



Development of a four-zone carousel process packed with metal ion-imprinted polymer for continuous separation of copper ions from manganese ions, cobalt ions, and the constituent metal ions of the buffer solution used as eluent

Se-Hee Jo^a, Chanhun Park^a, Sung Chul Yi^a, Dukjoon Kim^b, Sungyong Mun^{a,*}

^a Department of Chemical Engineering, Hanyang University, Haengdang-dong, Seongdong-gu, Seoul 133-791, South Korea

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

ARTICLE INFO

Article history:

Received 31 March 2011

Received in revised form 15 June 2011

Accepted 26 June 2011

Available online 3 July 2011

Keywords:

Carousel process

Metal-ion imprinted polymer

Copper separation

Continuous separation process

Heavy metal ions

ABSTRACT

A three-zone carousel process, in which Cu(II)-imprinted polymer (Cu-MIP) and a buffer solution were employed as adsorbent and eluent respectively, has been developed previously for continuous separation of Cu²⁺ (product) from Mn²⁺ and Co²⁺ (impurities). Although this process was reported to be successful in the aforementioned separation task, the way of using a buffer solution as eluent made it inevitable that the product stream included the buffer-related metal ions (i.e., the constituent metal ions of the buffer solution) as well as copper ions. For a more perfect recovery of copper ions, it would be necessary to improve the previous carousel process such that it can remove the buffer-related metal ions from copper ions while maintaining the previous function of separating copper ions from the other 2 impure heavy-metal ions. This improvement was made in this study by proposing a four-zone carousel process based on the following strategy: (1) the addition of one more zone for performing the two-step re-equilibration tasks and (2) the use of water as the eluent of the washing step in the separation zone. The operating conditions of such a proposed process were determined on the basis of the data from a series of single-column experiments. Under the determined operating conditions, 3 runs of carousel experiments were carried out. The results of these experiments revealed that the feed-loading time was a key parameter affecting the performance of the proposed process. Consequently, the continuous separation of copper ions from both the impure heavy-metal ions and the buffer-related metal ions could be achieved with a purity of 91.9% and a yield of 92.8% by using the proposed carousel process based on a properly chosen feed-loading time.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

A multi-column chromatographic process has been the center of attention in many separation tasks that were to be performed in a preparative-scale or a large-scale [1–14]. This was mainly because a multi-column process can allow the continuous separation of a feed mixture while maintaining high purity and high yield. Such advantages have led the multi-column process to surpass a single-column batch chromatographic process in productivity and economical efficiency [3,5–8].

Due to the aforementioned advantages, the multi-column process has served as a major tool for continuous separation of various mixture systems [1–14]. Among the multi-column processes developed so far, a carousel process is known to be well suited for removal or recovery of a certain heavy-metal ion in a continuous mode [9–14].

In general, such a carousel process can be classified into 2 groups according to its application scope and the kind of the adsorbent employed. The first group of carousel processes utilized conventional ion-exchange resins that could exert a strong attraction toward a wide range of heavy metal ions regardless of their respective identities. Thus, these types of carousel processes have been mostly applied to the removal of heavy metal ions from a mixture of heavy metal ions and non-metal substances such as biochemicals [9–13]. By contrast, the second type of carousel process, which was established recently [14], employed a kind of metal-ion imprinted polymer (MIP) resin with an extremely selective binding site for the targeted heavy-metal ions [15,16]. Such a unique property of the MIP resin led the second type of carousel process to become a highly suitable one for continuous recovery of only the targeted heavy-metal ions from a mixture of different heavy-metal ions.

In relation to the aforementioned second type of carousel process, it is quite worth noting a recent publication [14], in which a three-zone carousel process packed with Cu(II)-imprinted polymer (Cu-MIP) resin was developed for recovery of copper ions from a ternary mixture of heavy metal ions, which included copper ions,

* Corresponding author. Tel.: +82 2 2220 0483; fax: +82 2 2298 4101.
E-mail address: munsy@hanyang.ac.kr (S. Mun).

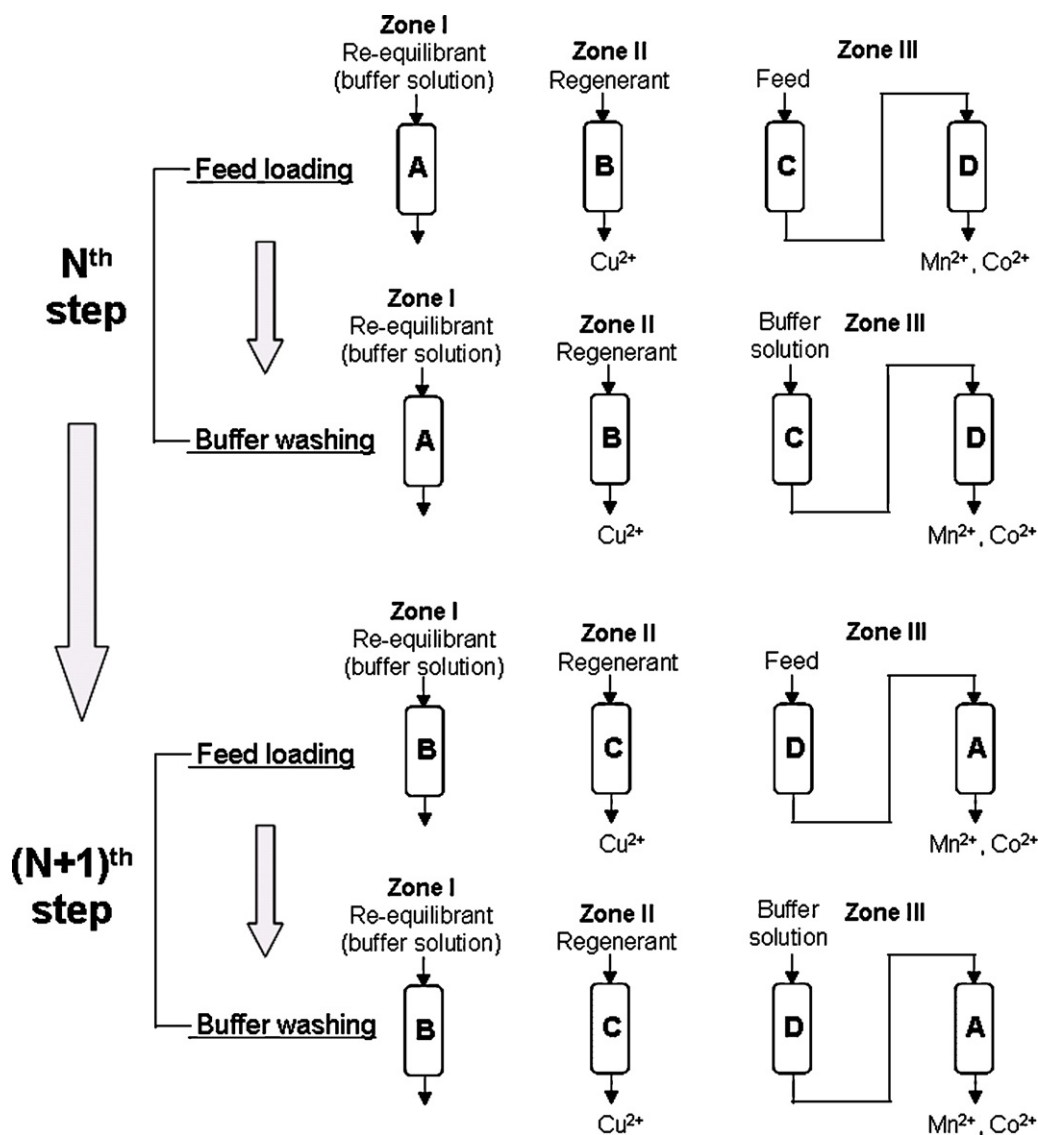


Fig. 1. Operation principle of the previous three-zone carousel process packed with Cu(II)-MIP resin for continuous separation of Cu^{2+} from Mn^{2+} and Co^{2+} . Reprinted with permission from Ref. [14]. Copyright 2010 Elsevier.

manganese ions, and cobalt ions. The operation methods of this process, which were delineated in detail in the previous publication [14], are summarized in Fig. 1. Notice that a total of 4 columns packed with Cu-MIP resin are employed in this process, where zone I and zone II each have one column and zone III has 2 columns. Among these 3 zones, zones I and II fulfill the re-equilibration task with the buffer solution containing sodium acetate and the regeneration task with nitric acid solution respectively while zone III is in charge of the substantial separation of interest.

As shown in Fig. 1, this carousel process has 3 inlet ports and 3 outlet ports, which are located in the top and bottoms of the 3 zones respectively. Under such an arrangement, a counter-current flow between liquid and solid phases is simulated by moving the ports by one column in the direction of the liquid-phase flow at a predetermined time interval (or switching time). Within each switching time, only zone III undergoes 2 different actions in series (Fig. 1). The first action is to load the feed mixture containing the 3 heavy-metal ions into the first column of zone III. During such a feed-loading action, the separation of copper ions from the other 2 impure heavy-metal ions (Mn^{2+} and Co^{2+}) occurs. As soon as this action is completed, the second action begins by eluting the buffer

solution through zone III. During such a buffer-washing action, the 2 impure heavy-metal ions are washed out of the first column in zone III. The lengths of these two-action periods along with the flow rates in zones I and II and the switching time were optimized in the previous study while fixing the flow rate of the separation zone (III) at 4 mL/min [14]. The three-zone carousel process based on such an optimized condition and Cu-MIP resin was reported to produce high-purity of copper ions through the zone II outlet (i.e., product port) while removing most of manganese ions and cobalt ions via the zone III outlet (i.e., impurity port) and minimizing the loss of copper ions through the zone III outlet. Further details for this three-zone carousel process can be found elsewhere [14].

However, one important problem to be solved is inherent in the above-explained three-zone carousel process. The problem is that the presence of the constituents of the buffer solution in the product stream is inevitable under the current configuration and operation method of the previous three-zone carousel process. As mentioned earlier, the buffer solution contains its constituent metal ions, which are the sodium ions coming from sodium acetate. Hence, the sodium ions, i.e., the buffer-related metal ions also need

to be separated from copper ions for more perfect recovery of copper ions. But this point was left out of consideration in the previous study, where only the 2 heavy-metal ions such as Mn^{2+} and Co^{2+} were regarded as the impurities against copper ions [14].

The goal of this study is to develop more efficient carousel process that can deal with the aforementioned problem. For this purpose, some modifications will be made in the operation method and the zone configuration of the previous three-zone carousel process, which will lead to the development of a four-zone carousel process based on more elaborated operation strategy in the present work.

To accomplish the above task, a series of single-column experiments will be performed first using the chromatographic column packed with Cu-MIP resin (hereafter, "MIP-column"). From these experiments, a proper strategy for separating copper ions from the buffer-related metal ions as well as manganese ions and cobalt ions in a carousel mode will be proposed. In addition, the operating parameters associated with the proposed carousel operation will be determined in a systematic way while keeping the flow rate of the separation zone the same as in the previous three-zone carousel process (4 mL/min). Under the resultant operating parameters and the proposed carousel configuration, a total of 3 carousel experiments will be carried out. The results from these 3 carousel experiments will then be used to clarify what is the major factor in securing the optimum of the proposed carousel process that can lead to high purity and high yield while treating the buffer-related metal ions as the same class of impurities with manganese ions and cobalt ions.

2. Approach

2.1. Straightforward method – replacement of only the buffer solution with water under the previous three-zone carousel configuration

One of the straightforward methods for implementing a continuous separation of Cu^{2+} from the other heavy metal ions (Mn^{2+} and Co^{2+}) while keeping the product stream (i.e., the stream containing Cu^{2+}) free from the buffer-related metal ions (Na^+) will be to replace all the employed buffer-solutions with water in the previous three-zone carousel process. This means that water is used as both the re-equilibrant in zone I and the eluent of washing period in zone III (Fig. 1). However, the feasibility of this method depends on whether a proper control of pH of the mobile-phase solution is practicable, because the nonuse of buffer solution can make it almost impossible to maintain the pH at a desirable value.

According to the previous publication [15], the adsorption capacity of Cu^{2+} onto the MIP resin and the selectivity between Cu^{2+} and other heavy metal ions on the MIP resin are significantly reduced as the pH value becomes lower. This phenomenon is mostly attributed to a unique ion-exchange equilibrium relationship between Cu^{2+} and H^+ in the system considered. Since only the dissociated hydrogen ions from the carboxylic groups of the MIP resin can be exchanged with copper ions in the liquid phase, the adsorption capacity of Cu^{2+} is largely affected by the number of deprotonated carboxylic groups ($\text{CH}_3\text{COO}^- \cdots \text{H}^+$) on the MIP resin. As the pH of the system is higher, the number of deprotonated carboxylic groups increases, which leads to an increase in the adsorption capacity of Cu^{2+} . On the other hand, if the pH is lower, the number of deprotonated carboxylic groups decreases and the number of protonated carboxylic groups (CH_3COOH) increases, which causes a decrease in the adsorption capacity of Cu^{2+} .

Therefore, if the separation performance of the carousel process is to be guaranteed, the pH of the columns in the separation zone (III) should be maintained higher (Fig. 1). The most important factor

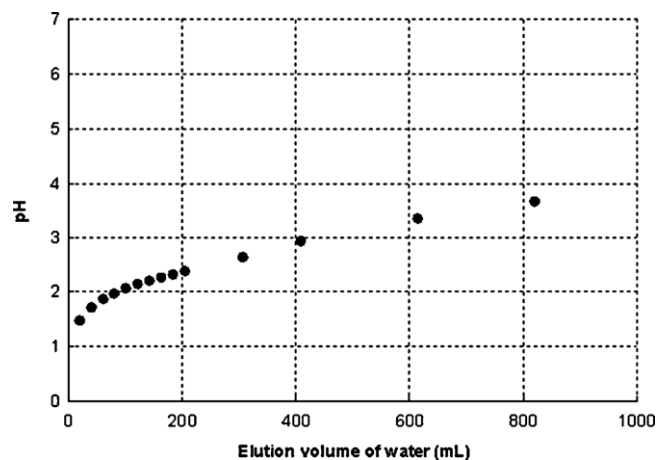


Fig. 2. Plot of the volume of water eluted through the MIP-column versus the resulting pH of the column effluent. The MIP-column used in this preliminary test had been pre-equilibrated with 0.1 M HNO_3 prior to the water elution. The length and diameter of this column were 11.6 cm and 1.5 cm respectively.

for maintaining such a condition throughout the carousel operation is virtually up to the pH of the column in the re-equilibration zone (I), because this column belongs to the separation zone at every time of the next port-switching.

To check whether water is suitable for the re-equilibrant in zone I, a preliminary experiment was carried out using the single MIP-column, which had been pre-equilibrated with 0.1 M HNO_3 in order to maintain the state of this column the same as that in the regeneration zone (II). This single column was then eluted with water while monitoring the pH of the column effluent. The result of this experiment is shown in Fig. 2. It can readily be seen that the pH was not sufficiently increased despite the elution of a very large amount of water, indicating that water is inefficient as the re-equilibrant of interest. This phenomenon is mostly due to the fact that water has no buffering function to take up the hydrogen ions inside the column.

Of course, an extremely large elution of water through the column for a long time can make it possible to increase the pH of the column up to 4 or higher value. However, this is by no means the end of the matter, because the principle of electro-neutrality forces a large amount of hydrogen ion to remain still attached to the fixed negatively charged-ionic sites of the MIP resin particles. If this column enters zone III and serves as a separation media in the next switching period, the hydrogen ions attached to the resin particles will be replaced by the heavy metal ions and then move into the mobile phase. Since such an outflow of H^+ from the resin particles to the mobile phase will decrease the pH significantly, the selectivity between Cu^{2+} and the other heavy-metal ions can be reduced accordingly. This will obviously lead to a severe reduction in throughput and product purity of the carousel process.

2.2. Proposed strategy – introduction of two-step re-equilibrations under a four-zone carousel configuration while using water as the washing solution in the separation zone

To overcome the underlying limitations in the aforementioned method, an alternative strategy is proposed in this section. The core of the proposed strategy is to use both buffer solution and water for re-equilibrating the column, i.e., for making the regenerated column ready for the separation task of the next step, while using only water as the eluent of the washing step in the separation zone.

The carousel process based on this strategy is illustrated in Fig. 3. Note that the proposed process has one more zone than the previous process. This is to perform the two-step re-equilibration tasks in

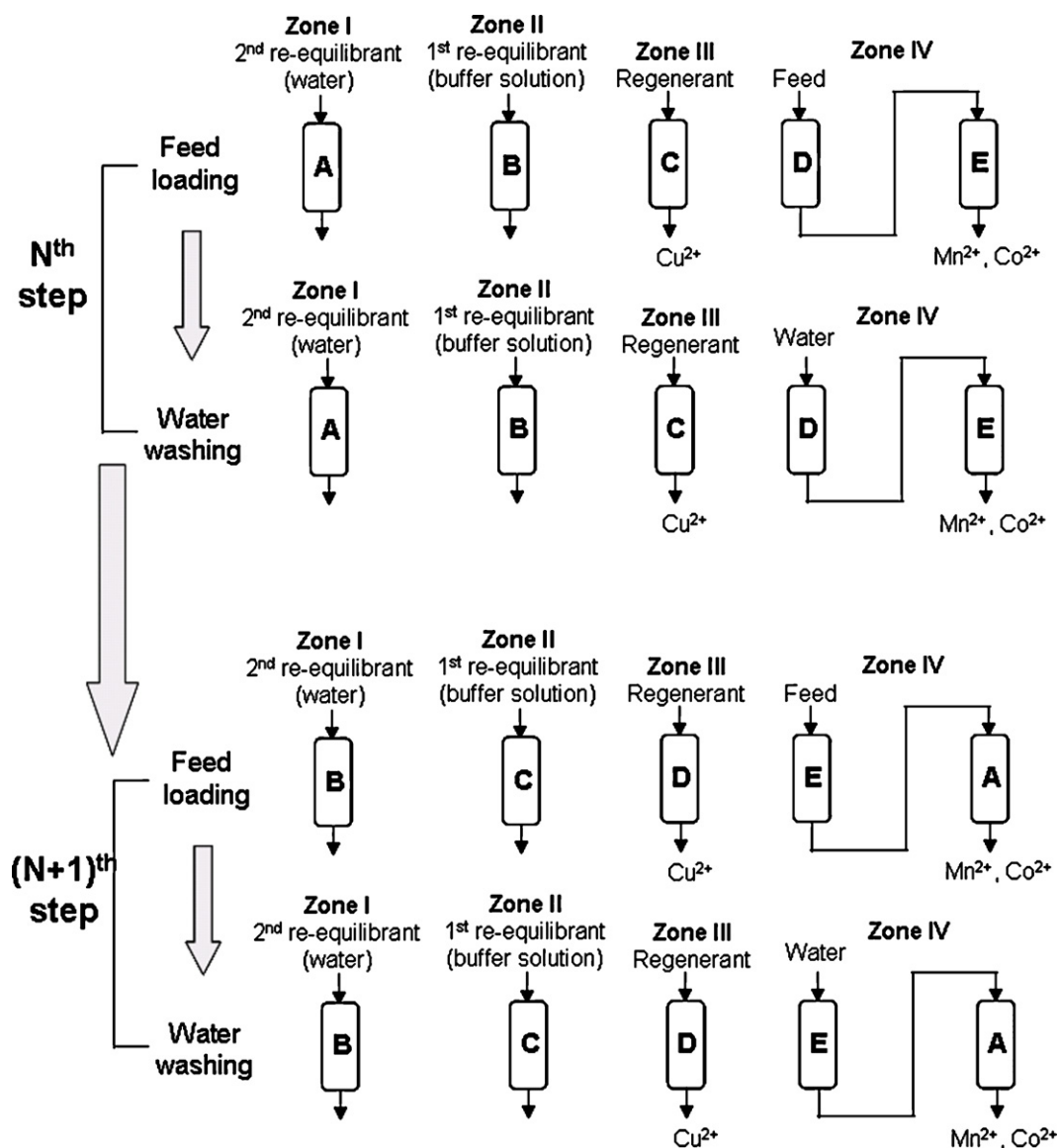


Fig. 3. Operation principle of the four-zone carousel process packed with Cu(II)-MIP resin for continuous separation of Cu^{2+} from Mn^{2+} , Co^{2+} , and the constituent metal ions of the buffer solution (i.e., the buffer-related metal ions).

2 adjacent zones (I and II) in series. As shown in Fig. 3, the first-step re-equilibration task is performed in zone II, where the regenerated column is eluted with a buffer solution for the following 2 purposes; (1) to remove most of the hydrogen ions staying in the column void and (2) to exchange the hydrogen ions attached to the MIP resin particles with a “third” metal ion belonging to the buffer solution (i.e., buffer-related metal ion). Once such a buffer-elution through the column is completed in zone II, the pH inside the column will reach a sufficiently high level due to the intrinsic property of the buffer solution. However, the column void will still be filled with the buffer-related metal ions. To clear these buffer-related metal ions out of the column, the second-step re-equilibration task is performed in zone I (Fig. 3), where the column that undergoes the first-step re-equilibration in the preceding zone is eluted with water.

The column that completes the aforementioned two-step re-equilibration tasks is then moved to the separation zone (IV) at the moment of port-switching (Fig. 3). As mentioned earlier, the most important issue to be considered in the separation zone is the pH inside the column. Recall that if the column would have been re-equilibrated with only water and then moved into the separation

zone, the pH of the column could be lowered to have an undesirable effect on the separation performance because the hydrogen ions onto the resin particles could be released to the mobile phase. Such a concern, however, is irrelevant to the proposed carousel process (Fig. 3), because the hydrogen ions onto the resin particles have been replaced by the buffer-related metal ions in the re-equilibration zones (I and II) before the column enters the separation zone (IV). Thus, the ions desorbed from the resin particles to the mobile phase by exchange with the heavy metal ions in a feed mixture are not hydrogen ions but the buffer-related metal ions. This will certainly help maintain a high pH in the separation zone, which can ensure the desired separation between Cu^{2+} and the other heavy-metal ions with high purity and high yield.

3. Experimental

3.1. Materials

Copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), cobalt(II) chloride hexa-hydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), and manganese(II) chloride (MnCl_2)

were purchased from Sigma–Aldrich Co. (St. Louis, MO) and utilized as the sources for the 3 heavy-metal ions considered. Magnesium acetate tetra-hydrate ($\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), which was supplied from Sigma–Aldrich Co. (St. Louis, MO), was used in the preparation of a buffer solution. Nitric acid was purchased from Matsunoen Chemicals Co. (Osaka, Japan) and used as a regenerant in the carousel experiments performed. The water used in this study belonged to the class of distilled deionized water (DDW), which was obtained from a Milli-Q system by Millipore (Bedford, MA).

The Cu–MIP resin was synthesized as reported elsewhere [15,16] and used as the adsorbent of this study. The synthesis of the Cu–MIP resin is based on a template polymerization technique where “host” molecules are prepared to recognize “guest ion” species specifically. In this technique, a template ion associates with functional monomers to form non-covalent bonded complex. This complex is then polymerized in the presence of lots of cross-linker to produce tight matrix structure. Removal of the template ion generates cavities in the polymer matrix. As these cavities memorize the spatial features and bonding preference of the template, the imprinted polymer selectively recognizes and thus rebinds the template from a mixture of ionic species.

The average diameter of the synthesized Cu–MIP resin was 250 μm . 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.

3.2. Equipment

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 experiments. This system consists of 2 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 and magnesium ion in the samples, which resulted from the single-column experiments and the carousel experiments.

The carousel equipment that had been built in-house in our previous study [14] was used in the present work after some modifications in accordance with the proposed process-configuration (Fig. 3). The modified carousel equipment consisted of 6 rotary valves, 5 pumps, and 5 columns. The rotary valve used was the ST valve from VICI Valco Instruments Co. (Houston, TX). The other details of this equipment can be found elsewhere [14].

3.3. Procedures

3.3.1. Selectivity measurement

To investigate the Cu^{2+} selectivity of the MIP resin, competitive adsorption experiment with Mn^{2+} and Co^{2+} was conducted in accordance with the procedures by Dam and Kim [15]. In this experiment, 1 g of the MIP particles were placed in 50 mL of a solution of these competitive ions (1 mM for each one), whose pH was adjusted at 6.0 by using the buffer solution. After adsorption equilibrium was reached, the concentrations of the 3 heavy metal ions in the remaining solution were measured by the Vario-6 atomic absorption spectrometer.

Table 1

The results from the selectivity studies for the MIP resin.

Heavy metal ion	Ionic charge	Distribution ratio (D)	Selectivity (α)
Cu	2	434.6	–
Mn	2	6.4	68.4
Co	2	15.6	27.9

3.3.2. Single-column and carousel experiments

The single-column experiments were performed to acquire the necessary data for the design of the proposed carousel process. The experiments performed for such a purpose included two-step re-equilibration tests, a frontal test, a washing test, and a regeneration test. To carry out these experiments, the column packed with Cu–MIP resin was installed between the pump and the fraction collector in the aforementioned FPLC system.

Three carousel experiments with different feed-loading times were carried out at room temperature using the aforementioned carousel equipment. The columns of the carousel equipment were pre-equilibrated with the buffer solution containing magnesium acetate prior to each carousel 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 first-step re-equilibrant (buffer solution) and the second-step re-equilibrant (water) were eluted through the columns of zones II and I respectively while the regenerant (0.1 M of nitric acid) was introduced into the column of zone III (Fig. 3). Also, the feed solution and the washing solution (water) were pumped into the first column of zone IV during the loading and the washing steps respectively (Fig. 3).

The feed solution was prepared by dissolving the 3 heavy-metal ions in water. The concentration of each heavy-metal ion in the feed was 1 mM. The concentrations of the samples resulting from the experiments were assayed by the Vario-6 atomic absorption spectrometer. The calibration curve was prepared in the range of 0 to 0.1 mM for each of the 3 heavy-metal ions (Cu^{2+} , Mn^{2+} , and Co^{2+}), and in the range of 0 to 0.05 mM for the buffer-related metal ion (Mg^{2+}). Every sample was diluted prior to its assay. The dilution ratios used were 1/20, 1/10, and 1 for the assay of the 3 heavy-metal ions, and 1/40 and 1 for the assay of the buffer-related metal ion.

4. Results and discussion

4.1. Selectivity studies

The selectivity of the MIP resin for Cu^{2+} over Mn^{2+} and Co^{2+} was investigated by carrying out the competitive adsorption experiment as explained in the previous section. Based on the results from this experiment, the distribution ratios and the selectivity of interest were estimated by following the same procedure as in the literature [15]. First, the distribution ratio (D) of each heavy metal ion was calculated from the following equation.

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

where v is the volume of the solution (mL), m is the mass of the MIP resin (g), and C_A and C_B are the initial and final concentrations of each heavy metal ion (mM), respectively. The resulting distribution ratio values are listed in Table 1.

Secondly, the selectivity (α) of the MIP resin for Cu^{2+} in the presence of Mn^{2+} and Co^{2+} was calculated from the following equation.

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

where D_{Cu} and D_{M} represent the distribution ratios of Cu^{2+} and another heavy metal ion, respectively. The resulting selectivity

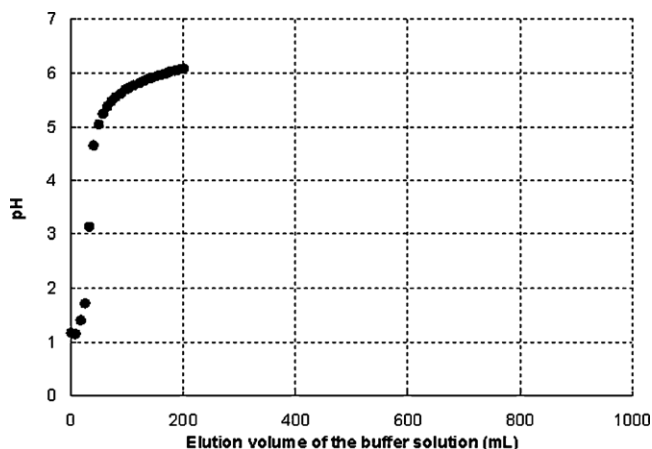


Fig. 4. The result of the first-step re-equilibration test where the pH of the effluent from the MIP-column was plotted as a function of the elution volume of the buffer solution (0.05 M $\text{Mg}(\text{CH}_3\text{COO})_2$). The MIP-column used in this test had been pre-equilibrated with 0.1 M HNO_3 prior to the elution of the buffer solution. The length and diameter of this column were 11.6 cm and 1.5 cm respectively.

values are presented in Table 1, which clearly demonstrates that the MIP resin has a significantly high selectivity for Cu^{2+} over both Mn^{2+} and Co^{2+} .

4.2. Single-column experiments for determination of the operating parameters of the proposed carousel process with four zones

4.2.1. Two-step re-equilibration tests with 0.05 M $\text{Mg}(\text{CH}_3\text{COO})_2$ and water in series

As part of the single-column experiments for determining the operating parameters of the four-zone carousel process proposed (Fig. 3), the re-equilibration test was carried out first. This test began by eluting the buffer solution of 0.05 M $\text{Mg}(\text{CH}_3\text{COO})_2$ through the single MIP-column that had been pre-equilibrated with the regenerant (0.1 M HNO_3). During this test, the pH of the column effluent was monitored. The resultant pH is presented as a function of elution volume in Fig. 4, which shows that about 200 mL of the buffer solution is quite enough for increasing the pH up to 6. This amount is, in fact, quite smaller, compared to the case where only water was eluted through the column with the same pre-equilibration condition (Fig. 2). This indicates that the buffer solution chosen (0.05 M $\text{Mg}(\text{CH}_3\text{COO})_2$) was suitable for the first-step re-equilibrant in the four-zone carousel process.

Following the aforementioned first-step re-equilibration, the second-step re-equilibration was performed by eluting the column with water while keeping the amount of the eluted water the same as that of the buffer solution in the preceding re-equilibration test (i.e., 200 mL). Since this amount corresponds to about 10 times the bed volume, most of the magnesium ions in the void space would be sufficiently expelled out of the column. The information on the elution volumes of the buffer solution and water that were used for the first- and second-step re-equilibrations respectively in this section will be applied later for the determination of the flow rates in zones II and I of the carousel process.

4.2.2. Frontal test with the mixture of heavy metal ions

The column that had undergone the first- and second-step re-equilibrations in the previous section was used in the frontal test, which was carried out by loading the mixture of heavy metal ions (Cu^{2+} , Mn^{2+} , and Co^{2+}) into the column. Since the purpose of this test was to obtain the clues to the operating parameters related to the separation zone of the carousel process, the flow rate in the front test performed was kept the same as that in the separation

zone (i.e., 4 mL/min as mentioned in Section 1). Under such flow rate, the feed-loading was continued for 160 min, which was sufficient to saturate the column with the feed mixture. The result of this test is presented in Fig. 5. One of the noteworthy phenomena is that the desorption wave of Mg^{2+} appears much earlier than the adsorption wave of Cu^{2+} . In other words, there exists a large time-gap between the extinction of Mg^{2+} and the breakthrough of Cu^{2+} . This will obviously help the carousel process attain a perfect separation of Cu^{2+} and the buffer-related metal ion, i.e., Mg^{2+} , which is, in fact, a matter of primary concern in the present work.

In addition, it can be confirmed in Fig. 5 that the impure heavy-metal ions (Mn^{2+} and Co^{2+}) showed much earlier breakthrough than the product heavy-metal ion (Cu^{2+}). Furthermore, it is clearly observed that Mn^{2+} and Co^{2+} created the “roll-up” phenomenon, which is that the effluent concentration becomes higher than the feed concentration in the initial stage of exiting time (Fig. 5). Selectivity for one ion over other is the reason for such a “roll-up” phenomenon.

If all the above-mentioned phenomena are put together for comprehensive analysis, the following inference can be drawn regarding the interactions among the 4 metal ions on the MIP resin. With the start of the feed-loading, most of the magnesium ions attached to the MIP resin particles are exchanged by the 3 heavy-metal ions and expelled out of the column. Since such exchanged ions from the resin particles to the mobile phase are not hydrogen ions but magnesium ions, the pH inside the column is still maintained high and it helps maintain a very high adsorption-affinity of copper ions to the MIP resin. This enables the copper ions to displace most of the impure heavy-metal ions while migrating through the column. It is thus expected that most of the resin particles inside the column can be occupied by only copper ions when a sufficient amount of copper ions will have swept over the entire resin phase.

On the bases of the above reasoning and the frontal experimental result in Fig. 5, the loading time of the carousel process could be determined in such a way that high purity and high yield are both guaranteed for the product ions (Cu^{2+}). First, for the purity of Cu^{2+} , it would be important to make the resin phase free of the other metal ions than Cu^{2+} until the end of the feed-loading step. Secondly, for the yield of Cu^{2+} , it would be important to minimize the amount of the copper ions exiting the column.

From the first criterion, it is evident that the carousel loading time must be at least longer than 75 min, which corresponds to the mass-center time of the breakthrough profile of Cu^{2+} in Fig. 5. By contrast, the second criterion requires that the loading period after the elapse of 75 min must be as short as possible.

The appropriate loading time in consideration of both criteria (i.e., purity and yield) will be determined on the basis of the results from the carousel experiment, which will be performed several times by varying the loading time.

4.2.3. Washing test with water

In the carousel process (Fig. 3), the loaded column in the separation zone needs to undergo one more procedure before it enters the regeneration zone for the recovery of Cu^{2+} . This procedure is to wash out the impure heavy-metal ions remaining in the column void, which is implemented by eluting the column with washing solution. As mentioned earlier, water was chosen as the washing solution in this study, because of the necessity for preventing the washing solution itself from becoming the source of another product-contamination. To determine a proper washing time, the washing test was performed at the same flow rate as that of the frontal test (4 mL/min) using the single MIP-column that had completed the front test in the previous section.

The result of the washing test is presented in Fig. 6, where the time of starting the water elution was set to zero in the x-axis. It is observed that the concentrations of Mn^{2+} and Co^{2+} become almost

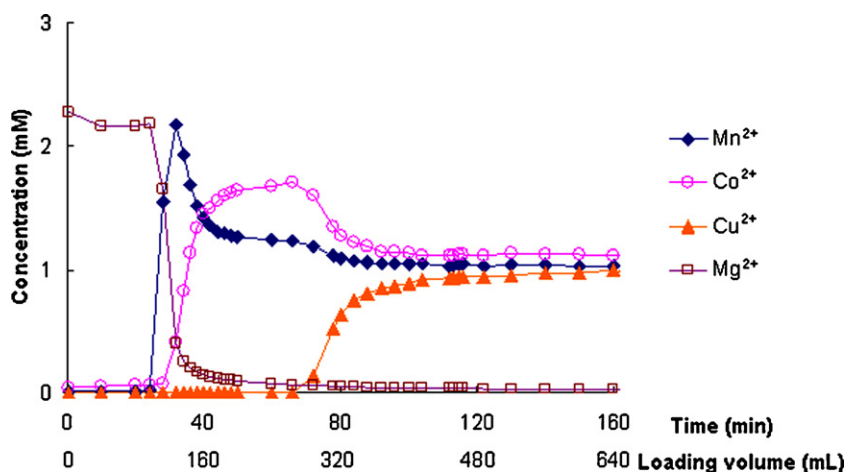


Fig. 5. The result from the frontal test where a mixture of the 3 heavy-metal ions were loaded into the MIP-column that had undergone the two-step re-equilibrations. In this test, the feed-loading was continued for 160 min, and the flow rate was 4 mL/min. Among the concentration data presented in the above figure, the first 4 concentrations of Mg^{2+} (>2 mM) and the sixth concentration (i.e., the highest concentration) of Mn^{2+} (>2 mM) were out of the corresponding calibration range.

zero about 15 min after the elution of water through the column. On the basis of this result, the washing time of the carousel process will be set at 15 min in the following stage of carousel design.

Besides the data for determining the aforementioned washing time of the carousel process, the result in Fig. 6 exhibits another interesting phenomenon, which is the “roll-up” of Cu^{2+} that can be observed between 3 min and 5 min. Such phenomenon may be related to the Cu–H equilibrium relationship during the elution of the washing solution. This equilibrium relationship will promote the desorption of some amount of copper ions from the solid phase during the washing operation, because the pore space will gradually be occupied by the washing solution (water). The desorbed copper ions will then be combined with the copper ions in the inter-particle space, which have been washed out and eluted through the column. Such a combination of the desorbed copper ions and the washed copper ions can lead to a sharp increase in the concentration of copper ion during the initial period of the washing operation. This may be the reason why the “roll-up” phenomenon of Cu^{2+} is observed between 3 min and 5 min in Fig. 6.

4.2.4. Regeneration test with 0.1 M HNO_3

The column that had undergone the feed-loading and washing procedures in the above sections was regenerated by eluting 0.1 M HNO_3 through the column. The purpose of this regeneration test was to clarify the required amount of regenerant (0.1 M HNO_3) for

recovering almost all the copper ions adsorbed onto the MIP resin. The result is shown in Fig. 7, where the concentration of Cu^{2+} in the effluent is plotted as a function of the regenerant elution volume. One can see that the concentration of Cu^{2+} is reduced to 1% of the feed concentration (i.e., 0.01 mM) when the elution volume reaches 489 mL (Fig. 7). This information will serve as a guide for designing the operating condition of the regeneration zone in the carousel process.

In this study, the concentration of the regenerant was fixed at 0.1 M. However, this regenerant concentration can sometimes be varied according to the degree of acid-resistance of the equipment materials employed. To provide against such a situation, the result of Fig. 7 can be re-expressed in terms of the following dimensionless parameter (τ):

$$\tau \equiv \frac{C_{\text{reg}} v_{\text{reg}}}{Q_{\text{bed}} V_{\text{bed}}} \quad (3)$$

where C_{reg} is the regenerant concentration (normality), v_{reg} is the elution volume of the regenerant, Q_{bed} is the capacity of the solid in the bed for copper ions (equiv./volume of the bed), and V_{bed} is the volume of the bed. The maximum capacity of the MIP resin for copper ions was reported to be $0.331 \text{ mmol g}^{-1}$ of solid [15], which was used to calculate the Q_{bed} in Eq. (3). The resulting Q_{bed} value was $0.305 \text{ equiv. L}^{-1}$ of bed volume. Based on this value and the above definition of τ , the x-axis in Fig. 7 is re-expressed into the

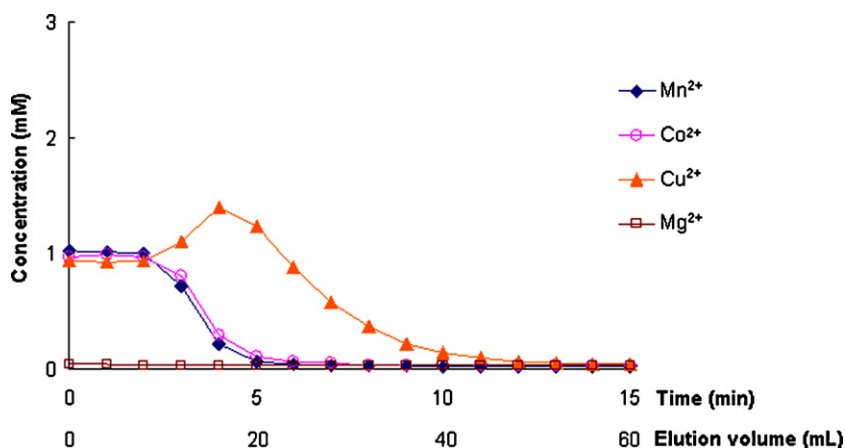


Fig. 6. The result from the washing test where water was eluted at the flow rate of 4 mL/min through the MIP-column that had completed the frontal test. The time of starting the water elution was set to zero in the x-axis.

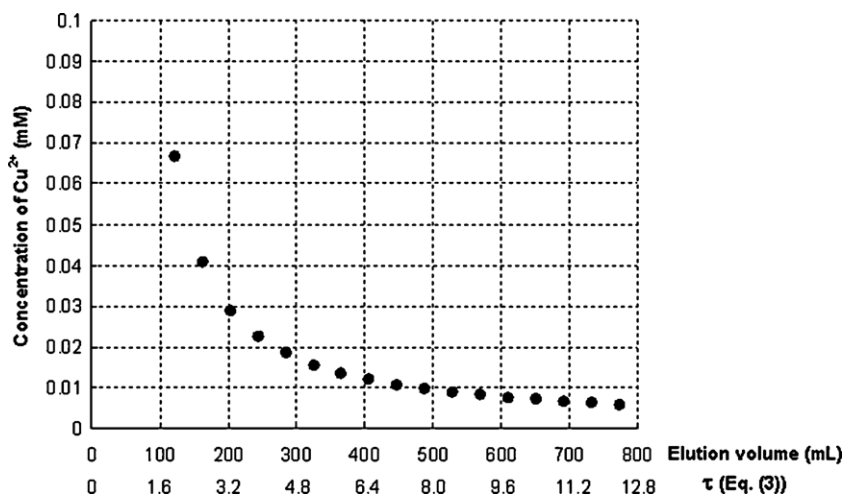


Fig. 7. The result from the regeneration test where the regenerant (0.1 M HNO₃) was eluted through the MIP-column that had undergone the frontal test and the washing test (i.e., the feed-loading and the water elution).

aforementioned parameter, τ . We see that the targeted regeneration task is accomplished at $\tau = 7.8$. This information will be more useful than the above-determined elution volume because the τ value can serve as more generalized criterion for the regeneration condition.

4.3. Determination of the operating parameters of the four-zone carousel process

Based on the results of the single-column tests performed in the previous sections, the operating parameters of the four-zone carousel process (Fig. 3) are determined in this section. First, the flow rates in zones II and I, where the first- and the second-step re-equilibrations are to be performed, are determined in the following manner.

$$\begin{aligned}
 Q^{\text{II}}(\text{1st step re-equilibration}) \\
 &= Q^{\text{I}}(\text{2nd step re-equilibration}) = \frac{200 \text{ mL}}{t_s(\text{min})} \\
 &= \frac{200 \text{ mL}}{t_{\text{load}}(\text{min}) + t_{\text{wash}}(\text{min})}
 \end{aligned} \quad (4)$$

where the value of 200 mL comes from the result of the previous re-equilibration test and the switching time (t_s) will be obtained by adding the loading time (t_{load}) to the washing time (t_{wash}).

In case of the washing time, its proper value had been confirmed to be 15 min from the previous washing test. By contrast, in case of the loading time, its definite value had not been obtained from the previous front test. Instead, only the guidelines on its effective range had been clarified. For this reason, 3 different loading times will be chosen within the effective range and the final decision on an optimal loading time will be made after completing 3 runs of carousel experiments based on the chosen loading times. Table 2 lists the 3 loading times chosen, which are then plugged into Eq. (4) along with the washing time of 15 min. The resultant flow rates of zones I and II are presented in Table 2.

Finally, the flow rate of regenerant (0.1 M HNO₃) in zone III is to be determined on the basis of the result from the previous regeneration test, in which the required amount of 0.1 M HNO₃ for completing the regeneration task up to the desired level was found to be about 489 mL. This amount of regenerant seems to be adequate for the column that had undergone the feed-loading for 75 min prior to the regeneration, because of the fact that the mass-center time of the breakthrough profile of Cu²⁺ in the frontal test was about 75 min (Fig. 5). This virtually implies that 489 mL of

regenerant can be fit for the 1st carousel design with the loading time of 75 min. By contrast, it would be necessary to increase the amount of regenerant in the cases of the 2nd and the 3rd carousel designs with the loading times longer than 75 min, because the adsorbed amount of copper ions in such cases could be larger than that in the case of the 1st carousel design. As a rule of thumb, the amount of regenerant for the 2nd and the 3rd carousel designs can be approximated on the assumption that the adsorbed amount of copper ions may be proportional to the loading time, which is

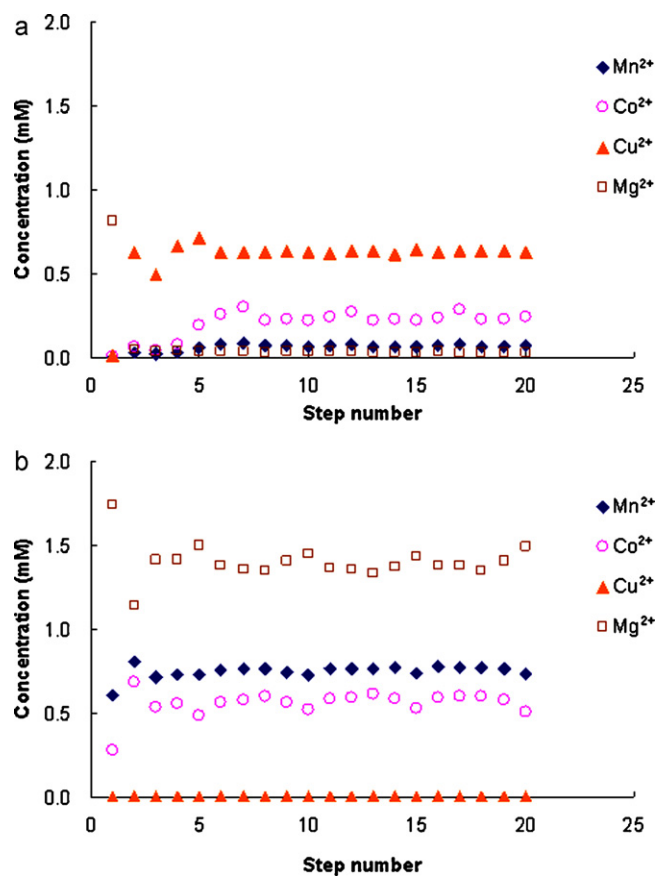


Fig. 8. The results from the 1st carousel experiment (loading time = 75 min). (a) Zone III outlet (product port), and (b) zone IV outlet. The concentrations were averaged over one switching period.

Table 2
Operating parameters of the four-zone carousel processes under consideration in this study.

		1st carousel design	2nd carousel design	3rd carousel design
Column configuration		1 – 1 – 1 – 2	1 – 1 – 1 – 2	1 – 1 – 1 – 2
Loading time (min)		75	119	145
Washing time (min)		15	15	15
Switching time (min)		90	134	160
Zone flow rates ^a (mL/min)	Zone I	2.22	1.49	1.25
	Zone II	2.22	1.49	1.25
	Zone III	5.43	5.79	5.91
	Zone IV	4.00	4.00	4.00
Inlet flow rates (mL/min)	Feed	4.00	4.00	4.00
	Wash	4.00	4.00	4.00

^a The flow rates in zones I, II and III are equal to the flow rates of the second-step re-equilibrant, the first-step re-equilibrant, and the regenerant, respectively.

virtually a conservative approach. The approximated amount of regenerant can then be divided by the switching time in order to obtain the zone III flow rate as follows.

$$Q^{\text{III}}(\text{regeneration}) = \frac{489 \text{ mL} \times t_{\text{load}} (\text{min}) / 75 \text{ min}}{t_s (\text{min})} \quad (5)$$

The resulting zone III flow rates (i.e., the regenerant flow rates) for the 3 cases of carousel designs are listed in Table 2.

4.4. Carousel experiments

Based on the operating parameters determined in the previous section, 3 runs of carousel experiments were carried out. From the experimental results, it was confirmed first that in all the 3 carousel experiments performed, the re-equilibration zones I and II fulfilled

their functions as desired and no loss of copper ions occurred in zones I and II.

The results for the other zones are presented in Figs. 8–10. One can see that the product stream from zone III contains almost no buffer-related metal ion (Mg^{2+}) throughout the operation, which is common in all the 3 carousel experiments performed. This phenomenon indicates that the carousel process developed in this study was successful in complete removal of the buffer-related metal ions from copper ions. This is certainly a key factor in enabling the carousel process developed in this study to become superior to the previous three-zone carousel process [14] in terms of application range.

Unlike the buffer-related metal ions, the amounts of the 3 heavy-metal ions in the zones III and IV outlet streams were largely affected by the loading time chosen in each carousel experiment. In case of the 1st carousel experiment with the loading time of

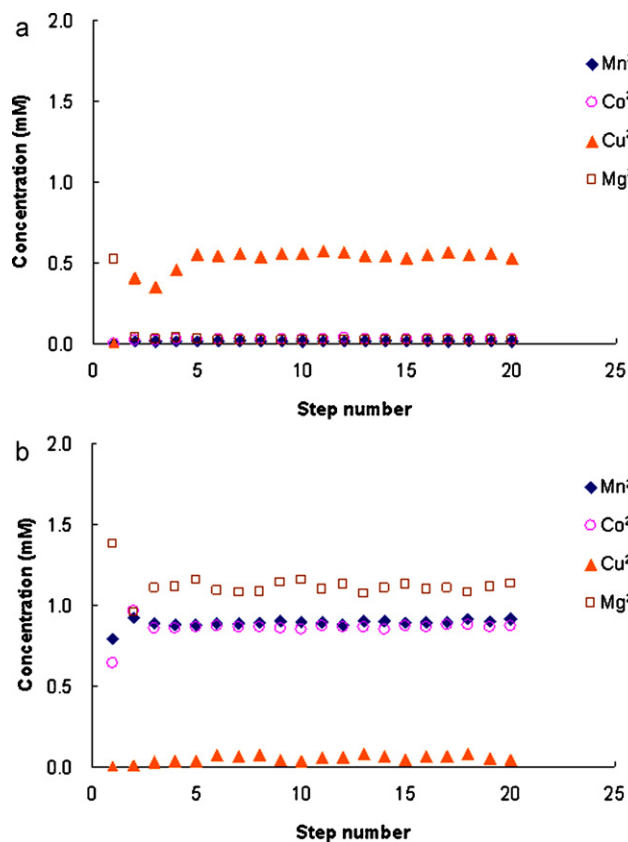


Fig. 9. The results from the 2nd carousel experiment (loading time = 119 min). (a) Zone III outlet (product port), and (b) zone IV outlet. The concentrations were averaged over one switching period.

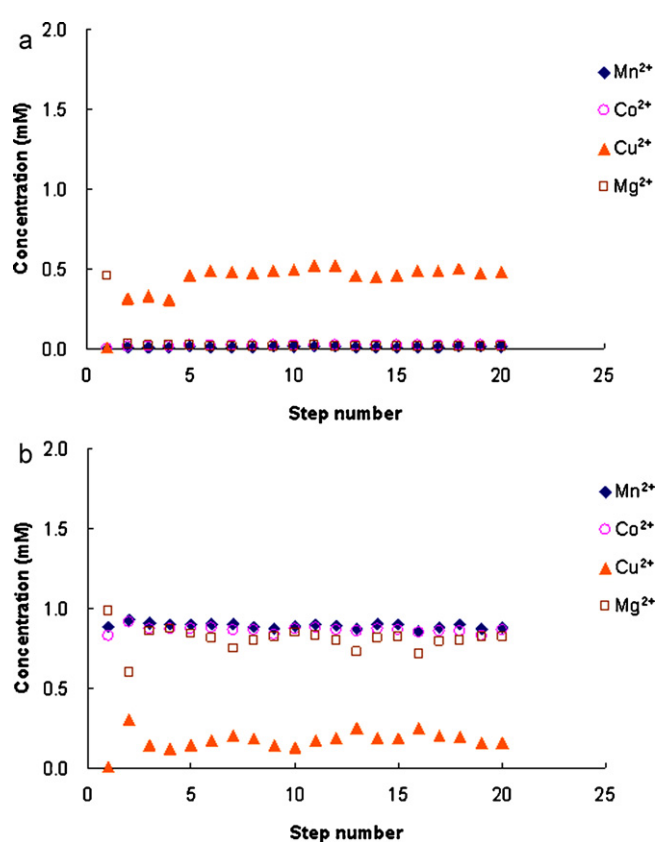


Fig. 10. The results from the 3rd carousel experiment (loading time = 145 min). (a) Zone III outlet (product port), and (b) zone IV outlet. The concentrations were averaged over one switching period.

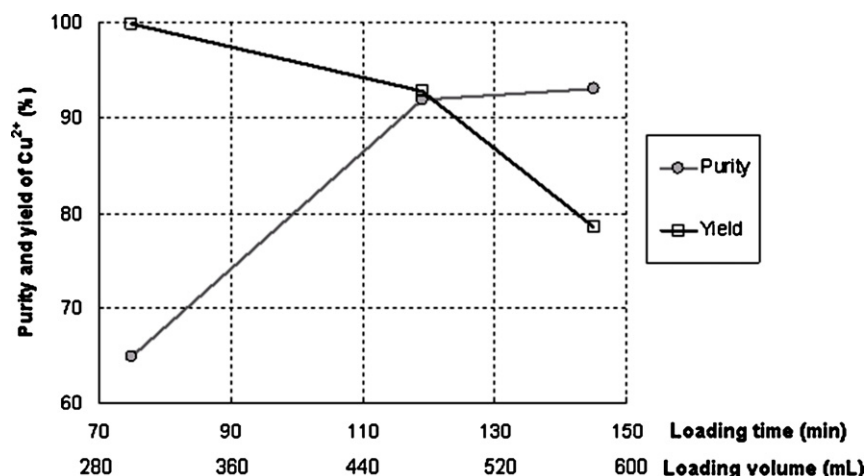


Fig. 11. Plot of the loading time in the carousel experiment performed versus the resultant purity and yield of Cu^{2+} .

75 min, it is evident that almost no loss of Cu^{2+} through the zone IV outlet occurs (Fig. 8b), which will be favorable for attaining high yield. However, a considerable amount of the impure heavy-metal ions were found to contaminate Cu^{2+} in the zone III outlet, i.e., the product port (Fig. 8a).

On the other hand, the behaviors of the 3 heavy-metal ions in the 3rd carousel experiment with the loading time of 145 min showed an opposite trend to that of the 1st experiment. As can be seen in Fig. 10a, the contamination of Cu^{2+} by the impure heavy-metal ions did not happen in the zone III outlet whereas a considerable amount of loss in Cu^{2+} occurred through the zone IV outlet.

The aforementioned 2 results support our previous inference regarding the interactions among the 3 heavy-metal ions. In other words, the displacement phenomenon occurring in zone IV caused a longer loading to eliminate most of the impurity metal ions from the resin particles at the cost of some loss of Cu^{2+} through the zone IV outlet. On the other hand, a shorter loading allows copper ions to stay within zone IV during the entire switching period at the cost of incomplete elimination of the impure heavy-metal ions from the resin particles.

Therefore, it is expected that the optimal loading time in consideration of product purity and yield can exist between the loading times of the 1st and the 3rd carousel experiments (i.e., between 75 min and 145 min). As expected, the 2nd carousel experiment with the loading time of 119 min revealed that the outflow of Cu^{2+} occurs mostly in zone III but little in zone IV (Fig. 9). Simultaneously, the outflow of Mn^{2+} and Co^{2+} occurs mostly in zone IV but little in zone III (Fig. 9). As a consequence, the purity and yield of Cu^{2+} from the 2nd carousel experiment reached 91.9% and 92.8% respectively, where the purity and yield of Cu^{2+} were evaluated from the following equations.

$$\text{Purity} = \frac{C_{\text{Cu}}^{\text{III}}}{C_{\text{Cu}}^{\text{III}} + C_{\text{Mn}}^{\text{III}} + C_{\text{Co}}^{\text{III}} + C_{\text{Mg}}^{\text{III}}} \quad (6a)$$

$$\text{Yield} = \frac{Q^{\text{III}} C_{\text{Cu}}^{\text{III}}}{Q^{\text{I}} C_{\text{Cu}}^{\text{I}} + Q^{\text{II}} C_{\text{Cu}}^{\text{II}} + Q^{\text{III}} C_{\text{Cu}}^{\text{III}} + Q^{\text{IV}} C_{\text{Cu}}^{\text{IV}}} \quad (6b)$$

where Q^j is the flow rate in zone j and C_i^j is the concentration of component i in the stream from the outlet of zone j at cyclic steady state. In this study, the value of concentration in the above equation was obtained by averaging those of the last 5 samples collected during the last 5 switching periods.

For comparison purpose, the purities and yields resulting from the aforementioned 3 carousel experiments are plotted as a function of the loading time in Fig. 11. It is clear from this figure that

the loading time must be a key parameter affecting the performance of the carousel process, which aims at separating copper ions from both the impure heavy-metal ions and the buffer-related metal ions. The result for the effect of loading time on the purity and yield in Fig. 11 is sufficiently predictable from the result of the previous frontal test in Fig. 5. One can observe in Fig. 5 that the bed is effectively equilibrated with the feed around 120 min after the feed-loading. It can thus be predicted that if the loading time will be shorter than 120 min as in the case of the 1st carousel operation (Fig. 8), a portion of the bed in the separation zone will inevitably hold the impure heavy-metal ions, resulting in a lower purity (Fig. 11). On the other hand, the adoption of the loading time longer than 120 min as in the case of the 3rd carousel operation (Fig. 10) will cause the feed-loading to be implemented too longer than is essentially needed, resulting in a lower yield (Fig. 11). As a consequence, the carousel operation with the loading time close to 120 min will lead to high purity and high yield as in the case of the 2nd carousel operation (Fig. 9).

5. Conclusions

The previous three-zone carousel process packed with Cu-MIP resin was successful in separating copper ions (product) from manganese ions and cobalt ions (impurities). The product stream of this process, however, included the buffer-related metal ions as well as copper ions, which was attributed to the use of the buffer solution containing its constituent metal ions as eluent. To solve this problem, a four-zone carousel process based on the following strategy was proposed in this study. The core of the proposed strategy was to perform the two-step re-equilibrations with the buffer solution and water while using only water as the eluent of the washing step in the separation zone.

The necessary data for determining the operating conditions of the proposed carousel process were acquired from a series of single-column experiments, which included the two-step re-equilibration tests, frontal test, washing test, and the regeneration test. From these single-column experiments, all the operating conditions of the proposed carousel process were determined except the feed-loading time. As for the feed-loading time, only a guiding principle on its proper selection was clarified. Thus, a total of 3 carousel experiments were carried out under the 3 different feed-loading times that were chosen on the basis of the principle derived from the aforementioned single-column experiments. The results of the 3 carousel experiments revealed that the feed-loading time was a key parameter affecting the performance of the proposed carousel process. As a consequence, the proposed carousel process based

on a properly chosen feed-loading time could separate copper ions continuously from both the impure heavy-metal ions and the buffer-related metal ions with high purity and high yield.

Acknowledgments

This work was supported by the Core Environmental Technology Development for Next Generation (Grant number 2008-02002-0048-0). Also, it was partially supported by the Manpower Development Program for Energy & Resources supported by the Ministry of Knowledge and Economy (MKE), Republic of Korea.

References

- [1] Y. Xie, D.-J. Wu, Z. Ma, N.-H.L. Wang, *Ind. Eng. Chem. Res.* 39 (2000) 1993.
- [2] J.L. Sung, B.S. Kim, J.-H. Kim, *J. Chem. Technol. Biotechnol.* 80 (2005) 1148.
- [3] K.B. Lee, C.Y. Chin, Y. Xie, G.B. Cox, N.-H.L. Wang, *Ind. Eng. Chem. Res.* 44 (2005) 3249.
- [4] Y. Kawajiri, L.T. Biegler, *AIChE J.* 52 (2006) 1343.
- [5] K.B. Lee, R.B. Kasat, G.B. Cox, N.-H.L. Wang, *AIChE J.* 54 (2008) 2852.
- [6] T.H. Yoon, E. Lee, J.M. Kim, W.S. Kim, I.H. Kim, *Korean Chem. Eng. Res.* 25 (2008) 285.
- [7] J.W. Lee, J.L. Kim, C.H. Lee, J.K. Kim, Y.M. Koo, *J. Liq. Chromatogr. Relat. Technol.* 30 (2007) 1859.
- [8] N.V.D. Long, T.H. Le, J.L. Kim, J.W. Lee, Y.M. Koo, *J. Sep. Sci.* 32 (2009) 1987.
- [9] M.V. Ernest, J.P. Bibler, R.D. Whitley, N.-H.L. Wang, *Ind. Eng. Chem. Res.* 36 (1997) 2775.
- [10] B.J. Hritzko, D.D. Walker, N.-H.L. Wang, *AIChE J.* 46 (2000) 552.
- [11] M.E. Huckman, M.I. Latheef, R.G. Anthony, *AIChE J.* 47 (2001) 1425.
- [12] S. Mun, C.Y. Chin, Y. Xie, N.-H.L. Wang, *Ind. Eng. Chem. Res.* 45 (2006) 316.
- [13] S. Mun, N.-H.L. Wang, *Ind. Eng. Chem. Res.* 45 (2006) 1058.
- [14] S.-H. Jo, S.-Y. Lee, K.-M. Park, S.C. Yi, D. Kim, S. Mun, *J. Chromatogr. A* 1217 (2010) 7100.
- [15] A.H. Dam, D. Kim, *J. Appl. Polym. Sci.* 108 (2008) 14.
- [16] A.H. Dam, D. Kim, *Ind. Eng. Chem. Res.* 48 (2009) 5679.