Preparation and Modification of Macroporous Epoxy-Triethylenetetramine Resin for Preconcentration and Removal of Hg(II) in Aqueous Solution

Junyan Pan, Sui Wang, Ruifeng Zhang

State Key Laboratory Base of Novel Functional Materials and Preparation Science, Ningbo University, Ningbo 315211, People's Republic of China

ABSTRACT: A novel macroporous resin was prepared from epoxy resin and triethylenetetramine through a polymerization with phase separation. In this experiment, the polyethylene glycol (PEG-1000) plays a very important part. It was used as solvent, as phase-separation reagent in the preparation processes, and as the pore-forming reagent through removing PEG-1000 from polymer by water-cleaning process after completing polymerization. The prepared resin was modified by carbon bisulfide and soaked in 1 mol L^{-1} NaOH. Its structure was characterized by Fourier transform-infrared spectra, scanning electron microscopy, and elemental analysis. The adsorption characteristic of the chelating resin was studied by series of experiments. The results show that the chelating resin possesses excellent adsorption characteristic toward trace Hg(II). The recovery can come to 100% when the concentration of Hg(II) is only 0.05 ppm, and the average maximum adsorption capacity of the chelating resin for Hg(II) is 122 mg g^{-1}. The precision (relative standard deviation) for six replicate adsorbent extraction of 0.01 μg mL^{-1} Hg(II) was 1.1%. The accuracy of the proposed procedure was verified by analyzing a standard reference material. Moreover, the chelating resin was applied to two natural samples and also got satisfactory results. That is to say, the chelating resin modified by carbon bisulfide exhibits a high chelating ability toward Hg(II) and can be used as adsorbent for preconcentration and removal of trace Hg(II) in aqueous solution. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2372–2378, 2006

Key words: macroporous polymers; phase separation; adsorption; mercury; ICP-AES

INTRODUCTION

In recent years, particular concern has been devoted to the presence of mercury species in natural waters, which is recognized as an area of major environmental concern.[1] As we all know, mercury is a poisonous heavy metal element and one of the most serious environmental pollutants. Mercury toxicity may represent the damnification to human brain, heart, liver, kidney, spleen, lung, etc.[2] The damnification of mercury to human health is mainly due to the environment pollution caused by the production of industry, for examples, thermometer, batteries, alloys, chemical factory, aurum-smelting factory, etc.[3] Therefore, several methods have been proposed and used for preconcentration and separation of trace Hg(II) according to the nature of the samples, the concentrations of the analytes, and the measurement techniques.[4–9]

Of all the preconcentration methods, chelating resin sorption method is one of the most effective methods because it can provide more flexible working conditions together with good stability, selectivity, high concentrating ability, high capacity of metal ions, and simple operation. So, many special chelating polymer resins have been prepared in the past decade.[10–12]

Among the various resins, the macroporous resin possesses higher adsorption capacity and velocity of mass transfer than general gel-resin does when it was used in adsorption of metal ions in aqueous solution, because the existence of macropores would provide convenient diffusion channels for metal ions into the interior of resin.[13–16]

Additionally, the incorporation of suitable functional groups into a polymeric matrix promotes the reaction with a particular metal under favorable conditions.[17–20] There are two ways to synthesize functional polymers for the preconcentration and removal of metal ions. In the first, monomer are modified with active and specific ligand to desired metal ions and polymerized. In the second way, after the polymerization, polymeric materials are modified by the active and specific ligand to one or more different metal ions.[21] For the extraction, determination, preconcentration, and removal of some heavy metal ions, different

types of new functional resins have been studied very intensively.[22–24] For the preconcentration and removal of mercury by chelating resin, the presence of a sulfur-containing group is desirable because of its selectivity and ability to form stable chelate complexes.[25–27]

In this study, a novel macroporous resin was prepared by epoxy resin and TETA through a polymerization with phase separation. In this experiment, the polyethylene glycol (PEG-1000) plays a very important part. It was not only used as solvent and phase-separation reagent in the preparation processes, but also as the pore-forming reagent through removing PEG-1000 from polymer by water-cleaning process after completing polymerization. Then the prepared resin was modified by carbon bisulfide. The chelating resin would be expected to have excellent adsorption ability for Hg(II).

In our knowledge, macroporous epoxy-TETA resin modified by carbon bisulfide has not been employed previously for the preconcentration and removal of trace Hg(II) from aqueous solution. In this article, we report the synthesis, structure, and characteristic of a novel macroporous epoxy-TETA resin modified by carbon bisulfide for preconcentration and removal of trace mercury in aqueous solution.

EXPERIMENTAL

Apparatus and reagents

An IRIS Advantage ER/S inductively coupled plasma spectrometer (TJA, USA) was used for all metal-determinations. The surface morphology of the resins was examined on a scanning electron microscope (S-570, Hitachi, Japan). The FTIR spectra of resins were analyzed by Nicolet NEXUS 670 FTIR spectroscopy (Nicolet Instrument, Madison, WI). Elemental analysis was done on a Perkin–Elmer 2400 elemental analyzer. A model pHS-3CT digital pH meter (Shanghai Dazhong Analysis Instrument Factory, China) was used to measure pH values. The flow rate of liquid through columns was controlled by a model BT00-100M peristaltic pump (Baoding Laonger Precision Pump Limited Company).

Stock solutions (1000 mg L^{-1}) of the elements were prepared by dissolving appropriate amounts of nitrate salts in 1.0% HNO_3 and further diluted daily prior to use. The pH was adjusted with diluted HNO_3 and $NH_3 \cdot H_2O$. Epoxy resin, triethylenetetramine, PEG-1000, carbon bisulfide and sodium hydroxide were purchased from Shanghai Chemistry Regent Limited Company, People's Republic of China. All reagents used in the experiments were of analytical grade and were not purified further. The two different samples were collected from Ningbo region, People's Republic of China. Among them, the wastewater was collected from the main drain of a chemical factory lied in Cixi. The river water was collected from Yongjiang River. The standard reference material (GBW 08619, water) was purchased from National Research Center for GeoAnalysis, People's Republic of China.

Unless otherwise stated, all water used in the experiments was 18 MΩ cm distilled de-ionized water (DDI) purified with a Milli-Q system (Millipore, USA) and all solutions were prepared with DDI water. Standard labware and glassware used were repeatedly cleaned with diluted HNO_3 and rinsed with DDI water according to a published procedure.[28]

Preparation of chelating resin

Six grams of epoxy resin and 2.0 g TETA were dissolved in 18.0 g melted PEG-1000 under strong stirring. The mixture was a transparent ropy solution and then placed into an oven at 50°C for 12 h. The liquid gradually turned into white as result of phase separation in the process of curing. Finally, a white bulk solid was obtained and washed with large amount of DDI water to remove PEG-1000 completely. The solid resin was dried at room temperature.

Then the resin was refluxed in carbon bisulfide for 1 h. After that, the resin was dried at room temperature and then soaked in 1 mol L^{-1} NaOH solution for 2 h. Finally, the prepared resin was cleaned by DDI water and dried in a vacuum oven at room temperature for 48 h. The sketch map of polymerization and modification reaction is shown in Scheme 1.

Batch experiments

A batch technique was applied to determine the metal binding ability of the synthesized adsorbents. An equal amount of dried resin particles was soaked in DDI water overnight. The standard solutions of metal ions (Hg^{2+}) were added into conical flasks. The solutions were adjusted to prefixed pH with dilute $NH_3 \cdot H_2O$ and HNO_3. The wetted resin particles were added to the metal ion solution. These mixtures in the flasks were shaken mechanically at room temperature for a certain period of time. After standing, the unadsorbed metal ions in the solutions were measured by an inductively coupled plasma atomic emission spectroscopy (ICP-AES) and the binding capacities of ions on chelating resin could be calculated. This method was used to study the effects of pH and the adsorption capacity of Hg(II) on the chelating resin.

Column experiments

Hundred milligrams of chelating resin was ground and screened. The particles with size in the range of 350–500 μm were selected and packed in a glass column (i.d. $0.5 \times 4 \ cm^2$). The solutions of Hg(II) were adjusted to a
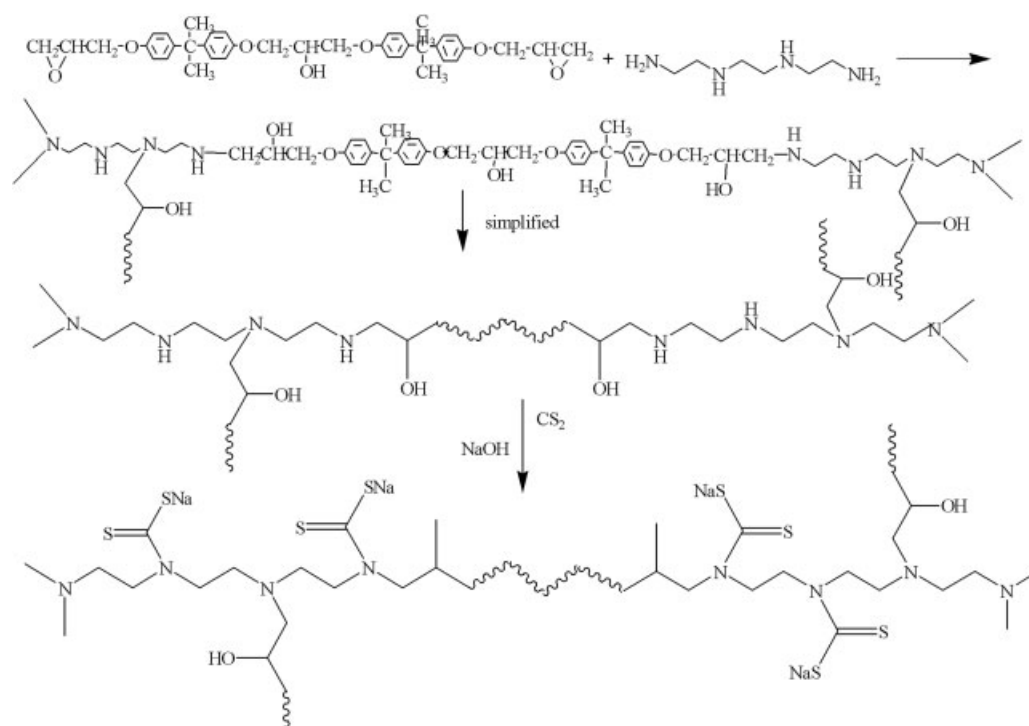
Scheme 1 The parts of possible reaction paths of epoxy-TETA chelating resin modified by carbon bisulfide.

suitable pH and passed through the adsorbing columns. The flow rate was controlled by peristaltic pump. The adsorbed resin particles were eluted with 0.1 mol L^{-1} HNO_3. The concentration of Hg(II) ions was determined by ICP-AES as described above.

General procedure of sample treatment

The bottles filled with the water samples were cleaned with detergent, DDI water, dilute nitric acid, and DDI water in sequence. The samples were immediately filtered by a cellulose filter membranes of 0.45 μm and were adjusted to pH 7.0 by the diluted HNO_3 and $NH_3 \cdot H_2O$.

RESULTS AND DISCUSSION

SEM observations of the resin

Generally, porous or gel resin could be differentiated by visual appearance, the former is white and opaque, the later is ivory-white and transparent.[29,30] The prepared epoxy-TETA resin is opaque and rigid. So, it should be regarded as porous resin. To testify further more, the porous structure of the chelating resin was analyzed by SEM image that was seen in Scheme 2. The image visually showed the morphology of the epoxy-TETA resin modified by carbon bisulfide. Abundant pores distributed on the surface of the chelating resin. Obviously, the pores were formed in the polymerization stage when phase

separation occurred and PEG-1000 was used as the pore-forming reagent.

To test the stability of the porous structure, a bit of the chelating resin was dried in a vacuum oven. At the beginning, the resin had no distinct change when the temperature was low. But when the temperature continuously increased till 110°C, the resin evidently shrunk and became transparent. That is to say, the macroporous structures of the resin would collapse under high temperature. However, the macro-pores were steady when the resin was filled with solvents in preparation process of the resin at about 50°C. When the resin was dried in a vacuum oven at room temper-
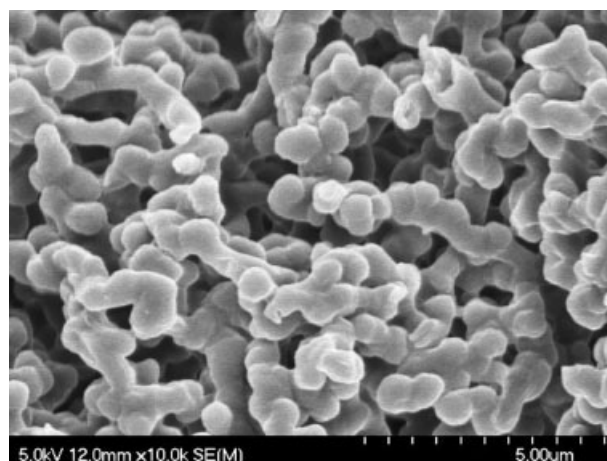
Scheme 2 SEM photograph of macroporous epoxy-TETA chelating resin modified by carbon bisulfide.
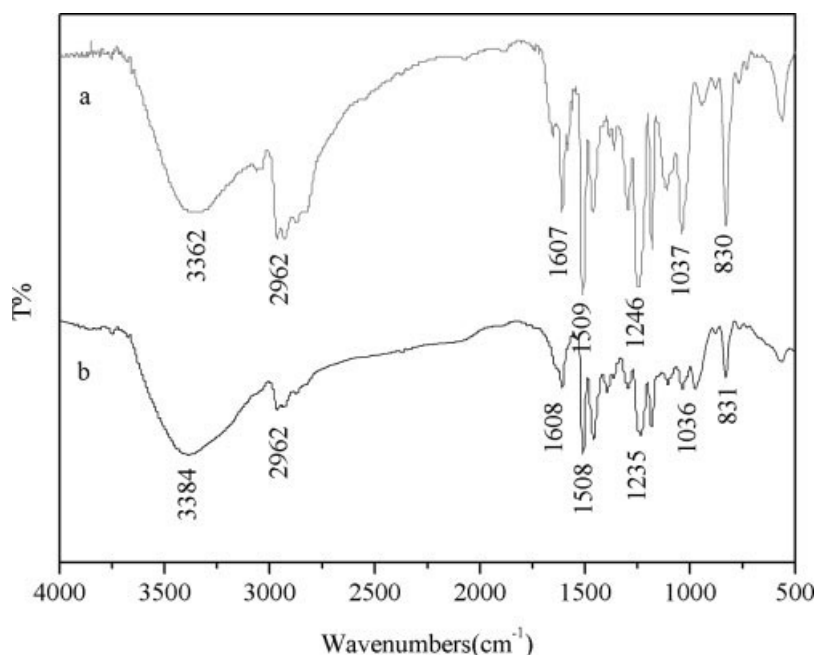
Figure 1 FTIR spectra: a, epoxy-TETA resin; b, chelating resin modified by carbon bisulfide.

ature, the dried resin also had no change. To retain the porous structure, the macroporous resin had better be hold in the distilled water on standby in routine experiments.

Analysis of FTIR spectra and elemental analysis

The existence of the functional groups in epoxy-TETA resin modified by carbon bisulfide was verified and analyzed by the FTIR (KBr) spectrum. Figure 1 shows the FTIR spectra of epoxy-TETA resin (curve a), chelating resin modified by carbon bisulfide (curve b). According to the reference,[31,32] the main absorption peaks can be assigned as follow: 3362 cm^{-1} (curve a) and 3384 cm^{-1} (curve b) (γ O—H and N—H), 2962 and 2962 cm^{-1} (γ C—H of CH$_2$ and CH), 1607 and 1608 cm^{-1} (γ C=C of Ar), 1509 and 1508 cm^{-1} (γ C=C of Ar), 1246 and 1235 cm^{-1} (γ_{as} C—O—C of O—Ar), (γ, stretching vibration; γ_{as}, antisymmetric stretching vibration; Ar, benzene).

To testify further more, the nonmodified resin and the resin modified by carbon bisulfide were analyzed by elemental analysis, respectively. The nonmodified resin does not have sulfur element. But the resin modified by carbon bisulfide has 8.37% of sulfur element. The results obviously show that carbon bisulfide has reacted with amidogen groups of the epoxy-TETA resin. However, the maximum content of sulfur element is theoretically 13.64% in case of complete modification. This difference maybe results from uncompleted reaction in the inner of the chelating resin microspheres.

### Effect of pH on sorption quantity

To obtain optimum extraction, the adsorption capacity of Hg(II) ions on chelating resin in different values of pH solutions was examined by batch experiments. Eight equal concentrations and equal volumes of Hg(II) ions standard solution (100-mL 10 μg mL^{-1}) were prepared and adjusted in the pH range 1–8 with diluted HNO$_3$ and NH$_3$·H$_2$O, respectively. Considering the hydrolysis of Hg(II) ion in strong alkali solution, pH above 8.0 was not tested.

The results show that the preconcentration and removal of Hg(II) was strongly affected by the solution pH. The chelating resin exhibited a low adsorption below pH 3.0. The optimal range of pH value for Hg(II) adsorption was 6.0–7.0 and pH 7.0 was chosen for further experiments.

TABLE I
Preconcentration and Removal of 100 ng mL^{-1} Hg(II) from Several Binary Mixtures with Other Metal Ions in a Sample Volume of 50 mL at pH 7.0^a

Foreign ions	Hg(II) recovery (%)
Cu(II)	93.5
Pb(II)	98.6
Cd(II)	95.2
Ni(II)	99.8
Fe(II)	98.8
Zn(II)	99.6
Mn(II)	98.4

^{a} Amount of each metal ion added was 10 μg.
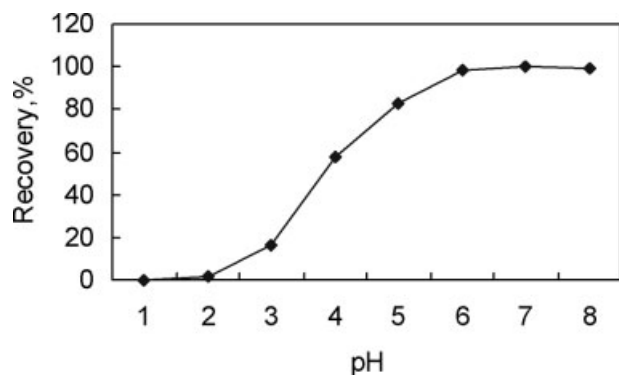
Figure 2 The effect of flow rate (mL min^{-1}) of Hg(II) solution on adsorption. Other conditions: 100 mg chelating resin; 100-mL 10 µg mL^{-1} Hg(II) solution; pH 7.0; room temperature.

Effect of diverse ions

To study the effects of diverse ions on the sorption of the mercury, solutions containing Hg(II) and other metal ions were prepared and analyzed by the proposed procedure. The results are presented in Table I. It is observed that other metal ions basically did not interfere in the recovery of the mercury. The reason for such a high selectivity for mercury is mainly based on the presence of sulfur-containing group.

Effect of flow rate

The flow rate of the Hg(II) solution through the chelating resin that was in the column is a very important parameter for the time controls of adsorption and analysis. In this experiment, sorption on the chelating resin modified by carbon bisulfide was studied at flow rate varying from 0.5 to 4 mL min^{-1} under optimum pH.

The results (Fig. 2) show that Hg(II) can be adsorbed quantitatively by the chelating resin at a flow rate below 2.0 mL min^{-1}. A flow rate <1.0 mL min^{-1} was not chosen due to the consequent long analysis time. However, a flow rate >2.0 mL min^{-1} causes a decrease in the percentage of sorption, the recovery was less than 95%. So 1.5 mL min^{-1} was chosen as optimal.

Adsorption capacity

At pH 7.0, by varying the concentration of Hg(II), adsorption capacity of Hg(II) on the chelating resin was investigated in batch experiments. The results show that the amount of mercury ions adsorbed per unit mass of the chelating resin increased with the initial concentration of the metal ions.

To test the adsorption capacity toward trace Hg(II), the minimum concentration of Hg(II) was diluted to 0.05 µg mL^{-1}, namely 0.05 ppm. To reach the "saturation," the initial mercury ion concentrations were increased till the plateau values were obtained. That is
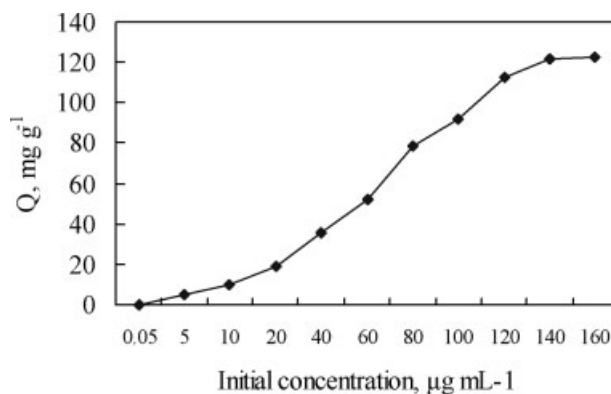
Figure 3 The effect of Hg(II) initial concentration on the adsorption quantity of resin. Other conditions: 100 mg resin; 100-mL Hg(II) solution; pH 7.0; room temperature.

to say, the adsorption capacity of the chelating resin increased almost linearly with the initial concentration of Hg(II) ions. The results were listed in Figure 3. The average maximum adsorption capacity of the chelating resin for Hg(II) is 122 mg g^{-1}.

Kinetics of sorption of Hg(II)

The adsorbing rate of Hg(II) on the chelating resin was studied using batch method. The beads of the resin (0.1 g) were equilibrated with 100-mL 140 µg mL^{-1} Hg(II) solution at room temperature for 20, 40, 60, 80, 100, 120, 140, and 160 min. The concentration of Hg(II) adsorbed by the resin and the amount remained in the solution were determined by the procedure described above. The results were shown in Figure 4. From the result, we can see that the equilibration rate $t_{1/2}$ for Hg(II) was 45 min. Considering the Brykina method,[33] the sorption rate constant k can be calculated using the following equation:

$$-\ln(1 - F) = kt, \quad \text{where } F = Q_t/Q$$

Q_t is the sorption amount at sorption time t and Q is the sorption amount at equilibrium. Putting the value of Q_t at different t (min) in the above equation, we
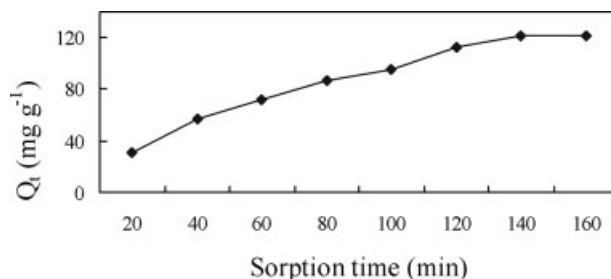
Figure 4 Kinetics of Hg(II) sorption on resin. Other conditions: 100 mg resin; 100-mL 140 µg mL^{-1} Hg(II); pH 7.0; room temperature.

TABLE II
Comparative Data from Some Previous Studies on Preconcentration and Removal of Hg(II)

Technique	System	Detection system	D.L.(3σ) ($\mu g \ L^{-1}$)	R.S.D. (%)	Reference
MIIP-SPE	Hg(II)-imprinted diazoaminobenzene-vinylpyridine copolymers	FAAS	0.05	2.4	34
SPE	Resin functionalized with a 1,2-bis(o-aminophenylthio) ethane moiety	CVAAS	0.09	1.0	1
SPE	2-Aminoacetylthiophenol functionalized Amberlite XAD-2	ICP-AES	0.23	<10	18
SPE	Anion-exchange resin loaded with 1,5-bis[(2-pyridyl)-3-sulphophenyl methylene] thiocarbonohydrazide	ICP-AES	4	3.6	35
SPE	1,3-Di-(4-nitrodiazoamino)-benzene loaded on β-cyclodextrin polymer	UV–vis	0.024	2.4	36
SPE	Macroporous epoxy-TETA resin modified by carbon bisulfide	ICP-AES	0.06	1.1	Present work

may get the corresponding value of k. The value of k for Hg(II) that linearly fitted according to the former five points is 1.53×10^{-2} min^{-1}.

Effect of elution rate

When the column procedure was used, the influence of the flow rate on desorption of the analytes from the columns with diluted HNO_3 solution was investigated. The experimental conditions show that, Hg(II) ions could be quantitatively eluted with 10-mL 0.1 mol L^{-1} HNO_3.

The whole procedure was carried just as above. HNO_3 (0.1 mol L^{-1}) solutions were passed through the chelating resin in the columns at a flow rate that could be controlled by peristaltic pump. The flow rate was carried from 0.5 to 4.0 mL min^{-1}.

The results show that Hg(II) ions can be quantitatively eluted at flow rates below 1.0 mL min^{-1}. So, the flow rate of 0.5 mL min^{-1} was selected for the elution flow rate.

Accuracy and precision of the analytical method

Under the selected optimum conditions, the recoveries of 0.01 μg mL^{-1} Hg(II) ions in 100 mL solutions, determined simultaneously six times, are 99–100%. The precision of the method for a standard, evaluated as the relative standard deviation (R.S.D., $n = 6$), was 1.1%. The limit of detection (3σ), defined as the concentration of analyte giving signals equivalent to three times, the standard deviation of the blank plus the net blank intensity for 100 mL of sample volume, was 0.06 ng mL^{-1}. A comparison of the presented procedure and some previous preconcentration procedures for Hg(II) determination in the literature are given in Table II.

The accuracy of the method was further validated through analyzing the standard reference material (GBW 08619, water). The analytical results for the standard material are in good agreement with the certified values.

Application of the chelating resin modified by carbon bisulfide

As a valid adsorbent for preconcentration and removal of Hg(II), the prepared chelating resin was applied to two water samples, which were collected from environment. The samples were treated by the sample procedure above. Then, these solutions were passed through the column system and the concentration of Hg(II) was determined in the same way as described previously. The obtained results as well as the recovery tests are listed in Table III. The results indicate the suitability of the present chelating resin for removal of Hg(II) from environment.

CONCLUSIONS

In this article, we prepared a novel macroporous resin by epoxy resin and TETA through a polymerization with phase separation. In the preparation process of polymer, the PEG-1000 was used as solvent at initial stage and phase-separation reagent at later stage of polymerization reaction. Then, the macroporous resin was modified by carbon bisulfide and soaked in 1 mol L^{-1} NaOH. The SEM image showed that the macroporous structure assuredly existed and was retained during the preparation steps. The results of FTIR spectra and the elemental analysis obviously show that carbon bisulfide has adequately reacted with amidogen groups of the epoxy-TETA resin. Moreover, the prepared chelating resin was applied to two natural samples and got satisfactory results. The prepared resin has shown

TABLE III
Removal and Determination of Hg(II) Ions from Two Natural Samples from Ningbo Region, Zhejiang Province, People's Republic of China

Sample[a]	Waste water sample	River water sample
Hg(II) found (μg L^{-1})	42.3 ± 0.28	4.3 ± 0.18
Recovery (%)	99.4	98.9

[a] Repeated three times.

an excellent adsorption characteristic for Hg(II). The results here show that the macroporous resin prepared via a simple method had a remarkable adsorptive capability for Hg(II) ions and can be used as adsorbent for preconcentration and removal of trace Hg(II) in aqueous solution.

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