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Fabrication method of extracting Cadmium(II) and Lead(II) in water samples using Nano Graphene modified 2-propyl-piperidine-1-carbodithioate

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ABSTRACT: A preconcentration/separation procedure is presented for the solid phase extraction of trace cadmium and lead ions as their 2-propylpiperidine-1-carbodithioate (PPCD) chelates in environmental samples on Nano Graphene, prior to cadmium and lead determinations by atomic absorption spectrometry. The preconcentration procedure was optimized by using model solutions containing cadmium and lead ions. The influences of pH of the model solutions, amounts of PPCD, eluent type and volume etc. were investigated. Also the effects of the matrix constituents of the samples were also examined. Separation of cadmium and lead from real samples was achieved quantitatively. The procedure presented was checked with the analysis of standard reference materials (IAEA-336 Lichen and SRM 1515 Apple leaves). The preconcentration procedure was applied for the lead and cadmium contents of the natural water samples, some salts with satisfactory results (recoveries >95%, relative standard deviations <7%).

Keywords: *Atomic absorption spectrometry; Cadmium(II); Extracting; Lead(II); Nano Graphene; Preconcentration; Solid phase extraction.*

INTRODUCTION

The transition metals including cadmium, chromium and lead etc. are an important risk for humans and animals. cadmium(II) and lead(II), at trace concentrations, acts as both a micronutrient and a toxicant in marine and fresh water systems (Leyden *et al.*, 1976; Narin *et al.*, 2000; Akama *et al.*, 2000; Ohta *et al.*, 2001; Cuculic *et al.*, 1997; Moghimi *et al.*, 2012). The direct determination of trace metals especially toxic metal ions such as Co, tin, arsenic, lead, antimony and selenium from various samples requires mostly an initial and efficient pre-concentration step (Leyden *et al.*, 1976). 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 techniques (Nambiar *et al.*, 1998; Caroli *et al.*, 1991). The application of solid phase extraction technique for pre- concentration of

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(*) Corresponding Author - e-mail: alimoghimi@iauvaramin.ac.ir trace metals from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects as well as sorption of the target species on the solid surface in a more stable chemical form (Alexandrova *et al.*, 1993). The normal and selective solid phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports which are mainly polyurethane foams (Arpadjan *et al.*, 1997), filter paper (Leyden *et al.*, 1975), cellulose (Gennaro *et al.*, 1983) and ion exchange resins (Grote *et al.*, 1985). 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 *et al.*, 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 1997; Mahmoud *et al.*, 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 cadmium(II) and lead(II) (Mahmoud, 1998 & 1999) and preconcentration of various cations (Leyden *et al.*, 1976; Narin *et al.*, 2000; Akama *et al.*, 2000; Ohta *et al.*, 2001; Cuculic *et al.*, 1997; Moghimi *et al.*, 2009; Thurman 1998; Pawliszyn 1997; Izatt *et al.*, 1996; Hagen *et al.*, 1990; Krueger 1995; Yamini *et al.*, 1994; Shamsipur *et al.*, 1999; Shamsipur *et al.*, 2001; Brunner *et al.*, 2003; Zelder *et al.*, 2004; Boll *et al.*, 2005; Nayebi *et al.*, 2006; Moghimi *et al.*, 2007; Moghimi 2007) and 2- mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations (Qiaosheng *et al.*, 1998). Ammonium hexahydroazepin-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 *et al.*, 1993). Mercapto-modified silica gel phase was used in preconcentration of some trace metals from seawater (Moghimi *et al.*, 2010). Sorption of cadmium(II) and lead(II) by some sulfur containing complexing agents loaded on various solid supports (Tajodini *et al.*, 2010) was also reported. 2-Amino-1- cyclopentene-1-dithiocaboxylic acid (ACDA) for the extraction of silver(I), cadmium(II) , lead(II) and palladium(II) (Moghimi *et al.*, 2009s), 2-[2-triethoxysilyl-ethylthio] aniline for the selective extraction and separation of palladium from other interfering metal ions (Narin *et al.*, 2000) as well as thiosemicarbazide for sorption of different metal ions (Campderros *et al.*, 1998) and thioanilide loaded on silica gel for pre-concentration of palladium(II) from water (Narin *et al.*, 2000) are also sulfur containing silica gel phases. This paper describes a preconcentration/separation procedure based on solid phase extraction of lead and cadmium in some natural water samples and some salts. The analytical parameters relevant quantitative retentions of lead and cadmium on Nano Graphene as PPCD chelates were investigated.

EXPERIMENTAL

Apparatus

A Varian SpectrAA model 200 atomic absorption spectrometer with deuterium background corrector was used in this study. A 10 cm long slot-burner

Table 1. Conditions for flame atomic absorption spectrometric determinations

Element	Wavelength (nm)	Slit (nm)	Lamp current (mA)	Flow rate of oxidant and fuel	
				Air (L/min)	Acetylene(L/min)
Pb	283.3	0.7	30	2.0	17.0
Cd	283.3	0.7	4	2.0	17.0

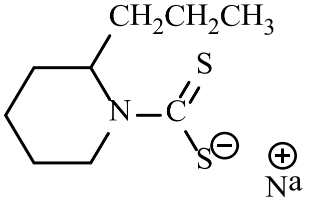
head, a lamp and an airacetylene flame were used. The operating conditions given in Table 1, adjusted in the spectrometer were carried out according to the standard guidelines of the manufacturers. The atomic absorption signal was measured as a peak height mode against an analytical curve. A pH meter, Metrohm model 691 digital pH meter was employed for measuring pH values in the aqueous phase.

Reagents and solutions

Synthesis of sodium 2-propylpiperidine-1-carbodithioate reagent.

Carbondisulphide (1.05 mol) was slowly added to a solution of 2-propyl-piperidine (1.43 mol) in 25 ml of water at 5 °C with constant stirring, followed by 1.0 mol of sodium hydroxide dissolved in 20 ml of water to form sodium 2-propylpiperidine-1- carbodithioate as shown in Fig. 6(a). The product was warmed to room temperature and washed 2–3 times with purified acetone. The reaction product was recrystallized from warm acetone. The purified compound has a melting point of 303–308 °C at 740mm pressure. Crystallization of water is less in 2-propylpiperidine-1-carbodithioate when compared with other carbodithioate, therefore, the extractability of the complex become easier. The metal salt of this reagent is a resonance hybrid of the structures, which contributed to the stability of metal complexes as shown in Fig. 6 (b).

Analytical reagent-grade chemicals from Merck, Darmstadt were employed for the preparation of all solutions. All aqueous solutions were prepared from distilled water (Milli- Q Millipore 18.2 MΩcm^{-1} resistivity). All the plastic and glassware were cleaned by soaking in dilute HNO_3 (1+9) and were rinsed with distilled water prior to use. Stock metal ion solutions, 1000 mg/L (Merck, Darmstadt) were diluted daily for obtaining reference and working solutions. Stock solutions of diverse elements supplied by Sigma Chem. Co., St. Louis, were prepared from high purity compounds. The calibration curves for analyte ions were established using the standard solutions prepared in 1M HNO_3 by dilution from stock solutions. The calibration standards were not submitted to the preconcentration procedure. The range of the calibration standards for cadmium and lead on flame atomic absorption spectrometric determinations were 0.02–2.0, and 1.0–10.0 mg/L, respectively. The correlation coefficient of the calibration curves were generally 0.997. Nano Graphene (60–80 mesh fraction, surface area: 600–700 m^2/g) (Sigma Chem. Co., St. Louis) was washed successively with methanol, water, 1M HNO_3 in acetone, water, 1M NaOH and water, sequentially, in order to eliminate trace metal ions and other inorganic and organic contaminants in the resin. The glass column, having a stopcock and a porous disk, was 10 cmlong, and 1.0 cm in diameter. The column contains about 600 mgresin (ca 2.0 cm bed). The columnwas prepared by aspirating water slurry of Nano Graphene into the glass column. It was conditioned with 10–15 mL of pH 9 buffer. The ligand; 2-propylpiperidine-1-carbodithioate (PPCD) was dissolved in a water / ethanol (75/25, v/v) mixture. Ammonium acetate buffer solutions (0.1 M) were prepared by adding an appropriate amount of acetic acid (Merck, Darmstadt) to ammonium acetate (Merck, Darmstadt) solutions for pH 3–6 and ammonium chloride buffer solutions (0.1 M) were prepared by adding an appropriate amount of ammonia (Merck, Darmstadt) to ammonium chloride



Schematic1. The molecular structure of Sodium 2 -propylpiperidine-1-carbodithioate

solutions for pH 8–10.

Preconcentration procedure

The column method was tested with model solutions. Model solutions (containing 5 µg of cadmium and 20 µg of lead in 40–60 mL) were adjusted to the desired pH. Then 2-propylpiperidine-1-carbodithioate (PPCD) was added to form the metal–PPCDchelates. After 5–10 min, the solutionwas loaded into the column. The flow of sample solution through the column was gravitationally performed. After passage of the solution finished, the column was washed with a chelating agent solution adjusted to the working pH. The metals were recovered with the aid of 8–10 mL of 1M HNO3 in acetone at 5.0 mL/min of flow rate. The eluent was evaporated over a hot plate to near dryness at 35 °C in a hood and was diluted to 2 mL or 5mL with 1M HNO_3. The metal concentrations in the final solution were determined by AAS.

Procedure for standard reference materials

Lichen (IAEA-336) and apple leaves (SRM 1515) standard reference materials (100 mg) were digested with 6mL of HNO_3 (65%), 2mL of H_2O_2 (30%) in microwave digestion system for 31 min and diluted to 50mL with deionized water. A blank digest was carried out in the same way. Final volume was 2 mL. Then the preconcentration procedure given above was applied to the final solutions.

Analysis of real samples

Analysis of the water samples

To assess the applicability of the method to real samples, it was applied to the extraction and determination of copper from different water samples. Tap water (Tehran, taken after 10 min operation of the tap) and Sea water (taken from Caspian Sea, near the Mahmoud-Abad shore) samples were analyzed (Table 3). As can be seen from Table 3 the added cadmium and lead ions can be quantitatively recovered from the water samples used. The water samples analyzed were filtered through a cellulose membrane filter (Millipore) of 0.45 µm pore size. The pH of the samples was adjusted to 9. Then PPCD solution was added. The sample was passed through the column. The PPCD chelates adsorbed on column were eluted with 1M HNO_3 in acetone. The effluent was evaporated to near dryness and made up to 2.0 mL with 1M HNO_3. The levels of the investigated analyte ions in the samples were determined by AAS.

Determination of cadmium and lead ions in salt samples

For the determination of analyte ions in alkaline salt samples, 3.0 g of each salt sample was dissolved in 3mL of distilled water and diluted to 100.0 mL with distilled water. The procedure given above was applied to these solutions. The analyte ions in the final solution were determined by atomic absorption spectrometry.

RESULTS AND DISCUSSION

Synthesis and characterization of graphene

Graphene nanoparticles were synthesized according to our previously reported study 36. The size and morphology of G was observed by scanning electron micros- copy (SEM) using an S-3000N microscope and X-ray diffraction (XRD) measurement was carried out using a Rigaku D/ max-rB diffractometer with Cu Ka radiation. In Fig. 1a, the SEM image shows the graphene agglomerate, consisting of al- most transparent carbon nanosheets with thin wrinkled and silk-like structures. XRD patterns in Fig. 1b reveal that the graphene nanosheets' peak at 2h = 26.2°, which is the characteristic peak of graphene.

Column preparation

Graphene (30.0 mg) was placed in a 3.0 mL SPE column using an upper frit and a lower frit to avoid adsorbent loss. Prior to extraction, the column was preconditioned with 10.0 mL meth- anol and 10.0

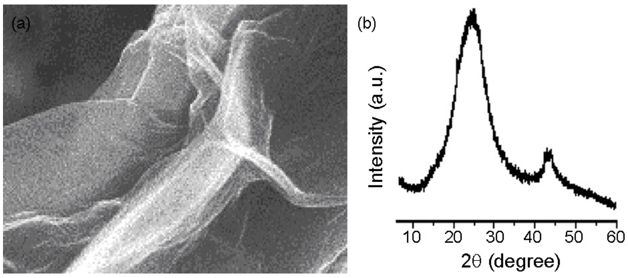


Fig. 1. SEM image and XRD pattern.

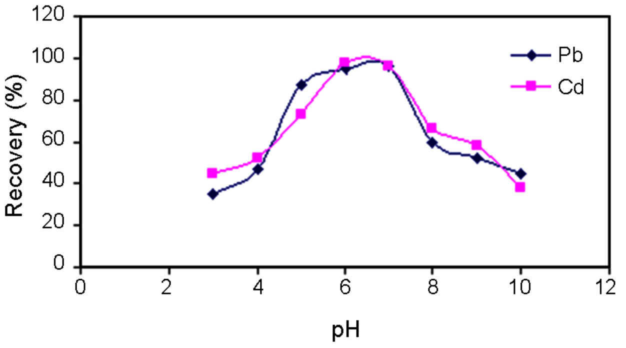


Fig. 2. Recoveries of cadmium and lead as a function of pH (eluent: 1M HNO3 in acetone, amount of resin: 600 mg, N= 3).

mL deionized water, respectively. The column was then conditioned to the desired pH with 5.0 mL of 0.2 mol.L^{-1} acetate buffer solutions.

Influences of pH of aqueous solutions on the retentions of cadmium and lead ions on Nano Graphene

The effects of the pH of the aqueous solution on the recoveries of the PPCD complexes of lead and cadmium were investigated in the pH range of 3–10 by using buffered model solutions containing 5 µg of cadmium(II) and 20 µg of lead(II). The results are depicted in Fig. 2. The recovery values for lead and cadmium ions were not quantitative at the pH values below 7. The recoveries increase with increasing pH and reach quantitative values at the pH range of 6-7 for both ions. All further studies were performed at pH 6 with acetic acid to ammonium buffer.

Ligand amounts

Prior to adsorption of traces heavy metal ions on a solid phase for preconcentration, generally metal ions were converted to a suitable form including metal chelates or metal inorganic complexes. Because of this point, 2-propylpiperidine-1-carbodithioate (PPCD) was selected as chelating agent for lead and cadmium ions. Different volumes of 1×10^{-2} M of PPCD solutions were added to model solutions containing 5 µg of cadmium(II) and 20 µg of lead(II). Then this solution passed through Nano Graphene column. Quantitative recoveries were obtained for lead and cadmium ions in the 2.0–4.0 mL of 1×10^{-2} MPPCD solution. Because of insufficient ligand amounts in the solutions, the recoveries of analytes were not quantitative when less than 2.0mL PPCD solution was used. After 4.0 mL of PPCD solution, the recoveries were below 95%, due to competition on the adsorption between PPCD–metal chelates and excess PPCD in the solution. In all further work, 3.0 mL of 1×10^{-2} M PPCD solution was added to the solutions.

Eluent type and eluent volume

Various elution solutions at 5 mL/min flow rate were examined to obtain quantitative recovery values for lead–PPCD and cadmium–PPCD chelates from Nano Graphene column. The recoveries of analytes were quantitative only with 1M HNO_3 in acetone. The recoveries were not quantitative when 1 and 2M HNO_3, 1 and 2M HCl and 1M HCl in acetone were used as eluent. 1M HNO_3 in acetone was used as the eluent all further work for quantitative recovery of metal ions from Nano Graphene. The volume of eluent (1M HNO_3 in acetone) that can completely strip the retained analytes from the solid phase is an important parameter for obtaining the maximum preconcentration factor. Thus some experiments were carried out in order to choose a proper eluent volume for the retained analyte ions on Nano Graphene. The recovery values for lead and cadmium ions from the Nano Graphene column were greater than 95%, in the eluent volume range of 5.0–10.0 mL. In the eluent volume lower than 5.0 mL, because of insufficient eluent volume, the recoveries of the analyte lions were not quantitative.

Effect of sample volume

The solid phase extraction technique is a common

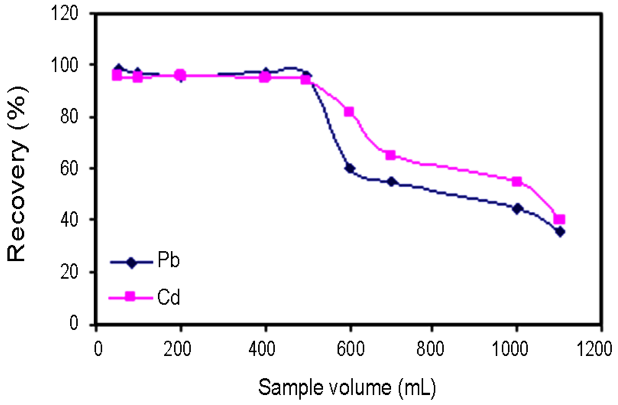


Fig. 3. Effects of sample volume on the recoveries of lead and cadmium ions on Nano Graphene (N= 3).

procedure for extraction and separation of metal ions from large sample volumes to obtain high preconcentration factor in the solid phase extraction studies. The recovery values as a function of sample volume were shown in Fig. 3. It was found that the recoveries were constant when up to 500 mL of the sample solution was used. At the higher volumes the recoveries for analytes decreased. Therefore a preconcentration factor of 250 can be achieved when using 500 mL of the sample and 2.0mL of final volume.

Amount of Nano Graphene

Due to the amounts of solid phase extractor is the one of the important factor for the quantitative retention of heavy metals at traces levels in the preconcentration studies based on solid phase extraction, the influences of the amount of Nano Graphene resin on the retention of cadmium and lead ions were examined by using the model solution containing analytes. The results are depicted in Fig. 4. Cadmium and lead ions were quantitatively retained in the range of 500–700 mg of Nano Graphene resin. The short glass column was filled with 600 mg of Nano Graphene for all further studies.

Influences of flow rates of sample and eluent solutions on the recoveries

The influences of the flow rates of sample and eluent solutions on the recoveries of cadmium and lead ions were investigated in the range of 1–10 mL/min. In the examination of the effects of sample and eluent solutions, 1M HNO_3 in acetone was used as eluent. The quantitative recovery values were obtained in the flow rate range of 1–8 mL/min for sample and eluent solution. After 8 mL/min of eluent solution, the recovery values of cadmium and lead ions were below 95%. Five milliliter per minute was selected as the flow rate for the all experiments for both flow rates of sample and eluent solutions.

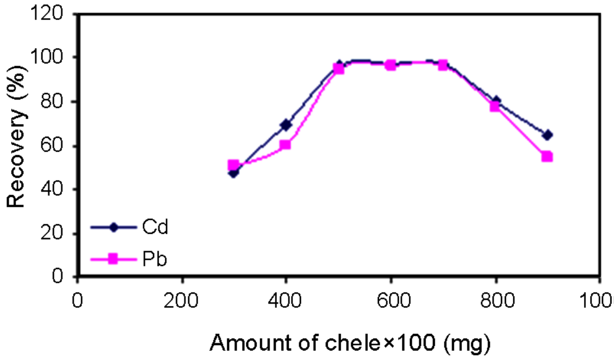


Fig. 4. Influences of amount of Nano Graphene on the retentions of cadmium and lead ions (N= 3).

Matrix effects

Because of the determination of the levels of traces metal ions of the highly saline samples were the goal, the influences of possible matrix ions in the environmental samples and some transition metals were also examined. The effect of potential interfering ions on the determination of lead and cadmium were investigated by adding known concentrations of each ion in a solution containing analytes and then determining the latter. The results were summarized in Table 2. The tolerated amounts of each ion were the concentration values tested that caused less than 5% the absorbance alteration. The ions normally present in water do not interfere under the experimental conditions used. Also, some of the transition metals at mg/L levels did not interfere with the recoveries of the analyte ions. This results show that the proposed preconcentration/ separation method could be applied to the highly saline samples and the samples that contains some transition metals including Ni^{2+}, Co^{2+}, Cr^{3+}, Zn^{2+}, Cu^{2+}, Fe^{3+}, Al^{3+} and Mn^{2+} at mg/L levels.

Figure of merits

The accuracy of the results was verified by analyzing the concentration after addition of known amounts of cadmium and lead into seawater, tap water, unrefined table salt and a refined salt sample. The results were given in Table 3. For all four samples, good agreements were obtained between the recoveries of analyte for spiked and control samples using the experimental procedure for analytes. The recoveries calculated for the additions were quantitative, thus confirming the accuracy of the present procedure and the absence of matrix effects. The analytical performance of the procedure can be calculated for the results from FAAS measurements. The reproducibility of the preconcentration and separation method was evaluated by passing 50 mL of solution containing analyte ions through the column and repeating this procedure ten times. The relative standard deviations (R.S.D.) were below 6%. The detection limits of the investigated elements based on three times the standard deviations

Table 2. Effect of the matrix ions on the recovery of metal ions (sample volume: 100 mL, N=3)

Ion	Added as	Concentration (mg/L)	Pb	Cd
Na^+	NaCl	10,000	96±2	98±3
		30,000	95±2	98±2
K^+	KCl	10,000	95±3	98±3
		20,000	95±2	96±3
Ca^{2+}	$CaCl_2$	10,000	98±2	97±2
		15,000	97±2	96±3
Mg^{2+}	$MgCl_2$	5000	98±2	98±2
		10,000	97±3	97±3
Cl^-	NaCl	10,000	97±3	98±3
		30,000	96±3	97±4
SO_4^{2-}	Na_2SO_4	5000	95±3	96±3
		10,000	94±2	95±3
PO_4^{3-}	Na_3PO_4	1000	96±3	97±3
		3000	95±2	96±4
F^-	NaF	1000	98±2	96±2
		3000	97±3	95±3
NO_3^-	KNO_3	5000	98±3	98±3
		10,000	97±3	97±2
Fe^{3+}	$FeCl_3$	25	97±3	96±2
		50	96±1	96±3
Al^{3+}	$Al_2(SO_4)_3$	25	97±3	96±3
		50	96±4	95±4
Mn^{2+}	$MnSO_4$	25	96±2	97±2
		50	96±3	96±3
Zn^{2+}	$ZnSO_4$	25	96±2	97±2
		50	96±3	97±3
Cu^{2+}	$CuSO_4$	25	98±3	98±2
		50	97±4	97±3
Cr^{3+}	$Cr(NO_3)_3$	25	98±3	95±3
		50	97±3	94±3
Co^{2+}	$CoSO_4$	25	98±2	96±2
		50	98±3	95±3
Ni^{2+}	$NiSO_4$	25	96±3	97±3
		50	95±2	96±2

of the blank (k=3, N= 20) on a sample volume 500 mL for cadmium and lead were 0.19 and 0.31 μg/L, respectively.

Adsorption isotherms and adsorption capacity

The adsorption behavior of Nano Graphene was determined by studying the amount of adsorbed cadmium and lead as a function of cadmium and lead concentrations; 50mL of solutions containing cadmium and lead at concentrations in the range 0.35–385 and 0.24–350 mg/L, respectively, were maintained under the optimum conditions determined before. The analytes in the eluents was determined by FAAS and the adsorption capacities of resin for cadmium and lead were calculated from Langmuir plots. The concentration of adsorbed cadmium(II) and lead(II) in mg/g (n) on to Nano Graphene as a function of its concentration in solution in mg/L (C) was investigated. The adsorption isotherms for cadmium and lead were shown in Fig. 5. The maximum adsorption capacity was obtained by

Table 3. Analysis of various samples spiked analyte ions (sample volume: 100 mL, final volume: 10 mL, N =4).

Refined table salt (3% (w/V))		Unrefined table salt (3% (w/V))		Sea water		Tap water		Added (µg)	Analyte
Found (µg) Recovery		Found (µg), Recovery		Recovery	Found (µg),	Recovery	Found (µg),		
x ± S.D[a] (%)		x ± S.D[a] (%)		(%)	x ± S.D[a]	(%)	x ± S.D[a]		
–	N.D.	–	N.D.	–	N.D.	–	N.D.	0	Pb
98 ± 3	9.8 ± 0.4	97 ± 3	9.8 ± 0.3	98 ± 3	9.8 ± 0.3	98± 3	9.8± 0.3	10	
98 ± 3	19.7 ± 0.7	97± 3	19.6 ± 0.6	98 ±3	19.7± 0.4	99 ± 3	19.8 ± 0.4	20	
99 ±2	39.5 ± 0.6	98 ± 2	39.2 ± 0.4	98 ± 3	39.6 ± 0.2	98 ±3	39.7± 0.5	40	
–	N.D.	–	N.D.	–	N.D.	–	N.D.	0	Cd
96 ± 2	2.4 ± 0.4	96 ± 3	2.4 ± 0.4	96 ± 3	2.4 ± 0.5	98±2	2.4± 0.5	2.5	
97 ± 2	4.9 ± 0.6	96 ± 2	4.8 ± 0.3	97 ± 2	4.8 ± 0.4	98± 3	4.9± 0.3	5	
96 ± 3	9.6 ± 0.4	96± 3	9.7 ± 0.3	98 ± 3	9.8 ± 0.5	98 ±3	9.9 ±0.5	10	

[a] S.D.: standard deviation, N.D.: not detected.

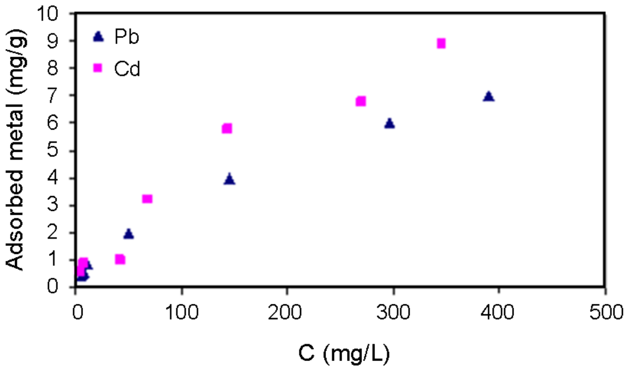


Fig. 5. Langmuir isotherm adsorption plots of lead(II) and cadmium(II) ions on Nano Graphene.

using a model Langmuir adsorption isotherm, based on following equation:

$$\frac{C}{n} = \frac{1}{n_m K} + \frac{1C}{n_m}$$

The maximum adsorption capacities (nm) of Nano Graphene for cadmium and lead were found to be 2.70 and 4.56 mg/g, respectively. The binding constants (K) were 0.211 l/mg for cadmium and 0.12 l/mg for lead.

Cadmium and lead contents of SRM samples

The method presented was checked to two different reference materials (IAEA-336 Lichen and SRM 1515 Apple leaves) for the determination of cadmium(II) and lead(II) ions. The certified and observed values for IAEA-336 Lichen and SRM 1515 Apple leaves were given in Table 4. The results found were in good

Table 4. The levels of lead(II) and cadmium(II) as µg/g in reference standard materials (final volume: 2 mL, N=4)

SRM 1515 Apple leaves		SRM (IAEA-336 Lichen)		Elements
Certified Value	Observed value	Certified value	Observed value	
0.50 ± 0.06	0.49	4.9 ± 0.2	5.0	Pb
0.015 ± 0.05	(0.015)[a]	0.117 ± 0.04	0.118	Cd

[a] The value in the parenthesis is not certified. Mean expressed as 95 %tolerance limit.

Table 5. Concentration of analyte ions in natural water samples as µg/L (N= 4, sample volume: 500 mL, final volume: 2 mL)

Cd	Pb	
1.8 ± 1.7	4.9 ± 1.1	Tap water from Tehran
1.5 ± 0.3	2.6 ± 0.8	Sea water from Caspian sea

Mean expressed as 95% tolerance limit.

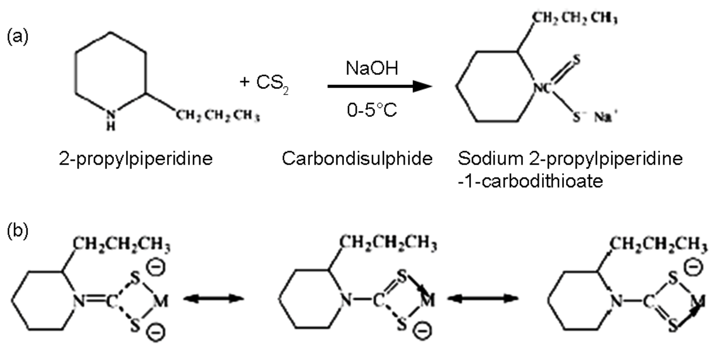


Fig. 6. (a) Synthesis of sodium 2-propylpiperidine-1-carbodithiodate reagent. (b) Resonance hybrid of the 2-propyl piperidine-1-carbodithioate with metal.

Table 7. Comparative data from recent papers on 2-propylpiperidine-1-carbodithioate (PPCD)used chelating agent on preconcentration studies

References	R.S.D. (%)	limit Detection (µg/L)	PF	Method and instrumental detection	Analytes
Moghimi, 2014	<5	0.8–23.2	50	SPE on Amberlite XAD-2/AAS	Cu(II), Cd(II), Pb(II)
Brunner, 2003	<5	50	–	SPE on aminocarboxylic amphoteric resin/DRS	Ni(II)
Shojai, 2015	1.6	0.024	100	SPE on surfactant-coated alumina/AAS	Cd(II)
Narin, 2000	0.74–1.8	0.12–0.26	15.9–16.3	CPE/CE	Cu(II), Co(II)
Present work	5–6	0.19 – 0.31	250	SPE on NanoGraphene /AAS	Pb(II), Cd(II)

agreement with the certified values of SRMs. If the concentration levels of the most common matrix constituents of reference standard materials analyzed and the accuracy of the presented method are considered together, it can be concluded that the proposed method is free from interferences of the various constituents.

Application to real samples

The PPCD/ Nano Graphene solid phase extraction procedure for lead and cadmium ions was applied to various environmental samples. The results for natural water and some salt samples were given in Tables 5 and 6, respectively.

Comparison with other preconcentration studies used 2-propylpiperidine-1-carbodithioate (PPCD)

2-propylpiperidine-1-carbodithioate (PPCD) is a reagent for the spectrophotometric determination of lots of transition metal ions. PPCD acts as a terdendate ligand complexing with metals through the hydroxyl oxygen atom, pyridine nitrogen atom and one of the azo group nitrogen atoms. PPCD has been also used for the separation and preconcentration of traces heavy metals as chelating agent from various media. Comparative data from some recent papers on preconcentration studies used 2-propylpiperidine-1-carbodithioate (PPCD) for traces metal ions for the figure 6 of the merits are summarized in Table 7.

The Nano Graphene /PPCD method presented in this study is most promising for the analyte ions as the preconcentration factor is 250. The preconcentration factor achieved with presented procedure is superior to solid phase extraction method given in Table 7 and some preconcentration/separation procedures including cloud point extraction, solid phase extraction, electroanalytical techniques. The detection limits of investigated elements are superior to those of some preconcentration/ separation techniques for analyses. The matrix effects with the method were reasonably tolerable. The elution of the analytes from the Nano Graphene column was easily performed with 1M HNO_3 in acetone. The good features of the proposed method showed that it’s convenient and low cost. Also the method is relatively rapid as compared with previously reported procedures for the enrichment of lead and cadmium ions. The Nano Graphene in the column can be used at least 200 times.

CONCLUSIONS

The reusability of Nano Graphene was as high as greater than 200 cycles without any loss in its sorption behavior. The system was also successful in preconcentrating metal ions from large sample volumes. In addition to validating the developed method by successfully analyzing standard reference materials (lichen (IAEA-336) and apple leaves (SRM 1515)), lead(II) and cadmium(II) content was established in natural waters, some salts samples by the developed preconcentration method.

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