patterns of silver-nanocomposite material before and after Hg treatment are shown in Supplementary Fig. 1A. The crystalline phases obtained with the formation of AgNPs within the GK matrix could be indexed to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of face-centered cubic bulk metallic counterparts [25]. All the diffraction peaks are sharp with (1 1 1) diffraction peak of the highest intensity. The formation of amalgam after addition of Hg^{2+} is confirmed by the XRD analysis. The lyophilized powder of AgNPs and Hg^{2+} reaction product showed XRD pattern closely matching with that of Ag_2Hg_3 alloy (pdf card no.: 03-065-3156 Supplementary Fig. 1A and b) thus demonstrating the reduction of Hg^{2+} by Ag^0. In order to confirm the role of Ag^0 oxidation in the above explained mechanism a small amount of Cl$^-$ions was added in the reaction mixture (Ag NPs and Hg^{2+}); appearance of white precipitate (AgCl Supplementary Fig. 1B) confirmed the presence of Ag$^+$ ions in the solution. Therefore, basically in the presence of Hg^{2+} first a portion of Ag NPs oxidizes to Ag$^+$ and causes the reduction of Hg^{2+} to Hg^0 which then forms amalgam with the remaining Ag NPs and forms the basis of decrease in colour of Ag NPs after reaction with Hg^{2+}. As the mechanism of Hg^{2+} detection by AgNPs occurs *via* oxidation of Ag^0 to Ag$^+$, it is obvious that halides (Cl$^-$, Br$^-$, I$^-$) which form a precipitate with Ag$^+$ ions would interfere in the analysis. No interference of halides was observed when they were spiked in the milliQ water and tested for the detection of Hg^{2+} at the LOQ reported for the method (discussed in detail in the later section).

3.2. *Selectivity and sensitivity of synthesized Ag NPs for Hg^{2+}*

Further investigations were carried out to assess the changes in the colour of Ag NPs that occurred 10 min after mixing 1.2×10^{-6} M of Na$^+$, K$^+$, Li$^+$, Mg^{2+}, Ba^{2+}, Ca^{2+}, Sr^{2+}, Hg^{2+} Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cd^{2+}, Zn^{2+}, As^{3+}, and Cr^{6+} with GK–Ag NPs. As depicted in Fig. 4a and b other than Hg^{2+}, no other element led to great decrease in the colour of the Ag NPs or any change in absorbance value, suggesting that the proposed GK–Ag NPs gives a highly selective reaction with only Hg^{2+}; hence it can act as good sensing probe for mercury detection. In order to test whether GK–Ag NP responds to only Hg^{2+} or other forms of mercury also, a solution of CH_3Hg^+ [1.0×10^{-6} mL^{-1}] was mixed with GK–Ag NP and no change/decrease in colour intensity was noticed indicating that the probes were selective to mercury (II) form only (Fig. 4c). Subsequently, an UV-irradiated solution of CH_3Hg^+, wherein the CH_3Hg^+ was converted to inorganic mercury [26], gave positive reaction (decrease in colour and absorption peak intensity) when mixed with nanoparticles solution. UV irradiation is well known to convert CH_3Hg^+ to Hg^{2+} which reacted with GK–Ag NPs. The result obtained not only confirms that GK–Ag NPs were highly selective for Hg (II) form of mercury but also shows a possibility of determining total mercury form in a given sample with a prior conversion of organic mercury to inorganic mercury. Sensitivity of GK–Ag NPs towards Hg^{2+} was evaluated so as to calculate minimum quantification limit (LOQ) and linear range of detection. When concentration of Hg^{2+} was increased from 0 to 1000 nM, the yellow colour of the silver solution decreased gradually with decrease in absorbance value at 400 nm with complete loss of colour and the peak at a concentration

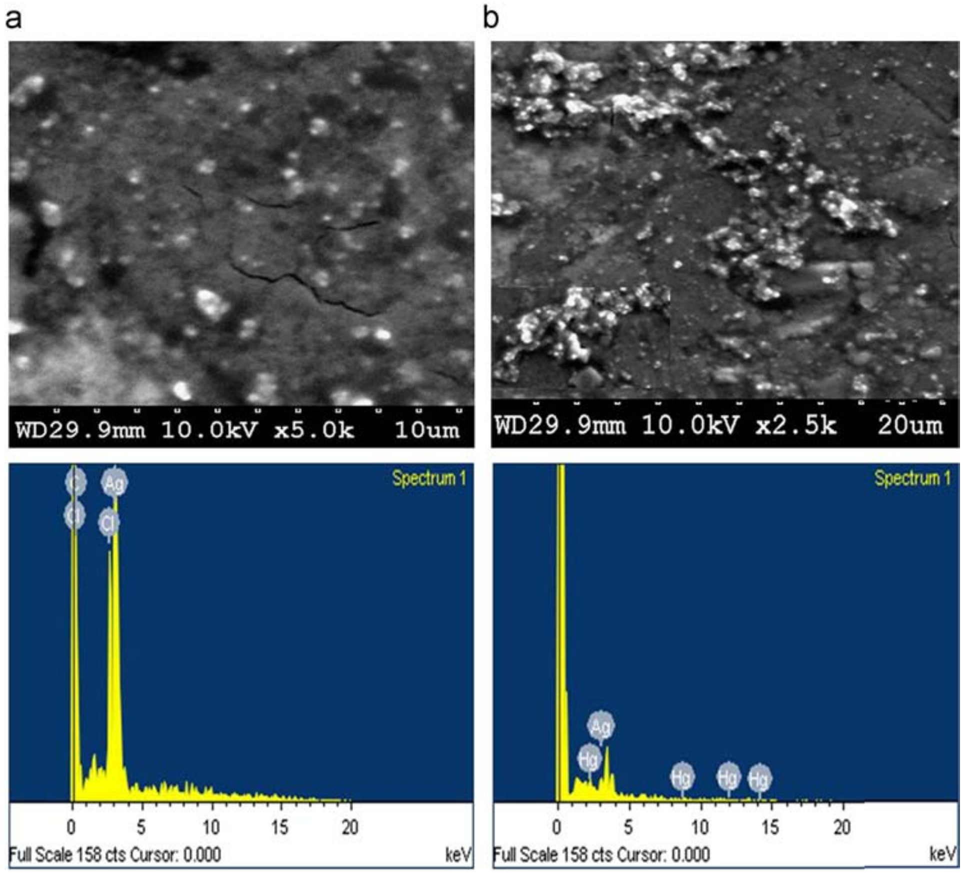

Fig. 3. SEM micrographs of Ag NPs (a) before and (b) after addition of Hg^{2+} and corresponding EDAX profiles.

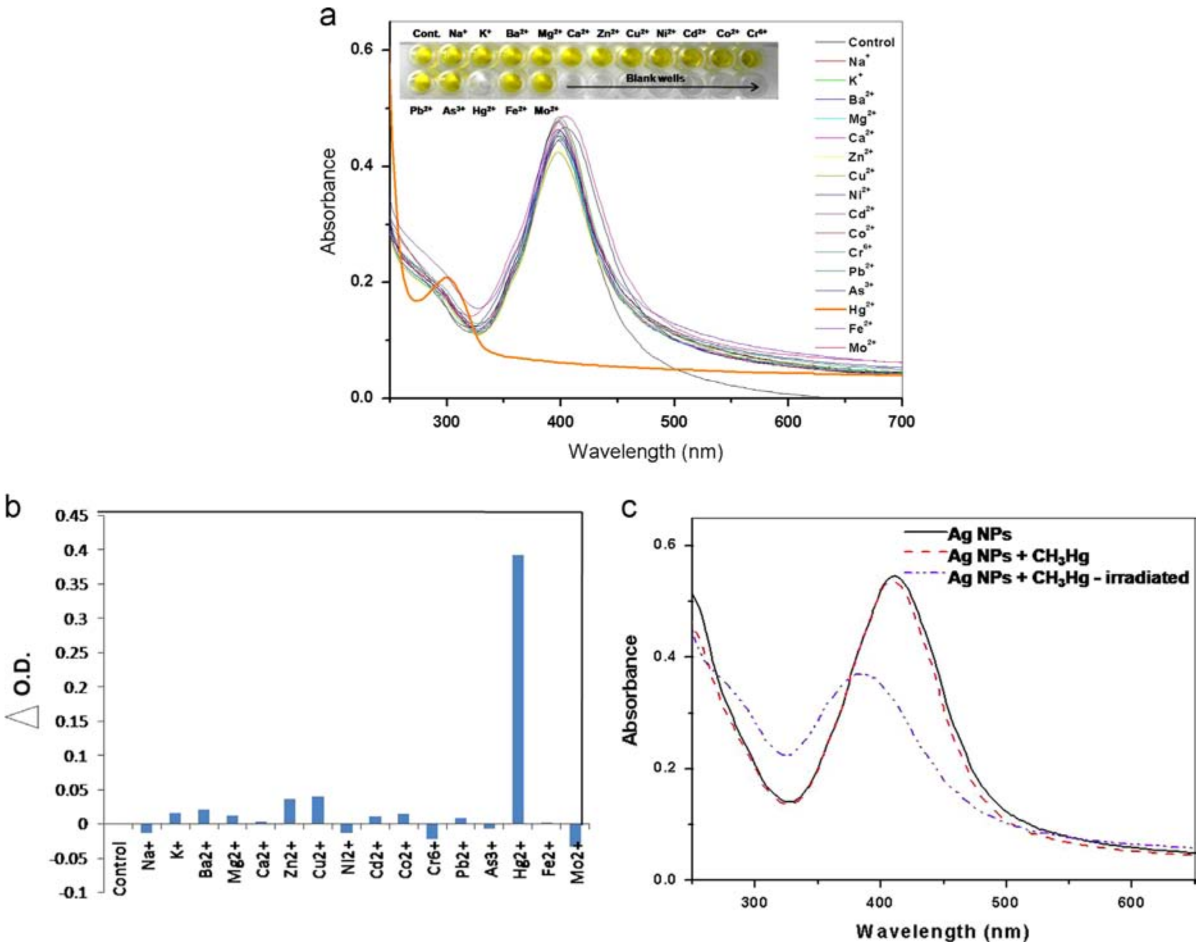

Fig. 4. (a) UV–visible spectra of GK–Ag NPs recorded in the presence of various cations, (b) the colorimetric response of GK–Ag NPs to various cations and (c) spectroscopic response of GK–AgGK–Ag NPs to CH_3Hg before and after irradiation.

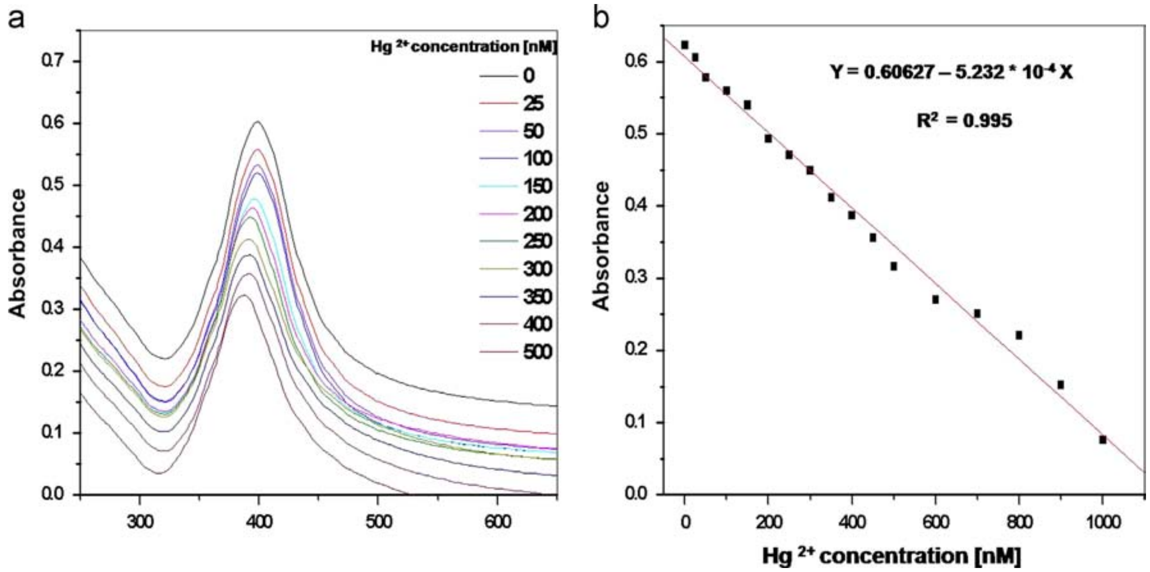

Fig. 5. (a) UV–visible spectra of GK–Ag NPs after addition of Hg^{2+} ions of various concentrations (0–500 nM) (b) Graphical plot between absorbance at 400 nm versus concentration of Hg^{2+} ions in nM.

of 1200 nM (Fig. 5a and b). It was observed that decrease in absorbance value upon addition of Hg^{2+} was linear in the range of 50–900 nM ($R^2=0.998$) with the LOQ of (4.9×10^{-8} mol L^{-1}). Very recently, Farhadi et al. [33] have shown potential of soap-root plant extract synthesized silver nanoparticles as Hg^{2+} sensor but the limit of detection reported was 2.2×10^{-6} mol L^{-1}. TEM analysis suggests that the synthesized GK–Ag NPs were spherical in shape and 5.0 ± 2.8 nm in size [Fig. 6]. The possible reason for higher

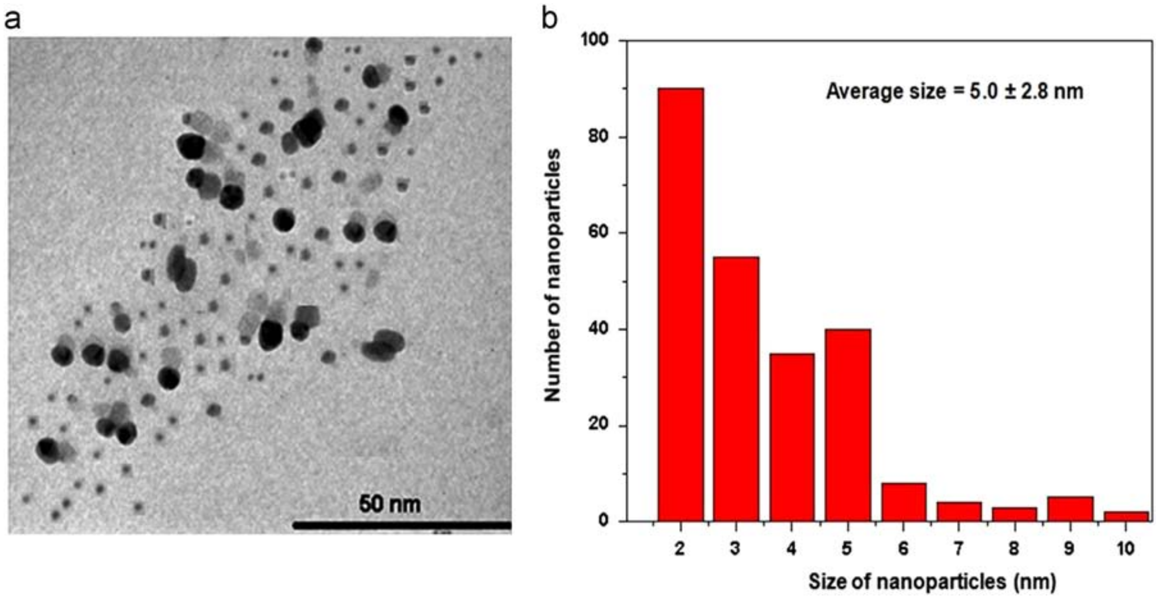

Fig. 6. (a) TEM micrograph and (b) size distribution of synthesized GK–Ag NPs.

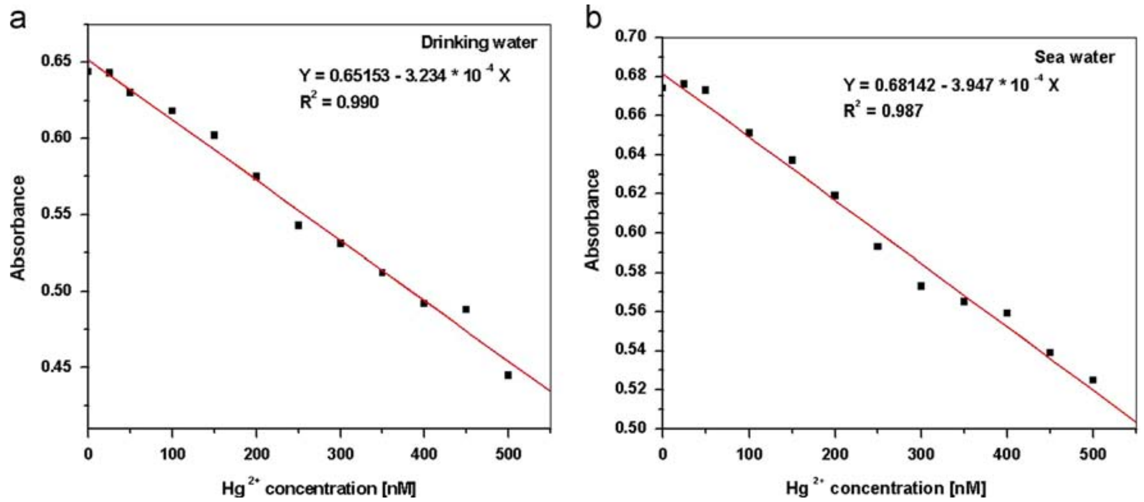

Fig. 7. A plot between absorbance of GK–Ag NPs at 400 nm versus concentration of Hg^{2+} ions in nM in (a) drinking water and (b) sea water.

sensitivity obtained in the present investigation can be attributed to the extremely small size of silver nanoparticles (~5.0 nm) as compared to earlier reported methods, wherein silver nanoparticles of the size 29–68 nm were used. It can be inferred that smaller the size of nanoparticles, more the surface area available for the interaction, which elicits a faster and more sensitive reaction.

3.3. Stability of GK–Ag NPs and determination of Hg^{2+} in different matrixes

The synthesized GK–AgNPs were found to be stable at various tested concentrations of salt (5–100 mM) as no significant change in the UV–visible spectra was observed. However, when tested at various pH conditions, the GK–AgNPs were stable in the range of pH 6–11 and at lower pH there was significant decrease in absorption intensity (Supplementary Fig. 2). So it may be required to neutralize the samples before analysing with the proposed method. In order to evaluate any interference due to halides (Cl^-, Br^-, I^-) spiking studies were carried out in milliQ water. No interference of spiked halides was observed in the analysis, as the developed method was capable of tolerating 2.8 mM of Cl^-, 300 μM of $I^-$and 450 μM of Br^-, without affecting the detection of Hg^{2+} at tested concentrations (50–1000 nM) (Supplementary Fig. 3). So, the inorganic anions such as Cl^-, $I^-$and Br^-could cause interference when present in concentration higher than this, but the fact is that they are present in very small amounts in drinking and ground water. In order to evaluate the practicality of present approach, the as synthesized GK–Ag NPs were used to analyse Hg^{2+} in drinking water and sea water. As depicted in Fig. 7, a linear response was obtained upon increasing spiked concentration of mercury in drinking water over a range of 50–500 nM ($R^2=0.990$) and in sea water over a range of 150–500 nM ($R^2=0.987$). Table 1 shows the minimum LOQ for Hg^{2+} to be 50 nM in drinking water and 150 nM in sea water.

3.4. Determination of Hg^{2+} in real samples

To test the potential of GK–Ag NPs for the determination of Hg^{2+} in environmental samples, the ground water samples collected were assessed for the presence of Hg^{2+} using the developed GK–Ag NPs method. The analytical results are tabulated in Table 2, which show the presence of high levels of Hg^{2+} in the

Table 1
Quantification of Hg^{2+} in different sample matrixes based on the GK–AgNPs.

Sl. no.	Matrix	Linear range of M[a]	R^2	LOQ (M)
1	Deionized water	5.0×10^{-8}–5.0×10^{-7}	0.998	5.0×10^{-8}
2	Drinking water	5.0×10^{-8}–5.0×10^{-7}	0.990	5.0×10^{-8}
3	Sea water	1.5×10^{-7}–5.0×10^{-7}	0.987	1.5×10^{-7}

[a] M=concentration of Hg^{2+} in moles, LOQ=limit of quantification.

Table 2
Determination of Hg^{2+} in ground water collected from in and around Hyderabad city zones exposed to polluted waste water. Comparison of GK–Ag NPs and CVAAS methods.

Sl. no.	Hg^{2+} by GK–Ag NPs [nM][a]	Hg^{2+} by CVAAS [nM][a]
1	1380 ± 124	1430 ± 115
2	2000 ± 120	2000 ± 125
3	1680 ± 145	1690 ± 130
4	1700 ± 125	1730 ± 120
5	1600 ± 135	1559 ± 150
6	1360 ± 126	1425 ± 115

[a] Analysis based on three independent samples, $n=3$.Values: Mean ± S.D.

samples. The same samples when subjected for Hg^{2+} analysis using CVAAS method also give Hg^{2+} concentrations which are in good agreement with the values obtained by GK–Ag NPs based method. The results suggest that GK–Ag NPs have great potential for determination of Hg^{2+} in environmentally relevant samples.

4. Conclusions

In conclusion, the study proposes, GK–Ag NPs as a facile, label free colorimetric probe for the sensitive detection of Hg^{2+} in aqueous systems, based on green approach. The proposed sensing mechanism is based on redox reaction between Ag NPs and Hg^{2+} in solution. Presence of Hg^{2+} could be easily monitored by a UV–vis spectrophotometer (in concentration range of 0–1000 nM) and by naked eye (at and above 1200 nM, yellow to colourless). The sensor (GK–Ag NPs) worked equally well in different aqueous materials like drinking water and sea water with minimum the detection limit of 50 nM and 100 nM respectively and good linearity range. Though the method was not able to respond to the Hg^{2+} at the concentrations (10 nM) permissible in drinking water according to US EPA, still the ease of preparation, analytical procedure and high stability of GK–Ag NPs should allow the application of the methodology as an effective sensor of mercury in various environmentally relevant aqueous samples. The main advantage of the GK–Ag NPs used in this method is the small size 5.0 ± 2.8 nm and narrow size distribution which could be obtained using a biological method. The small size could be a possible reason for increased sensitivity of as prepared AgNPs as compared to the Ag NPs prepared using other reducing and capping agents [33]. The only drawback of the as prepared AgNPs is that the time required for the synthesis is 1 h which is much higher than those of many other chemical methods of synthesis. The simplicity of the silver-nanoparticle based analytical method can be an excellent procedure for screening large number of aqueous samples contaminated with mercury.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.10.012.

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