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The Effects of Amine Additives and Flow Rate on the Performance of Mixed-bed Ion Exchange at Ultralow Concentrations

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Abstract−Experimental data were obtained to evaluate the effects of amine additives for pH control of solution and the volumetric flow rate of feed solution on the performance of mixed-bed ion exchange for the removal of ionic impurities in solution. The experiments were performed under various temperatures and cation resin ratios by using a continuous column system with NaCl solution. The breakthrough curves of ions, plotted as the ratio of the effluent to influent concentration versus run time or treated solution volume, give detailed results about the effects of the existence of the pH controller, such as ammonia and morpholine, and the variable flow rate on the fate of each ion in the units. The experimental results show that the morpholine breakthrough occurs earlier than the ammonia breakthrough and that the effect of ammonia on both sodium and chloride exchange rates is more significant than that of morpholine. The addition of ammonia in solution results in the decrease of cation resin capacity for the sodium removal much more than the addition of morpholine. The step changes in the flow rate affect significantly the shapes of sodium and chloride breakthrough curves. The effluent concentrations of sodium and chloride change according to the flow rate. However, the effect increases with decreasing operation capacity of cation resin, while it becomes serious around the breakthrough time of chloride and negligible after the time.

Key words: (Mixed-bed) Ion Exchange, Amine Additives, pH Controllers, Ultrapure Water, Volumetric Flow Rate

INTRODUCTION

The industrial applications of ion exchange are widespread, ranging from water purification, bio-separations, and the treatment of heavy metals [Kim et al., 2001, 2002; Rengaraj et al., 2004]. Mixed-bed Ion Exchange (MBIE) is an intimate mixture of cationic and anionic resins in the same column, used to deionize a contaminated liquid stream. In this, ion exchange is accompanied by a neutralization reaction, thereby reducing the bulk phase concentrations of hydrogen and hydroxide ions. MBIE is the traditional method of eliminating the final traces of ionic material from ultrapure water. The resistivity of the output from the MBIE system typically ranges from 16 to 18.3 MΩ. Presently, use of the MBIE units for the treatment of low level solids water requires realistic estimates of mixed-bed performance. However, the fundamental theories and detailed modeling of the ion exchange process are far behind the current technical applications.

Haub and Foutch [1986a, b] were the first to develop a mathematical model that can predict the MBIE performance operating at ultralow concentrations. Their model was for the hydrogen cycle MBIE with only two ions, Na^+ and Cl^-, considered for exchange with H^+ and OH^-, respectively. Zecchini [1990, 1991] extended the model for the ternary ionic systems with univalence. His model was also suitable for amine form operation, and was further extended to incorporate divalent ions by Pondugula [1992]. This model could predict the column effluent concentrations for a variety of industrial applications such as bed heels and bed cleaning. Bulusu [1994] extended the model to handle a multicomponent system of the ions with arbitrary valences. These mathematical models still have room to improve the accuracy through experimental data obtained under various industrial conditions.

To evaluate and improve the accuracies of the developed mathematical models, many experimental works have been performed. Yoon et al. [1994] studied the effect of the ratio of cation resin to anion resin on the MBIE performance at ultralow concentrations. Noh et al. [1996] obtained experimental data to evaluate the MBIE performance for the variable feed concentration and for the incomplete mixing of anion and cation resins. Kim et al. [1997] measured the selectivity coefficients of ion exchange resin for various ions as a function of temperature. Yoon et al. [1999] investigated the effect of temperature on the MBIE performance and reported that the exchange rates of cation and anion increased with temperature. Noh et al. [1999] evaluated the effects of divalent cations such as Ca^{++} and Mg^{++} on the fates of sodium and chloride in MBIE.

Many existing power plants have corrosion and erosion problems due to the contaminants present within process water [Sadler, 1986]. These problems impact the economic potential of the plants and safety considerations by reducing the operating life of the process vessels. The suspended and dissolved solids present in water are removed by filtration and ion exchange. Combining the purification steps with an alkaline pH control agent reduces the erosion and corrosion of the process equipment. This offers a reduction in corrosion due to fewer hydrogen ions available for interaction with metal surfaces.

Initially, ammonia was used as the primary pH control agent. Ammonia was added to increase pH of the feed water to the range 9.3-9.6 in the absence of copper alloy, and 8.8-9.2 in the presence of

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copper alloys [Sawochka, 1988]. These ranges are based primarily on laboratory and plant data obtained from the systems which use ammonia for pH control. Hydrazine is added as an oxygen scavenger. Alternatives to ammonia for the reduction of the pH excursion with increasing temperature have been considered. As an alternative to ammonia, morpholine has been used for pH control at several pressurized water reactor stations to reduce corrosion rates below those observed with ammonia/hydrazine control [Sawochka, 1988].

The criteria for a pH control agent are based on the dissociation constant, the distribution coefficient, the degradation characteristics of the resin, and the system toxicity [Zecchini, 1990]. The dissociation constant indicates the extent of ionization when dissolved in water. A large dissociation constant is desired for the pH control agent. The distribution coefficient is the ratio of the amount in the steam phase compared to the amount in the liquid phase. If the volatility is too low, the pH control of the steam and condensate will be difficult and then result in exacerbating corrosion in turbines and condensers. If the volatility is too high, loss of pH control will impact the steam generator. Base strength and volatility are discussed by Cobble and Turner [1985]. They tabulate predicted and experimental base strength and volatility data in the temperature range of 0 to 300 °C for ammonia, cyclohexylamine, and morpholine. The pH control agent must be thermally stable at all process conditions. If the pH control agent is unstable, then the effects of degradation products must be considered. The pH control agent should be nontoxic. Safety during material handling dictates this requirement.

The volumetric flow rates of the feed solution in the industrial MBIE units are not always constant, but fluctuate in a certain range, or involve upsurges beyond the range for a short time. Thus, this variable flow rate, as well as the pH controllers, make it difficult to estimate the performance of MBIE correctly, and as a result, the operating schedule of the units becomes ineffective. The objective of the present study is to evaluate experimentally the effects of the amine additives and the variable flow rate on the performance of MBIE. The data obtained in this study will provide a basic data for understanding the performance of MBIE operating under various conditions observed in full-scale industrial units and give a good design tool for an ion exchange process.

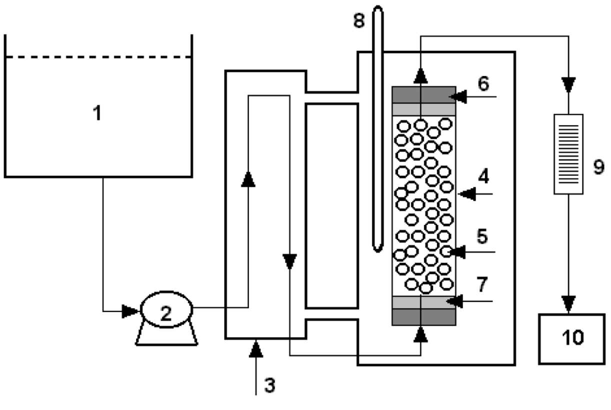

Fig. 1. Schematic diagram of the continuous column system.

1. Feed storage	6. Silicone stopper
2. Tubing pump system	7. Glass wool
3. Water bath system	8. Thermometer
4. Glass column	9. Flow meter
5. Cation resin	10. Ion chromatography

EXPERIMENTAL

The experiments for the present study were performed by using a continuous operation system. Fig. 1 shows the schematic diagram of the continuous MBIE experimental system utilized in this study. The system is composed mainly of an experimental column, its accessories for feeding, heating, and measuring the experimental parameters such as volumetric flow rate, temperature and pH, and a Dionex ion chromatograph (IC) (model DX-300) for measuring effluent concentration. The experimental column was made from the Pyrex glass that is transparent to see the resins loaded inside the column. Glass wool with stainless steel screens was used to support the mixed-bed resins and to ensure uniform flow distribution.

Because the feed concentrations for these experiments were very low, special attention was given to prevent water contamination. Ultrapure water was prepared by passing either distilled water or the effluent from the experimental column through high capacity MBIE columns in series. Resistivity greater than 18.2 MΩ-cm at room temperature was checked to ensure water quality. Water produced from the purification column was collected in a carboy and used to prepare either the feed solution or the chemicals for the IC. A leaching problem from the carboy became significant after about 48 hours, so water stored in the carboy more than 12 hours was fed into the purification columns again to ensure water quality.

The feed solution was prepared by diluting the concentrated solution with pure water, and the concentrated solution was obtained by dissolving the calculated weights of salts in a 100 ml flask with pure water. After pippetting 10 ml of the concentrated solution into a 10 liter carboy and adding pure water, vigorous agitation was used, and complete mixing was checked by conductivity measurement. Only a specified carboy was used for a certain duty. If necessary, the makeup feed water was made and added to the feed carboys.

Dowex Monosphere 650C (cation) and 550A (anion) resins provided by the Dow Chemical Company were used for the study. These resins were rinsed with pure water from the purification columns and stored in plastic containers. For the experiments, specific wet volumes of the cation and anion resins were taken from the resin containers and mixed. Then, the resins were placed in the experimental column carefully followed by being checked to ensure complete mixing and uniform packing throughout the column cross section. The column was filled with pure water fully, while being tipped to remove any air bubbles between the resin particles and to promote uniform packing. The air bubbles might be the source of carbonate or bicarbonate which affect the breakthrough curve of chloride strongly. After assembling the system, pure water was fed into the column and flowed downward until the desired experimental conditions were reached. To maintain a constant temperature, a constant-temperature reservoir and a heat exchanger were used. After the system was stabilized at the experimental conditions, the feed solution was introduced into the system.

When the feed solution reached the top portion of the column, the resistivity of the entrance portion would decrease. This point was considered as the starting point of the experimental run. Periodically, on-line resistivity and pH data were collected during the run and recorded on computer output files. For the continuous col-

Table 1. Experimental conditions for amine additive experiments

Parameter	Value
Column diameter	1.2 cm
Column depth	18-19 cm
Total resin wt.	11.6 g
Flow rate	10.8 L/hr
Feed concentration	NaCl 1.0×10^{-4} M ammonia 1.2×10^{-4} M morpholine 1.2×10^{-4} M
Temperature	20 °C, 30 °C
pH	7.0-9.4

umn experiments, an on-line IC procedure was utilized for the accurate sampling procedure. The IC was connected directly to the flow system and automatically collected and analyzed the effluent samples periodically and recorded the results on computer files. All the sampling and analyzing procedures were controlled by the AI-450 program. The post run processing of the chromatography data was performed by using utilities in the AI-450 program and a spreadsheet.

The experiments were mainly conducted with the cation resin more than the anion resin for conditions close to industrial practice. The amount of each resin was decided to have a reasonable experimental period so that it was possible to conduct an experimental run within a day.

To evaluate the effects of the amine additives on the performance of MBIE, the sodium and chloride breakthrough curves with the controllers in the feed solution were compared to those without the controllers. In addition, the breakthrough curves of the pH controllers themselves were also analyzed under the various conditions. Table 1 shows the experimental conditions for the amine additives experiments. To evaluate the effect of the variable flow rates, step changes in flow rate were arbitrarily introduced into the experimental column for 1-3 hours during the runs. Then, the effluent concentrations of cation and anion were compared to those obtained from the experiments with the constant flow rate. The normal flow rate was 10.8 liter/hr and the flow rates of the peaks were 21.6, 18.0, and 7.2 liter/hr. All experiments were carried out with the fraction of cation resin(FCR) to anion resin of 2 : 1 at 20 °C and the other conditions were approximately the same as those for the amine additives experiments.

RESULTS AND DISCUSSION

In general, the experimental data obtained by analyzing the effluent samples were plotted and presented in terms of the ratio of the effluent to influent concentration, C/C_o, versus run time in hours or treated volume of solution in liters. When plotted, the data showed smooth breakthrough curves, even though they tended to scatter at the early stage of each run.

1. Effect of Amine Additives

Figs. 2 and 3 show the effects of temperature and FCR on the concentration profiles of ammonia and morpholine, respectively, for the addition of ammonia or morpholine to the NaCl feed solution. At the first glance, it can be seen in these figures that different levels of initial leakage of each ion appear in the effluent of the exchange process. According to the previous study, these leakages might be due to the insufficient contact time between the solution and the resins, which results from the high flow rate and the relatively short bed depth [Noh, 1992]. The study concluded that the leakage did not affect the general trend of the breakthrough curve. Therefore, it can be said that the leakage gives no effect on the qualitative analysis of the curve. The flow rate and bed depth were selected to have the reasonable duration of the experimental runs in this study.

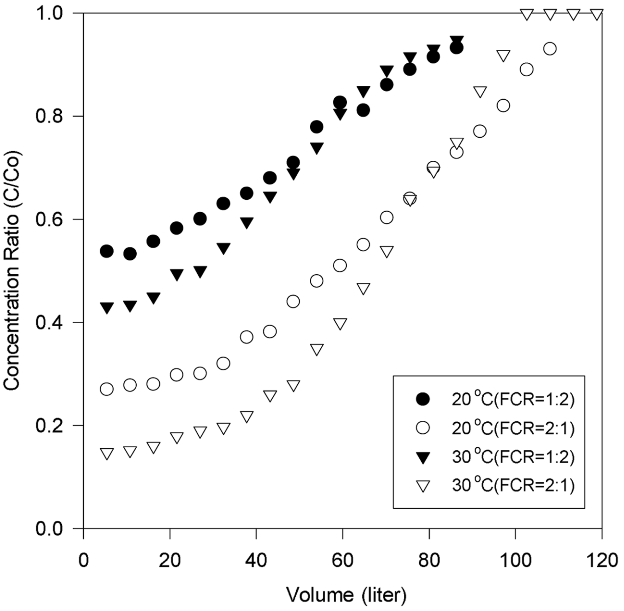

Fig. 2. Breakthrough curves of ammonia.

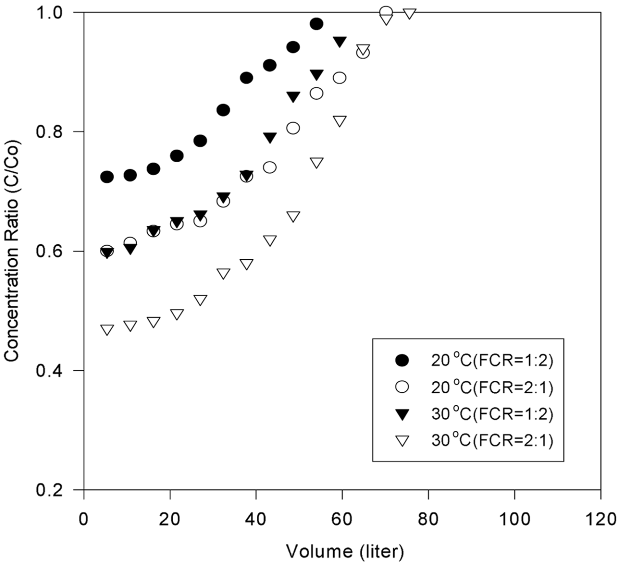

Fig. 3. Breakthrough curves of morpholine.

The figures also show that morpholine has higher initial leakage and faster breakthrough time than ammonia. This is due to the difference in selectivity coefficients of the cation resin. The selectivity coefficient of the resin for morpholine is lower than that for ammonia, which means that the resin has stronger affinity for ammonia than morpholine [Kim et al., 1997]. It has been said that as the selectivity coefficient is higher, the breakthrough curve is steeper and the equilibrium is more favorable [Helfferich, 1962].

It is observed in the figures that as temperature increases, the initial leakages of both ions decrease and the slopes of the curves increase. The temperature-dependent parameters, which affect the behavior of MBIE, are selectivity coefficients, ionic diffusion coefficients, ionization constant of water, and viscosity of the bulk solution phase [Divekar et al., 1987]. Among the parameters, the ionization constant of water and the ionic diffusion coefficients increase with temperature, while the two remaining factors decrease. However, the ionization constant and the ionic diffusion coefficients bring about the most significant changes in MBIE behavior with respect to the temperature and override the decreases in selectivity coefficients and viscosity. As a result, the rate of ion exchange increases with an increase in temperature. With an increase in the rate of ion exchange, the breakthrough time increases and the slope of the breakthrough curve becomes steep, as can be seen in the figures.

From the figures, it can be also seen that as FCR increases, the curves have longer breakthrough times and lower initial leakages. It is interesting that the slope of the curves of both ions do not change significantly with FCR, which can be concluded that FCR does not affect seriously the rate of ion exchange process.

Figs. 4 and 5 show the effects of the amine additives on the sodium breakthrough curves with FCR=1 : 2 and 2 : 1 at 30 °C, respectively. The effect of temperature on the curves will not be discussed in this part because it was already mentioned in the previous part for the breakthrough curves of the controllers. The figures indicate that the addition of the pH controllers decreases the exchange rate of sodium, as expected. The controllers exist as cation in solution and thus, they reduce the amount of sodium exchanged with hydrogen ion on the surface of the cation resin. The figures also show that ammonia affects the sodium curves more significantly than morpholine. The sodium curve with ammonia has higher initial leakage, shorter breakthrough time, and steeper slope than that with morpholine or without the controllers. The ammonia thus decreases the sodium removal capacity of the column much more than morpholine. This must be due to the difference in selectivity coefficients of the cation resin for the ions. The order of the selectivity coefficient of the resin is: NH_4^+>Na^+>H^+>morpholine [Kim et al., 1997]. Therefore, the possibility of the sodium removal with ammonia is relatively lower than with morpholine or without the controllers.

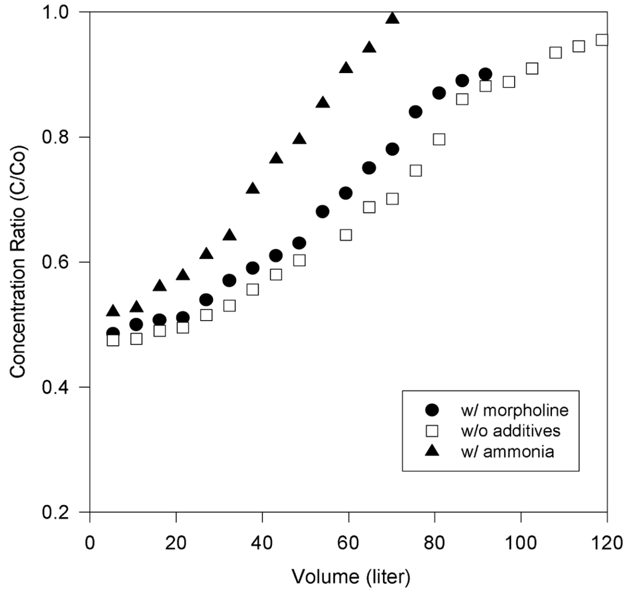

Fig. 4. The effects of amine additives on breakthrough curve of sodium with FCR=1 : 2 at 30 °C.

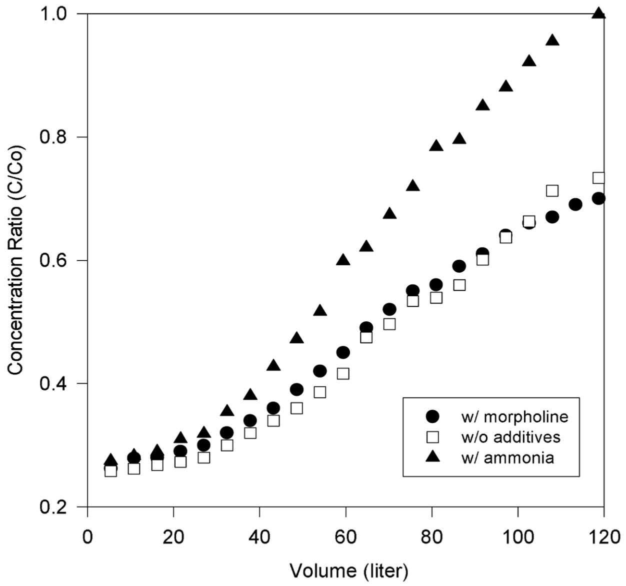

Fig. 5. The effects of amine additives on breakthrough curve of sodium with FCR=2 : 1 at 30 °C.

The effect of FCR on the sodium curves can be evaluated by comparison of Figs. 4 and 5. The increase of FCR causes the lower initial leakage and longer breakthrough time. The amount of the cation resin increases with FCR and thus, the removal capacity of the column increases. The figures also show that the curve with morpholine is very close to the curve without the controllers, while one with ammonia shows a big difference. According to the figures, it can be said that the effect of morpholine, which has the lower selectivity coefficient than hydrogen ion, on the sodium removal becomes insignificant as the amount of the cation resin increases. The slopes of the curves in these two figures are not likely to change with FCR. As mentioned earlier, FCR has no effect on the exchange rate and does not change the curve shape significantly.

The effects of the pH controllers on the chloride breakthrough curve are shown in Figs. 6 and 7. In general, the chloride curve has lower initial leakage and steeper shape than the sodium curve, resulting from the high selectivity coefficient of the anion resin for chloride. The controllers affect the chloride curves not as much as the sodium curve. The figures show that the curve with ammonia has longer breakthrough time and steeper slope than those with morpholine or without the controllers. This means that the addition of ammonia accelerates the exchange rate of chloride. In MBIE, it is known that the cation exchange is more favorable in an alkaline medium than a neutral or acidic medium because the mass transfer coefficient of sodium is higher in higher pH, while that of chloride

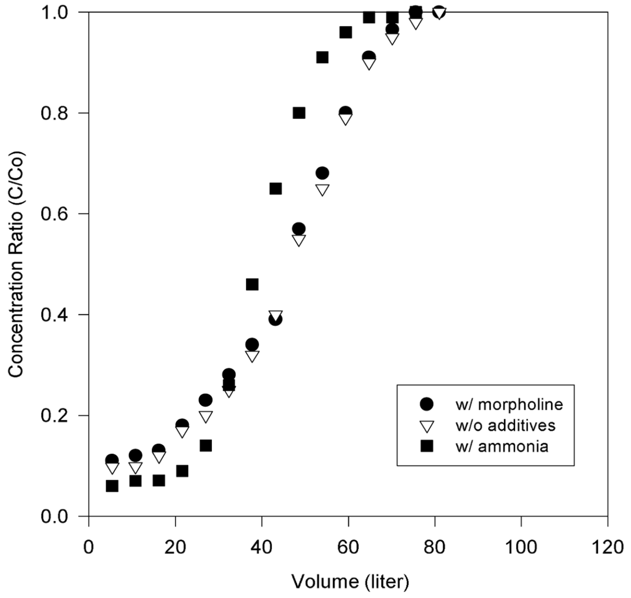

Fig. 6. The effects of amine additives on breakthrough curve of chloride with FCR=1 : 2 at 30 °C.

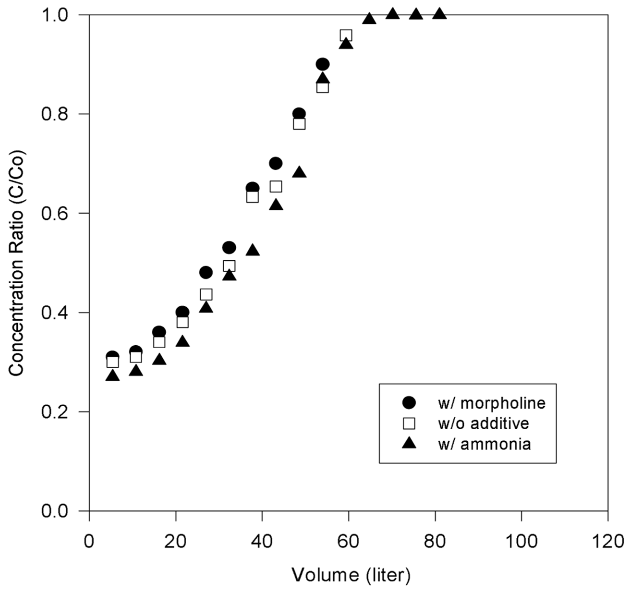

Fig. 7. The effects of amine additives on breakthrough curve of chloride with FCR=2 : 1 at 30 °C.

is higher in lower pH [Harries, 1988]. As the cation exchange rate increases, more hydrogen ions on the surface of the resin are exchanged with more cations in solution and thus, the solution becomes more acidic. Therefore, the exchange rate of chloride increases slightly. A close investigation of these figures gives that this effect of ammonia becomes less as the amount of the anion resin decreases.

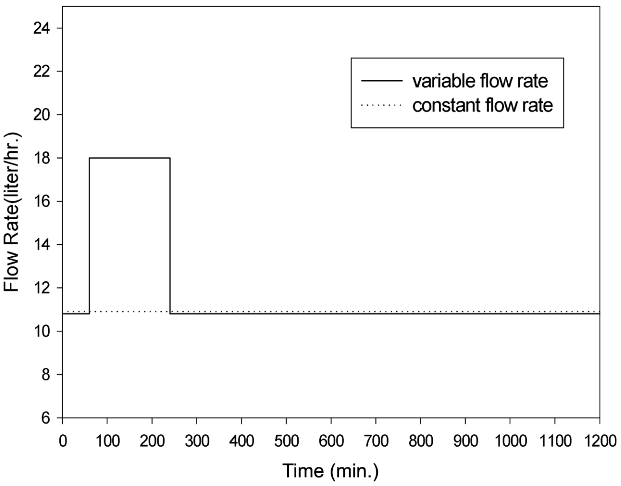

Fig. 8. Flow rate profiles for constant and variable flow rate experiments with one peak.

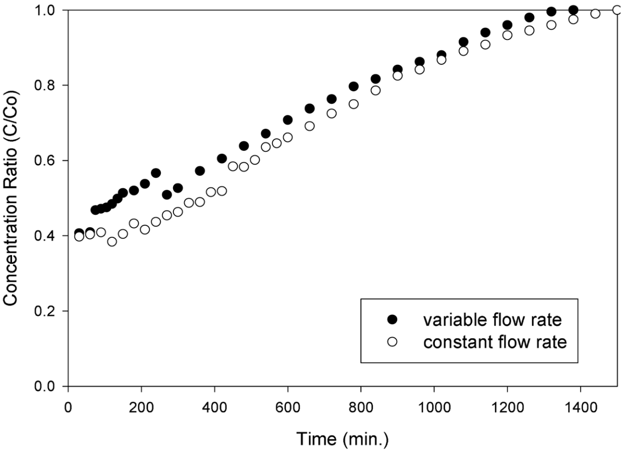

Fig. 9. The effect of one peak in flow rate on sodium breakthrough curve.

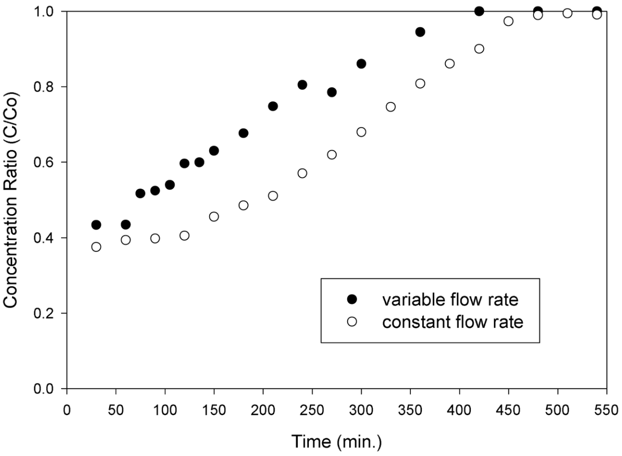

Fig. 10. The effect of one peak in flow rate on chloride breakthrough curve.

2. Effect of Variable Flow Rate

Fig. 8 shows the flow rate profiles for the constant and variable flow rate experiments with one peak in the flow rate profile. The peak, of which flow rate was 18.0 liter/hr, was introduced into the column 1 hour after starting the run and maintained for 3 hours. The flow rate was then dropped to the initial and kept constant for the rest of the run. The effect of this peak is shown in Figs. 9 and 10. These figures present the comparison of either sodium or chloride breakthrough curves from the constant and the variable flow rate experiments. In these figures, it can be seen that similar levels of initial leakage of each ion, $C/C_o=0.4$, appear in the effluent of the exchange process, resulted from the insufficient contact time between the solution and the resins.

As shown in Figs. 9 and 10, the flow rate has significant effect on the shapes of both cation and anion breakthrough curves, as expected. The effluent concentrations of sodium and chloride tend to change according to the flow rate. As the flow rate increases, the concentrations increase and as the flow rate decreases, those decrease. This means that the amounts of the ions removed by the exchange process decrease with the higher flow rate. Reynolds number increases in direct proportion with the flow rate of the solution. This increase in Reynolds number causes a decrease in the mass transfer coefficient of the column, as Reynolds number appears in the denominator of the formulas used in both Carberry's [1960] and Kataoka's [1973] mass transfer models. This decrease in the mass transfer coefficient causes less ions to be taken up by the exchange resins.

A close investigation of Figs. 9 and 10 gives that those two ions show different response quantitatively from each other to the step change in the flow rate. For sodium, the results of the experiments with the variable and the constant flow rate do not show much different in the slopes of the curves and times to reach equilibrium from each other, except around the peak. The effluent concentration of sodium for the variable flow rate increases to $C/C_o=0.6$ at the starting point of the peak and decreases close to that for the constant flow rate as the flow rate returns to the normal. However, chloride shows the increased effluent concentration of $C/C_o=0.8$ as the peak is introduced into the system and slightly decreases when the peak disappears, but shows large different concentration from that of the constant flow rate. For chloride, the breakthrough point is about 120 minutes for the constant flow rate and after this point, the operation capacity of the anion resin is reduced rapidly. The peak in the flow rate is maintained for 180 minutes and disappears 240 minutes after the run begins, which is beyond the breakthrough point. When the flow rate retrieves the initial, the operation capacity of the anion resin is almost exhausted. Therefore, even though the flow rate decreases, the ability of the anion resin to remove chloride does not improve as the cation resin does. The sodium breakthrough point is about 200 minutes and after the point, the capacity of the cation resin decreases slowly. This fact is obvious by comparing the curves of two ions directly.

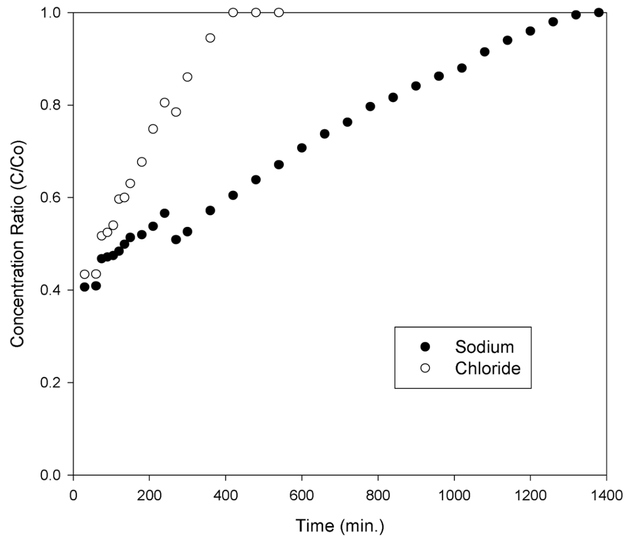

Fig. 11. Breakthrough curves of sodium and chloride for variable flow rate experiment with one peak.

Fig. 11 contains the same data of the variable flow rate experiment shown in Figs. 9 and 10. Usually, sodium shows relatively broad breakthrough curve compared to that of chloride and requires much longer time to reach the equilibrium than chloride. This is because the anion resin has a higher selectivity coefficient than the cation resin [Noh, 1992]. Moreover, less amount of the anion resin was used for the present study so that the total operation capacity of the anion resin is low compared to that of the cation resin, resulted in the different shapes of two curves.

Similarly, Fig. 12 shows the flow rate profiles of the constant and variable flow rates experiments with three step changes. The flow rate was maintained normal for the first 1 hour and increases rapidly

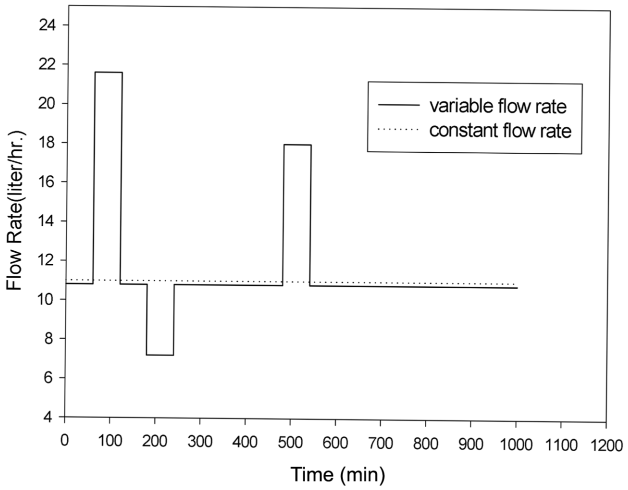

Fig. 12. Flow rate profiles for constant and variable flow rate experiments with three peaks.

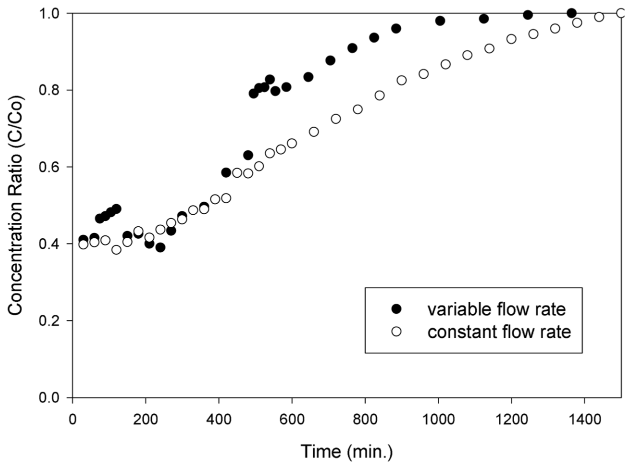

Fig. 13. The effect of three peaks in flow rate on sodium breakthrough curve.

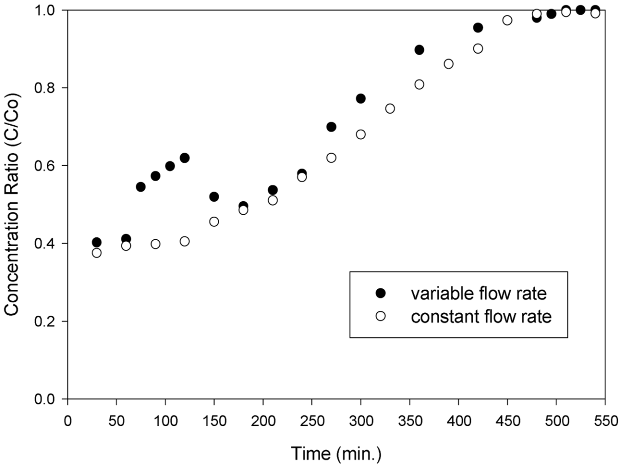

Fig. 14. The effect of three peaks in flow rate on chloride breakthrough curve.

to 21.6 liter/hr. One hour after the increase, the flow rate dropped to the initial flow rate and remained constant for 1 hour. Then, it decreased suddenly to 7.2 liter/hr and after 1 hour, retrieved the initial flow rate. The flow rate, after 4 hours, introduced the third peak of 18.0 liter/hr for 1 hour.

Figs. 13 and 14 show the effects of three peaks on the sodium and chloride breakthrough curves, respectively. As seen in the case of the one peak experiment, the effluent concentrations of both ions increase with the increased flow rate and decrease with the decreased flow rate. In Fig. 13, it can be seen that the effluent concentration of sodium increases as the initial flow rate changes rapidly and that as the flow rate returns to its initial value, it decreases to that of the constant flow rate. The second peak, of which flow rate is lower than the intial, results in the low concentration compared to the constant flow rate. The point which the second peak disappears is around the breakthrough time. The concentration increases much more than any other cases with the third peak, which is introduced into the system long time after the breakthrough time. After the third peak disappears, the concentration does not drop to the constant flow rate as it did before, but maintains higher concentration until the equilibrium. Therefore, it can be concluded that the effect of the flow rate on the sodium breakthrough curve becomes significant as the operation capacity of the cation resin gets exhausted.

The breakthrough curve of chloride, given in Fig. 14, shows a different trend from that of sodium. Before the breakthrough time, the concentration becomes close to that of the constant flow rate as the peak disappears. However, after the breakthrough time, the second and third peaks do not affect the concentration significantly. As a result, the effect of the flow rate on the anion breakthrough curve is serious before and/or around the breakthrough time when the operation capacity of the resin is still high. Otherwise, the effect becomes insignificant after the time. Fig. 15 shows the comparison of the cation and anion breakthrough curves for the variable flow rate experiment with three peaks.

CONCLUSIONS

The effects of amine additives for controlling pH of solution, such as ammonia and morpholine, and the variable volumetric flow rates on the performance of MBIE under the different temperatures and FCR at ultralow concentrations were experimentally evaluated in this study. For the amine additive experiments, the effluent concentration profiles of sodium and chloride were compared to those without the additives. The breakthrough curves of ammonia and morpholine were obtained to analyze their fates in the unit. For the variable flow rate experiments, step changes in flow rate were arbitrarily introduced into the experimental column. From both experiments, the following conclusions are drawn:

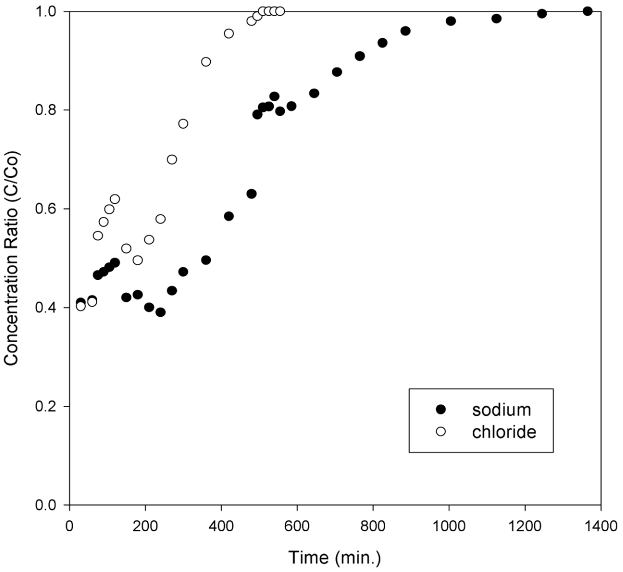

Fig. 15. Breakthrough curves of sodium and chloride for variable flow rate experiment with three peaks.

1. The breakthrough curve of morpholine shows higher initial leakage and faster breakthrough time than that of ammonia. As temperature increases, the exchange rates of the controllers increase, and the breakthrough curves of both ions show higher slopes and lower initial leakages. With an increase in FCR, the curves have longer breakthrough time and lower initial leakages. However, FCR is found not to affect the exchange rates of the ions.

2. The amine additives reduce the capacity of MBIE for the sodium removal significantly. However, the effect of ammonia is much more serious than that of morpholine. This is because the selectivity coefficient of the cation resin for ammonia is much higher than that for morpholine. The additives, especially ammonia, increase the exchange rate of chloride slightly at the early stage of the process. This is due to the difference of the mass transfer coefficient of chloride in an alkaline and an acidic solution.

3. Introducing step changes in flow rate affects the breakthrough times of sodium and chloride, but not the slopes of the curves. After the peaks are introduced, there is a low level of leakages of both ions due to insufficient contact time between the solution and the resins. When the flow rate returns to the normal, the leakage of chloride disappears. But, the sodium effluent starts to have higher concentrations after the peaks. Therefore, the amount of sodium removed until breakthrough time is more sensitive to the step changes in the flow rate than that of chloride. This would be due to the much

lower selectivity coefficient of sodium than the coefficient of chloride. The peaks affect the chloride breakthrough curve significantly until breakthrough time.

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