

Adsorption Properties of a Chelating Resin Containing Hydroxy Group and Iminodiacetic Acid for Copper Ions

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ABSTRACT: A chelating resin, PSGI, was synthesized by the radical polymerization of GMA-IDA, DVB, and styrene for the removal of Cu(II), Co(II), and Cd(II) from an aqueous solution. The characteristic functional groups and chemical composition of PSGI were analyzed by Fourier transform infrared spectroscopy and elemental analysis of C, H, and N. The equilibrium adsorption capacities of PSGI from their single-metal ion solutions were 1.46 mmol/g for Cu(II), 1.02 mmol/g for Co(II), and 1.10 mmol/g for Cd(II). The adsorption isotherm of Cu(II) by PSGI followed the Langmuir isotherm. Increasing the concentration (0–0.1 M) of KCl in Cu(II) solution affected the adsorption behavior slightly.

Within the pH range of 2–5.5, decreasing the pH of the Cu(II) solution did not produce remarkable changes in the equilibrium adsorption capacities. The adsorption capacities of PSGI for Cu(II) did not cause significant change during the repeated adsorption–desorption operations. The competitive adsorption tests verified that this resin had good adsorption selectivity for Cu(II) with the coexistence of Co(II) and Cd(II). © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2123–2130, 2004

Key words: adsorption; Langmuir isotherm; competitive adsorption; selectivity

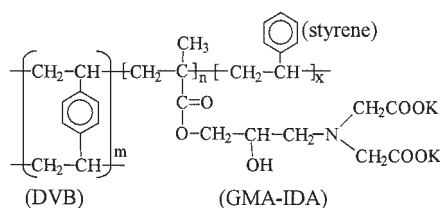
INTRODUCTION

In recent years, the effective treatment of heavy metal ions from an aqueous solution has received much attention because of their toxicities in relatively low concentration and tendency to bioaccumulate.^{1,2} Several methods, such as ion exchange, reverse osmosis, adsorption, and precipitation, have been investigated to remove metal ions from wastewater.^{2,3} Around these technologies, many publications concentrated on metal ion recovery using chelating polymers, because they are reusable and are easy to handle; as well they have higher adsorption capacities and efficiencies.^{2–4} Hence, numerous studies have either introduced low-molecular-weight ligands to various synthetic^{5–11} and natural polymeric matrices^{2,3,12–14} or synthesized a copolymer containing conventional chelating vinyl monomer^{15–18} to form a chelating resin. Additionally, many researchers have been concerned with synthesizing new chelating vinyl monomers^{19,20} because they are very useful in polymeric molecule design for copolymerization with other vinyl monomers.

Previous studies²¹ prepared a chelating vinyl monomer, GMA-IDA, via an epoxy group reaction of glycidyl methacrylate (GMA) with iminodiacetic acid (IDA). This monomer has the hydrophilic nature of hydroxy and iminodiacetate groups and has an ade-

quate affinity to metal ions. It can share four pairs of electrons with a single metal ion to stabilize the coordination bonds. The stability constants of GMA-IDA and its homopolymer (or copolymers) complexed with some metal ions were found to be close to 10^{11} . These results indicate that all of these water-soluble chelating polymers can form stable polymer–metal ion complexes in an aqueous solution. In this article, we extend our preliminary studies and focus on the synthesis of a chelating resin by radical copolymerization of GMA-IDA with styrene (SM) and divinylbenzene (DVB) for the removal of Cu(II) from an aqueous solution. The effects of solution conditions, such as pH value, metal ions, and salt concentrations, on the adsorption behavior were investigated. In addition, many researchers have been interested in the removal of metal ion from a single-metal-ion solution.^{2–6,9–12,18} However, this ideal situation rarely exists in a real wastewater system. Although a few papers^{7–8,13–17} presented the competitive adsorptions from the mixture of two metal ions, all of the studies have focused on the end results of competitive adsorptions. Investigations into the changes in concentrations of metal ions after the different competitive adsorption times, which can provide the maximum adsorption selectivity at the shortest adsorption time, have generally been disregarded. For example, Wan et al.¹³ and Pang et al.¹⁴ described the selectivity coefficients (α) of their chelating polymers after the competitive adsorptions for 12 h were $\alpha_{\text{Pb(II)/Cu(II)}} \cong 55.3$ and $\alpha_{\text{Ag(I)/Pb(II)}} \cong 9.8$, respectively. However, these selectivity coefficient

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Scheme 1

values may have occurred after 6 h, or they were not maximum values for 12 h. If the changes in concentrations of metal ions in the various competitive adsorption times were obtained, all problems would be resolved easily. For these reasons, the concentration changes of metal ions versus the competitive adsorption times for Cu(II) with the coexistence of Co(II) and Cd(II) were also studied in this article.

EXPERIMENTAL

Materials

The chelating vinyl monomer, GMA-IDA, was prepared as previously described.²¹ SM was purified by distillation under reduced pressure. Potassium persulfate (KPS) was recrystallized using standard procedures. The concentrations of CuCl₂, CoCl₂, and CdCl₂ solutions were determined by atomic absorption spectrophotometer (Perkin-Elmer, AAnalyst100). Divinylbenzene (ACROS), potassium hydroxide, hydrochloric acid, and potassium chloride (SHOWA) were used as received. All reagents were certified ACS reagent grade.

Preparation of chelating polymer

The chelating polymer, crosslinked poly(styrene-co-GMA-IDA), was prepared by radical polymerization of GMA-IDA with styrene and DVB at a molar ratio of 3:4:1 (GMA-IDA:SM:DVB) in a mixture of water with ethanol at 75°C for 12 h by adding KPS (0.3%) as an initiator. DVB was used as a crosslinking agent. The product obtained by the polymerization was filtered, washed thoroughly with distilled water, and dried by vacuum pump at 60°C to a constant weight. Finally, this chelating polymer, called PSGI, was ground and sieved to a narrow dispersion in granules sizes of 180–250 μm. Scheme 1 presents the chemical structure of PSGI resin.

Characterization of PSGI

The characteristic functional groups of PSGI and PSGI-metal ion complexes were analyzed by Fourier transform infrared spectroscopy (FT-IR, Bio-Rad, FIS-40A). The PSGI-metal ion complexes were conducted

by mixing PSGI (70–80 mg) and metal ions (30 mL, 7.87×10^{-3} M) in a flask with a magnetic stirrer for 24 h. After filtration, the solid products were washed thoroughly with distilled water and dried by vacuum pump at 60°C for 48 h. All samples were prepared by mixing with KBr and pressed to form pellets. The chemical compositions of PSGI were determined by elemental analysis (HERAEUS CHN-O rapid analyzer) of C, H, and N.

Adsorption experiment

Dynamic adsorption experiments were performed by mixing PSGI (70–80 mg) and 20 mL of metal ions in a flask with a magnetic stirrer at $25 \pm 0.2^\circ\text{C}$. The ionic strength of the metal ion solution was controlled by the addition of KCl. These solutions were adjusted to the corresponding pH values with 0.1 N HCl or with KOH solution. When the adsorption experiment was complete, the mixture was filtered and the metal ion concentration in the filtrate was determined by atomic absorption spectrophotometer. The adsorption capacities q (mmol/g PSGI) in various adsorption time were obtained as follows: $q = [(C_0 - C_f)V]/m$; where C_0 and C_f are the initial and final concentrations (mmol/L) of metal ion in the filtrate, respectively, V is the volume of metal ion solution (0.02 L in this article), and m is the weight of PSGI resin (g).

Desorption and repeated use

Desorption of metal ions was carried out in 3 M HCl solution. The PSGI-metal ion complexes were immersed in 3 M HCl solution and stirred with a magnetic stirrer for 120 min at 5°C. After filtration, the IDA functional groups in the chelating polymer were two carboxylic acids. Then they were immersed in 0.5 M KOH solution and stirred for 20 min at 5°C to convert carboxylic acids to carboxylic salts. These PSGI resins were filtered, washed thoroughly with distilled water, and dried by vacuum pump at 60°C for repeated use.

RESULTS AND DISCUSSION

Characterization of PSGI and PSGI-metal ion complexes

The chelating polymer, PSGI, was prepared by radical polymerization of GMA-IDA with styrene and DVB. Figure 1A displays the FT-IR spectrum of PSGI. The absorption band at 1725 cm^{-1} was caused by the stretching vibration of the ester carbonyl groups of GMA-IDA. Two strong bands were observed at 1635 and 1399 cm^{-1} , which ascribed to asymmetric and symmetric stretching of C=O in carboxylate salts (–COOK) of GMA-IDA. The aromatic C=C stretch absorption that occurred at 1600 cm^{-1} was overlapped

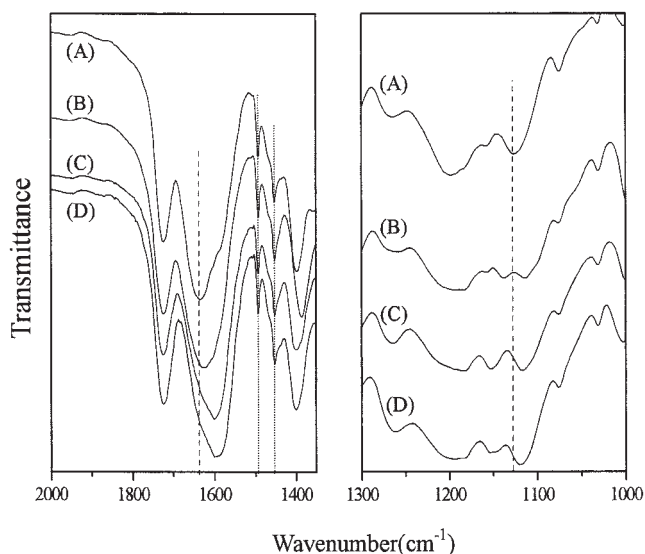


Figure 1 The FT-IR spectra of PSGI and its polychelates. (A) PSGI, (B) PSGI-Cu(II) complex, (C) PSGI-Co(II) complex, (D) PSGI-Cd(II) complex.

by the carbonyl absorption (1635 cm^{-1}) of carboxylate salts. However, two $\text{C}=\text{C}$ ring absorptions of styrene and DVB in PSGI appeared in the $1500\text{ to }1420\text{ cm}^{-1}$ region. That is, the polymerization of PSGI by GMA-IDA with styrene and DVB was carried out successfully. When the metal ions were adsorbed by PSGI, no shift occurred at $1500\text{--}1420\text{ cm}^{-1}$, indicating that there existed no chelating ability between $\text{C}=\text{C}$ ring of styrene and DVB with metal ions. However, the band at 1635 cm^{-1} shifted to a lower frequency, suggesting that the carboxyl group oxygens of carboxylate salts donate unshared electron pairs to the metal ions to form coordinate-covalent bonds.^{22,23} In addition, the absorption band of the C-N bond at 1130 cm^{-1} shifted to a lower frequency, implying that coordinate-covalent bonds also exist between nitrogen atoms and metal ions. To summarize, the FT-IR spectrum confirmed that the behaviors in the removal of metal ions by PSGI resin were chemical adsorptions and not physical ones. The chelating reactions occurred between metal ions and GMA-IDA units in PSGI.

Table I presents the chemical compositions of this polymer by elemental analysis of C, H, and N. The molar fraction of GMA-IDA in PSGI is 27.6%, which is less than that of the reaction condition. Prior to getting

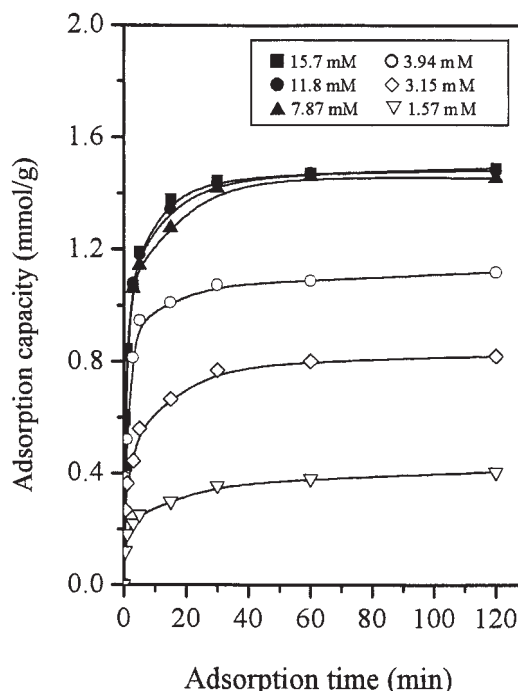


Figure 2 Effect of the adsorption time on the adsorptions of various concentrations of Cu(II) by PSGI at 25°C , pH 4.5.

PSGI, the product obtained by the polymerization was filtered and washed thoroughly with distilled water. A few polymers containing many GMA-IDA units dissolved in water caused the loss of GMA-IDA in PSGI. Notably, Table I also lists the theoretical maximum adsorption capacity (1.56 mmol/g) that is calculated by the complexation reaction ratios between metal ions with GMA-IDA units which are 1:1.²¹

Dynamic and isothermal metal ion adsorption

Figure 2 illustrates the effect of the adsorption time on the adsorptions of various concentrations of Cu(II) by PSGI. The adsorption capacities of Cu(II) increased with increasing adsorption time. However, all the adsorptions tended toward equilibrium at 40 min. Figure 3 depicts the influence of the initial concentration of Cu(II) on the equilibrium adsorption capacity. The equilibrium adsorption capacities increased first with the initial concentration of Cu(II) and then reached a plateau value at about an initial concentration of 360

TABLE I
The Chemical Compositions of Polymeric Chelating Resin (PSGI) Calculated from Elemental Analyzer

Polymer	Elemental analysis			Molar fractions in PSGI (%)			The maximum adsorption capacity in theory (mmol/g)
	N(wt %)	C(wt %)	H (wt %)	GMA-IDA	Styrene	DVB	
Crosslinked poly(styrene-co-GMA-IDA) (PSGI)	2.19	62.28	5.82	27.57	55.89	16.54	1.56

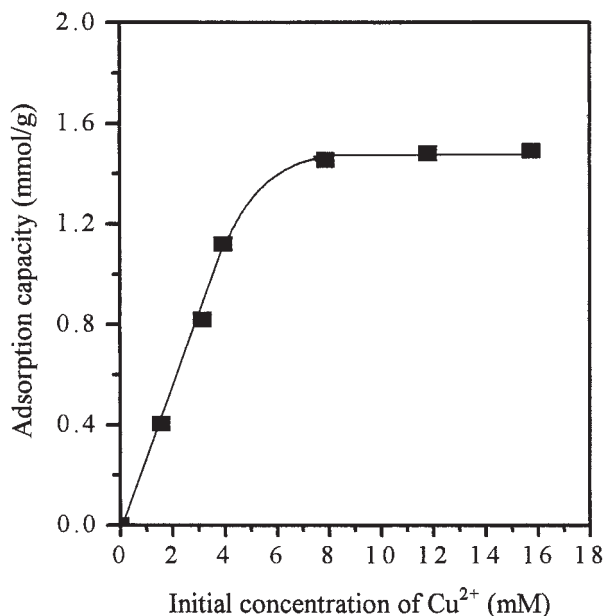


Figure 3 The influence of the initial concentration of Cu(II) on the equilibrium adsorption capacity at 25°C, pH 4.5.

ppm (5.7 mM). This is a typical curve of chemical adsorption,²⁴ which is in good agreement with the results of the FT-IR measurement. If the initial moles of Cu(II) in 20 mL solution are less than the theoretical maximum adsorption capacity of 75 mg PSGI resin, the equilibrium adsorption capacity will increase as the initial concentration of Cu(II) increases. However, when the initial moles of Cu(II) are greater than the theoretical maximum adsorption capacity of PSGI resin, the maximum adsorption efficiencies exceed 93% of the theoretical maximum adsorption capacity and there is no noticeable difference among the equilibrium adsorption capacities (or efficiencies). These fast adsorption rates and high adsorption efficiencies were attributed to the hydrophilic nature of GMA-IDA units in PSGI, which had an adequate affinity to metal ions. The long side chain of GMA-IDA leads to a higher free volume that can help the metal ions to diffuse toward the chelating groups easily. In addition, one GMA-IDA unit possesses a hydroxy and an iminodiacetate group that can share four pairs of electrons with a single Cu(II) ion and cage the metal ion tightly. Similar results are also shown in Figure 4, which describes the dependence of the adsorption rate on the initial concentration of Cu(II). When the initial moles of Cu(II) are less than the theoretical maximum adsorption capacity of PSGI resin, the log-log plot of the rate of adsorption versus initial concentration of Cu(II) gives a straight line. The slope of this line gives the order of the reaction (n) equal to 1.1 by applying the equation

$$\text{Adsorption rate} = k[\text{Cu}^{2+}]^n,$$

where k is the adsorption rate constant and $[\text{Cu}^{2+}]$ is the initial concentration of Cu(II). However, the slope of another straight line approaching zero could be observed at high initial concentration of Cu(II), which means that increasing the concentration of Cu(II) affected the adsorption rate only slightly.

A well-known model for the adsorption process, and particularly for the chemisorption process, was presented by Langmuir:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad (2)$$

where Q_0 is the maximum adsorption capacity of Cu(II) (mmol/g resin), b is the Langmuir constant (L/mmol), and C_e represents the equilibrium concentration (mmol/L) of metal ion after the adsorption experiment. Thus, the plot of C_e/q_e versus C_e gives a good linear relationship in Figure 5. The adsorption behavior follows the Langmuir adsorption isotherm and the equation can be expressed as

$$\frac{C_e}{q_e} = 0.6689C_e + 0.0318. \quad (3)$$

Hence, $b = 0.04,754$ (L/mmol) and $Q_0 = 1.50$ (mmol/g). The value of Q_0 is close to the theoretical maximum adsorption capacity given in Table I.

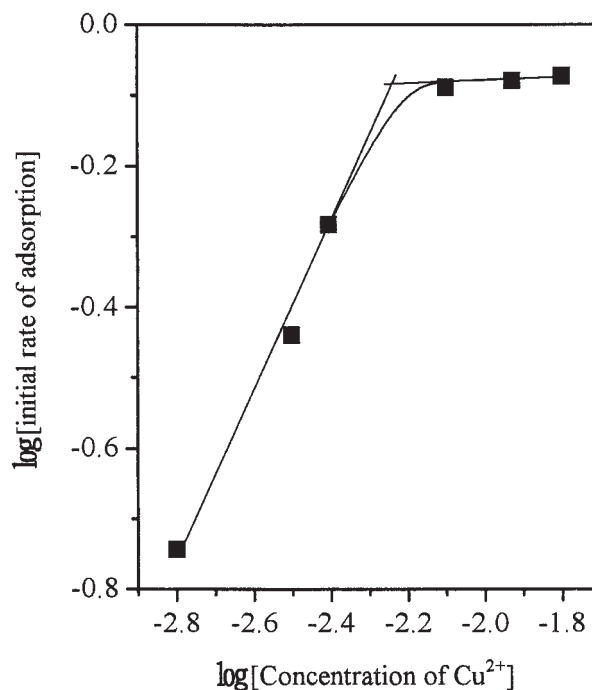


Figure 4 The dependence of the adsorption rate on the initial concentration of Cu(II) at 25°C, pH 4.5.

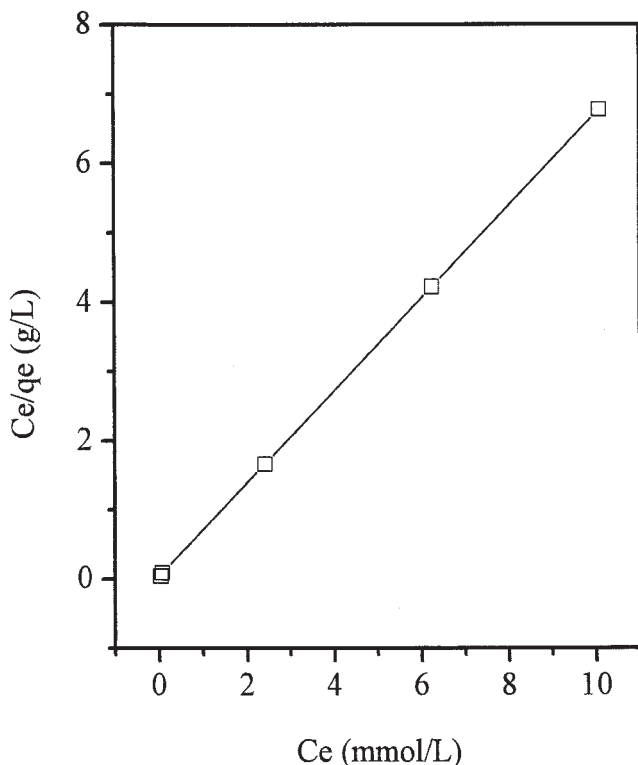


Figure 5 Langmuir adsorption isotherm of Cu(II) by PSGI resin at 25°C.

Effect of salt and pH value on adsorption

The presence of salts in wastewaters is one of the important factors that may affect the adsorption behaviors of metal ions. Therefore, Figure 6 shows the adsorption behavior of Cu(II) by PSGI in the presence of various concentrations (0–0.1 mol/L) of KCl solution. Obviously, the presence of KCl in Cu(II) solution was not an important controlling parameter in the adsorption process (<2.3%). Figure 7 reveals the effect of the pH on the adsorption of Cu(II) by PSGI. Notably, this article repeated the batch equilibrium studies in the range of pH 1.0–5.5 because the Cu(II) could be precipitated by OH⁻ to form a copper(II) hydroxide above pH 6. Except for pH < 2, as the pH value of the Cu(II) solution decreased, the equilibrium adsorption time and capacity decreased slightly. At low pH values, carboxylate ions (COO⁻) and amine groups in GMA-IDA can form protonation, which induces an electrostatic repulsion of Cu(II). Therefore, competition exists between protons and metal ions for adsorption sites and decreases the adsorption capacity. However, the first and second acid dissociation constants for the latex type of poly(styrene-co-GMA-IDA) are 10^{-4.5} and 10^{-10.2}, respectively.²¹ The stability constants of this polymer complexed with divalent metal ions are close to 10¹¹. These results indicate that metal ions can compete with hydrogen ions in adsorption by the carboxylate ions of GMA-IDA. In addition, the metal

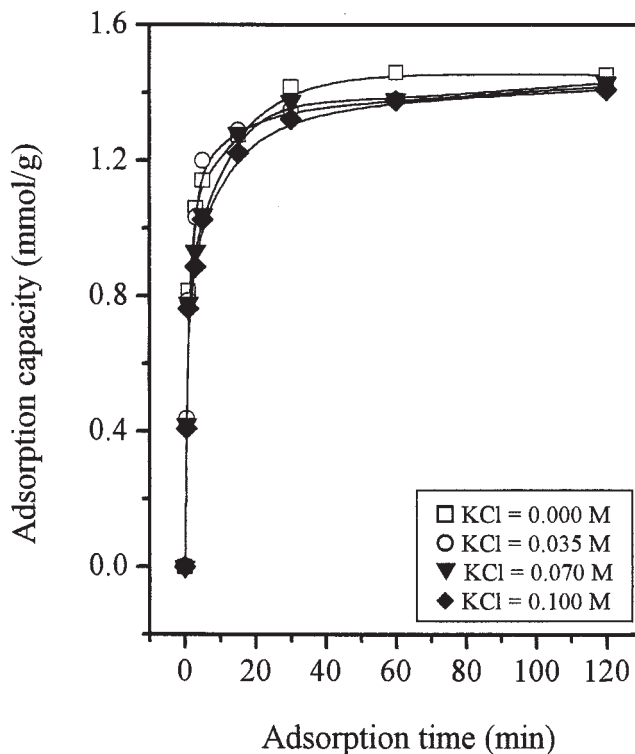


Figure 6 The adsorption of Cu(II) by PSGI in the presence of various concentrations of KCl solution at 25°C, pH 4.5 (initial concentration of Cu(II) = 7.87 × 10⁻³ M).

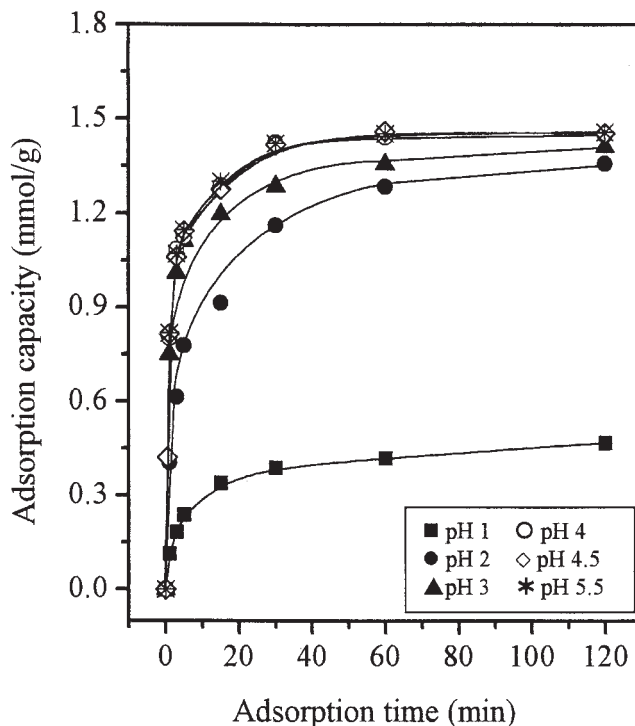


Figure 7 Effect of pH on the adsorption of Cu(II) by PSGI at 25°C (initial concentration of Cu(II) = 7.87 × 10⁻³ M).

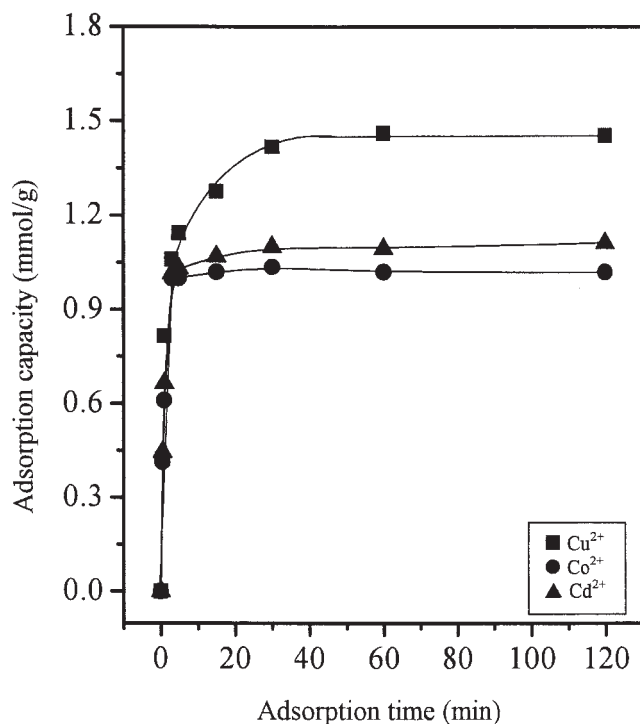


Figure 8 The adsorption kinetics of Cu(II), Co(II), and Cd(II) by PSGI under noncompetitive conditions at 25°C, pH 4.5.

ions were adsorbed onto GMA-IDA not only by carboxylate ions but also by triamine ($R_3-N:$) and hydroxy groups. That is, chelating reaction could be carried out even though the two carboxylate ions (COO^-) in GMA-IDA had protonated at high concentration of hydrogen ions (low pH value). Thus, high equilibrium adsorption capacity of Cu(II) can still be obtained at pH 2. In the case of pH 1, the adsorption of Cu(II) was limited because the carboxylate ions (COO^-) and amine groups formed protonation by very high concentration of hydrogen ions. In sum, the presence of salts in Cu(II) solution affected the adsorption behavior slightly. The removal of Cu(II) by PSGI resin can be operated well in the range of pH 2.0–5.5.

Desorption and repeated use

As described previously, many researchers concentrated on metal ion recovery by using chelating polymers because they were reusable. Furthermore, the readsorption tests were carried out to evaluate the practical utility of PSGI. Thus, after repeated adsorption–desorption operations, only 4% of the adsorption capacity decreased after 15 cycles. That is, PSGI is a good reusable adsorbent in the removal of Cu(II) from wastewater.

Competitive adsorption

The adsorption kinetics of Cu(II), Co(II), and Cd(II) by PSGI under noncompetitive condition is shown in

Figure 8. Although the equilibrium adsorption capacities of Co(II) and Cd(II) are less than that of Cu(II) (1.46 mmol/g), the equilibrium adsorption capacities are 1.02 mmol/g for Co(II) and 1.11 mmol/g for Cd(II), demonstrating that PSGI is also a good adsorbent for removal of Co(II) or Cd(II) from their single-metal-ion solutions. Furthermore, their adsorptions tended toward equilibrium at 15 min, which was earlier than that of Cu(II). This may be explained the fact that the adsorption capacities of metal ions increase with the increase of the contact time, but the polymer chains shrink and the fraction of the adsorption site decreases. Thus, metal ions are difficult to diffuse toward the chelating sites and the adsorption process will reach equilibrium. However, Cu(II) possesses the smallest ionic radius and the largest charge/radius ratio²⁵ that can still diffuse toward the adsorption sites and form stable polymer–metal complexes. That is, the equilibrium adsorption capacity of Cu(II) is greater than that of Co(II) and Cd(II), but it needs a longer time to reach equilibrium. Competitive adsorptions of Cu(II) with Co(II) and Cu(II) with Cd(II) under the same initial concentrations of metal ions ($7.87 \times 10^{-3} M$) are illustrated in Figures 9 and 10, respectively. Interestingly, only the initial adsorption rate of Cu(II) decreased slightly, and neither the equilibrium time and the adsorption capacity of Cu(II) was affected by the presence of Co(II) or Cd(II). On the contrary, adsorptions of Co(II) or Cd(II) under this condition were

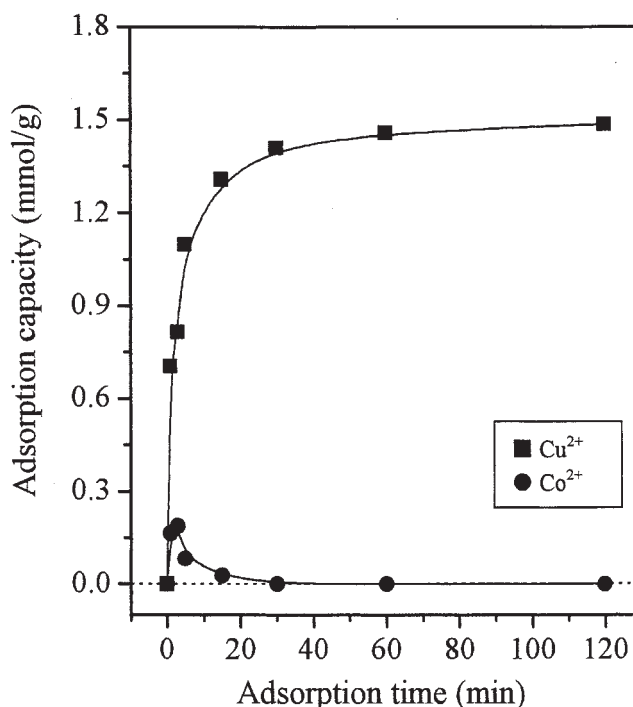


Figure 9 Competitive adsorptions of Cu(II) with Co(II) under the same initial concentrations of metal ions ($7.87 \times 10^{-3} M$) at 25°C, pH 4.5.

inhibited by the presence of Cu(II), and a maximum adsorption capacity was observed at 3 min. When the mixtures of the metal ions are adsorbed by PSGI first, all the metal ions have opportunities to occupy the chelating sites because there exist many unreacted chelating groups in this resin. When the most chelating sites adsorb the metal ions, no metal ions can diffuse toward the adsorption sites except Cu(II). The coordinate-covalent bond between the chelating group and Cu(II) is more stable than that of Co(II) and Cd(II). As the Cu(II) ions diffuse to the chelating sites of PSGI, they can replace the Co(II) or Cd(II) that have been adsorbed by the chelating groups in PSGI. Thus, a maximum adsorption capacity of Co(II) or Cd(II) is observed in Figures 9 and 10. In these competitive adsorption tests, the experimental results confirmed the adsorption capacities of Co(II) and Cd(II) declined to zero at 30 and 60 min, respectively. That is, the selectivity coefficient of Cu(II) with these two metal ions, at 25°C and pH4.5, are $\alpha_{Cu(II)/Co(II)} \rightleftharpoons \infty$ and $\alpha_{Cu(II)/Cd(II)} \rightleftharpoons \infty$ after a proper adsorption time. Figure 11 displays the competitive adsorption among Cu(II) with Co(II) and Cd(II) under the same initial concentrations of metal ions ($7.87 \times 10^{-3} M$). The adsorption behaviors of all the metal ions are similar to those of two metal ions' competitive adsorptions. To summarize, PSGI resin has good adsorption selectivity for Cu(II) with the coexistence of Co(II) and Cd(II). This can be applied to the separation of Cu(II) in aqueous systems containing Co(II) and Cd(II).

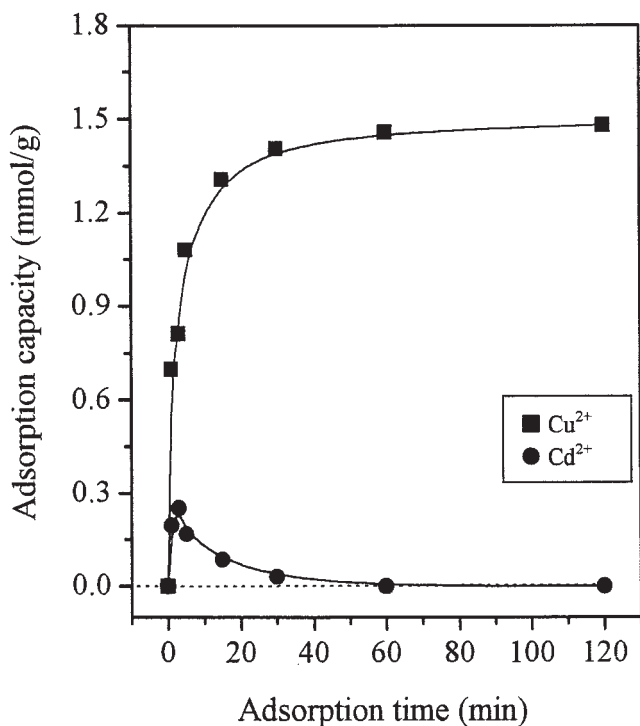


Figure 10 Competitive adsorptions of Cu(II) with Cd(II) under the same initial concentrations of metal ions ($7.87 \times 10^{-3} M$) at 25°C, pH 4.5.

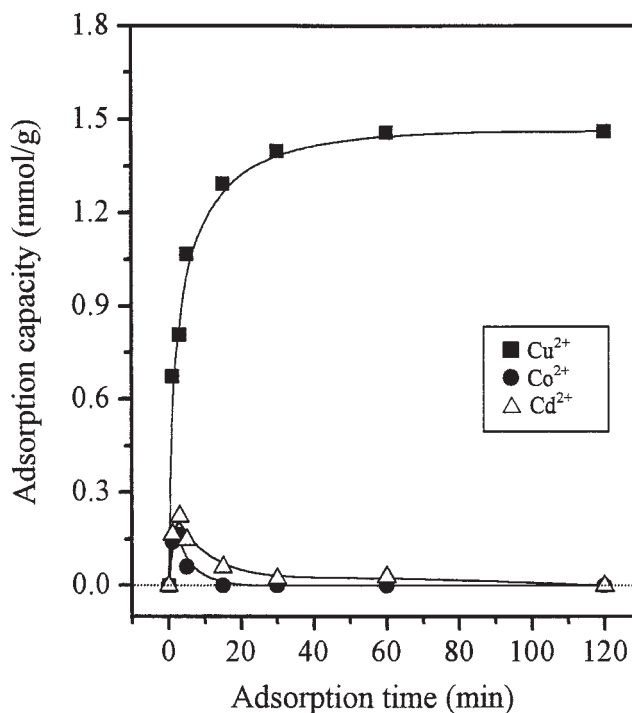


Figure 11 Competitive adsorptions of Cu(II) with Co(II) and Cd(II) under the same initial concentrations of metal ions ($7.87 \times 10^{-3} M$) at 25°C, pH 4.5.

CONCLUSION

A chelating resin, PSGI, was synthesized by the radical polymerization of GMA-IDA, DVB, and styrene. The equilibrium times and adsorption capacities of PSGI from their single-metal-ion solutions were 40 min, 1.46 mmol/g for Cu(II); 15 min, 1.02 mmol/g for Co(II); and 15 min, 1.10 mmol/g for Cd(II). The adsorption isotherm of Cu(II) on PSGI followed the Langmuir isotherm. The concentration of KCl of 0–0.1 M in Cu(II) solution did not produce remarkable changes in the adsorption behavior. Within the pH range of 2–5.5, the pH of the Cu(II) solution affected the adsorption behavior slightly. Repeated adsorption and desorption tests showed that only 4% of the adsorption capacity decreased after 15 cycles. In addition, the selectivity coefficient of Cu(II) with Co(II) and Cd(II) were $\alpha_{Cu(II)/Co(II)} \rightleftharpoons \infty$, $\alpha_{Cu(II)/Cd(II)} \rightleftharpoons \infty$ and $\alpha_{Cu(II)/(Co(II)+Cd(II))} \rightleftharpoons \infty$ after a proper adsorption time. That is, PSGI resin had good adsorption selectivity for Cu(II) with the coexistence of Co(II) and Cd(II).

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