

Extraction sorbent with nanographene with aminopropyltriethoxysilane (APTES) on surfactant coated C₁₈ for the preconcentration of Cd(II) in water

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ABSTRACT: Solid phase extraction (SPE) or liquid-solid extraction is popular and growing techniques that are used to sample preparation for analysis. Metal nanoparticles have been studied for decades, and this is due to the properties that these materials do not have in bulk state. In nanoscale materials, the numbers of surface atoms is high and hence, have significant surface effects. A novel, simple, sensitive and effective method has been developed for preconcentration of Cd(II) on nanographene with aminopropyltriethoxysilane (APTES) on surfactant coated C₁₈ solid-phase extraction adsorbent. Flame atomic absorption spectrometer was utilized for determination of Cd(II). Some of the important parameters on the preconcentration and complex formation were selected and optimized. Under the optimized conditions the limit of detection (LOD) and limit of quantification (LOQ) were 0.032 μg.L⁻¹, 163.7 ng L⁻¹ and the proposed method has a good reproducibility 0.81% (RSD %) and preconcentration factor was found to be 200. The methodology was applied for determination of Cd (II) in natural water samples and satisfactory results were obtained.

Keywords: Cd(II); Flame atomic adsorption spectrometry (FAAS); Nano graphene with aminopropyltriethoxysilane (APTES) on surfactant coated C₁₈; Preconcentration; Solid phase extraction

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INTRODUCTION

The properties of nano magnetic particles have attracted many studies on their functionality as magnetic carrier. This characteristic make these elements a fit candidate in a wide range of heavy metal ions application in biology and water samples (Deng *et al.*, 2005; Modoet

al., 2005; Margelet *al.*, 1997), also in medical imaging uses such as magnetic resonance imaging (MRI) (Bulte *et al.*, 2006), in isolating substances and materials in anions– cations pre-concentration (Afkhamei *et al.*, 2010). Cd, at trace concentrations, acts as both a micronutrient and a toxicant in marine and fresh water systems (Leyden *et al.*, 1976; Narinet *al.*, 2000; Akama *et al.*, 2000; Ohta *et al.*, 2001; Cuculicet *al.*, 1997; Moghimiet

al., 2012; Moghimiet *al.*, 2019; Moghimiet *al.*, 2009).The direct determination of trace metals especially toxic metal ions such as Cd, 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(Nambiaret *al.*, 1998;Caroliet *al.*, 1991). The application of solid phase extraction technique for pre- concentration of trace metals from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects as well as sorption of the target species on the solid surface in a more stable chemical form(Alexandrovaet *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(Arpadjanet *al.*, 1997), filter paper(Leyden *et al.*, 1975), cellulose(Gennaroet *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 (Kviteket *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 (Brueninget *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; Dadleret *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 Cd(II) (Mahmoud, 1998; Mahmoud, 1999) and pre-concentration of various cations (Leyden *et al.*, 1976; Narinet *al.*, 2000; Akamaet *al.*, 2000; Ohtaet *al.*, 2001; Cuculicet *al.*, 1997; Moghimiet *al.*, 2009; Thurman 1998; Pawliszyn 1997; Izattet *al.*, 1996; Hagen *et al.*, 1990; Krueger 1995; Yaminiet *al.*, 1994; Shamsipuret *al.*, 1999; Shamsipuret *al.*, 2001; Brunner *et al.*, 2003; Zelderet *al.*, 2004; Boll *et al.*, 2005; Nayebiet *al.*, 2006; Moghimiet *al.*, 2007; Moghimi, 2007) and 2-mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations (Qiaoshenget *al.*, 1998). Ammonium hexa-hydroazepin-1-dithiocarboxylate (HMDC)-loaded on silica gel as solid phase pre-concentration column for atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) was reported (Alexandrovaet *al.*, 1993). Mercapto-modified silica gel phase was used in pre-concentration of some trace metals from seawater (Moghimiet *al.*, 2010). Sorption of Cd(II) by some sulfur containing complexing agents loaded on various solid supports (Tajodiniet *al.*, 2010) was also reported. 2-Amino-1-cyclopentene-1-dithiocarboxylic acid (ACDA) for the extraction of Silver(I), Cd(II) and Palladium(II) (Moghimiet *al.*, 2009), 2-[2-triethoxysilyl-ethylthio] aniline for the

selective extraction and separation of palladium from other interfering metal ions (Narinet *al.*, 2000) as well as thiosemicarbazide for sorption of different metal ions (Campderroset *al.*, 1998) and thioanilide loaded on silica gel for pre-concentration of Palladium(II) from water (Narinet *al.*, 2000) are also sulfur containing silica gel phases. The main goal of the present work is the development of a fast, sensitive and efficient way for enrichment and extraction of trace amounts of Cd(II) from aqueous media by means of a surfactant coated C₁₈ modified with nanographene with aminopropyltriethoxysilane (APTES) Such a determination has not been reported in the literature. The structure of nanographene with aminopropyltriethoxysilane (APTES) is shown in Fig.1. The chelated ions were desorbed and determined by FAAS. The modified solid phase could be used at least 50 times with acceptable reproducibility without any change in the composition of the sorbent, GO-APTES or SDS. On the other hand, in terms of economy it is much cheaper than those in the market, like C₁₈ SPE mini-column.

EXPERIMENTAL

Reagents and Apparatus

Graphite oxide was prepared from purified natural graphite (SP-1, Bay Carbon, Michigan, average particle size 30 μ m) by the Hummers method and dried for a week over phosphorus

pentoxide in vacuum desiccators before use. 4-Isocyanatobenzenesulfonyl azide was prepared from 4-carboxybenzenesulfonyl azide via a published procedure. All solutions were prepared with doubly distilled deionized water from Merck (Darmstadt, Germany). C_{18} powder for chromatography with diameter of about 50 μm obtained from Katayama Chemicals from supelco. It was conditioned before use by suspending in 4 M nitric acid for 20 min, and then washed two times with water. Sodium dodecyl sulfate (SDS) obtained from Merck (Darmstadt, Germany) and used without any further purification.

Synthetic procedures

Preparation of GO–APTES

Zhang *et al.* reported the preparation of chemicalbonded graphene coating for SPME in a layer-by-layer manner (Fig. 1A) (Moghimi,2007). The silica fiber was first treated with NaOH and 3-amino propyltriethoxysilane (APTES) to introduce amino groups to the surface. Then, GO was bonded to the fiber via reaction of the carboxyl groups of GO with the amino groups. Repeating the treatment with APTES and GO four times gave a coating of 20 μm thickness (Fig. 1D). Finally, the fiber was aged at 60°C and reduced with hydrazine. SEM showed a rough tree-bark-like structure with a striped appearance (Fig. 1B), and the high-resolution image revealed a continuous folded, wrinkled structure (Fig. 1D).

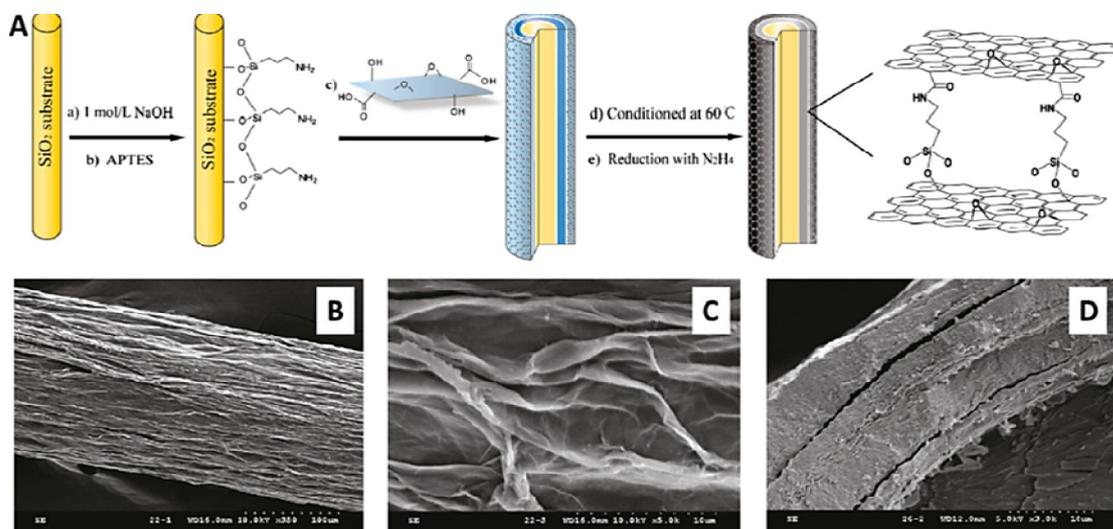


Fig. 1. (A) Layer-by-layer fabrication processes of chemical-bonded graphene-coated SPE fiber. (B–D) SEM images of an SPME fiber coated with graphene. The surface images at magnifications of (B) 350° and (C) 5000°; the cross-section image at magnifications of (D) 3000°.

Column preparation

GO-APTES(40 mg) were packed into an SPE mini-column (6.0cm ×9mm i.d., polypropylene). A polypropylene frit was placed at each end of the column to prevent loss of the adsorbent. Before use, 0.5 mol L⁻¹HNO₃ and DDW were passed through the column to clean it.

Apparatus

The pH measurements were conducted by an ATC pH meter (EDT instruments, GP 353) calibrated against two standard buffer solutions of pH 4.0 and 9.2. Infrared spectra of GO-APTES were carried out from KBr pellet by a Perkin-Elmer 1430 ratio recording spectrophotometer. Atomic absorption analysis of all the metal ions except Zn(II) were performed with a Perkin-Elmer 2380 flame atomic absorption spectrometer. Zn(II) determinations were performed by a Varian Spect AA-10. Raman spectrophotometer analyses were performed with a Perkin-Elmer.

Preparation of admicell column

To 40 ml of water containing 1.5 g of C₁₈, 150 mg of the above Schiff base-chitosan grafted multivalued carbon nanotubes was loaded after washing acetone, 1mol l⁻¹ HNO₃ solution and water, respectively, solution was added. The pH of the suspension was adjusted to 2.0 by addition of 4 M HNO₃ and stirred by mechanical stirrer for 20 min. Then the top liquid was decanted (and discarded) and the remained C₁₈ was washed three times with

water, then with 5 ml of 4 M HNO₃ and again three times with water. The prepared sorbent was transferred to a polypropylene tube (i.d 5 mm, length 10mm). Determination of Cd²⁺ contents in working samples were carried out by a Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hollow cathode lamp(HI-HCL) according to the recommendations of the manufacturers. These characteristics are tabulated in (Table 1). A metrohm 691 pH meter equipped with a combined glass calomel electrode was used for pH measurements.

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

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

Procedure

The pH of a solution containing 100 ng of each Cd(II) was adjusted to 2.0. This solution was passed through the admicell column with a flow rate of 5 ml min⁻¹. The column was washed with 10 ml of water and the retained ions were desorbed with 1 ml of 4 M HNO₃ with a flow rate of 2 ml min⁻¹. The desorption procedure was repeated 3 more times. All the acid solutions (4 ml all together) were collected in a 10 ml volumetric flask and

diluted to the mark with water. The concentrations of Cd in the solution were determined by FAAS at 283.3.

Determination of Cd in water samples

Polyethylene bottles, soaked in 1 M HNO₃ overnight, and washed two times with water were used for sampling. The water sample was filtered through a 0.45 µm pores filter. The pH of a 1000 ml portion of each sample was adjusted to 2.0 (4M HNO₃) and passed through the column under a flow rate of 5 ml min⁻¹. The column was washed with water and the ions were desorbed and determined as the above mentioned procedure.

Speciation of Cd in water samples

This procedure is reported in several articles. The method has been evaluated and optimized for speciation and its application on complex mixtures (Deng *et al.*, 2005; Modoet *et al.*, 2005; Margelet *et al.*, 1997). The chelating cation exchanger (Chelex-100) and anion exchanger, Dowex 1X-8 resins were washed with 1 M HCl, water, 1 M NaOH and water respectively. 1.2 g of each resin was transferred to separate polyethylene columns. Each column was washed with 10 ml of 2 M HNO₃ and then 30 ml of water. The C₁₈ bounded silica absorber in a separate column was conditioned with 5 ml of methanol, then 5 ml of 2 M HNO₃ and at the end with 20 ml of water. 5 ml of methanol was added on top of the absorber, and passed through it until the level of methanol reached just the surface of the absorber. Then water

was added on it and connected to the other two columns. A certain volume of water sample was filtered through a 0.45 µm filter and then passed through the three columns system, Dowex 1X-8, RP-C18 silica absorber and Chelex-100 respectively. The columns were then separated. The anion and cation exchanger columns were washed with 10 ml of 2 M HNO₃ and the C₁₈ column with 10 ml of 1 M HCl. The flow rate of eluents was 1 ml min⁻¹. The Cd content of each eluted solution was determined by FAAS.

RESULTS AND DISCUSSION

The treatment of nanographene with aminopropyltriethoxysilane (APTES) can Cd to the derivatization of both the edge carboxyl and surface hydroxyl functional groups via formation of amides (Moghimi, 2007) or carbamate esters, respectively.

Morphology

The amount of nanographene with aminopropyltriethoxysilane (APTES) sheet was evaluated by thermogravimetric analysis. As compared with the TGA results of pure graphite, which is thermally stable up to 900 °C under nitrogen, and GO which decomposes above 600 °C, after having lost the oxygenated species at 240 °C (i.e. 14.7% weight loss), the 6% weight loss occurred in the temperature range 250–550 °C for the GO–APTES material, is attributed to the decomposition of APTES (Fig.2).

The GO–APTES material forms a stable dispersion in DMF at a concentration not exceeding 1 mg mL⁻¹. The electronic absorption spectrum of GO–APTES in DMF (Fig. 3), shows (i) a broad signal monotonically decreasing from the UV to the visible region, which is attributed to GO and (ii) a characteristic band at 420 nm (Soret-band) corresponding to the covalently grafted APTES units (the Q-bands at 516, 557, 589 and 648 nm were flattened to the base line in the GO–APTES material).

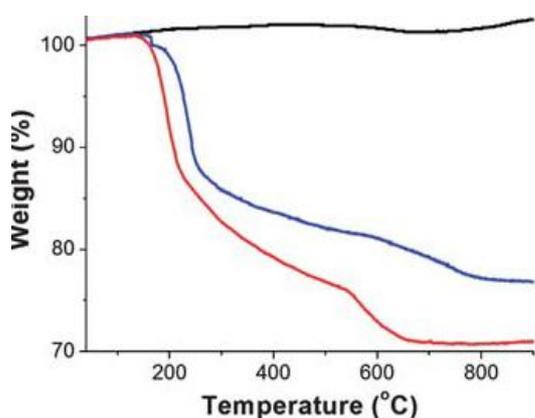


Fig. 2. The TGA graphs of graphite (black), GO (blue) and GO–APTES (red), obtained under an inert atmosphere.

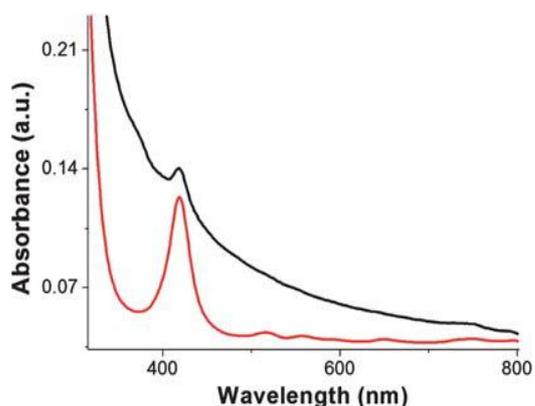


Fig. 3. The UV-Vis spectra of GO–APTES (black) and free APTES (red), obtained in DMF.

Interestingly, the absorption of porphyrin in the GO–APTES material is broadened, shortened and bathochromically shifted (ca. 2 nm) as compared to that of the free APTES, a result that corroborates not only the linkage of porphyrin with the GO sheets but also electronic interactions between the two species (i.e. GO and APTES) in the ground state. These results are in agreement with studies based on other hybrid systems consisting of porphyrins covalently grafted to carbon nanotubes and nanohorns (Moghimi,2007).

Stability studies

The stability of the newly synthesized GO–APTES phases was performed in different buffer solutions (pH 1, 2, 3, 4, 5, 6 and 0.1M sodium acetate) in order to assess the possible leaching or hydrolysis processes. Because the metal capacity values determined in Section 3.2 revealed that the highest one corresponds to Cd(II)s, this ion was used to evaluate the stability measurements for the GO–APTES phase. The results of this study proved that the GO–APTES is more resistant than the chemically adsorbed analog especially in 1.0, 5.0 and 10.0 M hydrochloric acid with hydrolysis percentage of 2.25, 6.10 and 10.50 for phase, respectively. Thus, these stability studies indicated the suitability of phase for application in various acid solutions especially concentrated hydrochloric acid and extension of the experimental range to very strong acidic media which is not suitable for

other normal and selective chelating ion exchangers based on a nano polymeric matrix. Finally, the GO–APTES phases were also found to be stable over a range of 1 year during the course of this work.

The IGO is insoluble in water. Primary investigations revealed that surfactant coated C₁₈ could not retain Cd(II) cations, but when modified with the GO–APTES retains these cations selectively. It was then decided to investigate the capability of the GO–APTES as a ligand for simultaneous preconcentration and determination of Cd on admicell. The C₁₈ surface in acidic media (1 < pH < 6) attracts protons and becomes positively charged. The hydrophil part of SDS (-SO₃⁻) is attached strongly to these protons. On the other hand, the GO–APTES are attached to hydrophobe part of SDS and retain small quantities of metallic cations (Deng *et al.*, 2005; Modoet *et al.*, 2005; Margelet *et al.*, 1997).

Effect of pH in does not occur.

The effect of pH of the aqueous solution on the extraction of 100 ng of each of the cations Cd(II) was studied in the pH rang of 1-10. The pH of the solution was adjusted by means of either 0.01 M H NO₃ or 0.01M NaOH. The results indicate that complete chelation and recovery of Cd(II) occurs in pH range of 2-4 and that of in 2-8 and are shown in Fig. 4. It is probable that at higher pH values, the cations might be hydrolyzed and complete desorption occur. Hence, in order to prevent hydrolysis of

the cations and also keeping SDS on the C₁₈, pH=2.0 was chosen for further studies.

Effect of flow rates of solutions

Effect of flow rate of the solutions of the cations on chelation of them on the substrate was also studied. It was indicated that flow rates of 1-5 ml min⁻¹ would not affect the retention efficiency of the substrate. Higher flow rates cause incomplete chelation of the cations on the sorbent. The similar range of flow rate for chelation of cations on modified C₁₈ with SDS and a GO–APTES has been reported in literature (Deng *et al.*, 2005; Modoet *et al.*, 2005; Margelet *et al.*, 1997). Flow rate of 1-2 ml min⁻¹ for desorption of the cations with 4 ml of 4 M HNO₃ has been found suitable. Higher flow rates need larger volume of acid. Hence, flow rates of 5 ml min⁻¹ and 2 ml min⁻¹ were used for sample solution and eluting solvent throughout respectively.

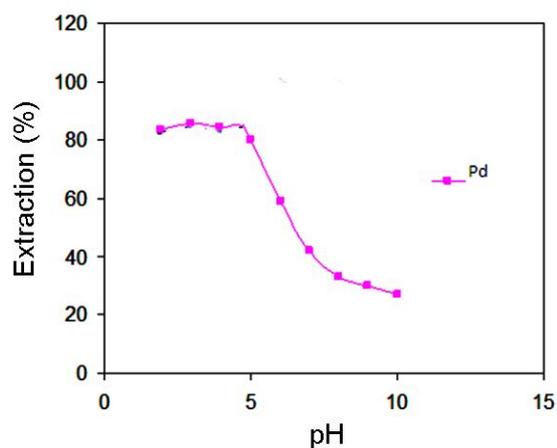


Fig. 4. Extraction percentage of Cd(II) against pH.

Effect of the GO–APTES quantity

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

Figures of merit

The breakthrough volume is of prime importance for solid phase extractions. Hence, the effect of sample volume on the recovery of the cations was studied. 100 ng of each cation was dissolved in 50, 100, 500 and 1000 ml of water. It was indicated that in all the cases, chelation and desorption of the cations were quantitative. It was then concluded that the breakthrough volume could be even more than 1000 ml. Because the sample volume was 1000 ml and the cations were eluted into 10 ml solution, the enrichment factors for both cations are 100, which is easily achievable. The maximum capacity of 1.5 g of the substrate was determined as follow; 500 ml of a solution containing 50 mg of each cation was passed through the column. The chelated ions were eluted and determined by FAAS. The maximum capacity of the sorbent for three individual replicates was found to be 15.2 ± 0.8 μg of each cation. The limits of detection (3σ) for the cations (Margelet *al.*,

1997) were found to be 3.20 ng l^{-1} for Cd ions. Reproducibility of the method for extraction and determination of 100 ng of each cation in a 50 ml solution was examined. As the results of seven individual replicate measurements indicated, they were 2.85% and 2.98% for Cd(II).

Effect of foreign ions

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

Analysis of the water samples

The prepared sorbent was used for analysis of real samples. To do this, the amounts of Cd were determined in different water samples namely: distilled water, tap water of Tehran (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 25 January 2013), Snow water (Tehran, 7 February 2013), and two synthetic samples containing different cations. The results are tabulated in Table 3. As it is seen, the amounts of Cd added to the water samples are extracted and determined quantitatively which indicates accuracy and precision of the present method. Separation and speciation of cations by three columns system It is possible to preconcentrate and at

the same time separate the neutral metal complexes of GO–APTES, anionic complexes and free ions from each other by this method (Deng *et al.*, 2005; Modoet *et al.*, 2005; Margelet *et al.*, 1997) Water samples were passed through the three connected columns: anion exchanger, C₁₈-silica absorber and chelating cation exchanger. Each species of Cd is retained in one of the columns; anionic complexes in the first column, neutral

complexes of GO–APTES in the second, and the free ions in the third. We have proposed a method for determination and preconcentration of Cd in water samples using surfactant coated C₁₈ impregnated with a Schiff's base. The proposed method offers simple, highly sensitive, accurate and selective method for determination of trace amounts of Cd(II) in water samples.

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

Diverse ion	Amounts taken (mg) added to 50 ml	% Found	% Recovery of Cd ²⁺ ion
Na ⁺	92.2	1.19(2.9) ^a	98.6(1.9)
K ⁺	92.2	1.38(2.1)	98.7(2.2)
Mg ²⁺	13.5	0.8(1.8)	96.9(2.7)
Ca ²⁺	23.3	1.29(2.0)	95.4(1.9)
Sr ²⁺	3.32	2.81(2.2)	98.2(2.1)
Ba ²⁺	2.26	3.16(2.4)	98.3(2.0)
Mn ²⁺	2.44	1.75(2.3)	98.5(1.8)
Co ²⁺	2.37	1.4(2.3)	98.1(2.2)
Ni ²⁺	2.25	2.0(2.14)	98.4(2.4)
Zn ²⁺	2.44	1.97(2.1)	98.7(2.2)
Bi ³⁺	2.3	2.7(1.4)	98.4(2.7)
Cu ²⁺	2.56	2.81(2.3)	97.7(2.5)
Fe ³⁺	2.4	3.45(2.4)	97.6(2.8)
Cr ³⁺	1.3	2.92(2.2)	96.3(2.4)
UO ₂ ²⁺	2.89	1.3(2.2)	97.3(2.2)
NO ₃ ⁻	5.5	2.3 (2.3)	96.4(2.6)
CH ₃ COO ⁻	5.3	2.2(2.6)	95.5(2.2)
SO ₄ ²⁻	5.0	2.9(3.0)	98.4(2.1)
CO ₃ ²⁻	5.4	1.8(2.5)	96.3(2.5)
PO ₄ ³⁻	2.6	2.1(2.0)	98.9(2.0)

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

Table 3. Recovery of Cd contents of water samples

Recovery of Cd contents of water samples		Amount added(μg)	Found(μg)	%Recovery
Sample Distilled water (100mL)	Cd	-	-	-
		0.050	0.043(2.40) ^a	96
		0.100	0.094(2.60)	97
Tap water(100mL)	Cd	-	0.015(3.0)	-
		0.050	0.068(2.42)	96
Snow water(50mL)	Cd	-	0.048(2.25)	-
		0.100	0.155(2.30)	98.0
Rain water(100mL)	Cd	-	0.045(2.25)	-
		0.100	0.143(2.40)	98
Synthetic sample 1 Na^+ , Ca^{2+} , Fe^{3+} , Co^{2+} Cr^{3+} , Hg^{2+} , 1 mg l^{-1}	Cd	-	-	-
		0.100	0.104(2.40)	98
Synthetic sample 2 K^+ Ba^{2+} , Mn^{2+} , Cd^{2+} Ni^{2+} , Zn^{2+}	Cd	-	-	-
		0.100	0.105(2.70)	99

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

CONCLUSIONS

In comparison with other methods reported for separation and measurement of Cd(II), this method enjoys considerable advantages in that it is simple and inexpensive and can be used quickly for environmental samples including natural water. In addition, it minimizes usage of organic, toxic, and expensive solvents. Furthermore, design and development of this method for preconcentration, separation, and measurement of Cd^{2+} are essential considering its significance in different industries and the low concentration of this

ion in most samples. Therefore, the aim of this research is to present an efficient, selective, inexpensive, and simple method for evaluation of the level of Cd(II) across different samples (in this research, the value of break through volume, limit of detection, and RSD has been obtained). This research indicated that measurement of Cd^{2+} occurs at an acceptable level without interference of any other interfering agent and thus the presented method can be used easily in measurement of the amount of Cd(II) in water samples.

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