

Full Length Research Paper

Preconcentration of Cd(II) by chemically converted graphene sheets adsorbed on surfactant-coated C₁₈ before determination by flame atomic absorption spectrometry (FAAS)

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A simple, highly sensitive, accurate and selective method for determination of trace amounts of Cd(II) in water samples is presented. A novel chemically converted graphene sheets (CCG) solid-phase extraction adsorbent was synthesized by CCG sheets. The stability of a CCG especially in concentrated hydrochloric acid was studied which used as a recycling and preconcentration reagent for further uses of CCG. The method is based on CCG of Cd(II) on surfactant-coated C₁₈, modified with a CCG. The retained ions were then eluted with 4 ml of 4 M nitric acid and determined by flame atomic absorption spectrometry (FAAS) at 283.3 nm for Cd. The influence of flow rates of sample and eluent solutions, pH, breakthrough volume, effect of foreign ions on chelation and recovery were investigated. 1.5 g of surfactant-coated C₁₈ adsorbs 40 mg of the Schiff's base which in turn can retain 15.2 ± 0.8 mg of each of the two ions. The limit of detection (3σ) for Cd(II) was found to be 3.20 ng L^{-1} . The enrichment factors for both ions are 100. The mentioned method was successfully applied on determination of Cd in different water samples. The ions were also speciated by means of three-column system.

Key words: Determination of Cd, preconcentration, chemically converted graphene sheets (CCG), flame atomic absorption spectrometry (FAAS).

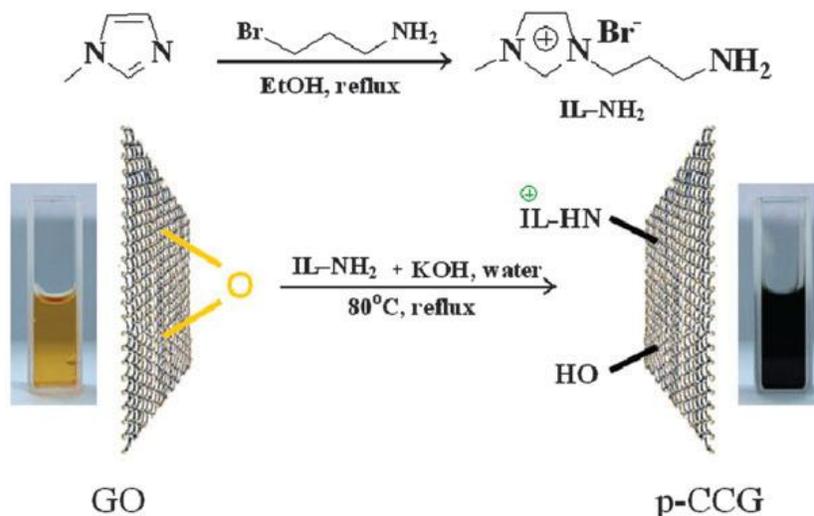
INTRODUCTION

Cd at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems (Izatt et al., 1985, 1991, 1995; Blake et al., 1996; Arca et al., 2001; Ghoulipour and Husain 2002; Hashemi et al., 2001; Shcherbinina et al., 1990). This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, Cd can bind to the cell membrane and hinder the transport process through the cell wall. Cd at nearly 40 ng ml^{-1} is required for normal metabolism of many living organisms (Gomes-Gomes et al., 1995; Unger, 1979). On the other hand, Cd is an important

element in many industries. Thus, the development of new methods for selective separation, concentration and determination of it in sub-micro levels in different industrial, medicinal and environmental samples is of continuing interest. The determination of Cd is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS), (Boudreau and Cooper, 1989) as well as spectrometric methods (Bruening et al., 1991; Mahmoud 1997a).

Solid phase extraction (SPE) methods are the best alternatives for traditional classic methods due to

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Scheme 1. Illustration of the preparation of CCG.

selective removal of trace amounts of metal ions from their matrices. SPE determinations can be carried out on different efficient ways. One of the most appropriate performance features of SPE is achieved by using octadecyl silica membrane disks. SPE reduce the use of toxic solvent, disposal costs, and extraction time (Mahmoud and Soliman, 1997; Mahmoud 1997b). The octadecyl silica membrane disks involves shorter sample processing time and decreased plugging due to the large cross-sectional area of the disk and small pressure drop which allows higher flow-rates; reduced channeling resulting from the use of sorbent with smaller particle size and a greater mechanical stability of the sorbent bed (Tong et al., 1990).

In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of chromium (Dadler et al., 1987; Ahmad et al., 2011; Moghimi, 2007) and Lead (Mahmoud, 1999). Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of Lead (Leyden et al., 1976; Moghimi et al., 2009; Liu et al., 1992), Copper (Liu et al., 1996; Mishenina et al., 1996; Wang et al., 1999), Silver (Wang et al., 1997; Zhang et al., 1982), Mercury (Zhou et al., 1983; Zargarani et al., 2008), Cadmium (Tabarzadi et al., 2010), Palladium (Shin et al., 2004), Ce (Nayebi and Moghimi et al., 2006) and UO₂ (Mahmoud, 1998).

The main goal of the present work is 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 chemically converted graphene sheets (CCG) (Scheme 1) (Yang et al., 2009).

Such a determination has not been reported in the literature. The structure of CCG is shown in Scheme 1. The chelated ions were desorbed and determined by

flame atomic absorption spectrometry (FAAS). The modified solid phase could be used at least 50 times with acceptable reproducibility without any change in the composition of the sorbent, CCG or Sodium dodecyl sulfate (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 nm) by the Hummers method and dried for a week over phosphorus pentoxide in a vacuum desiccator before use. 4-Isocyanatobenzenesulfonyl azide was prepared from 4-carboxybenzenesulfonyl azide via a published procedure (Tong et al., 1990). All solutions were prepared with doubly distilled deionized water from Merck (Darmstadt, Germany). The C₁₈ powder for chromatography with diameter of about 50 μm was obtained from Katayama Chemicals from supelco. It was conditioned before use by suspending in 4 M nitric acid for 20 min, and then washed 2 times with water. SDS was obtained from Merck (Darmstadt, Germany) and used without any further purification.

Synthetic procedures

Preparation of CCG

The preparation of CCG functionalized by IL-NH₂ is illustrated in Scheme 1. Details of the synthesis can be found in Yang et al. (2009).

Column preparation

CCG (40 mg) were packed into an SPE mini-column (6.0 cm × 9 mm i.d., polypropylene). A polypropylene frit was placed at each

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

end of the column to prevent loss of the adsorbent. Before use, 0.5 mol L⁻¹ HNO₃ 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 CCG 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 FAAS. Zn(II) determinations were performed by a Varian Spect AA-10. Raman spectrophotometer analysis was 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 multi walled carbon nanotubes was loaded after washing acetone, 1 mol 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 3 times with water, then with 5 ml of 4 M HNO₃ and again 3 times with water. The prepared sorbent was transferred to a polypropylen tube (i.d 5 mm, length 10 mm). 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.

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 2

times with water were used for sampling. The water sample was filtered through a 0.45 µm pores filter. The pH of a 1000 ml portion of each sample was adjusted to 2.0 (4 M 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 (Wang et al., 1997; Zhang et al., 1982). 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 adsorber 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 adsorber, and passed through it until the level of methanol reached just the surface of the adsorber. 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-column system, Dowex 1X-8, RP-C18 silica adsorber 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

Figure 1 is a typical Atomic Force Microscope (AFM) image of a CCG dispersion in water (0.25 mg ml⁻¹) after deposition on a freshly cleaved mica surface through drop-casting. The AFM analysis reveals that the average interlayer spacing for exfoliated CCG sheets obtained in this work was ca. 1.49 nm. When compared with well-exfoliated GO sheets, with a spacing of ca. 0.96 nm (Figure S1), the distance between CCG sheets is greater, as would be expected. This is due to both the presence of the ionic liquid chains grafted onto both sheet sides, as well as the electrostatic repulsion between the p-CCG sheets. Moreover, it is unavoidable that some solvent molecules are still trapped between the CCG sheets after drying (at ambient conditions for 24 h) and these

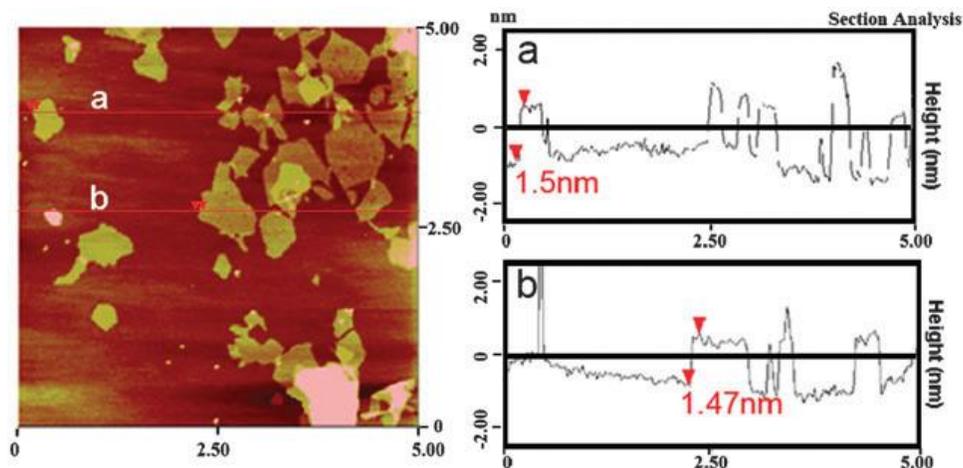


Figure 1. AFM image (left) of a p-CCG dispersion in water (0.25 mg ml^{-1}) on freshly cleaved mica surface through drop-casting, and height profiles (right) along the lines shown in AFM image.

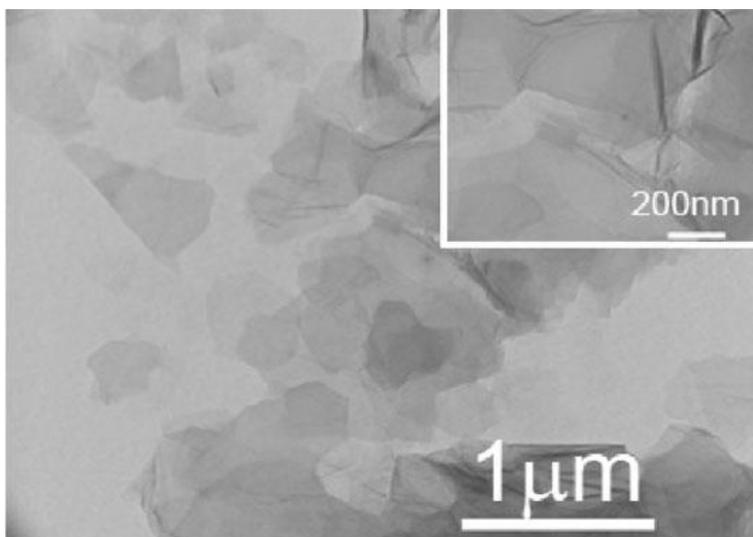


Figure 2. TEM image of p-CCG sheets.

molecules will have also contributed to the measured interlayer spacing. Similarly, an X-ray diffraction (XRD) analysis (Figure S2) was carried out in order to investigate and compare the exfoliation of GO and CCG. The (002) diffraction peak of graphite (Figure S2a) appears at *ca.* 26.6° , and the interlayer spacing is *ca.* 0.34 nm (Yang et al., 2009). The characteristic diffraction peak (001) of GO (Yang et al., 2009) was observed in Figure S2b, and corresponds to a GO interlayer spacing of $\sim 0.75 \text{ nm}$, as expected for well exfoliated sheets. However, it is worthwhile to note that, no obvious peaks attributed to graphite or GO could be found for CCG (Figure S2c), indicating that exfoliation of the layered CCG was obtained successfully in this work (Yang et al.,

2009). In conclusion, well exfoliated GO and CCG sheets were successfully obtained in this work.

It was found that the weight loss at around 200°C for the p-CCG composites was much lower than that of the GO composites, indicating a decreased amount of oxygenated functional groups. Finally, Transmission Electron Microscope (TEM) imaging of the CCG sheets was performed, and Figure 2 shows some multi- CCG flakes.

Stability studies

The stability of the newly synthesized CCG phases was

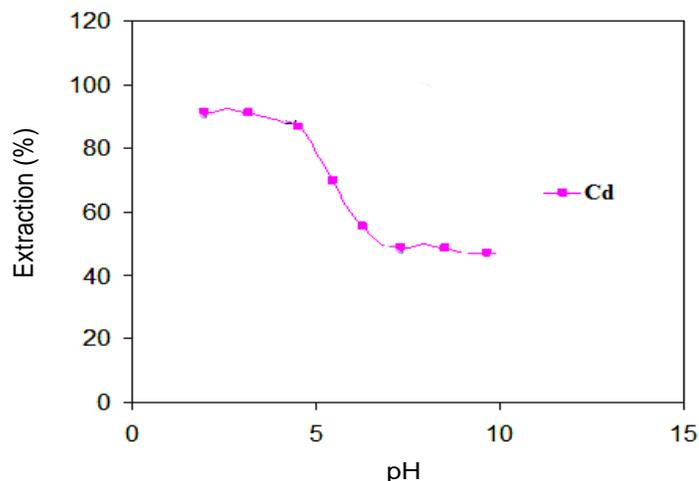


Figure 3. Extraction percentage of Cd(II) against pH.

performed in different buffer solutions (pH 1, 2, 3, 4, 5, 6 and 0.1 M sodium acetate) in order to assess the possible leaching or hydrolysis processes. Because the metal capacity values determined in the study revealed that the highest one corresponds to Cd(II)s, this ion was used to evaluate the stability measurements for the CCG phase (Mahmoud and Soliman 1997). The results of this study proved that the CCG 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 (Gomes-Gomes et al., 1995). Finally, the CCG phases were also found to be stable over a range of 1 year during the course of this work.

Primary investigations revealed that surfactant-coated C_{18} could not retain Cd(II) cations, but when modified with the CCG retains these cations selectively. It was then decided to investigate the capability of the CCG as a ligand for simultaneous preconcentration and determination of Cd on admicell.

The C_{18} surface in acidic media ($1 < \text{pH} < 6$) attracts protons and becomes positively charged. The hydrophilic part of SDS ($-\text{SO}_3^-$), is attached strongly to these protons. On the other hand, the CCG are attached to hydrophobic part of SDS and retain small quantities of metallic cations (Smith, 2009; Moghimi et al., 2009).

Non occurrence of the effect of pH

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 range of 1 to 10. The pH of the solution was adjusted by means of either 0.01 M HNO_3 or 0.01 M NaOH. The results indicate that complete chelation and recovery of Cd(II) occurs in pH range of 2 to 4 and that of 2 to 8 and are shown in Figure 3. 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 C_{18} , 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 to 5 ml min^{-1} would not affect the retention efficiency of the substrate. Higher flow rates cause incomplete chelation of the cations on the sorbent. The similar range of flow rate for chelation of cations on modified C_{18} with SDS and a CCG has been reported in literature (Smith, 2009; Moghimi et al., 2009). Flow rate of 1 to 2 ml min^{-1} for desorption of the cations with 4 ml of 4 M HNO_3 has been found suitable. Higher flow rates need larger volume of acid. Hence, flow rates of 5 and 2 ml min^{-1} were used for sample solution and eluting solvent throughout respectively.

Effect of the CCG quantity

In order to study optimum quantity of the CCG on quantitative extraction of Cd, 50 ml portions of solutions containing 100 ng of each cation were passed through different columns of the sorbent of which were modified with various amounts, between 10 to 50 mg of the CCG. The best result was obtained on the sorbent which was

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	98.6s(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⁺	2.30	2.7(1.4)	98.4(2.7)
Cu ²⁺	2.56	2.81(2.3)	97.7(2.5)
Fe ³⁺	2.40	3.45(2.4)	97.6(2.8)
Cr ³⁺	1.30	2.92(2.2)	96.3(2.4)
UO ²⁺	2.89	1.3(2.2)	97.3(2.2)
NO ₃ ⁻	5.5	2.3 (2.3)	96.4(2.6)
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.

modified with 40 mg of the CCG.

Figures of merit

The breakthrough volume is of prime importance for SPEs. Hence, the effect of sample volume on the recovery of the cations was studied. 100 ng of each cation was dissolved in 50, 100, 500 and 1000 ml of water. It was indicated that in all the cases, chelation and desorption of the cations were quantitative. It was then concluded that the breakthrough volume could be even more than 1000 ml. Because the sample volume was 1000 ml and the cations were eluted into 10 ml solution, the enrichment factor for both cations is 100, which is easily achievable.

The maximum capacity of 1.5 g of the substrate was determined as follows: 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 limit of detection (3σ) for the cations (Zargaran et al., 2008) was 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

Effect of foreign ions was 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. In order 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-column system is possible to preconcentrate and at the same time separate the neutral metal complexes of CCG, anionic complexes and free ions from each other by this

Table 3. Recovery of Cd contents of water samples.

Water sample		Amount added (μg)	Found (μg)	% Recovery
Sample distilled water (100 ml)	Cd	-	-	-
		0.050	0.043(2.40) ^a	96
Tao water (100 ml)	Cd	-	0.015(3.0)	-
		0.050	0.068(2.42)	96
Snow water (50 ml)	Cd	-	0.048(2.25)	-
		0.100	0.155(2.30)	98.0
Rain water (100 ml)	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⁺ Cd ²⁺ , Zn ²⁺ , 1 mg L ⁻¹ of each cation	Cd	-	-	-
		0.100	0.105(2.70)	99

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

Table 4. Results of speciation of Cd in different samples by three-column system.

Column	Tap water (1000 ml)	Water sample (1000 ml) ^a	River water (50 ml)
	Cd(μg)		
Dowex 1X8	-	-	-
Silica C-18	-	-	-
Chelex-100	0.012(4.0) ^b	0.104(2.9)	0.103(2.8)

^a, This was a solution containing 0.1 μg of each cation in 1000 ml of distilled water; ^b, values in parenthesis are CVs based on three replicate analysis. The samples are the same as those mentioned in Table 4.

method (Wang et al., 1997). Water samples were passed through the three connected columns: anion exchanger, C₁₈-silica adsorber and chelating cation exchanger. Each species of Cd is retained in one of the columns; anionic complexes in the first column, neutral complexes of CCG in the second, and the free ions in the third. The results of passing certain volumes of different water samples through the columns are listed in Table 4. According to the results, it is indicated that Cd is present only as cations. On the other hand, the t-test comparing the obtained mean values of the present work with those published indicate no significant difference between them. 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.

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