Journal of Hazardous Materials 169 (2009) 203–209

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Preparation of p-tert[(dimethylamino)methyl]-calix[4]arene functionalized aminopropylpolysiloxane resin for selective solid-phase extraction and preconcentration of metal ions

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A R T I C L E I N F O

Article history:
Received 28 November 2008
Received in revised form 3 March 2009
Accepted 19 March 2009
Available online 27 March 2009

Keywords:
p-Tert[(dimethylamino)methyl]-1,3-bisglyciyl-calix[4]arene
Aminopropylpolysiloxane
Solid-phase extraction
Heavy metal
Inductively coupled plasma optical emission spectrometry

A B S T R A C T

A new p-tert-[(dimethylamino)methyl]-1,3-bisglyciyl-calix[4]arene functionalized aminopropylpolysiloxane resin (APPS-CA) has been prepared and investigated for selective solid-phase extraction (SPE) of trace Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) prior to their determination by inductively coupled plasma optical emission spectrometry (ICP-OES). The characterization of the surface modification was performed on the basis of FT-IR spectroscopy, elemental analysis and thermal gravimetric analysis. The separation/preconcentration conditions of analytes were investigated, including effect of pH, the shaking time, the sample flow rate and volume, the elution condition, the interfering ions and stability test. At pH 4.0, the maximum adsorption capacity of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) were 47.2, 34.3, 52.8, 29.8 and 36.4 mg g^{-1}, respectively. The adsorbed metal ions were quantitatively eluted by 2.0 mL of 0.5 mol L^{-1} HCl. Common coexisting ions did not interfere with the separation. According to the definition of International Union of Pure and Applied Chemistry, the detection limits (3σ) of this method were found to be 0.58, 0.33, 0.47, 0.61 and 0.14 ng mL^{-1} for Cr (III), Cu (II), Ni (II), Co (II) and Zn (II), respectively. The relative standard deviation under optimum conditions is less than 4.0%. The application of this new adsorbent to preconcentration trace Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) of two water samples gave high accurate and precise results.

1. Introduction

The majority of industrial effluents may carry potentially toxic heavy metal ions [1,2]. Because of the toxic and harmful effect of heavy metal ions to aquatic life, human being and the environment, heavy metal ions removal from water or various industrial contaminations have been the subject of extensive technological research and recovering processes [3]. There are many processes available for the removal of heavy metal ions by conventional treatment technologies including chemical precipitation, ion exchange, reverse osmosis and adsorption, etc. [4–8]. Among all the treatments proposed, adsorption using adsorbents is one of the most applied methods for the treatment of aqueous streams contaminated with heavy metals. It is well known that solid-phase extraction (SPE) using adsorbents is one of the most efficient and popular methods for the removal of toxic metal ions from wastewater, especially, for low metal ion concentration due to the method is simple, higher enrichment factor, absence of emulsion, safety with respect of reagents, relatively low cost, flexibility and ease of automation [5–11].

The effective and economic methods are based on adsorption process, and an efficient solid phase should consist of a stable and insoluble porous matrix having suitable active groups that interact with heavy metal ions [12,13]. Calixarenes, which can be prepared by the ring-closing condensation of p-tert-butyl phenol and formaldehyde under alkaline conditions, are such cyclic oligomers composed of phenol units and are very well known as attractive and excellent ionophores because they provide a unique three-dimensional structure with almost unlimited derivatization possibilities [14,15]. Accordingly, calixarenes and its derivatives exhibit outstanding complex ability toward ions and organic molecules [16,17]. There are several recent reports for the applications of functionalized calixarenes or its derivatives for enrichment of metal ions, for instance, calix[4]arene tetraethyl ester and calix[6]arene hexaethyl ester were incorporated onto the surface of silica particles after hydrosilylation of the p-allyl calixarenes and were used as selective adsorbents for Na (I) ions [18,19]. Chelating calix[4]arene hydroxamates supported onto silica particles have been studied for their uptake of different transition metal ions [20]. A chelating resin has been synthesized by linking calix[4]arene semicarbazone derivatives on chloromethylated

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doi:10.1016/j.jhazmat.2009.03.084

polystyrene divinylbenzene copolymer for the separation of La (III), Ce (III), Th (IV) and U (VI) [21]. Amino/nitrile calix[4]arenas functionalized polymeric backbone has been studied for extraction of Cr (VI) [22].

On the other hand, polysiloxane resins can be easily prepared by a sol–gel technology based on cohydrolysis and polycondensation of functional organosilicone monomer with alkoxysilane, or sol–gel microparticles modified by organofunctional groups [23], exhibit nonswelling property and good diffusivity of solutes, excellent mechanical stability, and can be recovered and reused easily. For this reason, polysiloxane resins modified by organofunctional groups have been widely used as molecular adsorbents in analytical chemistry and separation science [24,25].

Accordingly, it is fascinating to study what happen when these two kinds of molecules are linked up. For this reason, a novel adsorbent of APPS-CA was synthesized by the ring-opening polycondensation of p-tert[(dimethylamino)methyl]-1,3-bisglyciyl-calix[4]arene (CA) and aminopropylpolysiloxane resin (APPS) that were prepared by the cohydrolysis and polycondensation of 3-aminopropyltriethoxysilane and tetraethylorthosilicate through a Shiff base bond formation [23]. The new adsorbent has a high adsorption capacity for the solid-phase extraction of trace Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) in the water samples by ICP-OES. Parameters that can affect the adsorption and elution efficiency of the heavy metal ions were studied in batch and column modes.

2. Experimental

2.1. Reagents and solutions

Unless otherwise stated, all reagents used were of analytical grade and all solutions were prepared by double distilled water. According to Zhai et al. [26], standard labware and glassware were used throughout and repeatedly cleaned with HNO_3 and rinsed with double distilled water.

Stock solutions ($1\,mg\,mL^{-1}$) of the selected heavy metals ions (Cr (III), Cu (II), Ni (II), Co (II) and Zn (II)) were prepared by dissolving a spectral pure grade and appropriate amounts of nitrate salts in 1.0% HNO_3 and further diluted daily prior to use. 1-Chloro-2,3-epoxypropane was purified by treatment with a molecular sieve and distilled before use, supplied by Resin Factory of the Hunan Yueyang Chemical Industry Co. (China). 3-Aminopropyltriethoxysilane and tetraethylorthosilicate were purchased from Chemical Company of Wuhan University (China). p-Tert-[(dimethylamino)methyl]-calix[4]arene was prepared according to known previous procedure [27,28]. The standard reference material (GBW 08301, river sediment) was provided by the National Research Center for Certified Reference Materials (Beijing, China). The other reagents were supplied by Shanghai Chemical Reagents Co. (Shanghai, China).

2.2. Instruments and apparatus

All metal ions were determined by an IRIS advantage ER/S inductively coupled plasma optical emission spectrometer (ICP-OES), Thermo Jarrel Ash (Franklin, MA, USA), the instrumental parameters were recommended by the manufacture. The pH value was controlled by a pHs-10C digital pH meter (Xiaoshan Instrument Factory, China). Fourier transform infrared spectra (FT-IR) in KBr were recorded on a Nicolet NEXUS 670 FT-IR apparatus (USA). A VarioEL element analyzer, Elementar Analysensysteme (Hanau, Germany), was used for elemental analysis. Thermogravimetric analysis (TG) was carried out on a Pyris Diamond TGA (Perkin-Elmer, USA). A 0.45 μm membrane (Jinteng Instrument Factory, Tianjin, China) was used to filter samples. A self-made glass column (20 cm × 4 mm i.d.) was used in column SPE procedure. The flow rate of solution through the columns was controlled with a model YL-110 peristaltic pump (The General Research Academe of Colored Metal, Beijing, China).

2.3. Sample preparation

Yellow River water was collected from Yellow River, Lanzhou, China. The water sample was firstly acidified (pH about 1.0), filtered through a 0.45 μm membrane, and then stored in pre-cleaned polyethylene bottles prior to use [29]. Tap water samples taken from our research laboratory (Lanzhou University, Lanzhou, China) were analyzed without pretreatment. The pH value was adjusted to 2.0 with $0.1\,mol\,L^{-1}$ HCl prior to use.

The certified reference material (GBW 08301, river sediment) was digested according to the literature [30]. A portion (50–100 mg) of the certified sediment sample was accurately weighed into a 50 mL beaker and 15.0 mL aqua regia was added to the sample. The beaker was covered with a watch glass and the mixture was evaporated on a hot plate at 95 °C almost to dryness. Then 8.0 mL of aqua regia was added to the residue and evaporated to dryness again. After cooling, resulting mixture was filtered through a 0.45 μm membrane. The sample was diluted to 10.0 mL with double distilled water and preconcentrated using the new adsorbent.

2.4. Synthesis

The reaction route and structure of compounds employed in this work are shown in Fig. 1.

2.4.1. Synthesis of CA

CA was prepared according to procedures reported in the literature [31] by the reaction of p-tert[(dimethylamino)methyl]-calix[4]arene with 1-chloro-2,3-epoxypropane in dry toluene and in the presence of anhydrous K_2CO_3 as the base. The mixture was refluxed for 6 h. After filtration and evaporation of solvent under reduced pressure, the residue was washed with toluene and water three times respectively and then dried under vacuum at 80 °C for 8 h.

2.4.2. Synthesis of APPS

6.6 g 3-aminopropyltriethoxysilane, 6.3 g tetraethylorthosilicate, 30 mL toluene and 1.2 mL of $1.0\,mol\,L^{-1}$ K_2CO_3 were added to a 100 mL three-neck round flask equipped with a magnetic stirrer. The mixture was stirred for 5 h at room temperature, and then refluxed at 100 °C for 3 h under nitrogen atmosphere. After 2.0 mL distilled water was added to the flask, the reactant was stirred continuously at reflux temperature for 3 h. The increase of the reactant viscosity and the formation of resin were observed, and the sample turned into a light yellow solid after cooling. The solid was filtrated and washed successively with acetone, distilled water, acetone, toluene, and acetone. Subsequently, the product was dried at 80 °C for 8 h.

2.4.3. Synthesis of APPS-CA

APPS-CA was prepared by the ring-opening polycondensation of the epoxy groups of CA and the amino groups of APPS. 5.6 g CA, 2.7 g APPS and 25.0 mL anhydrous acetonitrile were added to a 50 mL three-neck round flask equipped with a magnetic stirrer. The mixture was stirred for 48 h at 50 °C under nitrogen atmosphere. The product was filtrated and washed successively with toluene, acetone, distilled water, and acetone. Subsequently, the product was extracted with toluene for 24 h under nitrogen atmosphere, washed by acetone, and dried at 110 °C for 8 h. The structure of the APPS-CA obtained is illustrated in Fig. 1.

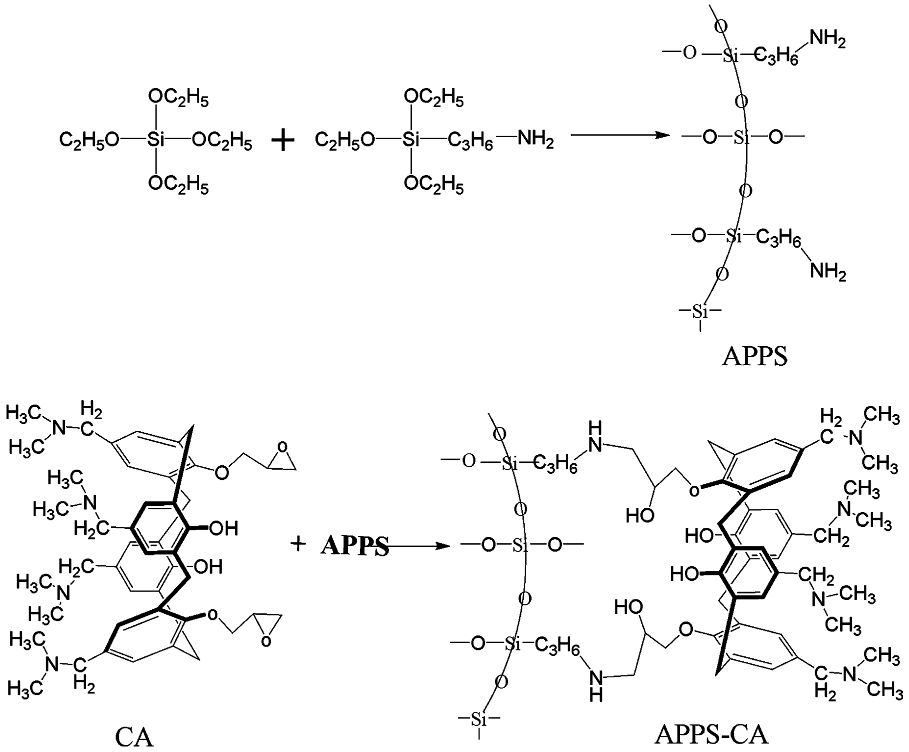

Fig. 1. Synthesis route of APPS and APPS-CA.

2.5. *Procedure*

2.5.1. *Batch procedure*

A series of standard or sample solutions containing Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) with known concentration was transferred into a 25 mL beaker, and the pH was adjusted to the desired value with ammonia or diluted HNO_3. Then the volume was adjusted to 10.0 mL with double distilled water. And 30 mg of APPS-CA was added. The mixture was shaken vigorously for 30 min at 25 °C to facilitate adsorption of the metal ions onto APPS-CA. After centrifuged, the concentrations of metal ions remaining in aqueous phase were determined by ICP-OES.

2.5.2. *Column SPE procedure*

A total of 50 mg of APPS-CA was packed in a glass column (20 cm × 4 mm i.d.) plugged with a small portion of glass wool at both ends in order to prevent loss of the particles during solution loading. Before using, the column was treated successively with 1.0 mol L^{-1} HCl and washed with double distilled water until free from acid. A suitable aliquot of standard or sample solutions containing Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) were passed through the column after adjusting their pH to 4.0, at a flow rate of 4.5 mL min^{-1} controlled with a peristaltic pump. The bound metal ions were stripped off from the column with 0.5 mol L^{-1} HCl and the analytes in the elution was determined by ICP-OES.

3. Results and discussion

3.1. *Characterization of APPS-CA*

FT-IR spectra were taken by using KBr to observe the functional groups of CA, APPS and APPS-CA and the spectra were shown in Fig. 2.

The data of main vibration adsorption bands [32,33] shown that the characteristic adsorption bands of the epoxy group of CA appear at 1293 and 942 cm^{-1}, and the bands disappear in the IR spectrum of APPS-CA. The bands of C–O and C–N stretching vibration (1197 and 1591 cm^{-1}) of CA are strong. The bands of Si–O–Si stretching vibration (about 1100 cm^{-1}) of APPS and APPS-CA are strong and broad, whereas the intensity of bands of Si–C stretching vibration (about 800 cm^{-1}) is weak. The bands of stretching vibration of C–O and Si–O of APPS-CA overlapped and shifted to a higher wave number (1126 cm^{-1}) than that of APPS (1090 cm^{-1}). In the IR spectrum of APPS, the adsorption bands of C–H stretching vibrations and C=C stretching vibrations of CA aromatic ring (3039 and 1591 cm^{-1}) are not characteristic, which can be attributed to the overlapping with the bands of O–H stretching vibration (3290 cm^{-1}) and bending vibration (1654 cm^{-1}) of NH_2 groups, respectively. Fig. 2 also shown that bending vibration bands of CH_2 and CH_3 groups are presented at about 1460 cm^{-1} for all samples determined.

Elemental analysis results of APPS and APPS-CA were given in Table 1, which confirmed that the modification of APPS by

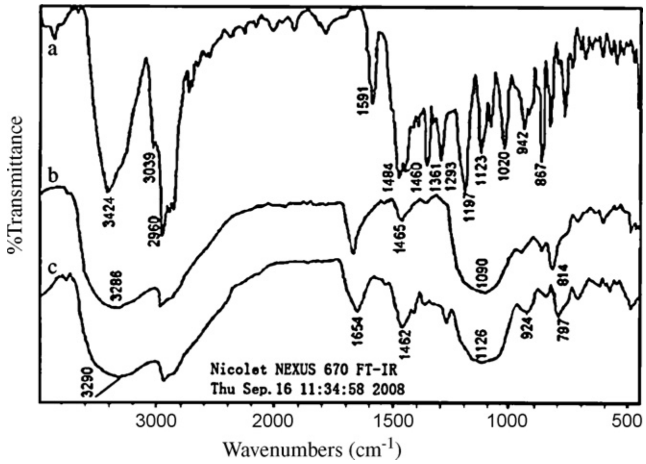

Fig. 2. IR spectra of (a) CA, (b) APPS and (c) APPS-CA.

Table 1
Results of elemental analysis for APPA and APPS-CA.

	%C	%H	%N	Bonded amount (mmol g^{-1})
APPS	19.74	5.59	7.71	–
APPS-CA	30.58	3.71	4.12	0.49

calix[4]arene derivative units was accomplished. It can be calculated that 1 g APPS-CA containing 0.49 mmol calix[4]arene derivative units according to the C and N content.

Thermogravimetry (TG) and the differential thermogravimetry (DTG) curves of CA and APPS-CA were presented in Fig. 3(a) and (b), respectively. As seen in Fig. 3, the starting temperature of weight loss for CA occurred at 378 °C, which is lower than APPS-CA (399 °C). The DTG curves indicated that the weight loss of APPS-CA is step by step from 399 to 700 °C, and the rate of the fastest weight loss for APPS-CA is much lower than CA. At 697 °C the weight losses of CA and APPS-CA are 62.3% and 19.1%, respectively. All of the results confirmed that bisglycidyl calix[4]arene derivative units are chemically bonded to polysiloxane resins and are relatively thermally stable. TG curves also shown that the weight is increased with increasing temperature under nitrogen atmosphere (200 mL min^{-1}) until 317 and 217 °C for CA and APPS-CA, respectively. The weight increased by 6.0% at 317 °C for CA and 11.0% at 217 °C for APPS-CA, respectively. The value of increase in weight is lower than that reported in the literature [23]. It is clear that the adsorption ability of the polysiloxane resins toward nitrogen is related to both the network structure and the amount of calix[4]arene derivative units loaded in the resins under an elevated temperature.

The above experimental results can demonstrate the APPS was successfully modified by CA.

3.2. Effect of pH

pH is one of the most important factors affecting the adsorption process. According to the batch procedure, the effect of pH on adsorption of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) was investigated in the pH range of 1–7 and then analyzed by ICP-OES. The adsorption experiments were in triplicates. It can be seen from Fig. 4 that the adsorption quantity of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) enhanced with increasing of pH value. The optimum pH values for maximum Cr (III) and Ni (II) have occurred at pH ≥ 3, Cu (II), Co (II) and Zn (II) at pH ≥ 4. In purpose of understanding the adsorption mechanism, the pH of the solutions was measured at the end of experiments. We found the pH value of the solutions changed from 3.0 to 2.24 for Cr (III) and 2.19 for Ni (II), and from 4.0 to 3.11 for Cu (II), 3.20 for Co (II) and 3.14 for Zn (II), respectively. These results indicated that the mechanism probably involves the competitive adsorption of H$^+$ with metal ions for the exchange site in the system [34,35]. In order to ensure quantitative adsorption and avoid precipitation at higher pH values, pH 4.0 was chosen as the optimum pH for further studies.

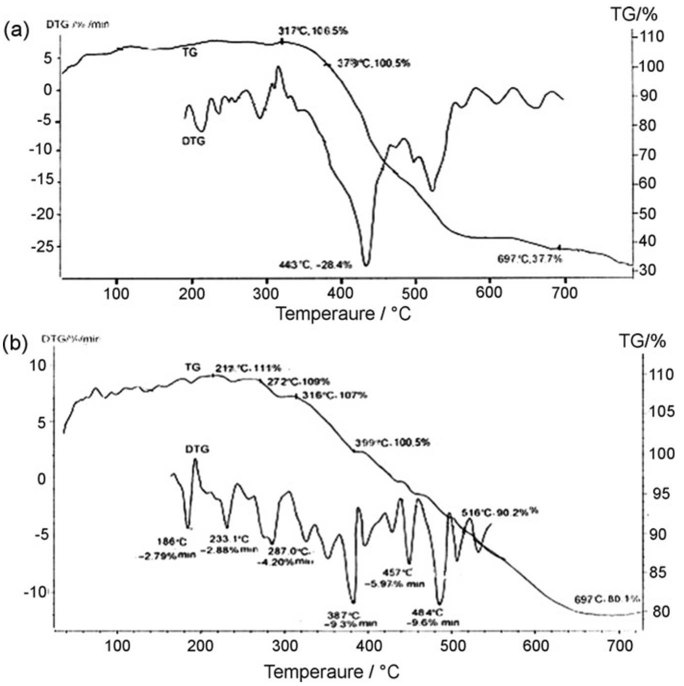

Fig. 3. TG and DTG curves of (a) CA and (b) APPS-CA.

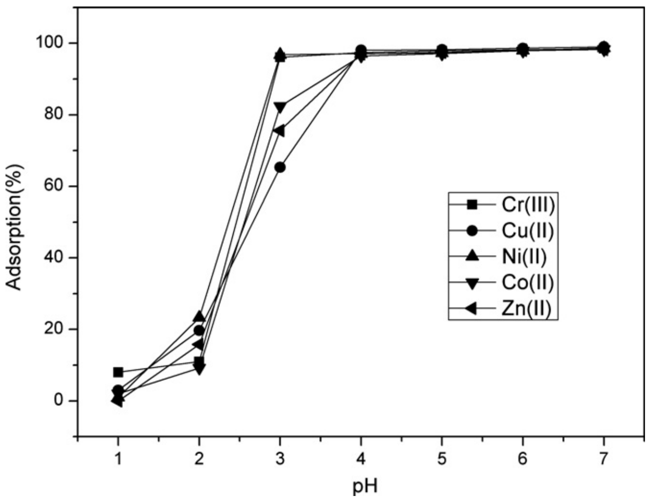

Fig. 4. Effect of pH on adsorption of 10.0 μg mL^{-1} Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) on APPS-CA. Other conditions: shaking time 30 min; temperature 25 °C.

3.3. Effect of shaking time

The effect of shaking time is another important factor in evaluating the affinity of APPS-CA to ions. To determine the rate of loading of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) on the APPS-CA, the recommended batch procedure was carried out. The studied time varied from 5 to 35 min and the results are shown in Fig. 5. The shaking

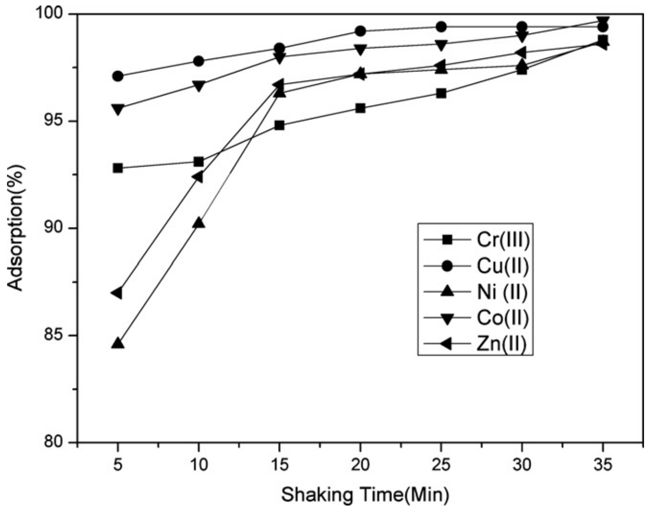

Fig. 5. Effect of shaking time of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) on APPS-CA. Other conditions: pH 4.0; temperature 25 °C.

Table 2
Elution recovery (%) for Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) adsorbed on APPS-CA.

	Eluent volume (mL)					
	1	2	3	4	5	6
Recovery[a] (%)						
Cr(III)	84.7 ± 2.4	96.6 ± 2.1	98.4 ± 3.4	100.9 ± 1.3	99.9 ± 2.6	101.4 ± 4.4
Cu(II)	100.2 ± 1.8	101.4 ± 3.7	100.7 ± 5.2	100.1 ± 3.0	101.5 ± 2.1	100.6 ± 2.7
Ni(II)	86.5 ± 1.3	96.6 ± 2.5	97.6 ± 2.2	99.3 ± 1.7	100.0 ± 1.7	100.3 ± 2.3
Co(II)	94.8 ± 3.2	100.1 ± 2.0	100.6 ± 2.6	101.5 ± 2.5	103.8 ± 1.3	100.8 ± 3.5
Zn(II)	97.5 ± 2.7	99.2 ± 1.6	100.0 ± 1.4	102.7 ± 3.8	104.4 ± 2.5	101.5 ± 3.1

0.5 mol L^{-1} HCl was used to select eluted volume.

[a] $\bar{X} \pm S$ $(n = 3)$. $\bar{X}$ value for three determinations, S standard deviation.

time of 10 min for Cu (II) and Co (II), 15 min for Zn (II) and Ni (II), and 20 min for Cr (III) were found to be sufficient to saturation at pH 4.0. The results indicated that APPS-CA has rapid adsorption kinetics. Hence, 20 min of stirring was enough to reach maximum values of simultaneous separation of all the metals. Therefore, it is suitable for application in flow system or using in the preconcentration of trace heavy metal ions.

3.4. *Effect of flow rate*

In a SPE system, the flow rate of solution through the packed bed column is a very important parameter for controlling the time of adsorption and analysis. Using the column procedure, the effect of flow rate on adsorption of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) were studied under optimum condition by passing 50 mL of standard solution through the column with a peristaltic pump. The result in Fig. 6 shown that the flow rate had a strong influence on the adsorption of Cu (II), Co (II) and Zn (II). The adsorption of Cu (II), Co (II) and Zn (II) decreased with increasing flow rate, but the adsorption values of Cr (III) and Ni (II) were not that much affected by flow rate. Quantitative recoveries of all target metal ions were obtained with 4.0–5.0 mL min^{-1}. Above 5.0 mL min^{-1}, the recovery of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) of less than 95% and flow rates of less than 4.0 mL min^{-1} were not employed to avoid the long extraction time. Thus, a flow rate of 4.5 mL min^{-1} was selected for column procedure.

3.5. *Adsorption capacity*

The capacity of the adsorbent is an important factor because it determines how much adsorbent is required to quantitatively remove a specific amount of metal ions from the solutions [36]. The adsorption capacity was tested following the batch procedure. 30 mg of APPS-CA was equilibrated with 50 mL of various concentrations of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) for 1 h, respectively. In order to reach the "saturation", the initial concentrations of metal ions were increased until the adsorption capacity values were obtained. The equilibrium concentration of ions in the aqueous phase was determined by ICP-OES.

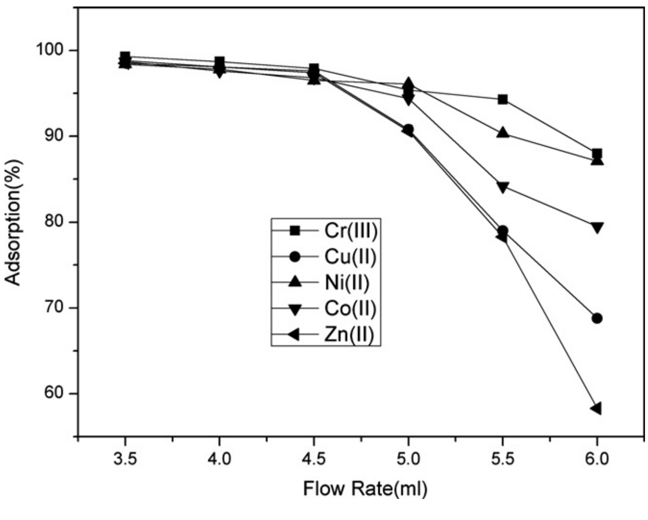

Fig. 6. Effect of solution flow rates on APPS-CA of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II). Other conditions: 50 mg of APPS-CA; volume 50 mL; pH 4.0; temperature 25 °C.

The maximum adsorption capacity has been found to be 47.2, 34.3, 52.8, 29.8 and 36.4 mg g^{-1} for Cr (III), Cu (II), Ni (II), Co (II) and Zn (II), respectively. The results shown that adsorption capacity of various heavy metal ions probably differ due to their size, degree of hydration and the value of their binding constant with the adsorbent.

In order to see the role of calix[4]arene units in modified polysiloxane resins, we also did the experiment of solid-phase extraction of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) using APPS. The maximum adsorption capacity of APPS has been found to be 4.4, 5.6, 5.8, 4.9 and 6.1 mg g^{-1} for Cr III), Cu (II), Ni (II), Co (II) and Zn (II), respectively, which implies that the adsorption capacity of APPS-CA is much higher than APPS. The results indicated that CA are successfully bonded to APPS, the higher adsorption capacity of APPS-CA can be attributed to the binding abilities of the calix[4]arenes derivative units which is related to the macrocycle ring sizes, their conformations and the nature of the functional groups [37].

3.6. *Effect of coexisting ions on the adsorption of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) on APPS-CA*

The effect of commonly occurring ions present in real samples on the adsorption of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) have been studied using the batch procedure. The tolerance limits of these ions are shown that in excess of 2000 μg mL^{-1} of K (I), Na (I), NO_3^-, Cl^-, NH_4^+; 500 μg mL^{-1} of Ca (II), Mg (II), SO_4^{2-}; 50 μg mL^{-1} of Cd (II), Mn (II) and 20 μg mL^{-1} of Fe (III) ions did not affect the separation processes. The results shown that high concentrations of the ions tested did not interfere with the separation and determination of the analytes. This may be due to the low adsorption capacity or rates for interfering ions.

3.7. *Maximum sample volume, enrichment factor and elution*

The enrichment factor was studied by the recommended column procedure using increasing volume of investigated heavy metal ions solutions while keeping the total amount of the ions loaded constant to 10.0 μg. The maximum sample volume can be up to 250 mL with 95% recovery.

In this work, the elution condition was studied in the column procedure using various concentrations and volumes of HCl for desorption of retained Cr (III), Cu (II), Ni (II), Co (II) and Zn (II). As shown in Table 2, 1.0 mL of 0.5 mol L^{-1} HCl was sufficient for 95% recovery for Cu (II) and Zn (II) and 2.0 mL of 0.5 mol L^{-1} HCl was sufficient

Table 3
Analysis results for the determination of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) in standard reference material (GBW 08301 river sediment).

Analyte	Found by present method[a] (μg g^{-1})	Certified value (μg g^{-1})
Cr(III)	87.8 ± 4.7	90.0 ± 8.0
Cu(II)	52.3 ± 4.3	53.0 ± 6.0
Ni(II)	30.9 ± 2.4	32.0[b]
Co(II)	66.5 ± 3.9	69.0 ± 4.0
Zn(II)	248.3 ± 5.6	251.0[b]

[a] $\bar{X} \pm S$ ($n = 8$). $\bar{X}$ value for eight determinations, S standard deviation.
[b] Reference value.

for 95% recovery for Cr (III), Ni (II) and Co (II). Quantitative recoveries of all metal ions were obtained with 2.0 mL of 0.5 mol L^{-1} HCl. Therefore, the high enrichment factor of 125 was obtained.

3.8. APPS-CA stability tests

To evaluate APPS-CA stability, several loading and elution batch operations were carried out. A 100 mg amount of APPS-CA was stirred with 100 mL of metal solution containing 1.0 mg mL^{-1} of metal concentration for 1 h at room temperature. The APPS-CA was filtered, washed with double distilled water and stripped for metal ions by shaking with 10 mL of 0.5 mol L^{-1} HCl for 1 h. 2–3% decrease in efficiency up to 10–12 repeated cycles may due to hydrolysis of APPS-CA treated with acids, which shown APPS-CA has good stability.

Table 4
Analytical results of natural water samples.

Ions	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
Yellow River water			
Cr(III)	0	3.29 ± 0.14	–
	5	8.17 ± 0.12	97.6
	10	13.10 ± 0.11	98.1
Cu(II)	0	55.77 ± 0.50	–
	5	60.59 ± 0.51	96.4
	10	65.65 ± 0.55	98.8
Ni(II)	0	3.84 ± 0.12	–
	5	8.78 ± 0.10	98.8
	10	13.75 ± 0.13	99.1
Co(II)	0	3.84 ± 0.12	–
	5	8.78 ± 0.10	98.0
	10	13.75 ± 0.13	100.4
Zn(II)	0	11.20 ± 0.45	–
	5	9.95 ± 0.09	101.0
	10	14.88 ± 0.19	99.8
Tap water			
Cr (III)	0	1.98 ± 0.10	–
	5	6.81 ± 0.10	96.6
	10	11.85 ± 0.11	98.7
Cu(II)	0	1.20 ± 0.11	–
	5	6.04 ± 0.07	96.8
	10	11.15 ± 0.15	99.5
Ni(II)	0	0.59 ± 0.09	–
	5	5.48 ± 0.13	97.8
	10	10.51 ± 0.19	99.2
Co(II)	0	0.43 ± 0.10	–
	5	5.30 ± 0.10	97.4
	10	10.46 ± 0.13	100.3
Zn(II)	0	2.25 ± 0.16	–
	5	7.10 ± 0.12	97.0
	10	12.14 ± 0.16	98.9

3.9. Accuracy and precision of the method

Under the selected conditions, eight portions of mixed standard solutions were enriched and analyzed simultaneously following the general procedure. In accordance with the definition of IUPAC, the detection limit of the method was calculated based on three times the standard deviation of eight runs of the blank solution. The detection limits (3σ) were found to be 0.58, 0.33, 0.47, 0.61 and 0.14 ng mL^{-1} for Cr (III), Cu (II), Ni (II), Co (II) and Zn (II), respectively (C = 50 ng mL^{-1}). The precision of the method (R.S.D.) of the eight replicate determinations was low than 4.0% (Cr (III): 2.7%, Cu (II): 3.1%, Ni (II): 2.2%, Co (II): 3.7%, Zn (II): 1.9%), which indicated that the method had good precision for the analysis of trace Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) in solution samples.

The accuracy of the proposed preconcentration methodology was evaluated by means of ions with determination in certified sample material (GBW 08301, river sediment), respectively. According to the results shown in Table 3, a good agreement was obtained between the estimated content by the proposed method and the certified values of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II). The results also indicated that the developed preconcentration method for Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) was not affected by potential interferences from the major matrix elements of the analyzed standard material.

3.10. Application of the method

The proposed method was then applied for the determination of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) in Yellow River water and tap water samples. For the analysis of the water samples, the standard addition method was used and the results for the recovery of all the metal ions are presented in Table 4. As shown in Table 4, the recoveries of analytes were in the range of 96.4–101.0%. It demonstrated the suitability of the APPS-CA for selective solid-phase extraction and preconcentration of trace Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) from environment samples.

4. Conclusions

In this study, a novel chemically modified polysiloxane resins containing calix[4]arene derivative units successfully synthesized and applied to solid-phase extraction and preconcentration of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) by ICP-OES. The proposed method was simple, low cost, and the short loading time of the present matrix makes the analytical procedure reasonably fast. The determination of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II) in the certified reference material shown good accuracy. Their separation curves demonstrated the efficiency of the resins for simultaneous separation in the presence compared to most of the other matrices used for enrichment of Cr (III), Cu (II), Ni (II), Co (II) and Zn (II). The modified polysiloxane resins exhibited good adsorption properties and enrichment factor for the selected heavy metal ions not only are these results related to both the special cavity and the network structure of resins, but the nitrogen atoms in resins also exert some auxiliary action. The resins were recycled many times without affecting its adsorption capacity.

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