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Combination of Solid Phase Extraction and Flame Atomic Absorption Spectrometry for Trace Analysis of Cadmium

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Um novo método seletivo foi desenvolvido para a separação e pré-concentração de íons Cd(II) tendo como base a formação de um complexo em uma mini-coluna contendo como suporte carvão ativado modificado com laranja de xilenol. Os íons Cd(II) pré-concentrados foram eluídos com 5,0 mL de solução 0,5 mol L^{-1} HNO_3 e determinados por espectrometria de absorção atômica com chama. Foram estudadas as condições de preparo do carvão ativado modificado, pH, vazões, bem como, o efeito de potenciais íons interferentes. Nas condições ótimas de trabalho, obteve-se um fator de pré-concentração de 200. O gráfico de calibração foi linear até 200 ng mL^{-1} de Cd(II) na solução inicial. O limite de detecção foi de 0,3 ng mL^{-1} Cd(II) e o desvio padrão relativo (RSD %) igual a 4,0% para uma solução 20,0 ng mL^{-1} Cd(II). O método foi aplicado com sucesso para determinar cádmio (II) em amostras de água e nos seguintes materiais de referência: lama de efluentes (CRM 144R) e água de mar (CASS 4).

A new selective method was developed for the separation and preconcentration of Cd(II) ions based on its complex formation with Xylenol orange loaded on activated carbon as a solid support in a mini-column. The preconcentrated ions were eluted by passing 5.0 mL 0.5 mol L^{-1} HNO_3 solution through the solid support and then the Cd(II) contents was measured by flame atomic absorption spectrometry. Conditions for preparation of the modified activated carbon, pH and flow variables were studied, as well as, the effect of potential interfering ions. A preconcentration factor of 200 was achieved using the optimum conditions. The calibration graph was linear up to 200 ng mL^{-1} Cd(II) in the initial solution. The detection limit of the method was 0.3 ng mL^{-1} Cd(II) and the relative standard deviation (RSD%) was 4.0% for 20.0 ng mL^{-1} Cd(II). The method was successfully applied to the determination of cadmium(II) in water samples and in two reference materials: sewage sludge (CRM 144R), and sea water (CASS 4).

Keywords: cadmium, activated carbon, xylenol orange, solid phase extraction, FAAS

Introduction

The transition metals including cadmium are an important risk for human and animals.[1,2] Because the main sources of heavy metals for humans and animals are the waters,[3,4] reliable and sensitive analytical methods and procedures have an important role to evaluate the impacts of metal pollutants. Flame atomic absorption (FAAS) and emission spectrometry are the most widely methods used for trace metals determination. Due to the limited sensitivity of the FAAS, high dissolved solid content of saline waters, and to the low cadmium concentration levels in natural samples, its determination frequently requires a previous separation and preconcentration steps.

Among the separation methods, solid-phase extraction (SPE) based on solid support modified with a suitable complexing agent is frequently used. Different solid phases with several complexing agents have been used for separation and preconcentration of Cd(II) as given in Table 1. Most of the reported methods has lower enrichment factor and/or suffer from many interfering ions for separation of Cd(II). Activated carbon is one of the important solid support that has been used either alone or modified with a complexing agent. In most of the previous studies, a ligand solution was needed for each experiment, because the chelating agent was used to wash metal ions from the surface of the sorbent.

The aim of this work is the development of a separation and preconcentration method for the determination of Cd(II) by FAAS for water samples, using activated carbon

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Table1. SPE preconcentration procedure for cadmium in combination with FAAS

Preconcentration reagent	Solid-phase material	pH	Calibration range (µg L^{-1})	LOD (µg L^{-1})	Enrichment factor	Applications	Interferences	Ref.
5,7-Dibromo-quinoline-8-ol	Benzophenone	6-8	0.1-50	0.1	200	Not reported. Waste water	Soils, Sea &	5
Diazoaminobenzene(DAAB)	Poly-Cd(II)-DAAB-VP	6	0.21-30	0.21	200	Ca^{2+}, Zn^{2+}, Hg^{2+}	Tap & River water	6
Bathocuproine disufonic acid	Chromosorb-108	8-9.5	20-2000	0.24	80	Al^{3+}, Ag^{+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Pb^{2+}	Tap & River water, Wine, Rice, Tea, Honey	7
1-(2-pyridylazo)-2-naphthol	Chromosorb-106	8-9	—	0.19	250	Fe^{3+}, Al^{3+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+}	River water, salt, tea, Human hair, tobacco	8
Iodide	Naphthalene- methyltrioctyl- amonium chloride	1.2-10	1-100	0.6	40	—	Tap & Persian Gulf water	9
O,O-Diethyldithiophosphate	Amberlite XAD-4	—	—	1-5	20	Not investigated	Biological samples	10
2-(62 -methyl-22 - benzothioazolylazo) chromatropic acid	Polyurethane foam	7.5	10-1000	0.8, 2.04	37, 22	Fe^{3+}	Natural & Tap water, Tea, Spinach	11
Vermicompost (humic material)	__	5.0	__	5	100	__	Mineral water	12
Cupferron	Silica Gel	5.5	__	0.5	30	Zn^{2+}, Cu^{2+}, Al^{3+}	Nail polish	13
Xylenol Orange	Amberlite XAD-7	4.5-5	500-2500	9	50	__	River water	18
Xylenol Orange	Activated carbon	6.0	0.5-200	0.3	200	__	Natural & Tap water	Present work

as sorbent and Xylenol orange (XO) as complexing agent. Activated carbon tightly adsorbed XO and thus, the adsorbed XO did not wash away during the elution step. This means that the modified activated carbon can be used several times without decreasing the enrichment factor.

Experimental

Reagents

All solutions were prepared with double distilled water. Otherwise stated, analytical-grade acids and other chemicals were obtained from Merck (Darmstadt, Germany).

Activated carbon, 40-60 mesh, was soaked in hydrochloric acid for 1 day; it was then washed with water and dried at 110 °C for 1 day.

Xylenol orange solution, 0.010% (m/v), was prepared by dissolving 0.010 g of the reagent in water. Samples were filtered through a cellulose membrane of pore size <2 µm.

Universal buffer (pH 3.0-11.0) was made of mixture of acetic acid, boric acid and phosphoric acid plus sodium hydroxide (0.04 mol L^{-1}) in water.

The following certified reference materials were used: CASS.4 seawater (National Research Council of Canada, Ottawa, Ontario) and CRM 144 R Sewage Sludge from Domestic Origin (Community Bureau of Reference, Brussels, Belgium).

Apparatus

A Perkin-Elmer (USA), Model 2380 atomic absorption spectrometer furnished with a cadmium hollow-cathode lamp was used. The instrument was set at a wavelength of 228.8 nm and the air-acetylene flame was adjusted according to the standard conditions. The schematic diagram of the preconcentration system is shown in Figure 1. The hardware of the system was composed of a 32 channel I/O card (PCL-720, Advantech, Taiwan) which has a power relay module to convert the output of I/O card to 220 V AC, a peristaltic pump (Ismatec, ISM 404, Switzerland), three 220 V AC electrical valves, a silicon rubber tubing pump (2.06 mm i.d.) and a PC computer, Pentium II (233 MHz). A program was written in Borland C^{++} by the authors to monitor and to control the system. The mini-column was made by packing of Teflon tubes (7 mm i.d.) with XO loaded activated carbon. Small amount of glass wool was plugged at the ends of each column to prevent material loss. A WPA Lightwave (UK), Model S2000 diode array UV-Vis spectrophotometer was used to measure the absorbance of the XO solution. The pH of aqueous solutions was checked using a Metrohm (Switzerland), Model 827 pH meter with a glass electrode.

Preparation of modified activated carbon

In a 1000 mL beaker, 2.0 g activated carbon was added to 800 mL of XO solution (6.0 mg/100 mL) and mixed well

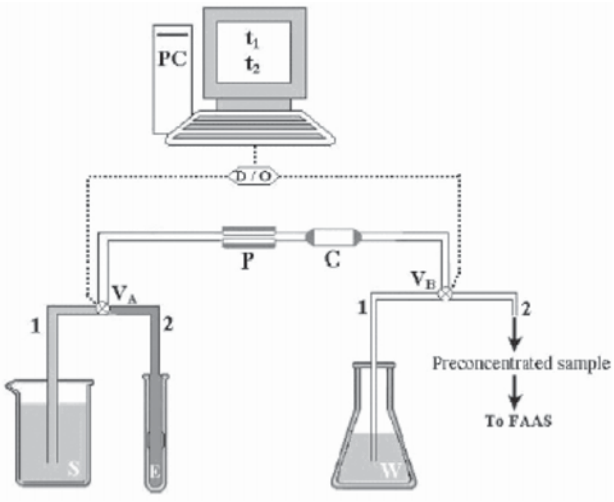

Figure 1. The schematic diagram of the preconcentration system. (P, Pump; C, Microcolumn; D/O: Analog to digital converter; S, Sample solution; V_A, valves A; V_B, valve B; E, Eluent solution (0.50 mol L^{-1} HNO_3) and PC, Computer).

at pH 10.0 (universal buffer, 0.04 mol L^{-1}). After 36 h, the mixture was filtered and washed with water three times, each time with 10 mL water, and then dried out. A Teflon column (42.9 cm length and 7.0 mm in diameter) was packed with 0.20 g of the modified activated carbon.

Procedure

The method was tested with model solution before its application to real samples. A 50 -1000 mL of Cd(II) solution, buffered at pH 6.0 (universal buffer, 0.04 mol L^{-1}), was passed through the column at a flow rate of 4.0 mL min^{-1} by opening the position 1 of electrical valves A and B (Figure 1). After finishing the sample solution, position 1 of valves A and B was closed, and position 2 of valves A and B was opened. Then, a volume of 5.0 mL of 0.50 mol L^{-1} nitric acid was passed through the column at a flow rate of 0.5 mL min^{-1} to elute the Cd(II) ions. The eluent was collected and Cd(II) was determined by flame atomic absorption spectrometry. The percent of metal ions adsorbed on the column for the concentration of Cd(II) was calculated from the amount of Cd(II) ions in the starting sample and the amount of Cd(II) eluted from the column.

The CASS4 Nearshore Seawater reference material for Cd(II) ions was analyzed. The pH of the sample was adjusted to 6 and the solution was passed through the column. Cadmium ions retained on the column were eluted with 5.0 mL of 0.5 mol L^{-1} HNO_3 and further introduced into the nebulizer of FAAS as described above.

For Sewage sludge, 100 mg of CRM144R Sewage sludge standard reference material sample was decomposed with 16 mL of aqua regia and the solution was evaporated to dryness.[14] This process was repeated twice. A volume of 10 mL of distilled water was added to the residue. The suspension was filtered through a blue band filtering paper and the insoluble residue was washed with distilled water. Afterwards, the above procedure was applied to the final solutions and the blank solution.

Results and Discussion

Xylenol orange (XO) (3,32 -bis[N,N-di(carboxymethyl) aminomethyl]-*o*-cresolsulfonephthalein) is a water-soluble dye of the triphenylmethane group. This is a metal indicator widely used for analytical determinations.[15,16] Silica gel modified Xylenol orange have been used as a solid phase extractor for Hg(II)[17] and Pb(II).[18] Tewari *et al.*[19] have used Amberlite XAD-7 impregnated with Xylenol orange as a chelating collector for preconcentration of Cd(II), Co(II), Cu(II), Ni(II), Zn(II) and Fe(III) at a pH range of 4-7. In the reported procedure, preparation of the solid phase needs long time (min. 2 h), and the limit of quantification for Cd(II) was 10 μg mL^{-1}. XO has a great formation constant with Cd(II). This ligand acts as a selective complexing agent for Cd(II) at pH 6.0. On the other hand, XO can be adsorbed on activated carbon surfaces. After the adsorption, the modified activated carbon is completely stable and does not wash off when using H_2O or HNO_3 solution as a washing solvent. This means that the activated carbon treated with XO can be used several times for separation and preconcentration of Cd(II) without decreasing the enrichment factor of the solid phase. This may be due to the similarity of the XO structure to that of activated carbon, producing strong π-π interaction.[20]

Optimization of variables

First of all, to obtain the best quantitative recoveries of Cd(II) ions, many parameters such as pH of adsorption of XO on activated carbon, pH of sample solution, sample volume, type and volume and the concentration of washing solution, sample flow-rate through the column, capacity of the modified activated carbon and the effect of matrix on the preconcentration step should be studied. In the optimization steps, 0.20 g of activated carbon was used.

To find the optimum pH for adsorption of XO on the activated carbon, buffer solutions were used. For this purpose, 6.0 mg of XO and 25.0 mL of buffer solutions (pH 4.0-11.0) were added into a series of 100 mL volumetric flasks and the solutions were diluted to 100 mL with water. The absorbances of the solutions were measured spectrophotometrically at an appropriate wavelength to find the molar absorption coefficient of XO at different pH values. Then, 6.0 mg of XO and 25.0 mL of the buffer solutions (pH 4.0-11.0) plus 0.20 g activated carbon were mixed in a series of 100 mL beakers. After 12 h, the mixtures were filtered, and the absorbances of the filtered solutions were measured spectrophotometrically to find non-adsorbed XO in each solution, according to the calibration curve. The results are given in Table 2. The results showed that the best pH for adsorption of XO on activated carbon was 10.0. Therefore, a buffer solution of pH 10.0 (universal buffer, 0.04 mol L^{-1}) was used to prepare the modified activated carbon.

The influence of time on the modification of activated carbon was studied by treating 6.0 mg of XO and 25.0 mL of buffer solution at pH 10.0 and 0.20 g activated carbon for different times. The results showed that maximum adsorption of XO on the surface of activated carbon took place after 36 h (Figure 2).

The capacity of activated carbon for XO was also checked. In order to measure the capacity of activated carbon for adsorption of XO at pH 10.0, 25 mL of the buffer solution (pH 10.0) plus 3.0 to 9.5 mg of XO was added into a series of 100 mL beakers and 0.20 g activated carbon was added to each beaker. After 36 h, the mixtures were filtered, and the absorbances of each solution were measured spectrophotometrically to find the free XO (non-adsorbed). The results are shown in Figure 3. From the results, we can calculate that 1.0 g of activated carbon could adsorb 30.0 mg of XO.

The influence of pH of sample solution on the preconcentration step of Cd(II) was also studied. For this purpose, 200 mL of 50.0 ng mL^{-1} Cd(II) at different pH values (3.0-10.0) was passed through the modified solid phase. Then the eluent solution was checked for Cd(II) concentration using FAAS (Figure 4). The results showed that a suitable pH for adsorption of Cd(II) on the modified activated carbon is around 6.0. This is due to the fact that in acidic solution, the constant formation of the Cd(II)-XO complex decreases due to the protonation of XO. Therefore,

Table 2. Influence of pH on adsorption of XO on activated carbon

pH	λ_{max}/nm	Absorbance
4.0	433	0.150
5.0	435	0.085
6.0	438	0.052
7.0	578	0.016
8.0	578	0.015
9.0	578	0.011
10.0	578	0.004
11.0	581	0.045

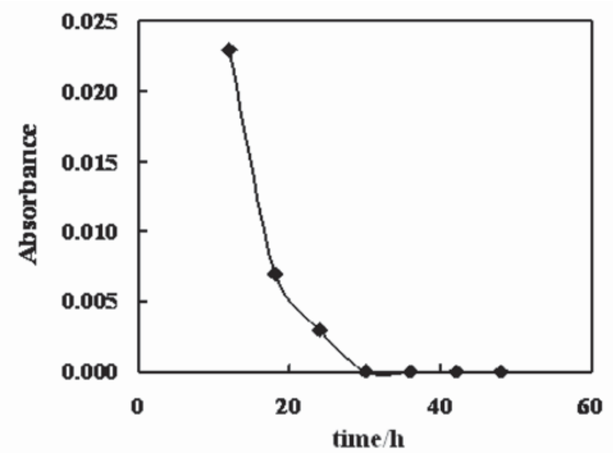

Figure 2. Influence of time on the modification of activated carbon with XO. Conditions: 100 mg activated carbon; 6.0 mg XO; at pH = 10.0.

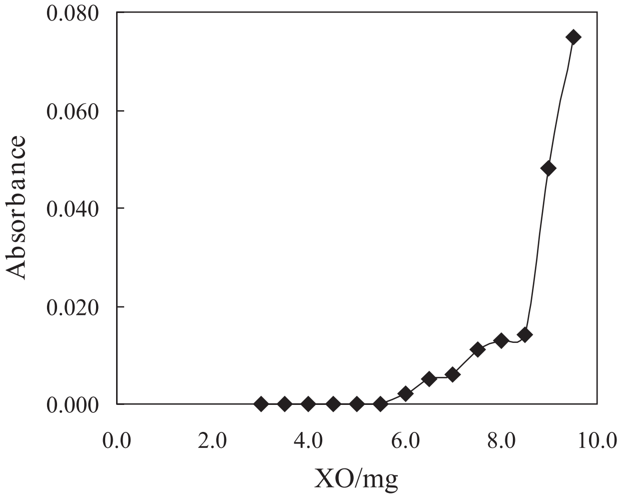

Figure 3. Capacity of activated carbon for XO. Conditions: 200 mg activated carbon; at pH 10.0; mixed and stored for 36 h.

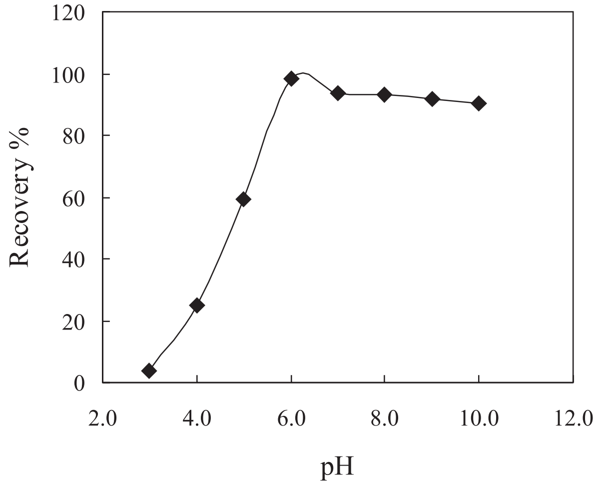

Figure 4. Influence of pH of the sample solution on adsorption of Cd(II) on the modified activated carbon. Conditions: Initial Cd(II) value, 200 mL of 50.0 ng mL^{-1}; Washing solution, 5 mL of 0.50 mol L^{-1} HNO_3.

a buffer solution (universal, 0.04 mol L^{-1}) at pH 6.0 was used for the preconcentration step.

For desorption of Cd(II) from the solid phase, different HNO_3 concentrations (5.0 mL) in the interval range of 0.5 to 2.0 mol L^{-1} with flow rate of 0.5 mL min^{-1} and with sample flow rate of 2.0 mL min^{-1} were tested for the quantitative elution of the adsorbed Cd(II) ions from the column. The results showed that 0.5 mol L^{-1} HNO_3 was suitable to remove (100 ± 1.3)% of Cd(II) from the solid sorbent. In order to optimize the volume of 0.5 mol L^{-1} HNO_3 solution, 50 mL of 200.0 ng mL^{-1} Cd(II) was passed through a series of the modified activated carbon under the optimum conditions. Then the solid phases were washed with different volumes of 0.50 mol L^{-1} HNO_3 (2.0-6.0 mL). The results showed that 5.0 mL 0.5 mol L^{-1} HNO_3 was suitable to remove (100 ± 1.5) % of Cd(II) ions from the solid phase.

The influence of the sample flow rate on preconcentration efficiency of Cd(II) ions through the column was also investigated. For this purpose, a volume of 50 mL of 200.0 ng mL^{-1} Cd(II) solution at pH 6.0 was passed through a series of modified columns at different flow rates. Then the adsorbed Cd(II) was washed with 5 ml of 0.5 mol L^{-1} HNO_3 solution and then the Cd(II) content was measured using FAAS. The results showed that using a sample flow rate greater than 5.0 mL min^{-1} caused a decrease of the Cd(II) ions recoveries from 100 to 95%. Therefore, a sample flow rate of 4.0 mL min^{-1} was used for further studies.

The effect of flow rate of HNO_3 (0.5 mol L^{-1}) on desorption efficiency of Cd(II) ions from the column was also checked in the range of 0.5-2.0 mL min^{-1}. The results showed that the recovery of cadmium was maximized when using elution rates up to 0.5 mL min^{-1}.

The capacity of the modified activated carbon for adsorption of Cd(II) was checked by passing 150 mL of Cd(II) solution containing 50.0-1000.0 µg L^{-1} Cd(II) through the column (containing 0.20 g modified activated carbon). The metal ions were stripped off the modified activated carbon with 5 mL 0.5 mol L^{-1} HNO_3 and measured by FAAS. The adsorption capacity was calculated as the following equation:

$$Q = (C_0 - C_e)\, v / m$$

where Q represents the adsorption capacity (µg g^{-1}), C_0 and C_e the initial and equilibrium concentration of Cd(II) (µg L^{-1}), m is mass of the modified activated carbon (g) and v is the volume of metal ions solution (L). The adsorbed Cd(II) on the solid phase was eluted with 5 ml of 0.5 mol L^{-1} HNO_3 and the desorbed Cd(II) was measured using FAAS. As it can be seen in Figure 5, the amount of Cd(II) adsorbed on the solid phase increased with the initial concentration of Cd(II). In order to reach the saturation, the initial Cd(II) concentrations were increased till the plateau values (adsorption capacity values) were obtained. It was established that the capacity of the solid adsorbent is equal to 0.50 mg of cadmium per 1.0 g of the modified activated carbon.

Reusability of the modified activated carbon was checked using the same solid phase for sorption-desorption of Cd(II) ions for fifty times the reusability was tested. The maximum change in the performance (sorption capacity) of the solid phase after the repeated use was less than 2%, indicating that its repeated use is feasible as leaching of the dye from the activated carbon matrix is insignificant. No change in the sorption capacity of the modified activated carbon was noticed after storing it for 5 months.

Limit of quantitative preconcentration, preconcentration factor and limit of detection

The lower limit of quantitative preconcentration (or limit of quantification) was determined by loading a fixed amount of Cd(II) ions - 0.5 mg for Cd(II) - onto the column containing 200 mg of the solid phase from a varying volume of the feed solution (100 to 2000 mL). The metal ions were desorbed as given in the recommended procedure into 5.0 mL of 0.5 mol L^{-1} HNO_3 and determined by FAAS. The results showed that the limit of quantitative preconcentration was 0.4 µg L^{-1} Cd(II) with a preconcentration factor of 200. Recoveries from further diluted solutions were not quantitative. The limit of detection values was equal to 0.3 µg L^{-1} Cd(II).

Interference Study and Applicability

The influence of matrix ions in water samples on the separation and recovery of Cd(II) ions was also

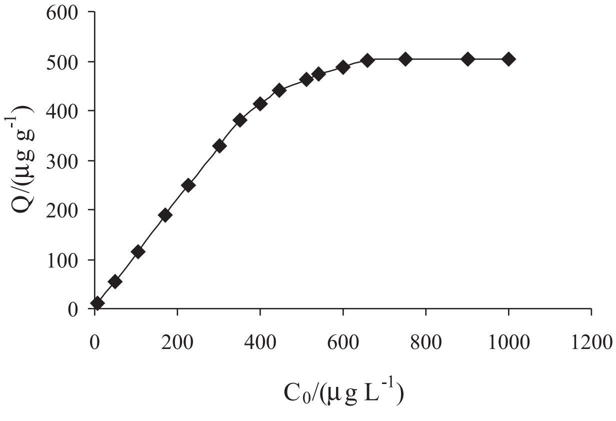

Figure 5. The effect of Cd(II) initial concentration on the adsorption quantity of the modified activated carbon. Other conditions: Modified activated carbon, 200 mg and pH 6.0.

investigated by passing different amounts of potential interfering ions plus 50.0 ng mL^{-1} Cd(II). The results showed that 10000-fold of alkaline and alkaline-earth ions, 5000-fold Zn(II), Fe(II), Ni(II), Pd(II), V(III), Mn(II), Cu(II), Hg(II), Al(III), Mo(VI), Co(II), Cr(III), Ag(I), Pb(II), chloride, nitrate, hydrogen carbonate, carbonate and sulfate did not interfere. The results confirm that the modified solid phase is highly selective for Cd(II) and interferences did not occur. The proposed method was used for three different water samples for Cd(II) determination: Zayandeh Roud River water (Isfahan city), tap water and waste water. The water samples were directly measured by the proposed method after filtering with a filter paper (Whatman No. 1) and spiking with various amounts of cadmium(II). For each sample, 250 mL of the spiked sample was passed through the column as explained in the recommended procedure. Then the Cd(II) contents in the washed solutions were determined by FAAS. In addition, the following reference materials: sewage sludge (CRM-144R), and sea water (CASS-4) were used to evaluate accuracy. CASS-4 reference material was spiked with various amounts of cadmium(II) to obtain the concentration of Cd(II). After that, cadmium(II) was determined using the separation/preconcentration system. The results showed that the new solid phase is capable to separate and preconcentrate Cd(II) ions from water at trace levels (Table 3). The results for spiked samples and reference materials also proved the suitability of the solid phase for water analysis.

Table 3. Determination of Cd(II) in water samples (n=4)

Sample	Cd(II) Added / (ng mL^{-1})	Cd(II) Found / (ng mL^{-1})	Recovery (%)
Tap water	—	4.8 ± 0.3	—
	20.0	24.4 ± 0.2	98.0
	30.0	35.1 ± 0.5	101.0
	40.0	44.6 ± 0.4	99.5
Zayandeh Roud River water	—	3.1 ± 0.4	—
	20.0	23.3 ± 0.6	101.0
	30.0	32.9 ± 0.5	99.3
	40.0	43.4 ± 0.4	100.8
Waste water	—	4.2 ± 0.2	—
	20.0	24.5 ± 0.3	101.5
	30.0	34.4 ± 0.5	100.7
	40.0	43.9 ± 0.4	99.2
CASS.4 Nearshore, Seawater reference material[a]	—	< DL	—
	10.0	10.2 ± 0.1	102.0
	20.0	19.8 ± 0.2 9	9.0
CRM-144R[b]	—	1.89 ± 0.10 µg g^{-1}	—

[a] Certified value: 0.026 ± 0.003 µg L^{-1}; < DL: below the detection limit; [b] Certified value: 1.84 µg g^{-1}.

Conclusions

The method could be applied for the separation, preconcentration and selective determination of trace amounts of cadmium(II) as low as 0.3 ng mL^{-1}. The modified activated carbon is stable for several treatments of sample solutions without the need for using any chemical reagent. The relative standard deviation for six independent determinations was 4.0 % for cadmium (20.0 ng mL^{-1}). Under the optimum conditions cadmium in aqueous samples was concentrated about 200-fold. The recoveries of spiked cadmium(II) were in the range of 99-104 %. The recoveries obtained by the present solid phase are also comparable with the widely used and recently reported chelating resins. The obtained results are in good agreement with the certified values, which proved the applicability of the developed method to the quantitative separation/preconcentration of cadmium in the sediment and sewage sludge samples. The lower acid concentration required for desorption of metal ion avoids the requirement of further dilution for AAS measurement and is among the advantage of the modified activated carbon, which also is not affected by leaching problems.

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