

The Effects of Resin Ratio and Bed Depth on the Performance of Mixed-bed Ion Exchange at Ultralow Solution

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Abstract

The effects of the cation-to-anion resin ratio and bed depth on ion exchange performance of mixed-bed were studied at ultralow solution concentration. Breakthrough curves were experimentally obtained for NaCl solution as functions of resin ratio and bed depth. The bed depth affects the pattern of the sodium breakthrough curve but not the chloride breakthrough curve in beds because of the selectivity difference. Resin selectivity determines the shape of breakthrough curves. Some sodium and chloride breakthrough curves crossed at a point as a function of resin ratio. The lower cation-to-anion resin ratio showed the higher effluent concentration or treated volume of the crossover point regardless of the total resin weight.

Key Words : Mixed-bed, Ion exchange, Ion exchange resin, Breakthrough curve, Resin ratio, Bed depth

1. Introduction

The mixed-bed ion exchange process was discovered during World War II by the Permutit technologists of New York. However, only small-sized mixed-bed demineralizers were used with the resins discarded after use¹⁾. The advent of spherical bead anion exchange resins with different densities from cation exchange resins allowed separation and regeneration by the hydraulic method. Since then, the mixed-bed ion exchange process has been used extensively in condensate purification units for applications in the power, electronics, and chemical industries.

The mixed-bed ion exchange process has been used predominantly in water treatment in several industries because this process provides an economical and convenient method to produce ultrapure water. This process

is equivalent to operate an infinite number of two stage cation and anion exchanges in series. In removing salt from the solution, the selectivity coefficient for salt ions is infinite. Therefore, the efficiency of mixed beds is better than cation and anion beds in series. A column, filled with an intimately mixed strong acid and strong base ion exchange resins, produces water with conductivity as low as 0.04 $\mu\text{S}/\text{cm}$, even lower than the conductivity of pure water, 0.055 $\mu\text{S}/\text{cm}$ at 25°C reported by Saunders²⁾.

Average sodium and chloride concentrations of less than 1 ppb in the polisher effluent are required as boiler feed water. Electric power generation facilities need a large volume of pure water. Thus ion exchange systems using deep mixed beds of bead form resin have supplied ultrapure water to industry³⁾.

Extensive use of mixed-bed ion exchange requires manufacturers to make high capacity resins for hundreds of applications. Especially in the field of ultrapure water production, the theory of ion exchange accompanied by chemical reaction is behind the corre-

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sponding technology. Thus, rigorous theoretical models and experimentation, that describe the actual industrial processes, are necessary to develop the basic understanding of this technology. Haub and Foutch^{4,5)} derived a mathematical model for the mixed bed ion exchange process operating in the hydrogen cycle at ultralow solution concentration. Their theoretical model can be evaluated by various experimental data, which show ion exchange performance in a mixed bed with breakthrough curve.

Many system parameters influence the shape of breakthrough curves in mixed-bed ion exchange. The parameters are; initial equivalent fractions of counterions in the cation resin and the anion resin, cation and anion resin particle diameters, bed void fraction, feed solution concentration, volumetric flow rate, system temperature, column diameter, height of packed resin, cation and anion resin capacities, types and ionic form of resins, selectivity coefficients for the sodium-hydrogen and chloride-hydroxide exchange, solution viscosity, solution density, cation-to-anion resin ratio, and diffusivities of the involved ions.

To evaluate the mathematical model of mixed-bed ion exchange, Noh et al.⁶⁾ obtained experimental data of ion exchange for the cases of various feed concentration and incomplete mixing of anion and cation resin at ultralow NaCl concentration. In addition, the effects of multicomponent systems of divalent cations on the performance of mixed-bed ion exchange in the concentration range used for ultrapure water processing were experimentally evaluated⁷⁾. 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 solution⁸⁾.

The objective of this research is to experimentally acquire breakthrough curves for sodium and chloride at different operating conditions in a mixed-bed and describe the effect of operating conditions on the shape of breakthrough curves. Among operating parameters in mixed-bed process, cation-to-anion resin ratio and bed depth were chosen as key parameters in mixed-bed. Experiments were performed to determine

effluent ion concentrations as a function of position and time in a mixed-bed column for NaCl concentration ranges below 10^{-4} M, that is typical allowable influent concentration range in ultrapure water production field.

2. Experimentation

2.1. Experimental system

In order to evaluate the effects of the cation-to-anion resin ratio and bed depth on mixed-bed ion exchange performance at ultralow solution concentrations, the effluent concentration of the solution as a function of time and position within the bed was measured from column experiments.

Fig. 1 shows the schematic diagram of the experimental system. It is mainly consisted of a large water purification column, a feed solution storage carboy, a solution feed pump, mixed-bed test columns, effluent solution storage carboys, and ion chromatography for measuring effluent concentrations. The water purification column is a large size mixed-bed ion exchange column, and is used to supply ultrapure water to make feed solutions with specific NaCl concentration. The column size was 10 cm ID \times 100 cm H, and resin depth was 70 cm. The produced water was good quality with a resistivity reading of 18.3 M Ω -cm, the standard of ultrapure water. The six test columns with the size of 2.54 cm ID \times 50 cm H were made with Pyrex

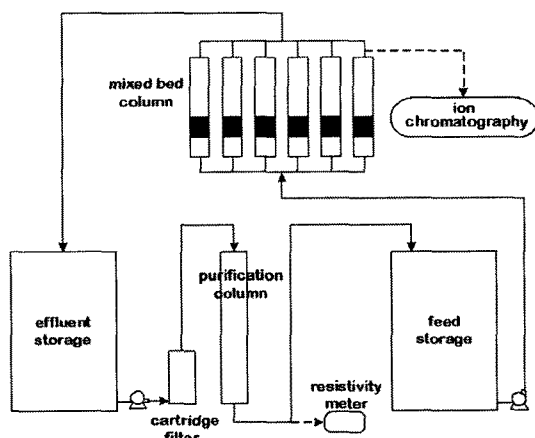


Fig. 1. Schematic diagram for the experimental system.

glass in order to watch directly the resin loaded inside the column and confirm the flows.

2.2. Ion exchange resins

Ambersep 200 H, for cation exchange, and Ambersep 900 OH, for anion exchange, provided by the Rohm and Haas Company, were used. Cation and anion resins were well mixed in a beaker and carefully loaded into a glass column. The physicochemical properties of the resins are shown in Table 1.

2.3. Experimental condition and procedure

All experiments were carried out at room temperature. The average temperature was $23 \pm 1^\circ\text{C}$. For time efficiency and data productivity, six test columns with different bed depths were simultaneously used to measure the concentration as a function of position as well as bed depth in the column. The flow rate was about 0.41-0.45 L/hr. Experimental runs were continued in all cases until effluent concentration was sure to reach breakthrough.

Very pure water, that was produced from the large water purification column, was used to prepare feed solution of 10^{-4} M NaCl. Feed solution was supplied to the test columns with the direction of bottom to top. The flow rate for each column was regularly checked and effluent samples were collected on a regular time basis. Collected samples were analyzed by ion chromatography.

Table 1. Characteristic values of ion exchange resins

Parameters	Cation	Anion
	H^+ type	OH^- type
Name	Ambersep 200 H	Ambersep 900 OH
Resin Bead Radius	0.80-0.85 mm	0.58-0.62 mm
Bulk Density	740-800 kg/m^3	630-700 kg/m^3
Exchange Capacity	1.6-1.7 eq/L	0.8-0.9 eq/L
Specific Gravity	1.18	1.06
Selectivity Coefficient	$\text{Na}^+ - \text{H}^+$ 2.0-2.5	$\text{Cl}^- - \text{OH}^-$ 15-18

3. Results and Discussion

The purpose of this study is to measure breakthrough curves for sodium and chloride in the conditions of various cation-to-anion resin ratio and bed depth, experimentally. Influent concentration of 10^{-4} M NaCl solution is chosen in this study. This meets maximum electrolyte concentration which is produced in condensate polishing plants.

As shown in Fig. 1, NaCl solution is continuously fed to the columns, and the treated solution is continuously removed. However, the mixture of cation and anion exchange resin in the column is exhausted gradually, so this is an unsteady-state process. The solution concentration will vary with both the bed position and elapsed time before cation and anion exchange resins are exhausted.

The experimental effluent concentration histories are given in dimensionless form of C/C_0 , i.e., effluent ion concentration divided by influent ion concentration, to interpret the results on a comparable basis.

Nine experimental conditions for breakthrough curves are shown in Table 2. The cation-to-anion resin ratios of 1/2, 1/1, and 2/1 were used for the total dry resin weights of 3.0, 6.0, and 9.0 g.

3.1. Breakthrough curve as a function of position

Figs. 2 through 4 for cation exchange and 5 through 7 for anion exchange, respectively, show the breakthrough curves of different total amount of mixed resin for each of the same cation-to-anion resin ratios. The abscissa of these figures is the amount of effluent volume treated, and the ordinate is C/C_0 .

Figs. 2 through 7 show that different levels of initial leakage appear in the effluent of the cation and anion

Table 2. Experimental conditions for breakthrough curves

Cation/Anion (dry weight)	Resin Amount(g/g)		
	3.0 g	6.0 g	9.0 g
1/2	1.0/2.0	2.0/4.0	3.0/6.0
1/1	1.5/1.5	3.0/3.0	4.5/4.5
2/1	2.0/1.0	4.0/2.0	6.0/3.0

exchange process. The initial leakage is not observed for anion exchange of mixed resin of 6.0 g or 9.0 g. For the mixed resin of 3.0 g, the initial leakage for anion exchange varies from 0.02 to 0.07, depending on anion resin amount in the bed. The initial leakage up to 0.24 is observed for cation exchange with cation resin of 1.0 g in Fig. 2. Cation exchange, except for the mixed resin of 9.0 g, shows the initial leakage depending on the bed depth. Under comparable conditions, the cation effluent concentration gives a higher level of leakage than anion effluent concentration. This will be due to the larger selectivity coefficient of anion exchange resin than cation exchange resin. The levels of leakage for anion exchange are almost constant, with a very low level for a lengthy period of time before the breakthrough curves started to rise. This is true except for very short beds due to insufficient contact between solution and resin. The levels of leakage for cation exchange are also almost constant for a long bed depth (total resin amount of 6.0 g or 9.0 g), but relatively broad compared to leakage levels for anion exchange.

Vermeulen and Hiester⁹⁾ pointed out that the shape and position of a breakthrough curve depend on equilibrium, rate, and stoichiometry. The equilibrium isotherms for the system influence the breakthrough curves especially when the equilibrium is very favorable or very unfavorable¹⁰⁾. Thus, the selectivity coefficient for the exchange influences the breakthrough curve, i.e., the relative steepness or sharpness of breakthrough curves. The more favorable the equilibrium is, the steeper the breakthrough curve. The limiting slope

of the breakthrough curve is reached in a shorter height of bed for a favorable equilibrium, while an unfavorable equilibrium gives a more gradual and non-sharpening breakthrough curve for a given set of diffusion coefficients. For a favorable equilibrium, breakthrough curves appear identical in pattern, while for an unfavorable equilibrium, breakthrough curves show a pattern of behavior proportionate to the bed volume or time through which it passes. The exchange wave continues to spread with distance through the column. Since the liquid-film diffusion rate control is assumed because of very low concentration range in this study, liquid-phase diffusion coefficients of ions, and selectivity coefficients for the sodium-hydrogen and chloride-hydroxide exchange will influence the breakthrough curve. Diffusion coefficients of the involved ions and selectivity coefficients for the exchange are properties of their own system. Thus, an accurate model which includes the rate expression with the appropriate system parameters predicts the behavior of the breakthrough curve.

Sodium breakthrough curves show that the leading band becomes diffuse as it progresses through the column, especially in Figs. 3 and 4 with relatively large cation resin amount. This is partly because of relatively unfavorable equilibrium of cation resin selectivity coefficient for sodium-hydrogen exchange of 2.0-2.5. Chloride breakthrough curves in Figs. 5 through 7 show a consistent pattern of behavior. However, the response is not as consistent as expected, considering the very favorable equilibrium as indicated by a selectivity coefficient for chloride-hydroxide of 15-18. This can

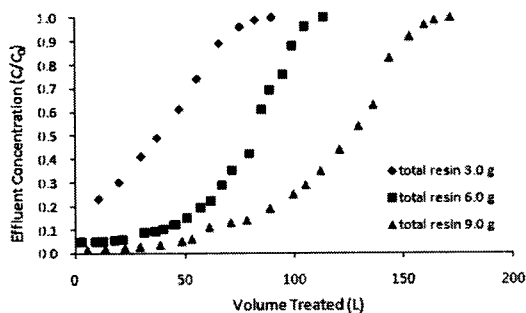


Fig. 2. Sodium breakthrough curves for cation/anion resin ratio of 1/2.

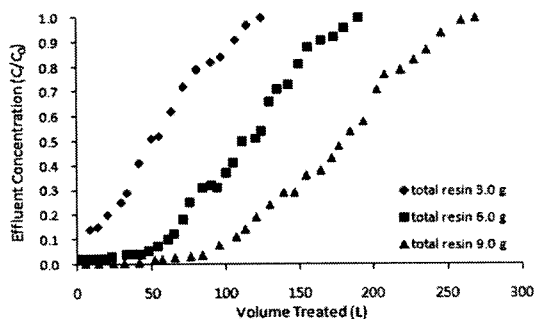


Fig. 3. Sodium breakthrough curves for cation/anion resin ratio of 1/1.

be explained by the claims of Coppola and Levan¹¹⁾ who studied adsorption with a constant pattern behavior in shallow beds. They claimed that the exchange wave approaches the constant pattern shape in deep beds with a favorable equilibrium, which corresponds to the maximum possible breadth of the mass-transfer zone. However, the mass-transfer zone can occupy a substantial fraction of the total bed length in shallow beds, so the constant pattern shape is not approached in shallow beds and the shape of breakthrough depends on the bed depth. The bed depths of our experimental columns are higher than typical shallow beds. For the total resin amount of 6.0 g or 9.0 g, the constant pattern is observed, but a slightly inconsistent pattern is observed for 3.0 g in Figs. 5 through 7. Inconsistent pattern in Fig. 7 is more serious than in Figs. 5 and 6. This effect is due to the bed depth, and our configuration is between shallow bed and deep bed. This trend is also observed in sodium breakthrough curves.

Thus, generally speaking, the parameter of bed depth affects the pattern of the sodium breakthrough curve but not the chloride breakthrough curve in sufficiently deep beds because of the selectivity difference.

3.2. Effluent concentration as a function of resin ratio

Using Figs. 2 through 7 from the experimental conditions in Table 2, the effects of the cation-to-anion resin ratio on the effluent concentration can be observed. Three resin ratios for the total dry resin weights of 3.0, 6.0, and 9.0 g give each three crossover points of cation and anion breakthrough curves. These are expressed in the Figs. 8 through 10, even though it is hard to distinguish the points in the figures. Table 3 presents the numerical values of crossover points of sodium and chloride breakthrough curves as a function of resin ratio.

Cation exchange resin and anion exchange resin

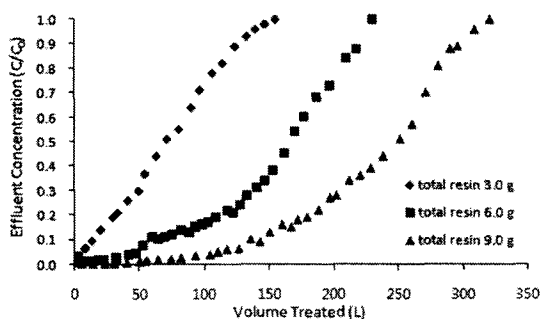


Fig. 4. Sodium breakthrough curves for cation/anion resin ratio of 2/1.

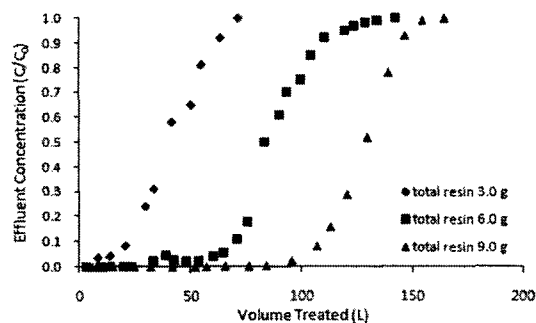


Fig. 6. Chloride breakthrough curves for cation/anion resin ratio of 1/1.

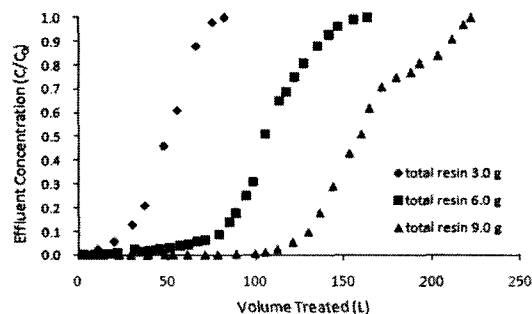


Fig. 5. Chloride breakthrough curves for cation/anion resin ratio of 1/2.

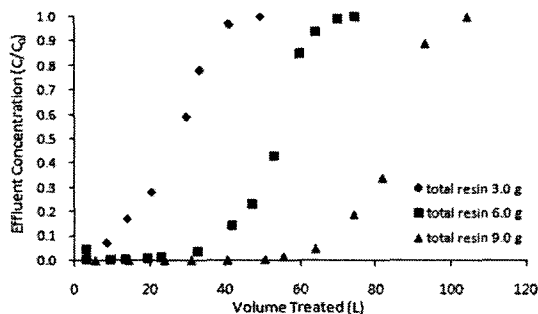


Fig. 7. Chloride breakthrough curves for cation/anion resin ratio of 2/1.

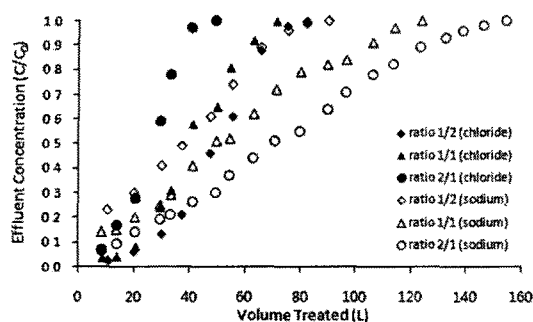


Fig. 8. Sodium and chloride breakthrough curves for various resin ratio at total resin of 3.0 g.

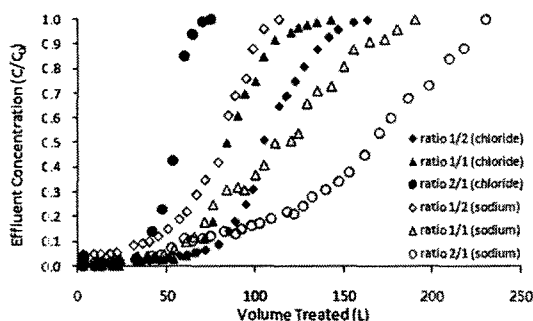


Fig. 9. Sodium and chloride breakthrough curves for various resin ratio at total resin of 6.0 g.

used in this study have different capacities. The conditions of the cation-to-anion resin ratios of 1/1 and 2/1 are expected to have higher cation exchange rates than anion exchange rates, while resin ratio of 1/2 is expected to have almost even cation and anion exchange rates. However, because of some other parameters which influence the ion exchange phenomena, the behavior of breakthrough curves are not simply dependent only on resin capacity. Selectivity coefficients of resins, mass-transfer coefficients for packed beds, and diffusion coefficients of ions are expected to affect the shape of the breakthrough curve. The selectivity of the resin towards the exchanging ions determines the sharpness of the exchange wave.

Some sodium and chloride breakthrough curves cross at a point regardless of the different total amounts of mixed resin in the column, and some do not cross. Since anion exchange resin has a higher selectivity coefficient than cation exchange resin, the chloride breakthrough curve is much steeper than the

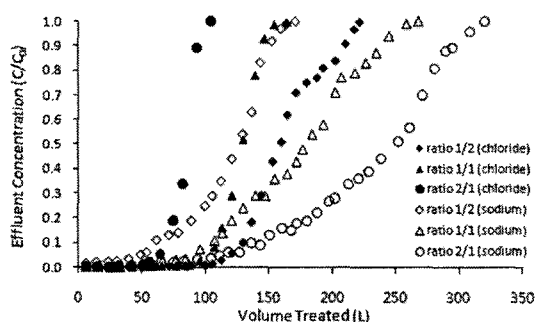


Fig. 10. Sodium and chloride breakthrough curves for various resin ratio at total resin of 9.0 g.

Table 3. Crossover points of sodium and chloride breakthrough curves

Cation/Anion (dry weight)	Volume Treated (L), C/C_0		
	3.0 g	6.0 g	9.0 g
1/2	74, 0.95	-	-
1/1	24, 0.22	70, 0.15	110, 0.15
2/1	-	10, 0.02	40, 0.01

sodium breakthrough curve as shown in Figs. 8 through 10. This is why sodium and chloride breakthrough curves meet at a point if the amount of one resin is not much larger or smaller than the other resin in the mixed bed. The crossover points of sodium and chloride breakthrough curves have the trends that the lower cation-to-anion resin ratio shows the higher effluent concentration or treated volume of the crossover point regardless of the total resin amount.

4. Conclusions

In light of the experimental results for the upward flow mixed-bed ion exchange column to obtain effluent concentrations as a function of time and bed depth, the following conclusions can be drawn in this study:

- Initial leakages depend on bed depth, thus different level of initial leakages is observed. The cation effluent concentration gives a higher level of leakage than anion effluent concentration. This will be due to the larger selectivity coefficient of anion exchange resin than cation exchange resin.

- Breakthrough curves are obtained as a function of

bed depth using the same cation-to-anion resin ratio and different total resin weight. The bed depth affects the pattern of the sodium breakthrough curve but not the chloride breakthrough curve in beds because of the selectivity difference.

• Resin selectivity determines the shape of breakthrough curves. Some sodium and chloride breakthrough curves cross at a point as a function of resin ratio. The lower cation-to-anion resin ratio shows the higher effluent concentration of the crossover point.

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