

# Metal Ion-Imprinted Polymer Microspheres Derived from Copper Methacrylate for Selective Separation of Heavy Metal Ions

Anh Hoang Dam, Dukjoon Kim

Department of Chemical Engineering, Sungkyunkwan University, Suwon, Kyunggi 440-746, Korea

Received 10 July 2006; accepted 28 September 2006

DOI 10.1002/app.26923

Published online 21 December 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Microbeads of metal ion-imprinted polymers (MIIPs) were prepared by a novel precipitation polymerization technique, in which copper methacrylate monomer and ethylene glycol dimethacrylate crosslinker were copolymerized in a rotary evaporator. The prepared microbeads had mono- or narrow size dispersity, and their sizes increased from 1 to 4  $\mu\text{m}$  with decreasing solvent amount or increasing initiator concentration. The absorption capacity and selectivity of the imprinted polymer for copper ion were determined in the presence of various competitive metal ions. As results, adsorption equilibrium

was quickly achieved in about 10 min with high absorbability (about 90%). The effects of pH, initial metallic ion concentration, and MIIP bead size on the absorption capacity were investigated. The Cu(II)-imprinted polymers exhibited extremely high selectivity, which was much higher than that of corresponding blank polymers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 14–24, 2008

**Key words:** imprinted polymer; separation; heavy metal ion; metal-containing monomer; precipitation polymerization

## INTRODUCTION

Molecular imprinting technique has been widely and successfully used to prepare polymers offering high-affinity binding sites for a variety of molecules, including organic, inorganic, and even biological molecules or ions.<sup>1–3</sup> These materials are useful for various application fields such as biomaterial, sensor technologies, molecular and ionic separations, and catalysis.<sup>4–30</sup>

The original concept of molecular imprinting was first inspired by Linus Pauling in the 1940s. However, the current interests in imprinted materials were aroused by Wulf and Sarhan,<sup>31</sup> who developed several approaches that came under the broad category of covalent molecular imprinting. They used the reversible formation of ester linkages between the sugar and phenylboronic acid.<sup>1</sup> Mosbach et al.<sup>32</sup> opened a new direction of preparing imprinted materials with noncovalent approach. They utilized a monomer, such as methacrylic acid (MAA) along with the crosslinker, such as ethylene glycol dimethacrylate (EGDMA), mixed with the template.

In the recent years, continuous progress in analytical chemistry has made it possible to develop new chemical separation techniques. Various techniques have been used for the separation or preconcentration of trace metals, including coprecipitation, liquid-liquid extraction, off-line preconcentration, and separation involving adsorption on activated carbon, dithizone-anchored poly-(EGDMA-HEMA) microbeads, polyurethane foam, amberlite XAD resins and other solid phases, and on-line flow injection. These methods often require large amounts of high purity, organic solvent, some of which are harmful to health and create environmental problems. Therefore, much more selective systems for the separation of metal ions are needed for the development of new extractants and adsorbents. Much of the current research in solid phase extraction is about the use of metal ion-imprinted polymers (MIIP) due to their low price and high stability in different environments and their higher selectivity than common techniques. There has been a rapid increase in the number of publications related to the synthesis of MIIP materials and their use in separation or preconcentration of metals. Many MIIPs have been prepared, including lanthanides, actinides, noble metals, and heavy metals, and transition elements such as Dy(III), Gd(III), UO<sub>2</sub>(II), Pd(II), Cu(II), Zn(II), Al(III), Pb(II), Ni(II), Ca(II), and Mg(II) imprinted ones.<sup>33,34</sup>

Monodispersed, micron-sized polymer spheres that have highly crosslinked structure cannot be easily

Correspondence to: D. Kim (djkim@skku.edu).

Contract grant sponsor: Core Environmental Technology Development Project for Next Generation; contract grant number: 022-051-014.

*Journal of Applied Polymer Science*, Vol. 108, 14–24 (2008)

© 2007 Wiley Periodicals, Inc.



obtained by any of the common polymerization methods such as bulk, solution, suspension, emulsion, and core-shell polymerization methods.<sup>35</sup> One of the most important points in preparing MIIP materials is the use of a high amount of crosslinker to hold the imprinting sites (high rigidity). Nowadays, most MIIP particles are prepared by solution polymerization or bulk polymerization techniques. These preparations however are confronted with problems such as (i) prolix grinding and sieving, (ii) partial destruction of imprinted structures during grinding, (iii) possible presence of residual guest, (iv) time-consuming process and yield for only moderate amounts of "useful" product, etc.<sup>36</sup> Although suspension polymerization and seed polymerization can probably provide spherical, molecularly imprinted polymer beads, they not only require use of either special dispersing phases, surfactants, or complicated swelling processes but also frequently compromise binding specificity.<sup>1,37-39</sup>

We report a novel precipitation polymerization method using a rotary evaporator for preparation of uniform MIIP microspheres bearing imprinted binding sites, quickly, cleanly, and with high yield. Importantly, the obtained MIIP microspheres show excellent selectivity against a range of "strong" competitive metal ions, including  $Mg^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Na^+$ , and  $Fe^{3+}$  ion. Copolymers of copper methacrylate ( $Cu(MAA)_2$ ) and EGDMA can be prepared by simple and economical precipitation polymerization, thermally initiated with 2,2'-azobisisobutyronitrile (AIBN) in isopropanol as a solvent, in which the stabilization mechanism is quite different from that in emulsion, dispersion, or suspension polymerization. Surprisingly, no chemical agent is involved in the stabilization mechanism for the formation of spherical particles from crosslinkable monomers-diethylene glycol dimethacrylate, as the stabilization of the particles originates from the resistance against the interfusion of particles probably caused by a high degree of crosslinker.<sup>35</sup>

## EXPERIMENTAL

### Materials and instruments

To remove the inhibitor prior to polymerization, MAA and EGDMA (Aldrich Chemical, USA) were distilled under vacuum and stored at 4°C until use. The initiator AIBN (Junsei Chemicals) was recrystallized from methanol. Copper carbonate (Aldrich), isopropanol, and other reagents were used as received.

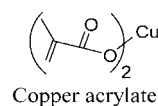
A Hitachi 180-70 Polarized Zeeman atomic absorption spectrophotometer (AAS) with deuterium background correction was used for the determination of  $Cu^{2+}$  ion and other metal ions during absorption and selectivity studies. An LI-120 digital pH

meter (ELICO, India) was used for pH measurements. An FTIR spectrum (Bruker, USA) was recorded in the range 0-4000  $cm^{-1}$ .

The surface morphology of the MIIP particles was studied using environmental scanning electron microscope (ESEM; Philips) with an accelerating voltage of 15 kV. An EDAX USL 30 analyzer attached to the ESEM was used to determine the chemical composition of the samples by energy dispersive X-ray spectrometer (EDX).

### Synthesis of monomer

Copper methacrylates were synthesized as reported elsewhere.<sup>40-49</sup> Briefly, copper carbonate was added to MAA in stoichiometric ratio and placed at room temperature for at least 2 days using dichloromethane as the solvent. The reaction mixture was filtered to remove any insoluble impurity, and residual MAA and dichloromethane solvent were evaporated under vacuum to obtain copper methacrylate monomer of solid form. The synthesis reaction and structure of copper methacrylate are as follows:



### Preparation of Cu(II)-imprinted polymer

Copper-ion imprinted microspheres were prepared by precipitation polymerization, in which the polymerization ingredients simply consisted of medium,  $Cu(MAA)_2$  and EGDMA co-monomer mixture, and AIBN. The molar ratio of EGDMA :  $Cu(MAA)_2$  ( $R$ ) in the monomer mixture was varied from 2 to 14 (in mol), and the total amount of monomers ( $Cu(MAA)_2$  and EGDMA) was varied from 2 to 20 wt/vol % of the medium. The amount of AIBN to the total amount of monomers was varied between 1 and 7 wt %. After charging the reactant mixture in 30 mL of isopropanol into a reactor (50 mL), it was sonicated for 5 min and purged with nitrogen for 15 min. The reactor was placed on a rotary evaporator and rotated around its oblique axis at 70 rpm. The temperature of the water bath was first ramped from room temperature to 70°C over 2 h, and then held at 70°C for 24 h under  $N_2$  atmosphere. After completion of the polymerization, the resulting particles were washed repeatedly with methanol and dried under vacuum at 50°C. The reproducibility of the results was confirmed through several repeated experiments.



**Figure 1** Photographs of Cu(II)-MIIP, MIIP, and non-MIIP from left to right, respectively. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Removal of the imprint ion from the synthesized polymers

The Cu(II) ions in the polymer particles were leached by stirring in  $\text{HNO}_3$  0.4M for 40 min. This process was repeated five times for the complete removal of Cu(II) ion, as checked by AAS. Following extraction, polymer particles were washed with deionized water and then dried in vacuum. The color of microparticles changed from blue to white after removal (Fig. 1), indicating the existence and removal of  $\text{Cu}^{2+}$  before and after extraction of the Cu(II)-MIIP, respectively.

### Adsorption of metal ions on MIIP microparticles

Adsorption of metal ions from aqueous solution was investigated in batch experiments. The effects of the initial concentration of metal ions, pH of the medium, and particle size on the adsorption rate and adsorption capacity were studied. The microparticles (0.1 g) were added to  $5 \text{ cm}^3$  of a solution containing  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2$ , in which the concentration of each metal ion was varied from 0.05 to 0.5 mM, and sealed in a test tube ( $10 \text{ cm}^3$  volume). The pH was adjusted to a desired value between 1.0 and 6.0 using a 100 mM acetic acid–sodium acetate solution and 100 mM nitric acid. The mixture was sonicated for 3 min and then shaken in a thermostated water bath at room temperature for between 5 and 60 min. The microparticles were then filtered off through a polyethylene membrane filter (Suplep LCR 25-LG, Nippon Millipore). The amount of metal ions absorbed on the microparticles was evaluated by their residual concentrations in the filtrated aqueous solution as measured by AAS. Adsorption values (mmol/g) were calculated as the difference in metal-ion concentration of the initial and final adsorption

solutions divided by the weight of dry microparticles. The experiments were performed in triplicate.

### Selectivity studies

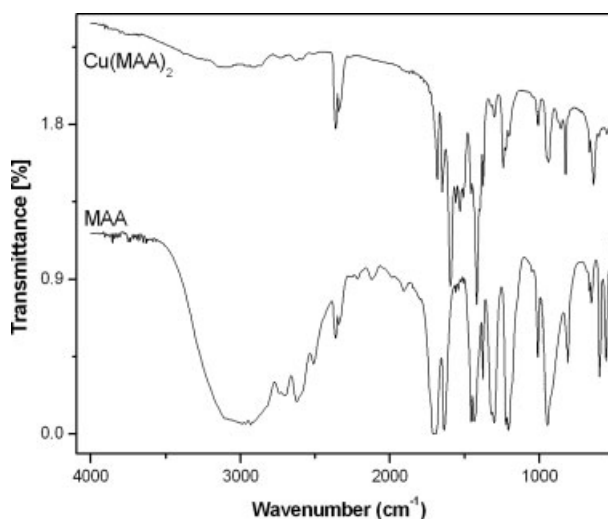
To show the  $\text{Cu}^{2+}$  selectivity of the imprinted particles, competitive adsorptions of  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Na}^+$ , and  $\text{Fe}^{3+}$  were also conducted, in which 0.1 g of the MIIP or comparative non-MIIP microparticles were treated with  $5 \text{ cm}^3$  of a solution of these competitive ions (0.3 mM for each one). After adsorption equilibrium was reached, the concentration of metal ions in the remaining solution was measured by AAS.

## RESULTS AND DISCUSSION

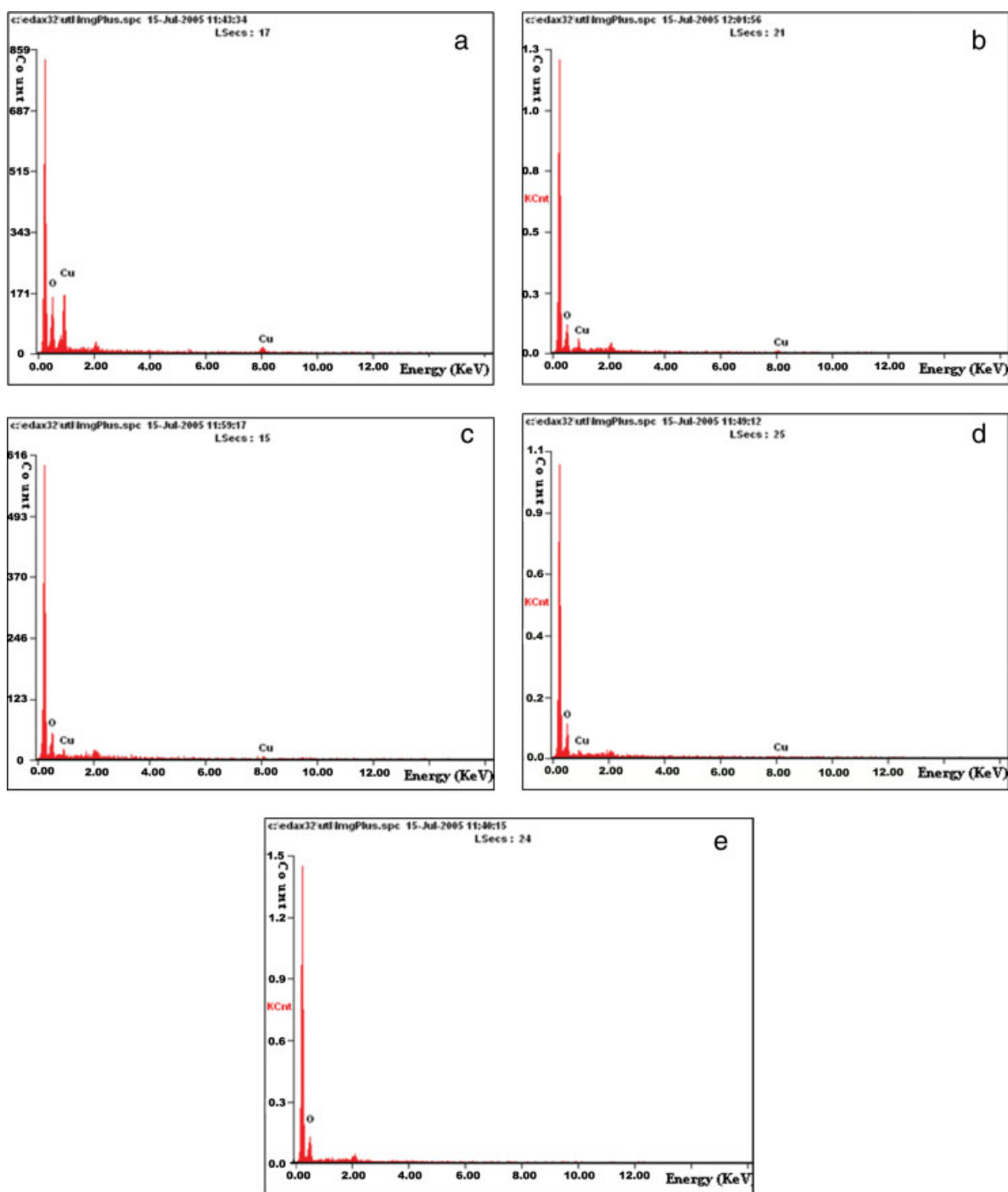
### IR spectra and EDX analysis

The IR spectra of MAA and  $\text{Cu}(\text{MAA})_2$  showed similar characteristic peaks (Fig. 2), indicating the similarity in the backbone structure of the different materials. As a result of the metal binding with the carboxyl group of MAA, the  $\text{C}=\text{O}$ ,  $\text{C}=\text{C}$ , and  $\text{C}-\text{O}$  stretching vibrations at 1693.4, 1639.4, and  $1203.5 \text{ cm}^{-1}$  in MAA were shifted to 1681.8, 1649.1, and  $1242.1 \text{ cm}^{-1}$  in the corresponding  $\text{Cu}(\text{MAA})_2$ , respectively. The  $-\text{OH}$  stretching vibration exhibited very strong peaks in the MAA spectrum but disappeared in that of  $\text{Cu}(\text{MAA})_2$ . The  $(\text{O}-\text{Cu})$  stretching vibration was observed at  $1595.1 \text{ cm}^{-1}$  in  $\text{Cu}(\text{MAA})_2$ , while  $\text{O}-\text{Cu}$  stretching was not observed in MAA. These results indicated that the synthesis of copper methacrylate was successfully conducted.

The presence and complete removal of  $\text{Cu}^{2+}$  in Cu(II)-MIIP and MIIP, respectively, were confirmed by EDX. As shown in Figure 3, the signal due to  $\text{Cu}^{2+}$  was clearly presented for Cu(II)-MIIP but



**Figure 2** FTIR spectra of (a)  $\text{Cu}(\text{MAA})_2$  and MAA and (b) Cu(II)-MIIP, MIIP and non-MIIP, respectively.



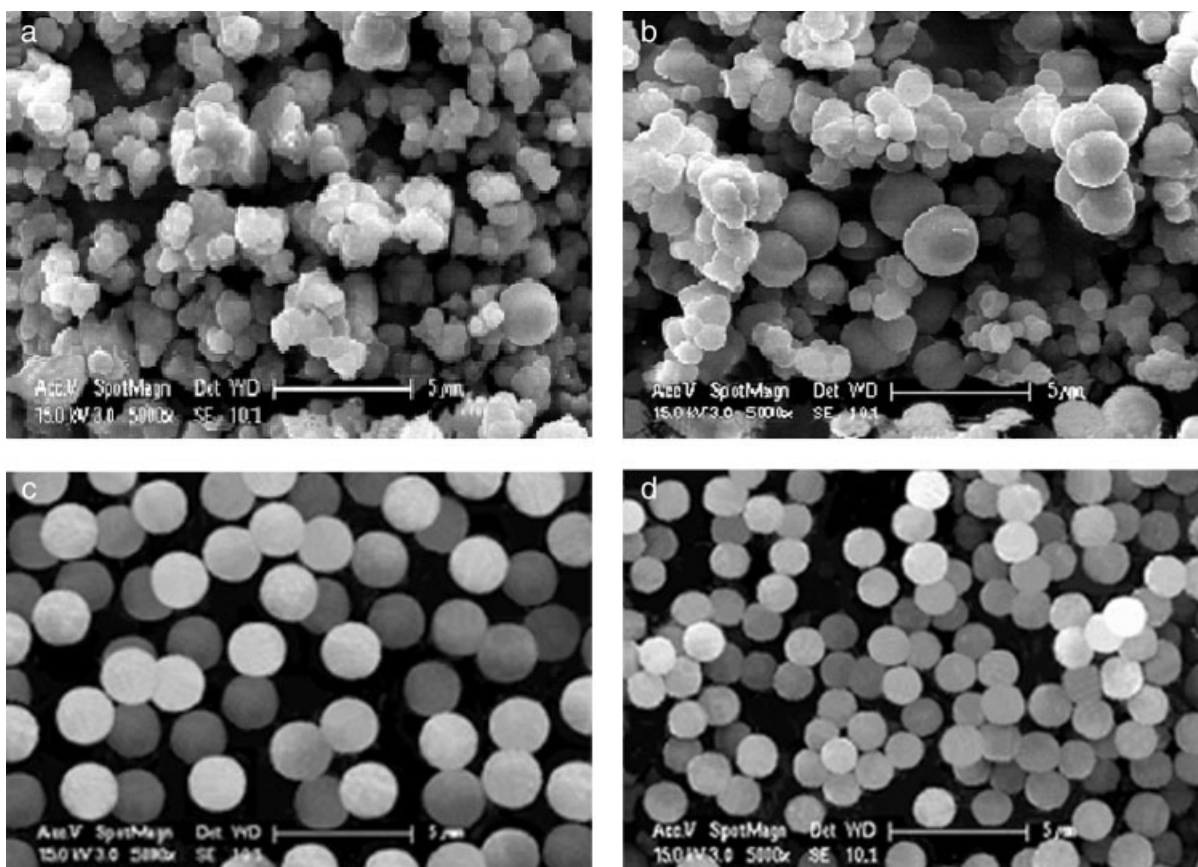
**Figure 3** EDX spectra of Cu(II)-MIIP (a–d) and MIIP (e). (a)  $R = 2$ ; (b)  $R = 6$ ; (c)  $R = 10$ ; (d)  $R = 14$ ; and (e)  $R = 10$ , respectively. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

absented for MIIP, and its intensity increased with the increasing concentration of  $\text{Cu}(\text{MAA})_2$  in the polymerization mixture.

### Morphology studies

The formation of stable microspheres in precipitation polymerization is strongly influenced by the degree of crosslinking, and the existence of a crosslinkable

monomer in high concentration is therefore essential. Since no stabilizing agents such as surfactants or steric stabilizers are used in precipitation polymerization, it is expected that the stability of the final particle will be significantly affected by the concentration of monomer, crosslinking agent, and initiator in the polymerization medium. To synthesize uniform MIIP microspheres, choice of the reaction solvent (medium) is critical.



**Figure 4** SEM image of Cu(II)-MIIP microparticles prepared at different crosslinking agent concentrations. (a)  $R = 2$ ; (b)  $R = 6$ ; (c)  $R = 10$ ; and (d)  $R = 14$ , respectively. Initiator concentration: 4 wt % AIBN, monomer concentration: 14 wt/vol % of solvent.

The final particle size is determined from the initial number and size of nuclei that grow to become individual particles at the end of polymerization. The number of nuclei strongly depends on the solubility of the polymerization medium. If the medium acts as a poor solvent for the nuclei, it hardly dissolves most of the small nuclei with low molecular weight, thereby increasing the number of nuclei and decreasing their size. When the nuclei are formed, monomers are adsorbed and polymerized onto its surface. Stable particles are generated by aggregation of the primary nucleus particles and absorption of oligomeric species, resulting in increased particle size. Numerous smaller nuclei in the initial stage of polymerization lead to smaller particle size after completion of the polymerization. In this experiment, we determined that isopropanol was the appropriate solvent based on the SEM images showing that the precipitation polymerization gives a uniform, microspherical particle with very high yield (99%).

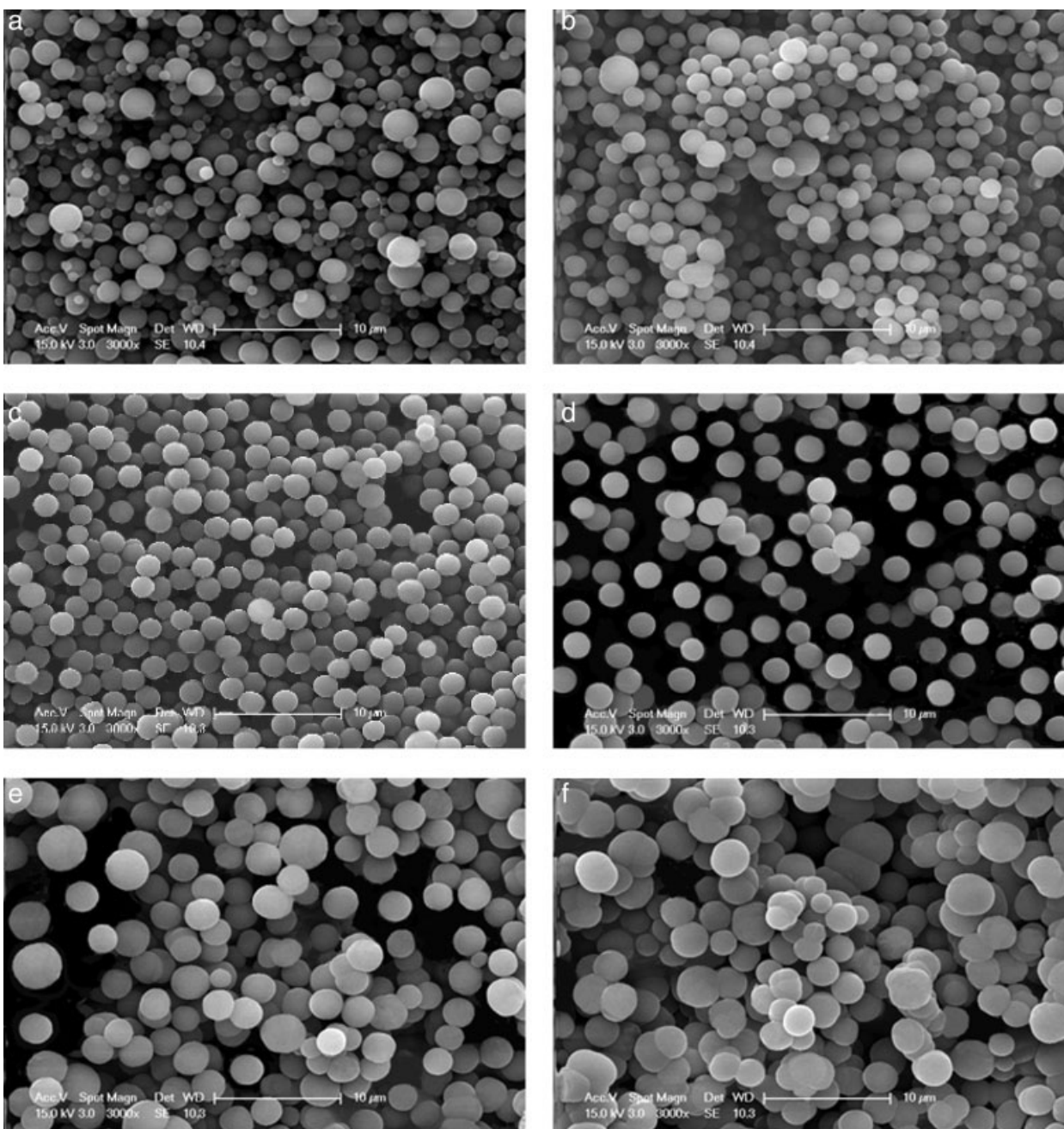
#### Effect of cross-linker concentration on MIIP morphology

The concentration of crosslinker plays an important role in determining the final particle size and uni-

formity. Figure 4 represents the morphology of the Cu(II)-MIIP microspheres synthesized at varying ratios of Cu(MAA)<sub>2</sub> to EGDMA in the monomer mixture (14 wt/vol % of total monomers in isopropanol) with 4 wt % AIBN. Coagulated particles were observed at the EGDMA : Cu(MAA)<sub>2</sub> ratio ( $R$ ) below 10 (in mol). With increasing  $R$ , the particle diameter decreased and the uniformity increased. With increasing EGDMA concentration in the monomer composition, the solubility of the nuclei in isopropanol decreased. The final particle size became smaller because of the large number of nuclei formed in the initial stage. Moreover, higher cross-linker concentrations reduced swelling and aggregation in the medium and hence produced smaller and more narrowly dispersed microspheres.

#### Effect of concentration of monomers in medium

The size and structure of microspheres are dependent on the initial monomer concentration and the solvent properties. Figure 5 shows the microphotographs of the microspheres produced, as the total monomer concentration was varied from 2 to 20 wt/vol % for  $R = 10$  with 4 wt % AIBN. The micro-

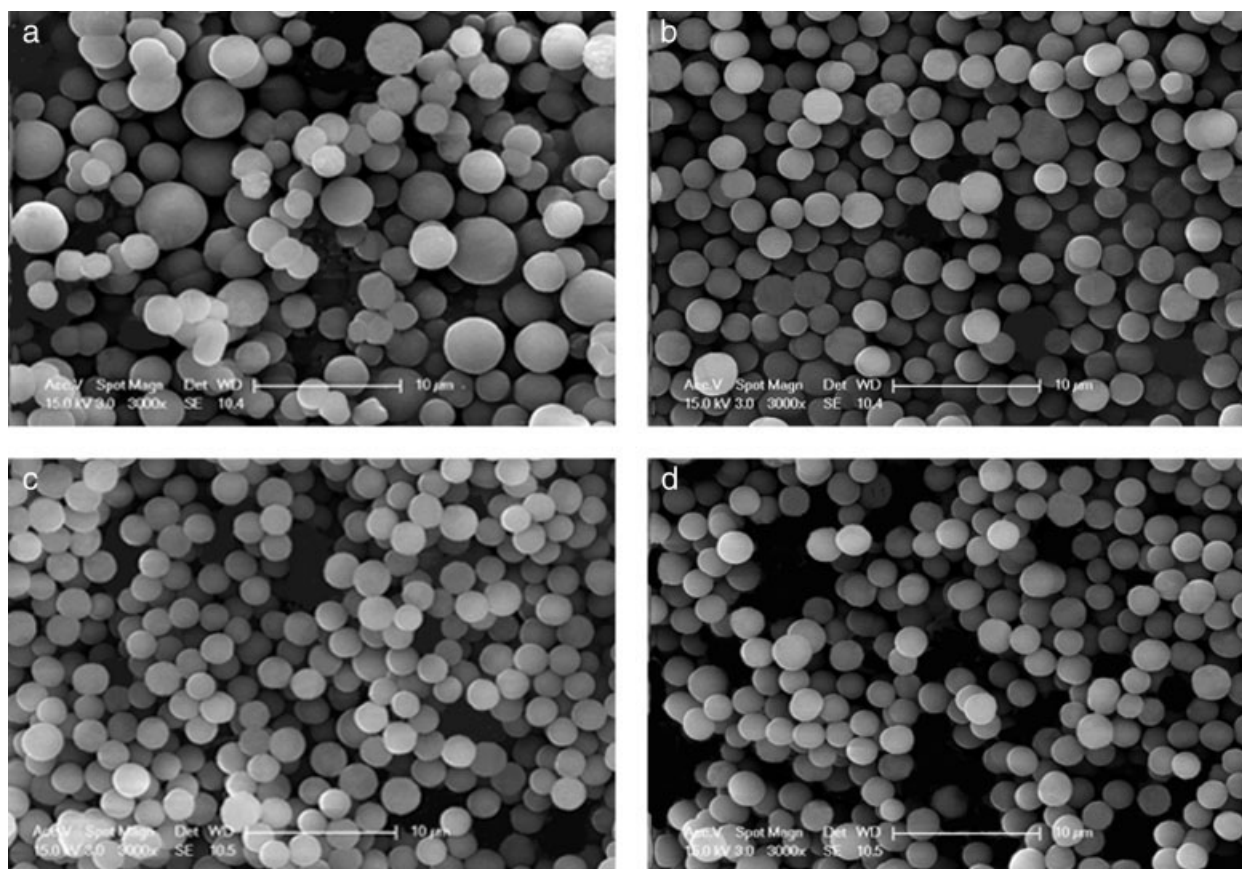


**Figure 5** SEM image of Cu(II)-MIIP microparticles prepared at different monomer concentrations. (a) 2; (b) 5; (c) 8; (d) 14; (e) 17; and (f) 20 wt/vol % of solvent, respectively.

sphere diameter increased monotonously from 1.7 to 3.4  $\mu\text{m}$  with monomer concentration, and microspheres were stable without severe coagulation, although small coagulated particles were obtained at high concentration above 20 wt/vol %. At low concentration of monomer (2 wt/vol %), the nuclei formed at the first state tended to grow by absorbing either monomers or oligomeric species rather than aggregating together, so that broader particle distribution was obtained.

#### Effect of initiator concentration

Figure 6 shows the SEM micrographs of MIIP microspheres ( $R = 10$ ) produced at different initiator (AIBN) concentrations. The size of the resulting particles decreased from 4 to 2.3  $\mu\text{m}$  as the AIBN concentration increased from 1 to 7 wt % (on the basis of  $\text{Cu}(\text{MMA})_2$  and EGDMA monomers). The increase in the initiator concentration increased the number of free radicals, resulting in more nuclei in the polymerization media.  $R$  of 10, monomer concentration of



**Figure 6** SEM image of Cu(II)-MIIP microparticles prepared at different initiator concentrations. (a) 1; (b) 2.5; (c) 4; and (d) 7 wt % of monomer, respectively.

14 wt/vol % and initiator concentration of 4% were used to produce MIIP particles for further studies.

### Removal studies

The removal behavior of Cu(II) ions from Cu(II)-MIIP particles is shown in Table I and Figure 7. Table I shows the theoretical/experimental removal percentages of  $\text{Cu}^{2+}$  from the Cu(II)-MIIP. There was close similarity between theoretical and experimental values. In Figure 7, the removal time was very quick to equilibrate (within 25 min). EDX in Figures 3 supports that all  $\text{Cu}^{2+}$  ions were completely removed from the particles.

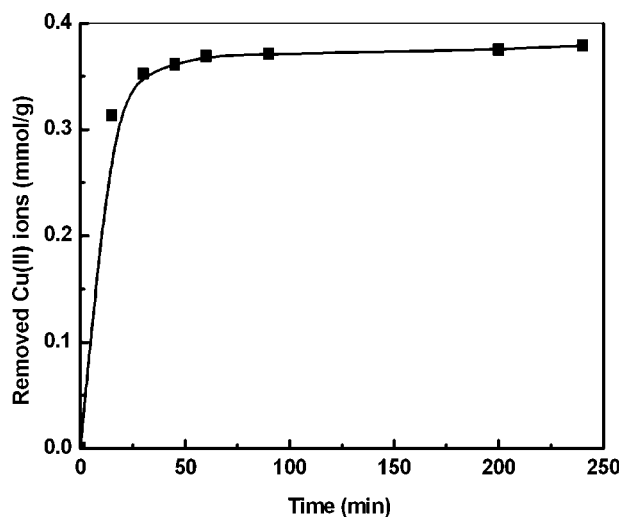
### Adsorption studies

#### Effect of initial concentration of metal ions

To investigate the effectiveness of the imprinting technique, the adsorption behavior of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cd}^{2+}$  from aqueous solution onto the imprinted polymer was studied at pH 5.6. As shown in Figure 8, the amount of metal ions adsorbed per unit mass of MIIP increased with increasing initial metal-ion concentration. Saturation of adsorption was achieved at a metal-ion concentration of about 0.35 mmol. The absorption of  $\text{Cu}^{2+}$  was much higher than that of other metal ions, and the maximum adsorption capacity of  $\text{Cu}^{2+}$  ions was  $0.331 \text{ mmol g}^{-1}$ .

**TABLE I**  
Effect of Crosslinker Concentration on the Amount of Cu(II) Ions Removed from Microparticles

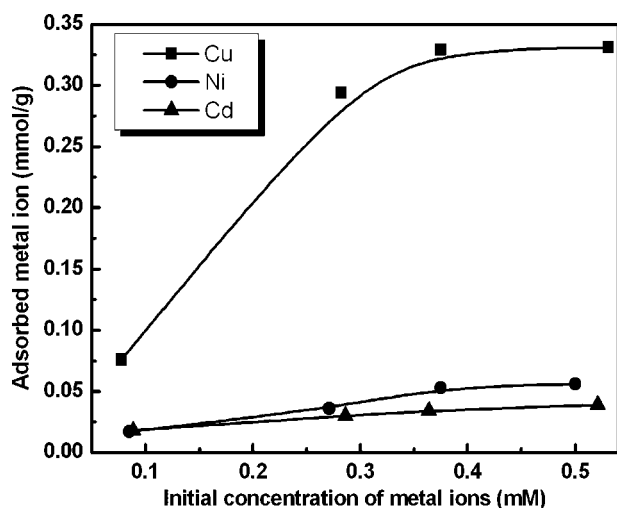
Cu(MAA) <sub>2</sub> : EGDMA (mol : mol)	1 : 2	1 : 6	1 : 10	1 : 14
Amount of removed Cu(II) ions (g/1 g particles)	0.095	0.040	0.027	0.020
Amount of Cu(II) ions following theoretical calculation, (g/1 g particles)	0.102	0.045	0.029	0.021



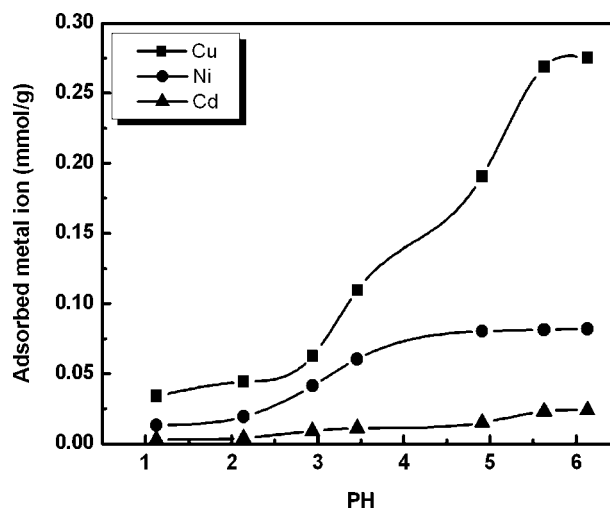
**Figure 7** Removal rate of Cu(II) ions from Cu(II)-MIIP microparticles.

#### Effect of pH

Increasing media pH increased the number of deprotonated carboxylic groups along polymeric chains, thus increasing the possibility of adjacent carboxylic groups forming a complex with copper ions. To determine the optimum pH for  $\text{Cu}^{2+}$  recognition, a series of solutions ranging from pH 1 to pH 6 were used for this study. Results demonstrated the significant influence of pH in the studied range. As shown in Figure 9, the sorption quantity of metals increases with increasing pH value, indicating that the proton dissociation of the carboxyl groups in the host molecules plays an important role in adsorbing metals. The sorption quantity is very low owing to the protonation of MIIP below pH 3.0. The Cu(II)-imprinted microspheres exhibited a higher absorptivity of



**Figure 8** Effect of initial concentration of metal ions on MIIP adsorption capacity.



**Figure 9** Effect of pH on MIIP adsorption capacity.

Cu(II) ions than other metal ions over the whole pH range and the sorption capacity was near the maximum capacity at pH 6.0. For this reason, pH 5.6 was used in all further studies.

#### Effect of time

Figure 10 shows the time dependence of adsorption capacities of metal ions on MIIP and non-MIIP. High adsorption rates were observed at the beginning of the adsorption process, after which adsorption equilibrium was quickly reached within 10 min. The maximum adsorption capacity for  $\text{Cu}^{2+}$  ions was 0.279 mmol per gram of dry imprinted microparticles. This fast adsorption equilibrium is probably due to high complexation rate and geometric shape affinity (or memory) between  $\text{Cu}^{2+}$  ions and  $\text{Cu}^{2+}$  cavities in the microparticle structure. It is well known that removal of the template from the polymeric matrix leaves cavities of complementary size, shape, and chemical functionality to the template. This template effect is attributed to the existence of copper ions memorized cavities on the polymer surface. A desirable coordination space is formed on the surfaces to facilitate the interaction with the imprinted copper ions.

#### Effect of particle size

The effect of particle size on absorption is shown in Figure 11. The amount of absorbed copper at equilibrium slightly increased with decreasing particle size because of increasing surface area of MIIP particles.

#### Selectivity studies

The selectivity of the imprinted polymer for copper ion was investigated by rebinding copper ion in the presence of various competitor metal ions.



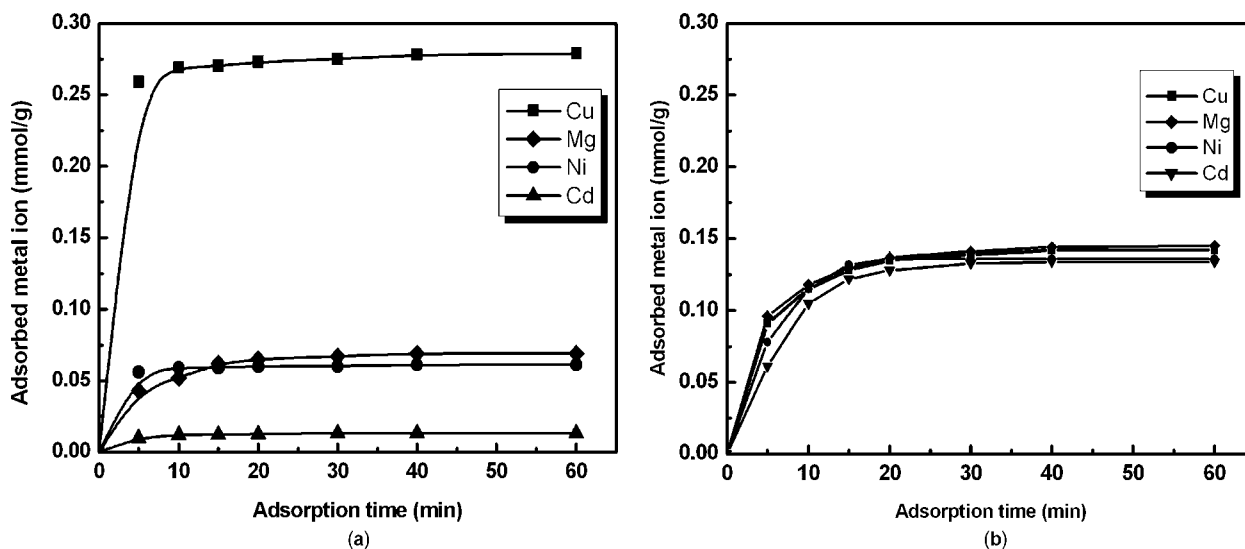


Figure 10 Comparison of adsorption rates of metal ions on (a) MIIPs and (b) non-MIIPs.

The distribution ratio, selectivity coefficient, and relative selectivity coefficient were calculated using the following equations:

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

$$D = \frac{C_A - C_B}{C_A} \times \frac{v}{m} \quad (1)$$

where  $v$  is the volume of the solution (mL) and  $m$  the mass of the polymer (g), and  $C_A$  and  $C_B$  are the initial and final concentrations of metal ions ( $\text{mmol l}^{-1}$ ), respectively.

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

$$\alpha = \frac{D_{\text{Cu}}}{D_M} \quad (2)$$

where  $D_{\text{Cu}}$  and  $D_M$  represent the distribution ratio of  $\text{Cu}^{2+}$  and of another metal ion, respectively.

A comparison of the selectivity coefficient of imprinted beads and nonimprinted beads with those metal ions allows an estimation of the effect of imprinting on selectivity. A relative selectivity coefficient  $\alpha_r$  can be defined as:

$$\alpha_r = \frac{\alpha_i}{\alpha_n} \quad (3)$$

where  $\alpha_i$  and  $\alpha_n$  represent the selectivity coefficient of MIIP and non-MIIP, respectively.

As shown in Table II, the  $D$  values of MIIP increased for Cu(II), but decreased significantly for other ions. Ni(II), with a smaller ionic radius (69 pm) than Cu(II) (71 pm), could enter into the imprinting sites easier than Zn(II) (74 pm) and Cd (92) could, and thus showed higher  $D_i$  than Zn(II) and much higher than Cd(II). Although Mg(II) has a

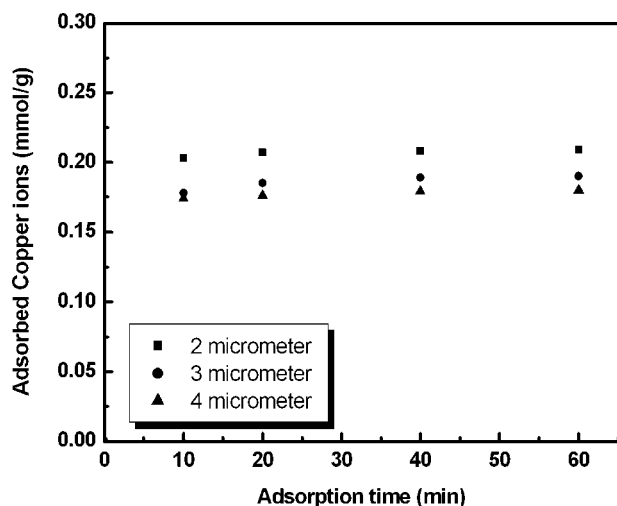


Figure 11 Effect of particle size on the absorption capacity of MIIPs.

TABLE II  
Selective Separation Properties of MIIP and Non-MIIP for Various Metal Ions

Metal ion	Ionic charge	Ionic radii (pm)	$D_i$	$D_n$	$\alpha_i$	$\alpha_n$	$\alpha_r$
Cu	2	71	450	42.3	–	–	–
Ni	2	69	10.9	39.1	41.3	1.08	38.2
Mg	2	71	14.3	43.9	31.5	0.96	32.8
Zn	2	74	10.1	46.3	44.6	0.91	49
Cd	2	92	2.2	38.1	204.5	1.11	184.2
Na	1	113	17.3	53	26.0	0.8	32.5
Fe	3	63	8.6	34.6	52.3	1.22	42.9

similar ionic charge and ionic radius, its arrangement in coordination geometry probably caused its lower  $D_i$  value than Cu(II). Na(I) showed a higher  $D_i$  and  $D_n$  than Ni(II), Mg(II), Zn(II), Cd(II), and Fe(III). It was expected that Na(I) would not fit into the imprinting sites but could associate with many functional sites. Fe(III) had a higher  $D_i$  than Cd(II) because Fe(III) enters into the imprinting sites easier than Cd(II) and occupies 2 sizeable fractions of the imprinting space or associates with a binding point in other manners. These explanations are supported by comparing  $D_i$  values of MIIP with  $D_n$  values of non-MIIP, which has random functional sites.

The relative selectivity coefficient is an indicator to express the adsorption affinity of recognition sites to the imprinted copper ions. From the study results, the relative selectivity coefficients of imprinted beads for Cu(II)/Mg(II), Cu(II)/Ni(II), Cu(II)/Zn(II), Cu(II)/Cd(II), Cu(II)/Na(I), and Cu(II)/Fe(III) were 32.8, 38.2, 49, 184.2, 32.5, and 42.9 times greater than that of the nonimprinted matrix, respectively.

These results indicate that the functional host molecules (memorized cavities) on the MIIP bead surfaces are immobilized with the strict configuration suitable for copper ions, and that the ionic recognition is influenced by the nature of metal ion, and its ionic radius and charge.

## CONCLUSION

MIIP microspheres were produced by a precipitation polymerization of EGDMA and Cu(MAA)<sub>2</sub>. By controlling the polymerization parameters, uniform MIIP microspheres were obtained in high yield and their average size was controlled to between 1 and 4  $\mu\text{m}$  in diameter. The adsorption time required to reach equilibrium was very short (10 min). The maximum adsorption capacity of MIIP for Cu(II) ions was 0.278 mmol/g of dry imprinted beads and was much higher than that of non-MIIP. The absorption values increased with increasing pH and metal-ion concentration, and a saturation value was achieved at pH 5.6 and a concentration of 0.35 mM. This imprinting effect of MIIP was even observed in the case of ions having similar chemical and physical properties with copper, and MIIP exhibited much higher efficiency and selectivity than the corresponding non-MIIP. The regular form and narrow size distribution of the microspheres make them easy to handle directly in various applications such as stationary phases in chromatography. As our novel precipitation polymerization technique using a rotary evaporator is very suitable for the preparation of metal-containing, monomer-derived MIIP having

very high selectivity and quick absorption kinetics, we expect that this method will open a new direction for the preparation of MIIPs in the future.

## References

- Bartsch, A. R. In *Molecular and Ionic Recognition with Imprinted Polymers*; ACS Symposium Series 703, ACS: Washington, D.C., 1998; p 1.
- Takeuchi, T.; Haginaka, J. *J Chromatogr B* 1999, 728, 1.
- Al-Kindy, S.; Badia, R.; Diaz-Garcia, M. E. *Anal Lett* 2002, 35, 1763.
- Al-Kindy, S.; Badia, R.; Suarez-Rodriguez, J.; Diaz-Garcia, M. E. *Crit Rev Anal Chem* 2000, 30, 291.
- Suarez-Rodriguez, J. L.; Diaz-Garcia, M. E. *Anal Chim Acta* 2000, 405, 67.
- Guo, T.-Y.; Xia, Y.-Q.; Wang, J.; Song, M.-D.; Zhang, B.-H. *Biomaterials* 2005, 26, 5737.
- Ramström, O.; Richard, J. A. *Chirality* 1998, 10, 195.
- Cunliffe, D.; Kirby, A.; Alexander, C. *Adv Drug Deliv Rev* 2005, 57, 1836.
- Rathbone, D. L. *Adv Drug Deliv Rev* 2005, 57, 1854.
- Hillberg, A. L.; Brain, K. R.; Allender, C. J. *Adv Drug Deliv Rev* 2005, 57, 1875.
- Matsui, J.; Akamatsu, K.; Hara, N.; Miyoshi, D.; Nawafune, H.; Tamaki, K.; Sugimoto, N. *Anal Chem* 2005, 77, 4282.
- Zhou, H.; Zhang, Z.; He, D.; Xiong, Y. *Sens Actuators B* 2005, 107, 798.
- Piletska, E. V.; Romero-Guerra, M.; Chianella, I.; Karim, K.; Turner, A. P. F.; Piletsky, S. A. *Anal Chim Acta* 2005, 542, 111.
- Greene, N. T.; Shimizu, K. D. *J Am Chem Soc* 2005, 127, 5695.
- Trojanowicz, M.; Marzena, W. *Anal Lett* 2005, 38, 523.
- Kempe, M.; Mosbach, K. *J Chromatogr* 1994, 664, 276.
- Dmitrienko, S. G.; Irkha, V. V.; Kuznetsova, A. Y.; Zolotov, Y. A. *J Anal Chem* 2004, 59, 808.
- Sellergren, B. *Anal Chem* 1994, 66, 1578.
- Andersson, L. I.; Miyabayashi, A. O'Shannessy, D. J.; Mosbach, K. *J Chromatogr* 1990, 516, 323.
- Ramstrom, O.; Andersson, L. I.; Mosbach, K. *J Org Chem* 1993, 58, 7562.
- Mayes, A. G.; Andersson, L. I.; Mosbach, K. *Anal Biochem* 1994, 222, 483.
- Nilsson, K.; Sakaguchi, K.; Gemeiner, P.; Mosbach, K. *J Chromatogr A* 1995, 707, 199.
- Valtakis, G.; Andersson, L. I.; Müller, R.; Mosbach, K. *Nature* 1993, 361, 645.
- Wulff, G.; Schauhoff, S. *J Org Chem* 1991, 56, 395.
- Glad, M.; Norrlöw, O.; Sellergren, B.; Siegbahn, N.; Mosbach, K. *J Chromatogr* 1985, 347, 11.
- Kempe, M.; Glad, M.; Mosbach, K. *J Mol Recogn* 1995, 8, 35.
- Venton, D. L.; Gudipati, E. *Biochim Biophys Acta* 1995, 1250, 126.
- Shea, K. J.; Spivak, D. A.; Sellergren, B. *J Am Chem Soc* 1993, 115, 3368.
- Ramström, O.; Ye, L.; Mosbach, K. *Chem Biol* 1996, 3, 471.
- Motherwell, W. B.; Bingham, M. J.; Pothier, J.; Six, Y. *Tetrahedron* 2004, 60, 3231.
- Wulff, G.; Sarhan, A. *Angew Chem Int Ed Engl* 1972, 11, 341.
- Mosbach, K. *Trends Biochem* 1994, 19, 9.
- Rao, T. P.; Daniel, S.; Gladis, M. *J Trends Anal Chem* 2004, 23, 28.
- Liu, Y.; Chang, X.; Wang, S.; Guo, Y.; Din, B.; Meng, S. *Anal Chim Acta* 2004, 519, 173.

35. Shim, S. E.; Yang, S.; Choe, S. *J Polym Sci A* 2004, 42, 3967.
36. Daniel, S.; Rao, P. P.; Rao, T. P. *Anal Chim Acta* 2005, 536, 197.
37. Ye, L.; Mosbach, K. *React Funct Polym* 2001, 48, 149.
38. Mayes, A. G.; Mosbach, K. *Anal Chem* 1996, 68, 3769.
39. Hosoya, K.; Tanaka, N. In *Molecular and Ionic Recognition with Imprinted Polymers*; ACS Symposium Series 703, ACS: Washington, D.C., 1998; pp 143–158.
40. Savostyanov, V. S.; Pomogailo, A. D.; Kritskaya, D. A.; Ponomarev, A. N. *J Polym Sci A* 1989, 27, 1935.
41. Pomogailo, D. A.; Savost'yanov, S. V. In *Synthesis and Polymerization of Metal-Containing Monomers*; Boca Raton: Florida, 1994; p 21.
42. Czerniawski, T.; Wojtczak, Z. *Eur Polym J* 1996, 32, 1035.
43. Czerniawski, T. *Eur Polym J* 2000, 36, 635.
44. Czerniawski, T.; Wojtczak, Z. *Acta Polym* 1989, 40, 409.
45. Czerniawski, T.; Wojtczak, Z. *Acta Polym* 1992, 43, 219.
46. Gupta, N.; Srivastava, A. K. *Polymer* 1994, 35, 3769.
47. Gupta, N.; Srivastava, A. K. *Macromolecules* 1995, 28, 827.
48. Sreenivasan, K. *J Appl Polym Sci* 2001, 80, 2795.
49. Gronowski, A.; Woztczak, Z. *J Therm Anal* 1983, 26, 233.