Synthesis and Characterization of Chelating Resins with Amino Moieties and Application on Removal of Copper(II) from EDTA Complexes

Cheng-Chien Wang,[1] Chun-Chih Wang[2]

[1]Department of Chemical Engineering, Southern Taiwan University of Technology, Tainan 710, Taiwan, Republic of China
[2]Department of Environmental Engineering and Health, Chia-Nan University of Pharmacy and Science, Tainan 717, Taiwan, Republic of China

ABSTRACT: Strong-field ligands (amino moieties) are introduced into a hydrogel resin to obtain a chelating resin via inversion suspension polymerization. The characteristics of chelating copolymers are measured by using Fourier transform IR spectroscopy (FTIR), elemental analysis (EA), and scanning electron microscopy (SEM). After chelating copolymers adsorb cupric ions, the absorption peak of stretch N—H is shifted to higher frequency because of a coordination reaction from the FTIR spectra. Furthermore, the mechanism of metal complex adsorption on the chelating copolymer is that the strong-field chelating ligand decomposes the bonding of the metal complexes and recoordinates the cupric ion to a chelating polymer, which is examined via FTIR, SEM with EA, and ionic chromatography analysis. The maximum adsorption capacity of cupric ions is 1.08 mmol/g and the adsorption capacity increases with the increase of the pH of the solution. The stability constant of the Cu chelating copolymer is $10^{18.72}$, and it can have competition adsorption with EDTA in aqueous solution. These amino chelating copolymers can be used not only to recover metal ions but also to move anion pollution in wastewater. It is interesting that parts of the cupric ions adsorbed on the chelating copolymer are reduced into cupreous ions and/or copper atoms after electron spectroscopy for chemical analysis measurement. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2457–2468, 2005

**Key words:** metal–polymer complexes; ion exchangers; hydrogel

INTRODUCTION

Chelating agents are widely used in the electroplating process.[1,2] The main function of the chelating agent is to stabilize the metal ions so that the electroplating can remain stable within a wide pH range. Thus, chelating agents in wastewater that frequently coexist with metal ions exhibit little or no tendency to be transferred to a metal hydroxide precipitate[3] in a high pH solution or to a chelating polymer (ion-exchange resins)[4–6] in an environmental treatment. Toxic heavy-metal ions are well known for their serious harm to human health. If the toxic metal ions can be recovered, the energy and material requirements of the wastewater treatment process can be simpler. Therefore, the development of high-performance chelating resins for removing heavy-metal ions from wastewater is considered not only as a research priority in the environmental field[7] but also as an area of interest in organic catalysts,[8–10] recovery of valuable trace metal ions,[11] the bioseparation field,[12] and so forth.

Commercially available chelating polymers are typically manufactured as porous microspheres. The active surface is unavailable in the fine pores of porous sorbents when large solute molecules or suspensions are present in wastewater. Hence, Kálalová et al.[13] prepared a water-swellable copolymer of glycidyl methacrylate (GMA)–ethylene dimethacrylate with an ethyl amine ligand to overcome this problem. In addition, Matejka and Zitkova[14] prepared a polyacrylamide that had oligo(ethyleneamine) moieties and pointed out those were able to effectively remove heavy-metal cations from neutral and alkaline solutions containing a strong chelating agent (EDTA). Moreover, Matejka and Zitkova[14] also proposed that the alkaline earth-metal cations did not coordinate to amine nitrogen atoms. Therefore, they did not affect the heavy-metal adsorption of chelating resins. This result was also proved by our previous study.[7] Consequently, the high metal stability constant of chelating hydrogel resins containing the strong-field ligand, pentaethylenehexamine (PEHA), was synthesized by
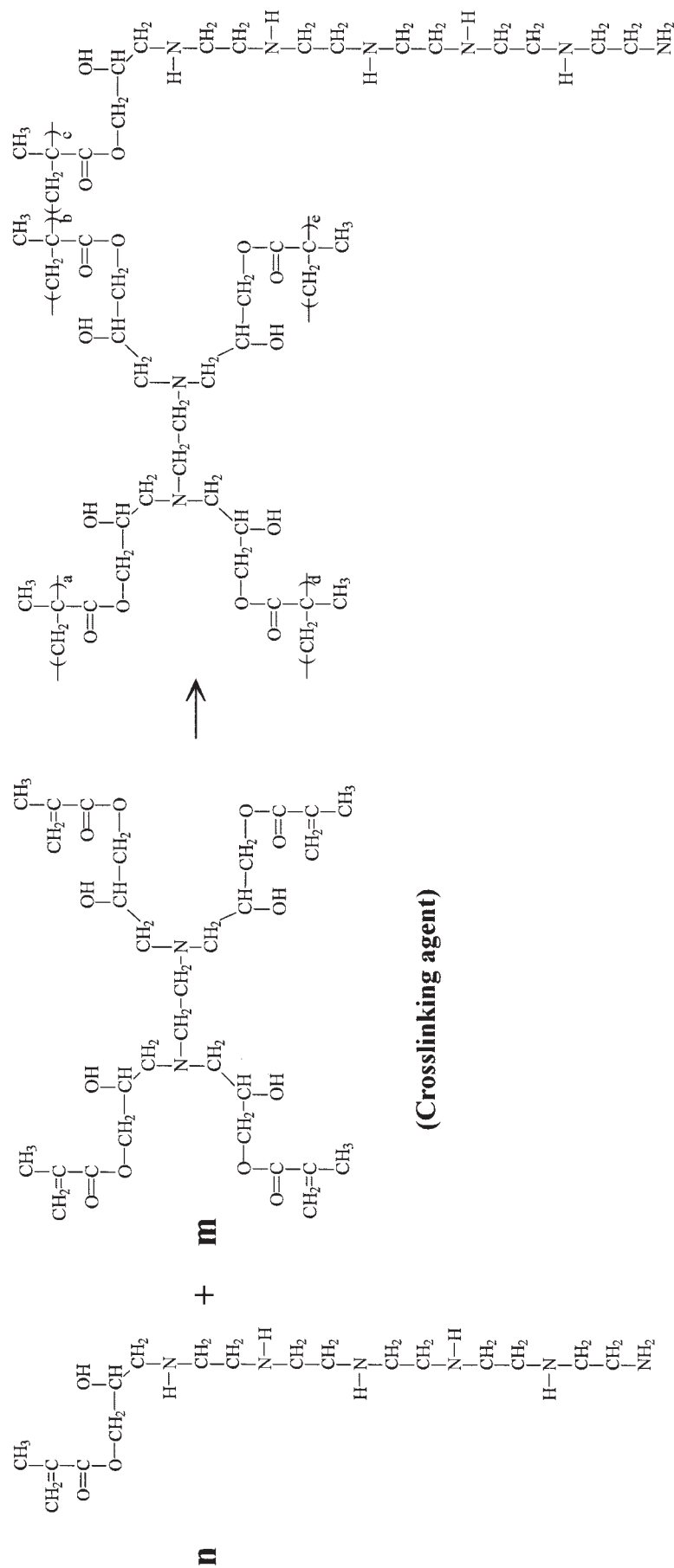
Scheme 1 The polymerization process of chelating hydrogel resins.

Symbol	Group	Chemical shift δ(ppm)
(1)	-CH$_3$	1.9
(2)	=CH$_2$	6.1、5.7
(3)	-CH$_2$-	4.5
(4)	-CH	4.2
(5)	-CH$_2$-	4.0
(6)	-NH	3.0
(7)	-OH	3.4
(8)	-CH$_2$-	2.7
(9)	-CH$_2$-	2.8
(10)	-CH$_2$-	2.9
(11)	-CH$_2$-	3.0

Figure 1 The ^{1}H-NMR spectrum of the chelating monomer.

EXPERIMENTAL

Preparation of chelating copolymer

GMA (Fluka Co. Ltd.) was purified by the distillation method. Copper(II) sulfate pentahydrate (Aldrich Co. Ltd.), disodium EDTA (EDTA-2Na$^+$, Ishisu Pharm. Co. Ltd.), ethylenediamine (ED, Fluka Co. Ltd.), and PEHA (Fluka Co. Ltd.) were used as received. The water-soluble acrylate monomer and crosslinking agent with an amino moieties chelating group were prepared from GMA reacted with PEHA and GMA reacted with ED at 60°C, as shown in Scheme 1. Then, the inversion polymerization of acrylate monomers[6,7] with an amino moieties chelating group was conducted in a 1-L, five-necked Pyrex kettle equipped
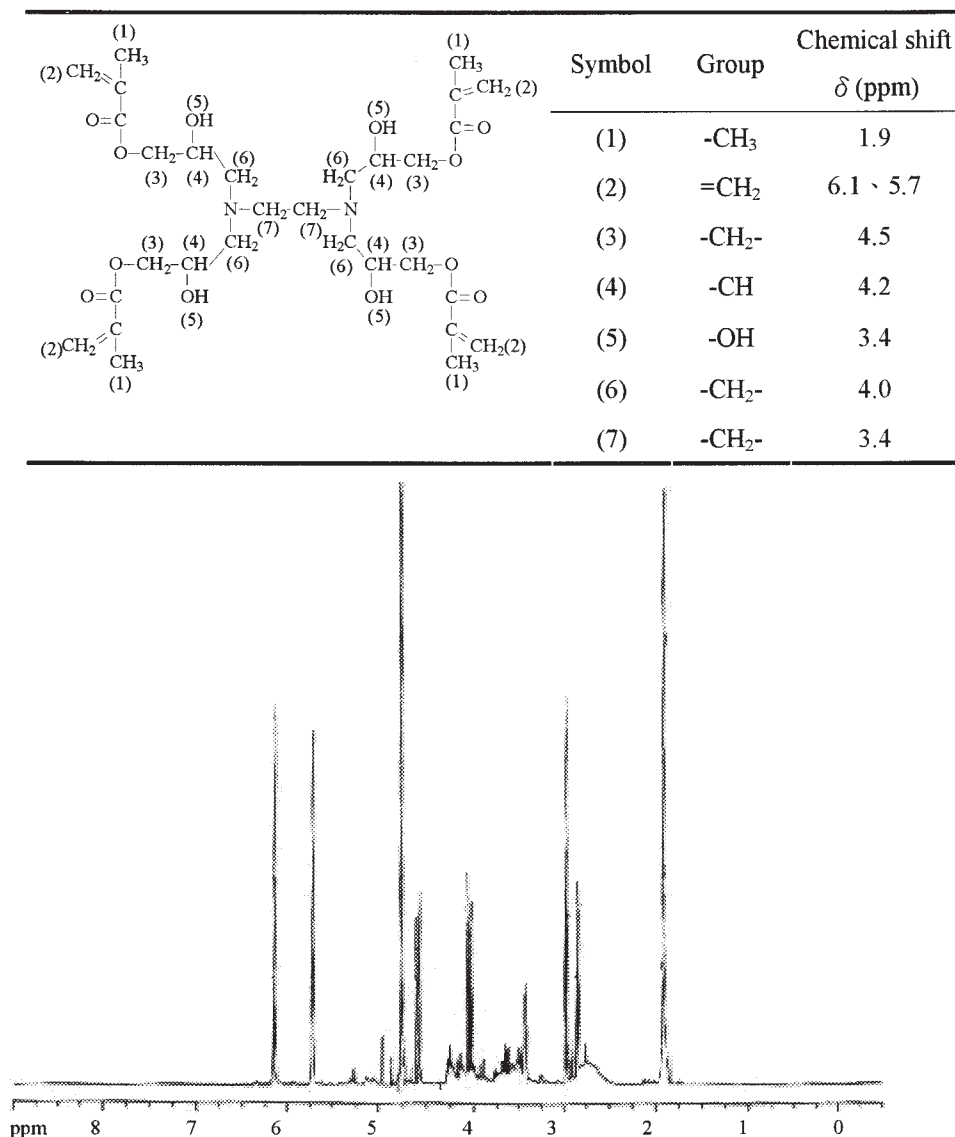
using inversion copolymerization in this study. The mechanism of the competition adsorption with the EDTA chelating agent and the stability constant were further investigated.

Symbol	Group	Chemical shift δ (ppm)
(1)	$-CH_3$	1.9
(2)	$=CH_2$	6.1、5.7
(3)	$-CH_2-$	4.5
(4)	$-CH$	4.2
(5)	$-OH$	3.4
(6)	$-CH_2-$	4.0
(7)	$-CH_2-$	3.4

Figure 2 The ^{1}H-NMR spectrum of the crosslinking agent.

with a stirrer, condenser, nitrogen inlet, and thermister. Potassium persulfate (0.3 g, Ishisu Pharm. Co. Ltd.) was used as an initiator. Toluene (300 mL, Merck Co. Ltd) and Span 60 (3 g, Ishisu Pharm. Co. Ltd.) served as suspension solvent and suspension agent, respectively. The reaction temperature was kept at 70°C. After cooling, the polymeric beads were separated from the polymerization medium by filtration and then washed with distilled water and methanol several times. The purified polymer was dried in a vacuum at 30°C to constant weight. The diameter of the polymeric beads (100–250 μm) was obtained by using a sieve.

Characteristics of chelating copolymer

A Fourier transform IR (FTIR) spectrophotometer (Bio-Rad Co. Ltd.) was employed to identify the functional groups of the chelating copolymer before and after metal ion adsorption. The samples were prepared by mixing with approximately 100 mg of dry, powdered KBr and pressing to form pellets. The contents of chelating functional groups in the copolymer were recorded by using an elemental analyzer (EA, HERAEUS CHN-O rapid analyzer). The metal ion dispersion and morphology of chelating copolymer particles were recorded by scanning electron microscopy (SEM; Hitachi S-4100 field emission scanning electron microscope, operating at 15.0 kV) with an energy dispersive spectroscopy (EDS) X-ray spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB Mark II system with Mg Kα radiation.

NMR measurement

The chelating monomers were characterized by the solution NMR technique (Bruker AMX-200 FT-NMR
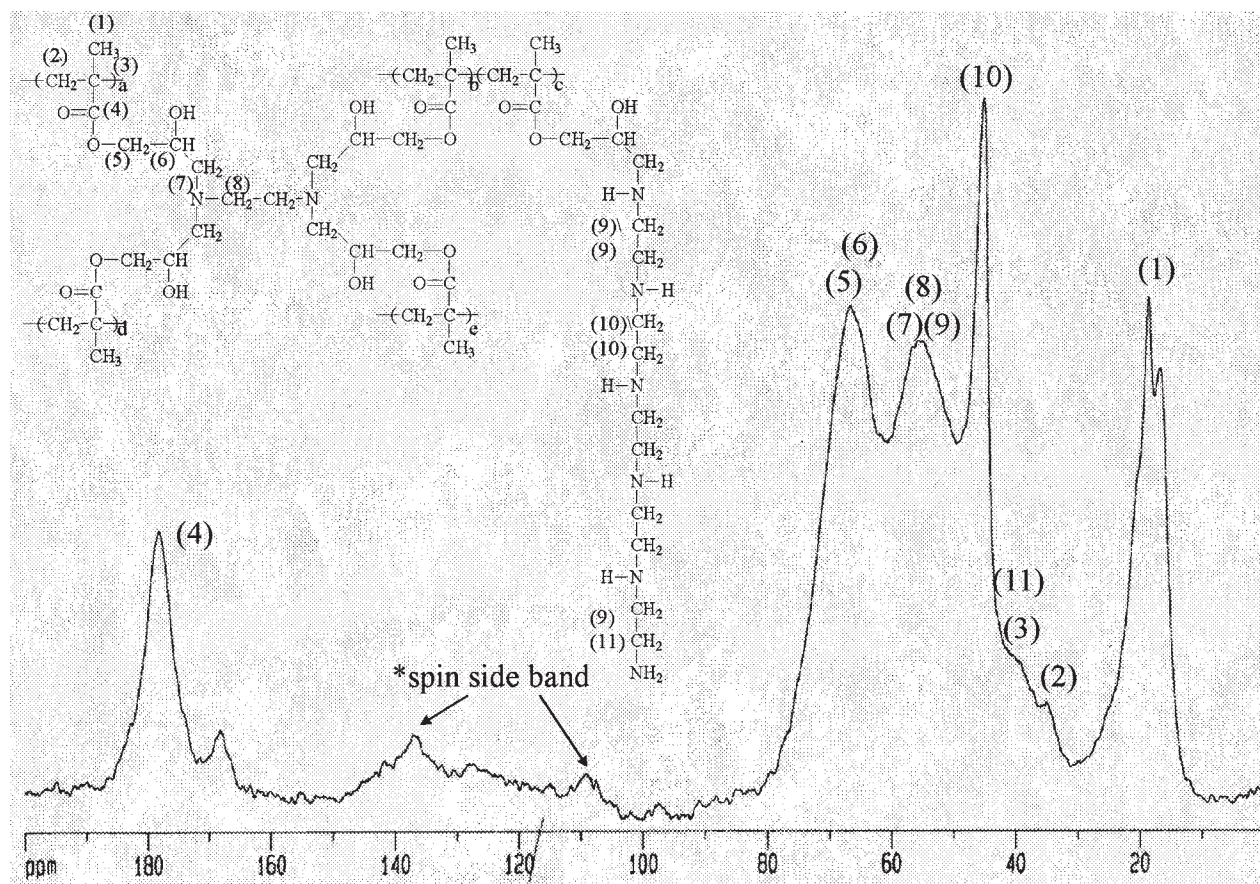
Figure 3 The CP/MAS ^{13}C-NMR spectra of the chelating hydrogel resin.

spectrophotometers), and D$_2$O was used as the solvent. For the chelating copolymers, solid-state NMR experiments were carried out on a Bruker AVANCE 400 spectrometer with an operating frequency of 100.61 MHz for the ^{13}C nucleus and 400.13 MHz for the ^{1}H nucleus at a constant temperature of 300 K throughout all experiments. The ^{13}C spectra were derived by performing cross polarization with magic angle spinning experiments, which use the Hartmann–Hahn transfer technique, and proton decoupling during acquisition to enhance the sensitivity of the spectra. The recycle delay time was 5 s. The 90° pulse width for ^{1}H excitation was 4 m, which corresponds to a B$_{1,H}$ field strength of 62.5 kHz, a contact time of 2 ms, an acquisition time of 0.0336 s, and a spectral width of 303 ppm for 560 scans at a spin rate of 7 kHz. The magic angle spinning frequency of tetramethylsilane was consistently used as the reference frequency for both the carbon and proton spectra.

Adsorption experiment

A fixed amount of dry chelating resin (0.1 g) and 50 mL of cupric ions (CuSO$_4$, Merck Co. Ltd.) or Cu–EDTA complex solution was placed in a thermostated

oscillation bath for 48 h for an isothermal adsorption experiment. After filtration, the concentration of cupric ions was measured by an atomic adsorption spectrophotometer (AA model 932, GBC Co. Ltd.). The amount of metal ions adsorbed (q_e, mmol/g) was obtained as follows:

$$q_e = \frac{(C_0 - C_e)V}{g}$$

where C_0 and C_e are the initial and equilibrium solution concentrations (mmol/L), respectively; V is the volume of solution (L); and g is the weight of the chelating resin (g).

RESULTS AND DISCUSSION

Characteristics of chelating monomers and resins

Figures 1 and 2 display the ^{1}H-NMR spectra of the GMA-PEHA chelating monomer and the GMA-ED crosslinking monomer, respectively. The characteristic peaks of the chelating monomers are assigned and shown in Figures 1 and 2. The ^{1}H chemical shifts at 6.1 and 6.7 ppm are the proton of ethylene (C=C) and the
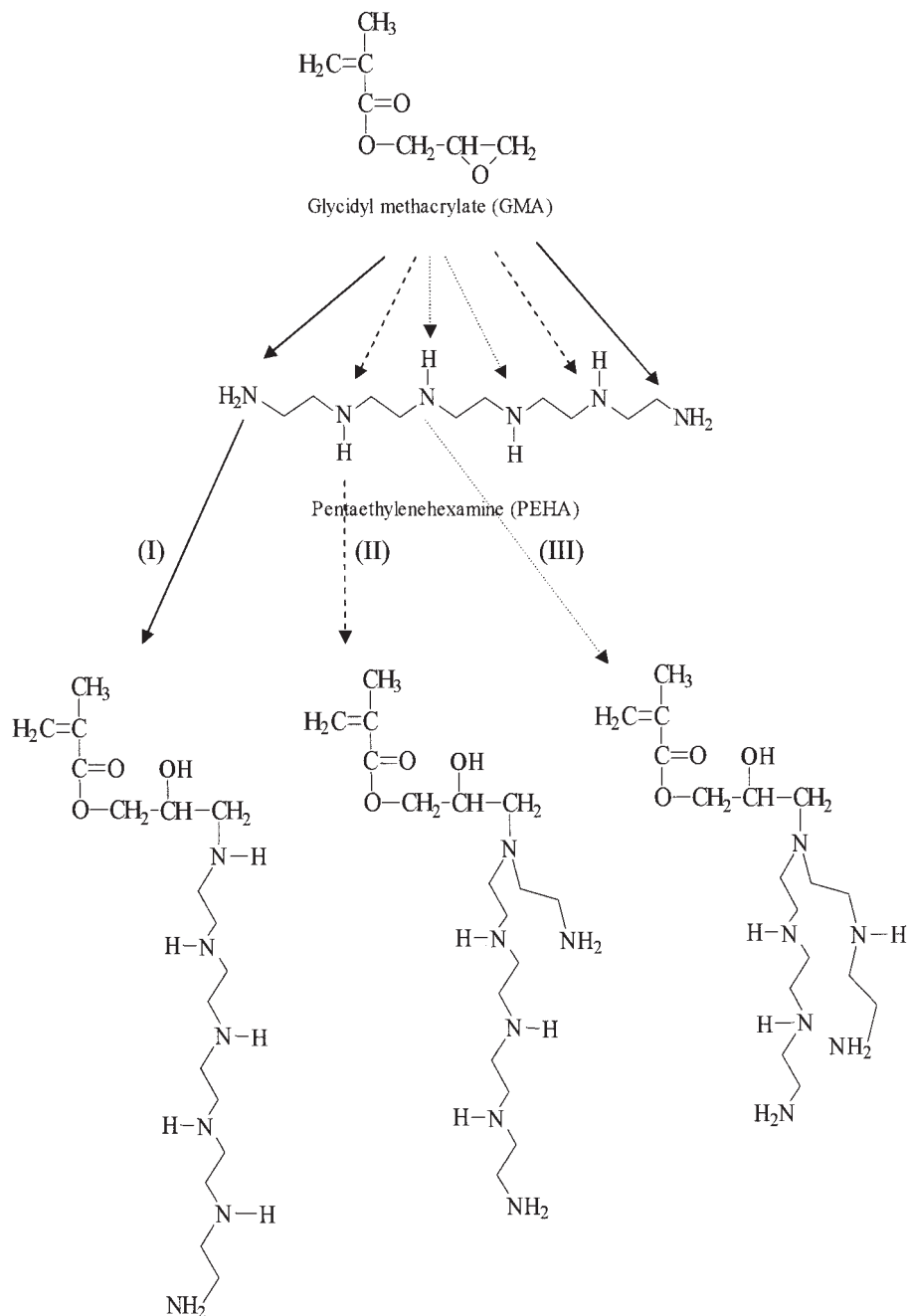
Scheme 2 The possible active aminogroup in PEHA reacted with the epoxy ring on GMA.

[1]H chemical shifts at 2.7–4.0 ppm are correlated from the amino moiety functional groups. These results illustrate that the chelating monomers and crosslinking monomers are obtained and both chelating monomers can be dissolved in water.

Figure 3 displays the solid-state (cross polarization with magic angle spinning) ^{13}C-NMR spectra of the chelating resin and the peak assignments. Observe that the characteristic peaks of the amino moiety appear in the spectrum of the hydrogel resin. In addition, the results of the EA, including nitrogen (7.4 wt %), hydrogen (8.5 wt %), and carbon (51.4 wt %), are consistent with the original recipe. Thus, the chelating resin was successfully prepared by this process. Because the PEHA includes primary and secondary amines, the stability constant of the chelating copolymer depends on the active sites of the amino group, which will react with the epoxy ring of the monomer. Scheme 2 depicts that the active amino groups of PEHA may react with the epoxy ring of the side chain of the monomer. Among them, structure (I) generally has the highest stability constant. Therefore, the stability constant of the copolymer may be determined from the ratio of structures (I), (II), and (III). Unfortu-
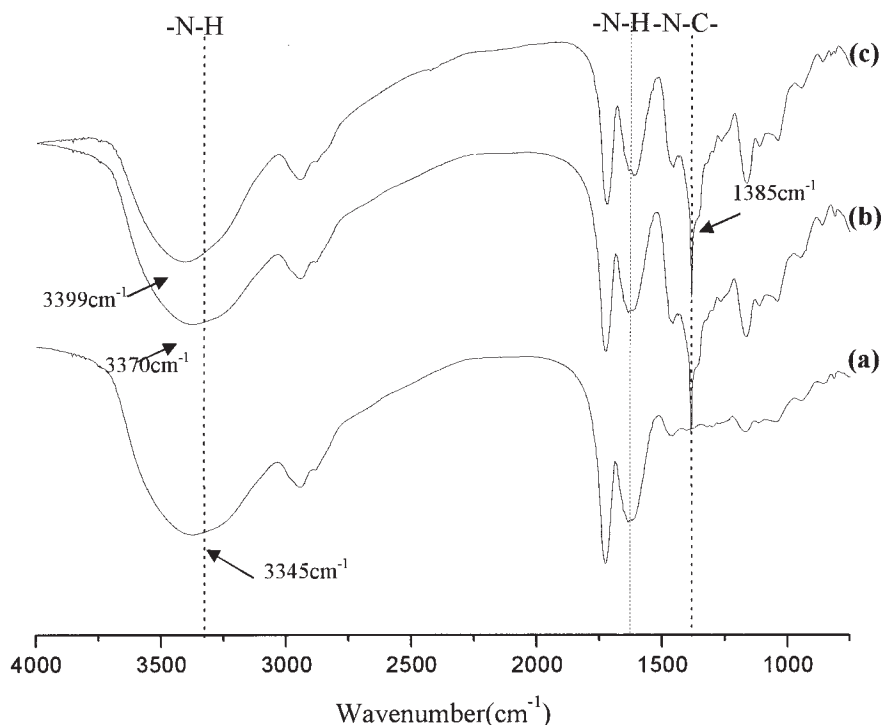
Figure 4 FTIR spectra of the chelating hydrogel resin before cupric ions are adsorbed (spectrum a), after cupric ions are adsorbed (spectrum b), and after Cu-EDTA is adsorbed (spectrum c).

nately, this determination is difficult because the characteristic peaks of the secondary and tertiary amines overlap seriously, as shown in Figures 1–3. We did not deconvolute the peaks to realize the ratio of each structure, but we believe that the grafting of PEHA on the side chain of the hydrogel copolymer involves all of the structures in Scheme 2. Therefore, the stability constant of the hydrogel resin will be related to the ratio of three structures.

Characteristics of chelating metal-complex uptake by resins having amino moiety

Figure 4 displays the IR spectra of chelating copoly(GMA-divinylbenzene-hydroxyethylmethacrylate-*graft*-PEHA) before and after the adsorption of a cupric ion and the cupric complex. The N—H group absorption bands at 1600 and 3345–3412 cm^{-1} are shifted to higher frequency when the cupric ion or Cu–EDTA is adsorbed, and an obvious triamine absorption band is observed at 1385 cm^{-1}, as shown in Figure 4(b,c). This result is attributable to coordinate bonding between cupric ions and a long pair of amino groups in chelating copolymers. Notably, the FTIR spectrum shows no characteristic absorption peak of EDTA [Fig. 4(c)]. Obviously, the metal complexes adsorbed onto the chelating copolymer are the stronger chelating copolymers, forcing the metal to release to EDTA, and the recoordination of the released cupric

ion into the chelating polymer. This spectral result is consistent with Matejka and Zitkova.[14] Moreover, other anions should replace EDTA around the copolymer beads because the chelating copolymer beads are electrically neutral. Some anion detecting experiments were conducted to establish this mechanism, as shown in Figures 5 and 6. Figure 5 exhibits the morphology of chelating copolymer beads after the cupric–EDTA complex has been adsorbed. The EA of the cross section inside the chelating copolymer beads was also performed by using an EDS spectrometer, as shown in Figure 5(c,d). Figure 6 presents the detection of the residual sulfate and chloride anion in the filtrate. Figure 5(b) shows small crystalline particles inside the chelating copolymer beads after the cupric ions have been adsorbed. The energy dispersive X-ray spectra in Figure 5(c,d) also demonstrate that elemental sulfur is really adsorbed into the chelating copolymer beads. In addition, the residual concentration of sulfate anions, which was measured by ionic chromatography (IC), is reduced 85 wt % by the chelating copolymer beads from the cupric isothermal adsorption experiments, which is depicted in Figure 6. In order to identify anion adsorption phenomena, 100 ppm NaCl was added into the isothermal adsorption system and the residual concentration of chloride anions was also measured by IC. The residual concentration of chloride anions obviously decreases with the increase in the amount of chelating resin, as shown in
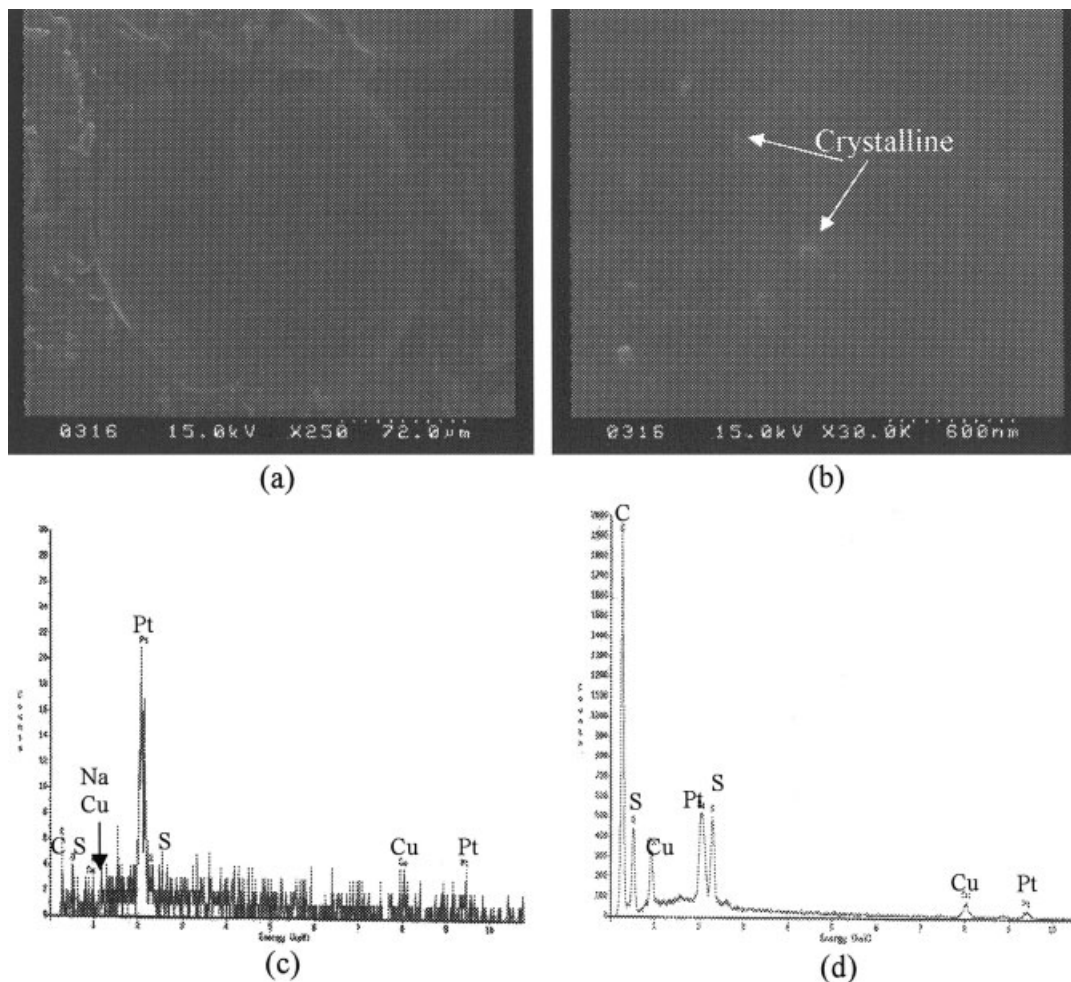
Figure 5 The SEM/EDS graphs of chelating hydrogel resin cross section at 100×; original magnifications (a) ×100 or (b) ×1000, (c) cupric ions adsorbed, and (d) Cu-EDTA adsorbed.

Figure 6. Hence, the mechanism of metal complex description above is proven to be reasonable.

Furthermore, the structure of the crystal within Cu^{2+} chelated copolymer resins is also elucidated by electron spectroscopy for chemical analysis (ESCA); Figures 7 and 8 show the results. Except for the C(1s) peak at 284.8 eV, the shoulder peak of C(1s) at 288 eV is attributed to the C=O group, coordinated with the metal ions as described in the literature,[15] and indicated in Figures 7(b) and 8(b). Thus, the C=O group in the chelating copolymer can be regarded as a weak-field ligand. It is notable that, regardless of whether Cu^{2+} or Cu^{2+}-EDTA is adsorbed by a hydrogel chelating–resin chelating copolymer, the peak of Cu $(2P_{2/3})$ in the XPS spectrum has a right shoulder peak, as depicted in Figures 7(c) and 8(c). The deconvolutions of the Cu $(2P_{2/3})$ spectra in Figures 7(c) and 8(c) have two and three resonance peaks, respectively. When the cupric ion is adsorbed onto the hydrogel chelating resin [Fig. 7(c)], the spectrum can be satisfactorily simulated using two components, CuO (933.3 eV)[16] and $CuSO_4$ (935.3 eV)[17], with a ratio of CuO/
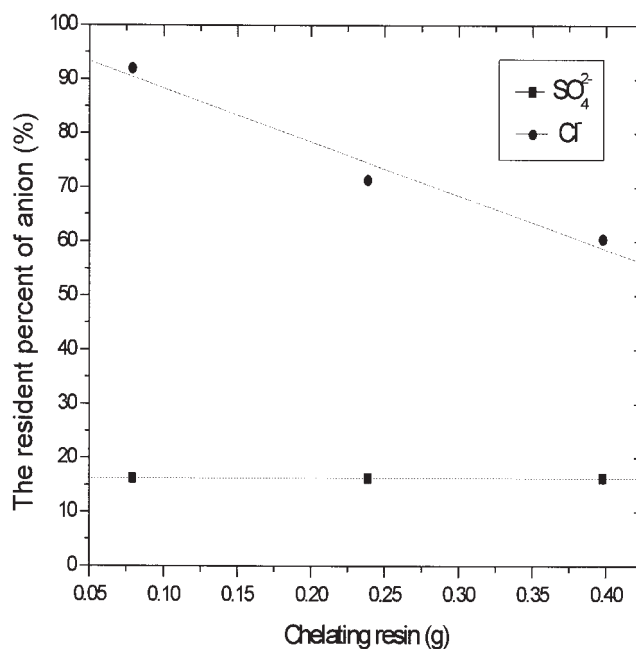

Figure 6 The residual percent of sulfate and chloride anions after the isothermal adsorption experiment.
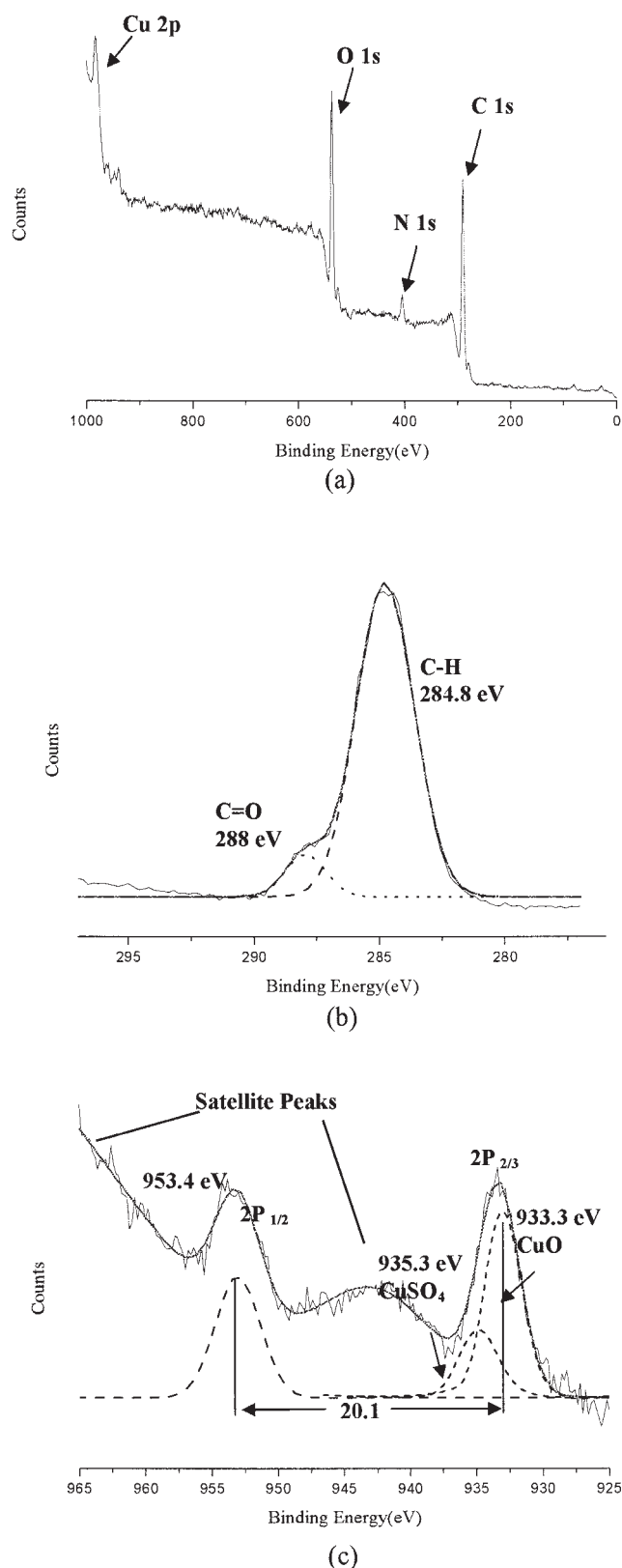
Figure 7 XPS spectra of Cu^{2+} adsorbed on the chelating hydrogel resin (a) in the fully binding energy range, (b) the binding energy of carbon, and (c) the binding energy of copper.

CuSO$_4$ areas of around 0.79:0.21. Interestingly, when the Cu^{2+}–EDTA complexes are adsorbed by the hydrogel chelating resin [Fig. 8(c)], Cu(0) [or Cu(I)][18,19] becomes visible at a lower binding energy (932.4 eV). The ratio of Cu(0) [or Cu(I)]/CuO/CuSO$_4$ is approximately 0.16:0.51:0.33. We do not illustrate this result because of no further information. However, a copper–ascorbic acid complex can catalyze the autoxidation of ascorbic acid and various substances, including phenylenediamines, phenols, and cysteine, to generate Cu(I) as an intermediate, according to the literature.[20] Hence, the amino group of the chelating copolymer may reduce Cu(II) into the Cu(I) and/or Cu(0) crystal. If the hydrogel chelating resin with amino moieties has this reduction ability, it may be able to be applied to prepare the nanocomposite via chemical metal deposition (or electroless plating).[21]

In summary, these amino chelating copolymers can be used not only to recover metal ions but also to move anion pollution in wastewater.

Competition of chelating copolymer with metal ion/Cu–EDTA

Figure 9 depicts the competition adsorption among chelating copolymers for various concentrations of Cu(II)–EDTA in aqueous solution. The maximum adsorption capacity of cupric ions is 1.08 mmol/g. With a ratio of concentrations of cupric ions to EDTA in the range 0–1.25, the equilibrium sorption capacity of Cu(II) adsorbed by the chelating resin remains reasonably good. In addition, the chelation capacity of cupric ions follows the decrease in the quantity of EDTA as the Cu–EDTA concentration increases, such as (Cu/EDTA = 1:0.5) > (Cu/EDTA = 1:0.75) > (Cu/EDTA = 1:1) > (Cu/EDTA = 1:1.25). This decreasing tendency is larger than that of Matejka and Zitkova,[14] who reported that resins can operate at a high molar ratio {EDTA/Cu} = 5. However, as the amount of EDTA in solution increases, more EDTA is available to compete with the chelating copolymer in cupric ion adsorption. When the Cu/EDTA ratio exceeds 0.75, the efficiency of removal of cupric ions is limited in this study.

Stability constants of metal-chelating copolymer complexes

The stability constant (K) measures the tendency of a metal ion to form a particular complex ion. According to the literature, general methods for estimating stability constants of chelating copolymers include ligand competition, metal competition, proton competition, and decomplexing. The ligand competition method is applied to determine the stability constant of a cupric-chelating copolymer complex, because the system herein is heterogeneous. The estimation pro-
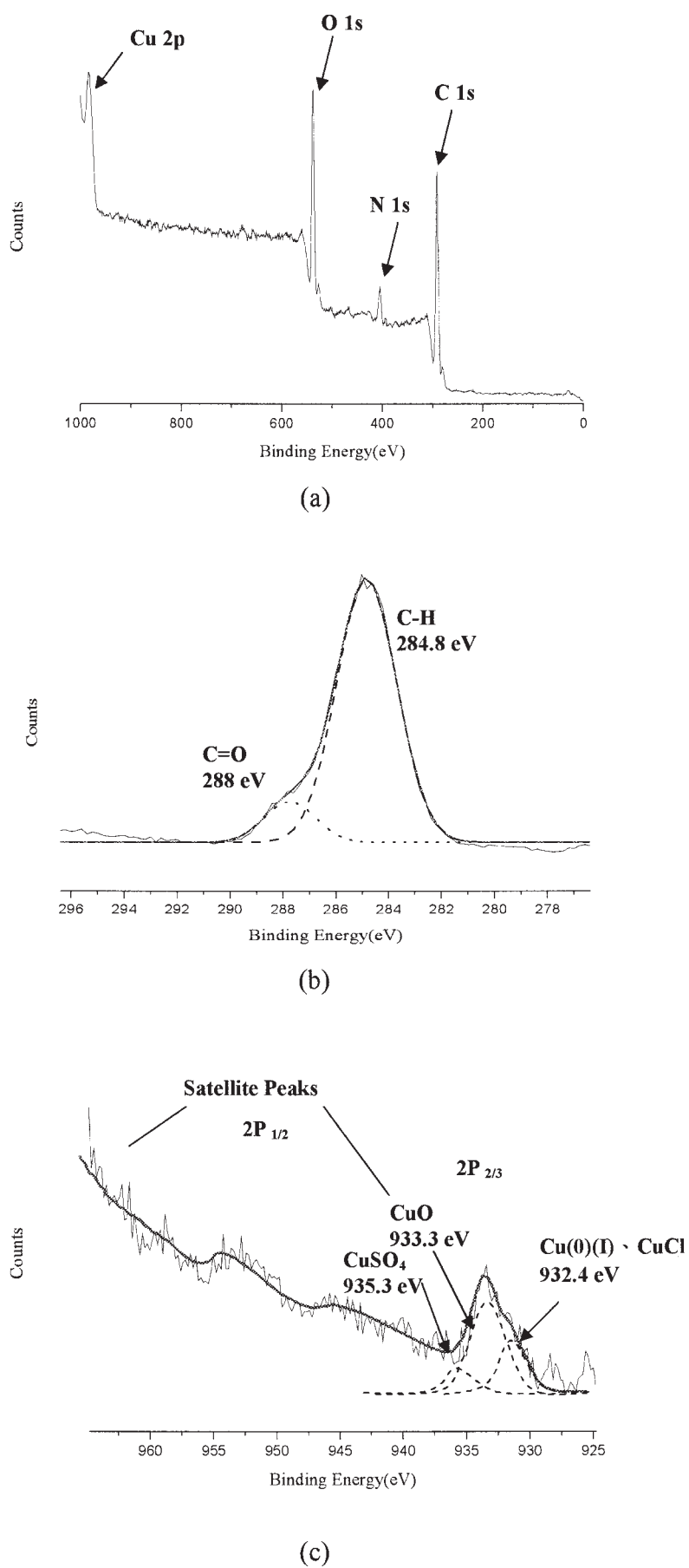
Figure 8 XPS spectra of Cu-EDTA adsorbed on chelating hydrogel resin (a) in the fully binding energy range, (b) the binding energy of carbon, and (c) the binding energy of copper.
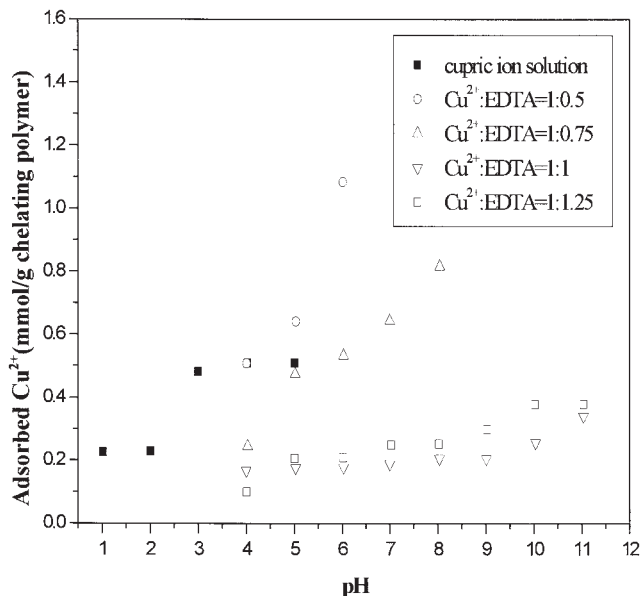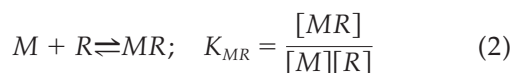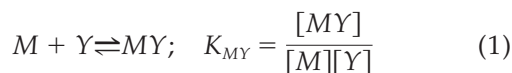
Figure 9 The 0.1-g chelating hydrogel resin competition with cupric ions/Cu-EDTA complex (300 ppm) solution at various pH values.

cedure of Loewenschuss and Schmucker[22] is the following:

$$M + Y \rightleftharpoons MY; \quad K_{MY} = \frac{[MY]}{[M][Y]} \quad (1)$$

$$M + R \rightleftharpoons MR; \quad K_{MR} = \frac{[MR]}{[M][R]} \quad (2)$$

where M represents the metal ion, Y is a competing ligand, and R is the synthesized chelating copolymer.

The overall reaction is

$$MY + R \rightleftharpoons MR + Y; \quad K_{overall} = \frac{[MR][Y]}{[MY][R]} = \frac{K_{MR}}{K_{MY}} \quad (3)$$

$$\log[R_{residue}] = \log\frac{[MR][Y]}{[MY]} - \log K_{overall} \quad (4)$$

The stability constant (K_{MR}) of the metal-chelating copolymer complex can be obtained from the intercept of graph b, which plots $\log(R)$ versus $\log[(MR)(Y)/(MY)]$. Table I presents the measurements of the equilibrium for the copper-chelating resin system. The stability constant obtained for the copper-chelating copolymer complex is $10^{18.72}$, which is lower than PEHA ($10^{26.6}$) because of the different reaction sites between GMA and PEHA, as described above. Fortunately, it is slightly higher than that of Cu–EDTA ($K_s = 10^{18.30}$) and suffices for the copolymer complex to compete with EDTA.

CONCLUSION

A hydrogel resin with amino moieties is successfully prepared by using inversion copolymerization. This kind of chelating resin not only has a high stability constant with Cu^{2+} but also can adsorb the anions in aqueous solution according to the results of the isothermal adsorption experiments and IC measurement. Although the stability constants of chelating resins with amino moieties is lower than that of the PEHA molecule, the minimum stability constant obtained for the copper-chelating copolymer complex was still high ($10^{18.72}$), which can have competition adsorption with EDTA in wastewater treatment.

TABLE I
Equilibrium Measurements for Copper–EDTA–Chelating Resin System

Cu (mmol)	EDTA (mmol)	CuR (mmol)	Cu/R (mmol)	Cu-EDTA/soln (mmol)	EDTA/soln (mmol)	K_{MR}	$\log\frac{K_{MR}}{K_{MY}}$	$\frac{X}{X+Y}$
0.7766	0.7855	0.0727	0.1786	0.5980	0.1875	19.5535	1.2535	0.2299
0.7766	0.7855	0.1084	0.1578	0.6187	0.1668	19.2556	0.9556	0.2032
0.7766	0.7855	0.1440	0.1762	0.6003	0.1852	18.4360	0.1360	0.2269
1.4820	1.5759	0.1452	0.3076	1.1744	0.4015	18.5788	0.2788	0.2076
1.4820	1.5759	0.2905	0.3327	1.1493	0.4265	18.3785	0.0785	0.2245
1.4820	1.5759	0.4347	0.3577	1.1244	0.4515	18.5703	0.2703	0.2413
2.2967	2.3622	0.3601	0.5903	1.7065	0.6557	18.5424	0.2424	0.2570
2.2967	2.3622	0.5038	0.5636	1.7332	0.6290	18.3271	0.0271	0.2454
2.2967	2.3622	0.6458	0.5849	1.7118	0.6503	18.8622	0.5622	0.2547

Cu, taken as the concentration of cupric ions, EDTA, taken as the concentration of EDTA; CuR, maximum adsorbed capacity of chelating resin; Cu/R, chelating resin adsorbed concentration of cupric ions; Cu-EDTA/soln, residue concentration of cupric ion in solution; EDTA/soln, residue concentration of EDTA in solution; R, after competing, without adsorbed chelating resin; X, Cu/R; Y, Cu-EDTA/soln.

References

1. Lie, Y. C. Waste Manag 1995, 15, 209.
2. Spearot, R. M.; Peck, J. V. Environ Prog 1984, 3, 124.
3. Cherry, K. F. Plating Waste Treatment; Ann Arbor Science: Ann Arbor, MI, 1982.
4. Kannan, P.; Kaliyappan, T. J Appl Polym Sci 1996, 60, 947.
5. Thomas, J. S. Environ Sci Technol 1986, 20, 1072.
6. Wang, C. C.; Chang, C. Y.; Chen, C. Y. Macromol Chem Phys 2001, 202, 882.
7. Wang, C. C.; Chang, C. Y.; Chen, C. Y. J Appl Polym Sci 2002, 84, 1353.
8. Wang, C. C.; Chen, H. C.; Chen, C. Y.; Shih, W. B. Polym Adv Technol 2003, 14, 349.
9. Wang, C. C.; Chen, C. Y.; Chen, H. C.; Chen, C. Y. React Funct Polym 2003, 57, 125.
10. Wang, C. C.; Li, W. S.; Chen, C. Y.; Chen, C. Y.; Kuo, J. F. React Funct Polym 2002, 51, 69.
11. Kabay, N.; Egawa, H. Sep Sci Technol 1993, 28, 1985.
12. Denizli, A.; Salih, B.; Piskin, E. J Appl Polym Sci 1997, 65, 2085.
13. Kálalová E.; Radová Z.; Švec, F.; Kálal, J. Eur Polym J 1977, 13, 293.
14. Matejka, Z.; Zitkova, Z. React Funct Polym 1997, 35, 81.
15. Zhang, Z.; Liu, W.; Xue, Q. Wear 1998, 215, 40.
16. Robert, T.; Bartel, M.; Ofergeld, G. Surface Sci 1972, 33, 128.
17. Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. Handbook of X-ray Photoelectron Spectroscopy; Chastain, J., Ed.; Perkin-Elmer Corp.: Norwalk, CT, 1992.
18. Schon, G. Surface Sci 1973, 35, 96.
19. Gaarensfroom, S. W.; Winograd N. J Chem Phys 1977, 67, 3500.
20. Nartell, A. E.; Calvin, M. In Chemistry of the Metal Chelate Compounds; Latimer, W. M., Ed.; Prentice–Hall: Englewood Cliffs, NJ, 1956.
21. Wang, P. H.; Wu, Y. Z.; Zhu, Q. R. J Mater Sci Lett 2002, 21, 1825.
22. Loewenschuss, H.; Schmucker, G. Talanta 1964, 11, 1399.