Preparation and Adsorption Selectivity for Hg(II) and Ag(I) of Chelating Resin Immobilizing Benzothiazolyl Group on Crosslinked Polystyrene via Hydrophilic Sulfur-Containing PEG Spacer

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ABSTRACT: A new chelating resin incorporating 2-mercaptobenzothiazole (MBZ) into macroporous chloromethylated polystyrene via hydrophilic spacer of polyethylene glycol containing sulfur was synthesized. The resin was characterized by elementary analysis and infrared spectra. The adsorption capacity of the resin for Ag^+, Hg^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} as a function of pH was determined. The effects of interference ions, such as Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}, on percent recovery were also investigated. The results showed that the resin could effectively remove Hg^{2+} and Ag^+ from solutions containing a large excess of Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}. In column operation, it was observed that Hg^{2+} and Ag^+ in trace quantities were effectively removed from binary metal ions. The percent recovery of the resin for Hg^{2+} and Ag^+ was >98.6% and >97.5%, respectively. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 5034–5038, 2006

Key words: chelating resins containing heterocyclic functional groups; spacer; adsorption

INTRODUCTION

Metal ions are nonbiodegradable in nature and their intake at a certain level is toxic, so it is necessary to design new materials that can effectively remove and recover toxic metal ions from aqueous solution. Chelating resins with covalently bonded functional groups containing nitrogen and sulfur atoms possess excellent adsorption and selectivity properties for metal ions, especially for heavy metal ions.[1–5] Such heterocyclic functional groups[6–17] as pyridine, imidazole, thiazole, and pyrazole, etc. show high affinity for silver and mercury; the earlier reports[18–20] have shown the usefulness of the chelating resins anchoring heterocyclic functional groups to polymeric support for the separation of Hg^{2+} and Ag^+ in trace quantities from geological, medicinal, and environmental samples.

The recent literatures report that the introduction of spacer arm containing oxygen between functional group and polymeric matrix can enhance the hydrophilicity of the chelating resin and increase the adsorption capacity of the chelating resin.[21,22]

In this study, we synthesized a novel chelating resin by incorporating 2-mercaptobenzothiazole (MBZ) into macroporous chloromethylated polystyrene via hydrophilic spacer arm of polyethylene glycol containing sulfur. Its structure was characterized by infrared spectra and elementary analysis. The adsorption properties and the percent recovery of the resin toward some metal ions were also investigated.

EXPERIMENTAL

Materials and methods

The macroporous chloromethylated polystyrene (degree of crosslinking 10% DVB, chlorine content 19.85%) was supplied by Chemical Factory of Nankai University of China. 2-(2-chloroethoxy) ethanol was purchased from Aldrich Chemical Co. and used as
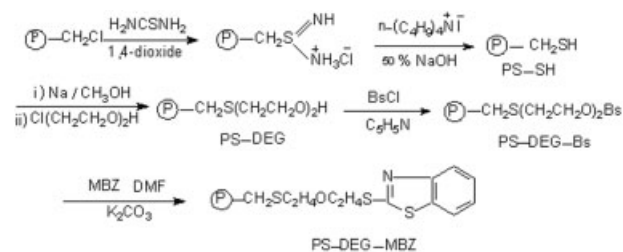
Scheme 1. Synthetic route of the resin.

received. Benzenesulfonyl chloride (BsCl), 2-mercaptobenzothiazole (MBZ), tetrabutyl ammonium iodide, thiourea, methanol, tetrahydrofuran, 1,4-dioxide and other reagents, solvents were of analytical grade quality and were used without further purification.

The content of S and N elementary analyses were carried out by central laboratory of Shandong University. The infrared spectra were recorded on a Nicolet MAGNA-IR550 (series II) spectrometer. The adjustment of pH was made on microprocessor pH meter (Model pH211).

Stock solutions of all the metal ions were prepared by dissolving appropriate amounts of analytical grade nitrates in distilled water and standardized with EDTA solution. The concentration of Ag^+, Hg^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} was determined on a GBC-932 atomic absorption spectrophotometer.

Preparation of the resin

The synthetic route of the intermediates and the resin was shown in Scheme 1.

PS-SH was synthesized according to the literature.[23] PS-DEG (4.92 g) was obtained according to the following procedure: 0.75 g sodium were added to a mixture of 20 mL of methanol and 20 mL of dioxide, after the reaction was over, 4.0 g PS-SH was added, and the entire mixture was shaken at room temperature overnight. Then, 5.0 g 2-(2-chloroethoxy)ethanol was added, and the mixture was then stirred at 50°C for 24 h. The polymeric beads were filtered and washed with distilled water and ethanol, and dried. PS-DEG-Bs was synthesized according to the following procedure: PS-DEG (4.3 g) together with 100 mL of pyridine was cooled in an ice-water bath, and 9 mL of BsCl was added dropwise. The mixture was stirred at room temperature for 24 h, and then the reaction were filtered and washed with distilled water and ethanol, and dried; 5.02 g of PS-DEG-Bs was obtained. At the last step, PS-DEG-Bs (5 g), 2-mercaptobenzothiazole (3.07 g), and K_2CO_3 (0.85 g) were suspended in DMF (80 mL), the reaction was stirred at 85°C for 24 h, the reaction was then filtered off and thoroughly washed with distilled water and ethanol, and dried; 5.70 g of PS-DEG-MBZ was obtained.

Water regain[24]

Water regain was defined as the amount of water absorbed by 1 g of polymer. It was measured according to the method: approximately 1 g of the resin was stirred in double-distilled water for 48 h, then filtered off by suction, weighted, dried at 100°C for 48 h. After cooling in a desiccator, the resin was reweighed. The water regain was calculated as $(m_w - m_d)/m_d$, where m_w was the weight of water swollen polymer, m_d was the dry weight.

Adsorption capacity

Adsorption capacities of the resin for different metal ions were determined by batch method. To a 50-mL glass bottle fitted with stopper, 50 mg of the resin, 18 mL of the perchloric acid of desired pH value, and 2.0 mL of 0.2 mol L^{-1} metal ion solution were added. After a shaking time of 20 h at 25°C, the solutions were separated from the adsorbent and the concentrations of metal ions were determined by means of AAS. The adsorption capacities were calculated according to eq. (1):

$$Q = \frac{(C_0 - C)V}{W} \tag{1}$$

Where Q is the adsorption amount (mmol/g); C_0 and C are the initial concentration and the concentration of metal ion in solution when the adsorbent is separated (mmol/mL); V is the volume (mL); and W is the dry weight of resins (in grams).

Desorption of metal ion

The resins-adsorbed metal ions were shaken with certain volume of desorbents for 1 h, after filtration, the concentrations of the effluents were determined by means of AAS. In this study, 10% thiourea in 0.1M $HClO_4$ and 5% thiourea in 0.1M $HClO_4$ were used for the desorbents of Ag^+ and Hg^{2+}.

Adsorption kinetic

The adsorption rate curve of the resin for the Hg^{2+} and Ag^+ were studied at the corresponding pH of maximum adsorption. The time taken for 50% uptake of metal ions ($T_{1/2}$) was determined. The experiments were carried out by shaking 50 mg of the resin with 18 mL of the perchloric acid of desired pH value and 2.0 mL of 0.2 mol L^{-1} metal ion solution at 25°C. At predetermined time intervals, the solutions were separated from the adsorbent. The concentration of metal ions was decided using the AAS. The adsorption amounts were calculated according to eq. (1).

TABLE I
Elemental Analysis, Functional Group Capacity, and Percent Conversion of Functional Group
of Precursors and the Resin

Polymer	Sulfur (%)	Nitrogen (%)	Functional group capacity (mmol FG/g)	Percent conversion of function group (%)
PS-SH	16.92	0.477	5.12	93.15
PS-DEG	12.54	0.310	3.97	77.53
PS-DEG-MBZ	19.62	3.522	3.67	92.44

Effect of diverse metal ions on adsorption capacities

To a 50-mL glass bottle fitted with stopper, containing 100 mg of the resin, 20 mL of standard solutions of Hg^{2+} or Ag^+ (10 μg mL^{-1}) and 25 mL of standard solutions containing the alkali and alkaline earth metal ions (Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}) (80 μg mL^{-1}) as interference were added; after a shaking time of 20 h, the resins-adsorbed metal ions were separated and completely eluted with desorbents; the concentrations of the effluents were determined using the AAS method.

Separation of Hg^{2+} and Ag^+ from several binary mixtures

Separation of Hg^{2+} and Ag^+ from several binary mixtures was performed by batch and column operation. The batch test was same as described earlier except for the amount of the resin was 100 mg instead of 50 mg. In column operation, a 50×5 mm^2 glass column was used. The column was packed with 100 mg resin. In batch operation, a 50 mL solution containing 250 μg of Ag^+ or Hg^{2+} and 500 μg of the competing ions (Cu^{2+}, Zn^{2+} and Pb^{2+}) was shaken for 20 h with 100 mg resin. In column operation, solutions of same amount of binary mixture were percolated through the resin bed at a rate of 0.5 mL min^{-1}.

The resins-adsorbed metal ions were completely eluted with corresponding eluent. The concentrations of Ag^+ or Hg^{2+} in the effluent were measured by means of AAS.

RESULTS AND DISCUSSIONS

Synthesis and characterization of the intermediates and the resin

By comparison with the IR spectrum curve of PS-DEG, the characteristic peak of O—H at 1072 cm^{-1} disappeared in that of PS-DEG-Bs and a series of new peaks involved in PS-DEG-Bs appeared at 1187 and 613 cm^{-1}. These new peaks were assigned the characteristic absorbance of benzenesulfonate,[25] which indicated that the benzensulfonate group was introduced into polymeric matrix. From the IR spectrum curve of PS-DEG-MBZ, we could find that the characteristic

absorption of benzensulfonate had disappeared. The appearance of new peaks at 1456 and 1426 cm^{-1} suggested that benzensulfonate group had been substituted with 2-mercaptobenzothiazole.

According to the data of elementary analysis, the functional group capacity and percent conversion of functional group of intermediates and the resin were listed in Table I.

Adsorption behavior of the resin for metal ions

The adsorption capacities of the resin were tested in aqueous solution for different metal ions by batch method at various pH values. Results for these experiments were summarized in Table II. It was observed that the resin had high adsorption capacities only for Hg^{2+} and Ag^+ over the pH range of 1.0–6.0. The resin exhibited no affinity for Cu^{2+}, Zn^{2+}, and Pb^{2+}, especially for Cu^{2+} and Zn^{2+}.

Under the optimum condition, the sorption rate curve of the resin for the Hg^{2+} and Ag^+ was studied. The sorption rate curves were shown in Figure 2.

The time required for 50% uptake of the maximum capacity for Hg^{2+} and Ag^+ ($T_{1/2}$) was listed in Table III.

According to Brykina method,[26] the adsorption rate constant could be calculated from:

$$-\ln (1-F)=kt$$

where $F = Q_t/Q$, Q_t and Q were the adsorption amounts at sorption time t and at equilibrium, respectively. The slope of straight line that was made by plotting $-\ln(1 - F)$ versus t, yielded the sorption rate

TABLE II
Adsorption Capacity of the Resin for Different Metal
Ions Versus pH (mmol g^{-1})

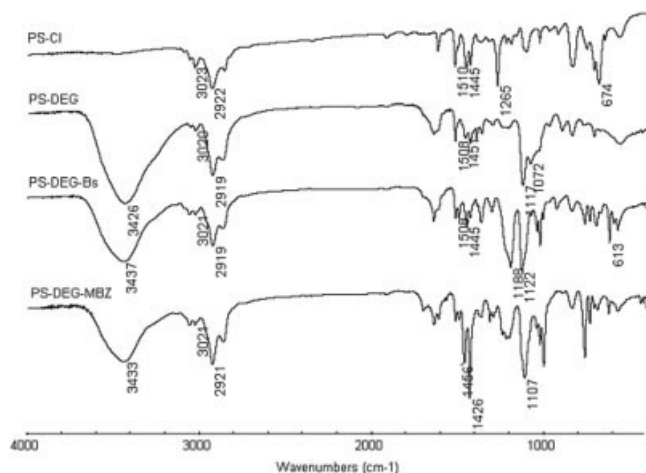| pH	Ag^+	Cu^{2+}	Hg^{2+}	Zn^{2+}	Pb^{2+}
1.0	1.38	0.00	1.37	0.00	0.06
2.0	1.35	0.00	1.16	0.00	0.03
3.0	1.24	0.00	1.35	0.00	0.01
4.0	1.27	0.00	1.44	0.00	0.07
5.0	1.21	0.00	1.23	0.00	0.00
6.0	1.25	0.00	1.35	0.00	0.01

Figure 1 The FTIR spectra of the intermediates and the resin.

k. The sorption rate k of the resin for Hg^{2+} and Ag^+ were 1.46×10^{-4} and 2.1×10^{-4} (s^{-1}). Then, the adsorption processes of PS-DEG-MBZ for Hg^{2+} and Ag^+ at 278 K could be described, respectively, as follows:

$$-\ln(1-F) = 1.46 \times 10^{-4}t \quad R^2 = 0.9890$$

$$-\ln(1-F) = 2.10 \times 10^{-4}t \quad R^2 = 0.9580$$

The water regain value of the resin was found to be 27 mmol g^{-1}, as was to be expected. The water regain of the resin was higher when compared with that of the resin without the spacer arm between polymer matrix and functional group (18 mmol g^{-1}). The improved performance of the resin could be attributed to the introduction of hydrophilic spacer arm of polyethylene glycol.
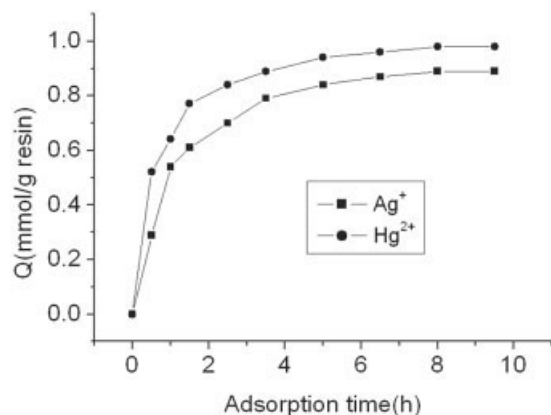

Figure 2 Adsorption rate curve of the resin for Hg^{2+} and Ag^+.

TABLE III
Adsorption Parameter of the Resin for Hg^{2+} and Ag^+

Ion	Adsorption capacity (mmol g^{-1})	Water regain (mmol g^{-1})	$T_{1/2}$ (min)
Hg^{2+}	1.44	27	40
Ag^+	1.38	27	45

The data, including adsorption rate constant, water regain, and $T_{1/2}$ showed that the resin was satisfactory for removing metal ions in column method.

Separation of Ag^+ and Hg^{2+} from alkali and alkaline earth metal ions

Separation of Hg^{2+} and Ag^+ from several binary mixtures with alkali and alkaline earth metal ions at their corresponding maximum absorbance pH was carried out (as shown in Table IV). At pH 4.0, Hg^{2+} solutions (containing 10-fold of alkali and alkaline earth metal ions) were treated with the resin, the percent recovery of Hg^{2+} was 100%. In case of Ag^+, the percent recovery was 97+%. These results indicate that the presence of large excess of alkali and alkaline earth metal ions do not affect the recovery of Hg^{2+} and Ag^+ from acidic solution.

Separation of Ag^+ and Hg^{2+} from other metal ions

The ability to selectively remove particular metal ions from aqueous solution, in a competitive situation, is of utmost importance in designing a resin for environmental remediation applications. The percent recovery of Ag^+ and Hg^{2+} by the resin in the presence of competing metal ions (Cu^{2+}, Zn^{2+}, and Pb^{2+}) was studied by both batch and column method. The results are shown in Table V.

From Table V, it could be seen that the percent recovery of the resin for Hg^{2+}, Ag^+ is >97.5% and >98.6%, respectively. The results show that the resin

TABLE IV
Separation of Ag^+ and Hg^{2+} from Binary Mixtures with Alkali and Alkaline Earth Metal Ions[a]

Diverse ions	Amount of diverse ion (μg)	Ag^+ found (μg)[b] pH = 1.0	Hg^{2+} found (μg) pH = 4.0
Na^+	2000	197 (98.6)	200 (100)
Mg^{2+}	2000	195 (97.4)	200 (100)
Ca^{2+}	2000	200 (100)	200 (100)
Ba^{2+}	2000	200 (100)	200 (100)

[a] The amount of Hg^{2+} or Ag^+ in the binary mixtures was 200 μg.

[b] The data in parenthesis are the percent recovery. It was calculated by formula [finding M^{n+}]/[starting M^{n+}] $\times$ 100.

TABLE V
Separation of Ag⁺ and Hg²⁺ from Other Metal Ions at Corresponding pH of Maximum Adsorption

Metal ions	Recovery (%)	
	Batch method (column method)	
	Ag^+	Hg^{2+}
Cu^{2+}	97.3 (98.6)	97.1 (98.6)
Zn^{2+}	95.2 (97.5)	98.8 (99.0)
Pb^{2+}	97.6 (99.4)	100.0 (99.6)

is selective for removing Hg^{2+} and Ag^+ from acidic solution, even in the presence of twofold excess of competing metal ions.

CONCLUSIONS

A new chelating resin incorporating MBZ into macroporous chloromethylated polystyrene via hydrophilic spacer of polyethylene glycol containing sulfur was synthesized and characterized. The resin was also shown to be selective for Hg^{2+} and Ag^+ even with a large excess of competing metal ions. The presence of diverse metal ions, such as Cu^{2+}, Zn^{2+}, Pb^{2+}, Na^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}, did not affect the adsorption and desorption of Hg^{2+} and Ag^+. This resin can efficiently remove Hg^{2+} and Ag^+ from acidic aqueous solution. The percent recovery of the resin for Hg^{2+} and Ag^+ was >98.6% and >97.5%, respectively. This resin has potential utility for the effective preconcentration and removal of Hg^{2+} and Ag^+ from industrial wastes and seawater.

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