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Simultaneous Preconcentration of Cadmium(II) and Lead(II) in Water Samples Using Resin Amberlite XAD-2 Functionalized with Nitroso R Salt and Determination with Atomic Absorption Spectrometry

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A preconcentration/separation procedure is presented for the solid phase extraction of trace cadmium and lead ions in environmental samples on Amberlite XAD-2 functionalized with nitroso R salt resin, 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 influence of pH on the model solutions, amounts of, eluent type and volume, *etc*. were investigated. 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, with satisfactory results (recoveries > 95 %, relative standard deviations < 7 %).

Key Words: Preconcentration, Cadmium(II), Lead(II), Amberlite XAD-2, Nitroso R salt, Solid phase extraction, Atomic absorption spectrometry.

INTRODUCTION

The transition metals including cadmium, chromium, lead, *etc*., are an important risk for human and animals[1-3]. Heavy metals at trace levels are also components of the natural biosphere. Because the main sources of heavy metals for human and animals are water, food and atmosphere[1,4,5], reliable and sensitive analytical methods and procedures have an important role to evaluate the impacts of metal pollutants. The determination of traces metal ions in these samples are continuously performed in the analytical chemistry laboratories around the world by using various instrumental techniques including atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), *etc*. Although, atomic absorption spectrometry and atomic emission spectrometry are among the most widely methods used for trace metal determination, their sensitivity is usually insufficient for monitoring the low level concentrations of metals in the environmental samples. The interfering effects of the matrix components of the samples are one of the main problems in the determination of trace heavy metals by AAS and or ICP-AES.

Also lower elements concentrations than the detection limits of the instrumental technique are another problem in the trace heavy metal determinations in environmental samples. Consequently, a preconcentration/ separation process is usually required[6-10].

Coprecipitation[11-13], membrane filtration[14,15], electrodeposition[16], cloud point extraction[17] and solvent extraction[18-21] are the popular methods for the pre-concentration and separation of the trace transition metal ions. Solid phase extraction (SPE) of trace metal ions is also an important preconcentration/separation technique[1,22-25].

Although, disadvantages such as significant chemical additives, solvent losses, complex equipment, large secondary wastes, unsatisfactory enrichment factors and high time consumption limit the application of these techniques. These problems could be addressed by the development of modular and compact processes that provide adequate separation and preconcentration without complex processes. The solvent microextraction technique effectively overcomes these difficulties by reducing the amount of organic solvent as well as allowing sample extraction and preconcentration to be done in a single step. The technique is faster and simpler than conventional methods. It is also inexpensive, sensitive and effective for the removal of interfering matrices. Solvent microextraction is a form of solvent extraction with phase ratio values higher than 100. Compared with the conventional solvent extraction, microextraction may provide poorer analyte recovery, instead the concentration in the organic phase greatly enhances. In addition, the amount of the organic solvent is highly reduced and only one step of manipulation is necessary, therefore, problems of contamination and loss of analytes vanishes.

Cloud point extraction (CPE)[26-31], homogeneous liquid-liquid extraction (HLLE)[32,33] and single drop microextraction (SDME)[34-38] are fairly new methods of sample preparation which are used in separation and preconcentration of metals and can solve some of the problems encountered with the conventional pretreatment techniques.

In the previous researches, we demonstrated a novel microextraction technique, named dispersive liquid-liquid microextraction (DLLME), which was successfully used, for the extraction and determination of polycyclic aromatic hydrocarbons (PAHs), organphosphorus pesticides (OPPs) and chlorobenzenes in water samples[39-41]. Dispersive liquid-liquid microextraction is a modified solvent extraction method and its acceptor-to-donor phase ratio is greatly reduced comparing with the other methods. In DLLME, the appropriate mixture of the extraction and disperser solvents is rapidly injected by syringe into aqueous samples containing analytes. Thereby, cloudy solution forms. In fact, the cloudy state results from the formation of fine droplets of the extraction solvent, which disperse in the sample solution. Then, this cloudy solution shall be centrifuged and the fine droplets sediment at the bottom of the conical test tube. The determination of anlaytes in sedimented phase can be performed by instrumental analysis. In this extraction method any component in the solution, directly or indirectly after previous (or simultaneous) derivatization reaction, interacts with the fine droplets of the extraction solvent and consequently gets extracted from the initial solution and concentrates in the small volume of the sedimented phase. Simplicity of the operation, rapidity, low sample volume, low cost, high recovery and high enrichment factor are some advantages of DLLME.

Dispersive liquid-liquid microextraction is a miniaturized sample pre-treatment technique. On the other hand, graphite furnace atomic absorption spectrometry (GF AAS) is a microamount sample analysis technique. Therefore, it makes it perfect when a combination of both DLLME and GF AAS is used. The applicability of the approach has been demonstrated for the determination of cadmium in water samples. This element was selected for evaluation of the procedure because cadmium is one of the principal heavy metals of analytical interest due to its extreme toxicity even at relatively low concentrations[42,43].

In our best of knowledge, SPE and preconcentration by Cd(II)-imprinted diazoaminobenzene-vinylpyridine copolymer packed-bed columns have not been employed for the separation and preconcentration of Cd(II) from aqueous solution. This paper reports the synthesis of Cd(II) imprinted and non-imprinted copolymers by copolymerizing cadmium chloride (or without it), diazoaminobenzene (DAAB) and vinylpyridine (VP) using ethyleneglycol dimethacrylate (EGDMA) as cross-linker in presence of 2,2'-azobisisobutryonitrile as initiator and its analytical applications for column preconcentrative separation of Cd(II) from natural water. Thus, it described a preconcentration/separation procedure based on solid phase extraction of lead and cadmium in some natural water samples and salts. The analytical parameters relevant quantitative retentions of lead and cadmium on Amberlite XAD-2 functionalized with nitroso R salt were also investigated.

EXPERIMENTAL

A Varian SpectrAA model 200 atomic absorption spectrometer with deuterium background corrector was used in this study. A 10 cm long slot-burner head, a lamp and an air acetylene flame were used. The operating conditions are 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.

Synthesis of resin: A modified version of a procedure described in the literature for similar reagents[44,45] was used to synthesize NRS-XAD. Amberlite XAD-2 (5 g) was treated with 10 mL of concentrated HNO_3 and 25 mL of concentrated H_2SO_4 and the mixture stirred at 60 ºC for 1 h on a water bath. Thereafter, the reaction mixture was poured into an ice-water mixture. The nitrated resin was filtered, washed repeatedly with water until free from acid and thereafter, treated with a reducing mixture of tin(II) chloride, conc. hydrochloric acid and ethanol. The system was refluxed for 12 h at 90 ºC. The precipitate was filtered off and washed with water

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

and 2 mol L^{-1} NaOH. The amino resin was first washed with 2 mol L^{-1} HCl and finally with ultrapure water to remove the excess of HCl. It was suspended in an ice-water mixture (150 mL) of 1 mol L^{-1} HCl and 1 mol L^{-1} $NaNO_2$. The diazotized resin was filtered, washed with ice-cold water and reacted with nitroso R salt (3.0 g in 250 mL of 5 % (w/v) NaOH solution) at 0-5 ºC for 24 h. The resulting dark-brown resin was filtered, washed with water and dried in air.

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. After 5-10 min, the solution was 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 1 M HNO_3 in acetone at 5.0 mL/min of flow rate. The eluent was evaporated over a hot plate to near dryness at 35 ºC in a hood and was diluted to 2 mL or 5 mL with 1 M 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 6 mL of HNO_3 (65 %), 2 mL of H_2O_2 (30 %) in microwave digestion system for 0.5 h and diluted to 50 mL 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 cadmium and lead 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-2). As can be seen from Table-2 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. The sample was passed through the column. The trace cadmium and lead ions adsorbed on column were eluted with 1 M HNO_3 in acetone. The effluent was evaporated to near dryness and made up to 2.0 mL with 1 M HNO_3. The levels of the investigated analyte ions in the samples were determined by AAS.

TABLE-2
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) x ± S.D.^{a}	Recovery (%)	Found (µg) x ± S.D.^{a}	Recovery (%)	Found (µg) x ± S.D.^{a}	Recovery (%)	Found (µg) x ± S.D.^{a}	Recovery (%)		
–	N.D.	–	N.D.	–	N.D.	–	N.D.	0	Pb
98 ± 3	9.8 ± 0.4	97 ± 3	9.8 ± 0.3	98 ± 2	9.8 ± 0.7	98± 3	9.8± 0.3	10	–
98 ± 3	19.7 ± 0.7	97± 3	19.6 ± 0.6	98 ±2	19.7± 0.7	99 ± 3	19.8 ± 0.4	20	–
98 ±3	39.5 ± 0.6	98 ± 2	39.2 ± 0.4	98 ± 3	39.6 ± 0.8	98 ±2	39.7± 0.8	40	–
–	N.D.	–	N.D.	–	N.D.	–	N.D.	0	Cd
96 ± 2	2.4 ± 0.7	96 ± 3	2.4 ± 0.4	96 ± 3	2.4 ± 0.5	98±2	2.4± 0.8	2.5	–
98 ± 3	4.9 ± 0.5	96 ± 2	4.8 ± 0.3	97 ± 2	4.8 ± 0.8	98± 4	4.9± 0.9	5	–
96 ± 3	9.6 ± 0.4	96± 3	9.7 ± 0.3	98 ± 3	9.8 ± 0.5	98 ±3	9.9 ±0.6	10	–

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

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 3 mL of distilled water and diluted to 100.0 mL with distilled water. The procedure given above was applied to this solution. The analyte ions in the final solution were determined by atomic absorption spectrometry.

RESULTS AND DISCUSSION

Influences of pH of aqueous solutions on the retentions of cadmium and lead ions on Amberlite XAD-2 functionalized with nitroso R salt: The effects of the pH of the aqueous solution on the recoveries of the trace cadmium and lead ions 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. 1. 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.

Resin characterization: Elemental analysis (found: C, 47.9 %; H, 3.1 %; N, 8.5 %; calculated for $C_{18}H_{13}N_3O_8S_2$: C, 46.6 %; H, 2.8 %; N, 9.1 %) shows that on an average one nitroso R salt molecule is present in the resin/repeat unit of the polymer. A structure according with elemental analysis is shown in Fig. 2. The infrared spectrum of NRS-XAD resin is compared with that of free Amberlite XAD-2. There are additional bands at 3460, 1540, 1440, 1400 and 1335 cm^{-1}, which appear to originate due to modification of resin by the ligand and are characteristic of O-H, -N=N-, C-N, N=O and C-OH vibrations, respectively.

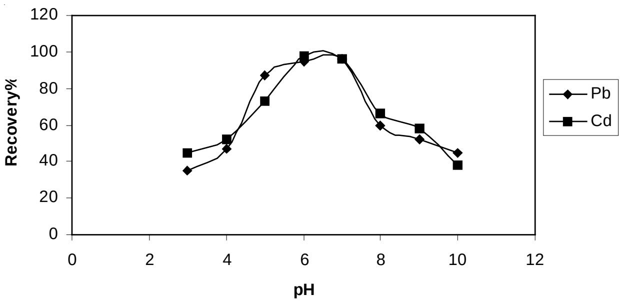

Fig. 1. Recoveries of cadmium and lead as a function of pH (eluent: 1 M HNO_3 in acetone, amount of resin: 600 mg, N = 3)

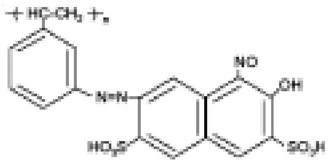

Fig. 2. Proposed structure for NRS-XAD

Eluent type and eluent volume: Various elution solutions at 5 mL/min flow rate were examined to obtain quantitative recovery values for lead and cadmium from Amberlite XAD-2 functionalized with nitroso R salt column. The recoveries of analytes were quantitative only with 1 M HNO_3 in acetone. The recoveries were not quantitative when 1 and 2 M HNO_3, 1 and 2 M HCl and 1 M HCl in acetone were used as eluent. 1 M HNO_3 in acetone was used as the eluent all further work for quantitative recovery of metal ions from Amberlite XAD-2 functionalized with nitroso R salt.

The volume of eluent (1 M HNO_3 in acetone) 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 Amberlite XAD-2 functionalized with nitroso R salt. The recovery values for lead and cadmium ions from the Amberlite XAD-2 column were more than 95 %, in the eluent volume range of 5.0-10.0 mL. In the eluent volume lower than 5 mL, because of insufficient eluent volume, the recoveries of the analyte ions were not quantitative.

Effect of sample volume: The solid phase extraction technique is a common 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 2.0 mL of final volume.

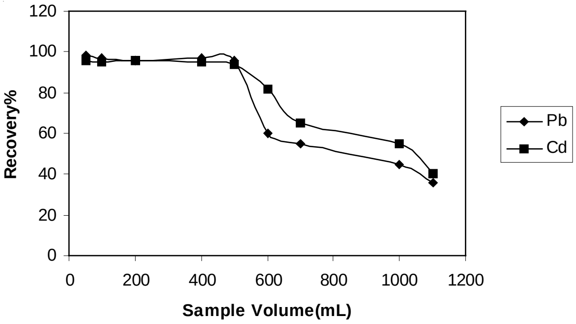

Fig. 3. Effects of sample volume on the recoveries of lead and cadmium ions on Amberlite XAD-2 functionalized with nitroso R salt (N = 3)

Amount of amberlite XAD-2 functionalized with nitroso R salt: The amounts of solid phase extractor are the one of the important factors 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 Amberlite XAD-2 resin on the retention of cadmium and lead ions were examined by using the model solution containing analytes. The results are shown in Fig. 4. Cadmium and lead ions were quantitatively retained in the range of 500-700 mg of Amberlite XAD-2 resin. The short glass column was filled with 600 mg of Amberlite XAD-2 for all further studies.

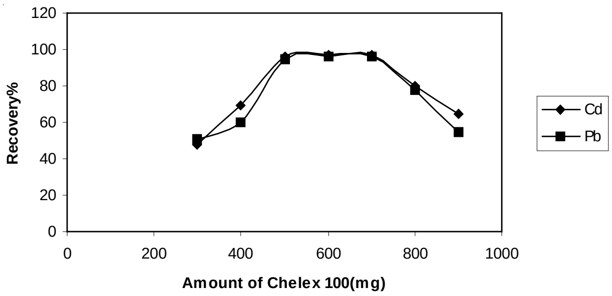

Fig. 4. Influences of amount of Amberlite XAD-2 functionalized with nitroso R salt resin on the retentions of cadmium and lead ions (N= 3)

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, 1 M 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 %. 5 mL/min was selected as the flow rate for the all the experiments for both flow rates of sample and eluent solutions.

Matrix effects: Because of the determination of the levels of trace 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-3. The tolerated amounts of each ion were the concentration values tested that caused less than 5 % the absorbance alteration.

TABLE-3
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
		25,000	95 ± 2	98 ± 2
K^+	KCl	10,000	95 ± 2	98 ± 3
		25,000	95 ± 2	96 ± 3
Ca^{2+}	$CaCl_2$	10,000	98 ± 2	97 ± 3
		10,000	97 ± 2	96 ± 2
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 ± 3
SO_4^{2-}	Na_2SO_4	4000	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 ± 2
		10,000	97 ± 3	97 ± 3
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
		60	96 ± 3	96 ± 3
Zn^{2+}	$ZnSO_4$	25	96 ± 2	97 ± 2
		40	96 ± 3	97 ± 3
Cu^{2+}	$CuSO_4$	35	98 ± 3	98 ± 2
		50	97 ± 4	97 ± 3
Cr^{3+}	$Cr(NO_3)_3$	35	98 ± 3	95 ± 3
		40	97 ± 3	94 ± 3
Co^{2+}	$CoSO_4$	25	98 ± 2	96 ± 2
		40	98 ± 3	95 ± 3
Ni^{2+}	$NiSO_4$	25	96 ± 3	97 ± 3
		40	95 ± 2	96 ± 2

The ions normally present in water do not interfere under the experimental conditions used. Some of the transition metals at mg/L levels did also 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 which contains some transition metals *e.g.*, 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 refined salt sample. The results were given in Table-2. For all the 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 10 times. The relative standard deviations (RSD) were below 6 %. The detection limits of the investigated elements based on three times the standard deviations 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 behaviour of amberlite XAD-2 functionalized with nitroso R salt was determined by studying the amount of adsorbed cadmium and lead as a function of cadmium and lead concentrations 50 mL of solutions containing cadmium and lead with 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 amberlite XAD-2 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 were obtained by using a model Langmuir adsorption isotherm[40,41], based on following equation:

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

The maximum adsorption capacities (nm) of Amberlite XAD-2 functionalized with nitroso R salt 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

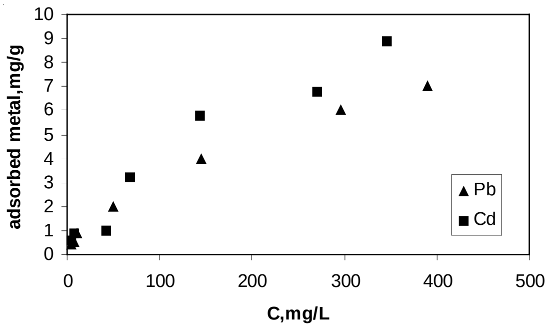

Fig. 5. Langmuir isotherm adsorption plots of lead(II) and cadmium(II) ions on Amberlite XAD-2 functionalized with nitroso R salt

and observed values for IAEA-336 Lichen and SRM 1515 Apple leaves were given in Table-4. The results found were in good 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.

TABLE-4
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)		Element
Certified value	Observed value	Certified value	Observed value	
0.50 ± 0.06	0.480	4.900 ± 0.20	5.000	Pb
0.015 ± 0.06	(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.

Application to real samples: The amberlite XAD-2 functionalized with nitroso R salt 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 amberlite XAD-2 functionalized with nitroso R salt: Amberlite XAD-2 functionalized with nitroso R salt is for the spectrophotometric determination of a number of transition metal ions[40,41]. Amberlite XAD-2 functionalized with nitroso R salt acts as a terdendate

TABLE-5
CONCENTRATION OF ANALYTE IONS IN NATURALWATER SAMPLES AS µg/L (N = 4, SAMPLE VOLUME: 500 mL, FINAL VOLUME: 2 mL)

Cd	Pb	
1.8 ± 1.3	4.9 ± 1.2	Tap water from Tehran
1.5 ± 0.4	2.6 ± 0.9	Sea water from Caspian sea

Mean expressed as 95 % tolerance limit.

TABLE-6
APPLICATION OF PRESENTED METHOD FOR THE LEVELS OF CADMIUM AND LEAD IN SOME SALT SAMPLES (FINAL VOLUME: 2 mL, N = 4)

	Concentration (μg/g)	
	Pb	Cd
Refined table salt	1.5 ± 0.3	0.14 ± 0.04
Unrefined table salt	2.6 ± 0.5	0.23 ± 0.05
Ammonium chloride (technical grade)	7.9 ± 0.4	0.42 ± 0.04
Sodium chloride (technical grade)	7.0 ± 0.4	0.38 ± 0.03

Mean expressed as 95 % tolerance limit.

ligand complexing with metals through the hydroxyl oxygen atom, pyridine nitrogen atom and one of the nitrogen atoms of the azo group. Amberlite XAD-2 functionalized with nitroso R salt has also been 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 amberlite XAD-2 functionalized with nitroso R salt for traces metal ions for the figure of the merits are summarized in Table-7.

The amberlite XAD-2 functionalized with nitroso R salt 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

TABLE-7
COMPARATIVE DATA FROM RECENT PAPERS ON 2-PROPYLPIPERIDINE-1-CARBODITHIOATE (PPCD) USED CHELATING AGENT ON PRECONCENTRATION STUDIES

Ref.	RSD (%)	Limit detection (μg/L)	PF	Method and instrumental detection	Analytes
46	0.96	200	25-50	SPE on naphthalene/DDP	In(III)
47	1.4-4.0	–	100	SPE on surfactant-coated alumina/AAS	Co(II)
48	1.1	20	40	SPE on naphthalene/spectrophotomety	Ir(III)
49	2.4	40	300	SPE on surfactant-coated alumina/AAS	Ni(II)
50	0.98	70	40	SPE on naphthalene/DDP	Cd(II)
51	< 10	0.38	115	CPE/AAS	Co
52	< 5	0.8-23.2	50	SPE on Amberlite XAD-2/AAS	Cu(II), Cd(II), Pb(II)
53	< 5	50	–	SPE on aminocarboxylic amphoteric resin/DRS	Ni(II)
54	1.6	0.024	100	SPE on surfactant-coated alumina/AAS	Cd(II)
55	0.74-1.8	0.12-0.26	15.9-16.3	CPE/CE	Cu(II), Co(II)
56	<10	15	–	Electroanalytical/voltammetry	Pb(II)
44	2.1-3.0	0.4	100	SPE on chloromethylated polystyrene/AAS	Hg(II)
Present work	5-6	0.19-0.31	250	SPE on Amberlite XAD-2/FAAS	Pb(II), Cd(II)

PF: preconcentration factor, CPE: cloud point extraction, SPE: solid phase extraction, CE: capillary electrophoresis, AAS: atomic absorption spectrometry, DDP: differential pulse polarography, DRS: diffuse reflection spectroscopy.

solid phase extraction method given in Table-7 and some preconcentration/separation procedures including cloud point extraction, solid phase extraction, electroanalytical techniques[42,43,46-55]. The detection limits of investigated elements are better to those of some preconcentration/separation techniques for analyses[42,43,46-56]. The matrix effects with the method were reasonably tolerable.

The elution of the analytes from the amberlite XAD-2 functionalized with nitroso R salt column was easily performed with 1 M HNO_3 in acetone. The good features of the proposed method showed that its convenient and economic. Also the method is relatively rapid as compared with previously reported procedures for the enrichment of lead and cadmium ions. The Amberlite XAD-2 functionalized with nitroso R salt resin in the column can be used at least 200 times.

Conclusion

The reusability of Amberlite XAD-2 functionalized with nitroso R salt was as high as more than 200 cycles without any loss in its sorption behaviour. 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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