

Tris(2-aminoethyl) amine functionalized silica gel for solid-phase extraction and preconcentration of Cr(III), Cd(II) and Pb(II) from waters

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Abstract

A new tris(2-aminoethyl) amine (TREN) functionalized silica gel (SG-TREN) was prepared and investigated for selective solid-phase extraction (SPE) of trace Cr(III), Cd(II) and Pb(II) prior to its determination by inductively coupled plasma atomic emission spectrometry (ICP-AES). Identification of the surface modification was characterized and performed on the basis of FT-IR. The separation/preconcentration conditions of analytes were investigated, including effects of pH, the shaking time, the sample flow rate and volume, the elution condition and the interfering ions. At pH 4, the maximum adsorption capacity of Cr(III), Cd(II) and Pb(II) onto the SG-TREN were 32.72, 36.42 and 64.61 mg g⁻¹, respectively. The adsorbed metal ions were quantitatively eluted by 5 mL of 0.1 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 for Cr(III), Cd(II) and Pb(II) were 0.61, 0.14 and 0.55 ng mL⁻¹, respectively. The relative standard deviation under optimum conditions is less than 4.0% (*n* = 11).

The application of this modified silica gel to preconcentration trace Cr(III), Cd(II) and Pb(II) of two water samples gave high accurate and precise results.

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1. Introduction

In recent years, the toxicity and the effect of trace elements which are dangerous to public health and environment are attracting more attention from pollution and nutritional fields. Cr(III) is considered to be an essential trace element for the maintenance of effective glucose, lipid and protein metabolism in mammals [1]. On the other hand, Cd(II) and Pb(II), even at very low concentrations, are well-known toxic elements. For humans, the main sources of Cd(II) and Pb(II) are water and food, so rapid and sensitive methods must be accessible for their determination in these samples [2]. Therefore, preconcentration and selective separation of trace or ultra-trace Cr(III), Cd(II) and Pb(II) from food and natural water are very important and need further study [3,4].

The traditional separation and preconcentration methods for metal ions include liquid–liquid extraction [5], coprecipitation

[6] and ion-exchange [7], etc. These methods often require large amounts of high purity organic solvents, some of which are harmful to health and cause environmental problems. Recently solid-phase extraction (SPE) technique has become known as a powerful tool for separation and enrichment of various inorganic and organic analytes [8–11]. The SPE has several major advantages that include (i) higher enrichment factor, (ii) simple operation, (iii) safety with respect to hazardous samples, (iv) high selectivity, (v) lower cost and less time, (vi) the ability to combine with different modern detection techniques [12]. Silica gel is used as the most common inorganic solid adsorbent in many application studies [13–16]. Chemically modified silica gel is one of the most successful adsorbents, because the silica gel supports do not swell or shrink like the polymeric resin [17]. The modified silica gel may be employed in aqueous and organic solvents media [17]; they present good thermal stability [17] and appropriate accessibility of ions to the adsorbent groups; in addition the modified silica gel exhibits higher sorption capacities than polymeric resins [13–17], because the number of organic molecules immobilized on the support surface is more, allowing more removal of ions from aqueous solution.

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So far as we know, there are several recent reports on the use of functionalized silica gel for enrichment of metal ions. The synthetic pathways of modified silica gel were similar to the reaction of organosilane with silanol groups on silica gel but the difference was the type of chelating molecules which selectively chelate with metal ions such as 2-aminothiazole [18], 2,5-dimercapto-1,3,4-thiadazole [19], 2-mercapto-5-phenylamino-1,3,4-thiadazole [20], formylsalicylic acid [21], 2,4-dichlorophenoxyacetic acid [22], 2-pyridinecarboxaldehyde phenylhydrazone [23], 4-amino-3,5,6-trichloropicolinic acid [24] and 2-mercaptobenzothiazole [25]. Thus, modified silica gel is a fast developing area for solid-phase extraction technology. However, most of the sorbents have drawbacks more or less such as poor adsorption capacity or long equilibrium time, etc.

The treeing ligand is a kind of new organic ligands with three-dimensional structure which has two or more swinging arms. Basing on the functional group of the arms, it can coordinate with metal ions of different radius, and it has high selectivity for metal ions. TREN is an example of treeing ligands with four nitrogen atoms. Therefore, it exhibits great absorption performance for metal ions.

In our work, TREN chemically modified silica gel was synthesized and characterized. The modified silica gel showed great affinity, high adsorption capacity and less equilibrium time for binding with heavy metal ions. The solid-phase extraction of Cr(III), Cd(II) and Pb(II) by batch and column modes was studied. Parameters that affect the sorption and elution efficiency of the metal ions were also studied. Then, the method was applied to preconcentrate trace metal ions from natural water samples with satisfactory results.

2. Experimental

2.1. Apparatus

An IRIS Advantage ER/S inductively coupled plasma spectrometer (TJA, USA) was used for all metal ions determination. The instrumental parameters were those recommended by the manufacturer. The wavelengths selected were as follows: Cr 283.563 nm, Cd 228.802 nm, Pb 220.353 nm. The pH values were adjusted with a PHS-10C digital pH meter (Xiaoshan Instrument Factory, China). The Infrared spectra were recorded with a Nicolet NEXUS 670 FT-IR (U.S.A.) using pressed KBr disks and a spectral resolution of 4 cm^{-1} , and each spectrum was obtained after acquiring the same KBr background spectra. A VarioEL element analyzer, Elementar Analysensysteme GmbH (Hanau, Germany) was used for elemental analysis. An YL-110 peristaltic pump (General Research Institute for Non-ferrous Metals, Beijing, China) was used in the separation/preconcentration process. A PTFE (polytetrafluoroethylene) column (50 mm \times 9.0 mm i.d.) was used.

2.2. Reagents and standard solutions

Reagents of analytical and spectral purity were used for all experiments and doubly distilled deionized water was

used throughout. TREN was used in this work (Aldrich Chemical Company). Silica gel (200–300 mesh) and 3-chloropropyltrimethoxysilane were purchased from Chemical Engineering Corporation of Ocean University of China (Qingdao, China).

Standard stock solution of Cr(III), Cd(II) and Pb(II) (1 mg mL^{-1}) were prepared by dissolving spectral pure grade chemicals $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ (The First Reagent Factory, Shanghai, China). Standard working solutions were further diluted prior to use.

2.3. Sample preparation

The river water samples were collected from Yellow River (Lanzhou, China). All water samples were filtered through a $0.45\text{ }\mu\text{m}$ polytetrafluoroethylene (PTFE) millipore filter (Tianjin Jinteng Instrument Factory, Tianjin, China), and acidified to pH of about 1 with concentrated HCl prior to storage for use [26]. Tap water samples were taken from our research laboratory (Lanzhou University, Lanzhou, China) without pretreatment. And the pH value was adjusted to 4 with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} $\text{NH}_3 \cdot \text{H}_2\text{O}$ prior to use.

2.4. Synthesis of SG-TREN

2.4.1. Synthesis of chloro-functionalized silica gel sorbent

The silica gel surfaces were activated by refluxing with concentrated hydrochloric acid under stirring for 8 h, then the activated silica gel was filtered and washed with doubly distilled water to neutral and dried under vacuum at $70\text{ }^\circ\text{C}$ for 8 h.

To prepare the chloro-functionalized silica sorbent, 5 g of activated silica gel was dispersed into toluene (50 mL) in a flask of total volume 100 mL, and then 3-chloropropyltrimethoxysilane (5 mL) was gradually added into the solution with continuous stirring. The mixture was refluxed for over night. The final product was filtered off, washed with toluene, alcohol and dried under vacuum at $70\text{ }^\circ\text{C}$ for 8 h.

2.4.2. Synthesis of SG-TREN

For the synthesis of SG-TREN, 2 g TREN was dissolved in 100 mL of dry toluene, and then 5 g of chloro-functionalized silica gel was added into the solution. The mixture was refluxed for 12 h with continuous stirring. After being filtered, the particles were washed with toluene, ethanol and diethyl ether and dried at $70\text{ }^\circ\text{C}$ for 8 h. The structure of the SG-TREN obtained is illustrated in Fig. 1.

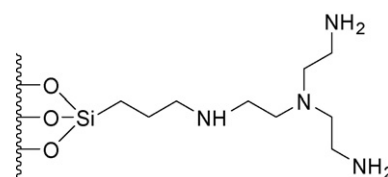


Fig. 1. Structure of SG-TREN.

2.5. Experimental procedure

2.5.1. Static method

A series of standard or sample solutions containing Cr(III), Cd(II) and Pb(II) were transferred into a 10 mL beaker, and the pH value was adjusted to the desired value with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} $\text{NH}_3 \cdot \text{H}_2\text{O}$. Then the volume was adjusted to 10 mL with doubly distilled deionized water. SG-TREN (50 mg) was added, and the mixture was shaken vigorously for 30 min to facilitate adsorption of the metal ions onto the SG-TREN. After centrifugation, the concentration of the metal ions in the solution was determined by ICP-AES.

2.5.2. Dynamic method

Firstly, the PTFE column was packed with 300 mg SG-TREN. A small amount of glasswool was placed at both ends to prevent loss of the particles during sample loading. Before using, HCl solution (pH 4) and doubly distilled deionized water were successively passed through the column in order to equilibrate, clean and neutralize it. Portions of aqueous standard or sample solutions containing Cr(III), Cd(II) and Pb(II) were prepared, and the pH value was adjusted to the desired pH value with 0.10 mol L^{-1} of HCl or 0.10 mol L^{-1} $\text{NH}_3 \cdot \text{H}_2\text{O}$. Each solution was passed through the column at a flow rate of 4.0 mL min^{-1} by a peristaltic pump. Afterwards, the metal ions retained on column were eluted with 0.10 mol L^{-1} HCl solution and the analytes in the elution were determined by ICP-AES.

3. Results and discussion

3.1. FT-IR characterization and elemental analysis

The modified silica gel was confirmed by FT-IR analysis. As shown in Fig. 2 the sharp features around 1099.24 cm^{-1} indicated Si–O–Si stretching vibrations [27]. The presence of adsorption water was reflected by νOH vibration around 3446.11 and 1621.55 cm^{-1} [27]. The bands around 803.74 and 468.10 cm^{-1} resulted from Si–O vibrations [27]. A characteristic feature of the SG-TREN adsorbents (b) when compared with the activated silica gel (a) was N–H and C–H of TREN around 1521.40 cm^{-1} and 2958.11 cm^{-1} [27–29]. These results showed that TREN had been grafted onto the surface of silica gel after modification. Comparison of the FT-IR spectra between SG-TREN (b) and SG-TREN saturated with Cr(III) (c), Cd(II) (d) and Pb(II) (e), respectively, revealed two differences. First, N–H band around 1521.40 cm^{-1} (b) disappeared. Second, there were new peaks at 1371.82 (c), 1382.77 (d) and 1383.75 cm^{-1} (e) appearing in the FT-IR spectra. Based on the above analysis, it is concluded that when SG-TREN chelated with Cr(III), Cd(II) and Pb(II), respectively, the N–H band would have a negative shift [29].

Elemental analysis indicated 7.887% carbon, 2.929% nitrogen and 1.960% hydrogen in SG-TREN. It could be calculated that 1 g silica gel contained 0.077 g TREN.

All these characteristic procedures can demonstrate that TREN was modified on SG surface.

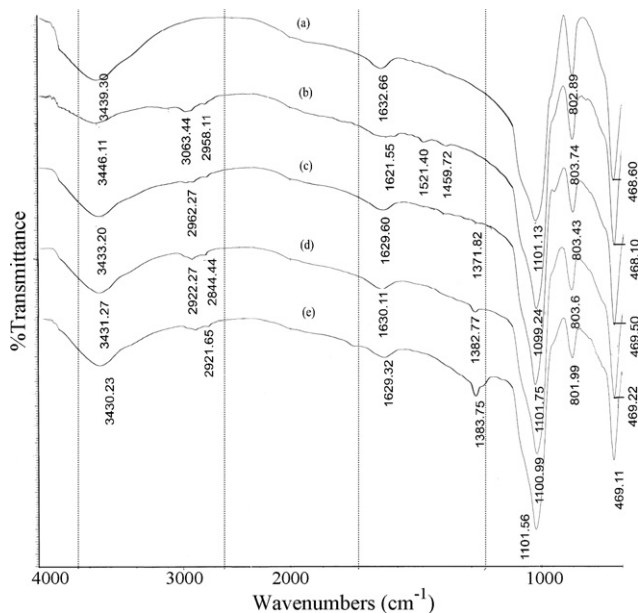


Fig. 2. FT-IR spectra of the activated silica gel (a), SG-TREN (b), SG-TREN saturated with Cr(III) (c), SG-TREN saturated with Cd(II) (d) and SG-TREN saturated with Pb(II) (e). The areas of $2800\text{--}3400 \text{ cm}^{-1}$ and $1300\text{--}1700 \text{ cm}^{-1}$ were expanded.

3.2. Effect of solution pH

According to the recommended procedure (static method), several metal ions, viz. Cr(III), Fe(III), Hg(II), Ca(II), Mg(II), Co(II), Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) were adsorbed by 50 mg SG-TREN in different buffer solutions, namely pH 1, 2, 3, 4, 5, 6 and 7. It is well-known that binding of metal ions to the chelate compound either in solution or loaded on solid support is mainly dependent on several factors such as nature, charge and size of the metal ions [30,31]; nature of the donor atoms and their binding characteristics [32,33]; the buffering conditions. These factors are documented very well in solution chemistry as well as in solid-phase extraction of certain metal by organic chelates immobilized on the surface of solid support such as silica gel, nanomaterials or polymeric species. Therefore, to evaluate the suitability of the newly synthesized SG-TREN for metal ions extraction and binding, we studied the effect of pH of metal ions solution on the metal capacity values as one of the most significant controlling factors in such process. The results are shown in Fig. 3.

Several trends were notable. First, it was the strong dependence of the metal capacity values on the pH value of the tested metal ions, and the metal capacity increased with the increasing of pH value. Second, it was found that the metal recovery values of Cr(III), Cd(II) and Pb(II) was higher than other ions in range of pH 4–7. To avoid hydrolyzing at higher pH and determine these elements simultaneously, pH 4 was selected as the enrichment acidity for further study.

In addition, Co(II), Ca(II), Mg(II), Ni(II), Zn(II) were not adsorbed by SG-TREN at pH 4; Cu(II), Hg(II), Fe(III) and Mn(II) could be adsorbed by SG-TREN about 20–30% at pH

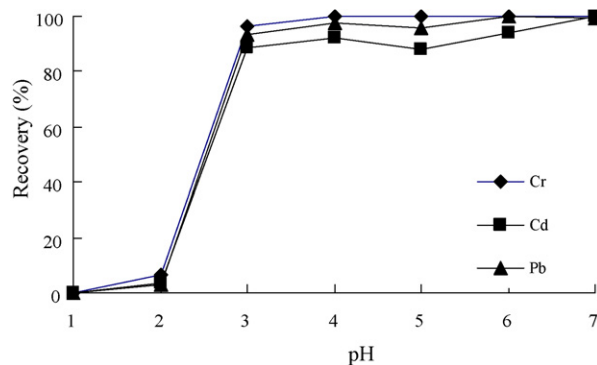


Fig. 3. Effect of pH on analyte recovery; Cr(III) $1.0 \mu\text{g mL}^{-1}$, Cd(II), Pb(II) $10.0 \mu\text{g mL}^{-1}$; SG-TREN 50 mg; shaking time 30 min.

Table 1

Effect of concentration of HCl (10.0 mL) solution on elution of Cr(III), Cd(II) and Pb(II) adsorbed on SG-TREN

HCl (mol L^{-1})	Recover (%)		
	Cr(III)	Cd(II)	Pb(II)
0.01	56.3	60.8	70.9
0.05	71.6	77.5	85.1
0.1	97.9	98.7	99.2
0.5	97.8	98.3	100.3
1	96.1	97.3	99.5
2	97.5	97.8	98.8
4	95.5	96.1	97.5

4, but they do not interfere with enrichment and determination of Cr(III), Cd(II), and Pb(II).

3.3. Effect of elution condition on recovery

Since the adsorption of cations at $\text{pH} < 2$ was negligible, one can expect that elution will be favoured in acidic solution. So different concentration and volume of HCl were used for the desorption of retained Cr(III), Cd(II) and Pb(II) following the above procedure (dynamic method). The obtained results were shown in Tables 1 and 2. It was found that quantitative recoveries ($>95\%$) with 5.0 mL of 0.1 mol L^{-1} HCl could be obtained. Therefore, 5.0 mL of 0.1 mol L^{-1} HCl was used as eluent in the following experiments.

3.4. Adsorption capacity of SG-TREN

The adsorption capacity is an important factor because it determines how much adsorbent is required to quantitatively

Table 2

Effect of volume of HCl (0.1 mol L^{-1}) solution on elution of Cr(III), Cd(II) and Pb(II) adsorbed on SG-TREN

Eluent volume (mL)	Recovery (%)				
	3	4	5	6	7
Cr(III)	83.5	89.9	98.2	99.2	98.9
Cd(II)	80.7	92.7	98.9	98.5	98.7
Pb(II)	85.8	94.5	99.2	100	100

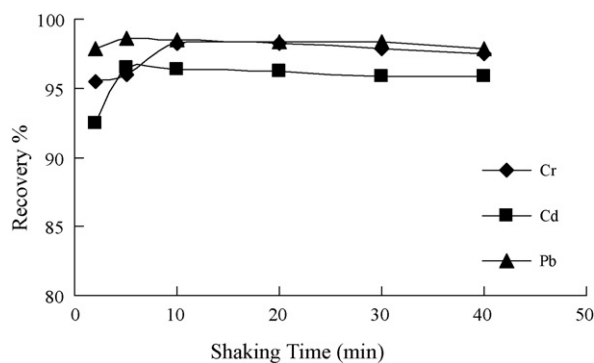


Fig. 4. Extraction percentage of Cr(III), Cd(II) and Pb(II) at different shaking time; Cr(III) $1.0 \mu\text{g mL}^{-1}$, Cd(II), Pb(II) $10.0 \mu\text{g mL}^{-1}$; SG-TREN 50 mg.

concentrate the analytes from a given solution. The capacity study was adopted from the paper recommended by Maquieira et al. [34]. A series of 20 mL of Cr(III), Cd(II) and Pb(II) ions solutions ($10\text{--}200 \mu\text{g mL}^{-1}$) were adjusted to the appropriate pH. The proposed separation and preconcentration procedures (Static method) described above were applied. A breakthrough curve was gained by plotting the concentration ($\mu\text{g mL}^{-1}$) vs. the micrograms of Cr(III), Cd(II) and Pb(II) adsorbed per gram of SG-TREN. From the breakthrough curve, the maximum adsorption capacity of SG-TREN for Cr(III), Cd(II) and Pb(II) are found to be 32.72, 36.42 and 64.61 mg g^{-1} at pH 4, respectively. However, Cr(III), Cd(II) and Pb(II) ions were adsorbed poorly on untreated silica gel at pH 4. The results showed that SG-TREN had a high adsorption capacity for Cr(III), Cd(II) and Pb(II).

3.5. Effect of shaking time

The shaking time is an important factor in determining the possibility of application of the SG-TREN for the selective extraction of metal ions. In this work, different shaking time (range from 2 to 40 min) was studied for the percentage extraction of three ions by SG-TREN. Fig. 4 shows the results of recoveries of Cr(III), Cd(II) and Pb(II) vs. the shaking time in minutes. It is evident from Fig. 4 that the percentage extractions of Cr(III), Cd(II) and Pb(II) reached above 95% in 5 min. Probably the reason for the fast adsorption of Cr(III), Cd(II) and Pb(II) on SG-TREN is that the sorbent contains lots of amino—which exhibit very good hydrophilicity, so it can reach the equilibrium in short time. Accordingly, the shaking time of 5 min was chosen as the adsorption equilibrium time.

3.6. Effect of the flow rate

As the retention of elements on adsorbent depends upon the flow rate of the sample solution, its effect was examined under the optimum conditions (pH, eluent, etc.) by passing 10 mL of sample solution through the column controlled with a peristaltic pump. The flow rates were adjusted in range of $1.0\text{--}6.0 \text{ mL min}^{-1}$. As shown in Fig. 5, the sorption of Cr(III), Cd(II) and Pb(II) were not affected obviously by flow rate. When the flow rates above 4.0 mL min^{-1} , there was a decrease for

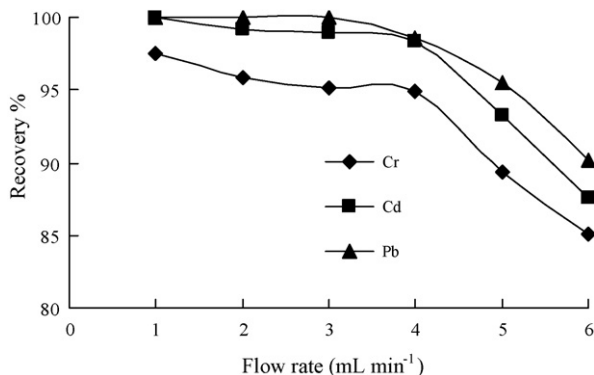


Fig. 5. Effect of flow rate on analyte recovery; pH 4; Cr(III) $1.0 \mu\text{g mL}^{-1}$, Cd(II), Pb(II) $10.0 \mu\text{g mL}^{-1}$; sample volume 10 mL.

Cr(III), Cd(II) and Pb(II). Thus, a flow rate of 4.0 mL min^{-1} was selected in this work.

3.7. Effect of the sample volume

To explore the possibility of adsorbing low concentrations of analytes from large volumes of solution, the effect of sample volume on the retention of metal ions was also investigated. For this purpose, 250, 500, 750 and 1000 mL of sample solutions containing $2.0 \mu\text{g Cd(II)}$, Pb(II) and $1.0 \mu\text{g Cr(III)}$ were passed through the column with the optimum flow rate. Fig. 6 indicates that the retention of all the metal ions examined was not affected by sample volumes up to 500 mL. when sample volumes above 500 mL, recovery values less than 95% for Cr(III), Cd(II) and Pb(II) were obtained. Therefore, 500 mL sample solution was adopted for the preconcentration of analytes from sample solutions. In this study, the final solution volume was 5 mL, so the concentration factors were 100 for the three metal ions.

3.8. Effect of coexisting ions

The effect of common coexisting ions on the adsorption of Cr(III), Cd(II) and Pb(II) on SG-TREN was investigated. In these experiments, solutions of $10.0 \mu\text{g mL}^{-1}$ of Cr(III), Cd(II), and Pb(II) that contain the interfering ions were analyzed according to the recommended procedure. The tolerance limit was set as the amount of ions causing recoveries of the examined elements

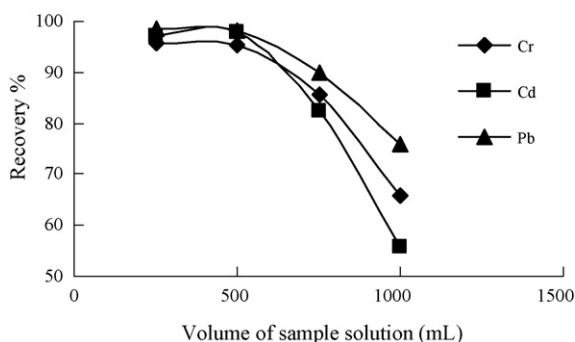


Fig. 6. Effect of the sample volume on analyte recovery; pH 4; SG-TREN 300 mg.

Table 3
Analysis of standard reference material

Element	Found ^a ($\mu\text{g L}^{-1}$)	Certified ^a ($\mu\text{g L}^{-1}$)
Cr	88 ± 1.2	90 ± 8.0
Cd	2.3 ± 0.2	2.4 ± 0.3
Pb	77 ± 5.0	79 ± 6

^a The value following “ \pm ” is the standard deviation ($n=3$).

to be less than 95%. The results showed that, excess of 1000-fold K(I), Na(I); 500-fold Ca(II), Mg(II); 50-fold Zn(II), Ni(II), Co(III), Fe(III) and 30-fold Cu(II), Mn(II) ions had no significant interferences in the determination of the analytes.

3.9. Analytical precision and detection limits

Under the selected conditions, eight portions of mixed standard solutions were enriched and analyzed simultaneously by following the recommended procedure. The relative standard deviations (R.S.D.s) of the method were low than 4.0% (Cr(III): 2.3%; Cd(II): 3.6%; Pb(II): 2.0%). It indicates that the method has good precision for the analysis of trace Cr(III), Cd(II) and Pb(II) from solution samples. According to the definition of IUPAC, the detection limits (3σ) of this method for Cr(III), Cd(II) and Pb(II) are 0.61 , 0.14 and 0.55 ng mL^{-1} , respectively ($n=11$, $C=50 \text{ ng mL}^{-1}$).

3.10. Analysis of real samples

The proposed method has been applied to the determinations of trace Cr(III), Cd(II) and Pb(II) in standard material (GBW 08301, river sediment), Yellow River water and tap water sam-

Table 4
Analytical results of natural water samples

Ion	Added ($\mu\text{g L}^{-1}$)	Found ^a ($\mu\text{g L}^{-1}$)	Recovery (%)
Tap water			
Cr(III)	0	2.13 ± 0.12	–
	5	6.93 ± 0.12	96.0
	10	11.87 ± 0.11	97.4
Cd(II)	0	–	–
	5	4.98 ± 0.11	96.6
	10	9.96 ± 0.15	98.1
Pb(II)	0	2.88 ± 0.10	–
	5	7.52 ± 0.10	92.8
	10	12.55 ± 0.13	96.7
Yellow River water			
Cr(III)	0	3.94	–
	5	8.79 ± 0.13	97.0
	10	13.83 ± 0.12	98.9
Cd(II)	0	–	–
	5	5.08 ± 0.09	99.2
	10	9.98 ± 0.11	98.6
Pb(II)	0	4.38 ± 0.10	–
	5	9.61 ± 0.12	104.6
	10	14.37 ± 0.19	100.2

^a The value following “ \pm ” is the standard deviation ($n=3$).

ples. The analytical results of the standard material in Table 3 were in good agreement with the certified values. For the analysis of natural water samples, the standard addition method was used. The analytical results are given in Table 4. The results indicate that the proposed method is reliable.

4. Conclusions

Functionalized silica gel have attracted widespread attention as highly selective adsorbents to remove metal ions selectively in the presence of other metal ions. In this study, a unique treeing ligand TREN was modified to the surface of silica gel and used for preconcentration and selective separation Cr(III) Cd(II) and Pb(II) as solid-phase extractant. The preparation of TREN functionalized silica gel was relatively simple and convenient. The SG-TREN adsorbent showed high affinity, selectivity and good accessibility for Cr(III) Cd(II) and Pb(II). Furthermore, this new developed method has been successfully applied to the determination of trace Cr(III) Cd(II) and Pb(II) in natural water samples with satisfactory results. This study also indicated that the design of treeing ligands to silica gel was very suitable for further development of solid-phase extraction techniques.

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