



Continuous separation of copper ions from a mixture of heavy metal ions using a three-zone carousel process packed with metal ion-imprinted polymer

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ABSTRACT

In this study, a three-zone carousel process based on a proper molecular imprinted polymer (MIP) resin was developed for continuous separation of Cu^{2+} from Mn^{2+} and Co^{2+} . For this task, the Cu (II)-imprinted polymer (Cu-MIP) resin was synthesized first and used to pack the chromatographic columns of a three-zone carousel process. Prior to the experiment of the carousel process based on the Cu-MIP resin (MIP-carousel process), a series of single-column experiments were performed to estimate the intrinsic parameters of the three heavy metal ions and to find out the appropriate conditions of regeneration and re-equilibration. The results from these single-column experiments and the additional computer simulations were then used for determination of the operating parameters of the MIP-carousel process under consideration. Based on the determined operating parameters, the MIP-carousel experiments were carried out. It was confirmed from the experimental results that the proposed MIP-carousel process was markedly effective in separating Cu^{2+} from Mn^{2+} and Co^{2+} in a continuous mode with high purity and a relatively small loss. Thus, the MIP-carousel process developed in this study deserves sufficient attention in materials processing industries or metal-related industries, where the selective separation of heavy metal ions with the same charge has been a major concern.

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1. Introduction

Chromatographic processes have been widely used in many industries for separation and purification of various systems including a petrochemical mixture or a biochemical mixture [1–3]. A matter of primary concern in such applications of chromatographic processes has been the attainment of high separation performance and high economic efficiency [4–6]. In regard to this matter, many researches have been performed previously in two directions: (1) preparation of improved adsorbent materials with higher separating capability (or selectivity) [7–13] and (2) application of a continuous counter-current process with multiple chromatographic columns [14–20].

In relation to the first direction, one of the proven approaches that have been developed recently was the introduction of molecular imprinting technique to the preparation of a chromatographic adsorbent [9–13]. In general, this approach begins with polymerization in the presence of a target molecule, resulting in an imprinted polymer matrix. Then, the imprinted target molecule is removed from the polymer matrix by extraction, which leaves behind a cavity complementary in size and shape to the target

molecule [9–13]. The presence of such a cavity with memory of the target molecule can allow the polymer matrix to serve as a highly effective adsorbent with an extremely selective binding site for the target molecule. The polymeric adsorbent based on this preparation method was referred to as molecular imprinted polymer (MIP) resin in the literature [9–13].

Due to the aforementioned advantage of high selectivity, the application scope of MIP resin as a chromatographic adsorbent has been focused mainly on a difficult separation system whose selectivity could no longer be improved under conventional adsorbents (i.e., non-MIP adsorbents). In this regard, it is worth noting several recent studies [12,13], in which MIP resin was prepared for selective separation of heavy metal ions with the same charge. In these studies, a proper polymer resin with cavities corresponding to a targeted heavy metal ion was obtained by a precipitation polymerization method based on a rotary evaporator. The resultant MIP resin was then applied to separation of a targeted heavy metal ion from a mixture of heavy metal ions. The results of these previous studies revealed that the developed MIP resin remarkably outperformed other conventional ion-exchange resins in terms of the separation performance for a targeted heavy metal ion [12,13].

However, the type of chromatographic processes used in all the aforementioned previous studies was confined to only a batch chromatographic process, which was known to be less suitable for a large-scale separation than a continuous counter-current chro-

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matographic process. In general, the latter process was reported to be more advantageous in attaining high production rate and high economic efficiency [3–6,17,21]. Therefore, it is quite worth considering the development of a continuous counter-current chromatographic process based on the aforementioned MIP resin for selective separation of a targeted heavy metal ion from a mixture of heavy metal ions.

This task will be performed in this study for the first time. For such a task, the Cu (II)-imprinted polymer (Cu-MIP) resin will be prepared in accordance with the polymerization method reported in the relevant literature [12,13]. Based on the prepared Cu-MIP resin, a three-zone carousel process for separation of Cu²⁺ from Mn²⁺ and Co²⁺ will be developed in a systematic way, which includes intrinsic parameter estimation, optimal process design, and experimental validation. The separation system under consideration (Cu²⁺, Mn²⁺, and Co²⁺) is an example system, which can be representative of a mixture of heavy metal ions that need to be separated in metal-related industries. A carousel, which is a process of interest in this study, is one of well-known continuous separation processes with multiple chromatographic columns and has been applied to several noteworthy separation tasks in the literature [14–18]. However, no previous carousel processes have hitherto attempted at the separation task of this study, i.e., the selective separation among heavy metal ions. For this reason, the results of this study will contribute to extending the application scope of a carousel process as well as confirming the possibility of using the Cu-MIP resin in a continuous counter-current chromatographic process. Furthermore, the MIP-carousel process developed in this study is expected to have sufficient possibility of application in the area of metal plating industry or semiconductor processing industry.

2. Simulation model

One of the important tools for developing a continuous separation process with multiple chromatographic columns is the detailed mathematical model that can allow prediction of the transport behavior of each species through a chromatographic column. The utilization of such a detailed model in the stage of process simulation and optimal design is effective in reducing the number of experiments required, leading to a saving of time and cost [22]. Hence, the approach of simulation based on detailed model will be used in part to development of the carousel process targeted in this study.

The simulation model consists of mass balance and mass-transfer equations for each component *i*, as presented below [3–6,20,22]:

$$\varepsilon_t \frac{\partial C_i}{\partial t} + (1 - \varepsilon_t) \frac{\partial q_i}{\partial t} + u_0 \varepsilon_b \frac{\partial C_i}{\partial z} - \varepsilon_b E_{b,i} \frac{\partial^2 C_i}{\partial z^2} = 0 \quad (1a)$$

$$\frac{\partial q_i}{\partial t} = k_{m,i} a_p (C_i - C_i^*) \quad (1b)$$

where the subscript *i* stands for different components; *C* and *q* are the concentrations in liquid and solid phases, respectively; *u*₀ is the liquid interstitial velocity; ε_t and ε_b are the total porosity and the inter-particle porosity, respectively; *C*^{*} is the liquid-phase concentration in equilibrium with the solid-phase concentration (*q*); *E*_b is the axial dispersion coefficient from the Chung and Wen correlation [23]; *k*_m is the mass-transfer parameter; *a*_p = 3/*R*_p for spherical particles; and *R*_p is the radius of solid particle.

The equilibrium relationship between *q*_{*t*} and *C*_{*i*}^{*} is usually expressed by an adsorption isotherm model, which is given below in the case of a single-component Langmuir adsorption model:

$$q_i = \frac{a_i C_i^*}{1 + b_i C_i^*} \quad (2)$$

where *a*_{*i*} and *b*_{*i*} are the Langmuir isotherm parameters of component *i*. For a multi-component system, it is a common practice to use the extension of the above Langmuir model, i.e., the multi-component Langmuir model, which is given below:

$$q_i = \frac{a_i C_i^*}{1 + \sum_{k=1}^n b_k C_k^*} \quad (3)$$

where *n* is the number of components; and *a*_{*i*} and *b*_{*i*} come from the single-component Langmuir isotherm parameters.

To solve the aforementioned model equations, a biased upwind differencing scheme (BUDS) was employed in conjunction with Implicit Euler integration having a step size of 0.05. The number of nodes in a column was set at 60. All of these numerical computations were carried out in Aspen Chromatography simulator.

3. Approach

3.1. Outline of separation system

Prior to the explanation on an approach to the design of the MIP-carousel process, a brief comment is given first regarding the separation system under investigation. As mentioned above, a feed mixture is comprised of three heavy metal ions such as Cu²⁺, Co²⁺, and Mn²⁺. The pH in the separation zone, which is the region of the columns in charge of separation between Cu²⁺ and the other metal ions, is kept constant by using the buffer solution as a liquid phase and an eluent. For the regeneration of the MIP-column after separation, nitric acid is employed.

3.2. Design of the three-zone MIP-carousel for separation of Cu²⁺ from Mn²⁺ and Co²⁺

There have been various types of carousel processes available in the literature [14–18]. Among them, a three-zone carousel process that was configured to complete both loading and washing operations within one switching period [17] was adopted in this study for the separation of interest.

Fig. 1 illustrates how such a three-zone carousel process can be applied to the separation of Cu²⁺ from the other metal ions (Co²⁺ and Mn²⁺). In step *N*, the feed containing the three metal ions is loaded into the first column (C) of zone III. During the feed loading, Cu²⁺ migrates much slower than the other metal ions because the cavities present in the adsorbent (i.e., MIP resin) molecules are oriented to catching only copper ions. As a result, most of copper ions will stay in column C whereas a large portion of cobalt and manganese ions will migrate toward column D. After the feed loading, the buffer solution is introduced into the feed port and eluted through the column C in zone III, which is continued until most of cobalt and manganese ions leave the column C (Fig. 1).

As soon as the column C becomes almost free of Co²⁺ and Mn²⁺, the next step (*N* + 1) begins with port switching (Fig. 1). During this step, the feed is loaded to column D, which corresponds to the first column in zone III. Simultaneously, the column C that has been filled with only copper ions in the previous step moves into zone II, where the column regeneration takes place and the desorbed copper ions are recovered from the product port. In the meantime, columns A and B, which have been in the re-equilibration and regeneration zones, respectively, in the previous step, moves into zone III and zone I, respectively (Fig. 1).

In step *N* + 2, the column C moves into zone I, where the column is re-equilibrated with the buffer solution. After this re-equilibration step, the column C is transferred to the second position of zone III (step *N* + 3) and utilized as the bed in charge of separation together with the first column of the same zone. If the step number becomes *N* + 4, the column C is located in the

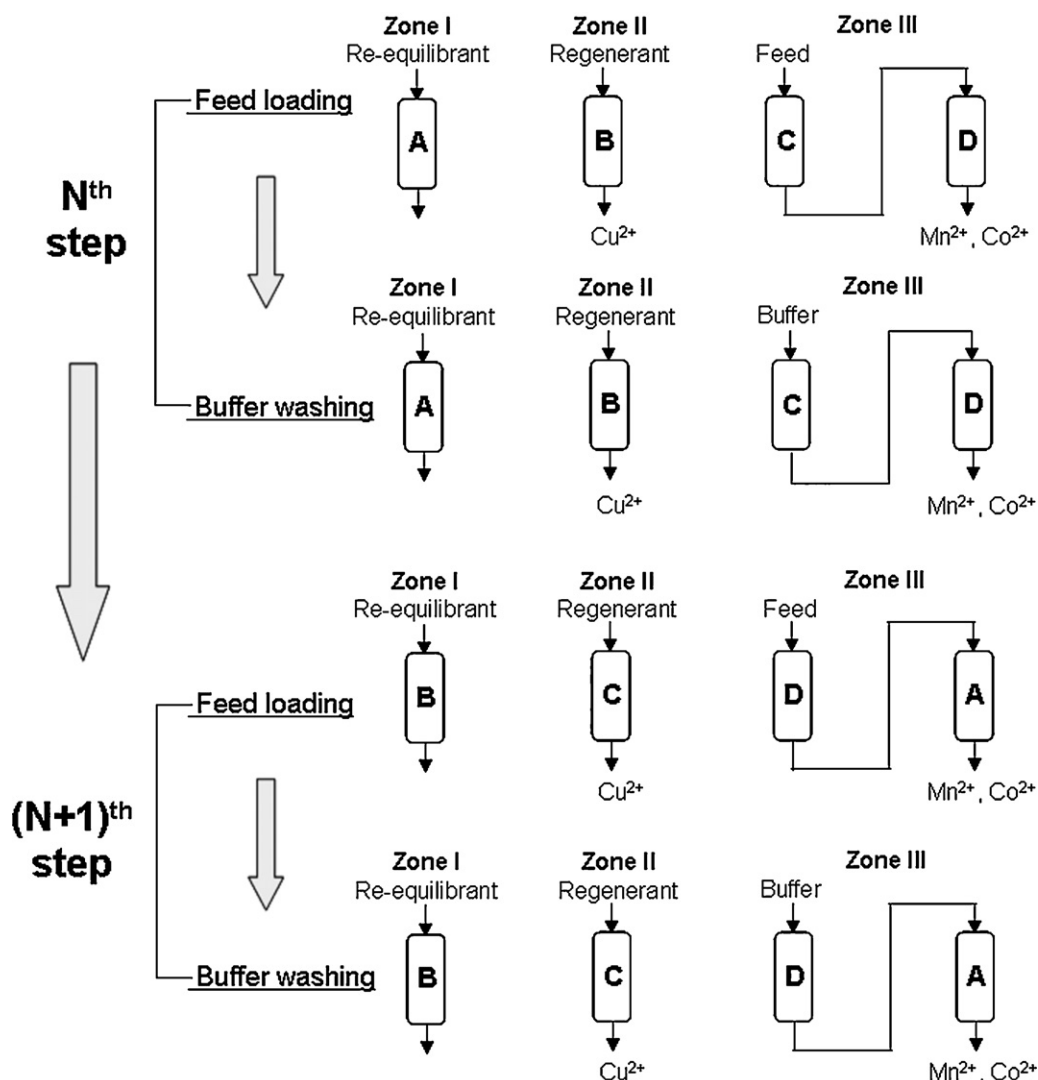


Fig. 1. Operation principle of the three-zone MIP-carousel process for continuous separation of Cu^{2+} from Mn^{2+} and Co^{2+} (re-equilibrant = buffer solution, regenerant = 1 M of nitric acid).

same position as in step N and it is loaded with the feed. The other columns A, B, and D are also located in the same position as in step N. All of these actions are implemented continuously in a cyclic manner, which can make possible continuous separation of Cu^{2+} from Co^{2+} and Mn^{2+} .

In the design of the aforementioned MIP-carousel process, the most important issue to be considered is the recovery of copper ions with high purity and small loss. To achieve such a separation goal, the operating parameters of the carousel process should be determined in a proper way. The operating parameters to be determined include flow rates, loading time, washing time, and switching time. The outline of approach to such a task for process design is presented in Fig. 2.

As stated in the outline (Fig. 2), the flow rate in the separation zone (III) will be fixed at 4 mL/min throughout the process design. Under such circumstances, all the other operating parameters will be determined through a series of simulation works and/or chromatographic experiments in such a way that high purity of copper ions can be recovered with a sufficiently small loss.

As the first step for the above task, the intrinsic parameters (i.e., adsorption isotherm and mass-transfer parameters) of Cu^{2+} , Co^{2+} , and Mn^{2+} will be estimated through a series of frontal experiments and iterative simulations (Fig. 2). The resultant intrinsic parameters

and the additional single-column experiments will then be used for determination of the operating parameters leading to high purity and small loss of copper ions. Finally, the carousel experiments will be performed to validate the operating parameters determined.

4. Experimental

4.1. Materials

Copper(II) sulfate penta-hydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), cobalt(II) chloride hexa-hydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), and manganese(II) sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) were purchased from Sigma-Aldrich Co. (St. Louis, MO) and utilized as the sources for the three heavy metal ions considered. Acetic acid and sodium acetate were supplied from Mallinckrodt Baker Inc. (Paris, KY) and Sigma-Aldrich Co. (St. Louis, MO), respectively, and they were used in the preparation of a buffer solution. Nitric acid was purchased from Matsuno Chemicals Co. (Osaka, Japan) and used as a regenerant in the MIP-carousel process developed. Distilled deionized water (DDW) was obtained from a Milli-Q system by Millipore (Bedford, MA).

The Cu-MIP resin was synthesized as reported elsewhere [12,13] and used as the adsorbent of this study. The average diameter of the

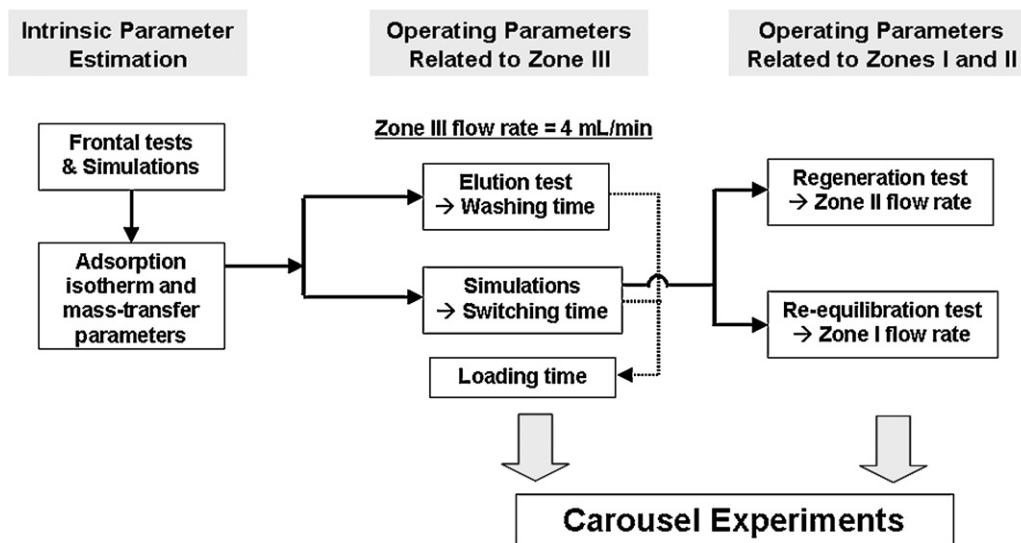


Fig. 2. The outline of approach to the design of the three-zone MIP-carousel process for continuous separation of Cu^{2+} from Mn^{2+} and Co^{2+} .

synthesized Cu-MIP resin was $250\ \mu\text{m}$. This adsorbent was packed into an omnifit chromatographic column, which was purchased from Bio-Chem Fluidics Co. (Boonton, NJ). The length and diameter of this column were 11.6 cm and 1.5 cm, respectively. The total porosity and the inter-particle porosity of the packed column were 0.746 and 0.380, respectively.

4.2. Equipments

An ÄKTA™ FPLC system, which was manufactured by Amersham Biosciences Co. (Piscataway, NJ), was used in the single-column experiments that were carried out prior to the carousel process design and the carousel experiments. This system consists of two pumps (Amersham Biosciences P-920), a high-performance monitor (Amersham Biosciences UPC-900), a flow division valve (Amersham Biosciences FV-903 Valve), and a fraction collector (Amersham Biosciences Frac-900). For an automatic control of this system, the Unicorn 5.1 software purchased from Amersham Biosciences Co. (Piscataway, NJ) was utilized in the Windows environment.

A Vario-6 atomic absorption spectrometer from Analytik Jena Co. (Jena, Germany) was used to analyze the concentration of each heavy metal ion in the samples, which resulted from the single-column experiments and the carousel experiments.

The carousel equipment was built in-house in a similar manner to that in the literature [17]. As shown in Fig. 3, the carousel equipment built consisted of five rotary valves, four pumps, and four columns. The rotary valve used was the ST valve from VICI Valco Instruments Co. (Houston, TX). This valve was connected to each column for implementation of periodic port movement, which occurs at the same time with the valve switching. All the actions associated with such a valve switching were controlled by a computer with Labview 8.0 software from National Instruments Co. (Austin, TX). For control of the flow rates, four pumps were employed in this equipment. A Series 200 Perkin-Elmer pump (Norwalk, CT) was used to control the flow rate of eluent that was introduced into the zone III inlet during the washing step. An Ismatec REGLO-CPF Digital pump (Glattbrugg, Switzerland) was used to control the flow rate of re-equivalent that was introduced into the zone I inlet. The other two pumps were Young-Lin SP-930D pumps (Anyang, Korea). One of them was used to control the flow rate of regenerant that was introduced into the zone II inlet, and the other the flow rate of feed that was loaded into the zone III inlet during the loading step.

4.3. Single-column experiments

The single-column experiments were performed to acquire the intrinsic parameters and the preliminary data for the carousel process design. The experiments performed for such purposes included a frontal test, an elution test, a regeneration test, and a re-equilibration test. To carry out these experiments, the column packed with the MIP resin was installed between the pump and the fraction collector in the aforementioned FPLC system.

First, the frontal test began by equilibrating the column with the buffer solution ($\text{pH}=4$). Then, a feed solution containing a single heavy metal ion or a mixture of heavy metal ions was loaded into the column. Such a feed loading was continued until the column was saturated with the feed solution.

In the elution test, the buffer solution ($\text{pH}=4$) was introduced into the column that had been pre-equilibrated with the feed solution containing a mixture of heavy metal ions. Such an elution was

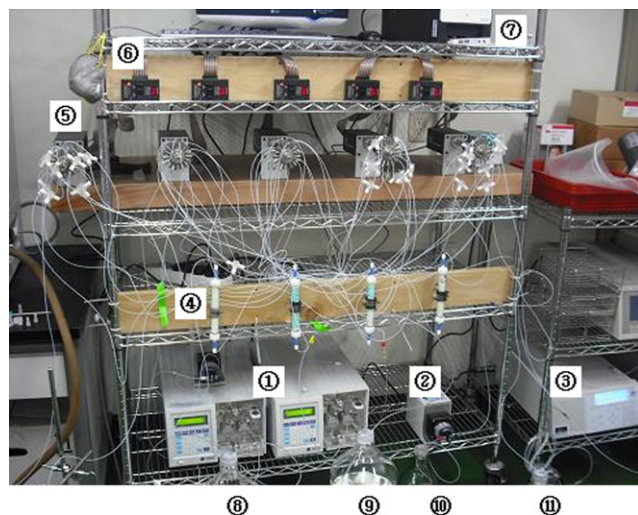


Fig. 3. Picture of the three-zone MIP-carousel equipment. (1) Young-Lin SP-930D pump, (2) Ismatec REGLO-CPF Digital pump, (3) Series 200 Perkin-Elmer pump, (4) MIP-column, (5) ST valve from VICI Valco Instruments Co., (6) Microelectric actuator, (7) Labview 8.0 software from National Instruments Co., (8) Regenerant (1 M of nitric acid), (9) Feed, (10) Re-equilibrant (buffer solution), and (11) Eluent (buffer solution).

continued until all the heavy metal ions other than copper ions were mostly eluted out of the column.

In the regeneration test, 1 M of nitric acid was eluted through the column that had been pre-equilibrated with the solution containing Cu^{2+} . The elution was continued until most of copper ions attached to the MIP resin were desorbed and eluted out of the column.

The regenerated column, which resulted from the above test, was utilized in the subsequent re-equilibrant test. In this test, the regenerated column was eluted with the buffer solution (pH = 4) until the column was completely re-equilibrated with the buffer solution, i.e., until the column was ready for use in the separation zone (III) in the subsequent switching period.

4.4. Carousel experiments

Two carousel experiments with different column configuration (allocation of the columns in the three zones) were performed at room temperature. The column configuration of the first experiment was 1–1–2 while that of the second experiment 1–1–1. The columns were equilibrated with the buffer solution (pH = 4) prior to each experiment. The carousel experiments were started by turning on the pumps and triggering the timer of the valve controller (Labview 8.0) simultaneously. During the experiments, the re-equilibrant (buffer solution) and the regenerant (1 M of nitric acid) were pumped into the columns of zones I and II, respectively (Figs. 1 and 3). Also, the feed solution and the eluent (buffer solution) were pumped into the first column of zone III during the loading and the washing steps, respectively (Figs. 1 and 3).

The feed solution was prepared by dissolving the three heavy metal ions in the buffer solution. The concentration of each heavy metal ion in the feed was 30 mg/L. The concentrations of the samples resulting from the experiments were analyzed by the Vario-6 atomic absorption spectrometer.

5. Results and discussion

5.1. Determination of intrinsic parameters of heavy metal ions

In order to characterize the adsorption behavior of the metal ions (Cu^{2+} , Co^{2+} , and Mn^{2+}) onto the MIP resin, preliminary batch tests were carried out and the breakthrough time of each metal ion was measured. The results showed that the breakthrough time decreased when the feed concentration increased. Since this is a major phenomenon occurring in Langmuir adsorption systems, the Langmuir model (Eq. (2)) was chosen in this study as the adsorption model for the three metal ions.

To exploit the Langmuir model for process design, its corresponding parameters (a_i and b_i) need to be specified for each species. Besides these two parameters (Langmuir isotherm parameters), there is an additional intrinsic parameter to be specified for describing the migration behavior of each metal ion through the MIP-column. It is the mass-transfer parameter ($k_{m,i}$), which relates the rate of concentration variation in the solid phase to the difference between the equilibrium and the actual concentrations in the liquid phase.

In the present study, the aforementioned three parameters (a_i , b_i , and $k_{m,i}$) were determined using inverse method [24,25], i.e., a least-square fitting of the simulation model (Eq. (1)) to the experimental chromatograms. For this task, three frontal experiments were performed in series for each metal ion with the single MIP-column while varying the feed concentration (10, 20, and 30 mg/L). During the experiments, the pH in the bed and the flow rate were maintained the same as in the separation zone of the MIP-carousel process (pH = 4 and flow rate = 4 mL/min).

Table 1
Langmuir isotherm and mass-transfer parameters of each heavy metal ion.

	Langmuir isotherm parameters		Mass-transfer parameter
	a_i (L/L S.V.)	b_i (L/mg)	$k_{m,i}$ (cm/min)
Mn^{2+}	0.9490	1.422×10^{-6}	3.825×10^{-4}
Co^{2+}	11.4052	1.662×10^{-1}	7.950×10^{-3}
Cu^{2+}	614.7710	1.751×10^{-1}	2.718×10^{-2}

The three chromatogram data obtained for each metal ion were then fitted simultaneously by tuning the Langmuir isotherm parameters and the mass-transfer parameter in the simulation model equations (Eqs. (1) and (2)). Such a tuning process was facilitated by employing the robust optimization tool based on genetic algorithm [6,25,26]. In each optimization run, the initial guesses of the Langmuir isotherm parameters were set on the basis of the breakthrough times of the acquired chromatograms. By contrast, it is not straightforward to predict the initial guess of the mass-transfer parameter. Thus, a wide range was first adopted for the searching region of the mass-transfer parameter, followed by narrowing down the searching region in stages.

The resulting values of the intrinsic parameters for each metal ion are listed in Table 1. Based on these parameter values, the model-predicted concentration profiles were generated and they are compared with the experimental chromatogram data in Fig. 4. A satisfactory agreement between the experimental and the model-predicted profiles is observed, indicating that the intrinsic parameter values in Table 1 can be utilized for design of the MIP-carousel process.

One of the noteworthy observations in Table 1 is that the adsorption strength of Cu^{2+} is much larger than those of Mn^{2+} and Co^{2+} . This trend can also be observed in Fig. 4, where the breakthrough time of Cu^{2+} is much longer than those of the other metal ions. Such a marked difference in the adsorption strength, which is obviously due to the unique property of the MIP resin used, will be of great advantage in the following design task for the development of the three-zone MIP-carousel process.

5.2. Validation of the Langmuir isotherm parameters for a mixture of the heavy metal ions

Prior to the use of the intrinsic parameters obtained in the above section, it was necessary to check whether the Langmuir isotherm parameters in Table 1 could be applied to a mixture of the metal ions. This is because the isotherm parameters in Table 1 were obtained for a single-component system. In case of a mixture system, a multi-component Langmuir model (Eq. (3)) is commonly employed, whose relevant isotherm parameters are based on those from a single-component Langmuir model. Such an approach was adopted in this study after some modification, which is presented below.

$$q_1 = \frac{0.9490C_1}{1 + 1.422 \times 10^{-6}C_1 + 1.662 \times 10^{-1}C_2 + 1.751 \times 10^{-1}C_3} \quad (4a)$$

$$q_2 = \frac{11.4052C_2}{1 + 1.422 \times 10^{-6}C_1 + 1.662 \times 10^{-1}C_2 + 1.751 \times 10^{-1}C_3} \quad (4b)$$

$$q_3 = \frac{614.7710C_3}{1 + 1.751 \times 10^{-1}C_3} \quad (4c)$$

where the subscripts 1, 2, and 3 stand for Mn^{2+} , Co^{2+} , and Cu^{2+} , respectively. Note that the Langmuir equations for Mn^{2+} and Co^{2+}

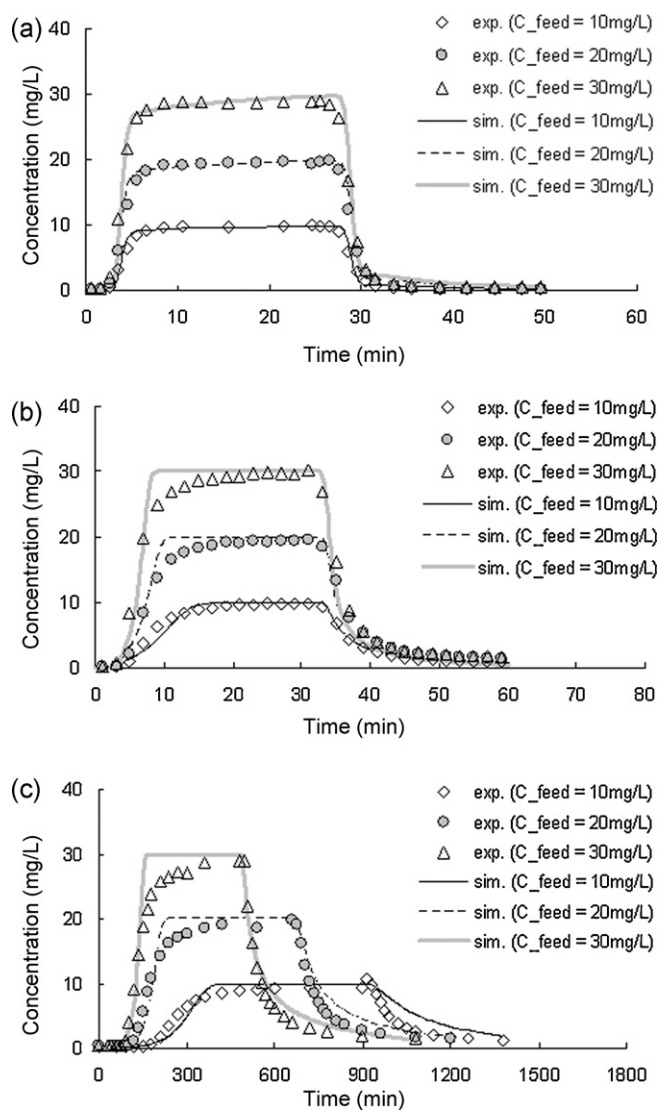


Fig. 4. Results from the frontal experiments performed for each heavy metal ion at the flow rate of 4 mL/min. (a) Mn²⁺, (b) Co²⁺, and (c) Cu²⁺.

were based on the type of multi-component model, which means that the presence of the other metal ions was taken into account. On the other hand, the single-component Langmuir equation was applied to Cu²⁺, which was due to a significantly large difference in the adsorption strength between Cu²⁺ and the other metal ions.

Based on the above Langmuir equations, the simulations were carried out for the case where a mixture of the three metal ions was loaded into the column while fixing the feed concentration of each metal ion at 30 mg/L. The simulation results were then compared with the data from the corresponding mixture frontal-experiment. As shown in Fig. 5, the simulation results are in reasonable agreement with the experimental data. This indicates the validity of the intrinsic parameters in Table 1 under a mixture condition as well as under a single-component condition.

5.3. Determination of the operating parameters related to zone III in the MIP-carousel process (1–1–2)

The intrinsic parameters (Table 1) obtained above were utilized in this section for design of the three-zone carousel process with four MIP-columns (1–1–2). The most important step in such a design task is to determine the operating parameters related to

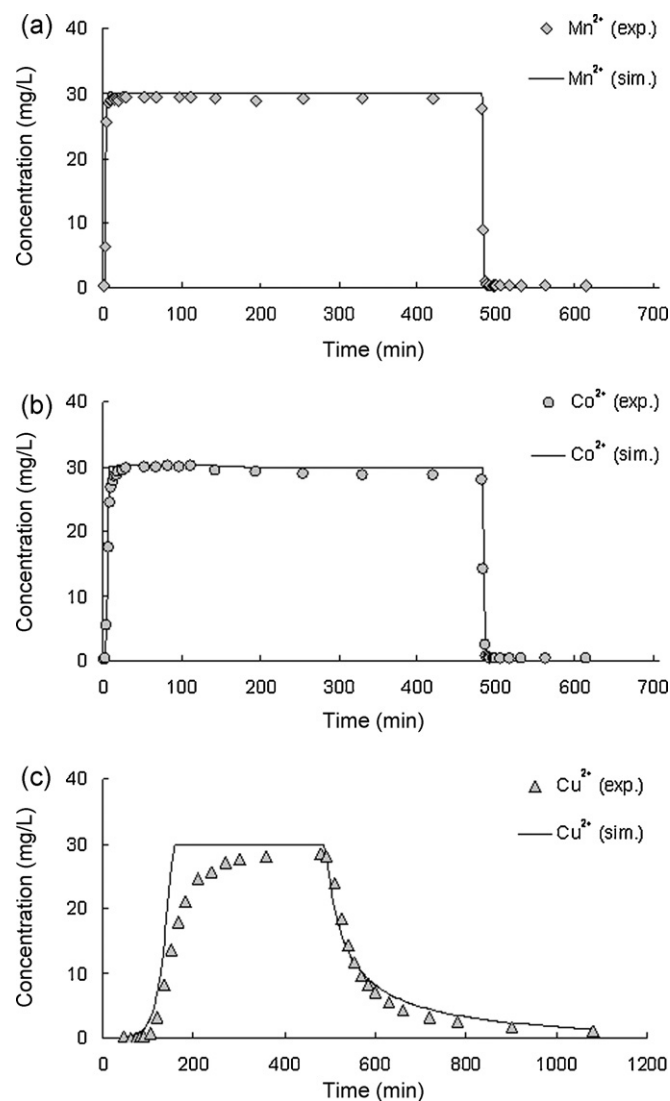


Fig. 5. Results from the frontal experiment performed for a mixture of the three heavy metal ions at the flow rate of 4 mL/min. (a) Mn²⁺, (b) Co²⁺, and (c) Cu²⁺.

zone III, because the purity and loss of product (Cu²⁺) are governed mostly by the migration behaviors of the metal ions in zone III. The operating parameters to be determined in this zone include the flow rates of feed loading and washing, washing time, switching time, and loading time.

First, the flow rates of feed loading and washing were both set at 4 mL/min, which was a natural result of the precondition that the flow rate in zone III should be kept at 4 mL/min as stated in the approach section (Fig. 2). Secondly, the washing time was determined from the elution test using the single MIP-column that had been pre-equilibrated with a mixture of the three metal ions whose feed concentrations were 30 mg/L each. In this test, the eluent (buffer solution) was eluted through the column at a flow rate of 4 mL/min, which was continued until most of Co²⁺ and Mn²⁺ staying in the chromatographic bed exited the column outlet. During the buffer elution, the concentration of effluent from the column outlet was measured. The measured concentration was then plotted as a function of time in Fig. 6, where the time zero indicates the instant of starting the buffer elution. Fig. 6 shows that the concentrations of Co²⁺ and Mn²⁺ decrease sharply with time and eventually become almost zero about 14 min after the buffer elution. On the evidence of this result, the washing time of the MIP-carousel process was determined to be 14 min (Table 2).

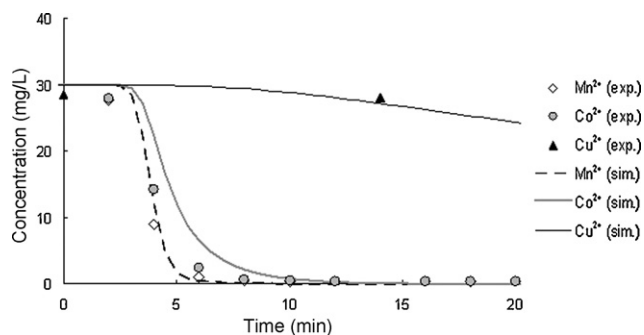


Fig. 6. Results from the elution test where the eluent (buffer solution) was eluted at the flow rate of 4 mL/min through the single MIP-column that had been pre-equilibrated with a mixture of the three heavy metal ions.

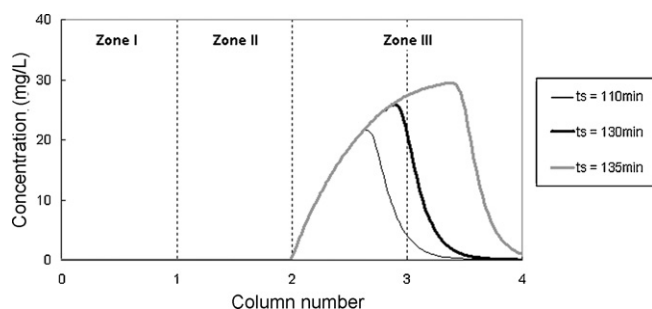


Fig. 7. Effect of switching time on the copper adsorption wave in the second column of zone III in the three-zone MIP-carousel process (1–1–2). This result was obtained from the simulations at the end of a switching period after a cyclic steady state was reached.

Thirdly, the switching time was determined through a series of detailed simulations, which were performed for the MIP-carousel process by varying the switching time under the fixed washing time of 14 min. In each simulation, the internal concentration profile of Cu^{2+} in zone III was obtained at the end of a switching period after a cyclic steady state was reached. The obtained concentration profiles were then used to examine the effect of switching time on the position of the front of copper adsorption wave in the second column of zone III. As shown in the simulation results in Fig. 7, an increase in the switching time made the copper front approach the

end of zone III. Since a longer switching time is advantageous for attainment of higher throughput, the simulations were carried out until the copper front nearly touched the end of zone III. It is evident from Fig. 7 that such an advantageous condition occurs at the switching time of 130 min. In case of the switching time longer than 130 min, the copper front was observed to overpass the boundary of zone III, which could obviously lead to a loss of copper ions. Considering these aspects, the switching time of the MIP-carousel process was chosen to be 130 min (Table 2).

Finally, the loading time was obtained by subtracting the washing time (14 min) from the switching time (130 min), because each switching period consists of only feed loading and washing steps in zone III. Thus, the loading time of the MIP-carousel process was set at 116 min (Table 2).

5.4. Determination of the operating parameters related to zones I and II in the MIP-carousel process (1–1–2)

Based on the switching time determined in the above section, the flow rate of regenerant in zone II and the flow rate of re-equivalent in zone I were determined in this section.

For the first task, the regeneration test was performed using the single MIP-column that had been pre-equilibrated with 30 mg/L of copper ion. The regenerant used was 1 M of nitric acid as mentioned in Section 4. The results from this test revealed that about 52.3 bed volumes of regenerant was required for desorbing and removing copper ions from the MIP-column.

For the second task, the re-equilibration test was conducted with the single MIP-column that had undergone the aforementioned regeneration. In this test, the pH of column effluent was measured in order to determine when the column became free of nitric acid and re-equilibrated with the buffer solution. It was confirmed that about two bed volumes of buffer solution was needed for re-equilibration of the column.

The aforementioned volumes of regenerant and re-equilibrant were then combined with the switching time in order to determine the flow rates in zones I and II (Q_1 and Q_2) as follows:

$$Q_1 (\text{Re-equilibration}) = \frac{2.0 \times BV}{t_s} \quad (5a)$$

$$Q_2 (\text{Regeneration}) = \frac{52.3 \times BV}{t_s} \quad (5b)$$

where BV stands for bed volume. Based on these two equations, the flow rates of re-equilibrant and regeneration in zones I and II were determined. In case of the re-equilibrant flow rate, the resulting value from the above equation (Eq. (5a)) was too low to keep accuracy throughout the operation. Thus, a little higher flow rate that could be better controlled was adopted as the re-equilibrant flow rate in zone I. The finalized flow rates of re-equilibrant and regenerant are reported in Table 2.

5.5. Experiment of the three-zone MIP-carousel process (1–1–2)

Based on the operating parameters (Table 2) determined in the previous sections, the three-zone carousel experiment was conducted for about 22 h or 10 switching steps. In this experiment, four columns packed with the MIP resin were used and their assignment to the three zones followed the configuration of 1–1–2. During the experiment, the effluents from the outlets of zones I, II, and III were collected in every switching period and the concentrations of the collected streams were analyzed. The analyzed concentrations were then plotted as a function of step number in Fig. 8, where the reported concentration represents the one averaged per each switching period.

Note first in Fig. 8b that the effluent from the zone II outlet (i.e., product port) contains a considerable amount of Cu^{2+} but almost

Table 2
Operating parameters and experimental results of the three-zone MIP-carousel processes under consideration in this study.

	Carousel-A	Carousel-B
Column configuration	1–1–2	1–1–1
<i>Zone flow rates^a (mL/min)</i>		
Zone I	1.00	2.00
Zone II	8.24	8.24
Zone III	4.00	4.00
<i>Inlet flow rates (mL/min)</i>		
Feed	4.00	4.00
Wash	4.00	4.00
Switching time (min)	130	74
Loading time (min)	116	60
Washing time (min)	14	14
<i>Experimental results^b</i>		
Purity of Cu^{2+} (%)	97.6	94.0
Loss of Cu^{2+} (%)	4.9	0.4

^a The flow rates in zones I and II are equal to the flow rates of re-equivalent and regenerant, respectively.

^b The experimental purities and losses were obtained by averaging those of the last four samples collected from the zone II outlet (product port) and the zone III outlet (impurity port), respectively, in the carousel experiments.

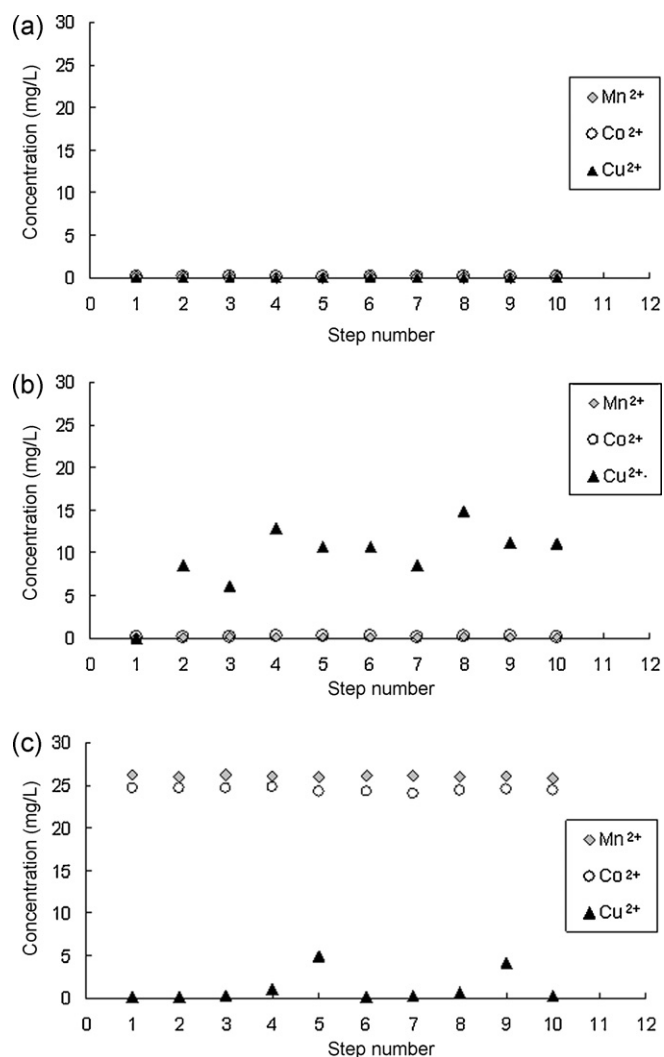


Fig. 8. Results from the carousel-A experiment (1–1–2). (a) Zone I outlet, (b) zone II outlet (product port), (c) zone III outlet. The concentrations were averaged over one switching period.

no impurity metal ions (Mn²⁺ and Co²⁺), resulting in high purity of Cu²⁺ in the product stream (Table 2). It was also confirmed from the effluent history at the zone I outlet (Fig. 8a) that the regeneration and re-equilibration were accomplished as designed.

On the other hand, the effluent history at the zone III outlet (i.e., impurity port) indicated that some loss of Cu²⁺ happened at certain step numbers, the 5th and the 9th steps (Fig. 8c). Since each column in the carousel process is located in the same zone at every four steps, the second column of zone III at the 1st, the 5th, and the 9th steps is virtually identical. It is therefore inferred that the MIP resin contained in the second column of zone III at the 1st step may have lower capacity than the MIP resin contained in the other three columns. In connection with this issue, additional supporting evidence was found in the effluent history at the zone II outlet. As shown in Fig. 8b, the copper concentration at the zone II outlet had a sharp decrease at the 3rd and the 7th steps. Considering that the column in zone II at the 3rd and the 7th steps becomes the second column of zone III at the 5th and the 9th steps, the aforementioned inference seems to be close to the truth. From a follow-up survey, it was revealed that only the MIP resin used in the problematic column (i.e., the second column of zone II at the 1st step) had been manufactured at a different date from that of the MIP resin used in the other three columns. This must be the most reliable reason for

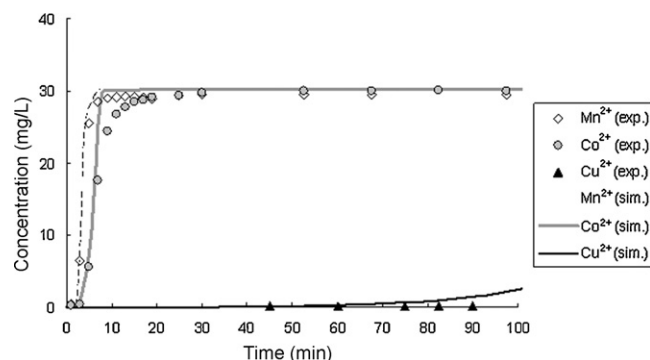


Fig. 9. Results from the breakthrough experiment for Cu²⁺ under the condition that a mixture of the three heavy metal ions were loaded into the single MIP-column.

having caused the non-uniformity in column capacity and leading to a considerable loss of copper ions as listed in Table 2.

5.6. Additional experiment of the three-zone MIP-carousel process (1–1–1)

To reduce the loss of copper ions by avoiding the non-uniformity in column capacity, additional carousel experiment was carried out using only the three columns that had been packed with the MIP resin of the same manufacturing date. Since the number of columns used in the carousel process was decreased from four to three, the column configuration was changed accordingly from (1–1–2) to (1–1–1). For the sake of convenience, the previous carousel with four columns (1–1–2) will be called “*carousel-A*” while the carousel with three columns (1–1–1) will be called “*carousel-B*” hereafter.

The operating parameters of the carousel-B process were determined from the batch experimental data that had already been acquired for the design of the carousel-A process. First, the washing time of the carousel-B was chosen to be the same as that of the carousel-A (14 min) because the washing condition remained the same between the two processes. Secondly, the switching time of the carousel-B was determined based on the breakthrough time of copper ion when a mixture of the three metal ions was loaded into the single column. This was due to the fact that the separation zone (III) of the carousel-B had only one column and this required copper ions to be confined within one column. The result of the copper-breakthrough experiment in Fig. 9 revealed that the breakthrough time of copper ion was about 75 min. Based on this result, the switching time of the carousel-B was set at 74 min. Thirdly, the loading time was obtained by subtracting the washing time (14 min) from the switching time (74 min).

Since the switching time of the carousel-B is shorter than that of the carousel-A, the flow rates of re-equivalent and regenerant in zones I and II in the carousel-B would need to be set higher than those in the carousel-A. Thus, the flow rate of re-equivalent in zone I in the carousel-B was set at 2 mL/min, which was two times higher than that in the carousel-A. On the other hand, the flow rate of regenerant in zone II in the carousel-B was not set higher but chosen to be the same as that of the carousel-A. This was because a considerable reduction in the amount of copper ion in the column of zone III could be expected as a result of the shortened loading time (116 min → 60 min), which could obviously reduce the load of regeneration in zone II.

All the above-determined operating parameters of the carousel-B are summarized in Table 2. Based on these operating parameters, the carousel-B experiment was performed and the results are presented in Fig. 10. It is clearly seen that the periodic change in copper concentration in zones II and III, which had been observed in the results of the carousel-A experiment (Fig. 8b and c), did not hap-

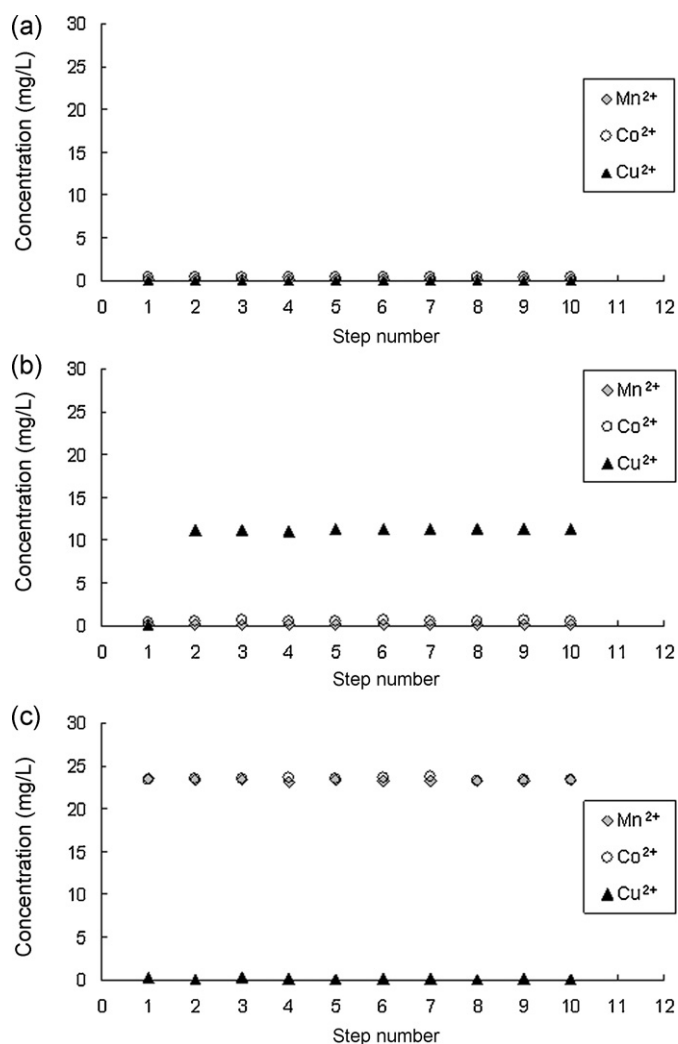


Fig. 10. Results from the carousel-B experiment (1–1–1). (a) Zone I outlet, (b) zone II outlet (product port), (c) zone III outlet. The concentrations were averaged over one switching period.

pen in the results of the carousel-B experiment (Fig. 10b and c). As a consequence, the loss of copper ion through the impurity port (i.e., the zone III outlet) was prevented in the carousel-B process, resulting in a smaller loss of copper ion than the carousel-A process (Table 2).

On the other hand, a little reduction in the purity of copper ion was observed in the carousel-B, compared to the carousel-A (Table 2). The possible reason for such phenomenon is that the metal-ion content of the column of zone III in the carousel-B is different from that of the first column of zone III in the carousel-A. In case of the carousel-B, a completely regenerated and re-equilibrated column that is free of metal ions is placed in zone III every at the beginning of a switching period. By contrast, in the zone III of the carousel-A, the second column containing a considerable amount of metal ions is placed in the position of the first column every at the beginning of a switching period. Therefore, the metal-ion content is maintained lower in the zone III column of the

carousel B, which causes the impurity metal ions (Mn^{2+} and Co^{2+}) in the carousel-B to be more strongly adsorbed. Since this will lead to more unfavorable condition for removing all the impurity metal ions completely from the zone III column of the carousel-B within the washing period, the carousel-B process has a lower purity of copper ions than the carousel-A process.

6. Conclusions

For continuous separation of Cu^{2+} from Mn^{2+} and Co^{2+} , the Cu (II)-imprinted polymer (Cu-MIP) resin was prepared and utilized as the adsorbent of the three-zone carousel process. As the first step for developing such a three-zone MIP-carousel process, the intrinsic parameters of the three metal ions were estimated through a series of frontal tests. The results from these frontal tests revealed that the adsorption behavior of each metal ion could be approximated by the Langmuir isotherm model. The estimated Langmuir isotherm and mass-transfer parameters were then used in the stage of designing the three-zone MIP-carousel process under consideration. Besides the intrinsic parameter estimation, the computer simulations and the additional single-column experiments such as elution, regeneration, and re-equilibration tests were performed for completion of the carousel process design. Based on the design results, the three-zone MIP-carousel experiments were conducted. The experimental results showed that the design method and the proposed MIP-carousel process can ensure the continuous separation of the targeted metal ion from a mixture of metal ions with high purity and small loss.

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