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Simultaneous separation and determination of trace amounts of Cd(II) and Cu(II) in environmental samples using novel diphenylcarbazide modified nanoporous silica

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ABSTRACT

A novel sorbent for simultaneous separation of cadmium and copper was prepared by functionalizing SBA-15 nanoporous silica with diphenylcarbazide. A solid-phase extraction method using the above sorbent has been developed to separate and concentrate trace amount of cadmium and copper ions from environmental samples by flame atomic absorption spectrophotometry measurements. The optimum experimental conditions such as pH, flow rates, type and the smallest amount of eluent for elution of cadmium and copper ions, break through volume and effect of coexisting ions on the separation and determination of cadmium and copper ions were evaluated. The extraction efficiency for cadmium and copper ions were greater than 98% and limit of detection (LOD) was 0.15 and 0.45 ng mL^{-1} for cadmium and copper, respectively. The preconcentration factor was 294 and 291 for cadmium and copper, respectively, and the relative standard deviation (RSD) of the method was <4% for 10 separate column experiments for the determination of 5.0 μg cadmium and copper ions. The adsorption capacity of the nanoporous silica was 198 mg g^{-1} for cadmium and 105 mg g^{-1} for copper on functionalized SBA-15 nanoporous silica. Validation of the outlined method was performed by analyzing certified reference materials (Soil (NCS DC 73323) and ore polymetallic gold Zidarovo-PMZrZ (206 BG 326)). The practical applicability of the developed sorbent was examined using real samples such as sea water, fish and sediment samples.

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1. Introduction

Determination of trace heavy metals is often a major task for the analytical chemists, as it is a good tool to monitor toxicants in environmental samples. Among heavy metals that exist in the environment, cadmium monitoring is very critical because cadmium concentrations in the environment are increasing drastically [1–4]. Cadmium exposure can be linked to diseases associated with aging such as osteoporosis, prostate and pancreatic cancer [5–7]. On the other hands, although copper is an essential element for our health, it is toxic at high concentrations [8–10]. For this reason its determination in environmental samples is warranted by the narrow window of concentration between essentiality and toxicity. However, the heavy metals concentration level in environmental samples is fairly low and preconcentration procedures are often required [11]. Among numbers of methods such as liquid–liquid extraction [12,13], chemical precipitation [14,15], ion exchange [16,17], reverse osmosis adsorption [18] and solid-phase extraction (SPE), solid-phase extraction attracted a considerable amount of interest for the preconcentration of toxic metal ions [19–25], due to the higher efficiency and low consumption of pure organic solvent. This method is simple, efficient, selective, cost-effective, and it is easy to automate without need for emulsion, and it is also safe, regarding to the reagents employed [26]. According to the nature of this method, the key point is choosing appropriate adsorbent, since this factor could have an effect on selectivity and sensitivity of method [27]. By advent of SPE, various sorbents have been proposed such as carbon nanotubes [28], activated carbon [29], polymeric adsorbent resin [30], Amberlite XAD-7 resin [31], synthetic zeolites [32], modified chromosorb [33], TiO_2 [34], activated alumina [35] and nanoporous silica [36]. Among these sorbents nanoporous silicas such as MCM-41, MCM-48 and SBA-15 have attracted great attention because of their good mechanical and thermal stability, and their lower susceptibility to swelling and shrinking [37]. In spite of these advantages, their applications without surface modifications and functionalizations are limited [38]. Furthermore, properties of these materials depend on the functional group that anchored to surface of nanoporous silica. Among lots of suitable

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ligands in coordination chemistry, diphenylcarbazide is a well-known ligand for coordinating to transition metals in general and cadmium and copper in particular [39,40].

In this work, for the first time, SBA-15 nanoporous silica was functionalized by diphenylcarbazide and utilized as an adsorbent for the separation of ultra-trace amounts of cadmium and copper ions. The effects of the pH, flow rates, type and the smallest amount of eluent for elution of cadmium and copper ions, break through volume and effect of coexisting ions on the separation and determination of cadmium and copper ions were investigated. The proposed method was applied to determine cadmium and copper ions in several environmental samples, and also the accuracy was confirmed by two standard materials.

2. Experimental

2.1. Reagents and materials

All reagents used in this study (HCl, HNO_3, NaOH, KCl, diphenylcarbazide, 3-choloro-propyltriethoxysilane, acetic acid, $Cd(NO_3)_2$, $Cu(NO_3)_2$, toluene and ethanol) were of analytical grade and purchased from Merck (Darmstadt, Germany). Colloidal silica with particle size below 0.5 mm and surface area of 200 $m^2\,g^{-1}$ was purchased from Merck Company and used as received. Double-distilled water from a Milli-Q purification system (Millipore, Bedford, MA, USA) was used for the preparation of solutions. A stock solution (1.0 $mg\,mL^{-1}$) of cadmium and copper ions was prepared by dissolving an appropriate amount of corresponding nitrate salts in double-distilled water. Soil (NCS DC 73323) and ore polymetallic gold Zidarovo-PMZrZ (206 BG 326) from Bulgaria was prepared as the reference material.

SBA-15 was prepared according to the previous report [41], and 3-choloro-propyltriethoxysilane was used to modify nanoporous silica surface, similar to the general procedure of modification of nanoporous silica by amines [42]. In a typical reaction, 1.0 g of SBA-15 was suspended in 50 mL toluene and the mixture was stirred for 1 h. Then 3-choloro-propyltriethoxysilane (2.0 g) was added to the mixture and was refluxed for 12 h under nitrogen atmosphere. The resulted solid was suspended in 100 mL of toluene and triethylamine mixture (1:1, v/v) and an excess amount of diphenylcarbazide (5.0 g) was added. After 24 h reflux the yellow solid was removed from solvent by filtration, washed with toluene and acetone and then dried at room temperature (Fig. 1). The synthesis of nanoporous silica and diphenylcarbazide-functionalized material (DPC-SBA-15) was characterized by IR spectroscopy, low-angle X-ray diffraction, BET surface area measurement and elemental analysis.

Diphenylcarbazide-functionalized colloidal silica was prepared similarly as described for the SBA-15. In a typical reaction, 1.0 g of colloidal silica was suspended in 50 mL toluene and the mixture was stirred for 1 h and then 3-choloro-propyltriethoxysilane (2.0 g) was added and the mixture was refluxed for 12 h under nitrogen atmosphere. The resultant solid was suspended in 100 mL toluene and triethylamine mixture (1:1, v/v) and an excess amount of diphenylcarbazide (5.0 g) was added. After 24 h reflux, the yellow solid was removed from solvent by filtration, washed with toluene and acetone and then dried at room temperature.

2.2. Apparatus

Cadmium and copper concentration was determined by an AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer (FAAS) in an air–acetylene flame, according to the user's manual, provided by the manufacturer. Cadmium and copper hollow cathode lamp was used as the radiation source with wavelength of 228.8 and 324.8 nm, respectively. The pH was measured at $25 \pm 1\,^{\circ}C$ with a digital WTW Metrohm 827 Ion analyzer (Herisau, Switzerland) equipped with a combined glass–calomel electrode. A peristaltic pump was obtained from Leybold (Cologne, Germany) and an adjustable vacuum gauge and controller were obtained from Analytichem International (Harber City, CA). The adjustable vacuum gauge allowed the control of the flow rate during extraction. The CHN analysis was performed on a Thermo Finnigan Flash EA112 elemental analyzer (Okehampton, UK). IR spectra were recorded on a Bruker IFS-66 FT-IR spectrophotometer. BET surface areas measured by nitrogen adsorption technique using a Micromeritics ASPS 2010 analyzer. Low angle X-ray diffraction patterns were obtained on a Philips-PW 17C diffractometer with Cu $K\alpha$ radiation. The transmission electron microscopy (TEM) images were taken on a JEOL JEM-2100F field emission transmission electron microscope.

2.3. Procedure

2.3.1. Column method

Hundred milligrams of DPC-SBA-15 was packed in a glass column with dimensions 120 mm in length and 20 mm in diameter, and blocked by two polypropylene filters at the ends to prevent loss of the nanoporous material during sample loading. Prior to extraction, the column was preconditioned successively with 5 mL absolute ethanol, 5 mL toluene, and 5 mL absolute ethanol and then washed with double-distilled water until it became free of organic solvent. A 25 mL of standard solution containing 1 $mg\,L^{-1}$ cadmium and copper ions, after adjusting the pH of sample to 6.0 by adding HNO_3 or NaOH solution, was passed through the column at a flow rate of 10 $mL\,min^{-1}$ using a peristaltic pump. The sorbed cadmium and copper ions were eluted from the column with HCl (2 $mol\,L^{-1}$) at a flow rate of 2 $mL\,min^{-1}$. Afterwards, the analytes in the eluent were determined by FAAS.

2.3.2. Real sample pretreatment and analysis

Fish and sediment samples were collected from two different sites of Musa Creek. Musa Creek is located in the northwest of Persian Gulf (21°30′–31°30′N, 52°48′E), and has several subsidiary Creeks. Among them, Jafar Creek marked as a polluted site and Behad Creek chosen as a reference site where it is far from petrochemical industries. Sampling was carried out in August 2010. The fish samples (platycephalusindicus) were stored in a plastic bag on ice and transported to the laboratory and were kept at $-20\,^{\circ}C$ before being used. A part of the muscles was taken out quickly and was dried in an oven at $70\,^{\circ}C$ for 48 h [43]. After grinding the dry tissue, 0.5 g of each sample was digested with 5 mL of concentrated HNO_3 in a Teflon beaker for 4 h at $100\,^{\circ}C$. Resulted mixture was filtered into 100 mL Erlenmeyer flask and then diluted with double distillated water up to 100 mL. Sediment samples were collected from each under investigation site, using Peterson grab sampler and stored in a plastic bag in ice and transported to the laboratory and was kept at $-20\,^{\circ}C$ until analysis. 1.0 g of sediment was digested with 6 mL of HCl (37%) and 2 mL of HNO_3 (65%) in a microwave digestion system. Digestion was carried out for 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W, 8 min at 550 W and then venting for 8 min [44]. The residue resulted from digestion was then diluted to 100 mL with deionized water.

3. Results and discussion

Extraction and preconcentration of cadmium and copper ions on DPC-SBA-15 were highly dependent on the different parameters such as pH of the sample, type, volume and concentration of eluent, sample and eluent flow rate, sample volume and concentration of

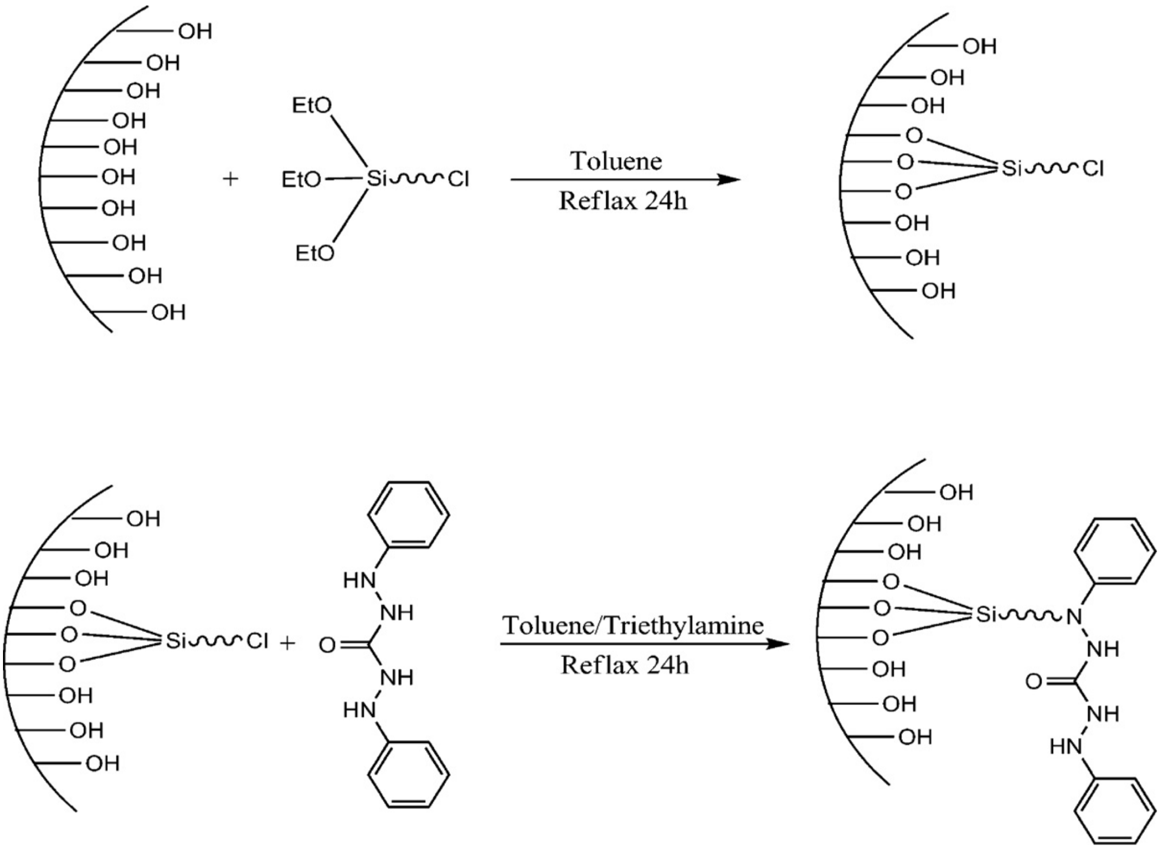

Fig. 1. A scheme for modifying SBA-15 with diphenylcarbazide.

coexisting ions. In this context, the procedure was optimized for the various analytical parameters.

3.1. Characterization of adsorbent

Elemental analysis of the diphenylcarbazide-functionalized nanoporous and colloidal silicas gave a diphenylcarbazide concentration of 1.95 and 0.36 mmol g^{-1}, respectively. The low-angle X-ray diffraction pattern of DPC-SBA-15 showed that the nanoporous structure of silica after functionalization with diphenylcarbazide remains intact (Fig. 2). The TEM study also confirmed that the nanopore structure of the SBA-15 remained intact after functionalization. As the image in Fig. 3 shows, the pores of SBA-15 with approximately 10 nm wide, bright spots, and the walls, dark spots, clearly are visible. Considering colloidal silica is not a porous material and has smaller surface area, lower efficiency, less capacity and preconcentration factor is expected in comparison with SBA-15.

The FT-IR spectra of SBA-15 and diphenylcarbazide functionalized SBA-15 (KBr pellets) was evaluated. The characteristic stretching vibration bands of diphenylcarbazide and organosilane (1652, 1548 and 2945 cm^{-1}, respectively) in the spectrum of the functionalized material confirmed the presence of diphenylcarbazide groups on the surface of the nanoporous silica. Furthermore,

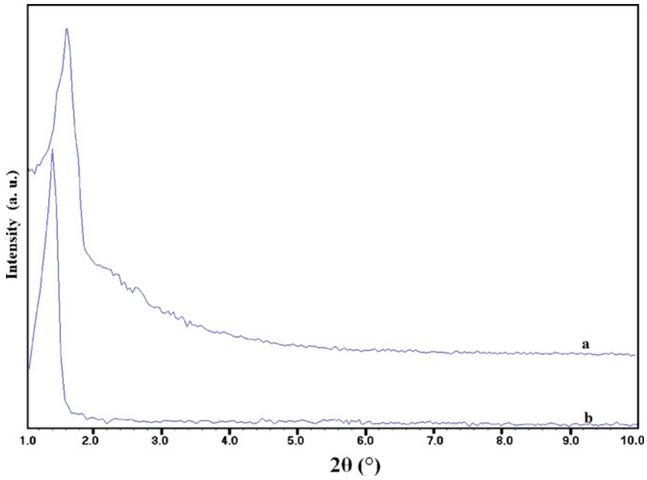

Fig. 2. The low-angle X-ray diffraction patterns of SBA-15 (a) and diphenylcarbazide-SBA-15 (b).

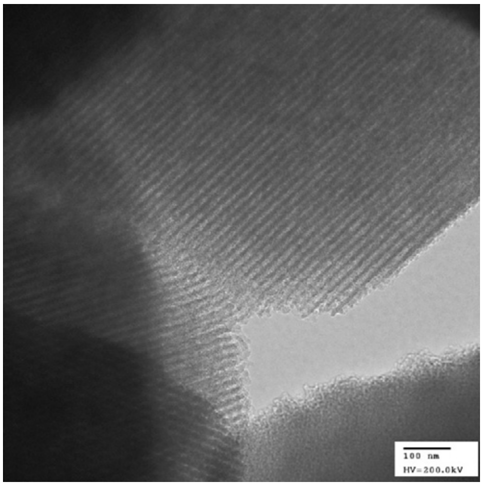

Fig. 3. TEM micrograph of diphenylcarbazide modified SBA-15.

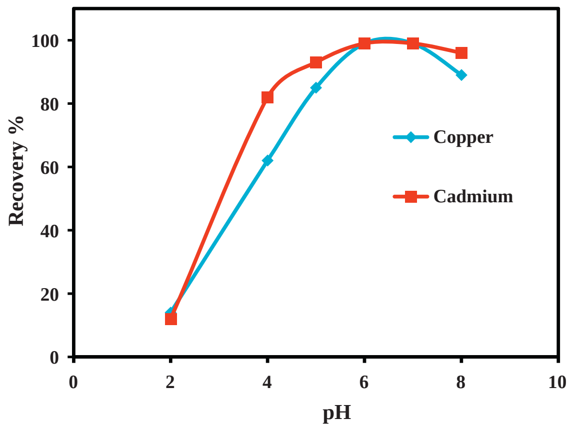

Fig. 4. Effect of pH of sample solutions on percent recovery of cadmium and copper ions by diphenylcarbazide-SBA-15. Conditions: sample concentration, 1 μg mL^{-1}; sample volume, 25 mL; eluent, 5 mL of HCl (2 mol L^{-1}); flow rate of eluent, 2 mL min^{-1}.

the Si—O—Si and Si—O—H stretching vibration bands of nanoporous silica appeared at 1038, 809 and 3000–3500 cm^{-1}, respectively.

3.2. Effect of pH

Among the tested variables, pH was found to be the most critical parameter for adsorption of metals on the nanoporous silica. To evaluate the effect of pH on the extraction efficiency, the pH of the 25 mL sample solutions containing 1 mg L^{-1} of cadmium and copper ions was adjusted to fit in the range of 2–8. The retained cadmium and copper ions were then eluted with 5 mL of HCl (2 mol L^{-1}). Cadmium and copper ions content in the eluent were determined by FAAS and the data graphed as a function of pH and are shown in Fig. 4. The quantitative recovery of DPC-SBA-15 was obtained in the pH of 6.0 for cadmium and copper ions. Lowering the pH value of the solution decreased the quantitative recovery of the sorbent due to the electrostatic repulsion of the protonated active sites on the sorbent with the positively charged cadmium and copper species. In consideration of hydrolysis, pH above 8.0 was not tested.

3.3. Effect of type, concentration and volume of eluent

In order to desorb cadmium and copper ions from DPC-functionalized nanoporous silica, a series of selected eluent solutions, such as HNO_3, HCl and CH_3COOH at different concentrations were used. As shown in Table 1, it was eventually found that HCl (2 mol L^{-1}) provided effective elution of cadmium and copper ions from DPC-functionalized nanoporous silica. The effect of eluent volume on the recovery of cadmium and copper ions was also studied. As Table 1 shows, quantitative recovery could be obtained with 5 mL of HCl (2 mol L^{-1}). Therefore, volumes of 5 mL of eluent for desorption of the cadmium and copper ions were used in the remaining experiments.

3.4. Effect of sample and eluent flow rate

To optimize the sample flow rate, 25 mL solutions of 1 mg L^{-1} cadmium and copper ions were adjusted to pH of 6.0, and then passed through the column at flow rates in the range of 1–16 mL min^{-1} with a peristaltic pump. The column was then washed with 10 mL of water to remove free metal ions. Subsequently, 5 mL of eluent was passed to desorb the coordinated cadmium and copper ions from DPC-functionalized SBA-15. The results in Table 2 demonstrated that sample flow rate variation in the ranges of 1–10 and 1–4 mL min^{-1} had no effect on the recovery of cadmium and copper ions on DPC-SBA-15 and DPC-SiO_2, respectively. On the other hand, quantitative recoveries for cadmium and copper ions were obtained at a flow rate range of 0.5–2.0 and 1.0–3.0 mL min^{-1} for DPC-SBA-15 and DPC-SiO_2 with HCl (2 mol L^{-1}).

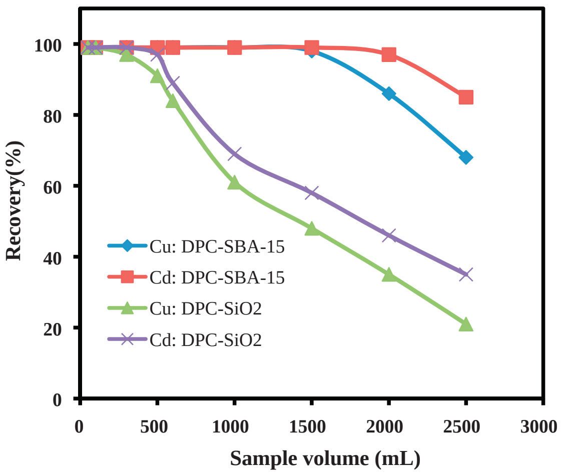

Fig. 5. Effect of sample solution volume on extraction recovery of cadmium and copper ions on DPC-SBA-15 and DPC-SiO_2. Condition: 0.1 mg of cadmium and copper ions; solution's pH 6; eluent, 5 mL of HCl (2 mol L^{-1}); flow rate of eluent, 2 mL min^{-1}.

3.5. Effect of the volume of sample solutions

A higher preconcentration factor can be obtained by increasing the sample to eluent volume ratio by either decreasing the eluent volume and/or increasing the sample volume. Therefore, the maximum volume of sample solution was investigated by increasing the volume of metal ion solution with a constant amount of ions (0.01 mg of cadmium and copper ions). Samples solution volumes of 50, 100, 300, 500, 600, 1000, 1500, 2000, and 2500 mL containing cadmium and copper ions were passed through the column. These results (Fig. 5) demonstrated that the dilution effect was not significant for sample volumes 2000 and 500 mL for cadmium on DPC-SBA-15 and DPC-SiO_2 and 1500 and 300 mL for copper ions on DPC-SBA-15 and DPC-SiO_2 respectively. It was found that the simultaneous quantitative recovery of cadmium and copper ions on DPC-SBA-15 and DPC-SiO_2 could be obtained for sample volume up to 1500 and 300 mL, respectively. As the elution volume was 5 mL for cadmium or copper ions, a pre-concentration factor of 294 for cadmium and 291 for copper was obtained by assuming a recovery greater than 97% and 98% for cadmium and copper ions, respectively. The preconcentration factor for simulate determination of cadmium or copper ions on DPC-SiO_2 is 58.2 with recovery greater than 97%.

3.6. Effect of foreign ions

To investigate the effect of various cations found in natural samples, elements representing alkaline, alkaline earth, and transition metals were added to 100 mL of solution containing 0.01 mg cadmium and 0.01 mg copper ions. The degree of tolerance for some alkaline, alkaline earth and transition metal ions are presented in Table 3. From the tolerance data, it can be seen that the foreign ions have no significant effects on preconcentration of cadmium and copper ions at pH 6.0.

Table 1
Effect of type, concentration and volume of eluent on extraction efficiency.

Eluent	Concentration (mol L^{-1})	Volume (mL)	R^a% ± S^b	
			Cd	Cu
HNO_3	3	10	84.0 ± 1.0	87.0 ± 1.5
HCl:CH_3COOH	2:1	10	82.0 ± 1.5	78.0 ± 2.0
HNO_3:CH_3COOH	2:1	10	73.0 ± 1.0	68.0 ± 3.0
CH_3COOH	3	10	69.0 ± 1.0	65.0 ± 2.0
HCl	3	10	99.0 ± 1.0	99.0 ± 1.0
HCl	2.5	10	99.0 ± 1.0	99.0 ± 1.0
HCl	2	10	99.0 ± 1.0	99.0 ± 1.0
HCl	1.5	10	87.0 ± 1.5	82.0 ± 1.0
HCl	1	10	68.0 ± 1.5	65.0 ± 1.5
HCl	0.5	10	57.0±.1.5	54.0 ± 1.0
HCl	2	7.5	99.0 ± 2.0	99.0 ± 1.0
HCl	2	5	99.0 ± 1.0	99.0 ± 1.0
HC	2	2.5	78.0 ± 2.0	64.0 ± 3.0

[a] Recovery.
[b] Standard deviation.

Table 2
Effect of sample and eluent flow rate.

Sample flow rate (mL min^{-1})		R^a% ± S^b		Eluent flow rate (mL min^{-1})	R^a% ± S^b	
		Cd	Cu		Cd	Cu
1	DPC-SBA-15	99.0 ± 1.5	99.0 ± 1.0	0.5	99.0 ± 2.0	99.0 ± 1.0
	DPC-SiO_2	99.0 ± 1.0	99.0 ± 1.0		99.0 ± 1.5	99.0 ± 1.0
2	DPC-SBA-15	99.0 ± 1.0	99.0 ± 1.0	1	99.0 ± 1.0	99.0 ± 1.0
	DPC-SiO_2	99.0 ± 1.0	99.0 ± 2.0		99.0 ± 1.0	99.0 ± 2.0
4	DPC-SBA-15	99.0 ± 1.0	99.0 ± 1.0	1.5	99.0 ± 1.5	99.0 ± 1.5
	DPC-SiO_2	99.0 ± 1.5	99.0 ± 1.0		99.0 ± 1.0	99.0 ± 2.0
6	DPC-SBA-15	99.0 ± 2.0	99.0 ± 1.5	2	99.0 ± 1.0	99.0 ± 2.0
	DPC-SiO_2	91.0 ± 2.0	93.0 ± 1.0		99.0 ± 1.0	99.0 ± 1.0
8	DPC-SBA-15	99.0 ± 1.0	99.0 ± 1.0	2.5	99.0 ± 1.0	92.0 ± 2.0
	DPC-SiO_2	–	–		99.0 ± 1.5	99.0 ± 1.0
10	DPC-SBA-15	99.0 ± 1.0	99.0 ± 1.0	3	87.0 ± 2.0	91.0 ± 3.0
	DPC-SiO_2	–	–		99.0 ± 1.0	99.0 ± 2.0
12	DPC-SBA-15	99.0 ± 1.0	91.0 ± 2.0	3.5	72.0 ± 3.0	82.0 ± 3.0
	DPC-SiO_2	–	–		98.0 ± 2.0	99.0 ± 1.0
14	DPC-SBA-15	87.0 ± 2.0	78.0 ± 3.0	4	54.0 ± 3.0	68.0 ± 4.0
	DPC-SiO_2	–	–		95.0 ± 1.0	97.0 ± 1.0

[a] Recovery.
[b] Standard deviation.

3.7. *Adsorption capacity*

The adsorption capacity of DPC-SBA-15 for cadmium and copper ions was studied by passing 500 mL portions of aqueous solutions containing 100 mg of cadmium and copper ions at optimal pH through the column. This was followed by determination of the effluent and retained metal ions using FAAS. The capacity of DPC-SBA-15, obtained for five replicate analyses, was found to be 198 ± 0.01 and 105 ± 0.03 mg g^{-1} of cadmium and copper ions, respectively.

3.8. *Analytical performance*

Under the optimized conditions, calibration curves were constructed for the determination of cadmium and copper ions, according to the general procedure. Linearity was maintained

Table 3
Influence of interfering ions.

Foreign ion	Tolerable concentration ratio X/Cd and Cu	R^a% ± S^b	
		Cu	Cd
K^+	10,000	99.0 ± 1.0	99.0 ± 2.0
Na^+	10,000	99.0 ± 2.0	99.0 ± 2.0
Cs^+	1000	99.0 ± 2.0	98.0 ± 2.0
Ca^{2+}	100	98.0 ± 2.0	97.0 ± 1.2
Mg^{2+}	100	98.0 ± 2.0	98.0 ± 1.0
Al^{+3}	100	98.0 ± 1.0	97.0 ± 1.0
Cr^{3+}	100	98.0 ± 1.0	98.0 ± 1.0
Pb^{2+}	100	95.0 ± 2.0	92.0 ± 1.0
Fe^{2+}	100	97.0 ± 2.0	98.0 ± 1.0
Ni^{2+}	100	96.0 ± 1.0	96.0 ± 1.0
Mn^{2+}	100	97.0 ± 1.0	96.0 ± 1.0

[a] Recovery.
[b] Standard deviation.

Table 4
Statistical and calibration parameters.

Analyte	Regression equation	r^2	LOD (ng mL^{-1})	DLR (ng mL^{-1})	PF	Recovery (%)	RSD (%)	Maximum sorption capacity (mg g^{-1})
Cadmium ion	$Y = 0.016X + 0.047$	0.998	0.15	1–100	100	97	3.4	198
Copper ion	$Y = 0.01X + 0.022$	0.997	0.45	1–150	100	98	3.8	105

Table 5
Comparison of analytical performance of DPC-functionalized nanoporous silica to DPC-immobilized silica adsorbents.

Adsorbent	Adsorption capacity		Sample flow rate		Sample volume	
	Cd (mg g^{-1})	Cu (mg g^{-1})	Cd (mL min^{-1})	Cu (mL min^{-1})	Cd (mL)	Cu (mL)
DPC-functionalized nanoporous silica	198	105	12	10	2000	1500
DPC-immobilized silica adsorbents	54	30	4	3	500	300

Table 6
Determination of cadmium and copper ions recovery in certified reference materials.

Sample	Element	Concentration (mg kg^{-1})		Relative error (%)
		Certified	Found	
Ore polymetallic gold Zidarovo-PMZrZ (206 BG 326)	Cu	0.51	0.494	−3.13
Soil (NCS DC 73323)	Cd	0.45	0.43	−4.44

Table 7
Analysis of cadmium in different real samples.

Sample	C_{added} (μg kg^{-1})	C_{found} (μg kg^{-1})	Recovery%	RSD%
Fish sample in Behad creek	–	4.2	–	
	10	14.4	101.5	3.8
Fish sample in Jafar creek	–	18.4	–	
	10	28.2	99.2	3.2
Sediment sample in Behad creek	–	19.5	–	
	10	29.8	101	3.4
Sediment sample in Jafar creek	–	42.4	–	
	10	51.8	98.8	4.2
Water sample	C_{added} (μg L^{-1})	C_{found} (μg L^{-1})	Recovery%	RSD%
Pure water	–	–	–	
	10	9.9	99	3.4
Tap water	–	–	–	
	10	10.03	100.3	3.6

1–100 ng mL^{-1} for cadmium and 1–150 ng mL^{-1} for copper in initial solution. The correlation of determination (r^2) was 0.998 for cadmium and 0.997 for copper ions. The limits of detection, defined as $C_{LOD} = 3Sb/m$, where Sb is the standard deviation of 10 replicate blank signals and m is the slope of the calibration curve after preconcentration, for a sample volume of 500 mL, were found to be 0.15 and 0.45 ng mL^{-1} for cadmium and copper ions, respectively. The relative standard deviation for 10 separate column experiments for the determination of 5.0 μg cadmium and copper ions in 100 mL water was 3.4 and 3.8%, respectively. The corresponding limit of detection (LOD), regression equation, dynamic linear range (DLR), correlation of determination (r^2), preconcentration factor (PF), recovery, and maximum sorption capacity were calculated under optimized conditions and summarized in Table 4.

Table 8
Analysis of copper in different real samples.

Sample	C_{added} (μg kg^{-1})	C_{found} (μg kg^{-1})	Recovery%	RSD%
Fish sample in Behad creek	–	54.2	–	
	10	64.5	100.4	2.6
Fish sample in Jafar creek	–	80.2	–	
	10	89.6	99.3	2.2
Sediment sample in Behad creek	–	328	–	
	50	378.8	100.2	3.6
Sediment sample in Jafar creek	–	862	–	
	50	909.5	99.7	3.4
Water sample	C_{added} (μg L^{-1})	C_{found} (μg L^{-1})	Recovery%	RSD%
Pure water	–	–	–	
	10	9.8	98	3.8
Tap water	–	10.1	–	
	10	20.2	100.4	2.8

3.9. Effect of nanopores on the analytical performance

To study the effect of pores on the analytical performance, the adsorption capacity, sample flow rate and sample volume of nanoporous was compared with diphenylcarbazide modified colloidal silica. As results show in Tables 2 and 5 and Fig. 5, the pores caused this sorbent to become a valuable material for separation and preconcentration of metal ions.

3.10. Validation of the method

The concentration of cadmium and copper ions that obtained by DPC-SBA-15 was compared with the standard materials. For this reason, the concentration of cadmium and copper ions was determined at optimum conditions in standard reference material (Soil (NCS DC 73323)) and ore polymetallic gold Zidarovo-PMZrZ (206 BG 326). As it can be seen in Table 6, good correlation was achieved between estimated content by present method and reference materials. Therefore, DPC-SBA-15 can be used as a reliable solid-phase for extraction and determination of cadmium and copper ions in environmental samples.

3.11. Determination of cadmium and copper in real samples

Since natural samples have complex matrices, non-specific background absorption was caused by interfering species of the sample matrix. To reduce this undesirable effect, nanoporous silica was applied for selective sorbent for cadmium and copper ions extraction in pH = 6. Tables 7 and 8 show the cadmium and copper ions recovery in the seawater, fish and sediment samples.

4. Conclusion

A simple, fast, reproducible and selective solid phase extraction procedure, based on modified nanoporous silica (DPC-SBA-15), for the determination of cadmium and copper ions have been developed. In comparison with other solid phases, DPC-SBA-15 has the advantages of high-capacity factor, low limit of detection and high enrichment factor. Due to the relatively high preconcentration factor, trace metal ions at ng mL^{-1} level in high-volume samples can be determined and separated by functionalized nanoporous silica.

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