PRECONCENTRATION AND SEPARATION OF ULTRA-TRACE AMOUNTS OF MERCURY(II) USING ULTRASOUND-ASSISTED CLOUD POINT-MICRO SOLID PHASE EXTRACTION BASED ON MODIFIED SILICA AEROGEL WITH [1-(3,5-DICHOLOROPHENYL)-3(2-ETHOXYPHENYL)] TRIAZENE

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ABSTRACT

In this study, a separation-preconcentration procedure, ultrasound-assisted cloud point-micro solid phase extraction (USA-CP-MSPE) with modified silica aerogel, was developed for the determination of Hg (II) from water samples- modified silica aerogel (SA) adsorbent coupled with metal chelating ligands of [1-(3,5-dicholorophenyl)-3(2-ethoxyphenyl)] triazene (DCPEPT). The adsorbent was characterized by fourier transform infrared spectra (FTIR) and scanning electron microscope (SEM). Some effective factors that influence the microextraction efficiency were investigated and optimized. Desorption study showed that over 96.25 % of Hg(II) could be desorbed from SA-DCPEPT with 1M KBr solution. The influences of some cations and anions on Hg(II) recoveries were also examined. An enhancement factor of 110 was achieved with 1mL sample. The detection limit for mercury(II) ions was 1.5 ng L^{-1}. This method is a simple, fast, accurate, highly stable and selective method which has successfully been applied to the speciation of mercury in water samples.

Keywords: Mercury(II); Triazene; Ultrasound-assisted cloud point-micro solid phase extraction; silica aerogel

INTRODUCTION

Mercury is a global pollutant identified as a highly toxic element due to its accumulative and persistent character in the environment and living organisms [1]. Mercury can induce damage to the central nervous system, lead to renal function impairment, and result in chest pain and dyspnea [2]. One of the main routes of incorporation of mercury into the human body is drinking water [3]. Therefore, determination of mercury is of utmost importance, especially in the water system. Different analytical techniques, such as spectrophotometry [4], inductively coupled plasma mass spectrometry (ICP-MS)[5], neutron activation analysis [6], electrothermal atomic absorption spectrometry (ETAAS) [7], atomic fluorescence spectrometry (AFS) [8], cold vapor atomic absorption spectrometry (CV-AAS) [9], and flow injection-inductively coupled plasma optical emission spectrometry (FI-ICP-OES) [10], can be used for the determination of trace Hg; for most applications, separation and preconcentration are still often recommended before detection due to its extremely low concentration in water samples. For this purpose, several techniques such as cloud point extraction [11], electroanalytical techniques [12], dispersive liquid-liquid microextraction [13], membrane separation [14], ion exchange [15], solid phase extraction (SPE) [16], and resin chelation [17] have been reported for preconcentration of trace mercury(II). Ultrasound-assisted cloud point-micro solid phase extraction (USA-CP-MSPE) investigated in this study is a simple and fast microextraction technique. Ultrasound-assisted cloud point-micro solid phase extraction (USA-CP-MSPE) presented by Falahnejad, M.(USA-CP-MSPE), is a simple, highly sensitive, efficient, and fast technique for the separation and preconcentration of traces of Pb (II) ions in water samples [18].

Nanomaterials, possessing high surface area and excellent adsorption ability, have received extensive attention in the field of preconcentration. Silica aerogels are commonly known as unique porous materials with highly cross-linked network structure having large specific surface area, high porosity, low density and very low thermal conductivity [19]. Furthermore, one of the most notable properties of silica aerogels is also the possibility to modify their surface chemical nature through the incorporation of organic functional groups [20]. In recent years, silica aerogel (SA) surface modifications with chelating agents for adsorption of metal ions, such as polyacramide [21], mercaptopropyl [22]and 4-amino-5-methyl-1,2,4-triazole-3(4H)-thion [23] have been reported with successful rates of incorporation.

In the present study, newly synthesized [1-(3,5-dicholorophenyl)-3(2-ethoxyphenyl)] triazene ligand (DCPEPT), as the metal chelating ligand, (see Fig. 1 for structure) was used and its application for separation-preconcentration of Hg(II) ion was examined. Triazene compounds, characterized by a diazoamino group (–N=N–N–), have been studied for over 130 years owing to their interesting structural and anticancer properties [24]. Recently, it has also been reported that synthesized triazene ligands are interestingly applicable for the determination of silver ions by solid phase extraction [25] and the determination of Hg(II) by an optical sensor [26].
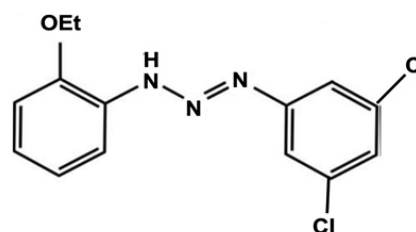

Fig. 1: Structure of [1-(3,5-dicholorophenyl)-3(2-ethoxyphenyl)] triazene (DCPEPT).

In the present study, USA-CP-MSPE based nanostructured modified silica aerogel (SA-DCPEPT) was used, as a new nanoadsorbent, for separation and preconcentration of Hg(II) ions in water samples. Various analytical parameters, including pH, adsorbent dose, time and temperature of ultrasonic bath etc., were optimized. The method has also been extended to include the extraction of Hg(II) from some water samples in the presence of a large amount of other ions.

EXPERIMENTAL

Reagents and apparatus

All chemicals used were of analytical-reagent grade and all solutions were prepared with doubly distilled deionized water. Hg(II) stock solution (1000 mgL^{-1}) was prepared by dissolving 0.3426 g Hg(NO$_3$)$_2$·H$_2$O in water and 0.5mL of 1 molL^{-1} HNO$_3$ diluted to 100mL in a standard flask. Tetramethoxysilane (TMOS) and methyltrimethoxysilane (MTMS) from Aldrich and other reagents used in the present study were of analytical grade from E. Merk. DCPEPT were prepared according to the method described in previous work[27]. Overall, 0.1% (m/v) of DCPEPT solution was daily prepared in acetonitrile mixture. A thermostated magnetic stirring bath (GongyiYuhua Instrumentation Factory, China), model DF-101S, was used and centrifugation was carried out using a Kokusan, H-11ncentrifuge (speed range 0-6000 rpm, timer 0-60 min). A pH meter (a Seven Mettler Toledo, Shanghai, China.) was employed for pH adjustments.

Adsorbents' synthesis

The 5.02 mL TMOS was diluted with 44.2 mL of methanol; then 1.5 mL of MTMS was added. Finally 1.2 mL F (0.1 molL^{-1}) solution was added to the mixture. Then the mixture was stirred at 20°C for 30 minutes. After the intermediate product was homogenized by a homogenizer (20000 rpm), 0.033g DCPEPT was added to the mixture. The mixture was poured into a Teflon beaker where the sol was aged into hydrogel within about ten minutes. After gelation, the gel was left for one day. Subsequently, the product was thoroughly

immersed into methanol for 24h and dried at room temperature for five days. Eventually, the SA-DCPEPT adsorbent was obtained.

Microextraction procedure

Hg(II) batch adsorption experiments were performed in glass conical flasks. 1mL of Triton X-100 1% (v/v) was added to 100mg of SA-DCPEPT. The flasks were kept for shaking at 200 rpm in an orbital shaker (Riviera, India) for one minute. 10 mL of the standard solution or pre-treated sample containing Hg(II), (10 mg L^{-1}), was added to the above mixture. The sample was kept in an ultrasound bath for five minutes. Then, this solution was placed in a thermostated bath at 50 °C for five minutes. Subsequently, the solution was cooled in an ice bath for five minutes. SA-DCPEPT was separated by centrifugation (three minutes, 4000 rpm). For desorbing the Hg(II) ions, 1mL of nitric acid (1 M) was added and shaken for about 60 minutes. Finally, 0.5 mL of this phase was removed and the concentration of Hg(II) was determined by atomic absorption spectrometry. Different parameters, such as pH, amount of nanoadsorbent, type and volume of eluent solvent, type and amount of surfactant, equilibrium temperature, and time and sonication times, were investigated. The extraction recovery was defined as the percentage of the total amount of analyte (m) that was extracted into the sedimented phase:

$$\%R = m_{sed}/m_o \times 100 = (C_{sed}/C_o)(V_{sed}/V_{aq}) \times 100$$

Where V_{sed}, V_{aq}, C_o and C_{sed} are the volumes of the sedimented phase and the sample solution, initial concentration of the analyte in the aqueous sample, and concentration of the analyte in the sedimented phase, respectively. The C_{sed} was calculated from the analytical curve.

Preparation of water samples

Water samples, including lake water and tap water, were collected from our lab and Kan Lake (Tehran, Iran). After sampling, all the real water samples were filtered through a 0.25 µm micro pore member prior to being applied to the removal of suspended particulate matter. Aliquots of 10.0mL from each sample solution were used for the analysis. All materials used for sampling activities were previously washed overnight with a 10% (v/v) HNO_3 water solution and rinsed with ultrapure water.

RESULTS AND DISCUSSION

Characterization

Figs. 2 (a) and (b) show the SEM micrographs of the SA and SA-DCPEPT. Silica aerogel particles range from 10 to 40µm; SA-DCPEPT particles fall between 30 and 80µm. In Fig. 3, the FTIR investigation of silica aerogels modified with SA-DCPEPT is shown in comparison to SA. The broad absorption band in the region 3440-3435 cm^{-1} and band at 1636-1642 cm^{-1} respectively attributed to the adsorbed water and surface silanol groups [28]. Silica aerogel exhibits bands in the 1250-1050 cm^{-1}region and 800 cm^{-1} and 457 cm^{-1} which are easily attributed to the Si-O-Si asymmetric and symmetric stretching vibrations of the silica network, respectively [29]. The strong and broad peaks obtained for SA-DCPEPT samples at 1100 cm^{-1} appear due to Si-OR group. At lower wavelength peaks, these samples appear due to asymmetry, symmetry and bending modes of SiO_2, respectively- as in the case of unmodified silica aerogel. As expected for SA-DCPEPT samples, new but weak and sharp peaks appeared at 3120 cm^{-1} due to NH groups. Moreover, new peaks appeared at 1315 cm^{-1} due to C–N groups, at 1496cm^{-1} due to N=N stretching vibration, and at 1180 cm^{-1} due to N–N groups [30-32]. These peaks are not observed for silica aerogel. Peaks at around 1600 cm^{-1} and 3400 cm^{-1} on both graphs correspond to O-H stretching, provided that they are sharper in the case of unmodified silica, which contains more O-H groups. These two peaks are the weakest in the case of SA-DCPEPT sample, where the amount of precursor amine group is increased. The above FTIR data indicates that strong interactions exist on the interface of silica aerogel and DCPEPT, and silica aerogel is successfully modified by DCPEPT.

Optimization of USA-CP-MSPE parameters
Effect of pH

The pH of the aqueous phase is one of the most important factors in extraction of metal ions from various media for the formation of metal complex [33]. In order to obtain the desired separation and preconcentration efficiencies, pH values were studied. The effect of pH on the complex formation of Hg(II) was studied in a range of 2.0-12.0 (Fig. 4. shows the removal percentage versus pH). For SA-DCPEPT, between pH values 3.0 and 6.0, the metal sorption increases sharply, reaching values that almost decrease for pH values

in the range of 7.0-12.0. At lower pH (<6), Hg(II) was in the free ionic form of Hg(II) [34], and the positively charged hydrogen ions may have competed with the Hg(II) for binding sites on the amino groups on the surface of the SA-DCPEPT. Once the amino groups were protonated, the strong electrical repulsion prevented Hg(II) from contacting the surface of the SA-DCPEPT, resulting in lower adsorption capacities at lower pH, which can be attributed to the decreased solubility of Hg(II) at high pH. At lower pH (>6), the surface of SA-DCPEPT was negatively charged, which negatively decreased surfactant coating through electrostatic force of repulsion. Consequently, adsorption decreased at pH values higher than 6. Therefore, pH 6.0 was selected for the subsequent experiments. In order to control the pH during the analytical procedure, it was adjusted to 6.0 with a buffer solution of acetate/acetic acid.
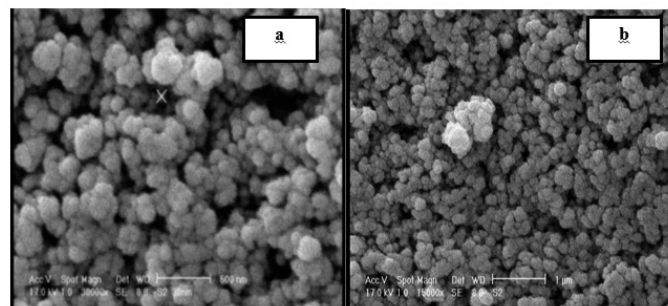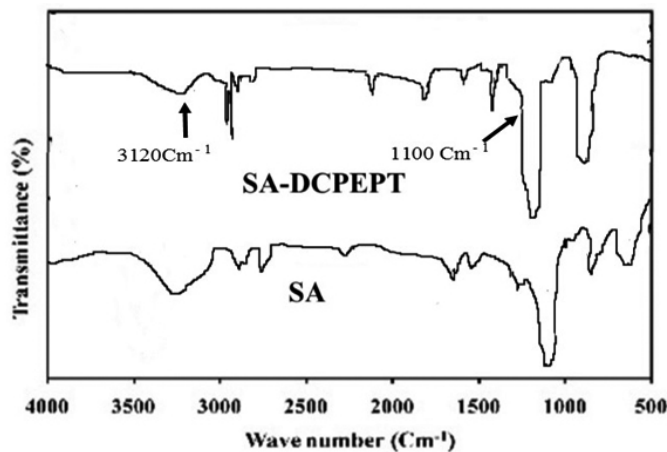

Fig. 2: The SEM image of (a) SA and (b) SA_ DCPEPT.

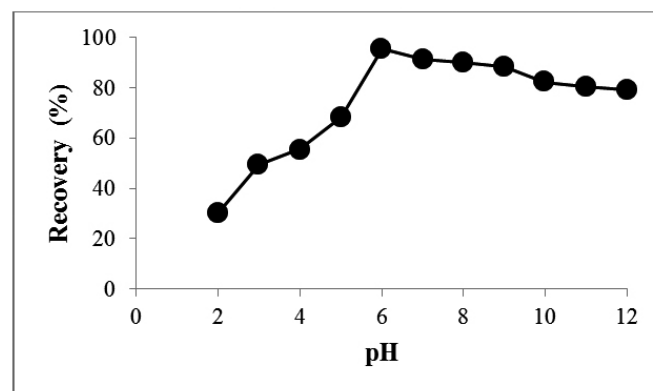**Fig. 3:** FTIR absorption spectra of aerogel samples SA, SA–DCPEPT

Fig. 4: Effect of pH on adsorption of mercury(II) ions.
$[Hg^{2+}]_0 = 10$ mgL^{-1} ; solution volume = 10 mL ; surfactant= 1.0 mL Triton X-100 (1%) ultrasound bath=6 min; thermostat water bath=5 min (50 °C); ice bath= 5 min; centrifugation=3 min (4000 rpm); elution solvent=1 mL HNO_3 (1M) t = 1 h , 20 °C.

Effect of adsorbent dose

The effect of the quantity of SA-DCPEPT on the enrichment-recovery of Hg(II) was investigated (Fig. 5). To investigate this effect, several quantities of these adsorbents were tested. Masses between 10 and 100 mg were used per experiment. The results showed that 50 mg of sorbent is sufficient for Hg(II) extraction in the sample and for adsorbent dosages higher than these values, mercury ions removal remained almost constant. Increases in adsorption with increases in adsorbent dosage are attributed to the availability of larger surface areas and more adsorption sites. Thus, in all experiments 50 mg of sorbent was chosen.
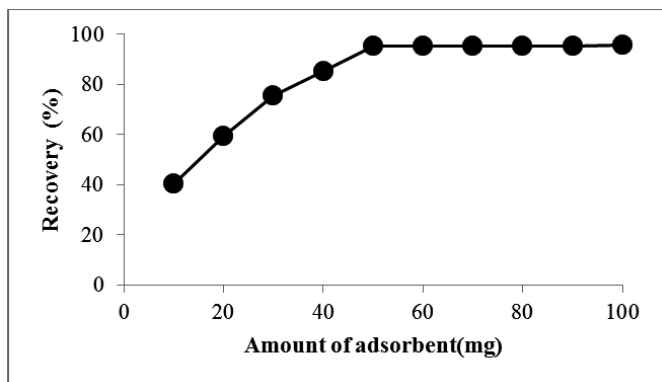

Fig. 5: Influence of adsorbent dose on mercury(II) adsorption. $[Hg^{2+}]_0 = 10$ mgL^{-1}; solution volume = 10 mL; pH= 6; surfactant= 1.0 mL Triton X-100 (1%)ultrasound bath=6 min; thermostat water bath=5 min (50 °C); ice bath= 5 min; centrifugation=3 min (4000 rpm); elution solvent=1 mL KBr (1M) t = 1 h , 20 ^{0}C.

Time and temperature of ultrasonic bath

Sonication time is a reflection of adsorption rate, which determines the time required for perfect adsorption. Different sonication times in the range of 2-16 minutes were examined according to the batch method. Removal percentage of Hg(II) versus sonication time is demonstrated in Fig. 6. As seen, 95% of the adsorption was accomplished during six minutes. Thus, a duration of five minutes was used in the subsequent experiments. The effect of ultrasonic testing in different temperatures on extraction was studied by varying the temperature. Three different temperatures of 20, 40, and 60 °C were considered. It can be observed that the removal percentage decreased for Hg(II) ions. Further increases in temperature induced a decrease in recovery. Hence, extraction was performed at room temperature.
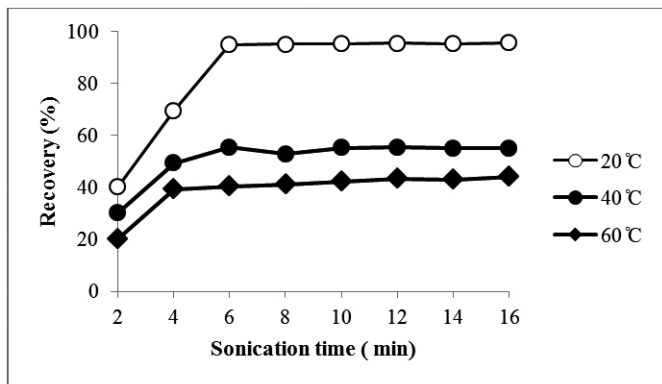

Fig. 6: Influence of sonication time on mercury(II) adsorption. $[Hg^{2+}]_0 = 10$ mgL^{-1}; solution volume = 10 mL; pH= 6; surfactant= 1.0 mL Triton X-100 (1%) ultrasound bath=6 min; thermostat water bath=5 min (50 °C); ice bath= 5 min; centrifugation=3 min (4000 rpm); elution solvent=1 mL KBr (1M) t = 1 h , 20 ^{0}C.

Effect of temperature and time on CPE procedure

The temperature in CPE procedure is an important factor affecting the reaction rate. In this study, the temperature was evaluated from 20 to 50°C.

The results illustrated that the extraction efficiency increased by increasing the temperature to 50°C. Accordingly, 50°C was chosen as the optimum temperature. Plus, various times were analyzed for extraction in the range of 5-25 minutes, and a duration of five minutes was chosen for extraction. The results also showed that the standing time of surfactant-enriched phase in an ice bath had no significant effects on the extraction efficiency. Accordingly, a standing time of five minutes in an ice bath was chosen for the next experiments. The effects of centrifugation rate on the absorbance of Hg(II) were studied. It was also found that when the solution was centrifuged at 4000 rpm for three minutes, the extraction performance increased. Hence, a duration of three minutes was chosen as the optimum time.

Desorption experiments

Desorption studies help elucidate the mechanism of sorption and recover metals from wastewater and sorbent (Fig.7). In order to evaluate the influence of the chemical nature of the elution solution, various eluents, such as Thiourea, and KSCN, HCl, KBr and HNO$_3$, were investigated for the elution of adsorbed Hg(II) ions from the solution. The highest desorption was observed for the KBr solution as the effluent (96.25%). Additionally, in order to investigate the reusability of the SA-DCPEPT, five adsorption-desorption cycles were carried out under optimum conditions (Table 1). Non-statistically significant differences in the sorption and desorption of Hg(II) were noted during one to five successive sorption–desorption cycles. These results showed that SA-DCPEPT could be repeatedly used in Hg(II) sorption studies.
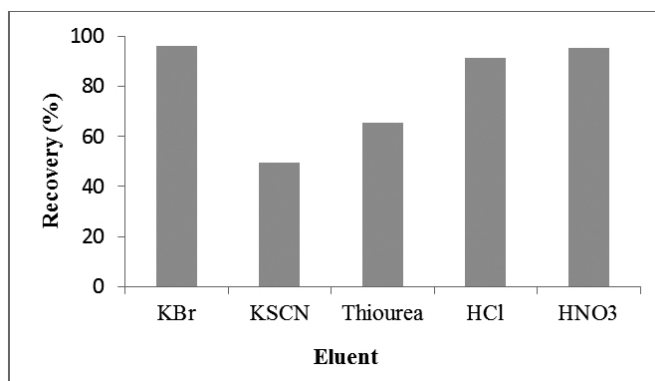

Fig. 7: Percentage of mercury recovered by using different eluant. $[Hg^{2+}]_0 = 10$ mgL^{-1} ; solution volume = 10 mL; pH= 6; surfactant= 1.0 mL Triton X-100 (1%) ultrasound bath=6 min; thermostat water bath=5 min (50 °C); ice bath= 5 min; centrifugation=3 min (4000 rpm); elution solvent=1 mL eluent (1M), t = 1 h , 20 ^{0}C.

Table- 1: Performance of fresh and recycled.

Cycle [a]	Fresh	(1st run)	(2nd run)	(3rd run)	(4rd run)
Recovery (%)	95.45	95.40	94.87	94.67	94.66

[a] $[Hg^{2+}]_0 = 10$ mgL^{-1} ; solution volume = 10 mL; pH= 6; surfactant= 1.0 mL Triton X-100 (1%) ultrasound bath=6 min; thermostat water bath=5 min (50 °C); ice bath= 5 min; centrifugation=3 min (4000 rpm); elution solvent=1 mL eluent (1M), t = 1 h , 20 ^{0}C

Interferences

The effects of potential interfering species were tested by the high selectivity for Hg-DCPEPT complex formation at pH 6 by using solutions containing 1mg.L^{-1}Hg(II) and adding various concentrations of potentially interfering ions. The tolerance limits of the coexisting ions, defined as the largest amount decreasing the recovery of Hg(II) ion to less than 5%. Table 2 shows the tolerance limits of the interfering ion concentrations. Most of the examined ions (Na$^+$, Mg^{2+}, and CH$_3$COO$^-$) did not interfere with the determination of Hg(II) at more than a 1000 fold excess, K$^+$, Al^{3+}, NO$_3^-$, Cl$^-$, Pb^{2+} and SO$_4^{2-}$ did not interfere at more than a 100-fold excess, and the cations (Mn^{2+}, Co^{2+}, Cr^{3+},Fe^{2+},Ni^{2+}, Zn^{2+} and Cu^{2+}) did not disturb determination at more than a 10-fold excess. According to the obtained data, most foreign cations and major cations in the water and real samples have no obvious influence on determination of Hg(II) ion under the selected conditions.

Table- 2: Tolerance limits of interfering ions in the determination of 1 mgL^{-1} of mercury.

Ion	Added as	Forein ion to Hg^{2+} concentration ratio	Recovery(%)
Na$^+$	NaNo$_3$	1000	95.40
Mg^{2+}	Mg(No$_3$)$_2$	1000	95.42
CH$_3$COO$^-$	CH$_3$COONa	1000	94.23
K$^+$	KNO$_3$	100	93.89
Al^{3+}	Al(No$_3$)$_2$	100	94.67
NO$_3^-$	NaNo$_3$	100	94.90
Cl$^-$	NaCl	100	93.69
Pb^{2+}	Pb(No$_3$)$_2$	100	93.11
SO$_4^{2-}$	Na$_2$SO$_4$	100	92.55
Mn^{2+}	Mn(No$_3$)$_2$	10	94.56
Co^{2+}	Co(No$_3$)$_2$	10	92.89
Cr^{3+}	Cr(No$_3$)$_3$	10	93.78
Fe^{2+}	Fe(No$_3$)$_2$	10	90.21
Ni^{2+}	Ni(No$_3$)$_2$	10	92.35
Zn^{2+}	Zn(No$_3$)$_2$	10	92.23
Cu^{2+}	Cu(No$_3$)$_2$	10	92.82

Analytical figures of merit

Under selected conditions, the calibration curves were observed as linear in the concentration range of 10^{-4}–10^{-8} molL^{-1} Hg(II) when using 10 mL of the solution. The regression equation was A = 0.170C + 0.0150 (where A is the absorbance and C is mercury concentration in µgL^{-1}), with a correlation coefficient(r) of 0.9997, which indicates good linearity in the mentioned concentration range. The limit of detection (LOD), based on a signal-to- noise ratio (S/N) of 3, was 1.5 ng L^{-1}. The relative standard deviation (RSD) of the method, determined by analyzing the standard solution at 10 mg L^{-1} of Hg(II) five times, was 1.5%, whereas the enhancement factor, defined as the slope ratio of two calibration curves for Hg(II) with and without preconcentration, was 110.

Samples analysis

The presented microextraction procedure was applied for preconcentration and determination of Hg(II) in several water (i.e., tap water and lake water) samples. Different amounts of Hg(II) were spiked to these samples in order to estimate the accuracy and applicability of the proposed method (Table 3). The recoveries for the spiked samples were in the acceptable range of 99-101%. Good agreement was obtained between the added and found analyte content using the recommended procedure. These results demonstrated that the proposed procedure could be satisfactorily used for the analysis of water samples.

Table- 3: Determination of mercury(II) in water samples .

Ion	Samples	Added (mgL^{-1})	Found (mgL^{-1}) [a]	Recovery (%)
Hg^{2+}	Tap wate	-	0.040±0.01	-
		10	10.234±0.03	101.94
		20	20.008±0.05	99.84
	lake water	-	0.160±0.03	-
		10	10.135±0.05	99.75
		20	20.101±0.08	99.70

[a] Mean of three experiments ± standard deviation.

Comparison of the proposed procedure with other methods

A comparison of the proposed method with others reported in preconcentration method for mercury determination is shown in Table 4. In comparison with other reported methods, the proposed method has low LOD and good RSD (%). This methodology is a reproducible, simple, and low-cost technique which does not require further instrumentation.

Table- 4: Comparison of USA-CP-MSPE method with other methods for determination of mercury(II).

Method	LOD (µgL^{-1})	RSD (%)	Sample volume (mL)	Reference
SDME-ETV-ICP-MS[a]	9.8×10^3	5.2	1.5	35
CPE-ETAAS	104	4	1	36
SPE-ICP-AES	100	4	1	37
L-LE- FICV-AAS[b]	2.3 ng L^{-1}	2.8	20	38
CPE-HPLC-ICP-MS[c]	4 ng L^{-1}	1.08	10	39
IL-SDME-LC[d]	22.8	11.6	12	40
PSIL-SPE-CVAAS[e]	2.4 ng L^{-1}	2.7	40	41
USA-CP-MSPE	1.5 ng L^{-1}	1.5	1	This work

[a] Single drop microextraction (electrothermal vaporization inductively coupled plasma mass spectrometry)
[b] Liquid–liquid extraction (flow injection-cold vapor atomic absorption spectrometry)
[c] Cloud point extraction (High performance liquid chromatography combined with inductively coupled plasma mass spectrometry)
[d] Ionic liquid-based single-drop microextraction (high-performance liquid chromatography)
[e] Polymer-supported ionic liquid solid phase extraction (cold vapor atomic absorption spectrometry)

CONCLUSIONS

In this study, modified silica aerogel with chelating ligands of [1-(3,5-dicholorophenyl)-3(2-ethoxyphenyl)] triazene (DCPEPT) was synthesized and applied to highly selective separation-preconcentration of Hg(II) ion from aqueous solution in ultrasound-assisted cloud point-micro solid phase extraction (USA-CP-MSPE) technique. Many effective factors in extraction of Hg(II), such as pH, adsorbent dose, time and temperature of ultrasonic bath, were optimized. The optimum pH for the adsorption was found to be 6.0 with the corresponding adsorbent dosage level of 50m g. Subsequently, equilibrium was achieved for Hg (II) with standing time of five minutes in an ice bath and sonication time of five minutes at room temperature. In addition, the effects of matrix ions presented in water samples were tolerable by the presented method.

These findings indicate that modified silica aerogel with DCPEPT can be used as an inexpensive, efficient, and environmentally safe adsorbent for separation–preconcentration of Hg(II) ion. With the proposed method, good LODs, precisions, accuracy and sensitivity and low RSD% were achieved. Moreover, a unique green solvent was introduced as an alternative to toxic organic solvents. Trace and ultra-trace mercury in water samples could be detected with good repeatability and spiked recoveries.

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