Synthesis, Structure, and Selective Separation Behavior of Copper-Imprinted Microporous Polymethacrylate Beads

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Metal ion-imprinted polymethacrylate beads with sizes ranging from 100 to 300 μm were prepared by suspension polymerization for the application of selective separation of target metal ions. The metal ion contacting area of the beads was enlarged via pore formation (BET 425 m^2/g) using toluene as a porogenic agent. The synthesis of the copper-imprinted porous beads was verified using FTIR, SEM, and ESCA. Separation capacity and selectivity were investigated carrying out column separation experiments. The selective adsorption behavior of the imprinted beads was significantly affected by flow rate, pH, and metal ion concentration in the solution. Adsorption of the copper ion, the template metal ion, onto the beads was highly selective, compared with other ions such as nickel and zinc, with the selective coefficients at approximately 5–10. The microporous particles possessing such high selectivity has a potential application as novel column packing materials especially requiring high selective efficiency, which is usually not achievable by commercial ion exchange resins. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 3248–3254, 2009

Keywords: polymer properties, polymerization, separation techniques, particle technology

Introduction

Treatment of industry waste is an important environmental protection issue. The pollutants in waste water to be dealt with include heavy metals such as copper, nickel, zinc, arsenic, and palladium, which have harmful effects on the ecology and living organisms. Accumulation of such heavy metals in the human body can cause cancer and brain damage.

The molecular or ionic imprinting technique is an approach to prepare "host" molecules that can recognize "guest" species (molecules or ions).[1,2] A template molecule or ionic species is self-assembled with the functional monomers to form a variety of bonded complexes. The complex is then polymerized in the presence of cross-linkers to produce a rigid network structure. When the templates are removed, the binding sites (cavities) are formed in the polymer matrix. As these cavities are spatially and functionally accessible to the templates, the imprinted polymers synthesized have strong selective recognition abilities towards the template molecule or ion from a mixture of chemical species. Figure 1 shows a general synthetic procedure of molecule or ion-imprinted polymer.

There has been a rapid increase in the number of reports related to the synthesis of metal ion imprinted polymers (MIIP) and their use in separation or preconcentration of a variety of metals.[1–13] In previous research, copper-imprinted polymers were prepared to study their application towards selective separation of copper ions from a mixture of metal ions.[14] The polymers were imprinted on either the bulk body or the surface layer. The particle size was very small, 1–3 nm, for batch separation process. In a continuous column separation process, however, the particle size should be

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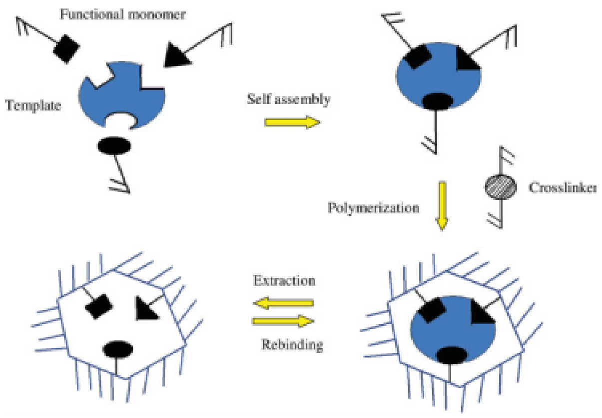

Figure 1. A schematic of typical synthetic procedure of molecule/ion-imprinted polymer.

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much bigger than nanoscale, considering the reasonable pressure drop in the column operation. The adsorption area (metal contacting area) decrease accompanied by the particle size increase can be compensated for by formation of pores through the entire body of the particles.

In this study, copper-imprinted polymer beads of size 100–300 μm were prepared by suspension polymerization using copper-methacrylate as a monomer and trimethylpropanol trimethacrylate as a cross-linker. The pores were provided using a selected porogenic solvent. The adsorption capacity and selectivity were measured for a mixture of metal ions to investigate potentials of these imprinted polymers for high selective column separation. The commercial resins developed so far are usually not able to separate the metal ions selectively because their adsorption function is given by a simple ion exchange on the polymer backbone in absence of such a rigid tailor made cavity structure.

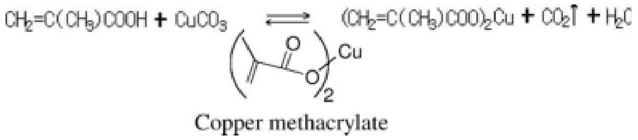
Experimental

Materials

Methacrylic acid (MAA), the monomer, and trimethylpropanol trimethacrylate (TRIM), the cross-linking agent, were supplied from Aldrich Chemical Company (Milwaukee, WI). These were vacuum distilled to remove the inhibitor and stored at 25°C prior to use. Azobisisobutyronitrile (AIBN, Aldrich) was used as an initiator for polymerization. Hydroxyethylcellulose (HEC, Aldrich) and polyvinyl alcohol (PVA, Aldrich) were used as stabilizers. Copper carbonate (Aldrich) was used as the covalently bonded template, and toluene (Daejung, Korea) the porogenic solvent. Other reagents were used as received.

Synthesis of the monomer

The copper-bound monomer was synthesized from the reaction of MAA and copper carbonate. Copper carbonate (0.09 mol) was mixed with MAA (0.36 mol) in a stoichiometric ratio and reacted at room temperature for at least 2 days in dichloromethane (150.0 mL). The resulting mixture was filtrated to remove any insoluble impurities or unreacted copper carbonate. The residual monomer and solvent were removed by evaporation under vacuum to obtain the pure copper methacrylate monomer as a solid.



$$CH_2{=}C(CH_3)COOH + CuCO_3 \rightleftharpoons (CH_2{=}C(CH_3)COO)_2Cu + CO_2\uparrow + H_2O$$

Preparation of Cu(II)-imprinted porous particles

The microporous copper-imprinted polymer particles were produced via a suspension polymerization method using toluene as a porogenic agent. This reaction was performed in a 250-mL three-neck flask fitted with a mechanical stirrer, reflux condenser, and nitrogen gas purging line. The monomer phase was composed of Cu-MAA (0.1344 g) and TRIM (1.5547 g) (monomer to cross-linker mol ratio = 1:8), and AIBN (2 % w/w total monomers). The volume of toluene was nine times that of the monomer phase. The aqueous phase was obtained by dissolving the PVA stabilizer (0.06 g) in DI water (60.0 mL). The ratio of the aqueous to organic phase was adjusted to 3:1. The organic phase was dispersed in the aqueous phase by sonication for 5 min, and then the polymerization reaction conducted in a thermostatic water bath at 80°C for 4 h under agitation. The porous materials produced were filtrated and then washed with DI water and acetone successively to remove residual surfactants, unreacted monomer, and any other impurities. The purified beads were dried under vacuum for 24 h.

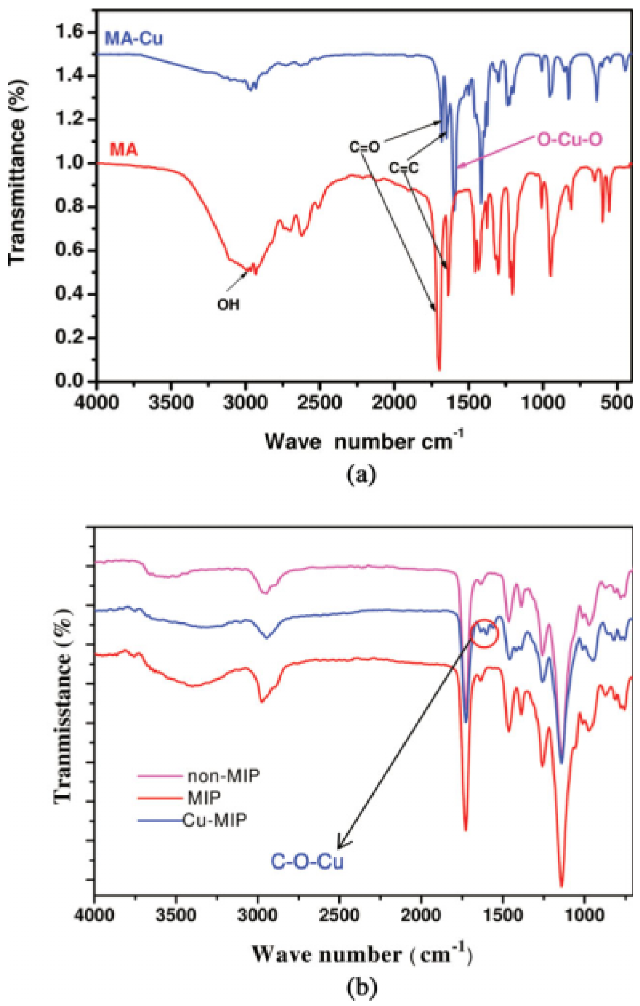
The metal ions contained in polymer particles were extracted by pacing the particles in 0.4 M HNO_3 aqueous solution, followed by vigorous stirring for 40 min. This process was repeated five times for complete removal of copper ions. After extraction of the template, the polymer particles were washed with de-ionized water several times and then dried in vacuum.

Sorption capacity measurement

A polarized Zeeman atomic absorption spectrophotometer (AAS; Model 180-70, Hitachi, Japan) with deuterium background correction was used to determine the presence and concentration of metal ions in aqueous solution during selective adsorption operation. An LI-120 digital pH meter (ELICO, India) was used for pH measurements.

Morphology and chemical structure identification

The morphology of the MIIP particles was studied using the environmental scanning electron microscope (ESEM, Philips XL-30, FEI, Hillsboro, Oregon) with an accelerating voltage of 15 kV. The formation of copper methacrylate was identified using an FT-IR (Vertex 80, Bruker, Billerica, MA) spectrophotometer. The samples were prepared blending 200.0 mg of IR spectroscopic grade KBr and 2.0 mg polymer. The atomic composition of the particle surface was carried out using a X-ray photoelectron spectroscopy (XPS, VG Scientific ESCA 2000 spectrometer) with an Mg-Kα X-ray source operating at a power of 170 W.



(a)

(b)

Figure 2. FTIR spectra of (a) monomers and (b) microporous polymer beads before and after extraction of copper, respectively.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Column separation experiment

The adsorption experiments were carried out in a packed-bed system with an internal diameter of 0.46 cm and a height of 25 cm. To study the adsorption capacity of the Cu(II)-imprinted polymer beads, the column was packed with 0.8 g of the stationary phase composed of prepared MIIP particles. To study the effect of the copper (II) concentration on adsorption capacity, the aqueous copper (II) solutions ranging from 5.0 to 100.0 mg/L were injected at a constant flow rate of 0.67 mL/min at pH 6.5. Effluent (2.0 mL) was collected and the Cu(II) concentration determined by AAS. The extraction percentage was calculated from $(C/C_0) \times 100$, where C is the concentration of the column effluent and C_0 that of the column influent. Similar experiments were conducted to study the effect of pH or flow rate on the adsorption capacity by varying the pH from 3 to 7, or flow rates from 0.67 to 5 mL/min, respectively. Desorption of copper ions adsorbed onto the Cu(II)-imprinted polymer was realized using 0.1 M HNO_3 solutions.

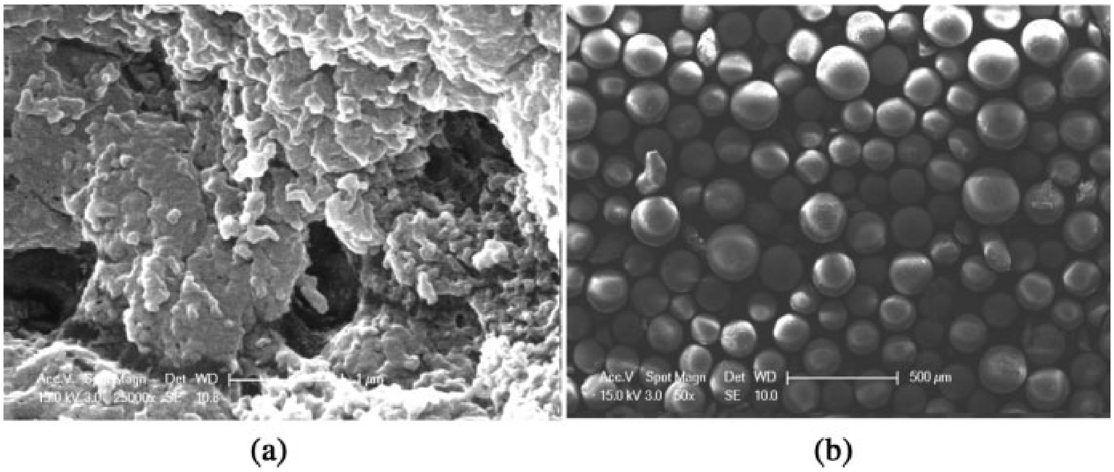
Selectivity measurement

To observe the selective adsorption behavior of the Cu^{2+} ion competitive adsorption experiments with Ni^{2+} and Zn^{2+} ions were conducted. At pH 5.6, an aqueous solution composed of Cu^{2+}, Ni^{2+}, and Zn^{2+}, 5 ppm for each ion, was flowed into the column at a rate 0.67 mL/min. After collecting 60.0 mL of effluent, the concentration of each metal ion was measured using AAS. The distribution ratio, selectivity coefficient, and relative selectivity coefficient were calculated using the following equations:

The distribution ratio (D) was given by Eq. 1:

$$D = \frac{C_A - C_B}{C_A} \times \frac{\upsilon}{m} \tag{1}$$

Here, v is the volume of the solution (mL) and m the mass of the polymer (g), with C_A and C_B the initial and final concentrations of the metal ions (mg/L), respectively.



(a)

(b)

Figure 3. SEM microphotographs of porous MIIP particles at magnification of (a) ×25,000 and (b) ×50, respectively.

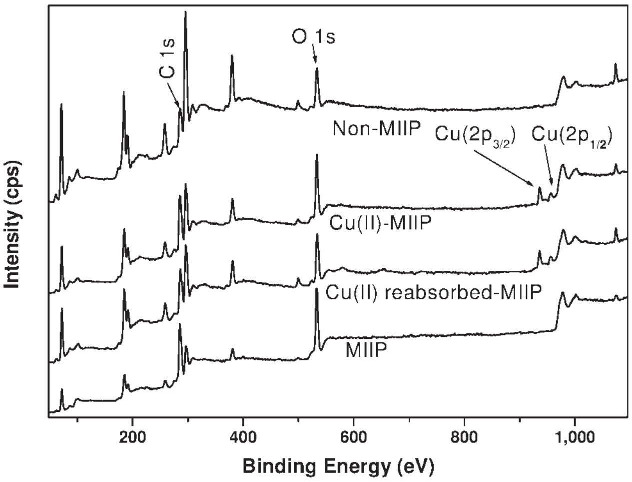


Figure 4. ESCA atomic spectra of microporous polymer beads.

The selectivity coefficient for the binding of a copper ion in the presence of other ion species can be obtained from the equilibrium binding data according to Eq. 2:

$$\alpha = \frac{D_{\mathrm{Cu}}}{D_{\mathrm{M}}} \tag{2}$$

Here, D_{Cu} and D_{M} represent the distribution ratios of Cu^{2+} and one of the other metal ions, respectively.

A comparison of the selectivity coefficient of imprinted beads with that of non-imprinted beads for each metal ion allows an estimation of the effect of imprinting on selectivity. A relative selectivity coefficient α_r is defined as:

$$\alpha_r = \frac{\alpha_i}{\alpha_n} \tag{3}$$

where α_i and α_n represent the selectivity coefficient of MIIP and non-MIIP, respectively.

Results and Discussion

Synthesis of the monomer and MIP polymer

The synthesis of MAA and $\mathrm{Cu(MAA)_2}$ was verified from FTIR spectra. The IR spectra of MAA and $\mathrm{Cu(MAA)_2}$ showed similar characteristic peaks (Figure 2), except for the metal-binding carboxylic acid group. As a result of the metal bound to the carboxyl group of MAA, the C═O, C═C, and C—O stretching vibration peaks at 1697.3, 1635.5, and 1205.4 cm^{-1} in the MAA were shifted to 1679.9, 1649.1, and 1201.6.1 cm^{-1} in the $\mathrm{Cu(MAA)_2}$, respectively. The —OH stretching vibration exhibited very strong peaks in the MAA spectrum, but disappeared in $\mathrm{Cu(MAA)_2}$. A (O—Cu) stretching vibration was observed at 1597.4 cm^{-1} in $\mathrm{Cu(MAA)_2}$, while not in MAA. These results indicated that the synthesis of copper methacrylate was successful. Figure 2b shows the IR spectra of porous materials with non-MIP, Cu-possessing polymer (Cu—MIP), and Cu-imprinted (removed) polymer (MIP). Figure 2b shows similar peak assignments among non-MIP, Cu-MIP, and MIP, except for the peak of the C—O—Cu bond, appearing at 1598 cm^{-1} in the spectrum of Cu—MIP from the presence of the Cu ion. No C—O—Cu band for MIP sample assures complete removal of Cu^{2+} during its extraction process.

Morphology, particle size, and BET surface area

Figure 3 shows the morphology of porous MIP beads in both high magnification (25000×: Figure 3a) and low magnification (50×: Figure 3b). Figure 3a and 3b show that the prepared particles were highly porous in spherical form with a size ranging from 100 to 300 μm. BET analysis shows that the average surface area of copper-containing porous polymer particles was 401.0 m^2/g, while the copper-imprinted was 481.9 m^2/g. The higher value of the surface area for the copper-imprinted particles was caused by depletion of copper ions form the polymer surface during its extraction process. The porosity of copper imprinted particles was 0.11 cm^3/g. The average particle diameter did not change by removal of

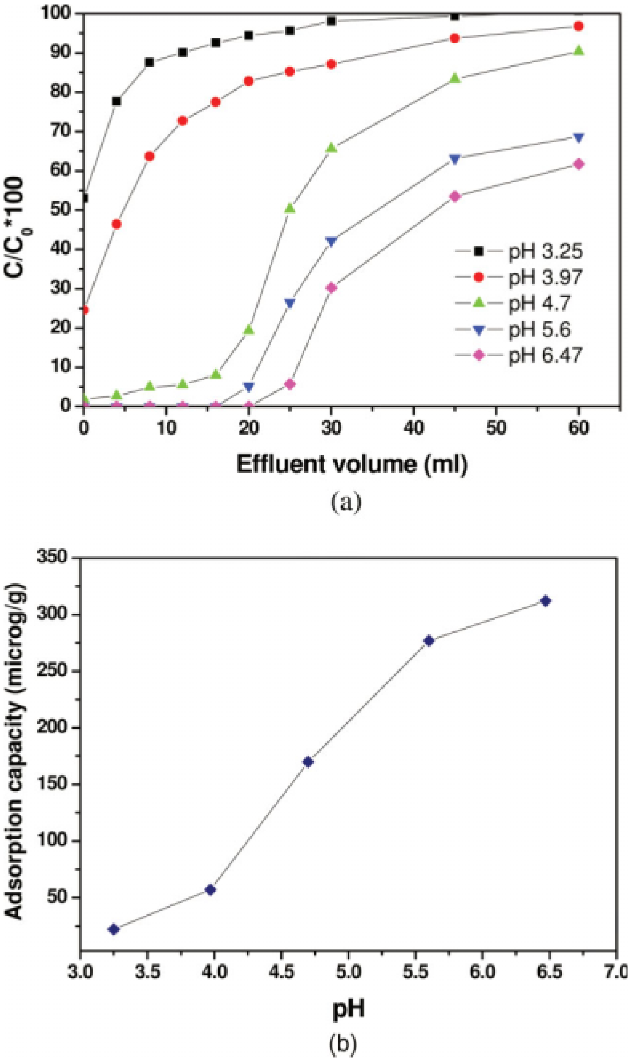


Figure 5. Effect of pH on (a) the adsorption rate and (b) the adsorption capacity for Cu at the flow rate of 0.67 mL/min.

The initial copper concentration is 4.86 ppm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

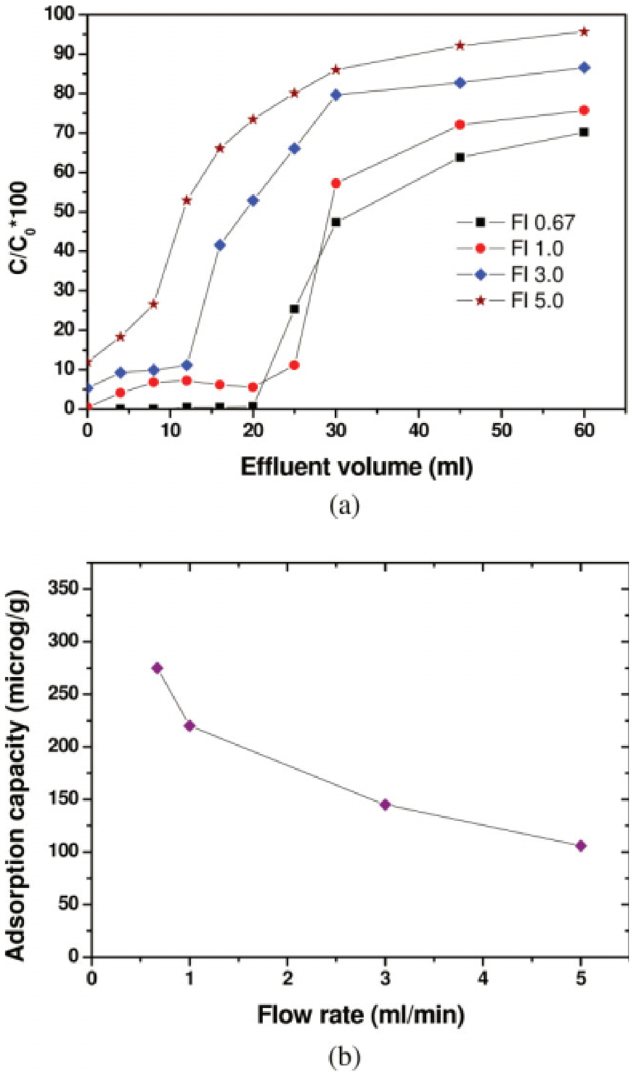


Figure 6. Effect of flow rate on (a) the adsorption rate and (b) the adsorption capacity for Cu at pH 5.6.

Initial copper concentration is 4.86 ppm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

copper ions due to such a high crosslinking density (crosslinker to monomer mol ratio of 8), and thus there was no packing efficiency difference between the two systems before and after extraction of template.

Atomic analysis of particle surface

The XPS spectra of Cu(II)-MIIP and Cu(II)-reabsorbed-MIIP particles were characterized by a dominant spin-orbit-split doublet occurring around 934.7 eV (Cu2p3/2) and 954.5 eV (Cu2p1/2) (Figure 4), respectively, suggesting the presence of Cu^{2+} on polymer particles. The absence of Cu2p peak in the MIIP spectrum indicates the 100% removal of copper ions from Cu(II)-MIIP surface. The position, width and shape of the Cu2p peaks of Cu(II) readsorbed-MIIP were exactly the same as those of Cu(II)-MIIP. This means that the shape of cavities formed after removal of Cu^{2+} from MIIP microsphere is suitable for coordination geometry of Cu^{2+} ions which is selectively adsorbed from a solution, and almost all carboxyl groups in the specific binding sites on MIIP surface interacts effectively with the copper ions.

Column separation analysis

Effect of pH. pH is an important factor in controlling adsorption characteristics. As shown in Figure 5a, not many copper ions were adsorbed onto the MIP porous materials at a low pH (below 4.7). The adsorption kinetics of the copper ions increased with increasing pH, up to 7, where the copper ion started to precipitate from the reaction with the —OH group. In Figure 5b, the equilibrium adsorption capacity of the copper ion also increased with increasing pH, indicating deprotonation of the carboxyl groups in the host molecules at high pHs.

Effect of Flow Rate. The effect of flow rate on the copper adsorption kinetics and equilibrium capacity at a fixed pH of 5.6 is shown in Figure 6a, b. As shown in Figure 6a, the outlet concentration of the copper ion increases with increasing flow rates. In the case of a relatively slow flow rate of 1.0 or 0.67 mL/min, the outlet concentration of the

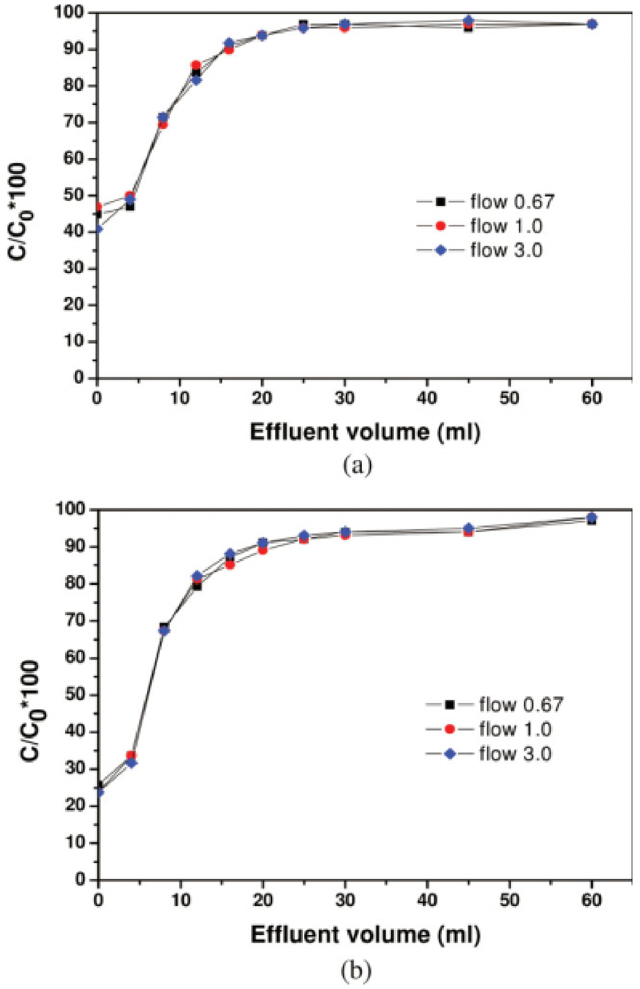


Figure 7. Effect of flow rate on the adsorption rate for (a) Zn and (b) Ni.

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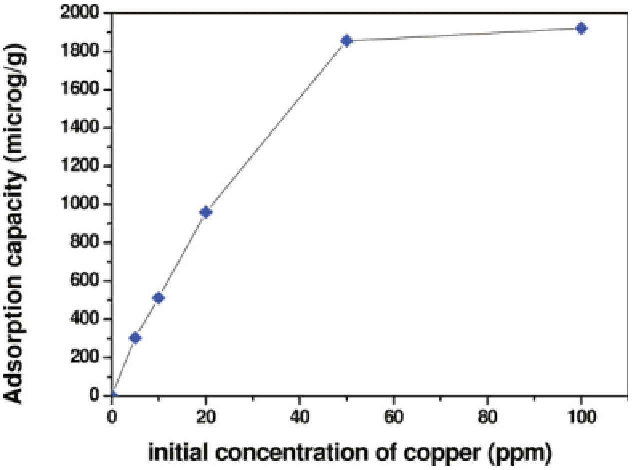

Figure 8. Effect of initial copper concentration of on the adsorption capacity for Cu at pH 5.6.

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copper ion was nearly undetectable within the first 20.0 mL, followed by its increase after that. At a high flow rate, copper ions could be caught only in the active binding sites of the particle surface. As there was not enough time for copper ions to move inside the pores of the particles, the outlet concentration of copper ions rapidly increased to reach the injection value. When the flow rate is small enough for copper ions to migrate into the pores, it makes possible adsorption onto the active binding sites of both surface and pores of the particles. Figure 6b shows the equilibrium adsorption capacity of microporous MIP particles. The adsorption capacity of the copper ion decreases from 275.0 to 106.0 μg/g with an increasing flow rate from 0.67 to 5.0 mL/min.

The imprinting effect of the polymer particles on adsorption capacity is well illustrated in Figure 7 where the aqueous solution containing other metal ions, such as nickel and zinc, were applied to column separation. As shown in Figure 7, there was not any difference in sorption capacity for these metal ions from the template copper ion.

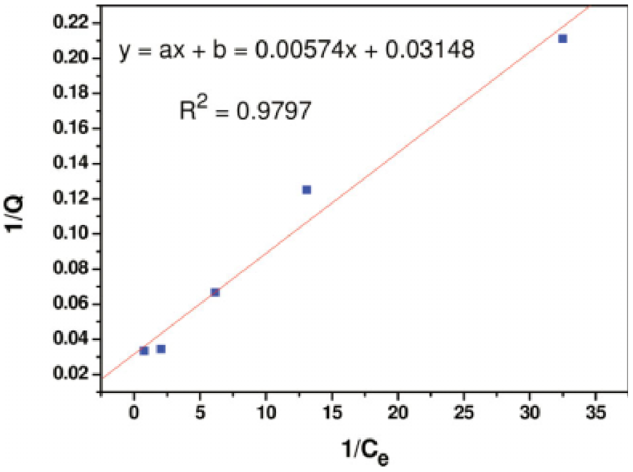

Figure 9. Langmuir adsorption isotherm.

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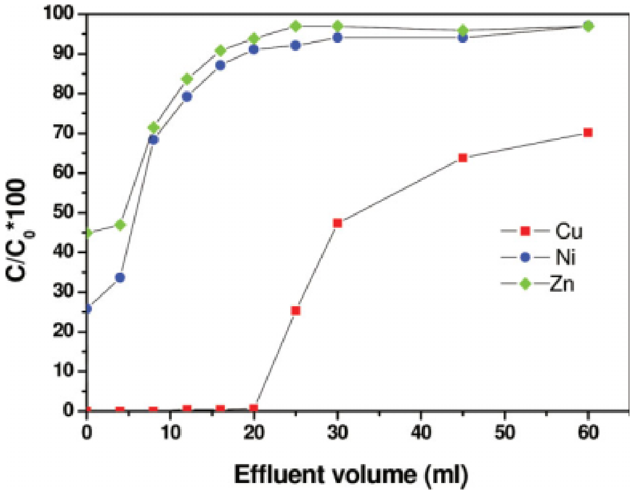

Figure 10. Adsorption behavior of copper, nickel and zinc on the copper imprinted microporous beads at pH 5.6.

The flow rate is 0.67 mL/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Effect of Initial Concentration Adsorption of Cu^{2+} from aqueous solution was investigated at different initial concentrations of the copper ion. As shown in Figure 8, the amount of copper ions adsorbed per unit mass of the polymer beads increased up to saturation (equilibrium adsorption amount, or adsorption capacity) with the initial concentration of copper ions.

Adsorption isotherms

In this batch sorption experiment, adsorption isotherms were used to evaluate the adsorption properties of MIP particles. The Langmuir model was applied in interpreting Cu(II) adsorption capacity of imprinted polymers. Figure 9 shows the dependence of the equilibrium concentration on the adsorbed amount of Cu(II) onto the porous MIP. The Langmuir adsorption isotherm is expressed by Eq. 4, assuming that the molecules/ions are adsorbed at a fixed number of well-defined sites, each of which holding one molecule. These sites are also assumed to be energetically equivalent and equidistant to each other so that there are not any interactions between molecules adsorbed to adjacent sites. The corresponding transformations of the equilibrium data for the Cu(II) ions gave rise to a linear plot, indicating that the Langmuir model could be applied in these systems and described by the equation:

$$Q = \frac{Q_{\max} b C_e}{1 + b C_e} \tag{4}$$

where Q is the adsorption capacity of copper ions (μmol/g); C_e the equilibrium of Cu(II) ion concentration in solution (μmol/

Table 1. Adsorption Capacity of Copper, Zinc, and Nickel

Metal Ions	Adsorption Capacity (μg/g)
Copper	277
Zinc	51
Nickel	38

Table 2. Selectivity Coefficient

	Cu-Imprinted Polymer		Nonimprinted Polymer		
Metal Type	D	α	D	α	α_r
Cu^{2+}	56.99		7.12		
Zn^{2+}	10.04	5.68	7.46	0.95	5.98
Ni^{2+}	7.62	7.45	6.53	1.09	6.83

L); b the Langmuir constant (g/μmol); and Q_{max} the maximum adsorption capacity (μmol/g). This equation can be linearized.

The maximum adsorption capacity (Q_{max}) data for the adsorption of copper ions were obtained from experimental data with a correlation coefficient (R^2) of 0.9797. The Langmuir adsorption model can be applied in this affinity adsorbent system. It should also be noted that maximum adsorption capacity (Q_{max}) was determined to be 2033 μg/g, which is very similar to the saturated value observed from the experiment (Figure 8).

Selectivity

Figure 10 shows the adsorption behavior of copper-imprinted polymer microporous particles for a few other metal ions, including not only copper, but also nickel and zinc as well. The metal ions selected in this study have the same valence number and similar radii one another—Cu(II) 71, Ni(II) 69, and Zn(II) 74 pm, respectively. Even though such similar effective sizes, there is a considerable difference in the adsorption capacity of those cupper imprinted beads between the template ion, Cu(II) and nontemplate ones, Ni(II) and Zn(II). The outlet concentration of zinc and nickel sharply increased within the first 10 min and rapidly reached the initial concentration. On the contrary, the copper ion was nearly adsorbed into the porous materials within the first 20 min, followed by an increase in outlet concentration; however, after 60 min it reached just 70 % of the initial concentration.

Tables 1 and 2 summarize the adsorption capacity and selectivity of copper-imprinted microporous polymer particles for copper, zinc, and nickel ions, respectively.

Conclusion

The copper-bound methacrylate monomer was synthesized to prepare the copper-imprinted polymethacrylate porous beads in sizes ranging from 100 to 300 μm, which is appropriate for column packing materials. The synthesis of the monomer and polymer was verified with FTIR and SEM and the selective separation behavior of the imprinted polymer beads by AAS. The adsorption capacity of the porous materials was very high (up to about 2,000 μg/g polymer) with the high selectivity coefficient of copper adsorption 5.68 times higher than Zn and 7.45 times than Ni metal, respectively, although those three metals possess the same valence number and similar ion radii one another. The microporous particles prepared in this study are suitable for column separation of metal ion mixtures especially requiring high selectivity.

Acknowledgment

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