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Extraction of mercury (II) from sample water by Schiff base-chitosan grafted multi-walled carbon nanotubes

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A functionalized Schiff base-chitosan-grafted multi-walled carbon nanotubes (S-CS-MWCNTs) material has been studied on pre-concentration and determination of trace mercury. In this process, the effects of solution pH solution, elution conditions on pre-concentration of trace mercury were studied and the effect of interfering ions was also investigated. A novel S-CS-MWCNTs solid-phase extraction adsorbent was synthesized by covalently grafting a Schiff base-chitosan (S-CS) onto the surfaces of oxidized MWCNTs. The stability of chemically modified S-CS-MWCNTs especially in concentrated hydrochloric acid was then used as a recycling and pre-concentration reagent for further uses of S-CS-MWCNTs. The application of S-CS-MWCNTs for sorption of a series of metal ions was performed by using different controlling factors such as the pH of metal ion solution and the equilibration shaking time by the static technique. Hg(II) was found to exhibit the highest affinity towards extraction by these S-CS-MWCNTs phases. The pronounced selectivity was also confirmed from the determined distribution coefficient or dissociation constant (K_d) of all the metal ions, showing the highest value reported for Hg(II) to occur by S-CS-MWCNTs. The potential applications of S-CS-MWCNTs for selective extraction of Hg(II) to occur from aqueous solution were successfully accomplished as well as pre-concentration of low concentration of Hg(II) (60 pg ml^{-1}) from natural tap water with a pre-concentration factor of 100 for Hg(II) off-line analysis by cold vapor atomic absorption analysis.

Key words: Pre-concentration, Hg(II), Schiff base-chitosan-grafted multiwalled carbon nanotubes (S-CS-MWCNTs).

INTRODUCTION

Mercury (Hg) has been considered as a human health hazard because it may cause kidney toxicity, neurological damage, paralysis, chromosome breakage and birth defects (Manahan, 1994). Mercury itself and compounds are included in all lists of priority pollutants and different regulations and guidelines have been developed limiting their levels in water and sediments (Hayes, 1997). But it plays an important role in science and technology and inevitably exists in the environment (IARC, 1993; Jin et al., 2003; Seiler et al., 1998). The detection of Hg(II) has long held the attention of the analytical community and, as such, a large number of protocols have arisen (Smith 1963; Kantipuly et al., 1990; Greenway and Townshend, 1993; Manzoori et al., 1998). On the other hand, the toxicity level of mercury is becoming lower and lower, the direct determination of mercury at sub-microgram per liter level is suffered from the matrix interferences. It is

evident that the use of separation and pre-concentration procedures is still often necessary before the determination step, despite recent advances in analytical instrumentation (Pereira and Arruda, 2003). Recently, the solid-phase extraction (SPE) is being utilized for pre-concentration of heavy metals due to its flexibility, economical and environmental-friendly, absence of emulsion, speed and simplicity, sampling in the field, safety and ease of automation (Thurman and Mills, 1998; Moghimi, 2010; Tabarzadi et al., 2010; Moghimi et al., 2011). But the selectivity associated with SPE using solid support such as active carbon (Moghimi et al., 2011), ion-exchange resins (Swain et al., 2000), chelating fibers (Chang et al., 2001; Yang et al., 2004) and chelating resins (Tewari and Singh, 2000; Guo et al., 2004a, b; Zhou et al., 1983) and so forth is still to be improved for specific element.

Table 1. Operating conditions for ICP-MS.

Nebulizer	Babington
Spray chamber	Quartz double pass
RF power (kW)	1.5
Carrier gas flow rate (L min ⁻¹)	0.9
Makeup gas flow rate (L min ⁻¹)	0.15
Sample uptake rate (mL min ⁻¹)	0.3
Detection mode	Auto
Integration time (s)	0.1
Analytical masses	Hg

Now a days, metal ion imprinted polymers (MIIP) have been investigated as highly selective sorbents for SPE in order to concentrate and clean up samples prior to analysis.

One potential application that has recently attracted widespread interest is their use for clean up and enrichment of analytes present at low concentrations in complex matrices (Bae et al., 1998; Daniel et al., 2003; Rao et al., 2004; Liu et al., 2004). This element was selected for evaluation of the procedure because Hg(II) is one of the principal heavy metals of analytical interest due to its extreme toxicity even at relatively low concentrations (Moghimi, 2010; Bingye et al., 2012). This work investigates the applications of Schiff base-chitosan-grafted multi-walled carbon nanotubes (S-CS-MWCNTs) for selective extraction and solid phase pre-concentration of Hg(II) from aqueous and natural water samples.

EXPERIMENTAL

Reagents and materials

MWCNTs PET (filaments: 130 and dtex 170) made in Textile Engineering Department, Amir Kabir University of technology, Tehran, Iran. Analytical grade nitrate salts of Acrylic acid, acryl amid, benzoyl peroxide, acetone, Hg, Mn, Fe and Hg(II), Li, Na, K, Mg, Ca, Sr, Ba, Zn, Cd, Pb(II), Ni(II), Co(II) and Cu(II) of reagent grade were of the highest purity. Ultra pure organic solvents were obtained from E. Merck, Darmstadt-Germany, high Purity deionized water was used throughout the experiments and 3-chloro propyl trimethoxysilane was received from Aldrich Chemical, USA. Organic solvents were dried according to conventional methods. For all solutions double distilled water was used and the buffer solutions were prepared from 1.0 M sodium acetate to which different volumes of 1.0M HCl; HNO₃ were mixed and the pH-value of the resulting solution was adjusted with the use of a pH- meter. CS (Sangon Biotech Co., Ltd. Shanghai, China) and 4- methylbenzaldehyde (Aladdin Reagent Co., Ltd., Shanghai, China) were used in this work. Oxidized MWCNTs (MWCNTs-COOH) were provided by the Chengdu Organic Chemicals Co., Ltd. (Chengdu, China). The lengths of the MWCNTs-COOH were in the range of 10 to 30 nm and their outer diameters were in the range of 20 to 30 nm (Zargarani et al., 2008). The optimum operating conditions and measurement parameters for ICP-MS are listed in Table 1.

Synthetic procedures

The synthesis of the S-CS-MWCNTs is illustrated in Figure 1.

Synthesis of S-CS

Purified CS was obtained according to the method reported in the literature (Wu et al., 2007). CS (1000 mg) was dissolved in 80.0 mL of Figure 1.

0.2% (w/w) aqueous acetic acid solution was allowed to stand overnight, and then 4.0 ml of 4-methylbenzaldehyde in methanol (2:1, v/v) were slowly added. After stirring for 24 h at room temperature, the resulting mixture was washed with ethanol several times, filtered, and dried in a vacuum oven at 40°C for 8 h. The obtained yellow powder was S-CS.

Synthesis of acyl-chloride-modified MWCNTs (MWCNTs-COCl)

MWCNTs-COOH (80 mg) were dispersed in 40.0 ml of thionyl chloride. The suspension was stirred for 24 h at 70°C. The residue was separated by filtration, washed with N,N-dimethylformamide (DMF), and dried under a vacuum at 80°C for 8 h to obtain MWCNTs-COCl.

Synthesis of S-CS-grafted MWCNTs-COOH

MWCNTs-COCl (50 mg) and S-CS (400 mg) were added in 30.0 mL of DMF. The mixture was stirred at 100°C for 48 h under a nitrogen atmosphere and filtered through a 0.22 µm microporous membrane. To remove the physically adsorbed compounds, the residue was washed with 0.2% acetic acid, ethanol, and DDW. The S-CS-MWCNTs adsorbent was obtained after drying overnight in an oven at 40°C.

Column preparation

S-CS-MWCNTs (40 mg) were packed into an SPE mini-column (6.0 cm x 9 mm i.d., polypropylene). A polypropylene frit was placed at each end of the column to prevent loss of the adsorbent. Before use, 0.5 mol L⁻¹ HNO₃ and DDW were passed through the column to clean it.

Apparatus

The pH measurements were conducted by an ATC pH meter (EDT instruments, GP 353) calibrated against two standard buffer solutions of pH 4.0 and 9.2. Infrared spectra of S-CS-MWCNTs were carried out from KBr pellet by a Perkin-Elmer 1430 ratio recording spectrophotometer. Atomic absorption analysis of all the metal ions except Hg(II) were performed with a Perkin-Elmer 2380 cold vapor atomic absorption spectrometer. Hg(II) determinations were performed by a Varian Spect AA-10. Raman spectrophotometer analysis was performed with a Perkin-Elmer.

Adsorption and removed processes of metal ions

The adsorption ions onto S-CS-MWCNTs for Ni (II), Cu (II), and Pb(II) ions were investigated using the batch method. Experiments were carried out in an Erlenmeyer flask at the desired pH and 25°C temperature. The flasks were agitated on a shaker for 2 h. The amount of adsorbed metal was determined by the difference between the initial metal ion concentration and the final one after

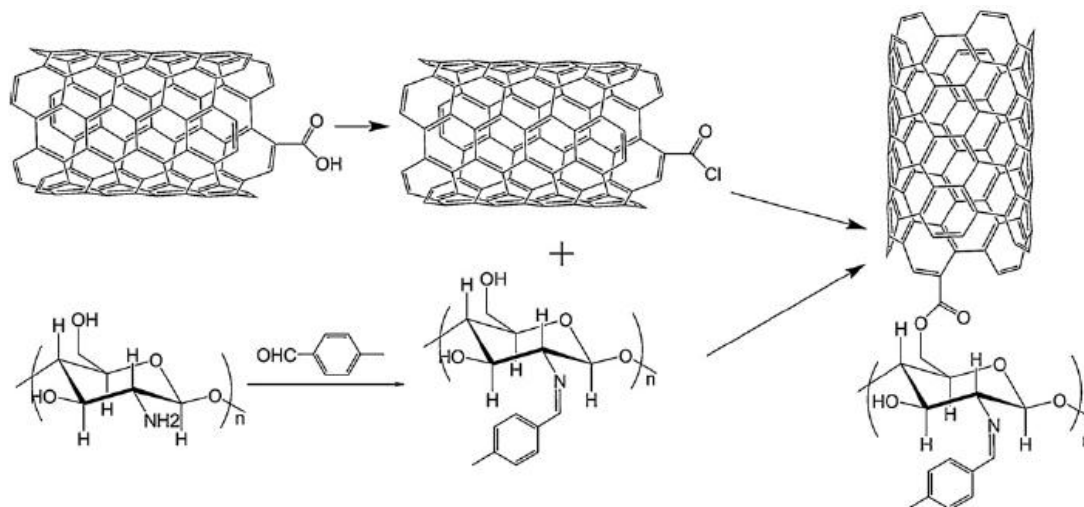


Figure 1. Schematic of synthesis and structure of S-CS-MWCNTs.

equilibrium (IARC, 1993). The concentration of ions was determined with a ICP-MS. The efficiency of metal ions recovery was estimated by the sorption yield (R%) and the q (mg/g) was calculated as:

$$R = (C_0 - C_t) / C_0 \times 100 \quad (1)$$

$$q = (C_0 - C_t) / G \times V \quad (2)$$

where C_0 is the initial metal ion concentration (mg/l), C_t is the ion concentration after the adsorption period, V is the volume of solution L and G is the dry mass of the S-CS-MWCNTs sample (in gram). The metal ions adsorbed on the S-CS-MWCNTs were then removed by placing 0.1 g of metal loaded MWCNTs in 10 ml of 1M HNO_3 solution for 30 min (Wu et al., 2007).

Stability studies

The stability of S-CS-MWCNTs phases in different buffer solutions (pH 1 to 6) and concentrated hydrochloric and nitric acids were studied by batch equilibration. In this procedure, 500 mg of the phase was mixed with 50 ml of the selected solution in 100 ml measuring flask and automatically shaken for 5 h. The mixture was filtered, washed with 500 ml water and dried in an oven at 80°C. Around 100 mg of the treated phase was added to 1.0 ml of 0.1 M Hg(II) and 9.0 ml of 0.1 M sodium acetate and the mixture was shaken for 30 min by an automatic shaker. The percentage of hydrolysis of Poly (ethylene terephthalate) from the surface of S-CS-MWCNTs phases in different acidic solutions was calculated from the determined $\mu\text{mol g}^{-1}$ value of each treated phase.

Sorption studies

Determination of metal capacity values ($\mu\text{mol g}^{-1}$)

The determination of metal capacity of 13 metal ions, viz. Ba(II), Ca(II), Co(II), Zn(II), Cu(II), Fe(III), Hg(II), Mg(II), Mn(II), Ni(II), Pb(II) and Hg(II) as a function of pH was studied by the static technique. Then 100 mg of the dry phase was added to a mixture of 1.0 ml of 0.1 M metal ion and 9.0 ml of the buffer solution (pH 1 to 10 and 0.1 M sodium acetate) in 50 ml measuring flask. The mixture was then automatically shaken for 30 min, filtered, washed with 50 ml water

and the unbound metal ion was subjected to complexometric titration using the proper buffer and indicator solutions and/or atomic absorption analysis. The effect of shaking time on the percentage extraction of metal ions was also studied for only Hg(II) by the static technique. In this, 100 mg of the S-CS-MWCNTs was added to 1.0 ml of 0.1M Hg(II) and 9.0 ml of 0.1M sodium acetate in 50 ml measuring flask and automatically shaken for the selected period of time (1, 5, 10, 20, 25, 30 and 35 min). The mixture was filtered, washed with 50 ml water and the free metal ion was determined as described earlier.

Determination of the distribution coefficient

About 100 mg of the S-CS-MWCNTs phase was mixed with 50 ml of the metal ion (1 mg ml^{-1}) in a 100 ml measuring flask and shaken for 3 h by an automatic shaker. The mixture was filtered, washed with water and diluted with 2% nitric acid solution in order to fit in the linear dynamic range of each metal ion. A standard solution for each metal ion was also prepared in a similar way.

Percentage removal of Hg(II) from aqueous solutions

One liter of Hg(II) solution, containing 10, 50 and 100 ng ml^{-1} was passed over a column (Bingye et al., 2012) packed with 500 and 1000 mg each of S-CS-MWCNTs. The flow rate was adjusted to 2.0 ml min^{-1} . The eluents were collected and 5ml was diluted with 20 ml of 2% nitric acid solution and subjected to ICP-MS.

Pre-concentration of Hg(II) from aqueous and natural tap water

Two liters sample solution spiked with 20 pg ml^{-1} of Hg(II) in both double distilled water (DDW) and natural tap water were prepared and passed over a column packed with 1000 mg of S-CS-MWCNTs with a flow rate of 2 ml min^{-1} . Then 10 ml concentrated hydrochloric acid (10.0 M) was then passed over the phase and adsorbed metal ion to desorb the bound-Hg(II). The desorbed metal ion was directly determined by ICP-MS. A standard solution and blank aqueous and tap water samples were also prepared and determined for evaluation.

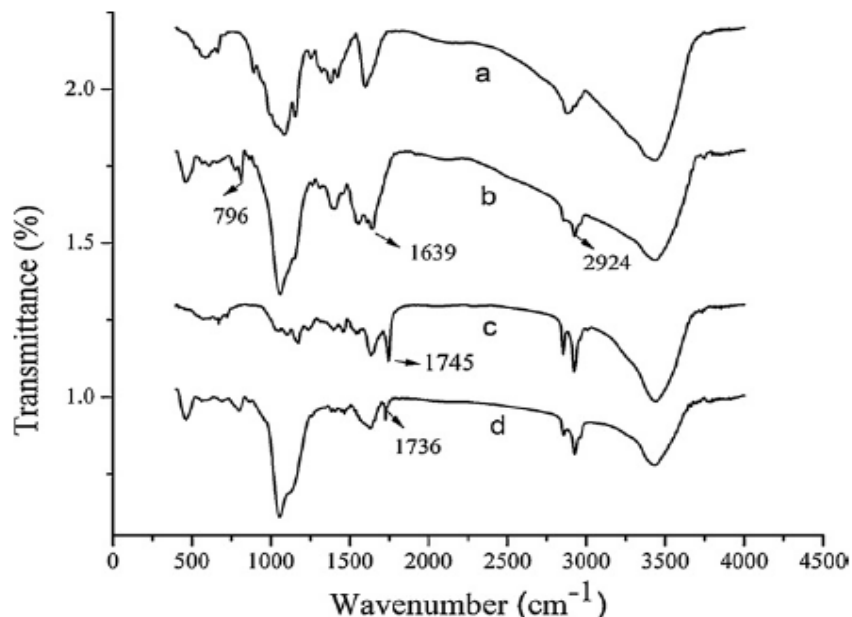


Figure 2. FT-IR spectra of (a) CS, (b) S-CS, (c) MWCNTs-COOH and (d) S-CS-MWCNTs.

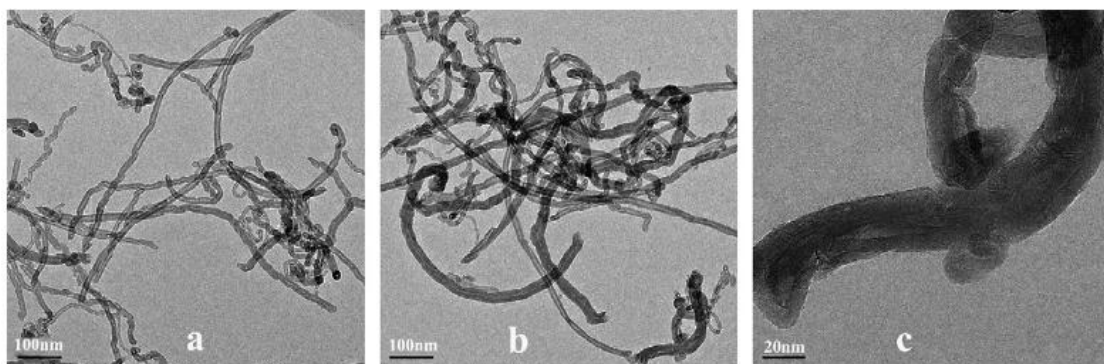


Figure 3. TEM images of (a) MWCNTs-COOH, (b) S-CS-MWCNTs and (c) S-CS-MWCNTs magnification.

RESULTS AND DISCUSSION

The FT-IR spectra of pure CS, S-CS, MWCNTs-COOH, and S-CS-MWCNTs were recorded. Their IR adsorption frequencies are shown in Figure 2a–d. A comparison of the FT-IR spectra of CS and S-CS showed that a new band at 1639 cm^{-1} appeared in the S-CS spectrum. This band was attributed to the C = N stretching vibration and indicated that the Schiff base had been successfully prepared. As a result of CS reacting with 4-methylbenzaldehyde, several new peaks also appeared in the S-CS, and they were assigned as follows. The peak observed at 2924 cm^{-1} was attributed to the stretching vibration of C H in CH_3 . The peak at 796 cm^{-1} resulted from the C H bending vibration of the benzene ring. In the MWCNTs-COOH spectrum, there was a strong absorbance at 1744 cm^{-1} , which corresponds to the C = O of

COOH. However, in the S-CS-MWCNTs, the absorbance at 1744 cm^{-1} was absent, and there was an absorbance at 1736 cm^{-1} , which indicated that the -OH of the CS had reacted with the MWCNTs to form ester bonds. The results confirmed the successful immobilization of S-CS on the surfaces of the MWCNTs. The surface microstructures of the grafted composites were observed using TEM. The TEM image of the MWCNTs-COOH is shown in Figure 3a. The average diameters of the MWCNTs-COOH were 20 to 30 nm. The TEM image of the S-CS-MWCNTs (Figure 3b) shows that their diameters were obviously larger than those of the MWCNTs, and we could clearly see that some of the S-CS was grafted onto the MWCNTs. In the higher-magnification TEM image (Figure 3c), a core-shell structure of S-CS-MWCNTs was clearly observed. The core of MWCNTs in the center was wrapped in grafted

Table 2. Metal capacity values determined in $\mu\text{mol g}^{-1\text{a}}$.

pH	Hg(II)	Pb(II)	Fe (II)	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Cd(II)	Ca	Mg	Ba
NaOAc	248	59	52	20	-	14	43	63	19	23	20	20
6	217	45	36	58	-	35	64	91	39	21	23	28
5	136	33	23	69	10	50	69	74	20	35	21	29
4	55	25	15	50	44	25	38	60	10	30	19	10
3	34	12	10	28	30	14	38	45	5	25	10	10
2	23	7	8	18	23	10	25	25	0	15	5	6
1	2	3	3	13	3	4	15	14	0	2	0	2

^a Values are based on $n = 3$ with standard deviation of 4.

S-CS, proving that the MWCNTs were coated with the polymer. These coated polymer layers could reduce the strong attractive interactions among the nanotubes and prevent aggregation of the MWCNTs, and could also increase the number of adsorption sites for metal ions.

Stability studies

The stability of the newly synthesized S-CS-MWCNTs phases was performed in different buffer solutions (pH 1, 2, 3, 4, 5, 6 and 0.1 M sodium acetate) in order to assess the possible leaching or hydrolysis processes. The values of the metal capacity determined revealed that the highest one corresponds to Hg(II), this ion was used to evaluate the stability measurements for the S-CS-MWCNTs phase (Chang et al., 2001). The results of this study proved that the S-CS-MWCNTs is more resistant than the chemically adsorbed analog especially in 1.0, 5.0 and 10.0 M hydrochloric acid with hydrolysis percentage of 2.25, 6.10 and 10.50 for phase, respectively.

Thus, these stability studies indicated the suitability of phase for application in various acid solutions especially concentrated hydrochloric acid and extension of the experimental range to very strong acidic media which is not suitable for other normal and selective chelating ion exchangers based on a nano polymeric matrix (Manzoori et al., 1998). Finally, the S-CS-MWCNTs phases were also found to be stable over a range of 1 year during the course of this work.

Metal capacity in various controlling factors

The metal capacity values determined in $\mu\text{mol g}^{-1}$ for the S-CS-MWCNTs in different buffer solutions were studied to evaluate the pH effect of metal ion on the extractability of the S-CS-MWCNTs phase. Table 2 compiles the $\mu\text{mol g}^{-1}$ values for the 12 tested metal ions, viz) Hg(II), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Fe (II), Cd(II), Ca, Mg, Ba and Pb(II). Several trends can be observed and outlined from the data given. First, is the strong dependence of $\mu\text{mol g}^{-1}$ extracted values from the metal ion solution for

most tested metal ions on the pH-value (Bae et al., 1998; Tao et al., 1998). The maximum value was found to be mainly at higher pH-values (pH 4 to 6 and 0.10 M NaOAc). Second, is the strong affinity of the S-CS-MWCNTs phase for extraction and removal of Hg(II) from aqueous solution compared to other tested metal ions, as shown by the higher $\mu\text{mol g}^{-1}$ values by S-CS-MWCNTs phases (Tao et al., 1998).

This behavior of S-CS-MWCNTs -loaded sulfur containing compounds for selective extraction and removal of Hg(II) from aqueous and natural water sample is well documented (Guo et al., 2004a, b) and reported based on different governing rules (Tewari and Singh, 2000). Third are the notably high $\mu\text{mol g}^{-1}$ values determined for chemically S-CS-MWCNTs phase in comparison with values found as given in Table 2. The comparison between the metal sorption properties of chemically and physically- S-CS-MWCNTs phases has been extensively studied (Daniel et al., 2003) and the results presented in this work are consistent with the surface activity of the donor atoms responsible for metal ion interaction, sorption, extraction and selective removal. In the case of the physically adsorbed phase, some of these donor atoms are involved in physical adsorption processes with the active surface, leading to the minimization of the reactivity of such donor atoms for metal interaction and binding processes. The product, S-CS-MWCNTs, in this case is tuned with the active donor atoms (N) directed with the capability and accessibility for fast and direct interactions with the free metal ion present in solution. Fourth, are the general orders of metal capacity values for all tested metal ions by the two phases which are in many respects consistent and similar. Therefore, the conclusion drawn from this section can be outlined as the high superiority of phase for selective extraction of Hg(II) as well as the higher metal uptake behavior of S-CS-MWCNTs phase. The effect of shaking time on the percentage extraction of metal ions at various equilibration time intervals (1, 5, 10, 15, 20, 25 min) was also studied and evaluated as $\mu\text{mol g}^{-1}$ and correlated to that determined at 30 min shaking time. Figure 4 represents the percentage extraction versus shaking time in min and clearly reflects the rapid

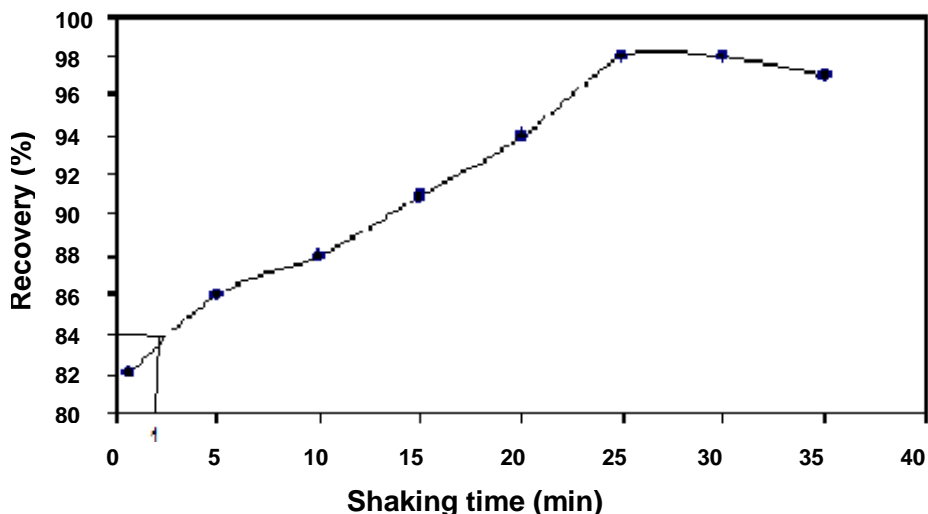


Figure 4. Effect of shaking time (min) on the percentage extraction of Hg(II) by the S-CS-MWCNTs phases.

Table 3. Distribution coefficient (K_d) values of various metal ions.

Metal ions	K_d
Mn(II)	90
Fe(III)	87
Co(II)	68
Ni(II)	57
Cu(II)	85
Cd(II)	530
Cu(II)	228
Hg(II)	2400
Pb(II)	120

exchange equilibrium between S-CS-MWCNTs phase and Hg(II). One minute shaking time was found to be sufficient to establish 84% of the determined $\mu\text{mol g}^{-1}$ value at 30 min whereas 10 min shaking time led to 88% extraction. The data and results presented in this section reveal the superiority of S-CS-MWCNTs phase as previously declared in the stability studies.

The distribution coefficient (K_d) data of the tested metal ions with the two newly S-CS-MWCNTs phase are summarized in Table 3. It is evident that Hg(II) is the strongest sorbed metal ion by S-CS-MWCNTs phase. The distribution coefficient values of Hg(II) by the loaded S-CS-MWCNTs phase were found to be much higher than those reported for ion exchange resins containing S-CS-MWCNTs derivatives (Manzoori et al., 1998). In addition, the K_d values for Hg(II) by S-CS-MWCNTs phase were found to come on the second place after Hg(II) which behavior can be interpreted on the basis of the affinity of both nitrogen and hydroxyl donor groups present in S-CS-MWCNTs for binding with Hg(II) (Guo et

al., 2004a, b). On the other hand, the various tested metal ions as shown in Table 3 were found to exhibit lower tendency to bind with S-CS-MWCNTs phase judging from the comparable low distribution coefficient values determined for these metal ions. The higher K_d value for Hg(II) and the lower ones for the other metal ions, except Hg(II), provide an additional evidence for the suitability of these two newly S-CS-MWCNTs phase for selective extraction of Hg(II) from aqueous solutions. It is also noteworthy that the conclusion drawn from the evaluation of the K_d values by S-CS-MWCNTs phase is consistent with the reported data.

Effect of pH

According to the recommended procedure solutions (the volume of each 100 mL) containing $0.5 \mu\text{g mL}^{-1}$ of Hg(II) was taken. Their pH values were adjusted in range 1.5 to 10 with HNO_3 , 0.01M acetate and/or phosphate buffer solutions and the mixture was shaken for 5 h. The 0.1 g of S-CS-MWCNTs in different pH value, namely pH 1.5, 2, 3, 4, 5, 6, 7, 8, 9 and 10 Hg(II) was determined. It also can be seen in Figure 5, the sorption quantity of Hg(II) increases with the pH value increases in the studied pH ranges. Below pH 2.0, the sorption quantity of Hg(II) is very low since the functional groups were protonated. Owing to hydrolysis at higher pH value, pH 4.0 was chosen as the optimum pH for further studies.

Selective pre-concentration of Hg(II) from natural water for off-line ICP-MS

This study was undertaken in order to evaluate the potential application of S-CS-MWCNTs phase for

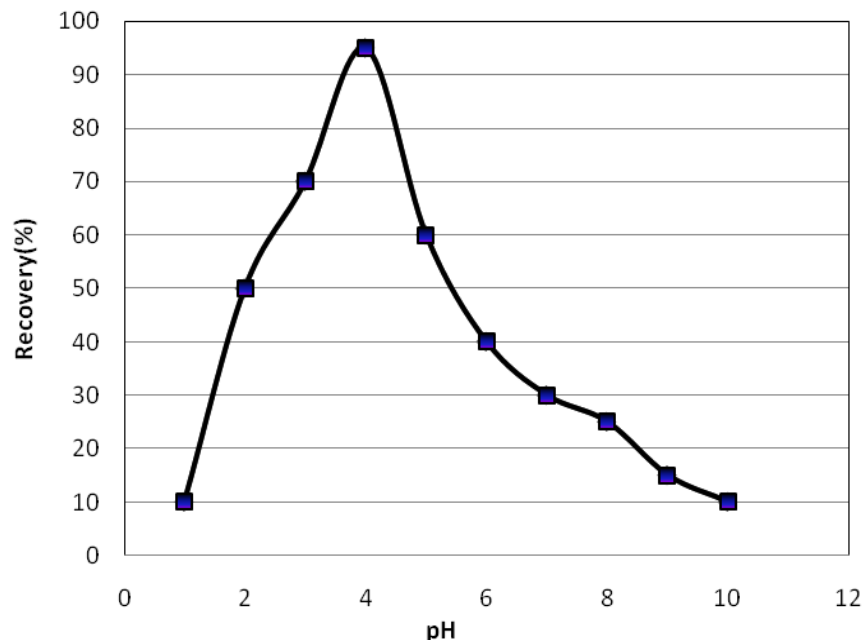


Figure 5. Effect of pH sorption of Hg(II) onto S-CS-MWCNTs. shaking time: 5 h, temperature: 25°C.

pre-concentration of trace levels of Hg(II) in natural water samples. Drinking tap water was used without prior treatments as an example and compared with double distilled water (DDW) to evaluate and investigate the matrix effect. Both drinking tap water and DDW (2 L) were spiked with 20 $\mu\text{g ml}^{-1}$ of Hg(II). Several pre-concentration reagents are well known and extensively examined for desorption of the bound metal ions from the surface of the stationary phase and these include mainly, hydrochloric and nitric acid, thiourea HCl (Manzoori et al., 1998). However, some of these reagents are usually characterized by adsorption on the surface of S-CS-MWCNTs which lead to severe change in the nature of packing material as well as non reproducible results if the column used in future applications. The efficiency of metal ion pre-concentration especially Hg(II), by 10.0 M HCl acid is found to be high without causing any notable change to the chemical nature of the organic S-CS-MWCNTs.

Therefore, 10.0 ml of 10.0 M HCl was used for the elution of the adsorbed Hg(II) from the column bed. The pre-concentration factor targeted from this study is 100 as given. As the results indicate, the off-line detection results of the eluted and pre-concentrated Hg(II) are very good with a satisfactory pre-concentration factor which can be further increased to 100-fold by simply increasing the water sample volume to 5 L instead of 2 L. Moreover, natural tap water sample was found to give very close results to that reported for DDW sample and this comparison indicates that the matrix effects of the dissolved inorganic and organic matters played an insignificant role in the aimed selective extraction,

removal and pre-concentration of Hg(II) by S-CS-MWCNTs phase.

Percentage removal of Hg(II) from aqueous solution

The use of a column technique is a common procedure for extraction, separation and selective extraction of metal ions from various aquatic systems (Pereira and Arruda, 2003). The column technique is characterized by major advantages over the batch or static equilibration method that is the possible application to large sample volumes (Chang et al., 2001; Moghimi, 2007; Yang et al., 2004; Ensing and Boer, 1999). This property enables the pre-concentration of metal ions at very low trace levels. The percentage removal of metal ions from aqueous solutions is essential for the evaluation of the method described and suggested here. This is mainly dependent on several well known factors such as the type and amount of packing stationary and mobile phases and the flow rate of the mobile phase (Daniel et al., 2003). In this study, we attempted to evaluate the percentage recovery of Hg(II) with different spiked concentrations, namely 10, 50 and 100 ng ml^{-1} from 1 L of 0.1 M NaOAc solution by the application of two different amounts (500 and 1000 mg) of S-CS-MWCNTs phase packing. The results of the percentage removal of Hg(II) from aqueous solutions are presented in Table 4 which clearly demonstrate the suitability and validity of S-CS-MWCNTs phase for removal and extraction of Hg(II) with ICP-MS. In addition, the effect of packing amount of silica gel phase is also evident in Table 3 where the near completion of

Table 4. Percentage removal of Hg(II) from aqueous solutions by S-CS-MWCNTs^a.

Hg(II) spiked (ng ml ⁻¹)	Phase (mg)	Percentage removal
10	500	94±2
50	500	96±3
100	500	97±4
10	1000	99±3
50	1000	95±2
100	1000	96±3

^aValues are based on triplicate analysis.**Table 5.** Preconcentration of Hg(II) from DDW and natural tap water samples^a.

Phase (mg)	Sample volume (ml)	Hg(II) spiked (pg ml ⁻¹)	Pre-concentration reagent	Pre-concentration factor	Hg(II) detected ^a (ng ml ⁻¹) with ICP-MS	Hg(II) detected ^a (ng ml ⁻¹) with CV-AAS	Percentage removal
1000	2000 Tapwater (Tehran)	20	10.0 ml of 10.0 M HCl	200	3.93±2.4	3.99±2.9	98.4±2.3
	2000 DDW				3.95±2.6	3.90±3.1	98.6±2.1

^a Values are corrected for blank concentration of water samples and based on triplicate analysis.

Hg(II) removal was accomplished by the use of 1000 mg phase. The results of the pre-concentration of Hg(II) from aqueous solutions are presented in Table 5 of Hg(II) from DDW and natural tap water samples.

Conclusions

In summary, a selective and sensitive method for the determination of trace levels of Hg(II) based on S-CS-MWCNTs as a sorbent for the determination of the analytes in biological samples as well as natural water samples. The sorption capacity for Hg(II) is 44.01 mg g⁻¹ that is higher than most of the sorbents. The faster sorption and desorption are other distinct advantages. In comparison to the commonly immobilized in silica gel, the present sorbent has a superior pre-concentration factor (100-folds) for Hg(II). In addition, the preparation of S-CS-MWCNTs is relatively simple and rapid. However, the S-CS-MWCNTs sorbent has some drawbacks include lower reusability and stability, which can be repeated only 10 cycles. This may make it difficult to put into practical use and should be a subject of further investigations.

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