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Full Length Research Paper

Solid phase extraction of Cd(II) using mesoporous organosilicas and determination by FAAS

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A simple and reproducible method for the rapid extraction and determination of trace amounts of Cd(II) ions using mesoporous organo-silicas mesoporous silica and atomic absorption spectrometry is presented. Common coexisting ions did not interfere with the separation and determination. The preconcentration factor was 100 (1 ml elution volume) for a 100 ml sample volume. The limit of detection of the proposed method is 0.7 ng L^{-1}. The maximum sorption capacity of sorbent under optimum conditions has been found to be 5 mg of Cd per gram of sorbent. The relative standard deviation under optimum conditions was 3.0% (*n* = 10). Accuracy and application of the method was estimated by using test samples of natural and synthetic water spiked with different amounts of Cd(II) ion.

Key words: Preconcentration, Cd(II), mesoporous organo-silica, solid phase extraction, flame atomic absorption spectrometry (FAAS).

INTRODUCTION

In the recent years, pollution of the environment by heavy metals has received considerable attention. These elements accumulate in living organisms and are of high toxic potential. Their wide technological use (fertilizers, mining, pigments), as well as their production from burning oil and coal and incineration of waste cause an extensive anthropogenic contamination of soil, air and water (Carasek et al., 2002). Several analytical techniques such as flame atomic absorption spectrometry (FAAS) (Moghimi, 2006; Anthemidis et al., 2004), inductively coupled plasma atomic emission spectrometry (ICP-AES) (Boevski et al., 2000) and inductively coupled plasma mass spectrometry (ICP-MS)(Xia et al., 2005) are available for the determination of trace metals with enough sensitivity for the most applications. Despite good developments in the modern analytical instruments, which allow great enhancement in aspects of analysis, in many cases the available analytical instrumentation does not have enough sensitivity for the analysis of natural samples. Sample preparation is still a bottleneck for over-all throughput because the involved steps often employ large volumes of hazardous organic solvents, are time consuming and/or expensive (Carasek et al., 2002). Although, the determination of trace metal ions in natural waters is difficult due to various factors, particularly their low concentrations and matrices effects. Pre-concentration and separation can solve these problems and can lead to a higher confidence level and easy determination of the trace elements. Several procedures have been developed for the separation and preconcentration of contaminants from environmental matrices, such as: liquid–liquid extraction (Welz, 1985; Marczenko, 1986; Anthemidis et al., 2003), co-precipitation (Atsumi et al., 2005; Saracoglu et al., 2003; Doner and Ege, 2005), solid phase extraction (SPE) (Yamini et al., 2003; Burham et al., 2006; Moghimi, 2007; Jamali et al., 2006; Bowles et al., 2006; Melek et al., 2006; Dos Santos et al., 2005; Lemos and Baliza, 2005; Wang, 2002).

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 with-out complex processes. The solvent microextraction technique effectively overcomes these difficulties by reducing the

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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 micro-extraction is a form of solvent extraction with phase ratio values higher than 100. Compared with the conventional solvent extraction, micro-extraction may provide poorer analytic recovery, instead the concentration in the organic phase greatly enhances. In addition, the amount of the used organic solvent is highly reduced and only one step of manipulation is necessary, therefore, problems of contamination and loss of analytes vanish.

Cloud point extraction (CPE) (Hinze and Pramaur, 1993; Stalikas, 2002; Paleogos et al., 2005; Borges et al., 2003; Nayebi et al., 2006; Zhu, 2006), homogeneous liquid–liquid extraction (HLLE) (Ghiasvand et al., 2005; Igarashi et al., 2000) and single drop micro-extraction (SDME) (Fan and Zhou, 2006; Li et al., 2006; Chamsaz et al., 2003; Fragueiro et al., 2004; Fragueiro et al., 2006) are fairly new methods of sample preparation which are used in separation and pre-concentration of metals and can solve some of the problems encountered with the conventional pretreatment techniques.

In the previous researches, we demonstrated a novel micro-extraction 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 (Rezaee et al., 2005; Berijani et al., 2006; Rahnama et al., in press). DLLME 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 disperses 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.

DLLME is a miniaturized sample pre-treatment technique. On the other hand, graphite furnace atomic absorption spectrometry (GF AAS) is a micro-amount sample analysis technique. Therefore, it makes it perfect when a combination of both DLLME and GFAAS 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 (Robards and Worsfold, 1991; Kaewsarn and Yu 2001; Tehrani et al., 2005).

In our 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.

In this study, we report the synthesis of this new sorbent and its application as a selective sorbent for separation, preconcentration and determination of Cd^{2+} ions by AAS determination.

EXPERIMENTAL

Apparatus

Determination of Cd^{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. Separation of sorbent was assisted using a centrifuge (centurion scientific model: K 240R, West Sussex, U.K.). The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353). A cadmium hollow cathode lamp, operated at a current of 8 mA and a wavelength of 228.8 nm with a spectral band pass of 0.7 nm was used.

Reagents and solutions

All reagents were of the highest purity available from Merck and were used as received. Analytical grade nitrate salts of litium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt(II), and copper(II) were of the highest purity. Ultra pure organic solvents were obtained from E.Merck, Darmstat, Germany, and High Purity double distilled deionized water was used throughout the experiments.

The stock standard solution of Cd^{2+} was prepared by dissolving 0.1000 g of the Cd powder in 10 mL concentrated nitric acid and diluted to 1000 mL with water in a calibrated flask. Working solutions were prepared by appropriate dilution of the stock solution.

The chemicals used for the preparation of mesoporous silica-based materials were used as received: tetraethoxysilane TEOS (>98% Merck), c-aminopropyltriethoxysilane APTES (99% Sigma–Aldrich), cetyltrimethylammonium bromide (CTAB) (98% Fluka), ethanol (95–96% Merck) and aqueous ammonia (28% Prolabo).

Preparation and characterization of the mesoporous organosilicas

The mesostructured amine-functionalised silica material was prepared according to a previously published procedure (Walcarius et al., 2004; Etienne et al., 2002). First 2.4 g of CTAB was dissolved in

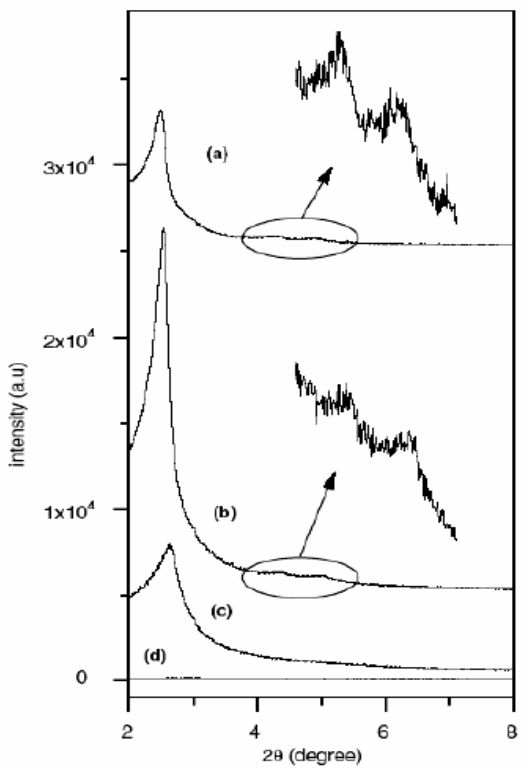


Figure 1. Powder XRD patterns for: (a) as-synthesised APS, (b) surfactant-extracted APS, (c) surfactant-extracted APS after deprotonation in alkaline ethanol, and (d) surfactant-extracted APS after deprotonation in alkaline aqueous medium (0.01M NaOH).

a solution containing 50 mL distilled water + 50 mL ethanol + 13mL ammonia 28%. Then, the precursors APTES and TEOS were introduced according to an APTES/(APTES + TEOS) molar ratio of 10%. The mixture was left under stirring at ambient condition for 2 h, then filtered on a Bu¨chner funnel, rinsed alternatively with distilled water and ethanol, and dried under vacuum ($<10^{-2}$ bar) for 24 h. Surfactant extraction was achieved by refluxing 1 g of the as-synthesised solid into 100 mL of 1 M HCl in ethanol for 18 h. The final product was recovered by filtration after washing three times with ethanol. It will be denoted ''APS'' (aminopropylsilica) afterwards. The particles have been characterized by powder X-ray diffraction (XRD), the resulting XRD patterns being collected with an X'PERT PRO from Philips equipped with a Cd anode (Kα1 radiation, k = 1.54056 A˚). Their porosity was analysed by the BET method on the basis of nitrogen adsorption– desorption measurements carried out at 77 K using a Coulter SA3100 apparatus after out gassing overnight at 323 K. Particle size distribution was measured using a light scattering analyser (model LA920, Horiba), based on the Mie scattering theory.

For some experiments, an amorphous silica material functionalised with the dipeptide carnosine was used as a solid-phase extractant for Cd(II) species. It was obtained by allowing TEOS to co-condensate with a precursor synthesized by amide coupling between the amino group of APTES and the carboxyl group of carnosine, using ethanol as co-solvent and ammonia in a catalytic amount (Sayen et al., 2003; Hamdoune et al., 2001). The copolymer precipitates several hours after mixing 1.21 g of the (triethoxysilyl)alkylamido-carnosine precursor with 1.95 g TEOS, in a solution containing 1.22 g water and 6.42 g ethanol, with 0.06 g NH_3 as the catalyst. The solvents are slowly evaporated to recover a dry white solid after about five days of reaction, the solid particles being washed thoroughly with dichloromethane and methanol before use. They are noted ''Scar'' (silica-carnosine) hereafter.

Procedure

A batch-wise process was employed for the extraction and preconcentration of Cd. Extraction was performed in test tubes containing Cd^{2+} in 10 ml acetate buffered solution (pH 3.0). Sixty milligrams mesoporous organo-silicas were added into the solution. After that, the mixture was shaken manually for an appropriate time to extract Cd completely from the solution. Finally, test tubes were placed in centrifuge and separation of sorbent was achieved by centrifugation for 2.5 min at 3500 rpm. The bulk aqueous phase was removed with a pipette and any residual aqueous phase was easily decanted. The back extraction was performed using 1.0 ml of 1.0 mol l^{-1} methanol solution. The Cd concentration was determined by Flame Atomic Absorption Spectrometry (FAAS).

RESULTS AND DISCUSSION

Some preliminary experiments were carried out in order to investigate the extraction of Cd by the mesoporous organo-silicas from solution. The results showed that mesoporous organo-silicas can extract it quantitatively.

Characterization of silica-based materials

The physico-chemical characteristics of both APS and Scar materials are as expected from previous studies (Sayen et al., 2003; Etienne et al., 2002).

X-ray diffractogramm of APS (Figure 1, curve ‘a’) reveals the existence of an ordered structure at the mesoporous scale, typical of a hexagonal MCM-41 structure, featuring one main correlation reflection at a 2 h angle of 2.49˚ and two weaker reflections at higher 2 h angles (diffraction planes indexed as 1 0 0, 1 1 0 and 2 0 0). The regular mesostructure was maintained after template removal (Figure 1, curve ‘b’), this step resulting however in slight lattice contractions (2 h angle of main line at 2.54˚) as previously observed for mesoporous organo-silicas prepared by the co-condensation route (Tehrani et al., 2005). Nitrogen adsorption–desorption isotherms were of type 5 (not shown here but similar as in Walcarius et al., 2004), in agreement with what was usually observed with mesoporous materials. A specific surface area of 950 m^2 g^{-1} and pore size of 22 A˚ was determined by BET and BJH analyses, respectively. The synthetic method applied to prepare the mesoporous APS material led to the production of spherical particles of an average diameter of 600 nm, but most of them were in the form of bigger aggregates displaying a particle size distribution centred at 6.5 ± 1.4 lm. The content of amino- propyl groups in APS were 1.1 mmol g^{-1}, as determined from elemental analysis. These groups, however, were in the form of propylammonium chloride as a consequence of template extraction performed in HCl/ethanol medium.

The silica-carnosine hybrid material, Scar, was des-

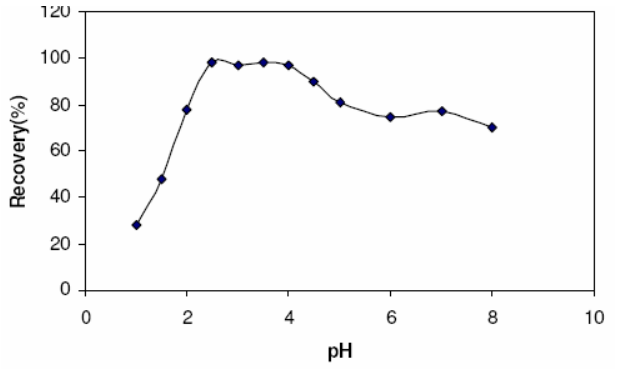
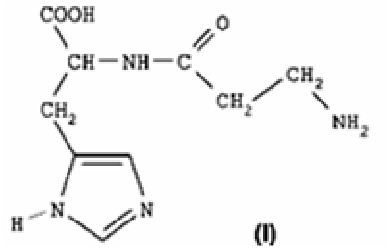


Figure 2. Effect of pH on the extraction of Cd. Experimental conditions: source, 10 ml of 0.1µgml^{-1} Cd^{2+} solution; amount of sorbent, 50.0 mg

cribed in Sayen et al. (2003), as an amorphous solid (flat XRD pattern) characterised by a specific surface area of 62 m^2 g^{-1}, a total pore volume of 0.279 cm^3 g^{-1}, and an average pore diameter of about 160 A˚ . Due to a treatment of Scar with gaseous HCl during the synthesis protocol (Sayen et al., 2003; Hamdoune et al., 2001), the carnosine groups (b-alanyl-Lhistidine I) attached to the silica framework were also protonated.

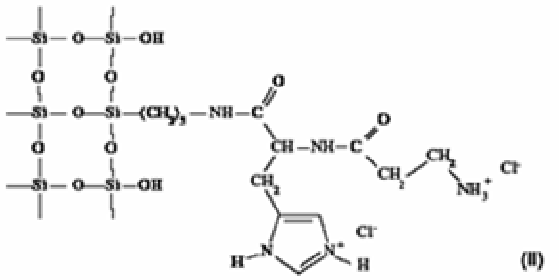


These materials are potentially good candidates for the extraction of Cd(II) species from dilute aqueous medium because of the well-known tendency of amine derivatives to form stable complexes with Cd(II). Indeed, both aminopropyl-grafted silica gels (Etienne et al., 2001) and carnosine functionalised silica (Walcarius et al., 2004) have been incorporated in carbon paste electrodes and successfully applied to electrochemical sensing of Cd(II) after preconcentration. In the present case, however, APS and Scar contain a great majority of their N centres in a protonated form. This is expected to limit their binding properties (decreasing stability of amine-Cd (II) complexes at pH below 7) (Etienne et al., 2001), thus requireing deprotonation of the material prior to use.

Deprotonation of APS without damage to the structural and chemical integrity of the material is not an easy task. As shown in curve ‘d’ on Figure 1, a treatment of APS in aqueous NaOH (0.01 M) resulted in the complete crashing of the mesostructure, which was accompanied by dramatic leaching of aminopropyl groups and silicon moieties in solution. A similar treatment in 95% ethanol was less destructive as some order was maintained (Figure 1, curve ‘c’) but the mesostructure was by far less ordered as the diffraction line corresponding to the 1 0 0 plane dropped significantly in comparison to the non treated solid while the weaker reflections at higher 2 h angles disappeared. This XRD pattern also revealed a shift of the diffraction line at higher 2 h values, indicating a significant contraction of the lattice with possible partial structure collapsing, as otherwise confirmed by BET measurements (specific surface area dropping by a factor of about 2.5 and pore volume by a factor 3).

Effect of pH

Basically, the approach described above for Cd(II) detection at APS-MCPE should be applicable to any modified electrode system involving N-bearing ligands that would require a modulation of their properties by a pH change. To point out this generalisation aspect, we have revisited an earlier work dealing with the use of an amorphous silica sample functionalised with carnosine groups (Scar), which was applied as modifier of a carbon paste electrode (Scar-MCPE) to Cd(II) preconcentration and detection (Sayen et al., 2003). The synthetic protocol to get the Scar material involved protection/deprotection processes resulting in N-bearing ligands under their protonated form, counter-balanced by chloride anions (compound II).



The effect of pH on the extraction of Cd^{2+} from water samples was studied in the pH range of 1.0–8.0. The higher pH values were not studied because functionnalized mesoporous silicates were not stable in alkali solutions due to the breaking of the Si–O–Si bonds by hydroxide ions attack. pH of the solution was adjusted at the required value by adding 1.0 mol l^{-1} sodium hydroxide and/or 1.0 mol l^{-1} nitric acid. As can be seen in Figure 2, extraction was nearly constant and quantitative in the pH range of 2–8.0. At lower pH (<2.5), the nitrogen atoms in mesoporous organo-silicas are protonated, so the stability of complex formation between the sorbent and Cd^{2+} is reduced. Therefore, the extraction of Cd decreased. Hence, pH of 3.0 was chosen as the optimum pH for extraction.

Choice of eluent

In order to choose the most effective eluent for desorbing

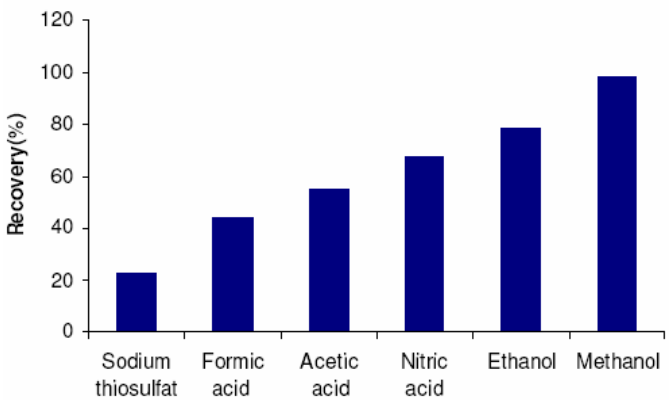


Figure 3. Effect of nature of eluent on the recovery of Cd. Experimental conditions: source, 10 ml of 0.1µgml^{-1} Cd^{2+} solution at pH 3.0; sorbent 50.0 mg.

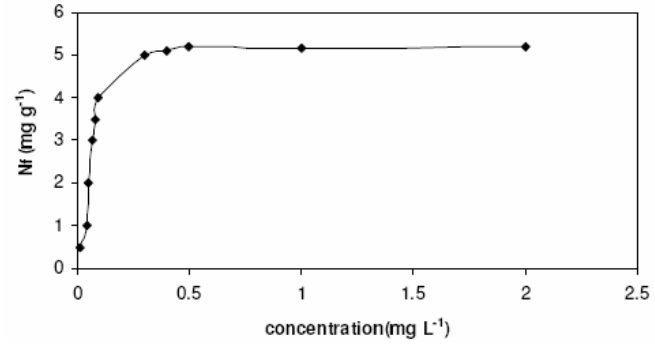


Figure 4. Adsorption isotherm of Cd(II) ion on sorbent.

Cdion from the sorbent surface aliquots of 10 ml of 0.1µgml^{-1} Cd ion solution was contacted with 50.0 mg of mesoporous organo-silicas. A series of selected eluent solution such as nitric acid, formic acid, acetic acid, sodium thiosulfate, ethanol and methanol was used. A total of 10.0 ml of 0.1 mol l^{-1} of the above men-tioned eluents were used for desorbing the adsorbed Cd ion. The amount of Cd ion back-extracted into the liquid phase by each eluent was measured using Flame Atomic Absorption Spectrometry (FAAS). Percent recoveries of Cd ion were calculated for each sample. The results (Figure 3) showed that recovery was the best when methanol was used as eluent. Also, higher concentra-tions of hydrochloric and nitric acid (0.5 and 1.0 mol l^{-1}) solutions were tested and the results showed the reco-very of Cd was not quantitative. Therefore, methanol was selected as eluent.

Effect of eluent concentration

The influence of the concentration of methanol on desorption of Cd ion was studied. For desorbing 1.0 µg Cd ion, already adsorbed on 50.0 mg of sorbent, 1.0 ml of different concentration of eluent (methanol) have been used. At a concentration of more than 0.7 mol l^{-1}, methanol desorbs (recovery of almost 100%) Cd ion completely from the sorbent surface. A concentration of 1.0 mol l^{-1} of methanol was selected for further studies.

Effect of the sample volume

In order to explore the possibility of concentrating low concentrations of Cd from large volumes, the maximum applicable volume must be determined. For this purpose, the effect of the sample solution volume on the recovery was studied by keeping the total amount of Cd^{2+} uptake constant (1.0 µg). The quantitative recoveries were obtained for sample volume of ≤100 ml. Therefore, the concentration factor was 100 for Cd^{2+} since the final elution volume was 1.0 ml.

Effect of the amount of mesoporous organo-silica

To test the effect of the amount of mesoporous organo-silicas on quantitative retention of analyte different amounts of sorbent (range from 2.0 to 200.0 mg) were added into the solution following the experimental method. The results showed that the extraction of Cd^{2+} was quantitative by using only 10.0 mg of mesoporous organo-silicas. Subsequent extraction experiments were carried out with 50.0 mg of mesoporous organo-silicas in order to achieve higher capacity and to account for other extractable species.

Adsorption capacity

The capacity of the sorbent is an important factor that determines how much sorbent is required to remove a specific amount of metal ions from the solution quantitatively. For investigation of adsorption isotherm of Cd ion, the same volumes of Cd ion solution with different concentrations of Cd ion were contacted with 0.1 g of sorbent in the batch mode. Then, the concentration of the remaining Cd in the solution was determined by Flame Atomic Absorption Spectrometry (FAAS). The adsorption isotherm that is the number of microgram absorbed per gram of adsorbent (N_f) versus the equilibrium concentration of cat ion (C_s) is shown in Figure 4. According to these results, the maximum amount of Cd that can be sorbed by mesoporous organo-silicas was found to be 5 mg g^{-1} at pH 3.0.

Effect of equilibrium time

In order to investigate the effect of shaking time on the extraction efficiency, extraction for a series of solutions containing 1.0 µgCd^{2+} were carried out. The results showed that the shaking time (from 20 to 350 s) has no effect on the extraction efficiency of Cd and the extrac-

Table 1. Effect of interferents on the recovery of 20 ng L-1 Cd(II) in water sample.

Interferent	Concentration (μgL^{-1})	Interferent/Cd(II) ratio	Recovery (%)
Na+	40,00,000	200,000,000	94.2
Li+	200	10,000	100.4
K+	200	10,000	98.3
Ca(II)	200	10,000	99.5
Mg(II)	200	10,000	100.8
Ba(II)	200	10,000	98.9
Sr(II)	200	10,000	100.2
Mn(II)	200	10,000	95.6
Co(II)	200	10,000	100.3
Al(III)	200	10,000	96.1
Fe(III)	200	10,000	98.4
Ni(II)	200	10,000	65.7
	20	1000	98.5
Zn(II)	200	10,000	52.6
	20	1000	93.5
Pb(II)	200	10,000	72.6
	20	1000	100.7
Fe(II)	200	10,000	73.6
	20	1000	98.7
Cu(II)	200	10,000	65.6
	20	1000	87.8
	2	100	96.8
Cr(III)	200	10,000	67.3
	20	1000	96.9
Cr(VI)	200	10,000	100.8
As(III)	200	10,000	69.9
	20	1000	98.6
As(V)	200	10,000	97.6
Hg(II)	200	10,000	22.7
	20	1000	65.8
	2	100	92.9
Cl^-	60,00,000	300,000,000	94.5
NO_3^-	200	10,000	99.2
CH_3COO^-	10,000,000	500,000,000	99.0
$H_2PO_4^-$	10,000,000	500,000,000	98.5

tion was quantitative. Although the extraction process can be continued during the centrifugation, however, the results showed that extraction was quantitative and very fast in all cases. Thus, the mixtures have been shaken for 20 s to reach equilibrium in the subsequent experiments.

Effect of ionic strength

The influence of ionic strength on the extraction of Cd was studied in the potassium nitrate solution with various concentrations from 0.01 to 1.0 mol l^{-1}. Results have shown that ionic strength has no considerable effect upon extraction efficiency up to 1.0 mol l^{-1} of KNO_3. These observations showed the specific tendency of mesoporous organo-silicas for Cd^{2+} and the possibility of using this method for separation of Cd from highly saline solutions (Table 1).

Effect of coexisting ions

The effects of common coexisting ions in natural water samples on the recovery of Cd were studied. In these experiments, 10 ml of solutions containing 0.1 µg l^{-1} of Cd and various amounts of interfering ions were treated according to the recommended procedure. An ion was considered to interfere when its presence produced a variation in the extraction recovery of sample more than

Table 2. Characteristic performance data obtained by using DLLME and other techniques in determination of cadmium in water.

Method	Calibration range (ng L^{-1})	Time (min)	Sample Consumption (mL)	Enrichment factor	R.S.D.[b] (%)	LOD[a] (ng L^{-1})	References
On-line solvent extraction–GF AAS	6–300	2	14.0	24.6	3.2	2.8	[8]
Co-precipitation–GF AAS	100–4000	>30	100.0	100	3.2	2.9	[9]
On-line SPE–GF AAS	20–200	4	3.0	59.4	1.3	1.3	[20]
CPE–GF AAS	0–20.0	>30	10.0	50	2.1	5.9	[26]
SDME–GF AAS	10–1000	>10	5.0	65	7.4	0.7	[29]
DLLME–GF AAS	2–21	<4	5.0	122	2.9	0.5	[Represented method]

[a] Limit of detection; [b] Relative standard deviation.

±5%. The results showed that, in excess of 10,000-fold Li^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+} and 1000-fold Cl^-,Br^-, SO_4^{2-}, Ag^+, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Pb^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+} and Hg^{2+} ions had no significant interferences in the extraction and determination of Cd. As can be seen, mesoporous organo-silicas have shown a high tolerance limit for alkali and alkaline earth metals. This is particularly useful for the analysis of Cd in natural water samples, for example, seawater, which contains large amounts of alkali and alkaline earth metal ions.

Reusability and stability of mesoporous organo-silicas

Reusability is one of the key parameters to assess the effectiveness of a sorbent. A series of sorption/desorption experiments were performed to understand the reusability of the synthesized mesoporous organo-silicas. After sorption, the sorbent was treated with 1.0 mol l^{-1} methanol to desorb Cd^{2+} and this sorption/desorption procedure was repeated five times. After each desorption step, the sorbent was washed with doubly distilled water to remove methanol and condition sorbent. On storing for a year under dark and dry conditions, the stability of sorbent was excellent and adsorption capacity did not change significantly.

Analytical performance

The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as the amount of analyte necessary to yield a signal equal to three times (3σ) and ten times (10σ) the standard deviation of the blank signals, respectively. Using sample volume of 100 ml a LOD of 0.7 ng $L^{-1}$and a LOQ of 0.9 ng L^{-1} were obtained for the determination of Cd. Ten replicate extraction and measurement of 1.0 µg of Cd^{2+} ion in 100 ml water solution gave a R.S.D. of 3.0%. Calibration graph was obtained using pre-concentration of 100 ml of standard solutions buffered at pH 3.0 with 50 mg of sorbent. For this purpose, standard solutions containing Cd ion in the range of 1–1000 µg l^{-1} were examined by the proposed procedure and it was observed that calibration curve were linear in this range. The regression equation was $I = 0.0083C$ (µg l^{-1}) + 0.0045 and the correlation coefficient was 0.9993.

Comparison to other methods

A comparison of the represented method with other reported preconcentration methods is given in Table 2. In comparison with other reported methods, this method has low LOD (0.7 ng L^{-1}), high enrichment factor (122), short extraction procedure (less than 4 min) and low sample consumption (5 mL). These characteristics are of key interest for routine laboratories in trace metal ion analysis.

Analysis of water samples

To assess the applicability of the method to real samples, it was applied to the extraction and determination of Cd from 100 ml of different water samples. Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 26 January, 2007), 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 Cd ions can be quantitatively recovered from the water samples used. The analytical results shown in Table 3 demonstrate that the results by using the present method are consistent with those obtained by ICP-MS.

Conclusion

Results presented in this work demonstrate well the tremendous possibilities offered by the solid phase extraction of trace amounts of Cd(II) in water samples using of mesoporous organo-silicas and its determination by FAAS. The method developed was simple, reliable, high capacity, good stability and fast adsorption and desorption kinetics for determining Cd in water. Also, the pro-

Table 3. Recovery of Cd(II) added to 100mL of different water samples (contaning 0.1M buffer acetic acid / acetate at pH= 3.0).

Recovery (%)	Cd^{2+} detected (ng ml^{-1}) with ICP-MS	Cd^{2+} detected	Cd^{2+} spiked	Sample
		(ng ml^{-1})	(ng ml^{-1})	
97.9	4.6 (2.8)[b]	4.8 (2.0)[b]	5.0	Sample 1[a]
98.6	9.6 (2.1)	9.7 (2.5)	10.0	
98.4	4.7 (3.0)	4.4 (3.0)	5.0	Sample 2[c]
98.3	9.2 (2.4)	9.3 (3.0)	10.0	
98.5	2.1 (2.5)	2.5 (2.4)	0.0	Tap water[d]
97.5	7.0 (2.9)	7.5 (2.9)	5.0	
98.3	12.1 (2.1)	12.3 (2.4)	10.0	
—	—	N.D.	0.0	Rain water[f]
98.4	5.2 (2.1)	4.9 (2.3)	5.0	
98.6	9.7 (2.0)	10.1 (2.6)	10.0	
99.3	14.2(2.5)	14.0(2.0)	0.0	Sea water[g]
96 .9	18.5 (2.4)	18.9 (2.3)	5.0	
98.1	24.4 (2.2)	24.0 (3.0)	10.0	

a Hg2+,Co2+,Cd2+,Fe3+,Ni2+,Cr3+ , 5000 ng ml−1 of each cation; K+ and Li+, 10,000 ng ml−1 of each. b R.S.D of three replicate experiments. c Hg2+,Co2+,Cd2+,Fe3+,Ni2+,Cr3+ , 2500 ng ml−1 of each cation; K+ and Li+, 5000 ng ml−1 of each. d From drinking water system of Tehran. e Not detected. f Tehran, 26january, 2007, Iran. g Caspian sea water.

posed method was free of interference compared to conventional procedures to determine Cd. The method can be successfully applied to the separation and determination of Cd in binary mixtures.

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