

Applications of organo-silica nanocomposites for SPNE of Hg(II)

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Abstract An analytical method using modified SiO₂ nanoparticles as solid-phase extractant has been developed for the preconcentration of trace amounts of Hg(II) in different water samples. Conditions of the analysis such as preconcentration factor, effect of pH, sample volume, shaking time, elution conditions and effects of interfering ions for the recovery of analyte were investigated. The adsorption capacity of nanometer SiO₂-APTMS was found to be 181.42 μmol g⁻¹ at optimum pH and the detection limit (3σ) was 0.45 μg L⁻¹. The extractant showed rapid kinetic sorption. The adsorption equilibrium of Hg(II) on nanometer SiO₂-APTMS was achieved just in 15 min. Adsorbed Hg(II) was easily eluted with 4 mL of 2.0 M hydrochloric acid. The maximum preconcentration factor was 75. The method was applied for the determination of trace amounts of Hg(II) in various synthetic samples and water samples.

Keywords SiO₂-nanoparticles · Solid phase extraction · Preconcentration · Separation

Introduction

In recent years, the toxicity and effects of trace elements to the danger of public health and environment have attracted increasing attention in the fields of pollution and nutrition. Hg(II) and its organometallic species are considered to be highly toxic to the environment, especially the aquatic system. Hg(II) is leached from rocks and soils into water system

by natural processes, some of which are accelerated by human activities. The World Health organization (WHO) recommends a limit of 1 μg L⁻¹ of Hg(II) in drinking water. Direct determination of mercury element at trace levels by conventional method is limited on account of its low concentration and matrix interferences. In trace analysis, therefore preconcentration or separation technique is frequently necessary to improve the detection limit and selectivity. It has become necessary to develop an accurate and sensitive method for quantitative determination of Hg(II) the environmental samples. One of the most important objectives for analytical chemists is metal quantification at low concentration level below μg L⁻¹ or ng mL⁻¹. Despite recent progress in instrumental techniques and increases in the selectivity and sensitivity of analytical techniques, direct determination of trace elements in sample is still difficult. Therefore, preconcentration and selective separation of trace elements from different water samples is very important and need much more attention.

Therefore, accurate and reliable methods sometimes must be developed for mercury determination. Because of their extremely low concentration, a preliminary concentration step i.e., preconcentration is usually necessary prior to the determination of the metals (Yaman 1999; Anezaki et al. 1998; Zolotov et al. 1995; Karadjova 1999; Shar and Soomaro 2004; Qufen et al. 2002). Nowadays, many separation/preconcentration techniques for metal ions determination include liquid–liquid extraction, (Liska 1993; Martinez et al. 2000; Bruzzoniti et al. 2000) ion-exchange resins, (Cao and Fang 1998; Yang et al. 2004) resin chelation and solid-phase extraction (Alonso et al. 2001; Henglein 1989; Xue and Xu 2003). Of all these methods, solid phase extraction has been widely used in comparison with traditional extraction techniques; since it is simple, rapid and inexpensive, less polluting to the environment

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and can be easily automated. Nowadays, nanometer materials have become more important owing to its special physical and chemical properties. The field of nanocomposite materials has received the attention, imagination and close scrutiny of scientists and engineer in recent years. These particles fall within the colloidal range, exhibiting typical colloidal properties. One of the specific properties of nanomaterials is that a high percent of atoms of the nanoparticle is on the surface. The surface atoms are unsaturated and can therefore bind with other atoms, possess high chemical activity. Nanoparticles exhibit intrinsic surface reactivity and high surface areas and can strongly chemisorb many substances. The size, surface structure and interparticle interaction of nanomaterials determine their unique properties and the improved performances and make their potential application in many areas (Xue and Xu 2003; Okuyama and Lenggoro 2003). Nanoparticles such as TiO_2 (Vassileva and Furuta 2001; Hosono et al. 2004), Al_2O_3 (Hiraide et al. 1997), ZrO_2 (Sarkar et al. 2003), CeO_2 (Ragai and Selim 1987) and modified silica nanoparticles have been used for the preconcentration of many metal ions and give promising results when used for trace element analysis of different samples. In present work, chemically grafted SiO_2 -APTMS nanoparticles were prepared by sol–gel method and characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR). These nanoparticles have been used for the preconcentration and separation of cadmium prior to their determination by spectrophotometric method.

Experimental

Apparatus

Absorbance of Hg(II) was measured with UV–Vis Shimadzu-1700 spectrophotometer. The pH values were controlled by century Cp-901 digital pH meter. Infrared spectra were recorded on a Perkin Elmer FT-IR analysis.

Reagents and standard solutions

All reagents used were of analytical grade unless otherwise stated and all solutions were prepared in double distilled deionized water. 3-Aminopropyltrimethoxysilane (APTMS) of GR grade was supplied by Acros Organics (Mumbai). The glassware was washed with chromic acid and soaked in 5 % nitric acid overnight and then cleaned with double distilled water before use. The pH adjustments were made with hydrochloric acid and sodium hydroxide and buffer solutions of acetic acid and sodium acetate, ammonia and ammonium chloride, boric acid and sodium tetraborate were prepared to maintain the pH of the solution.

Modification process

Surface modification of SiO_2 nanoparticles were performed in a 250 mL flask. Nanometer SiO_2 (1 g) was dispersed into dry toluene (30 mL), and then 3-aminopropyltriethoxysilane (4 mL) was gradually added, with continuous stirring. The mixture was refluxed for 6 h. The silylated nanometer SiO_2 was filtered off, washed with toluene and ethanol and dried at 60 °C for 3 h. Reaction mixture was filtered under vacuum and the chemically modified nanoparticles were stored in dessicator.

General procedure

Aliquots of cadmium sulphate containing 0.5 µg of Hg(II) was prepared and pH was adjusted to the 6.8 with 0.2 M sodium tetraborate/boric acid buffer, 35 mg of SiO_2 -APTMS particles were added, and the mixture was shaken vigorously for 15 min to facilitate adsorption of metal ion onto the adsorbent. 4 mL of 2 M hydrochloric acid was used for elution of Hg(II) from the adsorbent. Then, eluent was filtered and was determined by standard spectrophotometric method.

Results and discussion

Characterization of SiO_2 -APTMS modified nanometer sized SiO_2

The modification of nanometer-sized material is usually required to prevent a conglomeration of particles and to improve its consistency in relation to other materials, such as organic polymers. In addition, for the purpose of separation, the modification of nanometer-sized materials can improve the selectivity of nanometer-sized materials towards metal ions, organosiloxane is the most often used modifiers, in which one side is linked with the inorganic nanometer-sized materials, and the exposed end is the analytical functional group. The modified nanometer SiO_2 -APTMS was characterized by FT-IR and SEM.

Synthesis of silica nanoparticles by Sol–gel method

Bead size and the dispersity of the particle population depend strongly on the concentrations of alkoxysilane, ammonia and water. Temperature is also a controlling factor in the synthesis. A number of different approaches were investigated and it was found that the desired 100 nm spherical silica particles could be reproducibly prepared by the following procedure.

250 mL of methanol and 250 mL ammonium hydroxide ($\text{SG} = 0.88$) were mixed in a 1000 mL conical flask for

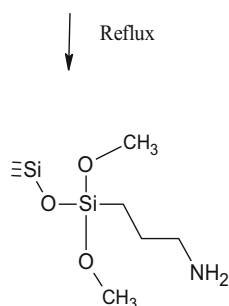
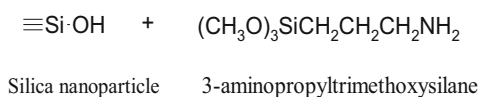
5 min using a magnetic stirrer. 5 mL of tetraethoxysilane was slowly added, whilst continuing the gentle stirring. The reaction was left to proceed at 20 °C for 1 h. The product was then centrifuged for 60 min at 3000 rpm at temperature of −4 °C and the supernatant was removed. The silica nanoparticles were rinsed with methanol several times, discarding the solvent at each stage after centrifugation. The silica nanoparticles were dried under vacuum and stored in a dry vial.

Modification of SiO₂ nanoparticles

Nanometer SiO₂ (1 g) was dispersed into dry toluene (30 mL) in a 250 mL flask, and then 3-aminopropyltrimethoxysilane (4 mL) was gradually added, with continuous stirring. The mixture was refluxed for 6 h. The silylated nanometer SiO₂ was filtered off, first washed with toluene and then with ethanol and dried at 60 °C for 3 h and stored in a dry vial.

Characterization of SiO₂-APTMS modified nanometer sized SiO₂

The modification of nanometer-sized material is usually required to prevent a conglomeration of particles and to improve its consistency in relation to other materials, such as organic polymers. In addition, for the purpose of separation, the modification of nanometer-sized materials can improve the selectivity of nanometer-sized materials towards metal ions, organosiloxane is the most often used modifiers, in which one side is linked with the inorganic nanometer-sized materials, and the exposed end is the analytical functional group. The modified nanometer SiO₂-APTMS was characterized by FT-IR and SEM.



Silica-APTMS nanoparticles

Determination of amino groups on the silica surface

The method is based on the reaction between primary amines and ninhydrin, which produces a complex purple compound, known as Ruhemann's purple, which absorbs strongly at 570 nm ($\epsilon = 22,000 \text{ mol L}^{-1} \text{ cm}^{-1}$).

Scanning electron microscopy (SEM)

The average diameter of the nanoparticles SiO₂ and SiO₂-APTMS was 100 nm and 1 μm confirmed by SEM. Figures 1a, b and 2a, b reveals the average size as well as the morphology of SiO₂ nanoparticles, SiO₂-APTMS and respectively.

FT-IR Spectrum Analysis

The main absorption peaks of nanometer SiO₂ (3448.0, 1642.5, 1404, 1070.2, 964.2, 798.8 cm^{-1}) are in agreement with standard spectrum of SiO₂. It reveals that peak at 2907.2 cm^{-1} is due to C–H stretching, peak at 1641.3 cm^{-1} is due to N–H stretching and peak at 1093.5 cm^{-1} C–O stretching in 3-aminopropyltrimethoxysilane Fig. 3.

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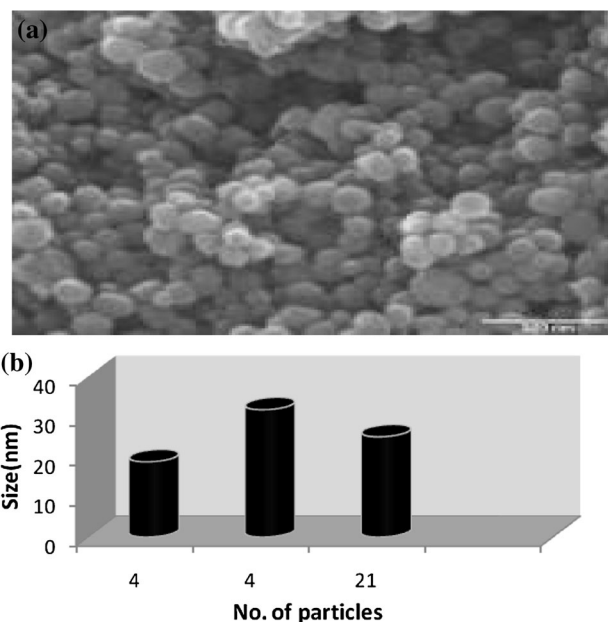


Fig. 1 a SEM micrograph of SiO₂ nanoparticles. b Particle size distribution plot for silica nanoparticles

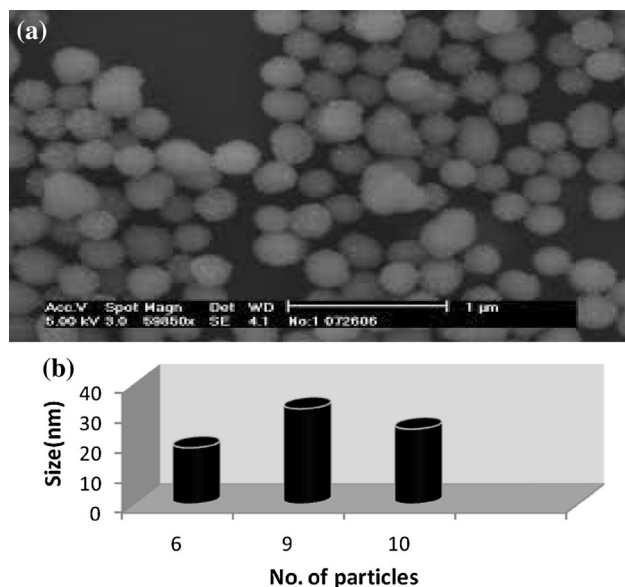


Fig. 2 **a** SEM micrograph of SiO₂-APTES nanoparticles. **b** Particle size distribution plot of APTES silica nanoparticles

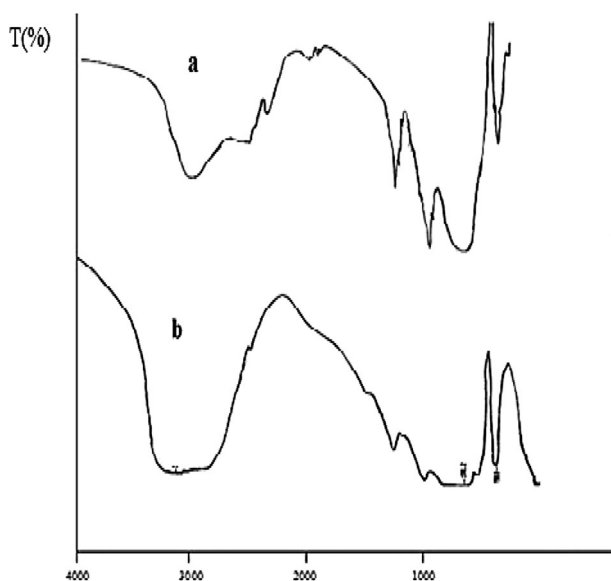


Fig. 3 FT-IR spectrum of **a** SiO₂-APTMS nanoparticles and **b** silica nanoparticles, respectively

Adsorption isotherm study

To investigate the relationship between the adsorbed species and their equilibrium concentrations, the data generated from the column studies were fitted to Langmuir, Temkin and Freundlich isotherm models.

Langmuir isotherm

The Langmuir isotherm is applicable to adsorption on homogeneous surfaces. According to this isotherm there are a constant number of available sites on the adsorbent surface. The linear form of this isotherm can be expressed as follows:

$$C_e/q_{\max} + 1/q_{\max} b$$

$$R_L = \frac{1}{1 + b_L C_0}$$

where b is a constant that increases with increasing molecular size and q_{\max} is the amount adsorbed to form a complete monolayer on the surface and C_e is the equilibrium concentration of the solute. The values of Langmuir constants q_{\max} and b were calculated from slope and intercepts, respectively, of plots of $\frac{C_e}{q}$ versus C_e . The values of q_{\max} and b for the removal of Hg(II) from aqueous solution were found to be 0.2565 mg g⁻¹ and 0.101 L mg⁻¹.

Freundlich isotherm

The Freundlich isotherm has also been widely used for many years to model analyte adsorption at equilibrium. The isotherm model describes the equilibrium on heterogeneous surfaces and hence does not assume a monolayer capacity.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

Temkin isotherm

The Temkin isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for analytes. The derivation of the Temkin isotherm indicates the multilayer adsorption on the adsorbent. The Temkin isotherm has generally been applied in the following form.

$$q_e = \frac{RT}{b_T \ln(A_T C_e)}$$

The Temkin isotherm can be expressed by following equation.

$$\frac{X}{M} = B \ln A + B \ln C_e$$

where C is the concentration of adsorbate in solution at equilibrium (mgL⁻¹), X is the amount of metal adsorbed (mg), m is the weight of adsorbent (mg) and A and B are constants related to adsorption capacity and intensity of adsorption. The generalized data pertaining to Hg(II) does not fit the Temkin isotherm as the isotherm constant obtained was $B = 0.049$ which is out of range (1–50). This

represents that there is no possibility for multilayer adsorption to take place.

It is clear that adsorption isotherm at temperature 35 °C can be fitted well using these isotherm models. However, the Langmuir model is more suitable than Freundlich model to describe the adsorption isotherm, as reflected with correlation coefficients. It suggests that adsorbent is homogenous and the adsorption is monolayer, the free energy (ΔG^0) of Hg(II) onto SiO₂-APTMS nanoparticles is calculated based on the adsorption isotherm.

$$\Delta G^0 = RT \ln b_L$$

where R is the universal gas constant; T (K) the 35 °C of the solution and b_L the Langmuir constant. The value of ΔG^0 is 20.2 kJ mol⁻¹. It is noted that the ΔG^0 value is negative, which indicate the feasibility and spontaneous adsorption of Hg(II) onto SiO₂-APTMS nanoparticles. The enthalpy change (ΔH^0) and entropy change (ΔS^0) could not be established because a linear relationship of $\ln b_L$ and $1/T$ in the Van't Hoff equation could not be established.

Effect of pH on enrichment recovery

The adsorption of Hg(II) on nanometer SiO₂-APTMS was studied at different pH value (3.4–10.0) following the recommended procedure. The results of effect of pH on the recoveries of the metal ions were shown in Fig. 4. It can be seen that a quantitative recovery ($\geq 95\%$) was found for Hg(II) in the pH range of 6.5–10.0.

Batch mode

Batch studies to measure the performance of the SPNEs in removing Hg(II) metal ions from waste water were conducted. For batch experiments the removal efficiency were tested by varying the dosage of the adsorbent,

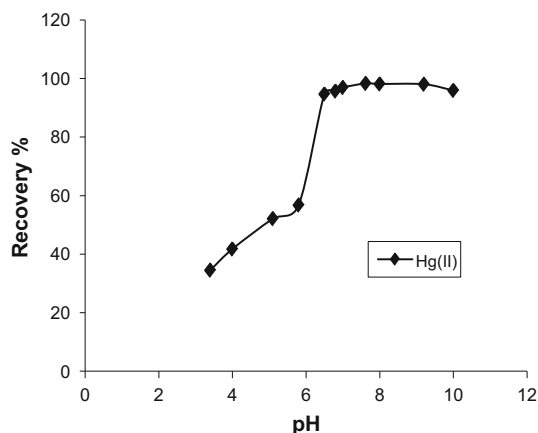


Fig. 4 Effect of pH on recovery (%) of analyte

concentration of the analyte solution, contact time and pH of the analyte solution. The pH of the solution was varied using the sodium hydroxide and hydrochloric acid. After the equilibrium time, the adsorbent was separated from the solution by centrifugation and then eluted with different concentrations of hydrochloric acid and determined by spectrophotometry. The amount of the analyte adsorbed per unit mass of the adsorbent was determined using the equation:

$$q = \frac{(C_0 - C_e) V}{W}$$

Effect of eluent concentration and volume

Since the adsorption of ferbam on nanometer SiO₂-APTMS at pH ≤ 2 is found to be negligible, elution will be favored in acidic solution. Elution of Hg(II) from nanometer SiO₂-APTMS extractant was investigated by using various concentrations of hydrochloric acid. It can be seen that quantitative recoveries ($\geq 95\%$) of Hg(II) can be obtained using 4 mL of 2 M hydrochloric acid as eluent. Therefore, 4 mL of 2 M of hydrochloric acid was used as eluent in subsequent experiments. The results of effect of eluent concentration and volume are given in Tables 1 and 2.

Effect of nanometer SiO₂-APTMS amount

To test the effect of amount of extractant on quantitative retention of analyte, different amount (5–50 mg) of nanometer SiO₂-APTMS were added into the solution following the experimental method. Quantitative extraction of the Hg(II) was obtained in the range of 5–50 mg of nanometer SiO₂-APTMS. 35 mg of nanometer SiO₂-APTMS as extractant was found to be sufficient for further studies. The results are shown in Fig. 5.

Effect of shaking time

The adsorption of Hg(II) on 35 mg of nanometer SiO₂-APTMS was studied for different shaking time (10–45 min).

Table 1 Effect of concentration of HCl solution on elution of Hg(II) ($n = 3$)

Concentration of eluent (M)	0.2	0.5	1.0	2.0	4.0	5.0
Recovery (%)	29.10	67.17	86.90	98.21	78.98	43.21

Table 2 Effect of volume of HCl solution on elution of Hg(II) ($n = 3$)

Volume of eluent (mL)	2.0	4.0	5.0	6.0	7.0	8.0
Recovery (%)	70.19	98.23	76.10	67.56	35.34	24.78

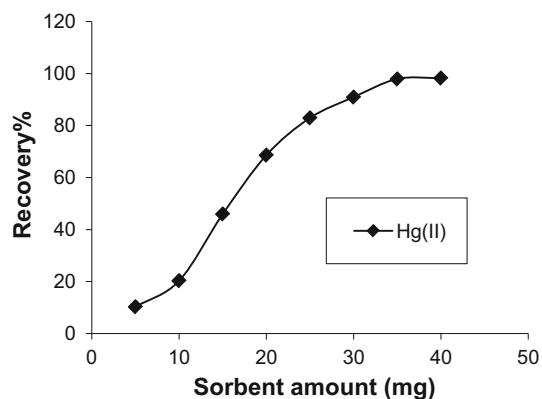


Fig. 5 Effect of sorbent amount on recovery (%) of analyte

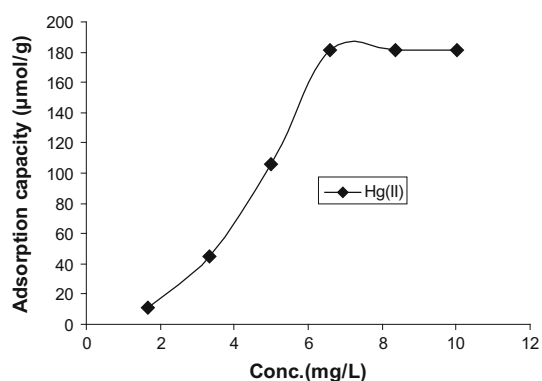


Fig. 6 Adsorption capacity of Hg(II) on nanometer SiO₂-APTMS

The results indicated that within 15 min the extraction percentage of Hg(II) $\geq 95\%$ was achieved. The results are shown in Fig. 6.

Adsorption capacity (Q_s)

The adsorption capacity (Mahmoud and Gohar 2000) is an important factor as it determines how much adsorbent is quantitatively required to concentrate the analytes from a given solution. A breakthrough curve was obtained by plotting the concentration (mg L^{-1}) versus the μmol of Hg(II) adsorbed per gram. From the breakthrough curve the amount of modified nanometer SiO₂-APTMS for Hg(II) was found to be $181.42 \mu\text{mol g}^{-1}$ at pH 6.8, respectively. The results are shown in Fig. 7.

Effect of sample volume

To explore the possibility of concentrating low concentration of analytes from large volumes, the effect of sample volume on the retention of metal ions was also investigated. For this purpose 50, 100, 150, 200, 250, 300 and 400 mL of the sample

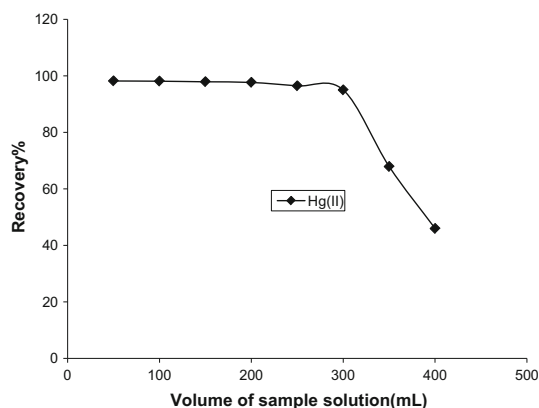


Fig. 7 Effect of sample volume on analyte recovery

solutions containing $1.0 \mu\text{g Hg(II)}$ was shaken, quantitative recoveries ($\geq 95\%$) were obtained for sample volume of $\leq 300 \text{ mL}$ for Hg(II). The results are given in Fig. 8.

Effect of coexisting ions

The effect of common coexisting ions on the sorption of Hg(II) was investigated. In these experiments, a solution of $1.0 \mu\text{g mL}^{-1}$ of Hg(II) that contains the added interfering ion was analyzed according to the recommended procedure. The tolerance of coexisting ions defined as the largest amount making the recoveries of Cd(II) less than 90% . In the determination of Hg(II), interfering ions like Cd(II), Cu(II) Fe(II) and Fe(III), were masked with 1 mL of 5% of sodium fluoride solution and Bi(II), Pb(II), Co(II) and Ni(II) were masked with 2 mL of 1 M sodium citrate. Besides, a lot of anions NO_3^- , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{C}_2\text{O}_4^{2-}$, H_2PO_4^- , I^- , CO_3^{2-} and Cl^- etc, did not interfere in preconcentration and determination of Hg(II).

Stability and reusability of adsorbent

The reusability and stability of the adsorbent was investigated. The capacity of the modified adsorbent was found to be apparently constant (less than 3%) after the repeated use of more than four cycles of sorption and desorption of the target analytes.

Salting out effect

Addition of an electrolyte can reduce the extraction time by increasing the ionic strength and reducing analyte solubility. The electrolytes generally used for this purpose are NaCl, NaHCO_3 , K_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$. The salting out effect makes SPE more effective.

Table 3 Analytical recovery of Hg(II) added to some water samples

Samples	Added ($\mu\text{g/L}$)	Found ($\mu\text{g/L}$)	Recovery (%)
Tap water	20.0	19.70	98.50
Mineral water	20.0	19.85	99.25
Waste water	0.0	8.57	–
	10.0	18.46	98.90

Table 4 Figure of merit of comparable methods for the determination of Hg(II) by solid-phase extraction

Support	Reagent	LOD ($\mu\text{g/L}$)	References
Silica gel	3-(2-Thioimidazolyl) propyl	5.0	(Stober et al. 1968)
Silica gel	Dithioacetal	10.0	(Toral et al. 2004)
Silica gel	3-Mercaptoimidazole	5.0	(Vassileva and Furuta 2001)
Silica gel	2-Amino-1,3,4-thiadiazole	5.0	(Yaman 1999)
Silica gel	Xylenol orange	10.0	(Yang et al. 2004)
Silica gel	Methyl thiosalicylate	10.0	(Zolotov et al. 1995)
Silica nanoparticles	APTMS	0.45	This work

The influence of ionic strength on the extraction of Hg(II) in batch method was studied using sodium/or potassium chloride, bromide, sulphate, nitrate, chlorate (pH 2) with concentrations (0.1 mol L^{-1} to saturation). The results showed no effect on the extraction efficiency. These observations showed the specific tendency of SiO_2 -APTMS nanoparticles for Hg(II) and the possibility of using this method for separation of Hg(II) from highly saline solutions.

Analytical precision and detection limit

Under the selected conditions, three portions of Hg(II) standard solutions was enriched and analyzed simultaneously following the experimental method. The relative standard deviation (RSD) of the method was 1.2 % for the determination of $6.0 \mu\text{g Hg(II)}$ in 100 mL water samples respectively. The detection limit of this method for Hg(II) was $0.45 \mu\text{g mL}^{-1}$.

Applications

The developed method has been applied for the determination of trace Hg(II) in tap water, mineral water, waste water samples. For analysis, 200 mL of tap, mineral or waste water were studied by the developed method. The relative standard deviation (RSD %) and the detection limit

of the method were 2.1 and $0.45 < \mu\text{g L}^{-1}$, respectively. Statistical analysis of these results using Student's *t* test showed that there was no significant difference between actual and found concentrations at 95 % confidence level. The results are given in Table 3.

Conclusions

The preconcentration method described by using 3-aminotripropyltrimethoxysilane anchored silica nanoparticles for the determination of Hg(II) in water samples has a good accuracy, repeatability and sensitivity. In this work, the advantages of nanoparticles as the sorbent including high adsorption capacity and facile extraction were combined with the advantages of spectrophotometric detection, including simplicity, speed, and inexpensiveness. Compared to other methods (especially complex hyphenated systems) the method had low detection limit and good precision. Moreover, the method was simple and fast. The results of comparison of preconcentration factor are given in Table 4.

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