Synthesis and Adsorption Properties of Magnetic Resin Microbeads with Amine and Mercaptan as Chelating Groups

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ABSTRACT: Three magnetic chelating resins containing amino and mercapto groups were prepared by the suspended condensation polymerization of 2-chloroethoxymethyl thiirane with diamines. The magnetic resins were microbeads whose diameter was in the range of 10 to 45 μm. The structure of the resins was characterized by XPS, IR, and elemental analysis. Their adsorption properties for Hg(II), Au(III), Pd(II), Pt(IV), Ag(I), Cu(II), Zn(II), and Pb(II) were investigated. The experimental results show the magnetic resins have high affinity for Hg(II) and noble metal ions. In the competitive adsorption, the resins predominantly adsorbed Hg(II) or Pd(II) in the coexistence of Cu(II), Zn(II), and Mg(II). Desorption of Pd(II) loaded on the resins was studied by using 2*M* hydrochloric acid solution containing 1% thiourea as desorbent. A high desorption ratio (up to 96.5%) was observed, and repeated adsorption/desorption operations showed the probability of repeated use of the magnetic resins. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1587–1592, 2001

Key words: magnetic chelating resins; adsorption; desorption; noble metal ion

INTRODUCTION

Magnetic chelating resins are conveniently used to treat industrial wastewater and recover metal ions because they are easily collected and precipitated rapidly in a magnetic field, which improves the operative technology of recovery and separation.[1,2] Therefore, such polymeric materials continue to attract the attention of many investigators.[3–5] Chelating resins with sulfur and nitrogen as donor atoms usually have excellent adsorption properties for mercury and noble metal ions.[6–8] In particular, the resins containing amine and mercaptan as chelating groups show better selectivity for noble metal ions.[9,10] However, only a few magnetic chelating resins, consisting of amino group and mercapto groups that selectively sorb noble metal ions, have been reported.

In this study, a series of core–shell microbeads of magnetic chelating resins containing amino and mercapto groups were synthesized, and their adsorption properties for Au(III), Pd(II), Ag(I), Pt(IV), Hg(II), Cu(II), Pb(II), and Zn(II) were investigated.

EXPERIMENTAL

Materials

2-Chloroethyl glycidyl ether was prepared by the reaction of epichlorohydrin and 2-chloroethanol

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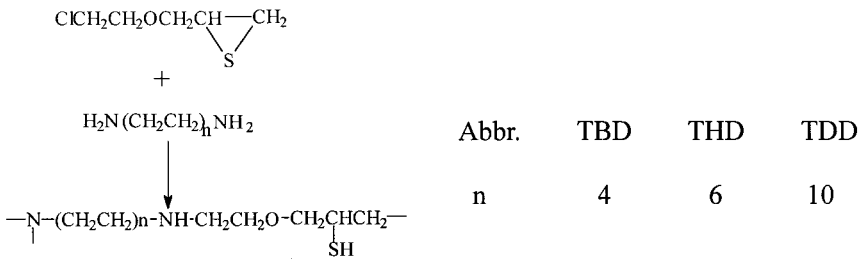

Figure 1 Reaction scheme for the synthesis of polymers and abbreviations for the magnetic resins.

by a previously reported method.[11] 2-Chloroethoxymethyl thiirane (CEMT) was synthesized by the reaction of 2-chloroethyl glycidyl ether and thiourea according to the procedure reported previously.[6] Magnetic particles of γ-Fe_2O_3 (0.1–0.5 μm, magnetization intensity 71.4 emu/g) were obtained from Wuhan Parrot Tape Co. The other starting materials were of reagent grade or higher grade and used without further purification.

Equipment

IR spectra were measured with a Nicolet 60 SXB Fourier transform infrared spectrophotometer (Nicolet Instruments, Madison, WI). Elemental analysis was performed by Perkin–Elmer Model 1106 Elemental analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT). Wide-angle X-ray diffraction patterns were obtained by a D/MAX-IIIA diffractometer (Rigaku, Tokyo, Japan) with a flat-film camera using nickel-filtered CuK_α radiation. A Hitachi 180-80 atomic absorption spectrophotometer (Hitachi, Tokyo, Japan) was used for the determination of the metal ion concentrations in aqueous solutions before and after adsorption. XPS spectra were measured with an ESCALAB (MgK_α II) spectrometer (British VG Scientific, West Sussex, UK). A 9500 VSM magnet analyzer (LDJ Electronics, Troy, MI) was used for the determination of magnetization intensity of the magnetic resins.

Surface Modification of Magnetic Particles

A 10-g sample of magnetic particles (γ-Fe_2O_3) was added to 30 mL ethanol solution containing 2% 3-(2′,3′-epoxypropoxy)propyl trimethoxy silane and stirred for 4 h at room temperature. Then, the mixture was filtered and dried at 80°C for 8 h, after which a black powder was obtained.

Preparation of Magnetic Chelating Resins

CEMT (7.61 g, 50 mmol) and diamine (34 mmol) were poured into a reaction flask and stirred for 2 h at room temperature. Then, magnetic particles (10.0 g) modified with coupling reagent were added and dispersed by high-speed stirring. After that, 40 mL 5% sodium hydroxide solution containing 2% hydroxyl-propyl methylcellulose was added, and the mixture was suspended into small drops. After the 10-h reaction at 75–80°C under nitrogen gas, the product was filtered, washed with water, and extracted with ethanol in a Soxhlet's extractor for 4 h to eliminate unreacted

Table I Synthesis of Magnetic Chelating Resins

Resin	CEMT (mmol)	H_2N—R—NH_2 R	(mmol)	Powder[a] (g)	Yield (%)	Diameter[b] (μm)	Elemental Analysis %C	%H	%N	%S	%Cl
TBD	50	C_4H_8	34	10.0	91	38	25.01	4.43	4.68	7.65	0.84
THD	50	C_6H_{12}	34	10.0	93	30	25.84	4.60	4.52	7.16	0.76
TDD	50	$C_{10}H_{20}$	34	10.0	96	36	31.92	5.59	4.24	6.64	0.63

[a] Magnetic powder with surface modification.
[b] Average diameter.

Table II Characterization of Magnetic Chelating Resins

Resin	Magnetization (emu/g)	—NH—/N (%)	SH Contents (mmol/g)	SH/S (%)	Polymer Contents (%)
TBD	41.5	48.3	1.78	74.5	41.8
THD	39.8	50.6	1.66	74.2	45.5
TDD	34.3	52.8	1.58	76.1	52.0

materials, and then was dried *in vacuo* at 85°C for 24 h. A yellow powder (average diameter 30–38 μm) was obtained. The reaction scheme for polymers and the abbreviations for the magnetic resins are shown in Figure 1. Yields and elemental analysis data for the products are listed in Table I.

Determination of Adsorption Capacities for Single Metal Ions

To 50 mL of an aqueous 1 mg metal L^{-1} solution of Au(III), Pd(II), or Pt(IV) chloride (in 2*M* HCl), 25 mg of magnetic chelating resins was added; to 25 mL of 0.1*M* solution of Ag(I), Hg(II), Cu(II), Zn(II), or Pb(II) nitrate [pH 5.6; Clark–Lubs buffer; Ag(I) in 1*M* HNO_3 or at pH 7], 100 mg of magnetic chelating resins was added. All the mixtures were shaken for 24 h at room temperature. The metal ion concentrations in the filtrate and initial solution were determined by atomic absorption spectrophotometry. Calculated adsorption capacities are shown in Table II.

Determination of Adsorption Selectivity for Metal Ions

Magnetic chelating resin (25 mg) was added to a mixed solution of 50 mL metal ions. For the aqueous system of Pd(II)–Cu(II)–Zn(II)–Mg(II), the concentration of Pd(II) was 2.5 m*M* and that of each of the other metal ions was 0.1 mol/L; for Hg(II)–Cu(II)–Zn(II)–Mg(II), the concentration of each of the metal ions was 0.05 mol/L. Adsorption was performed by the above-described procedure.

Desorption of Pd(II)

Desorption of TBD for Pd(II) was performed in a 0.1 mol/L HCl solution containing 1% thiourea. The magnetic chelating resins–loaded metal ions were placed in this adsorption medium and stirred at 400 rpm for 1 h at room temperature. The final concentration of Pd(II) in the aqueous phase was determined by atomic absorption spectrophotometry. The desorption ratio was calculated from the amount of metal ions adsorbed on the resins and final metal ion concentration in the desorption medium by the following equation:

$$\text{Desorption ratio} = \frac{\text{Amount of Pd(II)desorbed to the elution medium}}{\text{Amount of Pd(II)sorbed on the microbeads}} \times 100$$

RESULTS AND DISCUSSION

Synthesis and Characterization of Magnetic Chelating Resins

Three magnetic chelating resins were prepared by the suspended condensation polymerization of 2-chloroethoxymethyl thiirane and diamines (Fig. 1). Polymer contents in magnetic chelating resins of TBD, THD, and TDD are 41.8, 45.5, and 52.0%, respectively, calculated from the determined magnetization intensity of the magnetic resins (Table II). The XPS spectra of the resins show a lot of *sec*-amines in the resins have changed into *tert*-amines in the condensation reaction (shown in Fig. 2). The ratios of *sec*-N/total-N of the three

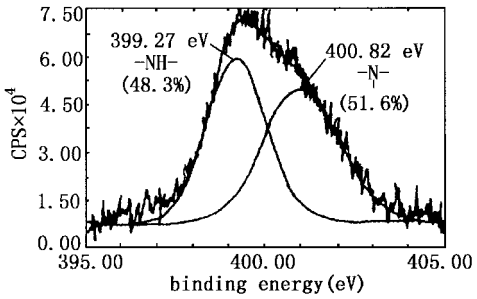

Figure 2 XPS spectrum (N_{1S}) of TBD.

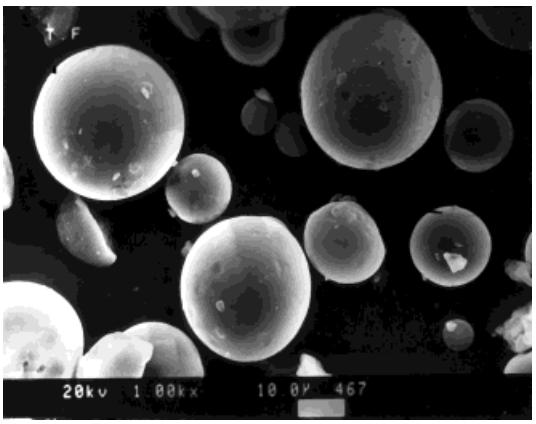

Figure 3 Microphotograph of unmagnetized TBD.

resins are 0.483, 0.506, and 0.528, respectively. This result demonstrates the resins are crosslinked. Furthermore, elemental analysis data of the magnetic resins accord with the resin structure determined by XPS. For example, the tested contents of N and S of TBD are 4.68 and 7.65%, respectively, which are close to the values calculated (N% 4.66, S% 7.47%) from the structure determined with XPS. In IR spectra of the resins, the characteristic absorption peaks of N—H, C—H, and S—H stretching vibrations appear at 3290, 1250, and 2529 cm^{-1} (weak), which are also consistent with the structure of the resins.

Because of the crosslinked structure of the resins, small molecules and other organic components should not be released from the resins in water and common organic solvent. Generally, polymers with crosslinked network structure are nontoxic.[12] In addition, the toxicity of the magnetic chelating resins to animal cells [e.g., dog kidney cell (MDCK) and pig kidney cell (PK-15)] were tested by microcalorimetry using an LKB-2277 bioactivity monitor (LKB Ultrascan XL, Bromma, Sweden) according to the method reported.[13] It was found that the magnetic chelating resins were inert in large dosages (up to 1 mg/mL), although the starting material (CEMT) inhibited the metabolism of the cells in a low concentration of 4 mg/L. This result demonstrates that magnetic chelating resins themselves could not cause pollution in the operation of recovery and separation.

Figure 3 is the microphotograph of unmagnetized TBD. The magnetic chelating resins are microbeads (diameter range of 10 to 45 μm), consisting of a thin polymeric shell and multiple aggregates of the magnetic particles as cores in each microbead, according to the findings of similar research in our earlier report.[2]

Adsorption Properties for Single Metal Ions

The adsorption capacities of the three magnetic resins for Au(III), Pd(II), Pt(IV), Ag(I), Hg(II), Cu(II), Zn(II), and Pb(II) were investigated in different aqueous media, which were chosen in our earlier work (as described in the Experimental section). Results are presented in Table III. It can be seen that the three resins show high affinity for noble metal ions used. The adsorptive ability of the magnetic resins for noble metal ions tested is TBD > THD > TDD, corresponding with the N and S contents of the resins. However, it was found that the adsorption capacity for Au(III) still increased with the adsorptive time after 24 h. The WAXD spectrum of TBD-sorbed Au(III), which accords with the diffractive peaks of crystalline gold, shows that some Au(III) sorbed on the resin was reduced (shown in Fig. 4). In addition, the magnetic resins have high adsorption capacities for Hg(II) and Cu(II), but lesser capacities for Pb(II) and Zn(II).

Table III Adsorption Capacities for Metal Ions (mmol/g)

	Metal Ion								
	In 2*M* HCl			Ag(I)		At pH = 5			
Resin	Au(III)[a]	Pd(II)	Pt(IV)	In 1*M* HNO_3	At pH = 7	Hg(II)	Cu(II)	Zn(II)	Pb(II)
TBD	4.55	2.44	1.49	1.78	3.69	3.86	1.34	0.58	0.31
TBD	4.24	2.27	1.27	1.66	3.41	3.02	1.05	0.42	0.22
TBD	3.36	2.16	1.11	1.58	2.94	2.81	1.06	0.68	0.34

[a] Au(III) was reduced.

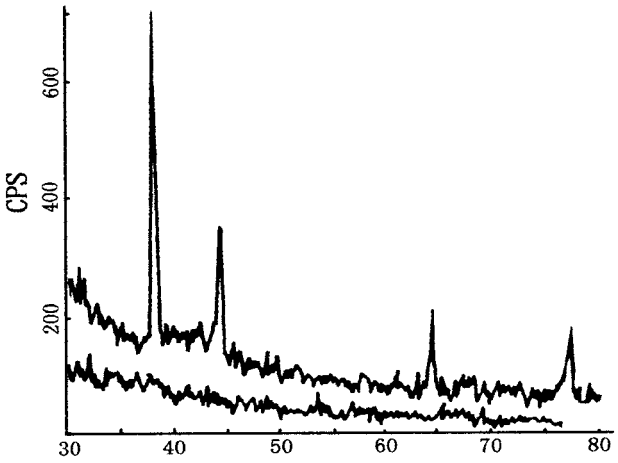

Figure 4 WAXD of TBD-sorbed Au(III).

Adsorption Selectivity of the Three Resins

Table IV shows that TBD, THD, and TDD possess excellent adsorption selectivity for Pd(II) in the presence of Cu(II), Zn(II), and Mg(II). This could be applied in the separation or concentration of Pd(II) in aqueous systems containing transition metal ions, such as Cu(II), Zn(II), and Pb(II).

The adsorption selectivity for Hg(II)–Cu(II)–Zn(II)–Mg(II) in 0.05*M* solution of each of the metal ions at pH 5 was also studied. As shown in Table V, the magnetic resins predominantly adsorbed Hg(II) in the coexistence of Cu(II), Zn(II), and Mg(II). Therefore, they could be used to remove hazardous mercury from wastewater, especially from an aqueous system with suspended substance from which the magnetic resins are conveniently collected and separated under an extramagnetic field.

Desorption of TBD for Pd(II)

The desorption of the adsorbed Pd(II) from microbeads of TBD was investigated with 2 mol/L hydrochloric acid solution containing 1% thiourea as desorption agent. The desorption ratio of the microbeads carrying maximum amounts of Pd(II) was very high (up to 96.5%).

To obtain the reusability of the magnetic resins, the adsorption–desortion cycle was repeated five times by using the same adsorbent. The result listed in Table VI demonstrates that the desorption ratio did not significantly change during repeated adsorption–desorption operations.

Table IV Adsorption Selectivity for Aqueous Solution Containing Pd(II), Cu(II), Zn(II), and Mg(II) at pH = 1

	Adsorption Capacity (mmol/g)			
Resin	Pd(II)	Cu(II)	Zn(II)	Mg(II)
TBD	2.45	0.06	0.05	0
THD	2.21	0.08	0	<0.01
TDD	2.10	0.02	0.02	0

Table V Adsorption Selectivity for Aqueous Solution Containing Hg(II), Cu(II), Zn(II), and Mg(II) at pH = 5

	Adsorption Capacity (mmol/g)			
Resin	Hg(II)	Cu(II)	Zn(II)	Mg(II)
TBD	3.64	0.13	0.01	0.01
THD	3.00	0.21	0	0
TDD	2.91	0.08	0	0

CONCLUSIONS

Three magnetic resins with amine and mercaptan as chelating groups were prepared by the suspended condensation polymerization of 2-chloroethoxymethyl thiirane and diamines, and the structures of the resins were characterized by XPS, IR, and elemental analysis. Their adsorption properties for Au(III), Pd(II), Pt(IV), Ag(I), Hg(II), Cu(II), Zn(II), and Pb(II) were also studied. The magnetic resins show high affinity for noble metal ions and Hg(II), and predominantly adsorbed Pd(II) or Hg(II) in the coexistence of Cu(II), Zn(II), and Mg(II). Therefore, they would be useful for the separation and concentration of noble metal ions or environmental pollution treatment from aqueous systems with suspended substance because of the convenient operation of magnetic chelating resins in an extramagnetic field.

Table VI Desorption Ratio of TBD for Pd(II)

Times	1	2	5
Ratio (%)	96.5	95.4	94.2

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