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Preconcentration and determination of Mercury(II) from natural water and milk sample by Histidine functionalized multi-walled carbon nanotubes (MWCNTs-His)

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A simple method has been developed for the preconcentration of Mercury(II) [Hg(II)] based on the adsorption of its histidine functionalized multi-walled carbon nanotubes (MWCNTs-His) complex. The stability of a chemically MWCNTs-His were determined especially in concentrated hydrochloric acid which was then used as a recycling and pre-concentration reagent for further uses of MWCNTs-His. The application of this MWCNTs-His for adsorption 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 MWCNTs-His phases. The pronounced selectivity was also confirmed from the determined distribution coefficient (K_d) of all the metal ions, showing the highest value reported for Hg(II) to occur by MWCNTs-His. The potential applications of MWCNTs-His 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) (40 µg ml⁻¹) from natural tap water and milk sample with a pre-concentration factor of 200 for Hg(II) off-line analysis by cold vapor atomic absorption analysis. The pre-concentration factor attainable for quantitative recovery (>96%) of Hg(II) was 100 for a 1000 ml sample volume.

Key words: Pre-concentration, Mercury(II), histidine functionalized multi-walled carbon nanotubes (MWCNTs-His).

INTRODUCTION

Direct determination of trace metals especially toxic metal ions such as Mercury (Hg), tin, lead and metalloids arsenic, antimony and selenium from various samples requires mostly an initial and efficient pre-concentration step (Leyden et al., 1976a). This pre-concentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte of interest (Jones et al., 1983). This can be performed simply in many ways including liquid and solid phase

extraction (SPE) techniques (Nambiar et al., 1998; Caroli et al., 1991). The application of SPE technique for pre-concentration of trace metals from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects as well as adsorption of the target species on the solid surface in a more stable chemical form (Alexandrova and Arpadjan, 1993). The normal and selective solid phase extractors are those derived from the immobilization of the organic

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compounds on the surface of solid supports which are mainly nano polyurethane forms (Arpadjan et al., 1997), filter paper (Leyden et al., 1975), cellulose (Gennaro et al., 1983) and ion exchange resins (Shamsipur et al., 2005). Silica gel, alumina, magnesia and zirconia are the major inorganic solid matrices used to immobilize the target organic modifiers on their surfaces (Unger, 1979) of which silica gel is the most widely used solid support due to the well documented thermal, chemical and mechanical stability properties compared to other organic and inorganic solid supports (Boudreau and Cooper, 1989). The surface of silica gel is characterized by the presence of silanol groups, which are known as weak ion exchangers, causing low interaction, binding and extraction of the target analytes (Kvitek et al., 1982). For this reason, modification of the silica gel surface with certain functional groups has successfully been employed to produce the solid phase with certain selectivity characters (Bruening et al., 1991). Two approaches are known for loading the surface of solid phases with certain organic compounds and these are defined as the chemical immobilization which is based on chemical bond formation between the silica gel surface groups and those of the organic modifier, and the other approach is known as the physical adsorption in which direct adsorption of the organic modifier with the active silanol groups takes place (Unger, 1979).

Selective solid phase extractors and pre-concentrators are mainly based on impregnation of the solid surface with certain donor atoms such as oxygen, nitrogen and sulfur containing compounds (Mahmoud, 1979; Mahmud and Soliman, 1997; Tong et al., 1990; Dadler et al., 1987). The most successful selective solid phases for soft metal ions are sulfur-containing compounds, which are widely used in different analytical fields. Amongst these sulfur-containing compounds are dithiocarbamate derivatives for selective extraction of Hg(II) (Mahmoud, 1998, 1999) and pre-concentration of various cations (Leyden et al., 1976; Moghimi et al., 2009; Tehrani et al., 2005) and 2- mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations (Moghimi et al., 2009). Ammonium hexa-hydroazepin-1-dithiocarboxylate (HMDC)-loaded on silica gel as solid phase pre-concentration column for atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) was reported (Alexandrova and Arpadjan, 1993). Mercapto-modified silica gel phase was used in pre-concentration of some trace metals from seawater (Moghimi et al., 2009). Sorption of copper(II) by some sulfur containing complexing agents loaded on various solid supports (Moghimi et al., 2011) was also reported. 2-Amino-1-cyclopentene-1-dithiocarboxylic acid (ACDA) for the extraction of silver(I), Hg(II) and palladium(II) (Moghimi, 2006), 2-[2-triethoxysilyl-ethylthio] aniline for the selective extraction and separation of palladium from other

Interfering metal ions (Tehrani et al., 2005) as well as thiosemicarbazide for sorption of different metal ions (Moghimi et al., 2011) and thioanilide loaded on silica gel for pre-concentration of palladium(II) from water (Tehrani et al., 2005) are also sulfur containing silica gel phases.

Ion adsorption onto solid chelating nano polymer materials is now considered as one of the most promising techniques for selective concentration, removal and recovery of metal ions from a wide variety of sources. Among different types of polymer adsorbent, polymer fibers have attracted great interest in recent years (Tahaei et al., 2008). This can be related to their structure and characteristics, like high specific surface, small cross-section, uniformity in diameter (in macroscopic scale) and long length of fiber to diameter (Abdouss and Mousavi-shoushtari, 2012).

Raw acrylic fibers (RAF), due to their chemical and thermal stability, are a good substrate for the modification. The mentioned advantages are mainly attributed to the high adsorption capacities, fast adsorption equilibrium, high recycling rate and low cost of these polymeric fibers. The use of commercial fiber and introducing functional groups on its structure are of the important methods for producing ion adsorbent fibers. The properties of the fiber can be maintained in this method (Abdouss and Mousavi-shoushtari, 2012).

In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of Hg (Ahmad et al., 2011; Tuzen et al., 2009a). Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of lead (Tahaei et al., 2008). This paper describes the applications of multi-walled carbon nanotubes (MWCNTs-His) for selective extraction and solid phase pre-concentration of Hg(II) from aqueous and natural water samples.

EXPERIMENTAL

Reagents and materials

Analytical grade nitrate salts of Hg, Mn, Fe, Cr, lithium sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt(II) and copper(II) of reagent grade were of the highest purity. Ultra pure organic solvents were obtained from Merck Chemical Company, Darmstat, Germany, and 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 (Moghimi et al., 2006). 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 1.0 M HCl; HNO₃ were mixed. It is obvious that pH should be adjusted by the use of a pH- meter.

Preparation of histidine functionalized multi-walled carbon nanotubes (MWCNTs-His) synthesis of MWCNTs-His

Figure 1 illustrates the scheme for the synthesis of MWCNTs-His. Briefly, the oxidized MWCNTs (MWCNT-COOH) were prepared as

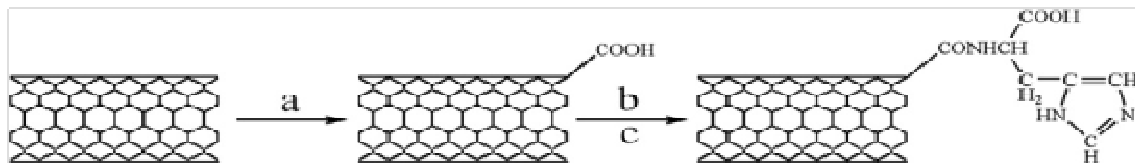


Figure 1. Scheme for the synthesis of histidine functionalized MWCNTs (a) sonicated 2 h; H₂SO₄/HNO₃ (3:1, v/v), 55°C, 7 h; (b) EDC/DMF; NHS/DMF, rt, 5 h; (c) histidine, rt, 24 h.

reported elsewhere (Niyogi et al., 2002). The MWCNT-COOH was dispersed with 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) in dimethyl formamide (DMF), and stirred for 5 h. Then the product was separated and dried under vacuum before mixed with histidine in anhydrous DMF and stirred for 24 h. After the resultant solid was washed with DMF and double distilled water (DDW), the prepared MWCNTs-His was dried under vacuum (Yang et al., 2006).

Apparatus

The pH measurements were conducted by an automatic temperature compensation (ATC) pH meter (EDT instruments, GP 353) calibrated against two standard buffer solutions of pH 4.0 and 9.2. Infrared spectra of MWCNTs-His were carried out from KBr 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 flame atomic absorption spectrometer. Hg(II) determinations were performed by a Varian Spect AA-10 plus atomic absorption spectrophotometer equipped with VGA-76 vapour generation.

Adsorption and removed processes of metal ions

The adsorption ions onto MWCNTS-HIS 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 equilibrium (Nambiar et al., 1998). The concentration of ions was determined with a flame atomic absorption (FAA) spectrometer (Philips model, PU9100). The efficiency of metal ions recovery was estimated by the sorption yield (R%) and the q (mg/g) was calculated as:

$$R = (C_0 - C_t) / C_0 \times 100 \quad (2)$$

$$q = (C_0 - C_t) / G \times V \quad (3)$$

Where C₀ 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 MWCNTS-HIS sample (in grams). The metal ions adsorbed on the MWCNTS-HIS were then removed by placing 0.1 g of metal loaded MWCNTs-His in 10 ml of 1 M HNO₃ solution for 30 min (Tahaei et al., 2008; Tuzen and Soylu, 2005).

Stability studies

The stability of MWCNTs-His phases in different buffer solutions

(pH 1–6) and concentrated hydrochloric and nitric acids was 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 0.1M 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 MWCNTs-His from the surface of MWCNTs-Hisphases in different acidic solutions was calculated from the determined μmol g⁻¹ value of each treated phase.

Sorption studies

Determination of metal capacity values (μmol g⁻¹)

The determination of metal capacity of 13 metal ions, viz. Ba(II), Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Hg(II), Mg(II), Mn(II), Ni(II), Pb(II) and Zn(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 6 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 MWCNTs-His phase was added to 1.0 ml of 0.1M Hg(II) and 9.0 ml of 0.1 M 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 thus.

Determination of the distribution coefficient

About 100 mg of the MWCNTs-His 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 Mercury(II) from aqueous solutions

One liter of Hg(II) solution, containing 10, 50 and 100 ng ml⁻¹ was passed over a column (Mazlum et al., 2003) packed with 500 and 1000 mg each of MWCNTs-His. The flow rate was adjusted to 2.0 ml min⁻¹. The eluents were collected and 5 ml was diluted with 20 ml of 2% nitric acid solution and subjected to cold vapor atomic absorption spectrometric analysis (CV-AAS).

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

Two liters sample solution spiked with 20 $\mu\text{g ml}^{-1}$ of Hg (II) in both double distilled water (DDW) and natural tap water were prepared 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 CV-AAS. A standard solution and blank aqueous and tap water samples were also prepared and determined for evaluation.

RESULTS AND DISCUSSION

Stability studies

The stability of the newly synthesized MWCNTs-His 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. Because the metal capacity values determined revealed that the highest one corresponds to Hg(II), this ion was used to evaluate the stability measurements for the MWCNTs-His phase (Mahmoud, 1997). The results of this study proved that the MWCNTs-His 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.

However, the use of nitric acid with different concentration values (1.0, 5.0 and 10.0 M) was found to change the color of MWCNTs-His from dark brown into reddish brown which is interpreted on the basis of chemical changes of the organic nano MWCNTs-His modifier via oxidation. In addition, stability of phases was also confirmed from the interaction with 10.0 M hydrochloric acid for more than 1 week. This test proved a reasonable stability of MWCNTs-His phase compared to non-treated silica gel phases judging from the color change of the two phases as well as the metal capacity values determination of Hg(II) and comparison of these with those of the original non-treated MWCNTs-His phases.

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 (Shamsipur et al., 2005; Tuzen et al., 2009b). Finally, the MWCNTs-His phases were also found to be stable over a range of one 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 MWCNTs-His in different buffer solutions were studied to evaluate the pH effect of metal ion on the extractability of

the MWCNTs-His phase. Table 1 compiles the $\mu\text{mol g}^{-1}$ values for the 13 tested metal ions, Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ca, Mg, Ba, Pb(II) and Hg(II). Several trends can be observed and outlined from the data given. First subject 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 (Moghimi et al., 2006).

The maximum value was found to be mainly at higher pH-values (pH 5 to 6 and 0.10 M NaOAc). Second subject is the strong affinity of the MWCNTs-His 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 MWCNTs-His phases (Moghimi, 2006).

This behavior of MWCNTs-His-loaded sulfur - containing compounds for selective extraction and removal of Hg(II) from aqueous and natural water sample is well documented (Mahmoud, 1998, 1999) and reported based on different governing rules (Tong et al., 1990). Third subjects are the notably high $\mu\text{mol g}^{-1}$ values determined for chemically MWCNTs-His phase in comparison with values found as given in Table 1. The comparison between the metal sorption properties of chemically and physically- MWCNTs-His phases has been extensively studied (Leyden et al., 1976b) 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, MWCNTs-His, 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 subject 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 MWCNTs-His phase.

The effect of shaking time on the percentage extraction of metal ions at various equilibration time intervals (1, 5, 10, 15, 20 and 25 min) was also studied and evaluated as $\mu\text{mol g}^{-1}$ and correlated to that determined at 30 min shaking time. Figure 2 represents the percentage extraction versus shaking time in min and clearly reflects the rapid exchange equilibrium between MWCNTs-His 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 MWCNTs-His phase as previously declared in the stability studies.

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

pH	Hg(II)	Pb(II)	Cr(III)	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Ca	Mg	Ba
NaOAc	280	53	50	24	-	16	47	63	19	40	20	20	30
6	200	40	39	56	-	35	68	91	39	68	28	29	40
5	1355	30	20	68	15	56	60	78	29	39	39	33	29
4	56	23	14	57	46	20	39	69	10	25	36	14	44
3	37	14	10	26	30	15	32	40	5	19	25	10	19
2	28	10	8	18	23	14	23	26	7	8	15	5	6
1	7	8	3	13	6	5	12	15	00	7	2	00	7

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

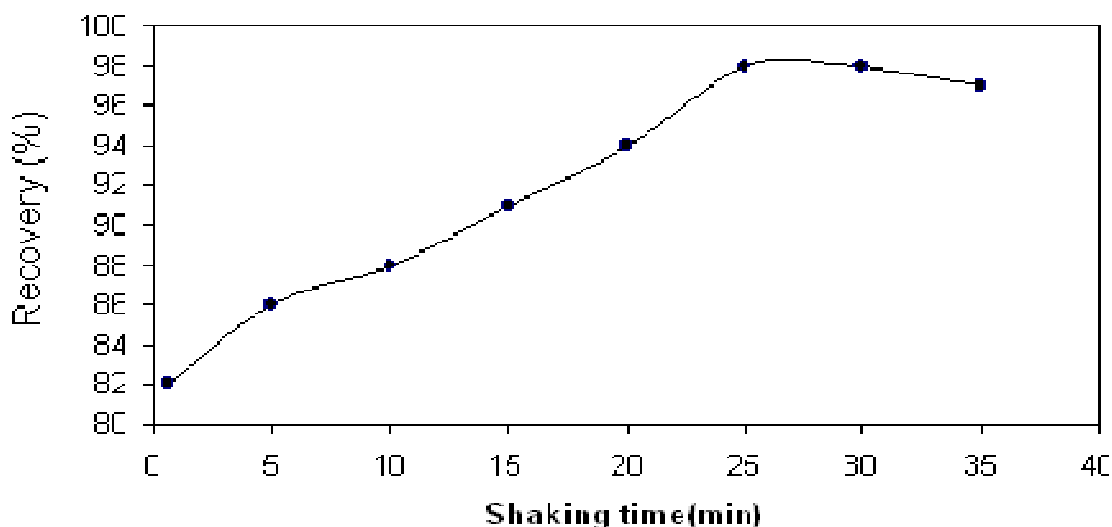


Figure 2. Effect of shaking time (minute) on the percentage extraction of Hg(II) by the MWCNTs-His phases.

The distribution coefficient (K_d) data of the tested metal ions with the both newly MWCNTs-His phases are summarized in Table 2. It is evident that Hg(II) is the strongest sorbed metal ion by MWCNTs-His phase. The distribution coefficient values of Hg(II) by the loaded MWCNTs-His phase were found to be much higher than those reported for ion exchange resins containing MWCNTs-His derivatives (Shamsipur et al., 2005). In addition, the K_d values for Cu(II) by MWCNTs-His 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 MWCNTs-His for binding with Cu(II) (Mahmoud 1998, 1999).

On the other hand, the various tested metal ions as shown in Table 2 were found to exhibit lower tendency to bind with MWCNTs-His 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 Cu(II), provide an additional evidence for the suitability of these two newly MWCNTs-His 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 MWCNTs-His phase is consistent with the reported data.

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 (Unger, 1979). The column technique is characterized by major advantages over the batch or static equilibration method that is the possible application to large sample volumes (Mahmoud, 1979; Mahmoud and Soliman, 1997; Tong et al., 1990; Dadler et al., 1987). 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

Table 2. Distribution coefficient (K_d) values of various metal ions.

Metal ion	K_d
Cr(III)	40
Mn(II)	30
Fe(III)	50
Co(II)	68
Ni(II)	45
Cu(II)	990
Zn(II)	479
Cd(II)	119
Hg(II)	11000
Pb(II)	300

Table 3. Percentage removal of Hg(II) from aqueous solutions by MWCNTs-His phase^a.

Hg(II) spiked (ng ml ⁻¹)	Phase (mg)	Percentage removal
10	500	96 ± 2
50	500	97 ± 3
100	500	97 ± 5
10	1000	98 ± 3
50	1000	99 ± 2
100	1000	98 ± 3

flow rate of the mobile phase (Leyden et al., 1976b). 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 MWCNTs-His phase packing. The results of the percentage removal of Hg(II) from aqueous solutions are presented in Table 3 which clearly demonstrate the suitability and validity of MWCNTs-His phase for removal and extraction of Hg(II). In addition, the effect of packing amount of silica gel phase is also evident in Table 3, where the near completion of Hg(II) removal was accomplished by the use of 1000 mg phase.

Selective pre-concentration of Hg(II) from natural water for off-line CV-AAS

This study was undertaken in order to evaluate the potential application of MWCNTs-His phase for 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 DDW to evaluate and investigate the matrix effect. Both drinking tap water and DDW (2 L) were spiked with 20 pg 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 (Shamsipur et al., 2005) as well as ethylenediaminetetraacetic acid (Moghimi, 2006).

However, some of these reagents are usually characterized by adsorption on the surface of MWCNTs-His 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 MWCNTs-His. 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 200 as given in Table 4. 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 500-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 MWCNTs-His phase.

Effect of pH

According to the recommended procedure solutions (the volume of each 100 ml) containing 0.51 g ml⁻¹ of Hg(II) was taken. Their pH values were adjusted in range 1.5-7 with HNO₃, 0.01 M acetate and/or phosphate buffer solutions and the mixture was shaken for 5 h. Hg (II) was determined by the 0.1 g of MWCNTs-His in different pH value, namely pH 1.5, 2, 3, 4, 5, 6 and 7. It also can be seen in Figure 3, the sorption quantity of Hg(II) increases with the pH value and increases in the studied pH ranges. Below pH 2.0, the sorption quantity of Ni(II) is very low since the functional groups were protonated. Owing to hydrolysis at higher pH value, pH 2.8 was chosen as the optimum pH for further studies.

Comparison to other methods

A comparison of the represented method with other reported pre-concentration methods is given in Table 5. Generally, the detection limit obtained by the present method is comparable to those reported in the literature, and the adsorption capacity and the enrichment factor of MWCNTs-His are better than other sorbents for Hg(II).

Table 4. Pre-concentration 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)	Percentage removal
1000	2000 Tap water (Saveh)	20	10.0 ml of 10.0 M HCl	200	3.90 ± 2.4	99.6 ± 2.7
1000	2000 DDW	20	10.0 ml of 10.0 M HCl	200	3.90 ± 2.8	98.4 ± 2.9
1000	2000 milk	20	10.0 ml of 10.0 M HCl	200	3.69 ± 2.8	97.3s ± 2.6

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

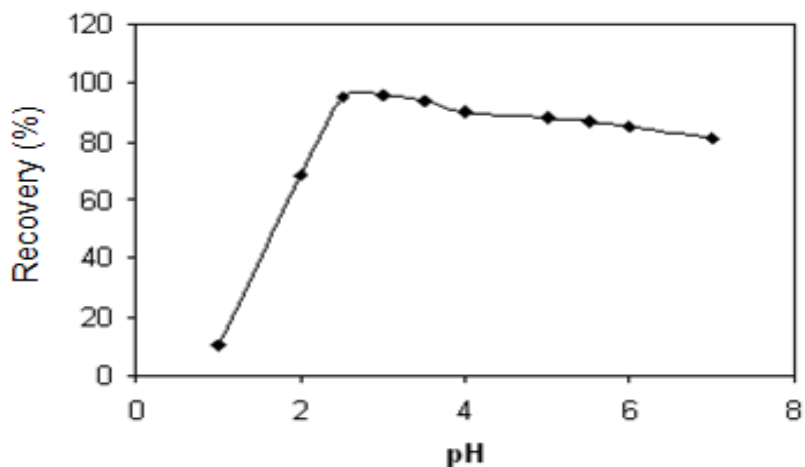


Figure 3. Effect of pH sorption of Hg (II) onto MWCNTs-His, shaking time: 5 h, temperature: 25°C.

Table 5. Comparison of the published methods with the proposed method in this work.

Adsorbent	Adsorption capacity (mg g ⁻¹)	Enrichment factor	Detection limit (µg L ⁻¹)	References
Naphthalene	-	40	0.6	Moghimi et al. (2006)
Chelating resin	7.3	50	0.42	Tahaei et al. (2008)
Activated carbon	0.08	-	1.0	Abdouss et al. (2012)
Al ₂ O ₃	0.89	21.9	0.08	Moghimi et al. (2011)
Biosorbent	-	32	1.7	Choi et al. (2003)
MWNTs	9.5	80	0.45	Tuzen et al. (2009b)
MWCNTs-His	44.01	200	40	This work

^a Values are based on triplicate analysis. MWNTs: multiwalled carbon nanotubes

Furthermore, the proposed system for Hg(II) was used for 50 subsequent pre-concentration cycles without any loss of the adsorption behaviours of MWCNTs-His throughout of the work.

Conclusions

Thus, a selective and sensitive method for the determination of trace levels of Hg (II) based on

MWCNTs-His as a sorbent for the determination of the analytes in milk sample 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 (Ahmad et al., 2011). 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) (Abdouss and Mousavi-shoushtari, 2012; Ahmad et al., 2011; Shin et al., 2004; Tabarzadi et al., 2010).

In addition, the preparation of MWCNTs-His is relatively simple and rapid. But the MWCNTs-His sorbent has some drawbacks such as lower reusability and stability, which can be repeated to use 10 cycles. This may make it difficult to put into practical use and should be a subject of further investigations.

The potential applications of MWCNTs-His 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) (40 pg mL⁻¹) from natural tap water and milk sample with a pre-concentration factor of 200 for Hg(II) off-line analysis by cold vapor atomic absorption analysis. The pre-concentration factor attainable for quantitative recovery (>96%) of Hg(II) was 100 for 1000 ml sample volume.

Results presented in this work demonstrate well the tremendous possibilities offered by the SPE of trace amounts of Hg(II) in water samples its determination by cold vapor atomic absorption analysis. The method developed was simple, reliable, and precise for determining Hg(II) in water. Also, the proposed method was free of interference compared to conventional procedures to determine Hg(II) (Choi and Choi, 2003; Moghimi, 2006; Tuzen et al., 2009a). The method can be successfully applied to the separation and determination of Hg(II) in binary mixtures.

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