

ORIGINAL RESEARCH PAPER

## Selective determination of mercury (II) in coastal water using bio-functionalized gold nanoparticles

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### ABSTRACT

The key to simple and rapid detection of a large volume of samples lies in the hands of solution-based nanomaterial sensors. Quantification of mercury in the river and coastal water is analytically challenging due to the potential interference of the matrix. In this endeavor, lysine-capped gold nanoparticles (Lys-AuNPs) based colorimetric sensors are demonstrated here towards efficient detection of trace amounts of mercury ions ( $\text{Hg}^{2+}$ ) in coastal and estuarine water. The colorimetric behavior of Lys-AuNPs is related to surface plasmon resonance (SPR)

During analysis, interestingly a decrease in the intensity of the original SPR peak at 530 nm was observed, with the concomitant appearance of a new peak at a longer wavelength due to agglomerated Lys-AuNPs. Developed sensors exhibit excellent performance in different environmental samples with high selectivity towards  $\text{Hg}^{2+}$  ions in the presence of other metal ions. For the analysis of coastal water samples, a low value of regression coefficient was observed due to the potential interference of salt in the sample. To overcome this, matrix-matching experiments were carried out. Developed Lys-AuNPs show good selectivity towards  $\text{Hg}^{2+}$  in matrixed matched diluted coastal water samples. With a sensitivity of 0.02 ppm, the sensor can be utilized to screen large numbers of coastal water samples for their  $\text{Hg}^{2+}$  content to satisfy coastal regulation norms. As a whole, this method is simple, sensitive, selective, cost-effective and can be used to screen large numbers of samples across the coastal area for monitoring  $\text{Hg}^{2+}$  concentration.

**Keywords:** Coastal water; Mercury ions; colorimetric sensing; Matrix effect; Surface Plasmon Resonance; lysine capped nanoparticle.

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### INTRODUCTION

Seawater contaminations by anthropogenic chemicals pose one of the worst problems to coastal and estuarine ecosystems around the world. When coastal water is used for recreational purposes, the toxicity of a metal present in it is attributable significantly to its labile fraction. These metal ions, especially heavy metal ions such as mercury, and  $\text{Hg}^{2+}$  are reported to be highly toxic even at very low levels in the aquatic environment. Mercury is reported to be among the first four toxic pollutants.

Reported literature also supports the high amount of  $\text{Hg}^{2+}$  across the coast, [1-4]. Considering the immense potential of coastal areas for recreational activities and the threat due to reported  $\text{Hg}^{2+}$  level, its quantification is very important. To monitor our estuarine/coastal water quality for these toxic pollutants, analytical methods, which are simple, economical, having high throughput capability with minimal sample preparation, are needed for an hour. The developed method should work excellently as a screening tool where discrimination between permissible and non-permissible limits should be easily possible. Regulatory bodies

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across the globe have also specified guidelines for these toxic components in recreational water [5] whereas the major emphasis is given to microbial contamination. A guideline for inorganic contaminants such as metal ions is missing. Reports by the United State Environmental Protection Agency (US-EPA) [6] for guidelines for heavy metals in seawater are among the rare guidelines in this area. The guidelines are summarized in Table 1.

In the table, the criterion on maximum concentration (CMC) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect, whereas criterion continuous concentration (CCC) stands for the highest concentration for indefinite exposure. According to WHO guidelines for coastal water 2003 (WHO report, 2003) [7], environmental quality standards for chemicals in recreational waters should be based on the assumption that recreational water makes only a relatively minor contribution to intake. They assumed a contribution for swimming of an equivalent of 10% of drinking-water consumption. Since most authorities (including WHO) assume consumption of 2 liters of drinking- water per day, this would result in an intake of 200 ml per day from recreational contact with water. With guidelines for mercury ion for drinking water as 1ppb (European standards) [8], and 2ppb (for Hg<sup>2+</sup> by WHO), the guidelines for recreational purposes can be relaxed tenfold i.e., 20 ppb for Hg<sup>2+</sup>. From Table 1, it is also evident that Hg is the highest priority contaminant among the listed ones. The significant reasons behind this include the high toxicity of organic mercury, the high solubility of inorganic mercury i.e. 69 g/L at 20 °C, and continuous conversion of organic, inorganic, and elemental Hg into each other forms [9]. The list of ill health effects associated with trace Hg<sup>2+</sup> through oral or dermal exposure is endless which includes gastrointestinal problems, kidney damage, dermatitis, discoloration of the nails, corrosion of the mucous membranes, and sometimes corrosive burns. It should be noted here

that the concentration of Hg<sup>2+</sup> can be interpreted into its more toxic forms such as organic mercury which makes sensing inorganic mercury ions (Hg<sup>2+</sup>) more significant.

Monitoring Hg<sup>2+</sup> in the complex matrix is a challenging task as speciation change of metal ions takes place during pre-treatment /extraction of metal ions. Thus, the analytical method for on-site determination is required. A variety of optical methods has been developed in the last few years for this where colorimetry and fluorimetry sensors are significant ones. These sensors became more attractive due to their simplicity, high sensitivity, selectivity, and capability for on-site analysis. To the best of our knowledge, there are very few reports on the applications of colorimetric sensors for the metal Hg<sup>2+</sup> analysis in seawater, especially because of the lack of selective recognition ligands and interference due to matrix components [10-11]. Surface plasmon resonance (SPR), is advantageous due to the unique optical, electrical, and chemical properties of nanoparticles. Recently, the nanomaterial-based colorimetric assay has been widely used for the sensing and removal of toxic compounds from environmental and biological samples [12-14]. SPR or localized SPR (LSPR) has a strong absorption band at a wavelength of about 521 nm, so it shows a deep red color. The colorimetric performance of gold nanoparticles AuNPs is associated with their SPR, which keenly depends on the shape, geometry, inter-particle distances, particle size, and refractive index. Any variation in these factors changes surface-plasmon frequency, which affects the strength and color of plasmonic enhancement [15]. A solution containing smaller separated gold nanoparticles shows deep red color whereas larger particles or aggregates of smaller particles showed a purple to deep blue color.

In recent years, an increasing number of works focused on the development of novel nanoparticle-based sensors for Hg<sup>2+</sup> detection, mainly motivated by the need for low-cost portable devices capable of giving a fast and reliable on-site analytical response, thus contributing to the analytical decentralization.

Table 1. Safety limits (criteria) set by US-EPA for concentration of heavy metals on Sea water

Element	Criterion of maximum concentration (CMC, µg/L)	Criterion of constant concentration (CCC, µg/L)
Cadmium	40	8.8
Copper	4.8	3.1
Lead	210	8.1
Mercury	1.8	0.94
Arsenic	69	36

Some of the significant work includes [16] where the colorimetric method for determination of  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  ions based on stabilization of AuNPs by redox-formed a metal coating in the presence of ascorbic acid (AA) is reported. Chaudhary et al., 2015 [17] also reported AuNPs based system for  $\text{Hg}^{2+}$  ions but with modification with Lys and dithiothreitol (DTT). The detection limit of these assays is reported as 27 pM and 58 pM for deionized water and tap water, respectively. Selvakannan et al., 2003 [18] reported that capping aqueous AuNPs with the amino acid i.e., lysine helps in stabilizing the particles in solution electrostatically and also renders them water-dispersible. Apart from the advantages known to us, these bio-inspired colorimetric sensing systems include cost-effective production, facile usage, and a visual color change for the detection method [19]. The above sensors allowed for reaching detection limits within the pM and nM range for different water samples whereas limited work is published on coastal water analysis [20-21]. Wang and Sun 2006 [22] have reported that optical limiting is observed in the presence of ionic salt where NaCl causes a slight decrease in UV-vis absorption signal as compared to KCl. This limits the applicability of the sensor in coastal water analysis.

Although most of these reported sensors proved their suitability in detecting and quantifying  $\text{Hg}^{2+}$  ions in synthetic solutions or spiked water samples, the state of the art in these technologies is still behind the standard methods of mercury quantification, such as cold vapor atomic absorption spectrometry and inductively coupled plasma techniques, in terms of reliability and sensitivity. This is mainly because the response of nanoparticle-based sensors is highly affected by the sample matrix. The developed analytical nanosystems may fail in complex real samples because of the negative incidence of the ionic strength and the presence of exchangeable ligands. Capping of lysine on AuNPs is reported to be serving both purposes. Among the reported work in seawater for  $\text{Hg}^{2+}$ , Lin et al. 2010 [21] have reported tween 20-modified AuNPs for selective detection of  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  in seawater. Here the surface of citrate-capped AuNPs was modified with Tween 20, which stabilizes the citrate-capped AuNPs against conditions of high ionic strength.

From the reported data it is clear that AuNPs have been effectively used for sensing  $\text{Hg}^{2+}$  in various water samples, mainly drinking and tap water. The application of the above sensor for

coastal water analysis is limited where a LOD of 0.1  $\mu\text{M}$  is reported by Lin et al., 2010. In this work, the use of surface-modified gold nanoparticles as an LSPR-based chemical sensor for the colorimetric detection of  $\text{Hg}^{2+}$  in coastal water samples is demonstrated. The method is based on the color change of amino acid-modified AuNPs from red to purple with the addition of  $\text{Hg}^{2+}$ . This color change is caused due to the shift in the LSPR band due to the inter-particle coupling effect. The aim of our study is also to develop a simple analytical method with minimal sample preparation for on-site analysis. The usefulness of this method for the critical analysis of  $\text{Hg}^{2+}$  in coastal and estuarine is successfully demonstrated here.

The highlights of the above work are

- Successful demonstration of a simple nanoparticle-based method for on-site analysis of  $\text{Hg}^{2+}$  in coastal and estuarine water.
- The method with minimal sample preparation where mere dilution is used as a sample preparation step.
- Limit of detection (LOD) of developed sensor for  $\text{Hg}^{2+}$  in coastal water is 0.02 ppm (0.0583mM),
- Application of developed sensor method for sensing  $\text{Hg}^{2+}$  in a coastal area of Goa where hardly any work is reported. Considering the potential of Goa, India for recreational activities and related revenue generation this study is important.

## EXPERIMENTAL

### *Chemicals and Instruments*

Sodium Citrate tribasic dihydrate, (Molychem) Gold (III) chloride trihydrate, Cysteine, Lysine, Copper nitrate hexahydrate, Cobalt nitrate hexahydrate, Lead nitrate, Nickel nitrate hexahydrate, Ferric nitrate nonahydrate, Zinc hydrate hexahydrate, Calcium nitrate, Aluminium nitrate, Potassium nitrate, Mercuric nitrate monohydrate, Sodium chloride, Nitric acid, Hydrochloric acid (Avra). For recording spectra, a Shimadzu UV-1800 spectrophotometer is used. Scanning Electron Microscopic images were taken using the SEM instrument.

### *Synthesis of lysine-capped gold nanoparticles and sensing of $\text{Hg}^{2+}$*

The AuNPs were prepared by the Turkevich method [15] in which the gold chloride salt is reduced using sodium citrate tribasic dihydrate. 12 ml of preheated sodium citrate solution (1% W/V) was added to 100 ml of boiling water containing

8.5 mg of gold chloride salt. The solution was vigorously stirred for 30 minutes until the solution turned a deep red color. Finally, the solution was cooled to room temperature and the volume of the gold nanoparticle solution was adjusted to 100 ml by using double distilled water. AuNPs were characterized by UV-visible spectrometry. These stabilized colloidal AuNPs exhibited characteristic SPR peaks at 519 nm and appeared red. 1 ml of AuNPs solution prepared as mentioned above was mixed with 1 ml of lysine solution (0.4 mM) at room temperature. The resultant solution was mixed to get Lys-AuNPs solution. Similarly, cysteine-capped AuNPs (Cys-AuNPs) was also prepared and used for detecting  $\text{Hg}^{2+}$  in a water sample. (Spectra in Supplementary information; SI-1)

In a typical experiment, 1.0 mL of Lys-AuNPs was mixed with 0.4 mL of  $\text{Hg}^{2+}$  solutions (in deionized / tap/river water) at different concentrations to give a final  $\text{Hg}^{2+}$  concentration in the range of 0.02 ppm to 1 ppm. Finally, the color change from red to blue was detected by the naked eye and/or by recording the UV- vis absorption spectra in the wavelength range 200 to 800 nm.

Similarly, the detection of  $\text{Hg}^{2+}$  by using Cys-AuNPs was also performed in the studied range. For understanding morphological changes, SEM analysis of citrate-capped AuNPs, lysine-capped AuNPs, and cysteine-capped AuNPs with and

without the addition of mercury was carried out. (Spectra in Supplementary information; SI-2)

#### *The selectivity of the Colorimetric Sensor*

To investigate the selectivity of the method, several metal ions such as  $\text{Ni}^{2+}$ ,  $\text{K}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ca}^{2+}$  including  $\text{Hg}^{2+}$  were added to the prepared lysine-capped gold nanoparticle (Lys- AuNPs). The corresponding color change was observed and the UV- visible absorption spectra were recorded. In addition, controlled experiments were performed in the absence of lysine and for high reproducibility; all experiments were performed in triplicate.

#### *Sample collection and preparation*

For the collection of water samples, the sampling sites were selected along the Goa coast. Sampling was carried out by the grab method in the post-monsoon period. Samples of water were analyzed on the same day (within 2 hours) without any prior acidification. The analyzed water samples include water from different sampling locations across the Zuari river/estuary / coastal area of goa i.e. S-1 to S-15. A figure representing details of the sampling location is given below (Fig 1). In practice, for sample pre-treatment, water samples were centrifuged (4470 RPM for 10 minutes), filtered (0.45  $\mu\text{m}$  pore size filter paper), and diluted (if required) before analysis. The pre-treated sample is then reacted with Lys- AuNPs.

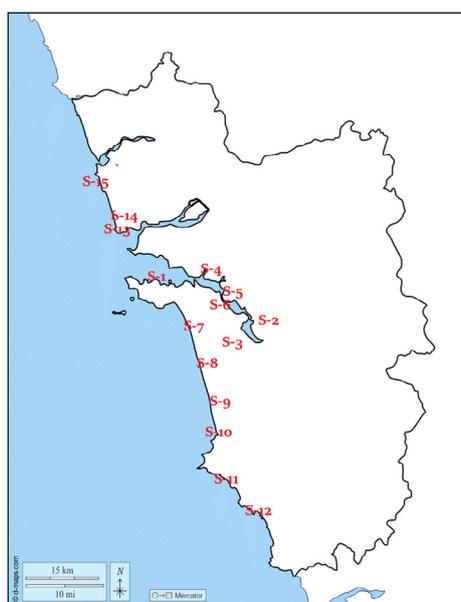


Fig. 1. Map illustrating the study area and sampling locations at coastline of Goa, India Sampling site code; S-1: Vasco, S-2: Borim, S-3: Rassai, S-4: Cortalim, S-5: Adpai, S-6: Zuari river, S-7: Arossim, S-8: Majorda, S-9: Betal batim, S-10: Colva, S-11- Khola, S-12: Sernabatim S-13: Miramar, S-14: Bogmalo S-15: Caboderam

### Real Samples Analysis

The proposed method was applied for the determination of  $Hg^{2+}$  in different water samples. In the case of nanoparticle-based colorimetric sensing for coastal water samples, matrix effects are reported to be more serious. The constituents of the coastal water ( $Na^+$  and  $Cl^-$ ) pose significant interferences. Thus, reporting the concentration of analytes without separation from the matrix may include huge errors [26]. During coastal water analysis, we observed that color is highly dependent on the concentration of the matrix. Therefore, experiments were conducted to minimize the effect of the matrix by decreasing the concentration of  $Na^+$  and  $Cl^-$ . Dilution seems to be an economical and effective approach for it and thus optimized.

For optimization, initially artificial seawater and natural seawater with various dilutions were reacted with Lys-AuNPs. Optimum dilution was calculated where the matrix gave negligible effect. Then, the samples were spiked with different concentrations of  $Hg^{2+}$ , and recovery studies were performed. Similar studies were carried out with Cys-AuNPs which gave a high positive error in the presence of NaCl (as for the colorimetric response of Cys-AuNPs, the presence of NaCl is essential). Thus, for coastal water analysis, Lys-AuNPs with optimized dilution for minimal matrix interference were finalized. The main objective of matrix matching is to obtain optimum color and  $\lambda_{max}$  in the adsorption spectrum.

### Statistical Analysis

Statistical Analysis was conducted to determine the difference between metal ion concentrations among the inter-day and intra-day analysis. The coefficient of variation was also calculated for real sample analysis to check the precision of  $Hg^{2+}$  analysis in coastal water.

## RESULTS AND DISCUSSION

### Proposed mechanism of $Hg^{2+}$ analysis

The colorimetric  $Hg^{2+}$  sensing principle can be explained by a two-step mechanism. In the first step, lysine was immobilized on the AuNP surface and formed a shell around the particles. Then,  $Hg^{2+}$  addition to this solution induces aggregation of Lys-AuNPs and results in a rapid color change from red to purple because the distance between the Lys-AuNPs decreases than the average particle diameter. Thus causing the broadening and shifting of the surface plasmon resonance (SPR) peak [15].

From Fig 2 (b) it is clear that AuNPs or Lys-AuNPs when characterized by UV-visible spectrometry show a characteristic SPR peak at 519 nm and appear red. But after the addition of  $Hg^{2+}$  solution, the intensity of the peak decreases, and the peak emerges at a longer wavelength. The peak shows a bathochromic shift. The role of lysine in the SPR signal is that it contains two amino groups which can interact strongly with  $Hg^{2+}$  ions and forms a bridge. This bridging leads to the aggregation of AuNPs leading to a shift in wavelength.

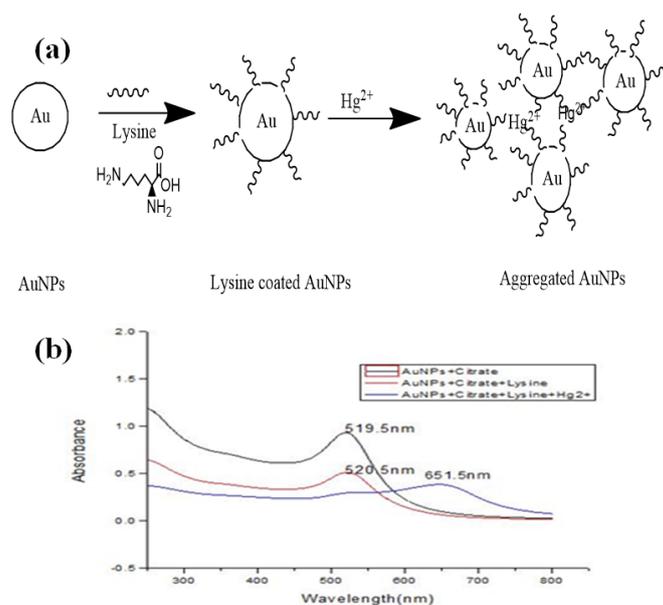


Fig. 2. a) Proposed  $Hg^{2+}$  sensing mechanism of the colorimetric assay, b) Spectra indicating peak for  $Hg^{2+}$  -lysine capped AuNP

### Colorimetric detection of Hg<sup>2+</sup> using lysine-capped gold nanoparticles

For the calibration curve, different concentrations of Hg<sup>2+</sup> were added to the Lys-AuNPs solution. With the increase in Hg<sup>2+</sup> concentration from 0.02 to 1 ppm (0.02 ppm = 0.058 μM), the SPR band around 643 nm was gradually enhanced, demonstrating a sensitive response to Hg<sup>2+</sup>.

The high correlation coefficient (R<sup>2</sup>) of 0.9873 in Fig 2. shows the good linear relation between Hg<sup>2+</sup> concentration and response for the selected method at maximum wavelength. Also, the increase in intensity has been observed concerning an increase in concentration as shown in the supplementary information, SI-3 for different Hg<sup>2+</sup> concentrations. Significant analytical features of merit for the given method are tabulated in Table 2.

### The selectivity of the Colorimetric Sensor

The selectivity of this colorimetric sensor in the presence of Ni<sup>2+</sup>, K<sup>+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>, Cu<sup>2+</sup>, and Ca<sup>2+</sup> was carried out. Controlled experiments were also performed in the absence of lysine. From the spectra obtained the results demonstrated that only Hg<sup>2+</sup> could cause the significant color change of the Lys-AuNPs, and Ni<sup>2+</sup>, K<sup>+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>, Cu<sup>2+</sup>, Ca<sup>2+</sup> species had no obvious effect on the SPR band and the color of the colloid. With the increase in Hg<sup>2+</sup> concentrations, there is a

significant increase in agglomeration of AuNP-lys was also observed. The larger atomic weight and lower electronegativity of Hg<sup>2+</sup> might be the prime reason behind preferential sensing. The above results indicated that this developed method could effectively distinguish the inorganic mercury, while other metal ions had no disturbance.

### Water sample analysis

Quantification of Hg<sup>2+</sup> concentration in water samples collected from different sampling sites was carried out. In practice, to understand the matrix effect, the calibration curve was plotted in all matrices. Hg<sup>2+</sup> solutions corresponding to standard calibration curves in all these matrices were prepared and analyzed. Table 2, represents a summary of the calibration curve for different water samples

The slopes of the calibration graphs prepared by the standard curve method for the tap, distilled and wastewater samples were found to be almost identical to that of the standard addition plot. Whereas for coastal seawater, the values for slope and correlation coefficient (R<sup>2</sup>) are relatively less. This indicates the interference of the salt matrix in coastal seawater analysis. To overcome this, matrix matching for coastal seawater samples is required before analysis. Considering this, the experiments were performed where the concentration of Hg<sup>2+</sup>

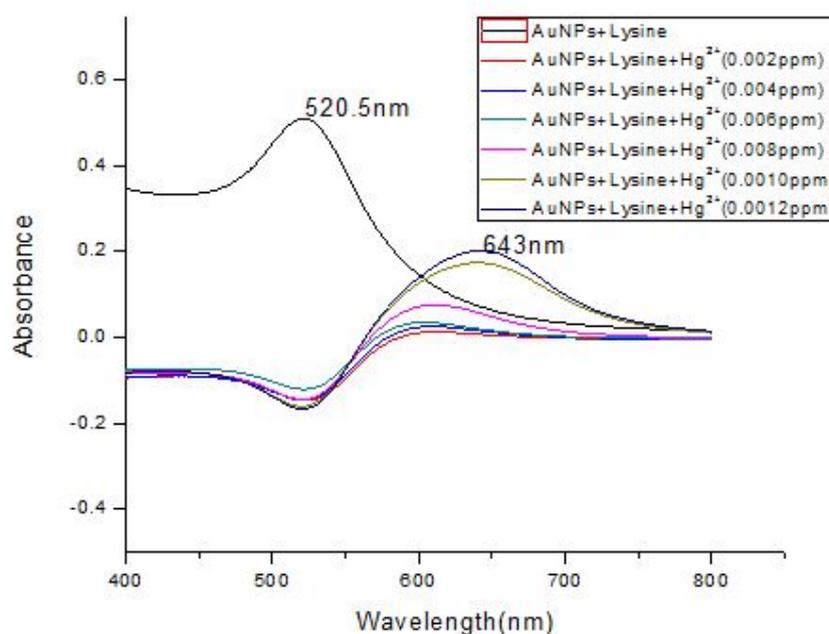


Fig. 3 Spectra for sensing different Hg<sup>2+</sup> concentrations

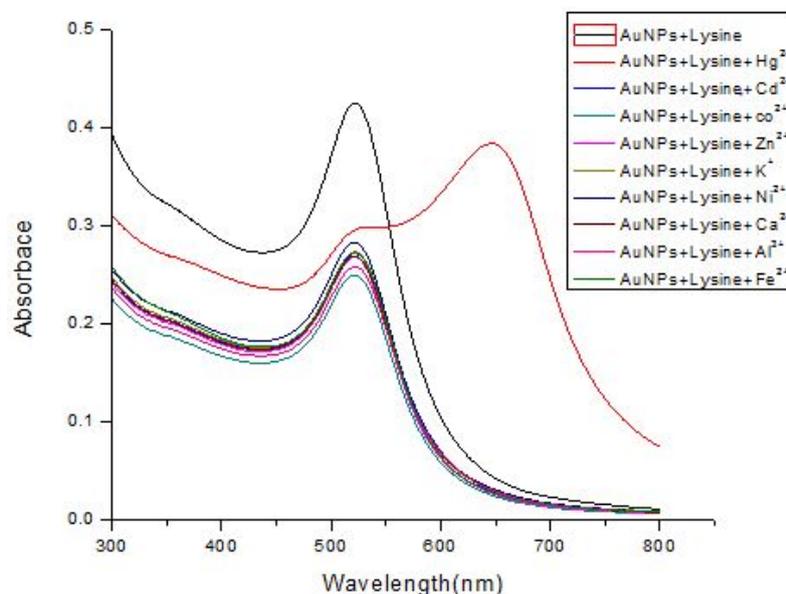


Fig 4. Selectivity of the colorimetric response for Hg<sup>2+</sup> analysis

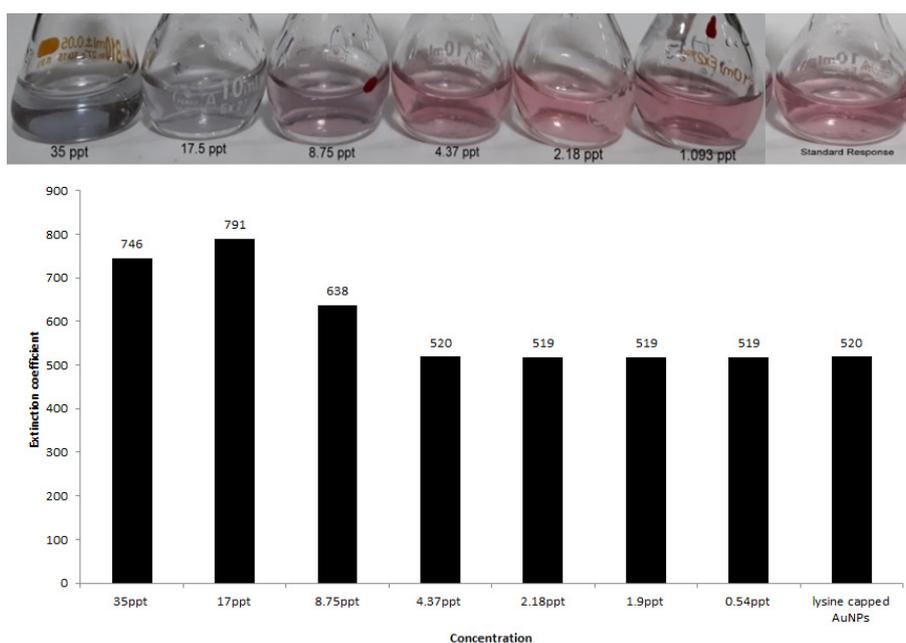


Fig 5. Matrix matching indicating optimum salt concentration of sea water for sensor response

and Lys- AuNPs is kept constant and various dilutions (with distilled water) of coastal seawater samples have interacted. The various dilutions used for this study are; Neat sea water (ASW-1), 1:1 dilution of seawater (ASW-2), 1:2 dilution of seawater (ASW-3), 1: 3 dilution of seawater (ASW-4) and so on. The color change was detected by the

naked eye. Also, the UV- visible absorption spectra were recorded in the wavelength range of 200-800 nm. The absorbance and extinction coefficient for each sample was calculated and compared with the reaction of Lys- AuNPs in distilled water. Fig 5, Represent matrix matching for artificial coastal water by dilution.

Table 2. Calibration curve in different matrix

Sample	Range	Slope	R <sup>2</sup>	Equation for linear fit
Distilled water	0.02- 1 ppm	0.2581	0.9944	0.2581X + 0.0781
Tap water	0.02- 1 ppm	0.1928	0.9822	0.0928X + 0.0830
Waste water	0.02- 1ppm	0.1509	0.9798	0.1509X + 0.0603
Coastal water	0.02- 1 ppm	0.1265	0.8948	0.1265X + 0.1008

Table 3. Analytical data for Hg<sup>2+</sup> determination in real samples. (With and without spiking. For spiking all samples were spiked with 0.1 ppm Hg<sup>2+</sup> concentration.

Sample	Actual Conc. in ppm	Observed Conc. in ppm after spiking	Recovery %	RSD%
S-1	0.0210	0.1210	121	2.5
S-2	BDL	0.108	108.0	2.1
S-3	BDL	0.1113	111.3	3.4
S-4	0.0188	0.1188	118.8	3.1
S-5	BDL	0.1123	112.3	2.5
S-6	BDL	0.1014	101.4	2.9
S-7	BDL	0.0864	86.4	2.6
S-8	BDL	0.0941	95.1	2.8
S-9	BDL	0.1015	101.5	3.1
S-10	BDL	0.0978	97.82	3.4
S-11	BDL	0.1025	102.5	2.1
S-12	BDL	0.1019	101.9	3.8
S-13	BDL	0.0978	97.82	2.9
S-14	BDL	0.1032	103.2	2.4
S-15	BDL	0.1036	106.7	2.5

\*The results are reported as the average values from three measurements

It was observed that with a dilution of seawater, the extinction coefficient changes and ultimately matches the value for the reaction of Lys- AuNPs in distilled water. With 1: 4 dilutions (i.e. ASW-4 in fig.), the extinction coefficient of Lys-AuNPs as well as absorbance value matches. This indicates that with 1: 4 dilutions, the matrix interference is negligible. Using matrix matching, samples from different locations (containing different Hg<sup>2+</sup> concentrations) were analyzed (representative spectra are given in supplementary information (SI-4) Later, spiking studies were also carried out to compare the response of matrix-matched sample and Hg<sup>2+</sup> with standard Hg<sup>2+</sup> in the calibration curve. It was observed that for a few samples, the concentration is below the detection limit (BDL) of the developed method i.e., 0.02ppm whereas for a few samples the quantified amount was above BDL.

Recovery (%) for all spiked samples was carried out. Here, the recovery values calculated for the added standards are observed to be higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects. Also, high accuracy and precision of data can be confirmed by %RSD values which are less than 5. From data in Table 3, for a few samples with actual concentration

below BDL the % recovery values are around 100 % whereas, for a few samples, higher recoveries in the range of 100-110 were observed. The data obtained for these samples also matches that of data without spiking. Relatively high recovery values for sites 1 and 4 were observed which may be due to the presence of Hg<sup>2+</sup> present in the seawater sample that may add to the signal and thus give a higher recovery value. The results obtained for high heavy metal concentrations at these sites are also consistent with earlier reported studies by Sarkar, A., et al., 2008 [26]. The occurrence of Hg<sup>2+</sup> at these sites may be due to the nearby hotels, restaurants, and port activities that discharge effluents into the water and thus pollute them. Also, an alarming signal for site S-1 is obtained indicating Hg<sup>2+</sup> concentration more than the permissible limit. For a few samples, low recovery values were observed. This may be due to the presence of the interfering ions in the matrix that may not allow the analyte to react with lys-AuNPs.

Statistical Analysis was conducted to determine the difference between metal ion concentrations among the inter-day and intra-day analysis. Inter-day and intra- day variations for samples were within the limit. The coefficient of variation was

Table 4. Summary of nanoparticle-based sensor for Hg<sup>2+</sup> in water

Sensor	LOD	Sample	Reference
AuNPs -diethyldithiocarbamate	10 nM	Drinking water	[9]
AuNPs-Lys	2.9 nM	Distilled and tap water	[15]
AuNPs	5 nM	Drinking water	[16]
AuNPs	58 pM	Tap water	[17]
Citrate capped AuNPs	0.1 μM	Drinking and sea water	[21]
AuNPs-DNA	100 nm (=20 ppb)	Drinking water	[23]
AuNPS-2-mercapto succinic acid	Ppb	Water, soil and plant residues	[24]
AuNPs-Lys	0.0583 μM (0.02ppm)	Coastal water estuarine water Waste water	This work

also calculated for real sample analysis to check the precision of Hg<sup>2+</sup> analysis in coastal seawater. It is clear from Table 4 that for real sample analysis, with different matrix % RSD is within 5 % which confirms that data is precise.

#### *Comparison of Colorimetric Determination of Hg<sup>2+</sup> for Water Samples Using Lys-AuNPs as a Chemical Sensor*

Linearity range and LOD value obtained with the present work are compared with other NPs based sensors for determination of Hg<sup>2+</sup> from a variety of samples (Table 4).

With our method, the LOD obtained for coastal water is 0.02 ppb i.e., 0.058 μM which is much below the published work for coastal water analysis and guidelines for recreational water. The added advantage of our method is minimal sample preparation. The other reported methods are found to be tedious, time-consuming, and multiple steps procedures. With our sensor, the cost of one test performed using our colorimetric assay is very low (around 0.5 cents), which is calculated based on reagent prices. Because of its simplicity (single-step reaction), excellent sensitivity, and selectivity, our colorimetric assay is advantageous over several metal nanoparticle-based methods (Table 2) and feasible for practical applications for on-site analysis of coastal water.

#### CONCLUSION

In this paper, a highly selective lysine-capped gold nanoparticles optical sensors method for ppb levels of Hg<sup>2+</sup> ions in coastal seawater has been shown in the range of 0.02-1 ppm. The range is useful to discriminate between polluted and non-polluted recreational water samples as per international guidelines. This method does not require any

costly and laborious sample preparation steps. This method is highly selective for Hg<sup>2+</sup> ions, and almost all metal ions examined gave no response at that wavelength. The developed method has the potential for performing on microwell plates and thus can serve as a high throughput screening method.

Unlike most of the chemosensors for Hg<sup>2+</sup> which have been evaluated in organic media or organic-aqueous mixtures owing to their low water-solubility, the high-water solubility of the AuNPs-Lys probes allow this assay to be performed in aqueous media without the need for organic co-solvents. In all, the simplicity of the developed sensor makes it a potent screening technology for Hg<sup>2+</sup> in seawater for the future.

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#### DISCLOSURE STATEMENT

No potential conflict of interest was reported by the authors.

#### SUPPLEMENTARY INFORMATION

Please find Supplementary Information on [Journal website](#).

#### REFERENCES

1. Ram A, Rokade M and Zingde MD, 2009. Mercury enrichment in sediments of Amba estuary. Indian Journal of Marine science, 38-96. <http://re.indiaenvironmentportal.org>.

- [in/files/Mercury%20enrichment.pdf](#)
- Ram A., Rokade M, Borole D V, Zingde M.D, 2003. Mercury in sediments of Ulhas estuary Marine Pollution Bulletin,7: 846-857. [https://doi.org/10.1016/S0025-326X\(03\)00065-1](https://doi.org/10.1016/S0025-326X(03)00065-1)
  - Dimitrakakis E, Hahladakis J, Gidarakos E, 2014. The "Sea Diamond" shipwreck: environmental impact assessment in the water column and sediments of the wreck area, Int. J. Environ. Sci. Technol.,11: 1421-1432. <https://doi.org/10.1007/s13762-013-0331-z>
  - Shanbehzadeh S, Dastjerdi M, Hassanzadeh A, Kiyanzadeh T, 2014. Heavy Metals in Water and Sediment: A Case Study of Tembi River. Journal of Environmental and Public Health, 1-5. <https://doi.org/10.1155/2014/858720>
  - Fujioka R, Sologabriele H, Byappanahalli M, Kirs M, 2015. US recreational water quality criteria: A vision for the future, Int. J. Environ. Res. Public Health,12: 7752-7776. <https://doi.org/10.3390/ijerph120707752>
  - USEPA report 1995, National Recommended Water Quality Criteria - Aquatic Life Criteria Table <https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table>.
  - Guidelines for Safe Recreational Water Environments: Coastal and fresh waters, Volume 1 by World Health Organization, 2003. <https://apps.who.int/iris/bitstream/handle/10665/42591/9241545801.pdf;jsessionid=B675308EB2911FF8EAD5F242410DF884?sequence=1>
  - European Standards for Drinking-water. [https://apps.who.int/iris/bitstream/handle/10665/40025/European\\_standards\\_for\\_drinking-water.pdf?sequence=1](https://apps.who.int/iris/bitstream/handle/10665/40025/European_standards_for_drinking-water.pdf?sequence=1)
  - Mason, R, Fitzgerald W and More Fm 1994. The biogeochemical cycling of elemental mercury: atherogenic influences. Geochim. Cosmochim. Acta, 58: 3191-3198. [https://doi.org/10.1016/0016-7037\(94\)90046-9](https://doi.org/10.1016/0016-7037(94)90046-9)
  - Mehdinia A, Mashkani M & Jabbari A, 2016. Polythionine-decorated magnetic nanoparticles as a robust and highly effective sorbent for mercury determination in environmental water samples, International Journal of Environmental Analytical Chemistry, 11: 1091-1104. <https://doi.org/10.1080/03067319.2016.1232719>
  - Chen L, Li J and Chen L, 2014. Colorimetric Detection of Mercury Species Based on Functionalized Gold Nanoparticles Appl. Mater. Interfaces, 6:15897-15904. <https://doi.org/10.1021/am503531c>
  - Priyadarshini E, Pradhan N, 2006. Metal-induced aggregation of valine capped gold nanoparticles: An efficient and rapid approach for colorimetric detection of Pb<sup>2+</sup> ions, Scientific Reports, 7: 9278. <https://doi.org/10.1038/s41598-017-08847-5>
  - Roushenas S., Nikzad M F, Ghoreyshi A A., ghorbani M, 2022, Magnetic pectin nanocomposite for efficient adsorption of heavy metals from aqueous solution, Journal of Water and Environmental Nanotechnology. 7:69-88. <https://doi.org/10.22090/jwent.2022.01.006>
  - Dutta-Borah S, Baruah S, Soliman W and Dutta J. Heavy Metal Ion Sensing By Surface Plasmon Resonance on Gold Nanoparticles, 2015. ADBU-Journal of Engineering Technology, 1-4. <https://doi.org/10.1016/j.gsd.2015.12.004>
  - Wang Z, Lee J-H, and LuY, 2008. Label-Free Colorimetric Detection of Lead Ions with a Nanomolar Detection Limit and Tunable Dynamic Range by using Gold Nanoparticles and DNAzyme, Adv. Mater. 20: 3263-3267. <https://doi.org/10.1002/adma.200703181>
  - Senser G., Uzun L., Denizil A. 2014, Lysine - promoted colorimetric response of gold nanoparticles: A simple assay for ultrasensitive Mercury (II) detection. Analytical Chemistry, 86: 514-520. <https://doi.org/10.1021/ac403447a>
  - Lou T., Chen Z., Wang Y and Chen L, 2011. Blue-to-Red Colorimetric Sensing Strategy for Hg<sup>2+</sup> and Ag<sup>+</sup> via Redox-Regulated Surface Chemistry of Gold Nanoparticles ACS Appl. Mater. interfaces, 3: 1568-1573. <https://doi.org/10.1021/am200130e>
  - Chaudhary A, Dwivedi C, Chawla M., Gupta A and Nandi C, 2015. Lysine and dithiothreitol promoted ultrasensitive optical and colorimetric detection of mercury using anisotropic gold nanoparticles J. Mater. Chem. C, 3: 6962. <https://doi.org/10.1039/C5TC01397F>
  - Selvakannan P, Mandal S, Phadtare S, Pasricha R and Sastri M, 2003. Capping of Gold Nanoparticles by the Amino Acid Lysine Renders Them Water-Dispersible, Langmuir, 19: 3545-3549. <https://doi.org/10.1021/la026906v>
  - Sarkar B and Mondal P. 2021. Colorimetric Sensors of Hg<sup>2+</sup> Ion Based on Functionalized Gold and Silver Nanoparticles, J. Water Environ. Nanotechnol., 6(1): 22-40. <https://doi.org/10.22090/jwent.2021.01.003>
  - Liu B and Wang M, 2014. Selective Determination of Iron (III) in Sea Water by Gold Nanoparticles Self-assembled with N-carboxyl- L-cysteine, Journal of New Materials for Electrochemical Systems.17: 1-4. <https://doi.org/10.14447/jnmes.v17i1.274>
  - Lin C-Y, Yu C-J, Lin Y-H and Tseng W-L, 2010. Colorimetric Sensing of Silver (I) and Mercury (II) Ions Based on an Assembly of Tween 20-Stabilized Gold Nanoparticles. Analytical Chemistry, 82: 6830-6837. <https://doi.org/10.1021/ac1007909>
  - Wang G and Sun W, 2006. Optical Limiting of Gold Nanoparticle Aggregates Induced by Electrolytes, J. Phys. Chem. B. 110, 20901-20905. <https://doi.org/10.1021/jp0638843>
  - Lee J-S, Han M and Mirkin C, 2007. Colorimetric Detection of Mercuric Ion (Hg<sup>2+</sup>) in Aqueous Media using DNA-Functionalized Gold Nanoparticles, Angew. Chem. Int. Ed. 46: 4093 -4096. <https://doi.org/10.1002/anie.200700269>
  - Kiran K,2015. Gold nanoparticles for mercury determination in environmental water and vegetable samples. Appl Nanosci, 5:361-366. <https://doi.org/10.1007/s13204-014-0325-2>
  - Velswamy P, Vincet A, Iswariyaa S, Perumalc P and Tiruchirappalli Uma, 2016. Gold nanoparticle based nano systems for the colorimetric detection of Hg<sup>2+</sup> ion contamination in the environment, RSC Advances, 00: 1-13.
  - Sarkar A., Gaitonde D., Sarkar A., Vashistha D., D'Silva C., Dalala S, 2008. Evaluation of impairment of DNA integrity in marine gastropods (Cronia contracta) as a biomarker of genotoxic contaminants in coastal water around Goa, West coast of India. Ecotoxicol. Environ. Saf. 71:471-482. <https://doi.org/10.1016/j.ecoenv.2008.01.006>