

Selective sorption behavior of metal(II) ion-imprinted polymethacrylate microspheres synthesized via precipitation polymerization method

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Abstract—Metal methacrylate complex was synthesized from methacrylic acid and metal carbonate to prepare metal ion-imprinted polymer (MIIP) particles by the precipitation polymerization method. Three types of metal ions, Cu(II), Ni(II), and Pb(II), were used as the template ions in this synthesis. The produced MIIP particles were spherically well-defined with 0.5–2 μm diameter in the order of Cu(II)-MIIP > Ni(II)-MIIP > Pb(II)-MIIP. The imprinted polymers exhibited a much higher adsorption capacity and selectivity toward the target (template) ion than other competitive metal ions. The MIIP particles, Cu(II)-MIIP, Ni(II)-MIIP, and Pb(II)-MIIP, synthesized in this study guaranteed the selective separation of the target metal ion from the mixtures, although their competitive strengths of the adsorption capacity and selectivity were different.

Keywords: Adsorption, Separation, Metal Ion Imprint, Polymer

INTRODUCTION

Although heavy metal ions are widely used in diverse industries, they are one of the main causes of wastewater pollution. Copper, nickel, and lead are typical heavy metals frequently used in battery manufacturing, metallurgy, metal coating and finishing, and chemical industries. As they are so harmful to human nervous system causing brain disorders, their removal from wastewater is quite imperative.

In recent years, owing to the continuous progress in analytical chemistry, new chemical separation techniques have been developed. Various techniques [1–10] have been used for the separation or preconcentration of metals including coprecipitation, liquid-liquid extraction, and adsorption with diverse adsorbent. However, these techniques often require large amounts of high purity organic solvents, and some of them are harmful to health and create environmental problems. Therefore, much more selective extractants and adsorbents for the specific separation of metal ions are needed.

An approach to the preparation of “host” molecules that can recognize “guest” species is the template polymerization technique called “molecular imprinting.” Molecular imprinting has been widely and successfully used in the preparation of polymers, offering high affinity binding sites for a variety of molecules including organic, inorganic, and even biological molecules or ions [11–14]. These materials are useful in various application fields such as biomaterial, sensor technologies, molecular and ionic separations, and catalysis [15–24].

Most of the current researches in the solid phase extraction are

focused on the use of metal ion-imprinted polymers (MIIPs) owing to their cost effectiveness, high stability in different environments, and high selectivity compared to common separation techniques [22–29]. The ion-imprinted polymer particles are generally prepared by the solution, bulk, suspension polymerization, or surface imprinted technique [30–33]. Those preparation methods, however, are confronted with some problems, such as (i) involvement of prolix grinding and sieving step, (ii) partial destruction of imprinted structures during grinding, (iii) possible presence of residual guest, (iv) time-consuming process yielding only moderate amounts of desired product, (v) complex preparation process due to the inclusion of stabilizer, solvent, and porogens, and (vi) expensive preparation cost associated with those problems mentioned above.

Several types of MIIP particles including Cu(II)-, Ni(II)-, and Pb(II)-imprinted particles in diameter ranging from 100 to 500 μm were formerly synthesized from our laboratory, basically using suspension polymerization. General adsorption behaviors, such as pH and initial concentration dependence of adsorption capacity, adsorption kinetics, selectivity, and regeneration behavior, were measured and analyzed for the synthesized microporous MIIP particles. [23, 34–36]. Although excellent adsorption capacity and selectivity were observed, their synthetic procedure was quite complicated, as the functional monomers were different from the polymerizable monomers, the stabilizing agent must be used to stabilize the growth of particle in different phase, and porogenic solvent must be used to establish porous structure. In this synthetic way, the particle size was hardly reduced to $\sim 1 \mu\text{m}$ scale.

To enhance the adsorption capacity in the absence of the porous structure, the adsorbent size is very important. Reduction of particle size leads to large surface area for quick and high adsorption capacity. The monodispersed, micron-sized polymer spheres with highly crosslinked structure cannot be easily obtained by any of the common polymerization methods such as bulk, solution, emulsion, and core-shell as well as suspension polymerizations. One of the

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^{*}This article is dedicated to Prof. Hwayong Kim on the occasion of his retirement from Seoul National University.

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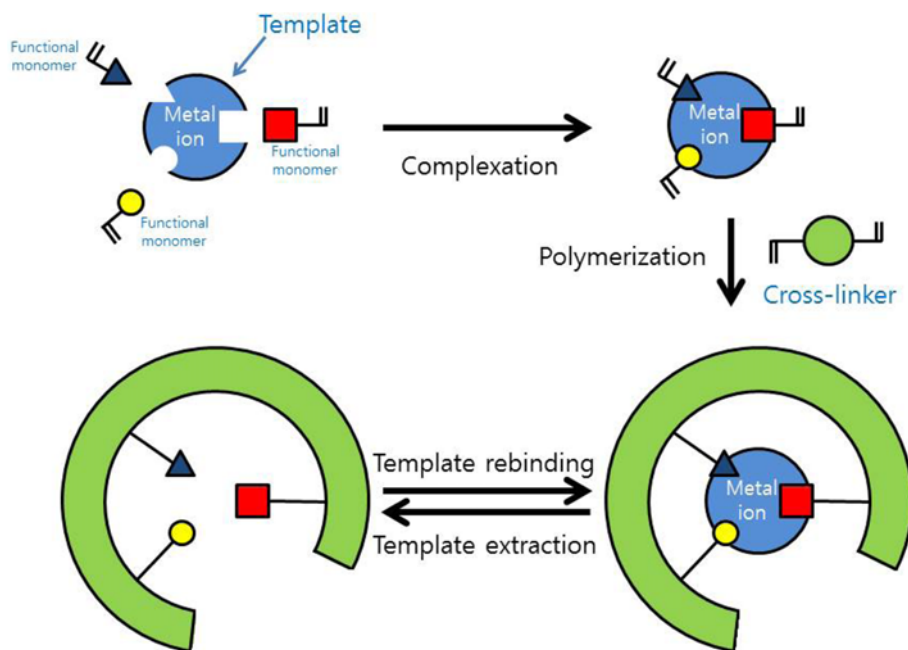


Fig. 1. Synthetic scheme of MIIP from functional monomers and metal ion template.

most important issues in preparing MIIP particles is the use of high amounts of crosslinker to hold the imprinting sites with high rigidity. Although the suspension polymerization or seed polymerization is able to produce spherical polymer beads, this not only requires special dispersing agents, surfactants, or complicated swelling processes, but also frequently compromises the binding specificity. In this study, we propose a novel, quick, and clean precipitation polymerization method using a rotary evaporator to prepare MIIP microspheres bearing imprinted binding in high yield. MIIPs were prepared from the presynthesized metal-containing monomers and then cross-linked at high concentration. In this synthesis, almost all the binding sites (COO-M binding) on the polymer particle surface are in “working state.” The synthesized MIIP microspheres show excellent selectivity against a range of ‘strong’ competitive metal [M] ions. No chemical agent was involved in the stabilization of spherical particles, as the stabilization of the particles originates from the resistance against the interfusion of particles associated with a high degree of crosslinking. Another novelty of this study includes the use of the same functional monomer to synthesize different metal ion - imprinted polymers, which has a great advantage over the previous reports, regarding its synthetic process simplicity.

EXPERIMENTAL

1. Materials

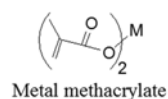
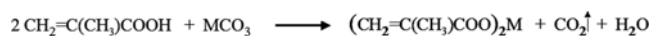
Methacrylic acid (MAA) monomer and ethylene glycol dimethacrylate (EGDMA) crosslinker were purchased from Sigma-Aldrich Chemical Company (Milwaukee, WI, USA). MAA and EGDMA were vacuum distilled at 40 °C prior to the polymerization to remove any inhibitor in the reactants. The AIBN initiator (Junsei Chemicals, Japan) was recrystallized from methanol for the purification before use. Metal carbonates including copper carbonate, lead carbonate, or nickel carbonate were purchased from Sigma-

Aldrich and used as the metal ion template in aqueous solution. Isopropanol, dichloromethane, and other solvents were also purchased from Sigma-Aldrich and used as received.

2. Preparation of Imprinted Polymers

In the preparation of MIIP, a template ion was interacted with one or more functional monomers to form a covalent or noncovalent-bonded complex. This complex was then polymerized with a crosslinker to produce a rigid polymer. Upon removal of the template species, cavities were formed in the polymer matrix. These cavities memorize the spatial features and bonding preference of the template so that the imprinted polymer selectively rebinds the template from a mixture of chemical species (Fig. 1).

Prior to the synthesis of MIIP, metal methacrylate ($M(\text{MAA})_2$) complex was first synthesized by self-assembling. Each metal carbonate (copper carbonate, lead carbonate, or nickel carbonate) was added to MAA in a stoichiometric ratio and placed at room temperature for at least 2 d in dichloromethane. Any insoluble impurity in the reactant mixture was removed by filtration, and the residual MAA and dichloromethane was evaporated under vacuum to obtain pure $M(\text{MAA})_2$ complex in solid form. The synthetic reaction and structure of $M(\text{MAA})_2$ are schematically shown as follows:



where M (metal) indicates copper, nickel, or lead.

MIIP microspheres were prepared by precipitation polymerization, where the polymerization ingredients simply consisted of $M(\text{MAA})_2$, EGDMA crosslinker, AIBN initiator, and polymerization reaction medium. The molar ratio of EGDMA : $M(\text{MAA})_2$ in the monomer

mixture was 8 : 1, and the total amount of monomers ($M(MAA)_2$ and EGDMA) was varied from 10 wt/vol% of the medium. The amount of AIBN to the total amount of monomers was 2 wt%. After charging the reactant mixture in 30 mL isopropanol in a 50 mL reactor, it was sonicated for 5 min and purged with nitrogen for 15 min. The reactor was placed in 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 for 2 h, and then held at 70 °C for 24 h in N_2 atmosphere. After the 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 by several repeated experiments.

The metal ions contained in the polymer particles leached out by stirring the polymer products in 0.4 M HNO_3 solution for 40 min. This process was repeated five times for complete removal of metal ions, and their removal was confirmed using an atomic absorption spectrophotometer (AAS, A 180-70 polarized Zeeman, Hitachi, Japan). After the extraction of the template ion, the polymer particles were washed with deionized water and then dried in vacuum.

3. Characterization of Chemical Compound and Structure of MIIP Microparticles

The formation of $M(MAA)_2$ was confirmed using Fourier transform infrared spectroscopy (FTIR, Bruker, USA). The thermal stability of the polymer and the amount of metal conjugated in the MIIP were investigated using a thermogravimetric analyzer (TGA-50H, Shimadzu, Japan). The temperature was scanned from room temperature to 600 °C at a scanning rate of 20 °C min^{-1} under nitrogen atmosphere. The shape and morphology of the MIIP particles were investigated by using the environmental scanning electron microscopy (ESEM, Philips Co.) at an accelerating voltage of 15 kV. The energy dispersive X-ray spectrometer (EDX, EDAX USL 30) attached to the ESEM was used to determine the chemical composition of the MIIP samples.

4. Adsorption Experiment of Metal Ions on MIIP Microparticles

A 180-70 polarized Zeeman atomic absorption spectrophotometer (AAS, Hitachi, Japan) with deuterium background correction was used for the determination of the concentration of metal ions in the extraction medium during adsorption experiment. An LI-120 digital pH meter (ELICO, India) was used for the pH measurement of the extraction medium. The adsorption of metal ions on the MIIP particles from the aqueous solution was investigated in the batch mode. The MIIP particles (0.1 g) were added to 5 mL of an aqueous solution containing one of $Cu(NO_3)_2$, $Ni(NO_3)_2$, or $Pb(NO_3)_2$ in a 10 cm^3 volume test tube, and the concentration of each metal ion was varied from 0.05 to 0.5 mM. The test tube was sealed. The mixture was sonicated for 3 min and then shaken in a thermostated water bath at room temperature for 5 to 60 min. The microparticles were then filtered off through a polyethylene membrane filter (Suplep LCR 25-LG, Nippon Millipore, Ltd.). The amounts of metal ions adsorbed on the microparticles were evaluated by their residual concentrations in the filtrated aqueous solution by AAS. The adsorption amount ($mmol\ g^{-1}$) was calculated from the difference in the metal ion concentration of the initial and final adsorption solutions divided by the weight of dry microparticles. The experiments were performed in replicates of three,

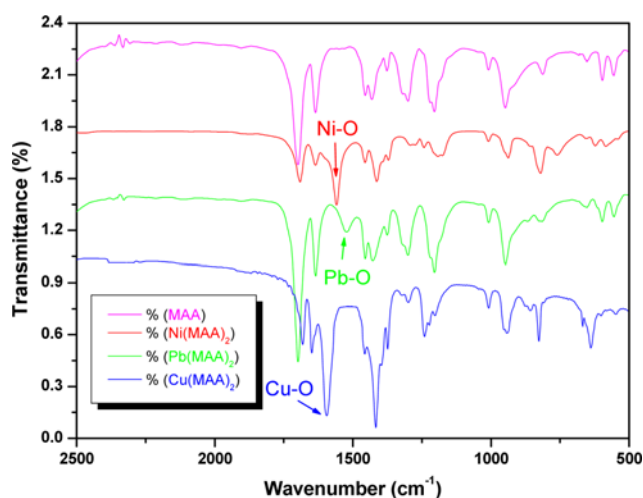


Fig. 2. FT-IR spectra of MAA and metal methacrylates.

and the average value was taken. To investigate the selective adsorption behavior of the imprinted particles, the competitive adsorption experiments toward $Ni(II)$, $Pb(II)$, and $Cu(II)$ ions were investigated. The MIIP or non-MIIP microparticles (0.1 g) was placed in 5 mL of a solution containing these competitive ions at 0.3 mM concentration for each ion. After the adsorption equilibrium was reached, the concentration of the metal ions in the remaining solution was measured by AAS.

RESULTS AND DISCUSSION

1. Characterization of Chemical and Physical Structure

The IR spectra of MAA and $M(MAA)_2$ are shown in Fig. 2 for comparison. The IR bands at 1,701 and 1,635 cm^{-1} correspond to the stretching vibration of C=O and C=C bonds of MAA monomer, respectively. The IR spectra of $M(MAA)_2$ show slight shifts of those band positions because of the binding of the metal to the monomer although their shifts are not noticeably observed for $Pb(MAA)_2$ complex. The IR spectra of $Ni(MAA)_2$ and $Cu(MAA)_2$ show clear shifts of the C=O stretching vibration band from the corresponding MAA band toward high wavelengths of 1,691 cm^{-1} for $Ni(MAA)_2$ and 1,681 cm^{-1} for $Cu(MAA)_2$. A shift of the C=C stretching vibration band from 1,635 cm^{-1} for MAA to 1,650 cm^{-1} for $Cu(MAA)_2$ and 1,630 cm^{-1} for $Ni(MAA)_2$ was also observed.

The big difference in the IR spectra of MAA and $M(MAA)_2$ is the appearance of the IR band associated with O-M bond in $M(MAA)_2$. The (O-M) stretching vibration bands were observed at 1,595.1, 1,559, and 1,522 cm^{-1} in $Cu(MAA)_2$, $Ni(MAA)_2$, and $Pb(MAA)_2$ spectra, respectively, whereas the corresponding O-M stretching band was not observed in the IR spectrum of MAA. These results indicate that the synthesis of metal methacrylate complex was successfully performed.

The adsorption and removal of $Cu(II)$, $Ni(II)$, and $Pb(II)$ ions on/from the imprinted polymers were confirmed by EDX. The EDX spectra of the MIIPs before and after removal of $Cu(II)$, $Ni(II)$, and $Pb(II)$ ions are shown in Fig. 3. The signals because of the presence of $Cu(II)$, $Ni(II)$, and $Pb(II)$ ions adsorbed on the MIIPs are clearly

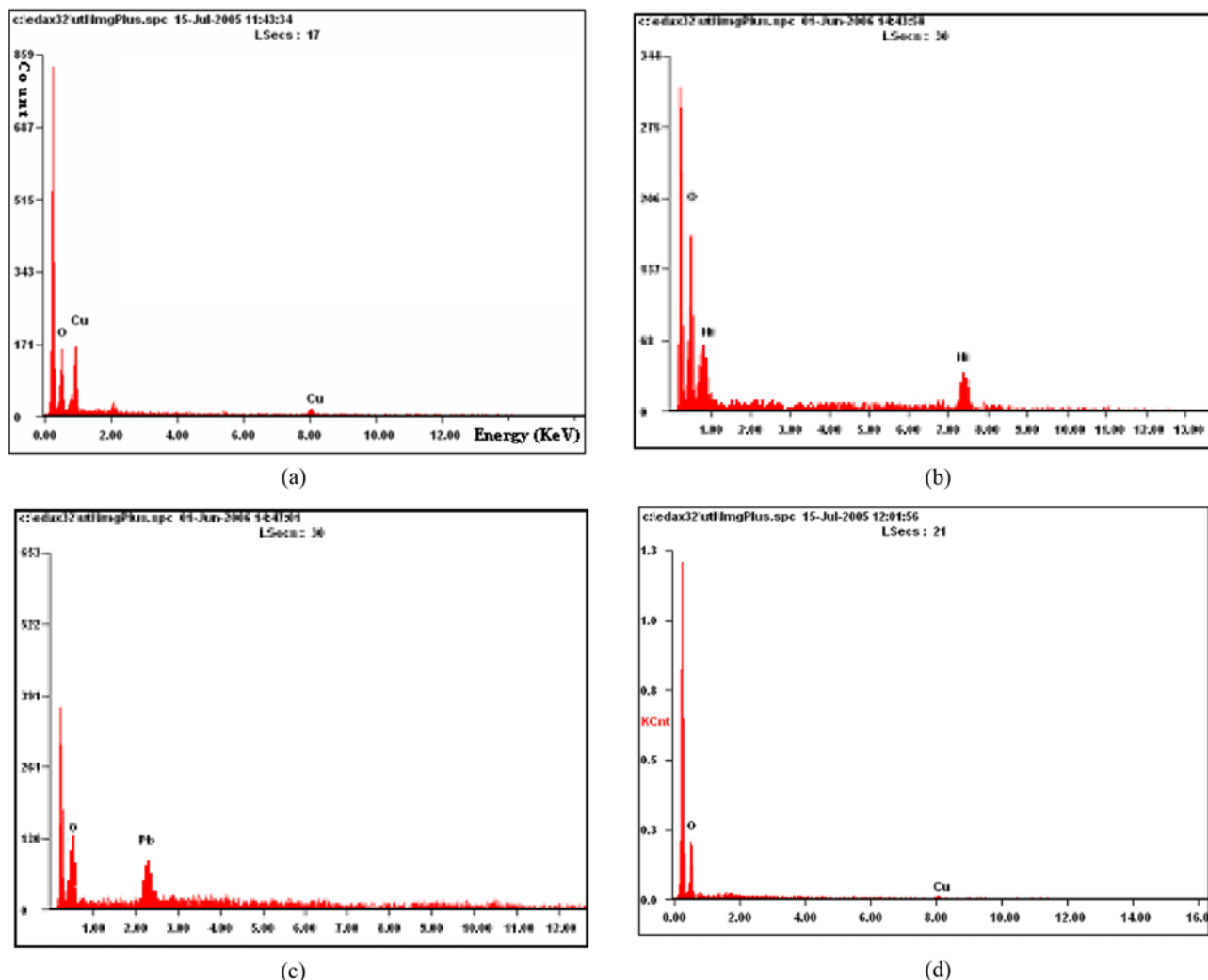


Fig. 3. EDX analysis of (a) Cu(II)-MIIP, (b) Ni(II)-MIIP, (c) Pb(II)-MIIP, and (d) MIIP particles.

shown in Figs. 3(a), 3(b), and 3(c), respectively; however, the absence of those metal ions after their removal is clarified in Fig. 3(d).

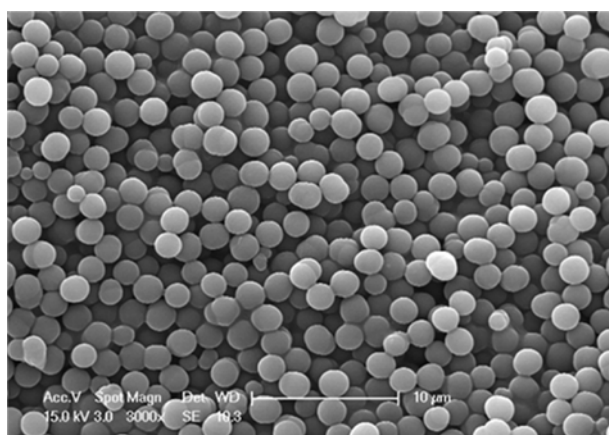
2. Morphology of MIIP Particles

The precipitation polymerization technique produces uniform polymer microspheres without the presence of any stabilizers. Thus, it is an ideal method for the preparation of MIIP microspheres, as the reaction conditions are not only simple but also adaptable to the synthesis of other metal ion imprinting systems. In the presence of excess solvent (typically >95% by volume) depending on the solubility parameter of the polymer and solvent, the uniform microspheres bearing imprinted binding sites were obtained in high yields (>85%), whereas the reaction solvent affects the morphology of the imprinted microspheres, and the presence of the template ion also affects the particle size of the produced microspheres. For a given template ion (and accordingly the functional monomer and crosslinker), the composition of the reaction system was finely tuned to control the phase separation behavior to yield uniform MIIP microspheres. In this precipitation polymerization using a rotary evaporator, the uniform and microspherical particles were directly obtained without grinding or sieving process. Figs. 4(a),

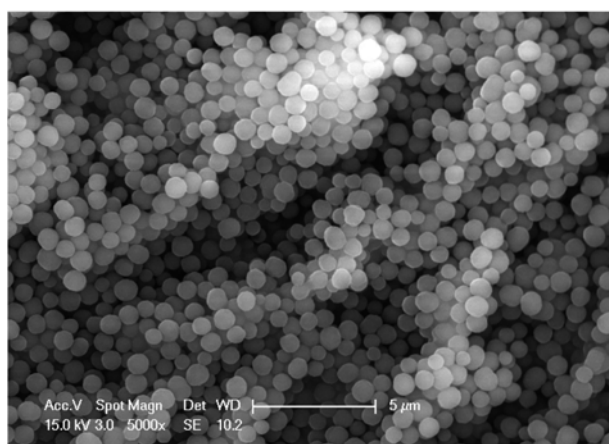
4(b), and 4(c) show the SEM microphotographs of Cu(II)-MIIP, Ni(II)-MIIP, and Pb(II)-MIIP particles, respectively. The imprinted microspheres were obtained in ~80-90% yields with the volume-averaged diameter of 1.5, 0.8, 0.5 μm for Cu(II)-MIIP, Ni(II)-MIIP, and Pb(II)-MIIP particles, respectively, with a very narrow distribution.

3. Thermogravimetric Analysis

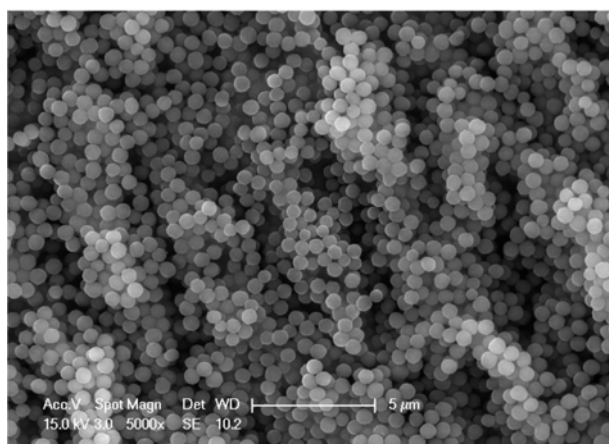
The TGA plots of the polymer particles synthesized before and after the removal of the metal template, Cu(II) contained MIIP and Cu(II)-MIIP, are shown in Fig. 5. For the Cu(II) contained MIIP (before Cu(II) ion removal), its weight was stable up to 210 $^{\circ}\text{C}$, but then dramatically reduced at >210 $^{\circ}\text{C}$, probably because of the decomposition of COO-Cu bonding and oxidative destruction of metal bonded polymers that occurred in the presence of oxygen. At 450 $^{\circ}\text{C}$, only 0.0308 g of residual copper per 1 g of particles, similar to both the theoretically calculated and experimentally determined values, was obtained. Cu(II)-MIIP shows much superior thermal stability compared to Cu(II) contained MIIP, as it was stable up to 450 $^{\circ}\text{C}$ owing to a fully crosslinked chemical structure. Other metal imprinted polymers showed similar TGA behavior.



(a)



(b)



(c)

Fig. 4. SEM images of (a) Ni(II)-MIIP and (b) Pb(II)-MIIP particles.

4. Absorption Capacity and Selectivity Studies

Our focus was mostly on the adsorption capacity and selectivity of the MIIP microparticles (with $\sim 1 \mu\text{m}$ diameter), as the general adsorption and desorption behavior such as the pH dependence of adsorption capacity, adsorption kinetics, and regeneration behavior, were already profoundly studied for the similar metal ion - imprinted polymer particles with $\sim 400 \mu\text{m}$ diameter in porous struc-

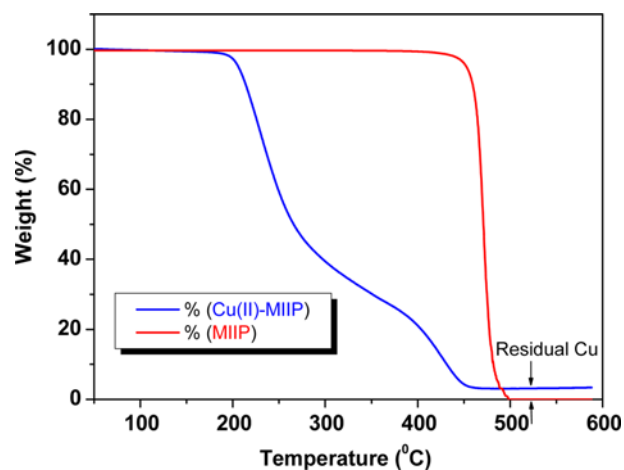


Fig. 5. TGA thermograms of Cu(II)-MIIP and MIIP.

ture [23,34-36]. The adsorption capacities were measured at pH 6 in metal ion contained aqueous solutions to find out the maximum adsorption capacity of the imprinted polymer. The amount of the adsorbed metal ion per unit mass of the imprinted polymer increased with increasing initial metal ion concentration. At the maximum adsorption capacity, all the binding sites were occupied by the metal ions. The distribution ratio, selectivity coefficient, and relative selectivity coefficient were calculated by 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), C_A and C_B are the initial and final concentrations of metal ions (mmol L^{-1}), respectively.

The selectivity coefficient for the binding of a template metal ion in the presence of other ion species was calculated from the equilibrium binding data according to Eq. (2).

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

where D_{Tem} and D_M represent the distribution ratios of template metal ion and one of other metal ions, respectively.

A comparison of the selectivity coefficient of the imprinted beads and nonimprinted beads with those metal ions allows an estimation of the effect of imprinting on the selectivity. A relative selectivity coefficient α_r can be defined as Eq. (3).

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

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

The competitive adsorption capacity of Cu(II)/Ni(II), Cu(II)/Pb(II), Ni(II)/Cu(II), Ni(II)/Pb(II) and Pb(II)/Cu(II), Pb(II)/Ni(II) for the three metal imprinted polymers, Cu(II)-MIIP, Ni(II)-MIIP, and Pb(II)-MIIP, respectively, was also investigated by the batch

Table 1. Selective adsorption properties of MIIP and non-MIIP particles

Metal ion	Non-MIIP	Cu(II)-MIIP				Ni(II)-MIIP				Pb(II)-MIIP			
	D_n	D_i	α_n	α_i	α_r	D_i	α_n	α_i	α_r	D_i	α_n	α_i	α_r
Cu ²⁺	35.6	450				17	0.79	5.95	7.5	20	0.73	5.4	7.4
Ni ²⁺	28	10.9	1.27	41.28	32.5	101.1				17.6	0.93	6.2	6.7
Pb ²⁺	26	7.5	1.37	60	43.8	8.1	1.08	12.48	11.6	108.7			

procedure. The D value of each MIIP was much higher for the corresponding template metal ion than other metal ions. The competitive adsorption capacity of MIIP microsphere for the corresponding template metal ion is higher than those of the nonimprinted ones as shown in Table 1. The α_r values of Cu(II)/Ni(II), Cu(II)/Pb(II) for Cu(II)-MIIP particles were 32.5 and 43.8, respectively. Moreover, the α_r values of Ni(II)/Cu(II) and Ni(II)/Pb(II) for Ni(II)-MIIP particles and Pb(II)/Cu(II) and Pb(II)/Ni(II) for Pb(II)-MIIP particles were 7.5 and 11.6 and 7.4 and 6.7, respectively, indicating that all the metal ion imprinted polymers synthesized in this study have superior adsorption selectivity to the nonimprinted polymer particles. The α_r values were analyzed for the microporous MIIP particles with much larger diameter (~400 μm) in our laboratory. In comparison of α_r values between the present and previous MIIP systems synthesized, the α_r of Cu(II)/Ni(II) for the present Cu(II)-MIIP particles, 32.5, was slightly lower than that of the Cu(II)-MIIP microporous particles, 38.2. The α_r values of Ni(II)/Cu(II) for the present Ni(II)-MIIP particles, 7.5 and Pb(II)/Ni(II) for Pb(II)-MIIP particles, 6.7 were, however, higher than those of microporous particles 5.8 and 6.3. As the α_r values were higher than 5 and not in big difference, excellent selective behavior was assured for both systems.

CONCLUSION

MIIP microspheres were prepared by the precipitation polymerization from EGDMA and Cu(MAA)₂. By optimizing the polymerization condition, the MIIP microspheres between 0.5 and 2 μm diameters with a narrow distribution were produced in high yield. As the imprinting effect of MIIP particles was observed even for the ions with the similar size, MIIP particles exhibited much higher selectivity than the non-MIIP ones. The uniform shape and narrow size distribution of the microspheres make them possible to be applied in various molecular and ionic separations. As the α_r values were higher than 5 and not in big difference from the microporous particles previously reported, the excellent sorption selectivity is assured. As the present novel polymerization technique using a rotary evaporator is very suitable for the preparation of MIIPs having very high adsorption capacity and selectivity associated with very small size compared to the previously reported ones, it is expected that this method will open a new direction for the preparation of MIIPs in the future.

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