Chemical Engineering Journal 166 (2011) 435–444

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Effect of solvent/monomer feed ratio on the structure and adsorption properties of Cu^{2+}-imprinted microporous polymer particles

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ARTICLE INFO

Article history:
Received 30 July 2010
Received in revised form 1 November 2010
Accepted 1 November 2010

Keywords:
Ion-imprint
Self-assembled
Suspension polymerization
Adsorption
Selectivity

ABSTRACT

The effect of solvent/monomer (S/M) feed ratio on the structure and adsorption properties of copper(II)-imprinted microporous polymer particles was investigated. Copper(II) ion-imprinted microporous particles were prepared from two functional monomers, methacrylic acid (MAA) and vinyl pyridine (4-VP), by forming a complex with the template copper ion by ionic interactions. The self-assembled copper/monomer complex was polymerized in the presence of an ethylene glycol dimethacrylate (EGDMA) cross-linker by a suspension polymerization. The diameter of the prepared microparticles was 200–700 μm. The chemical structure, morphology and adsorption capacity of the Cu(II)-imprinted microporous particles were analyzed using scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) test, atomic adsorption spectroscopy (AAS), furrier transform infrared spectroscopy (FTIR), and energy dispersive X-ray spectrometer (EDX). The adsorption capacity of the imprinted beads for the template ion, Cu(II), was significantly affected by the initial concentration and pH of the feed solution. The imprinted particles showed high selectivity for the copper ion, as the adsorption capacity for the Cu(II) ion was much higher than that of other metal ions such as Ni(II), Zn(II), and Cd(II). The adsorption capacity, adsorption kinetics, and selectivity of the imprinted particles prepared in this study, however, were not significantly affected by the S/M feed ratio.

1. Introduction

Heavy metal ions contained in industrial wastewaters are an important contributor to the serious problems of worldwide pollution. Heavy metal ions released into the environment can affect ecological life by their tendency to accumulate in living organisms. Many methods have been applied to remove such toxic ions, including filtration, chemical precipitation, neutralization, chelating ion exchange and adsorption [1–5]. The latter is generally preferred due to its efficiency, controllability, selectivity, and cost [6].

Molecular imprinting is a novel technique for selective adsorption [7–12]. Imprinted polymers are usually prepared by three steps. The template and polymerizable ligands are mixed and self-assembled, and then polymerized to obtain co-polymers in the presence of many cross-linkers, followed by extraction of the template from the co-polymer [13]. The molecular imprinting technique is extensively applied in a variety of fields such as sensor and on-chip devices [14,15], drug delivery [16], separation and screening of compounds of biological origin [17], membranes for biomolecules and proteins in aqueous medium [18,19], and sensors for monitoring toxic uranium [20].

Recently, our group has developed a few types of copper-imprinted polymeric particles with different morphologies and imprinting features, ranging from bulk- and surface-imprinted to pore-imprinted [21,22]. We compared two different methods, one- and two-step synthetic methods in suspension phase, in the preparation of imprinted polymers. Although extensive studies on the effects of cross-linker and porogenic solvent concentration on the particle shape, morphology, and separation properties have been conducted, discussions on other effects such as temperature, surfactant, and solvent/monomer (S/M) feed ratio have been rare.

In industrial production of polymer particles via suspension polymerization, the S/M feed ratio is an important economic factor as it determines the productivity of the process. In order to reduce the S/M feed ratio and thereby enhance the productivity, the surfactant concentration is usually increased. In this study, a few primal synthetic variables such as surfactant concentration and temperature are controlled to reduce the S/M ratio for the production of well defined particles. The effect of S/M feed ratio on the morphology and selective separation behavior of the synthesized molecularly imprinted polymer (MIIP) is also studied and discussed.

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doi:10.1016/j.cej.2010.11.006

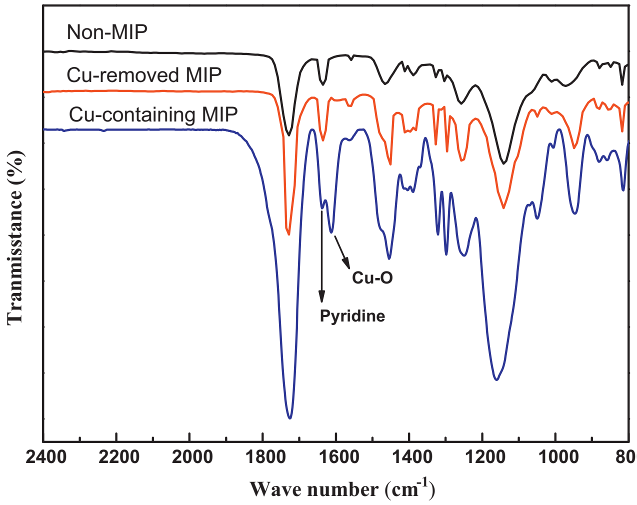


Fig. 1. FTIR spectra of Cu(II)-containing and Cu(II)-removed MIIPs along with non-imprinted polymers.

This type of imprinted polymer can be used for a selective separation of metal ion. Although copper ion is chosen as a model ion in this study, its application can be extended to a variety of heavy metal ions of interests—sometimes for selective recovery of highly valuable metal ions or sometimes selective removal of highly toxic ones from ionic mixtures. This is a unique and potential importance in the application of imprinted polymers compared to other conventional ion exchange resins.

2. Experiment

2.1. Materials

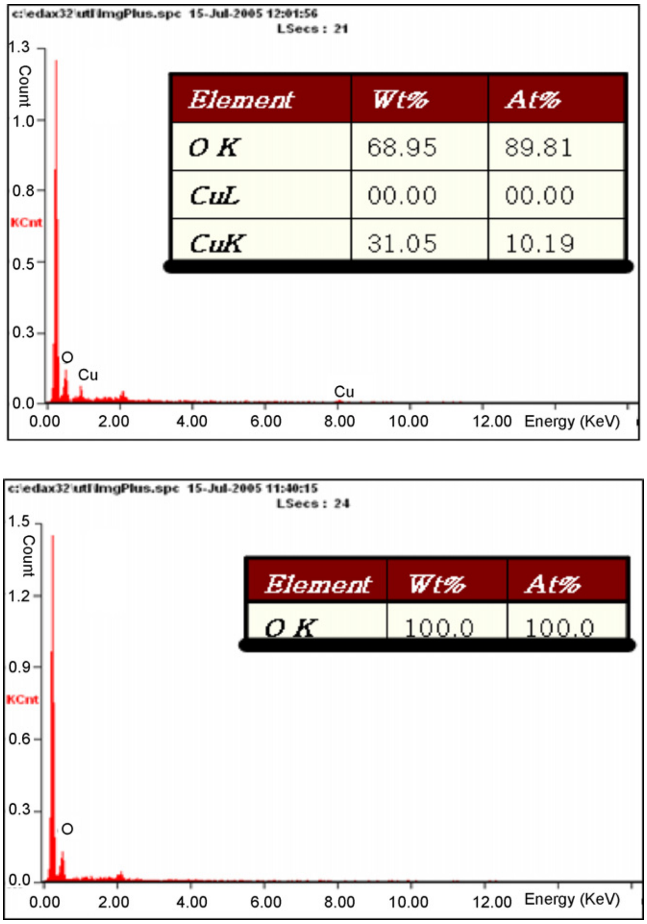
The copper salt $CuSO_4{\cdot}5H_2O$, as the template, was supplied from Daejung (Korea). The functional monomers of methacrylic acid (MAA), 4-vinyl pyridine (4-VP), and the cross-linker, ethylene glycol dimethacrylate (EGDMA), were supplied from Sigma–Aldrich (Milwaukee, WI, USA). The monomers were vacuum distilled for storage at 4 °C prior to use. Azobisisobutyronitrile (AIBN, Sigma–Aldrich, Milwaukee, WI, USA) was used as initiator and hydroxyethyl cellulose (HEC, Daejung, Korea) as a stabilizer in the polymerization reaction. All other chemical species were purchased as reagent grade from Sigma–Aldrich. The water used in this experiment was de-ionized (DI water).

2.2. Preparation of Cu(II)-imprinted microporous particles

Metal ion-imprinted polymers (MIIP) were prepared in microspherical form by suspension polymerization with the ingredients of Cu^{2+}, MAA, 4-VP, EGDMA and AIBN. The composition of Cu^{2+}, MAA, 4-VP, and EGDMA was 1:2:2:8 in molar ratio, and the amount of AIBN to the total amount of monomer system was 2 wt% in DI water. A series of S/M feed ratios was applied in the MIIP preparation. The S/M feed ratio was defined as the ratio of the solvent system amount (water and porogenic solvent (toluene)) to the monomeric system amount (MAA, 4-VP and EGDMA).

The reaction was performed in a 500-mL, three-neck reactor fitted with a mechanical stirrer. Toluene (10 mL) and the HEC aqueous solution were placed into the reactor. The concentration of HEC was 1–7 wt% to the monomeric system (monomer + cross-linker). The polymerization reaction was conducted at an agitation speed of 250 rpm for 15 min at room temperature, followed by 6 h at 70 °C under a N_2 atmosphere. After completion of the polymerization, the resulting particles were washed repeatedly with DI water and acetone to remove impurities and any remaining un-reacted monomer. The purified beads were dried under vacuum for 24 h. The same experiments were performed at different temperatures of 80 and 85 °C. The non-imprinted polymer was also prepared by the same procedure at the same condition except without use of Cu^{2+} for comparison in structure and adsorption behavior with imprinted ones.

The metal ions within the polymer particles were leached out by stirring in 1 M HNO_3 aqueous solution for 1 h. This process was repeated 20 times for complete removal of all metal ions, followed by washing and deionization with water and drying in vacuum.



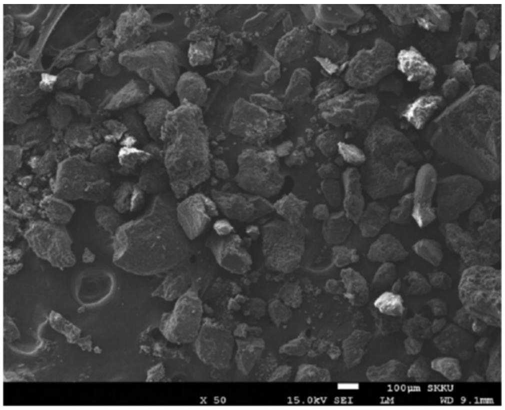
Element	Wt%	At%
O K	68.95	89.81
CuL	00.00	00.00
CuK	31.05	10.19

Element	Wt%	At%
O K	100.0	100.0

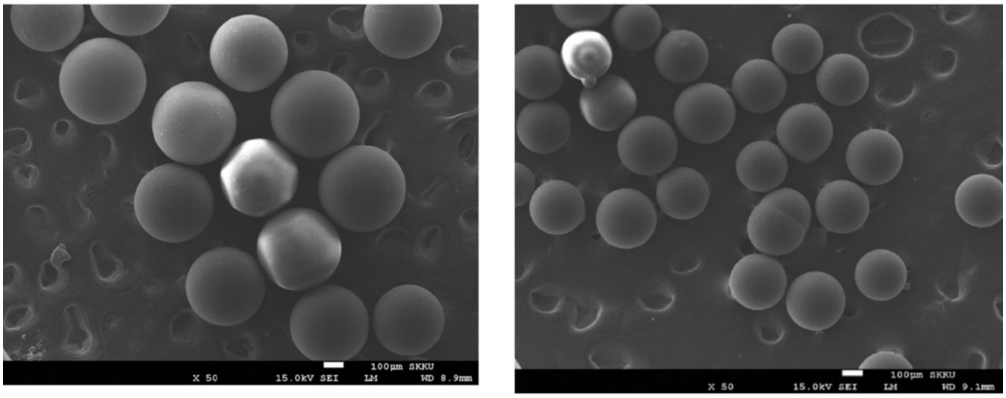
Fig. 2. EDX analysis of (a) Cu(II)-containing and (b) Cu(II)-removed MIIP.

2.3. Particle structure and size

Fourier transform infrared spectroscopy (Bruker IFS-66/S, FTIR, Bruker, Ettlingen, Germany) was used to identify the chemical structure of Cu(II)-imprinted microporous particles before and after extraction of the copper ions. The surface morphology of the MIIP particles was studied using an field emission scanning electron microscope (FESEM) (JSM7000F, JOEL, Tokyo, Japan) with an accelerating voltage of 15 kV. An EDAX USL 30 analyzer attached to the FESEM was used to determine the chemical composition of the samples by energy dispersive X-ray spectrometer (EDX). The Brunauer–Emmett–Teller (BET) test was conducted to characterize the surface area, width and volume of the pores of the MIIP powders using a porosimetry analyzer (ASAP 2010, Micromeritics, Norcross, GA, USA). The polymer sample (0.2 g) was degassed overnight at 100 °C to remove the adsorbed gases and moisture, after which the dry polymer was used for nitrogen adsorption and desorption isotherms at 77 K by BET.



a HEC 1 wt%



b HEC 2.5 wt% c HEC 3.5 wt %

Fig. 3. Effect of stabilizer concentration on the MIIP particle size and structure at an S/M feed ratio of 7.1.

2.4. Adsorption experiments

The adsorption of metal ions from the metal ion-containing aqueous solution was investigated in batch experiments. The effects of the initial concentration of metal ions and pH of the medium on the adsorption capacity were studied. A sample of 0.1 g of MIIP microparticles was added into a 100-mL solution containing Cu^{2+} in the concentration of 2.5–70 ppm, and the solution was sealed in a test bottle (250 mL volume). The pH was adjusted to a desired value between 3.0 and 7.0 using 100 mM sodium hydroxide and 100 mM hydrochloric acid aqueous solutions. The mixture was stirred for 4 h at room temperature using a magnetic bar. The microparticles were then filtered off through a polyethylene membrane filter (Sumplep LCR 25-LG, Nippon Millipore Ltd., Japan). The amount of metal ions absorbed on the microparticles was evaluated by measuring their residual concentrations in the filtrated aqueous solution by using atomic adsorption spectroscopy (AAS, Z-6100, Hitachi, Japan). The feed flow rates and pressures of fuel (acetylene) and oxidant (air) were 1.7 L min^{-1} at 20 kPa and 15 L min^{-1} at 160 kPa, respectively, at room temperature. The measurement was conducted at a wavelength of 324.8 nm. The adsorption capacity was calculated by the following equation:

$$Q = \frac{(C_0 - C_e)V}{M} \tag{1}$$

Here, Q is the loading capacity of the polymer (mg g^{-1}), C_o and C_e are the concentrations of the ions in the initial solution and in the aqueous phase after adsorption, respectively (mg L^{-1}), V is the volume of the aqueous phase (mL), and M is the amount of polymer (g).

In order to investigate the selective adsorption behavior of the imprinted particles, a competitive adsorption test was conducted for Cu^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+}. A sample of 0.1 g of the MIIP microparticles was treated with 100 mL of a mixture composed of these four component ions. After adsorption equilibrium was reached, the concentration of metal ions in the remaining solution was measured using AAS.

The distribution ratio, enrichment factor, and relative enrichment factor are calculated using the following equations:

The distribution ratio (D) is given by Eq. (2)

$$D = \frac{C_0 - C_e}{C_0} \times \frac{V}{M} \tag{2}$$

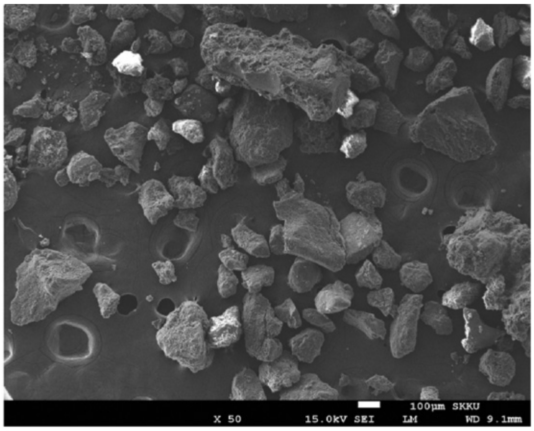
The enrichment factor for the binding of a copper ion in the presence of other ion species can be obtained from the equilibrium distribution ratio according to Eq. (3).

$$\alpha = \frac{D_{Cu}}{D_M} \tag{3}$$

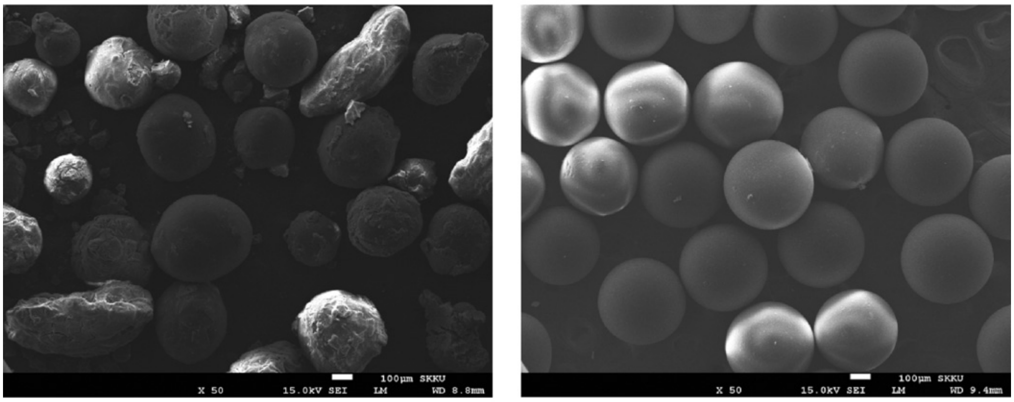
where D_{Cu} and D_M represent the distribution ratios of Cu^{2+} and one of other metal ions, respectively. A comparison of the enrichment factor of imprinted beads with that of non-imprinted beads for each metal ion allows an estimation of the effect of imprinting on selectivity. A relative enrichment factor α_r is defined as

$$\alpha_r = \frac{\alpha_i}{\alpha_n} \tag{4}$$

where α_i and α_n represent the enrichment factors of MIIP and non-MIIP, respectively.



a HEC 1 wt %



b HEC 1.5 wt % c HEC 2.5 wt %

Fig. 4. Effect of stabilizer concentration on the MIIP particle size and structure at an S/M feed ratio of 4.7.

3. Results and discussion

3.1. Synthesis of imprinted polymers

Fig. 1 shows the FTIR spectra of Cu-imprinted polymers before and after removal of template (copper ion) and non-imprinted polymer. The characteristic IR band at 1610 cm^{-1} originates from Cu–O bond and this band is clearly observed for Cu(II)-containing polymer, but not for Cu(II)-imprinted (removed) and non-imprinted polymers. Also, the Cu(II)-imprinted and non-imprinted polymers show the similar IR bands. From this IR spectra, a successful synthesis of Cu(II)-imprinted polymers was assured.

The energy dispersive X-ray analysis (EDX) was used to investigate the elemental composition of the Cu(II)-imprinted microporous particles, and the result is shown in Fig. 2. As the signal caused by the presence of Cu^{2+} was clearly observed for Cu(II)-containing polymer but not for Cu(II)-imprinted ones, the complete removal of Cu(II) was confirmed during extraction(washing) process.

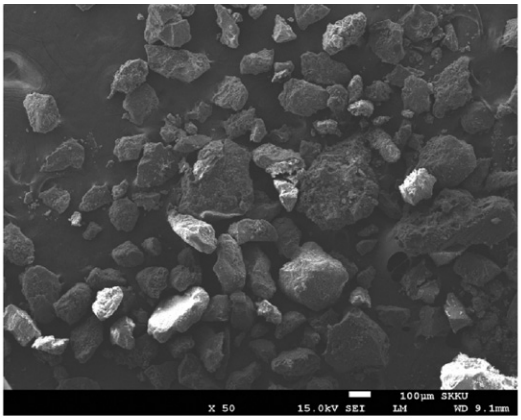
3.2. Particle size and morphology

3.2.1. Effect of stabilizer concentration

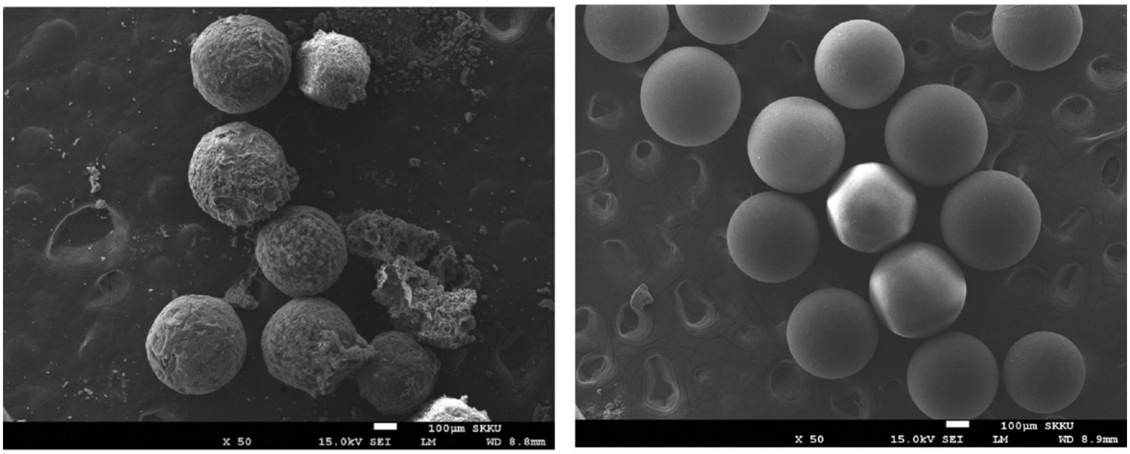
Two primary synthetic variables affecting the particle size and properties, stabilizer concentration and temperature, were investigated to reduce the S/M ratio as far as possible. MIIP particles were prepared at 70 °C at different S/M feed ratios. The minimum stabilizer concentration to obtain spherical and uniformly shaped particles in a desired size range was determined. Fig. 3 shows the size of MIIP particles produced at an S/M feed ratio of 7.1 over a stabilizer (HEC) concentration range of 1–3.5 wt%. The surfactant plays an important role in particle formation and aggregation. With insufficient stabilizer (below 2.5 wt%) (Fig. 3a), the resulting particles were not spherical and were aggregated with one another. At the initial stage of polymerization, the surfactant covering of the particle cores prevented aggregation. With the particle growth, however, some incomplete covering allowed some of the particles to coagulate with one another. The particle size decreased and became uniform with further increase of the stabilizer concentration, indicating that the surfactant aids their growth in the mono-dispersing mode. As the particle size became uniform from 2.5 wt%, the lowest stabilizer concentration of 2.5 wt% was chosen as the optimal stabilizer concentration to produce MIIP particles at an S/M feed ratio of 7.1.

Similarly, Figs. 4–6 show the stabilizer (HEC) concentration effects on the size and shape of MIIP particles produced at the S/M ratios of 4.7, 3.5 and 2.7, respectively. When the HEC concentration was increased from 1 to 2.5 wt% (Fig. 4a–c), 1 to 5 wt% (Fig. 5a–c), and 1 to 7 wt% (Fig. 6a–c), the particles were aggregated at concentrations lower than 2.5, 5, and 7 wt%, respectively. For the same aforementioned reason, the optimal (lowest) stabilizer concentrations to prepare well defined particle shapes was set as 2.5 wt%, 5 wt% and 7 wt% at the S/M ratios of 4.7, 3.5 and 2.7, respectively.

At S/M feed ratios lower than 2.7, it was difficult to disperse the monomer systems efficiently in the dispersing media, resulting in coagulation of polymeric particles without formation of a spherical shape, even at a stabilizer concentration as high as 9 wt% at 70 °C



a HEC 1 wt %



b HEC 3 wt %

c HEC 5 wt %

Fig. 5. Effect of stabilizer concentration on the MIIP particle size and structure at an S/M feed ratio of 3.5.

at a stabilizer concentration as high. At S/M feed ratios lower than 2.7, the particles formed rapidly, and thus tended to coagulate into larger particles until broken by mechanical stirring.

Fig. 7 shows a plot of the optimum surfactant concentration for production of spherical MIIP particles at different S/M feed ratios. The optimal S/M ratio decreased with increasing surfactant content, but its effect became negligible with decreasing S/M ratio and no further information of the reduction of S/M ratio was afforded below 2 in this present system in references.

3.2.2. Effect of temperature

Temperature was also expected to play an important role in controlling the particle size and uniformity. Fig. 8 presents the morphology of the MIIP particles produced at different temperatures at an S/M feed ratio of 2.7 and HEC concentration of 3.5%. The increase of the reaction temperature to 80 °C possibly led to the production of spherical particles that have never before been achieved at 70 °C at HEC concentrations below 7 wt%. In free radical polymerization, the reaction kinetics increases with temperature. The growth and termination of the chains thus possibly led to the formation of microspherical particles before aggregation at elevated temperature.

3.2.3. BET analysis

Table 1 shows the BET results for the MIIP particles produced at different S/M feed ratios at 70 °C. When the S/M feed ratio was decreased (i.e., the monomer concentration increased) from 7.1 to 2.7, the specific surface area was decreased from 0.3518 to 0.0323 $m^2\,g^{-1}$, and the pore volume from 0.000498 to 0.000095 $cm^3\,g^{-1}$, respectively (Fig. 9a–d). The pores are generated mostly by the evolution of the porogenic solvent, toluene, in the formation of spherical particles during polymerization. Because the relative concentration of the porogen (toluene) increased with increasing S/M ratio, the surface area and volume of the pores increased.

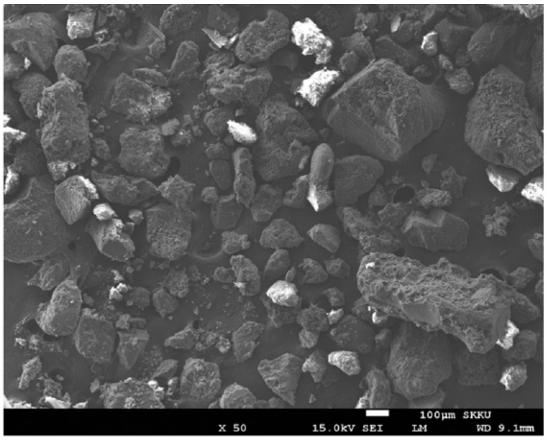
3.3. Adsorption characteristics

3.3.1. Adsorption capacity

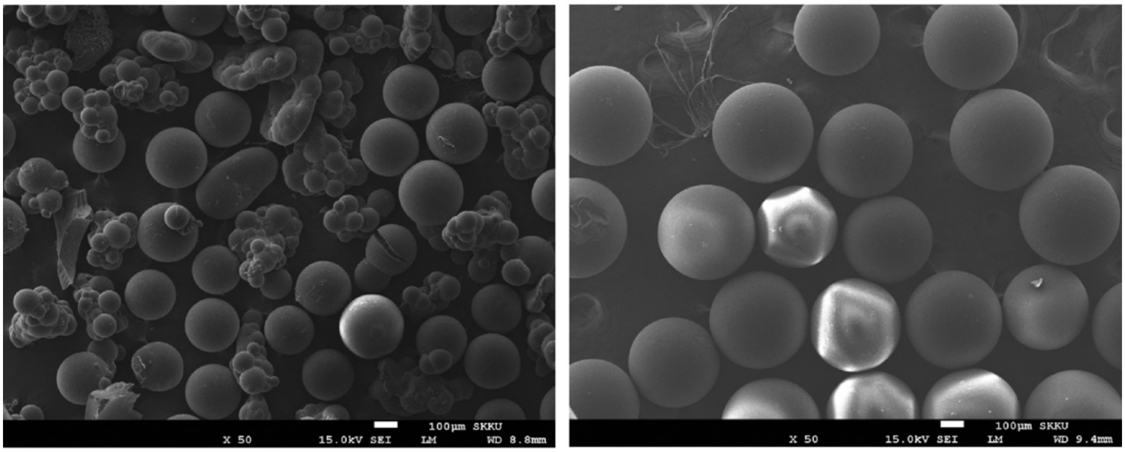
Molecular- or ionic-imprinted polymers can recognize a target material (template) specifically by means of the following mechanisms. First, a specific interaction between monomer and template—in this case, an ionic bonding between Cu(II) and carboxylic acid in monomer. Second, the tailored cavity provided by high cross-linking, followed by subsequent extraction of template in preparation process. Being different from the commercial cross-

Table 1
BET results of the MIIP samples prepared at 70 °C at different S/M feed ratios.

S/M ratio	Surface area ($m^2\,g^{-1}$)	Total pore volume ($cm^3\,g^{-1}$)
7.1	0.3518	0.000498
4.7	0.1632	0.000131
3.5	0.0323	0.000095
2.7	0.0158	0.000073



a HEC 2.5 wt %



b HEC 5 wt % c HEC 7 wt %

Fig. 6. Effect of stabilizer concentration on the MIIP particle size and structure at an S/M feed ratio of 2.7.

linked polymeric materials, the cross-linking density of MIIP is generally so huge that the bond ligands and cavity are highly firm. Thus, the resulting polymer is capable of binding the target materials with high specificity [7–12].

The adsorption of the Cu(II)-imprinted particles was studied at pH 6.2, the concentration of Cu^{2+} was 10 ppm. As shown in Fig. 10, the adsorption capacity, i.e., the amount of metal ions adsorbed per unit mass of MIIP, increased with increasing initial metal ion concentration up to a concentration of 350 μmol g^{-1} polymer, which is the maximum adsorption capacity of the prepared MIIP particles. The effect of the S/M feed ratio on this adsorption capacity was negligible, as the Cu^{2+} concentration in the monomeric system was invariant even at different S/M feed ratios. This result implies that the surfactant concentration did not strongly influence the imprinting efficiency of the Cu^{2+} ions on the polymers in their synthesis.

In order to determine the optimum pH for Cu^{2+} recognition, adsorption isotherms were obtained over a pH range of 3–7. The results demonstrated the significant influence of pH on the adsorption capacity of the MIIP particles. As shown in Fig. 11, the adsorption capacity for Cu^{2+} increased with increasing pH, indicating that the proton dissociation of the carboxyl groups in the host molecules plays an important role in adsorbing metals. The sorption capacity was very low owing to the protonation of MIIP in the acidic condition. As the Cu(II)-imprinted microspheres sorption capacity was near its maximum at pH 6.2, this pH was used in the further adsorption studies. The S/M feed ratio effect on the pH dependence of the adsorption capacity remained negligible for the same aforementioned reason.

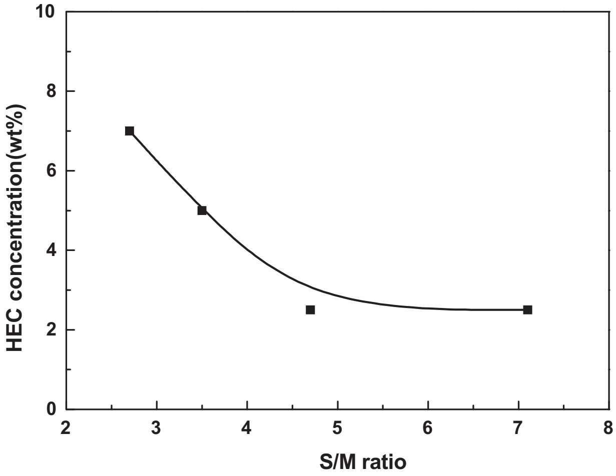
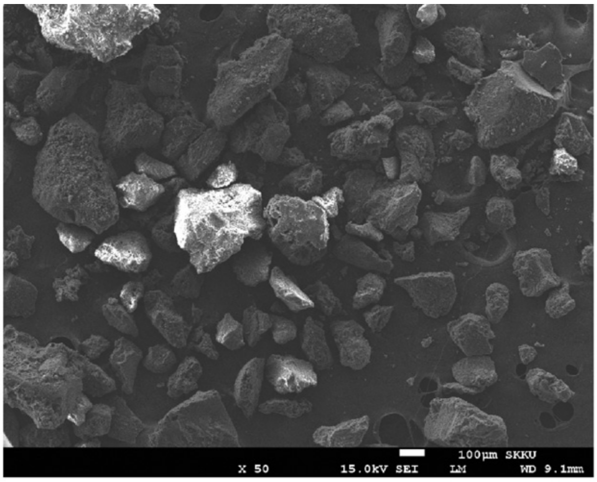
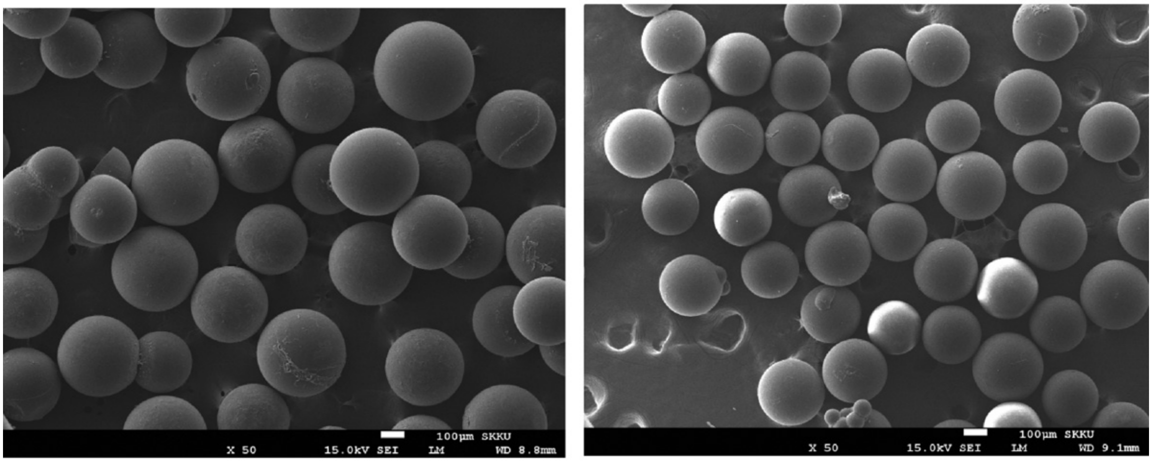


Fig. 7. Optimal HEC concentration for production of spherical MIIP particles at different S/M feed ratios.



a 70°C



b 80°C c 85°C

Fig. 8. Effect of temperature on the MIIP particle size and shape at an S/M feed ratio of 2.7 in the presence of 3.5 wt% HEC.

3.3.2. Selective separation behavior

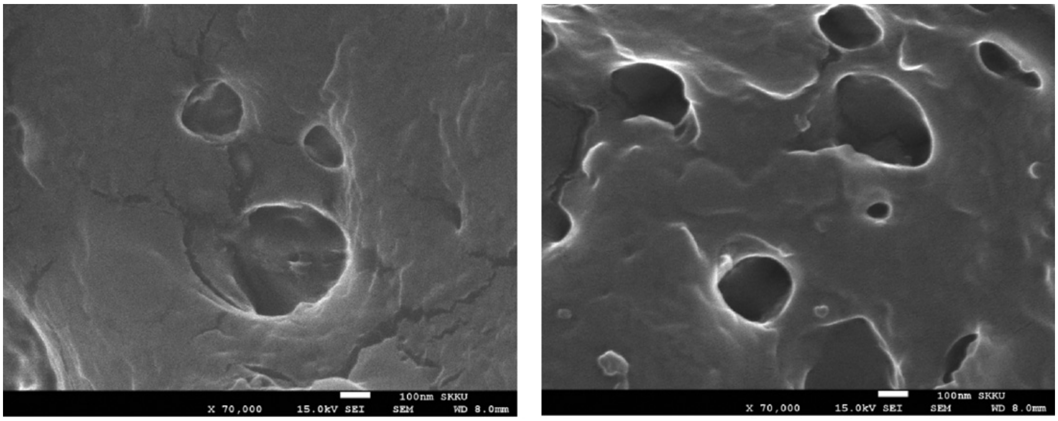
To investigate the selective separation behavior of the Cu(II)-imprinted polymer, the adsorption behavior of Cu^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} from aqueous solution onto the imprinted polymer was studied at pH 6.2, the concentration of each metal ions was 10 ppm. As shown in Fig. 12, the adsorption became saturated at a copper ion concentration of about 100 μmol g^{-1} polymer. This adsorption amount of Cu^{2+} was much higher than that of the other metal ions, Zn^{2+}, Ni^{2+} and Cd^{2+}, no significant S/M ratio effect on the selective separation behavior was observed. For the non-imprinted polymer, all metal ions are adsorbed almost at the same degrees, and thus no selective separation behavior was observed. Table 2 shows the distribution ratio (D), enrichment factor (α), and relative enrichment factor (α_r) of imprinted beads. The enrichment factors (α) for Cu(II)/Zn(II), Cu(II)/Ni(II), and Cu(II)/Cd(II) pairs were 5.92, 10.09 and 25.24 times greater than those of the non-imprinted polymers, respectively.

3.3.3. Adsorption kinetics

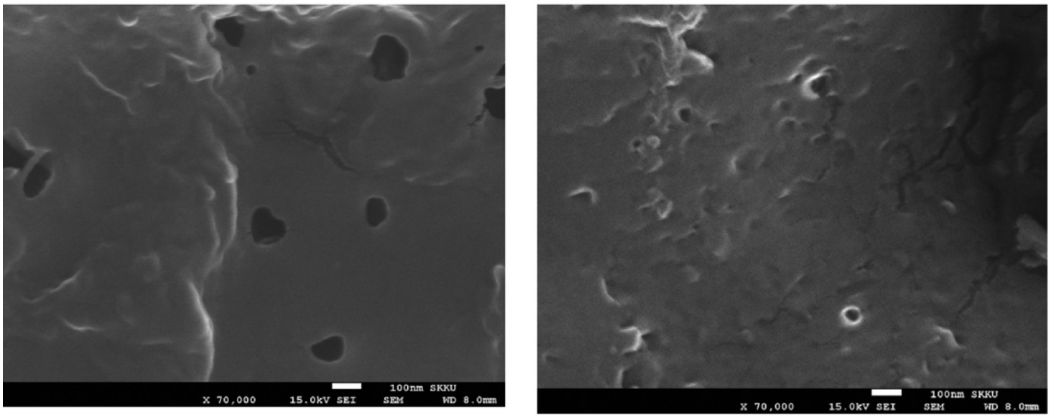
Pore volume is an important parameter controlling the adsorption kinetics of MIIP particles. When the pore volume was decreased by reducing the S/M feed ratio, the adsorption time to reach equilibrium was lengthened, as shown in Fig. 13a. The adsorption occurred rapidly in the first 1 h, after which the adsorbed amount was only slowly changed and the adsorption capacity reached equilibrium after 2 h. In order to investigate the reproducibility of the adsorption behavior of MIIP particles, the adsorption test was repeated several times using the same MIIP sample. Fig. 13b illustrates the adsorption behavior of the MIIP samples after repetition up to 6 times. Although the adsorption capacity decreases with repetition, its decrement degree is not so

Table 2
Distribution ratio (D), enrichment factor (α), and relative enrichment factor (α_r) of Cu(II)-imprinted polymer and non-imprinted polymer.

	Cu(II)-imprinted	Non-imprinted	Cu(II)-imprinted repeat
D_{Cu}	823.23	486.3	619.68
D_{Zn}	136.26	475.51	133.41
D_{Ni}	71.29	458	84.15
D_{Cd}	29.92	446.51	53.95
$\alpha_{Cu/Zn}$	6.04	1.02	4.64
$\alpha_{Cu/Ni}$	11.55	1.06	7.36
$\alpha_{Cu/Cd}$	27.51	1.09	11.49
$\alpha_{r\,(Cu/Zn)}$	5.92		
$\alpha_{r\,(Cu/Ni)}$	10.9		
$\alpha_{r\,(Cu/Cd)}$	25.24		



a S/M ratio 7.1 b S/M ratio 4.7



c S/M ratio 3.5 d S/M ratio 2.7

Fig. 9. Pore structure of MIIP particles prepared at different S/M feed ratios.

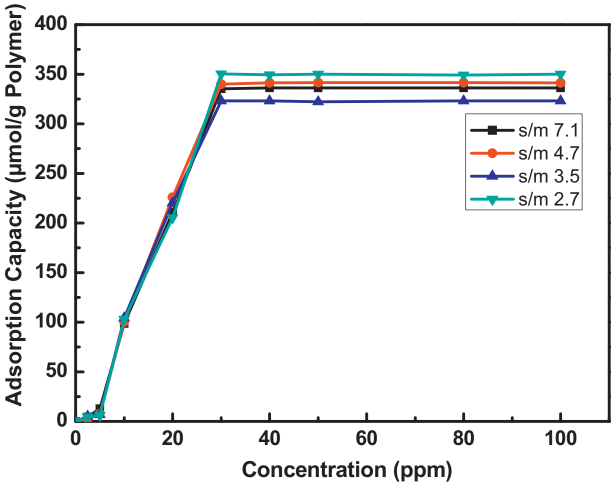


Fig. 10. Effect of S/M feed ratio on the initial concentration dependence of the adsorption capacity of MIIP particles.

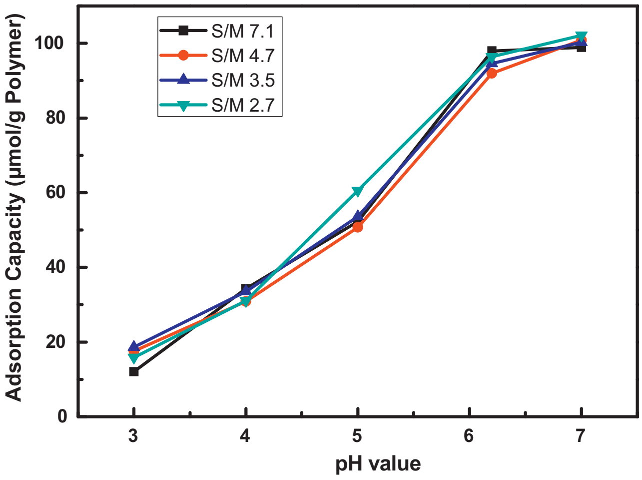


Fig. 11. Effect of S/M feed ratio on the pH dependence of the adsorption capacity of MIIP particles.

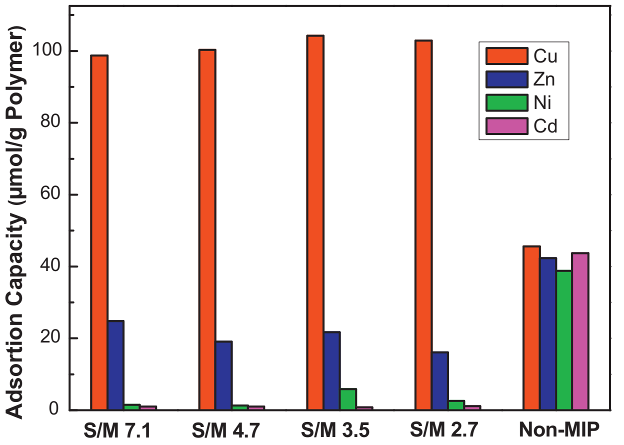


Fig. 12. Selective adsorption behavior of Cu(II)-imprinted polymer particles according to S/M feed ratios.

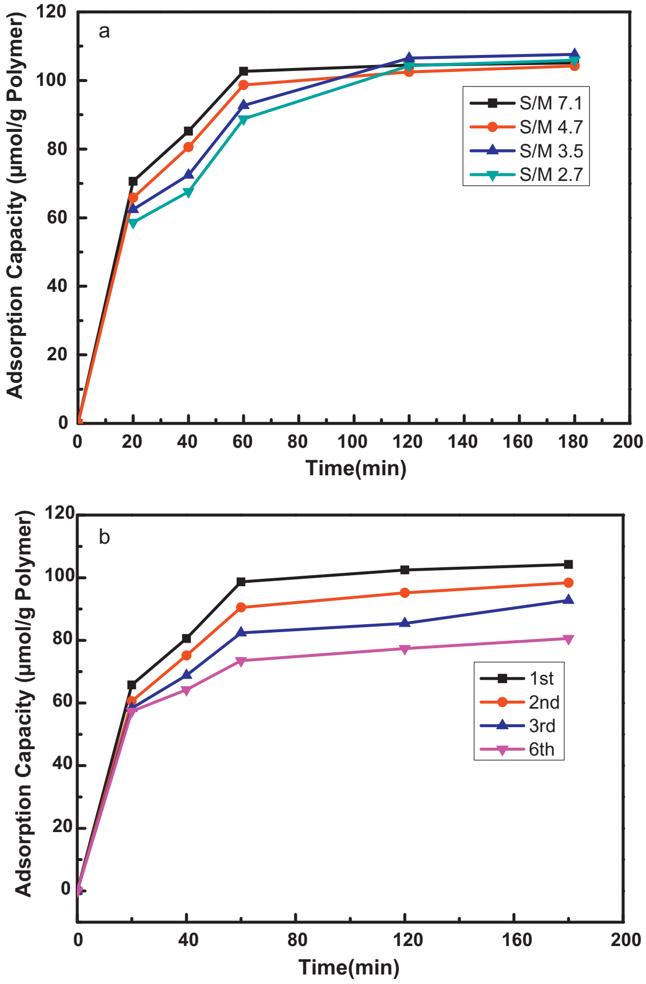


Fig. 13. Adsorption kinetics for Cu^{2+} ions of the samples prepared at (a) different S/M feed ratios and (b) S/M feed ratio of 4.7 in repeated experiments.

significant, and thus it demonstrates a good re-utilization property of MIIP. Not only the adsorption capacity but the selective characteristic is still kept after repetition, compared to the non-imprinted ones (see Table 2), although the selectivity decreases by about 50% (30–70% depending on the metal ion pairs) after 6th repetition.

4. Conclusion

In order to produce well defined spherical MIIP particles using a reduced S/M ratio, the surfactant concentration had to be increased. Increasing temperature also exerted a strong influence on the reduction of the S/M ratio. For the MIIP samples prepared at 70 °C, the maximum adsorption capacity of Cu^{2+} was about 350 μmol g^{-1}. The adsorption capacity for the template increased with increasing initial metal ion concentration. When the pH was increased to 6.2, the adsorption capacity was close to its maximum value. The effect of S/M ratio on the adsorption capacity and selectivity was negligible, due to the invariant Cu^{2+} concentration in the monomeric system. The adsorption kinetics increased with increasing S/M feed ratio, due to the increasing porosity. The very similar adsorption behavior, even in the second, third and tenth adsorption experiments, demonstrated the potential for the Cu-MIIP particles to be utilized repeatedly. The absorption capacity of Cu^{2+} was much larger than that of Cd^{2+}, Ni^{2+} and Zn^{2+} for Cu^{2+}-imprinted MIIP particles, which further exhibited the excellent selective separation characteristics.

Acknowledgment

This work was supported by the Core Environmental Technology Development Project for Next Generation (Grant number: 2008-02002-0048-0).

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