

Synthesis of Chelating Resins with Iminodiacetic Acid and Its Wastewater Treatment Application

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ABSTRACT: The chelating resins have high potential applications for the selective removal and recovery of metal ions from industrial waste solutions. The hydrophilic acrylate monomer with the iminodiacetic acid chelating group was prepared from glycidyl methacrylate and iminodiacetic acid at 60°C. The microbeads, prepared from acrylate monomer with the iminodiacetic acid chelating group, were employed by inversion suspension polymerization. In the pH range of 2–6, a reasonably good equilibrium sorption capacity is maintained for Cr³⁺ (ca. 2.7 mmol/g) and Cu²⁺ (ca. 1.8 mmol/g) in the chelating resins. The adsorption of Cd²⁺ and Pb²⁺ on microbeads is clearly affected by the pH of the solution, such that these ions' adsorption capacity increased with the pH of the aqueous solution. The adsorption of Cd²⁺ (ca. 1.25–1.87 mmol/g) and Pb²⁺ (ca. 0.99–1.89 mmol/g) showed a maximum at approximately pH = 5 and 6, respectively. The adsorption isotherms of Cr³⁺ and Cu²⁺ adsorbed on microbeads were following the Langmuir isotherm, but the adsorption behavior of Cd²⁺ and Pb²⁺ were not. The concentration of alkaline earth–metal cations on the range of 0–200 ppm had no influence on metal ions adsorbed capacity of chelating resins. Additionally, NTA (nitrilotriacetic acid) had no significant influence on metal ion adsorption by chelating resins. Furthermore, phenol pollutant can be adsorbed effectively by metal ions chelated microbeads; therefore, the microbeads were useful not only in recovering metal ions but also in the treating phenol pollutants in wastewater. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1353–1362, 2002; DOI 10.1002/app.10243

Key words: hydrogels

INTRODUCTION

The development of high-performance adsorbents for removing heavy metal ions from wastewater is considered a research priority in the environmen-

tal field. Metal ions are present in water as hydrated ions or as a complex species associated with various anions. In the electroplating industry, chelating agents in wastewater frequently coexisting with metal ions exhibit little or no tendency to be transferred to a chelating polymer (ion-exchange resins).¹ The charge on a metal ion must be neutralized, and some or all of its water hydration must be replaced before the ion is converted into an extractable species. Undesirable multivalent ions such as Ca²⁺ and Mg²⁺ replace monovalent ions, reducing the adsorption capac-

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ity of ion-exchange resins. Toxic metal ions represent a small fraction of a solution of many other ions in wastewater; if the toxic metal ions can be recovered specifically, the energy and material requirements of the wastewater treatment process can be more simply.

Fortunately, special chelating polymer resins can solve this problem. The chelated polymer is a high-performance material. The strength, glass transition temperature, conductivity, and the dielectric constant of materials can be improved by metal ion coordination with a chelated polymer.²⁻⁴ These materials have been used as semi-conductive materials, organic catalysts,⁵ and wastewater treatments,⁶ in the recovery of valuable trace metal ions, etc. Many researchers have prepared highly selective chelating resins for particular ions over the last decade. For example, new copper-selectivity chelating resins containing a salicylaldoxime group⁷ were designed for the large-scale hydrometallurgical separation of copper from its ores. Egawa et al.⁸ have synthesized certain chelating resins containing mercapto functional groups. Because the associated waste solution contains much Na^+ , Ca^{2+} , Mg^{2+} , Li^+ , and K^+ , the sorption of arsenic (III) on the chelating polymer was tested in the presence of sodium chloride and calcium chloride, and found not to be influenced by the presence of 10,000–40,000 ppm Na^+ or Ca^{2+} . Volkan et al.⁹ modified silica gel by incorporating mercapto chelating groups, and used it to preconcentrate Zn^{2+} , Cu^{2+} , and Pb^{2+} from seawater, yielding 90–95% recovery. The retention of traces of Zn^{2+} , Cd^{2+} , Pb^{2+} , Cu^{2+} , and UO_2^{6+} extracted from seawater by immobilizing alizarin Red-S on Amberlite XAD-2⁵ and amidoximes^{10,11} has also been investigated. Matejka et al.¹² prepared poly(acrylamide) with oligo(ethyleneamine) moieties, and stated that the presence of alkaline earth-metal cations in the loading solution significantly improved the sorption capacities toward the chelated heavy metal. Chitosan, derived from the deacetylation of chitin, is nature's most common biopolymer after cellulose.¹³ Chitosan dissolves in both mineral and organic acids, and can selectively bind trace amounts of group III transition metal ions in the presence of high concentrations of other metal ions. Restated, chelating resins have many potential applications in the selective removal and recovery of metal ions from industrial waste solutions.¹⁴

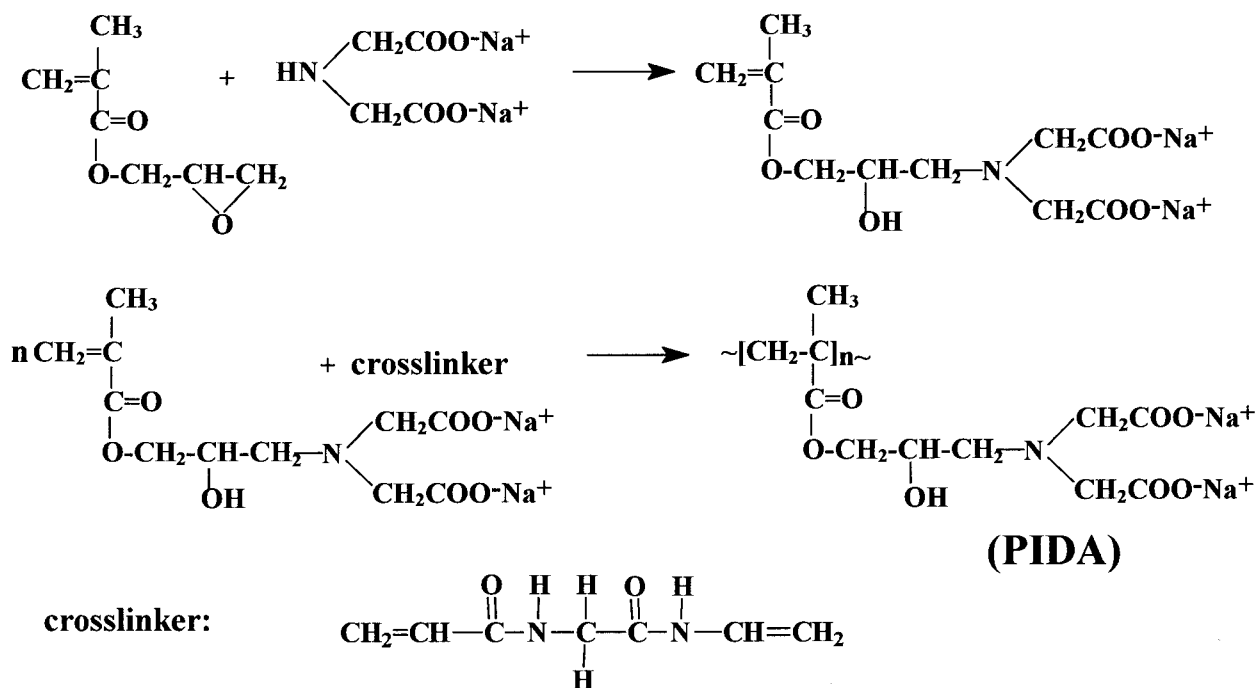
The large-scale commercial use of chelating resins is common with simple ion-exchange res-

ins. Few of the chelating resins have been used chiefly in analytical applications, and those not for the recovery of toxic metal ions from wastewater due to the prohibitive cost. The 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. Accordingly, Denizli¹⁵ prepared the water-swallowable poly(ethylene glycol dimethacrylate-hydroxyethyl methacrylate) microbeads with a new ligand, congo red, to overcome this problem. However, preparing a versatile chelating resin is easier if the vinyl monomers contain a chelating group. Therefore, the water-swallowable polymeric microbeads was synthesized using the hydrophilic monomer with an iminodiacetic acid chelating group, in this study. The tendency of sorbents to remove important heavy metals such as Cr(III), Cu(II), Cd(II), Pb(II), and phenol pollutant, often responsible for environmental pollution, was evaluated.

EXPERIMENTAL

Polymerization

The chelating polymer was prepared by glycidyl methacrylate (GMA = 0.4 M) (Ferck Co. Ltd.) with iminodiacetic acid (IDA = 0.4 M) (Sigma Co. Ltd.) sodium salt. $\beta\text{m}\beta'$ -Methylenebisacrylamide (0.1 M) (Ferck Co. Ltd.) was used as the crosslinking agent. The polymerization process was shown in Scheme 1. The hydrophilic acrylate monomer with iminodiacetic acid chelating group, was prepared from GMA and IDA at 60°C. Then, the inversion polymerization of acrylate monomer with iminodiacetic acid chelating group was conducted in a 1-liter, five-necked Pyrex kettle equipped with stirrer, condenser, nitrogen inlet, and thermister. Potassium persulfate (0.3 g) (Ishisu Pharm. Co. Ltd.) was used as an initiator. Toluene 300 mL (Ferck Co. Ltd) and Span 60 (3 g) (Ishisu Pharm. Co. Ltd.) were served as suspension solvent and suspension agent, respectively. The reaction temperature was kept at 70°C. After cooling, the polymeric beads (c.a. 100–250 μm) were separated from the polymerization medium by filtration, and then washed with distilled water and methanol several times. The purified polymer was dried in vacuum at 40°C to constant weight.



Scheme 1 Polymerization process of microbeads with an iminodiacetic acid chelating group.

Adsorption Experiment

The metal ions solutions were prepared by dissolving $\text{Cr}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$ (Ferck Co. Ltd.) with distilled water (Waters Millipore Purifying System). The pH of the solution was controlled by 0.01 N HCl and NaOH solution. A fixed amount of dry chelating polymer (0.1 g) and 50 mL of metal ion solution were placed in a thermostated oscillation bath for 48 h for isothermal adsorption experiment. After filtration, the pH of solution was measured by the pH meter (Muller Co. Ltd.) and the concentration of metal ions was measured by atomic adsorption spectrophotometer (AA model 932; GBC Co. Ltd.). The amount of metal ions adsorbed q_e (mg/g) was obtained as follows: $q_e = [(C_o - C_e)V]/L$; where C_o and C_e are the initial and equilibrium concentrations (mg/L) of metal ions, respectively; V is the volume of the solution (liter); and L is the mass of microbeads (g).

Different amounts of the alkaline earth-metal cations (Ca^{2+} and Mg^{2+}) and chelated agent nitrilotriacetic acid (NTA) (Ferck Co. Ltd) were added into the loading solution to study the metal ions selectivity of the chelating polymer.

A fixed amount of dry metal chelated microbeads (0.1 g) and 50 mL of phenol (500 ppm)

solution were placed in a thermostat with a magnetic stirrer for dynamic adsorption experiments. The concentration of sample was analyzed by UV/

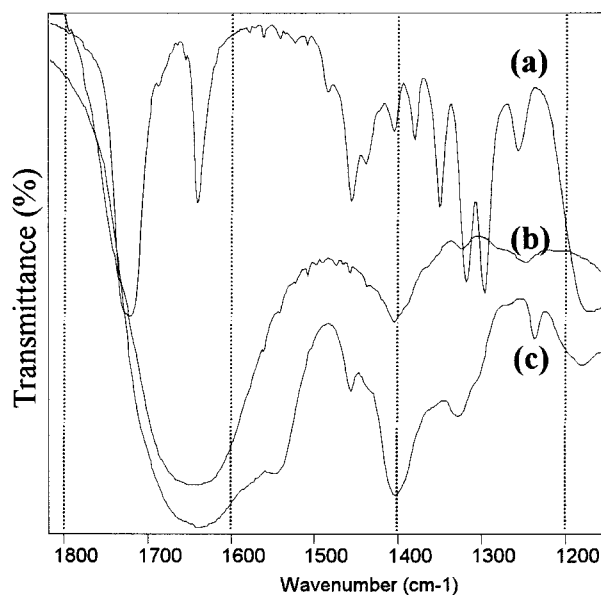


Figure 1 The FTIR spectra of (a) glycidyl methacrylate; (b) iminodiacetic acid; and (c) acrylate monomer with an iminodiacetic acid chelating group.

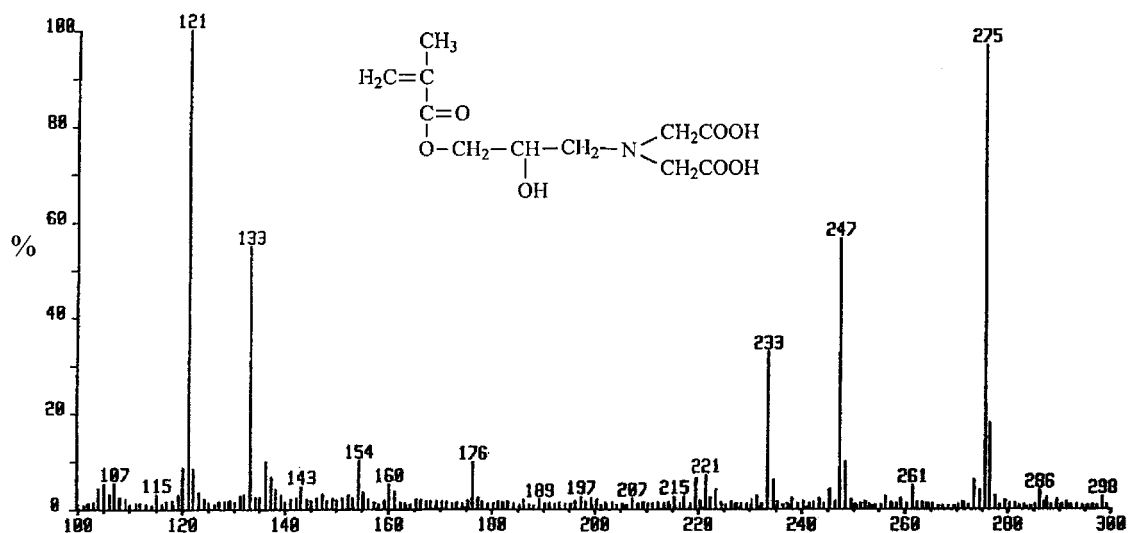
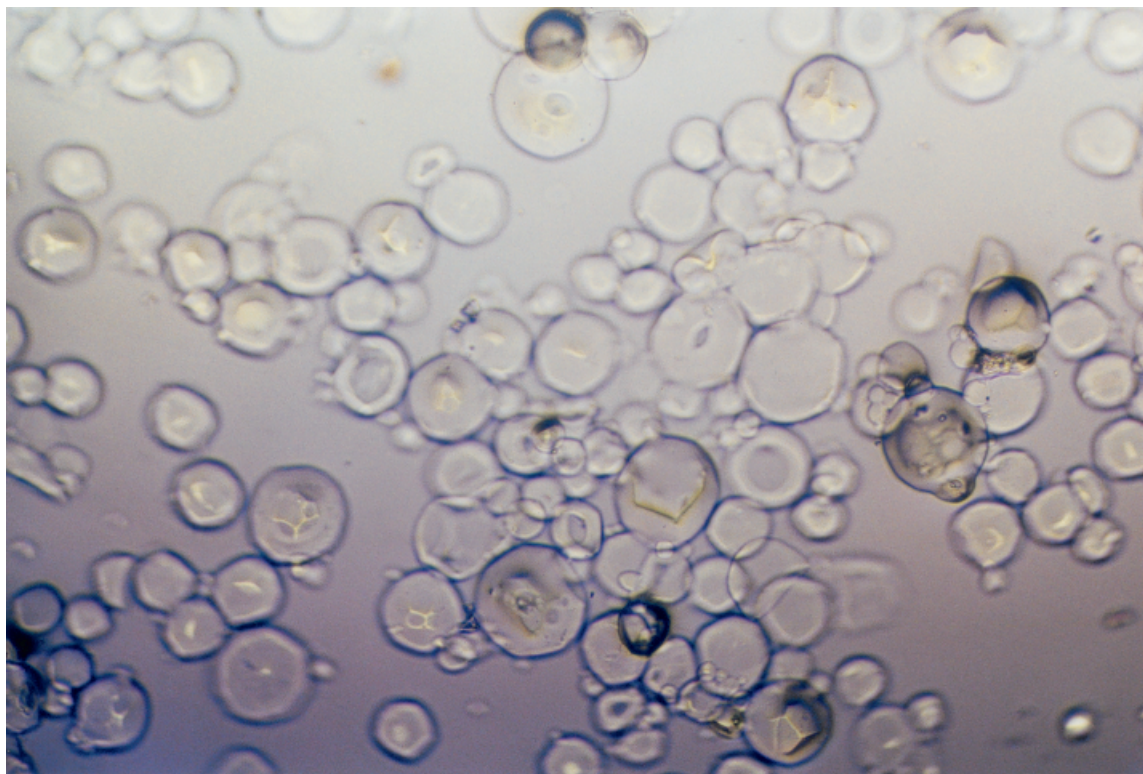


Figure 2 GC-MASS spectra of acrylate monomer with iminodiacetic acid chelating group.



200 μm

Figure 3 The optical micrograph of chelating microbeads. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

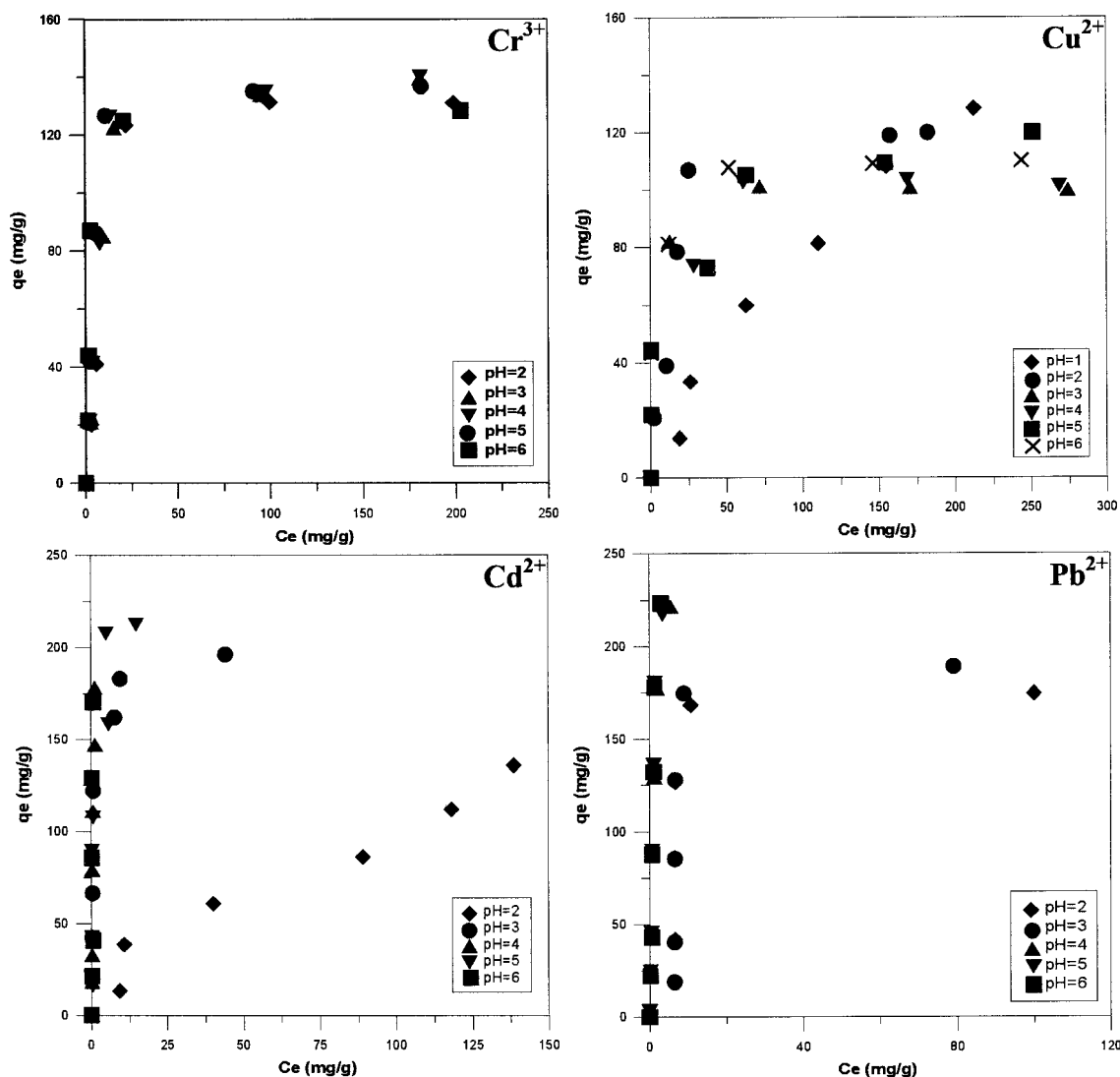


Figure 4 Effect of pH on adsorption of chelated Cr^{3+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} .

Visible spectrophotometer (Jasco Co. Ltd.) at appropriate intervals.

RESULTS AND DISCUSSION

Polymerization

The hydrophilic monomer with a chelating group was prepared by the epoxidizing glycidyl methacrylate (GMA) with iminodiacetic acid sodium salt (IDA-2Na). Figure 1 displays the FTIR spectra of the (a) GMA, (b) IDA-2Na, and (c) GMA-IDA-2Na chelating monomer. The C—C—O of the alkyl peroxide absorption band in the $1176\text{--}1198\text{ cm}^{-1}$ region and the symmet-

rical stretching band of the epoxy ring at 1260 cm^{-1} for the GMA monomer disappeared when the iminodiacetic acid sodium salt was connected to the GMA monomer. A strong asymmetrical stretching band near 1650 cm^{-1} and a weaker, symmetrical stretching band at 1400 cm^{-1} were attributed to the carboxylate ions' absorption of IDA-2Na in GMA-IDA-2Na, as presented in Figure 1(c). Figure 2 shows that the molecular weight of GMA-IDA was 275 from GC-Mass determined after the sodium ions in GMA-IDA-2Na were exchanged for H^+ . The maximum molecular weight (298), which corresponds to GMA-IDA-Na-H, was due to incomplete ion-exchange treatment. Therefore, the

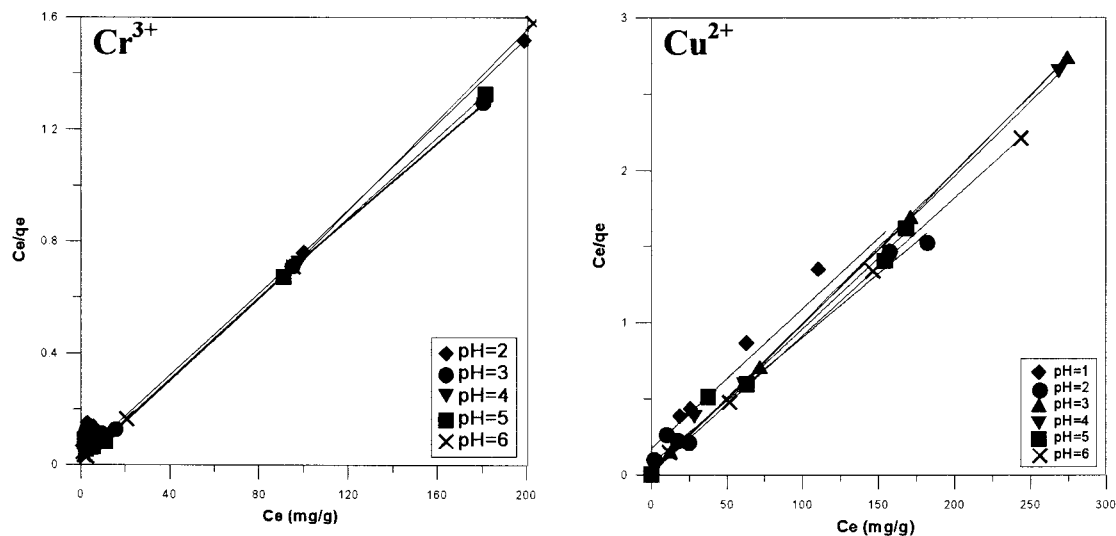


Figure 5 Langmuir adsorption isotherms of chelated Cr^{3+} and Cu^{2+} by microbeads.

chelating monomer $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}(\text{OH})\text{CH}_2-\text{N}(\text{CH}_2\text{COOH})_2$ was successfully prepared according to the above result.

Inverse suspension polymerization was used to prepare microbeads since the GMA-IDA-2Na chelating monomer was soluble only in water. Interestingly, the abnormal shape of microbeads is formed if the small amount of alcohol is not added to the toluene solvent. Alcohol changes the surface tension between the monomer/polymer droplets and the toluene solvent, acting as a cosuspension agent in this polymerization system. Figure 3 shows a photograph of the microbeads.

Isothermal Adsorption of Metal Ions

The hydrolysis and precipitation of the metal ions are influenced by the concentration and form of soluble metal species. Hydrolysis of metal ions becomes significant at around pH = 8.5, 6.5, and 7.5 for Cd^{2+} , Cu^{2+} , and Pb^{2+} at high concentration, respectively. Therefore, the adsorption experiment was conducted entirely in the range, pH = 2–6 and with a metal ion concentration under 500 ppm. Figure 4 plots the adsorption isotherm for Cr^{3+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} on the chelating resin microbeads against pH value. In the pH range of 2–6, a reasonably good equilibrium sorption capacity is maintained for Cr^{3+} (ca. 2.7 mmol/g) and Cu^{2+} (ca. 1.8 mmol/g) in the chelating resins. The adsorption of Cd^{2+} and Pb^{2+} on the microbeads is clearly affected by the pH of the solution, such that these ions' adsorption capacity

increased with the pH of the aqueous solution. The adsorption of Cd^{2+} (ca. 1.25–1.87 mmol/g) and Pb^{2+} (ca. 0.99–1.89 mmol/g) showed a maximum at approximately pH = 5 and 6, respectively. Morris¹⁶ observed similar behavior in the adsorption of Pb^{2+} on anionic microgels, and postulated that the carboxyl groups of anionic microgels are associated, and that negligible electrostatic attraction exists between the microgel and the Pb^{2+} ; thus, adsorption is minimal. $\text{Pb}(\text{OH})_2$ is formed under neutral aqueous conditions, lowering the ionic charge and removing the obstructive solvation energy, such that columbic and chemical energy contributions dominate, sharply enhancing adsorption. However, metal ions were adsorbed onto iminodiacetic acid chelating resins not only by carboxyl groups but also by tri-amine (R_3-N) groups. Thus, amounts of Pb^{2+} could be adsorbed onto microbeads at pH 2. Although the Cd^{2+} adsorption isotherm on chelating microbeads exhibited similar adsorption behaviors, the amount of Cd^{2+} adsorbed in a pH 2 loading solution was lower than that adsorbed in a high pH solution, due to the low stability constant of $\text{IDA}-\text{Cd}^{2+}$. Data concerning adsorption isotherms were characterized by the Langmuir adsorption isotherm that was followed by only Cr^{3+} and Cu^{2+} , as shown in Figure 5. The adsorption behaviors of Cd^{2+} and Pb^{2+} approximately followed the Langmuir adsorption isotherm. This result might follow from the "pore blockage mechanism."¹³ As metal ions adsorb onto iminodiacetic acid sites near the outer surface, the newly ad-

Table I The $q_{e_{\max}}$ of Langmuir Isotherm for Chelated Polymer in the Different pH Value of Solution

	Cr^{3+}		Cu^{2+}		Cd^{2+}		Pb^{2+}	
	(mg/g)	(mmol/g)	(mg/g)	(mmol/g)	(mg/g)	(mmol/g)	(mg/g)	(mmol/g)
pH = 2	131.6	2.53	119.8	1.87	140.2	1.25	204.1	0.99
pH = 3	140.8	2.71	120.5	1.88	191.2	1.71	238.1	1.15
pH = 4	140.8	2.71	102.8	1.61	193.2	1.73	297.6	1.44
pH = 5	137.0	2.63	107.5	1.67	210.3	1.87	355.2	1.72
pH = 6	128.2	2.47	110.6	1.73	196.9	1.76	390.0	1.89

sorbed metal clusters may constrict or block free volume, rendering iminodiacetic acid sites deep within the interior of the microbeads inaccessible for adsorption with metal ions. The larger diameters of the metal ions adsorbed, such as Pb^{2+} (1.19 Å) > Cd^{2+} (0.95 Å) > Cr^{3+} (0.62 Å) > Cu^{2+} (0.57 Å), and that of the nonporous hydrogel especially promote blockage. However, the $q_{e_{\max}}$ (maximum absorbed) values were determined from the Langmuir adsorption equation and presented in Table I. The values of $q_{e_{\max}}$ for both Pb^{2+} and Cd^{2+} are different from the experimental results.

The adsorption–desorption cycle was repeated five times using the same sorbent. The adsorption capacity of microbeads for Cu^{2+} did not significantly change during the repeated adsorption–desorption operation.

The Alkaline Earth–Metal Cation Effect

Table II shows the effect of Ca^{2+} or Mg^{2+} in the loading solution. With the concentration of alkaline earth–metal cations ranging from 0 to 200 ppm, a reasonably good equilibrium sorption capacity is maintained for four kinds of toxic metal ions adsorbed in chelating resins. The alkaline earth–metal cations do not coordinate with amino N-atoms,¹² and consequently, are not taken up by the triamine of the chelating resins. The result shows that the iminodiacetic acid chelating resins are suitable in recovering wastewater containing Ca^{2+} and/or Mg^{2+} ions.

The NTA Chelate Effect

Figure 6 shows the effect of NTA (nitrilotriacetic acid) in the loading solution. With the concentra-

Table II The Quantity of Heavy Metal Adsorbed by Chelating Resins in Presence of Ca^{2+} and Mg^{2+} Solution, Respectively

		Ca^{2+} (ppm)			Mg^{2+} (ppm)		
		100	150	200	100	150	200
Cr^{3+}	50 ppm	23.4	23.3	23.6	24.2	24.0	24.1
	100 ppm	46.7	46.8	46.5	46.0	46.6	47.1
	150 ppm	69.1	70.1	71.1	70.1	70.3	71.1
	200 ppm	92.4	93.0	92.1	91.2	91.9	91.6
Cu^{2+}	50 ppm	24.0	23.6	24.4	23.8	23.7	24.4
	100 ppm	47.8	47.0	49.0	48.6	48.0	47.3
	150 ppm	72.5	71.1	70.9	69.2	71.5	69.0
q_e (mg/g)	200 ppm	87.9	87.9	88.6	83.9	85.6	86.8
	Cd^{2+}	50 ppm	24.6	24.8	24.7	24.5	24.2
100 ppm		49.1	48.9	48.5	49.7	49.3	49.7
150 ppm		72.1	73.5	72.2	73.5	72.8	74.0
200 ppm		96.1	96.3	97.8	97.8	98.2	95.7
Pb^{2+}	50 ppm	24.8	24.4	24.8	24.4	24.4	24.5
	100 ppm	49.4	49.1	49.5	49.6	47.9	49.0
	150 ppm	73.6	73.8	74.0	73.6	74.5	72.0
	200 ppm	98.4	99.1	96.0	97.3	97.4	97.4

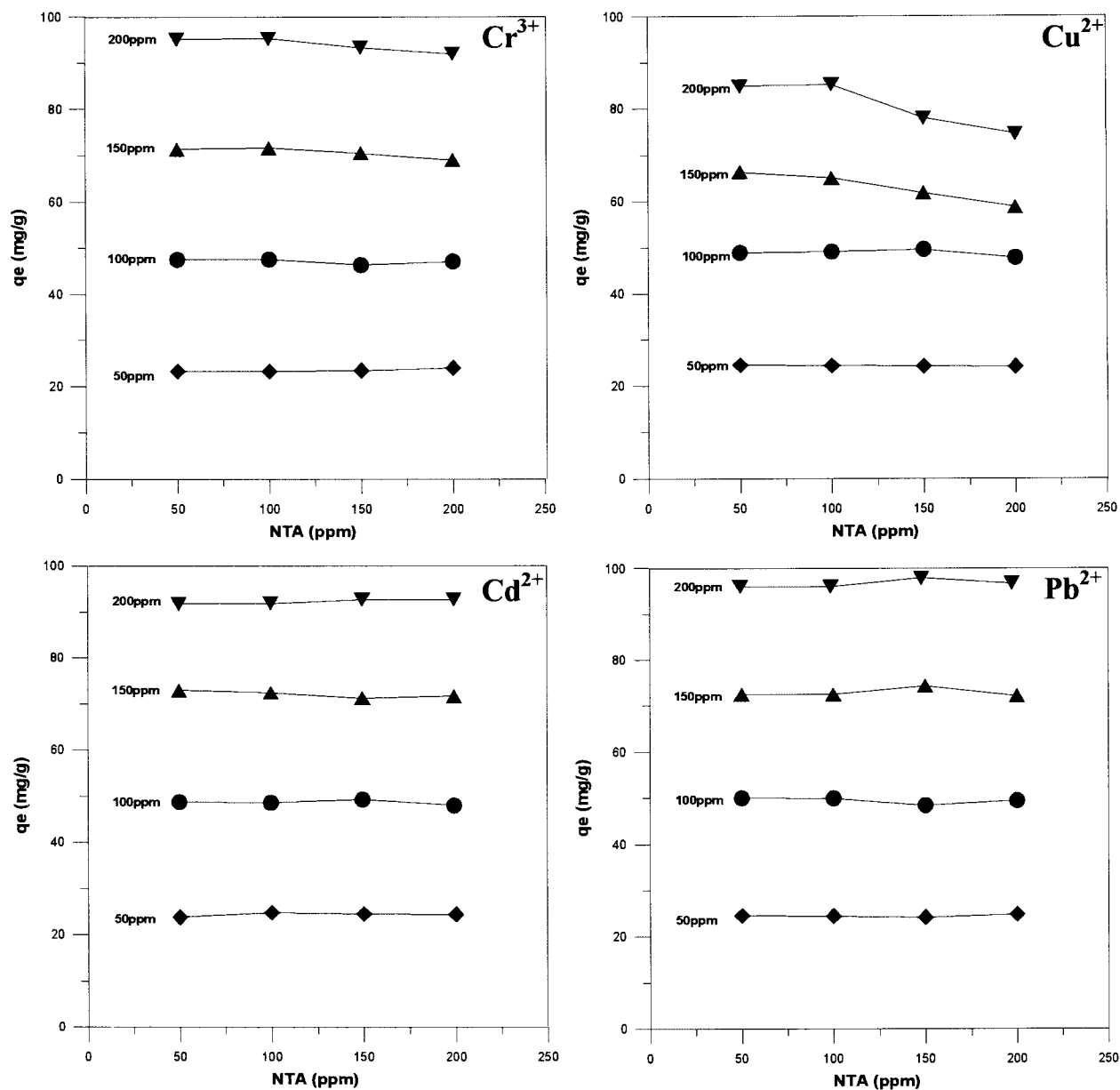
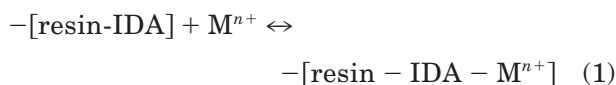


Figure 6 The effect of NTA chelate's concentration on metal ions adsorbed by microbeads.

tion of metal ions ranging from 50 to 100 ppm, a good equilibrium adsorption is maintained in the presence of different concentrations of NTA in the loading solution. More metal ions (100–200 ppm) in the loading solution correspond to a greater concentration of $[\text{M}^{n+}\text{-NTA}]$ complexes, especially for a high stability constant for NTA- Cu^{2+} . Consequently, the equilibrium adsorption capacity for chelated metal ions tends to decline with an increasing concentration of metal ions. The result is illustrated below.



$$K_s = \frac{-\text{[resin - IDA - M}^{n+}]}{-\text{[resin - IDA]}\text{[M}^{n+}]} \quad (2)$$



$$K_s = \frac{\text{[NTA - M}^{n+}]}{\text{[NTA]}\text{[M}^{n+}]} \quad (4)$$

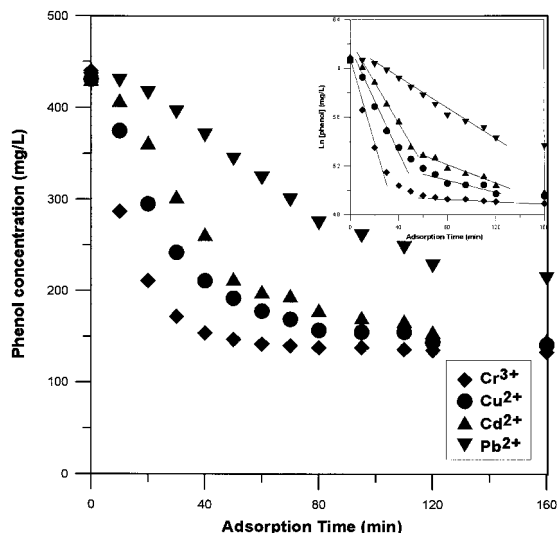
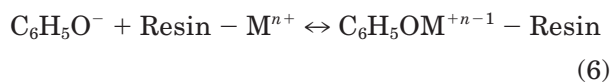


Figure 7 Adsorption of phenol pollutant on metal-chelated microbeads.

The mass of resin-IDA remained constant. The concentration of $[\text{resin-IDA-M}^{n+}]$ and $[\text{NTA-M}^{n+}]$ complexes increased when the concentration of metal ions was increased. The concentration of $[\text{NTA-M}^{n+}]$ increased again and the concentration of $[\text{resin-IDA-M}^{n+}]$ decreased simultaneously, when the concentration of [NTA] was increased, according to Le Chatelier's principle. However, this tendency was only slightly exhibited at a high concentration of metal ions. Therefore, the adsorption capacity of iminodiacetic acid chelating resins should be superior to that of NTA in this system according to the above result.

Adsorption of Phenol Contaminants by Metal Chelated Microbeads

Phenol is a well-known weak acid, and can be removed effectively from wastewater using anion-exchange resins.¹⁷ However, phenol can also be adsorbed effectively by metal ions of chelated microbeads, as shown in Figure 7, as metal cations can combine with phenol anions, as described below.



The quantity of phenol adsorbed corresponded to the quantity of metal ions adsorbed in the chelat-

ing microbeads; therefore, the chromic ion chelated microbeads were superior to the others, as shown in Figure 7. The amounts of phenol pollutant adsorbed on Cr^{3+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} chelated microbeads were 153.5, 145.0, 142.5, and 109.0 mg/g, respectively. The phenol adsorption rate for metal-chelated resins followed the two-step adsorption model, if a first-order adsorption rate was assumed, as shown in the upper right corner of Figure 7. However, no phenol was adsorbed on microbeads, as metal ions had not yet chelated with chelating resins. Further details of phenol adsorption by metal chelated microbeads will be reported in further work.

In summary, the microbeads were useful not only in recovering metal ions but also in the treating phenol pollutants in wastewater.

CONCLUSION

The hydrogel microbeads with iminodiacetic acid were successfully prepared by using inversion polymerization. Ethanol must be added as a co-suspension agent in polymerization system. With the pH range of 2–6 a reasonably good value of equilibrium sorption capacity is maintained for Cr^{3+} (ca. 2.7 mmol/g) and Cu^{2+} (ca. 1.8 mmol/g) adsorbed in chelating resins. Additionally, the adsorption of Cd^{2+} and Pb^{2+} were clearly influenced by the pH of the solution that their adsorption capacity was increased with the pH of aqueous solution. The adsorption isotherms of Cr^{3+} and Cu^{2+} adsorbed on microbeads were following the Langmuir isotherm, but the adsorption behavior of Cd^{2+} and Pb^{2+} were not. The concentration of alkaline earth-metal cations range of 0–200 ppm did not influence on metal ions adsorption capacity of chelating resins. In addition, NTA were also not significantly influence on metal ion adsorption of chelating resins. Furthermore, phenol pollutant can be adsorbed effectively by metal ions chelated microbeads; therefore, the microbeads were useful not only in recovering metal ions but also in the treating phenol pollutants in wastewater.

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