Available online at www.elixirpublishers.com (Elixir International Journal)

Applied Chemistry

Elixir Appl. Chem. 77 (2014) 28881-28886

ISSN: 2229-712X

Preconcentration of Pb(II) by Ethylenediamine-functionalized multi-walled carbon nanotubes(E- MWCNTs)on surfactant coated C_{18}

Ali Moghimi

Department of Chemistry, Varamin (Pishva) Branch Islamic Azad University, Varamin, Iran.

ARTICLE INFO

Article history:

Received: 20 June 2014;

Received in revised form:

19 November 2014;

Accepted: 29 November 2014;

Keywords

Determination of lead,

Preconcentration,

Ethylenediamine-functionalized multi-walled carbon nanotubes (E-MWCNTs), FAAS.

ABSTRACT

A simple, highly sensitive, accurate and selective method for determination of trace amounts of Pb(II) in water samples is presented. a novel ethylenediamine-functionalized multi-walled carbon nanotubes(E-MWCNTs) solid-phase extraction adsorbent was synthesized by covalently O-(7-azabenzotriazol-1-yl)-N,N,N´,N´-tetramethyluronium hexafluorophosphate onto the surfaces of multi-walled carbon nanotubes (MWCNTs). The stability of a chemically ethylenediamine-functionalized multi-walled carbon nanotubes(E-MWCNTs) especially in concentrated hydrochloric acid was studied which used as a recycling and pre-concentration reagent for further uses of (E-MWCNTs). The method is based on (E-MWCNTs) of Pb(II) on surfactant coated C_{18}, modified with a ethylenediamine-functionalized multi-walled carbon nanotubes(E- MWCNTs). The retained ions were then eluted with 4 ml of 4 M nitric acid and determined by flame atomic absorption spectrometry (FAAS) at 283.3 nm for Pb. The influence of flow rates of sample and eluent solutions, pH, breakthrough volume, effect of foreign ions on chelation and recovery were investigated. 1.5 g of surfactant coated C_{18} adsorbs 40 mg of the Schiff's base which in turn can retain 15.2±0.8mg of each of the two ions. The limit of detection(3σ) for Pb(II) was found to be 3.20 ng l^{-1}. The enrichment factor for both ions is 100. The mentioned method was successfully applied on determination of lead in different water samples. The ions were also speciated by means of three columns system.

Introduction

Carbon nanotubes (CNTs) are relatively new materials with an increasing number of applications due to their unique electrical, mechanical, optical and chemical properties [1,2]. These excellent properties make CNTs promising materials for numerous applications,such as hydrogen storage [3], catalyst supports [4], chemical sensors [5] and nanoelectronic devices [6]. Since it has been proven that CNTs possess potential for the removal of many kinds of pollutants from water because of their ability to establish $\pi-\pi$ electrostatic interactions and their large surface areas, CNTs have attracted great attention in analytical chemistry and environmental protection [7,8]. CNTs have shown exceptional adsorption capabilities and high adsorption efficiencies for various organic pollutants, such as aniline, phenol and their substitutes [9], as well as diazinon [10]. In addition, CNTs were found to be superior sorbents for several divalent metal ions [8,11,12].

Some of these methods suffer from poor limit of detection and harmful solvents are being used in some others. On the other hand, effect of foreign ions on theanalyte is not negligible in many instances. In such cases, preconcentration of the analyte makes the determination easier and the composition of the sample less complicated. In recent years, solid phase extraction(SPE) has offered attractive possibilities in trace analysis. It has reduced the solvent and time consumption drastically[13,14]. In order to increase the preconcentration or extraction power of SPE an organic or inorganic ligand is used in conjunction with the sorbont. Some of the ligands used for determination of lead and copper are: Amberlit XAD-2 with 3,4-dihidroxybenzoic acid [15], silicagel modified with 3-aminopropyl triethoxysilane [16], Levatit with di(2,4,4–trimethylpentyl)phosphinic acid[17], silicagel functionalized with methyl thiosalicylate [18], silicagel modified with zirconium phosphate[19] and C18 diskes modified with a sulfur containing Schiff's base[20,28-32].

Comparing these examples with the presented method, they have either a lower enrichment factor or a higher limit of detection. On the other hand, the C_{18} disks can be used only a few times, while the proposed sorbent could be used more than 50 times without loss of efficiency.

Surfactant coated alumina modified with chelating agents has been used for extraction and preconcentration of environmental matrixes and metals [21,22]. Here, the surfactant molecules have been associated on the alumina surface forming an admicell or hemimicell. Organic molecules attach themselves on the hydrophobe part and low concentration of metallic elements also on the hydrophobe part, which includes the chelating agent [22]. The Schiff's bases which are obtained from salisylaldelyde are known as multidentate ligands. These agents can form very stable complexes with transition metal ions [23,24].

The main goal of the present work is development of a fast, sensitive and efficient way for enrichment and extraction of trace amounts of Pb(II) from aqueous media by means of a surfactant coated C_{18} modified with ethylenediamine-functionalized multi-walled carbon nanotubes(E- MWCNTs). Such a determination has not been reported in the literature. The structure of ethylenediamine-functionalized

---

Tele:

E-mail addresses: alimoghimi@iauvaramin.ac.ir

multi-walled carbon nanotubes(E- MWCNTs)is shown in Fig. 1. The chelated ions were desorbed and determined by FAAS. The modified solid phase could be used at least 50 times with acceptable reproducibility without any change in the composition of the sorbent, E- MWCNTs or SDS. On the other hand, in terms of economy it is much cheaper than those in the market, like C_{18} SPE mini-column.

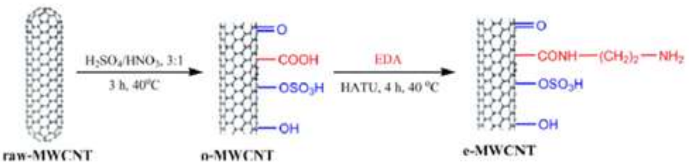
Experimental

Reagents and Apparatus

MWCNTs prepared by a chemical vapor deposition (CVD) method were used as received ithout purification. The purity of MWCNTs was more than 95% and the outer and inner diameters were 20–30 and 5–10 nm, respectively and the length between 5 and 200μm. All other reagents such as EDA, N-HATU, concentrated H_2SO_4 acid, concentrated HNO_3 acid and methanol were used as received. Millipore deionized (DI) water (18MΩcm resistance) was used for sample washing and solution preparation. All chemicals and MWCNTs were obtained from Sigma-Aldrich. Analytical-grade cadmium nitrate standard (Baker) was employed to prepare a stock solution containing 1000 μgmL^{-1} of Pb^{2+}, which was further diluted with DI water to the required Pb^{2+} concentrations for the sorption measurements. All solutions were prepared with doubly distilled deionized water from Merck (Darmstadt, Germany). C_{18} powder for chromatography with diameter of about 50 μm obtained from Katayama Chemicals from supelco. It was conditioned before use by suspending in 4 M nitric acid for 20 min, and then washed two times with water. Sodium dodecyl sulfate (SDS) obtained from Merck (Darmstadt, Germany) and used without any further purification.

Material preparation

The raw-MWCNTs were first treated with a (v/v 3:1) mixture of concentrated H_2SO_4 and HNO_3 (Scheme 1). This mixture was then sonicated for 3 h at 40 °C in an ultrasonic bath to introduce oxygen groups onto the MWCNT surface. After cooling to room temperature, the o-MWCNTs were added dropwise to 300mL of cold DI water and vacuum-filtered through a 0.05μm pore size PTFE membrane filter. The filtrant was washed with DI water until the pH was neutral. The sample was dried in a vacuum oven at 80 °C for 8 h. The oxidized nanotubes (100 mg) were dispersed in EDA (60 mL). The coupling agent, N-HATU, (8 mg) was added and the dispersion was sonicated for 4 h at 40 °C (Scheme 1). The obtained product was diluted with 300mL of methanol and vacuum filtered using a 0.05μm pore size PTFE membrane filter, after which the filtrant was washed extensively with excess methanol. Thus obtained e-MWCNTs were dried in a vacuum oven at 60 °C for 8 h.



Scheme 1. Schematic presentation of the functionalization of MWCNTs

Characterization of MWCNTs

Fourier-transform infrared (FTIR) spectra were recorded in the transmission mode using a BOMEM (Hartmann & Braun) spectrometer. Thermogravimetric analysis (TGA) was performed using a TA Instruments SDT Q600 from 20 to 800 °C at a heating rate of 20 °C min^{-1} and a nitrogen flow of 200mLmin^{-1}. Elemental analyses were performed using a VARIO EL III Elemental analyser. The BET specific surface area, pore specific volume and pore diameter were measured by nitrogen adsorption/desorption at 77.4K using a Micromeritics ASAP 2020MP gas sorption analyzer. The pH values at the point of zero charge (pH_{PZC}) of the samples were measured using the pH drift method [14]. The zeta potential measurements of the raw-MWCNT, o-MWCNT and e-MWCNT samples were performed using a Zeta-sizer Nano-ZS equipped with a 633nm He-Ne laser (Malvern). Suspensions of the samples at a concentration of 100mgL^{-1} in DI water were sonicated for 5min and the pH values of the suspensions were measured after the zeta potential measurements. The acidic and basic site concentrations were determined using the Boehm titration method [32].

Column preparation

E- MWCNTs (40 mg) were packed into an SPE mini-column (6.0 cm ×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} HNO_3 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 E- MWCNTs were carried out from KBr pellet by a Perkin-Elmer 1430 ratio recording spectrophotometer. Atomic absorption analysis of all the metal ions were performed with a Perkin-Elmer 2380 flame atomic absorption spectrometer

***Preparation of admicell column*:** to 40 ml of water containing 1.5 g of C_{18}, 150 mg of the above Schiff base-chitosan grafted multiwalled carbon nanotubes was loaded after washing acetone, 1mol l^{-1} HNO_3 solution and water, respectively, solution was added. The pH of the suspension was adjusted to 2.0 by addition of 4 M HNO_3 and stirred by mechanical stirrer for 20 min. Then the top liquid was decanted (and discarded) and the remained C_{18} was washed three times with water, then with 5 ml of 4 M $HNO_3$and again three times with water. The prepared sorbent was transfered to a polypropylen tube (i.d 5 mm, length 10mm).

Determination of Pb^{2+} contents in working samples were carried out by a Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hallow cathode lamp(HI-HCl) according to the recommendations of the manufacturers. These characteristics are tabulated in(Table 1). A metrohm 691 pH meter equipped with a combined glass calomel electrode was used for pH measurements.

Procedure

The pH of a solution containing 100 ng of each Pb(II) was adjusted to 2.0. This solution was passed through the admicell column with a flow rate of 5 ml min^{-1}. The column was washed with 10 ml of water and the retained ions were desorbed with 1 ml of 4 M HNO_3 with a flow rate of 2 ml min^{-1}. The desorption procedure was repeated 3 more times. All the acid solutions (4 ml all together) were collected in a 10 ml volumetric flask and diluted to the mark with water. The concentrations of lead in the solution were determined by FAAS at 283.3.

Determination of lead in water Samples

Polyethylene bottles, soaked in 1 M HNO_3 overnight, and washed two times with water were used for sampling. The water sample was filtered through a 0.45 μm pores filter. The pH of a 1000 ml portion of each sample was adjusted to 2.0(4 M HNO_3) and passed through the column under a flow rate of 5 ml min^{-1}.

The column was washed with water and the ions were desorbed and determined as the above mentioned procedure.

Results and Discussion

MWCNTs characterization

The FTIR spectra of raw-MWCNT, o-MWCNT and e-MWCNT are compared in Fig. 1a. The H_2SO_4-HNO_3 treatment produced carboxyl group on the external surface of the MWCNTs due to oxidation, as indicated by the presence of characteristic peaks at ≈3438 and ≈1726cm^{-1} of the stretching vibrations of υ(OH) and υ(C= O) of the carboxylic groups (COOH), respectively (Fig. 1a) [14,29,33].

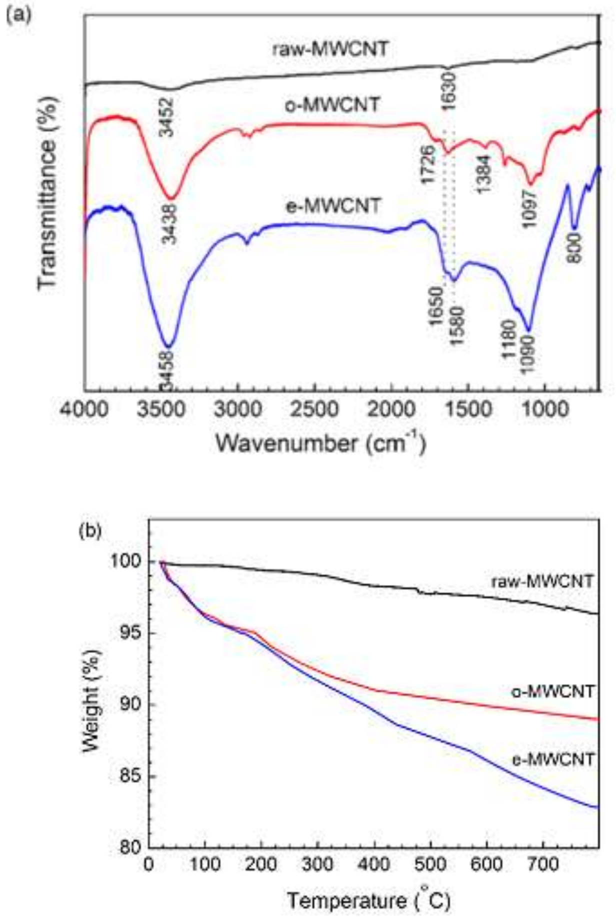


Fig 1. (a) FTIR transmission spectra and (b) TGA curves of raw-MWCNT, o-MWCNT and e-MWCNT

The asymmetric and symmetric stretching vibrations $\upsilon_{as}(CH_2)$ and $\upsilon_s(CH_2)$ were situated at ≈2924 and ≈2856cm^{-1}. Overlapped vibrations of double bonds C= C and carbonyl groups C= O were present at ≈1631cm^{-1}. The peak at ≈1384cm^{-1} was due to sulfate groups $\upsilon(OSO_3H)$ and δ(OH) bending vibration of COOH. The peak at ≈1097cm^{-1} was assigned to the υ(C–O) stretching vibration. The increased intensity of the O–H peak after oxidation and the appearance of C–H, C= O, C–O and OSO_3H bonds suggest that oxidation of the MWCNTs successfully introduced COOH, OH, C=O and OSO_3H groups onto the walls of the nanotubes [14,29,33]. The FTIR transmission spectrum of e-MWCNT (Fig. 1a) showed the absence of the band at ≈1726cm^{-1} and the simultaneous appearance of a band at a lower frequency (≈1650cm^{-1}), assigned to stretching of the amide carbonyl (C= O). In addition, the presence of new bands at ≈1580 and ≈1180cm^{-1}, correspond to N–H in-plane and C–N bond stretching, respectively. The peaks at≈3300–3600cm^{-1} were due to the NH_2 stretch of the amine group. A band at ≈800cm^{-1} was due to the out-of-plane NH_2 bending mode [22,29]. The FTIR results verify that amines were covalently attached to the MWCNTs. All of these groups introduced on surface of the MWCNTs can provide numerous sorption sites and thereby increase the sorption capacity of oxidized and amino-functionalized MWCNTs [12].

Thermogravimetric analysis, TGA, gave useful information about the functionalized MWCNTs, because most of the organic functional moieties on the MWCNTs were thermally unstable, i.e., most of the organic functional groups were decomposed before the onset of MWCNTs weight loss (Fig. 1b). The pristine MWCNTs sample was stable and hardly decomposed below 800 °C while the o-MWCNT exhibited a weight loss of about 12 wt% (Fig. 1b). The thermal degradation of o-MWCNT and e-MWCNT was multistage processes due to the different functional groups introduced onto the surface of the nanotubes. The first weight loss interval below 200 °C of all the samples was attributed mainly to the evaporation of saturated water [30]. At higher temperatures, the weight loss can be attributed to the thermal decomposition of side-groups. Thus, according to the TG analysis, the amount of amine covalently bonded to the MWCNTs was estimated, based on the total weight of e-MWCNT, to be about 7 wt% in relation to the o-MWCNT. The attachment of amine at the surface of e-MWCNT was further confirmed by elemental analysis (Table 1). No nitrogen could be detected from the raw-MWCNT but a small amount of nitrogen (0.49%) was observed for o-MWCNT due to the oxidation. Based on the results presented in Table 1, the nitrogen content (4.08%) of e-MWCNT can also provide an estimation of the amount of attached amine (around 7 wt%), which is in accordance with the TGA results. Furthermore, the found decrease in the oxygen content of e-MWCNT (13.50%) in comparison to that of o-MWCNT (15.56%) may also provide direct evidence for the attachment of amines.

Stability studies

The stability of the newly synthesized E- MWCNTs phases was performed in different buffer solutions (pH 1, 2, 3, 4, 5, 6 and 0.1M sodium acetate) in order to assess the possible leaching or hydrolysis processes. Because the metal capacity values determined in Section 3.2 revealed that the highest one corresponds to Pb(II)s, this ion was used to evaluate the stability measurements for the E- MWCNTs phase [14]. The results of this study proved that the E- 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 [9]. Finally, the E- MWCNTs phases were also found to be stable over a range of 1 year during the course of this work. Primary investigations revealed that surfactant coated C_{18} could not retain Pb(II) cations, but when modified with the E- MWCNTs retains these cations selectively. It was then decided to investigate the capability of the E- MWCNTs as a ligand for simultaneos preconcentration and determination of lead on admicell. The C_{18} surface in acidic media($1<pH<6$) attracts protons and becomes positively harged. The hydrophyl part of SDS($-SO_3^-$), is attached strongly to these protons. On the other and, the E- MWCNTs are attached to hydrophobe part of SDS and retain small quantities of metallic cations[22].

Table 1. The operational conditions of flame for determination of lead

Slit width	0.7 nm
Operation current of HI-HCL	10 mA
Resonance fine	283.3
Type of background correction	Deuterium lamp
Type of flame	Air/acetylene
Air flow	7.0 $mL.min^{-1}$
Acetylene flow	1.7 $mL.min^{-1}$

Table 2. Effect of foreign ions on the recovery of 100 ng of Pb

Diverse ion	Amounts taken (mg) added to 50 mL	% Found	%Recovery of Pb^{2+} ion
Na^+	92.2	1.19(2.9)[a]	99.6s(1.9)
K^+	92.2	1.38(2.1)	99.7(2.2)
Mg^{2+}	13.5	0.8(1.8)	96.9(2.7)
Ca^{2+}	23.3	1.29(2.0)	95.4(1.9)
Sr^{2+}	3.32	2.81(2.2)	99.2(2.1)
Ba^{2+}	2.26	3.16(2.4)	98.3(2.0)
Mn^{2+}	2.44	1.75(2.3)	99.5(1.8)
Co^{2+}	2.37	1.4(2.3)	99.1(2.2)
Ni^{2+}	2.31	2.0(2.14)	99.4(2.4)
Zn^{2+}	2.44	1.97(2.1)	99.7(2.2)
Cd^{2+}	2.63	1.9(2.0)	99.8(2.6)
Bi^{3+}	2.30	2.7(1.4)	99.4(2.7)
Cu^{2+}	2.56	2.81(2.3)	97.7(2.5)
Fe^{3+}	2.40	3.45(2.4)	97.6(2.8)
Cr^{3+}	1.30	2.92(2.2)	96.3(2.4)
UO^{2+}	2.89	1.3(2.2)	97.3(2.2)
NO_3^-	5.5	2.3 (2.3)	96.4(2.6)
$CH3COO^-$	5.3	2.2(2.6)	95.5(2.2)
SO_4^{2-}	5.0	2.9(3.0)	99.4(2.1)
CO_3^{2-}	5.4	1.8(2.5)	96.3(2.5)
PO_4^{3-}	2.6	2.1(2.0)	99.9(2.0)

[a]: Values in parenthesis are CVs based on three individual replicate measurements

Table 3. Recovery of Pb contents of water samples

		Amount added(μg)	Found(μg)	%Recovery
Sample Distilled water (100mL)	Pb	-	-	-
		0.050	0.043(2.40)[a]	96
		0.100	0.094(2.60)	97
Tap water(100mL)	Pb	-	0.015(3.0)	-
		0.050	0.068(2.42)	96
Snow water(50mL)	Pb	-	0.048(2.31)	-
		0.100	0.155(2.30)	99.0
Rain water(100mL)	Pb	-	0.045(2.31)	-
		0.100	0.143(2.40)	99
Synthetic sample 1 Na^+, Ca^{2+}, Fe^{3+}, $Co^{2+}Cr^{3+}$, Hg^{2+}, 1 mgL^{-1}	Pb	-	-	-
		0.100	0.104(2.40)	99
Synthetic sample 2 K^+ Ba^{2+}, Mn^{2+}, $Cd^{2+}Ni^{2+}$, Zn^{2+} , 1 mg L^{-1} of each cation	Pb	-	-	-
		0.100	0.105(2.70)	99

[a]: Values in parenthesis are CVs based on three individual replicate measurements.

Effect of pH in does not occur

The effect of pH of the aqueous solution on the extraction of 100 ng of each of the cations Pb(II) was studied in the pH rang of 1-10. The pH of the solution was adjusted by means of either 0.01 M H NO_3 or 0.01M NaOH. The results indicate that complete chelation and recovery of Pb(II) occurs in pH range of 2-4 and that of in 2-8 and are shown in Fig. 4. It is probable that at higher pH values, the cations might be hydrolysed and complete desorption occur. Hence, in order to prevent hydrolysis of the cations and also keeping SDS on the C_{18}, pH=2.0 was chosen for further studies.

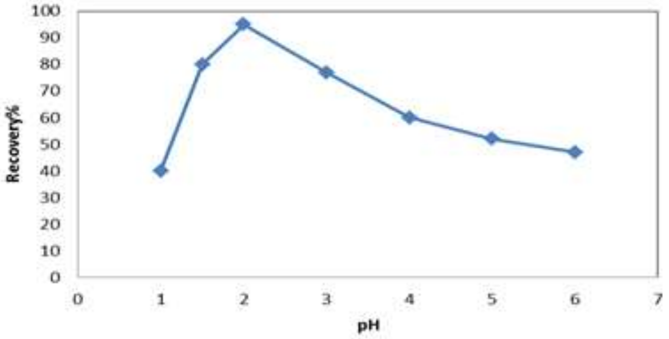


Fig. 4. Extraction percentage of Pb(II) against pH

Effect of flow rates of solutions

Effect of flow rate of the solutions of the cations on chelation of them on the substrate was also studied. It was indicated that flow rates of 1-5 ml min^{-1}would not affect the retention efficiency of the substrate. Higher flow rates cause incomplete chelation of the cations on the sorbent. The similar range of flow rate for chelation of cations on modified C_{18} with SDS and a E- MWCNTs has been reported in literature[21,22]. Flow rate of 1-2 ml $min^{-1}$for desorption of of the cations with 4 ml of 4 M HNO_3has been found suitable. Higher flow rates need larger volume of acid. Hence, flow rates of 5 ml $min^{-1}$and 2 ml min^{-1}were used for sample solution and eluting solvent throughout respectively.

Effect of the E- MWCNTs quantity

To study optimum quantity of the E- MWCNTs on quantitative extraction of lead, 50 ml portions of solutions containing 100 ng of each cation were passed through different columns the sorbent of which were modified with various amounts, between 10-50 mg of the E- MWCNTs. The best result was obtained on the sorbent which was modified with 40 mg of the E- MWCNTs.

Figures of merit

The breakthrough volume is of prime importance for solid phase extractions. Hence, the effect of sample volume on the recovery of the cations was studied. 100 ng of each cation was dissolved in 50, 100, 500 and 1000 ml of water. It was indicated that in all the cases, chelation and desorption of the cations were quantitative. It was then concluded that the breakthrough volume could be even more than 1000 ml. Because the sample volume was 1000 ml and the cations were eluted into 10 ml solution, the enrichment factor for both cations are 100, which is easily achievable. The maximum capacity of 1.5 g of the substrate was determined as follow; 500 ml of a solution containing 50 mg of each cation was passed through the column. The chelated ions were eluted and determined by FAAS. The maximum capacity of the sorbent for three individual replecates was found to be 15.2±0.8 µg of each cation. The limit of detection (3σ) for the catoins[30] were found to be 3.20 $ngl^{-1}$for lead ions. Reproducibility of the method for extraction and determination of 100 ng of each cation in a 50 ml solution was examined. As the results of seven individual replicate measurements indicated, they were 2.85% and 2.99% for Pb(II).

Effect of foreign ions

Effect of foreign ions were also investigated on the measurements of lead. Here a certain amount of foreign ion was added to 50 ml of sample solution containing 100 ng of each Pb(II) with a pH of 2.5. The amounts of the foreign ions and the percentages of the recovery of lead are listed in Table 2. As it is seen, it is possible to determine lead without being affected by the mentioned ions.

Analysis of the water samples

The prepared sorbent was used for analysis of real samples. To do this, the amounts of lead were determined in different water samples namely: distilled water, tap water of Tehran (Tehran, taken after 10 min operation of the tap), rain water(Tehran, 20 January, 2014), Snow water (Tehran , 12 February ,2014), and two synthetic samples containing different cations. The results are tabulated in Table 3. As it is seen, the amounts of lead added to the water samples are extracted and determined quantitatively which indicates accuracy and precision of the present method.

Separation and speciation of cations by three columns system It is possible to preconcentrate and at the same time separate the neutral metal complexes of E- MWCNTs, anionic complexes and free ions from each other by this method[27]. Water samples were passed through the three connected columns: anoin exchanger, C_{18}-silica adsorber and chelating cation exchanger. Each species of lead is retained in one of the columns; anionic complexes in the first column, neutral complexes of E- MWCNTs in the second, and the free ions in the third. We have proposed a method for determination and preconcentration of Pb in water samples using surfactant coated C_{18} impregnated with a Sciff's base. The proposed method offers simple, highly sensitive, accurate and selective method for determination of trace amounts of Pb(II) in water samples.

Acknowledgments

The authors wish to thank the Chemistery Department of Varamin branch Islamic Azad University for financial support.

References

[1] S. Iijima, Helical microtubules of graphitic carbon, Nature 354 (1991) 56–58.

[2] L.M. Dai, A.W.H. Mau, Controlled synthesis and modification of carbon nanotubes and C60: carbon nanostructures for advanced polymeric composite materials, Adv. Mater. 13 (2001) 899–913.

[3] S.M. Lee, Y.H. Lee, Hydrogen storage in single-walled carbon nanotubes, Appl.Phys. Lett. 76 (2000) 2877–2879.

[4] G.L. Che, B.B. Lakshmi, E.R. Fisher, C.R. Martin, Carbon nanotubule membranes for electrochemical energy storage and production, Nature 393 (1998) 346–349.

[5] P.G. Collins, K. Bradley, M. Ishigami, A. Zettl, Extreme oxygen sensitivity of electronic properties of carbon nanotubes, Science 287 (2000) 1801–1804.

[6] P.G. Collins, A. Zettl, H. Bando, A. Thess, R.E. Smalley, Nanotube nanodevice, Science 278 (1997) 100–102.

[7] M. Valcarcel, S. Cardenas, B.M. Simonet, Role of carbon nanotubes in analytical science, Anal. Chem. 79 (2007) 4788–4797.

[8] G.P. Rao, C. Lu, F. Su, Sorption of divalent metal ions from aqueous solution by carbon nanotubes: a review, Sep. Purif. Technol. 58 (2007) 224–231.

[9] K. Yang, W. Wu, Q. Jing, L. Zhu, Aqueous adsorption of aniline, phenol, and their substitutes by multi-walled carbon nanotubes, Environ. Sci. Technol. 42 (2008) 7931–7936.

[10] H. Katsumata, T. Matsumoto, S. Kaneco, T. Suzuki, K. Ohta, Preconcentration of diazinon using multiwalled carbon nanotubes as solid-phase extraction adsorbents, Microchem. J. 88 (2008) 82–86.

[11] Y. Liu, Y. Li, X.P. Yan, Preparation, Characterization, and application of l-cysteine functionalized multiwalled carbon nanotubes as a selective sorbent for separation and preconcentration of heavy metals, Adv. Funct. Mater. 18 (2008) 1536–1543.

[12] D. Xu, X. Tan, C. Chen, X. Wang, Removal of Pb(II) from aqueous solution by oxidized multiwalled carbon nanotubes, J. Hazard. Mater. 154 (2008) 407–416.

[13] R.E. Majors, LC-GC 4 (1989) 972.

[14] Z. Gao, T.J. Bandosz, Z. Zhao, M. Han, J. Qiu, Investigation of factors affecting adsorption of transition metals on oxidized carbon nanotubes, J. Hazard. Mater. 167 (2009) 357–365.

[15] V.A. Lemos, P.X. Baliza, R.T. Yamaki, M.E. Rocha, A.P.O. Alves, Talanta, 61 (2003) 675.

[16] N. Tokman, S. Akman, M. Ozcan, Talanta, 59 (2003) 201.

[17] Ibarra L, Jorda C. Effect of a diazide as adhesive agent in elastomeric matrix-short polyamide fibers composite. J Appl Polym Sci 1993;48(3):375–81.

[18] M. Zougagh, A.G.D. Torres, E.V. Alonso, J.M.C. Povon, Talanta, 62 (2004) 503.

[19] E. Matoso, L. T. Kubota, S. Cadore, Talanta, 60 (2003) 1105.

[20] N. Karousis, A. S. D. Sandanayaka, T. Hasobe, S. P. Economopoulos, E.Sarantopouloua , N. Tagmatarchis, J. Mater. Chem., 2011, 21, 109.

[21] Smith MB, March J. March's advanced organic chemistry: reactions,mechanisms, and structure. New York: John Wiley & Sons Inc.; 2001. p. 1182–3.

[22] J. Yu, M. Tong, X. Sun, B. Li, Biomass grafted with polyamic acid for enhancement of cadmium(II) and lead(II) biosorption, React. Funct. Polym. 67 (2007) 564–572.

[23] S.L. Zhang, Z. Du, G.K. Li, Anal. Chem. 83 (2011) 7531.

[24] L. Xu, J. Feng, J. Li, X. Liu, S. Jiang, J. Sep. Sci. 35 (2012) 93.

[25] .H. effery, Chemical Analysis, 5th ed., John Wiley & Sons, Inc., New York, 1991.

[26] O. Abollino, M. Aceto, C. Sarzanini, E. Mentasti, Anal. Chim. Acta, 411 (2000) 233.

[27] D.Bingye, C.Meirong,F. Guozhen,L. Bing,D. Xv,P. Mingfei,W. Shuo *Journal of Hazardous Materials* 219– 220 (2012) 103– 110.

[28] M. Groschner, P. Appriou, Anal. Chim. Acta, 297 (1994) 369.

[29] G. Vukovic, A. Marinkovic, M. Obradovic,V. Radmilovic, M. Colic, R. Aleksic, P.S. Uskokovic, Synthesis,characterization and cytotoxicity of surface aminofunctionalized water-dispersible multi-walled carbon nanotubes, Appl. Surf.Sci. 255 (2009) 8067–8075.

[30] J. Xu, P. Yao, X. Li, F. He, Synthesis and characterization of water soluble and conducting sulfonated polyaniline/para-phenylenediaminefunctionalized multi-walled carbon nanotubes nano-composite, Mater. Sci. Eng. B 151 (2008) 210–219.

[31] P.Nayebi;A. MOGHIMI, Oriental Journal of Chemistry 22(3)(2006)507.

[32] H.P. Boehm, Some aspects of the surface chemistry of carbon blacks and other carbons, Carbon 32 (1994) 759–769.

[33] R. Yu, L. Chen, Q. Liu, J. Lin, K.L. Tan, S.C. Ng, H.S.O. Chan, G.Q. Xu, T.S.A. Hor,Platinum deposition on carbon nanotubes via chemical modification, Chem. Mater. 10 (1998) 718–722.

[34] Goran D. Vukovic, Aleksandar D. Marinkovic, Miodrag Colic, Mirjana D. Ristic, Radoslav Aleksic, Aleksandra A. Peric-Grujic, Petar S. Uskokovic, Removal of cadmium from aqueous solutions by oxidized and ethylenediamine-functionalized multi-walled carbon nanotubes, Chemical Engineering Journal 157 (2010) 238–248.