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Parametric Studies on the Performance of Anion Exchange for Nitrate Removal

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Abstract–Ion exchange performance to remove nitrate in surface and underground water was studied experimentally in batch and continuous operation systems under various conditions. Data were collected by using commercially available strong-base anion-exchange resins of Cl^- and OH^- types. Equilibrium curves, obtained through the batch system and plotted as the concentration ratio versus run time, were used to evaluate the effects of temperature, resin type, and initial feed concentration on the equilibrium characteristics of nitrate. The selectivity coefficients of the resins were correlated as a function of temperature by using the Kraus-Raridon equation. Breakthrough curves, obtained through the continuous column system and plotted as the ratio of effluent to influent concentration versus solution volume passed through the experimental column, gave detailed results about the effects of the system parameters, such as temperature, resin type, feed concentration, volumetric flow rate, column diameter and height on the performance of the anion exchange to remove nitrate. The results of this study could be scaled up and used as a design tool for a water-purification system of real ground water and surface water treatment processes.

Key words : Ion Exchange, Denitrification, Nitrate Removal, Selectivity Coefficient

INTRODUCTION

Nitrate concentration in underground and surface water is increasing all over the world due to natural sources as well as animal, human and industrial waste. Nitrate concentrations in surface water are generally less than 5 mg/L due to the dilution by surface runoff, plant uptake and biological denitrification which transforms nitrate to harmless nitrogen gas into the atmosphere. However, nitrate concentration in underground is generally higher than surface water because of limited dilution with surface water, minimum plant uptake and the absence of a suitable carbon source for denitrification.

Nitrate is so toxic, especially to pregnant women and infants, that the USEPA and Korean standards of 10 mg NO_3^--N/L or less in drinking water were established for human health. Even though not yet proven, there might be some relationship between nitrate concentration and cancer occurrence. A portion of the nitrate consumed in drinking water is converted to nitrite in the body. Nitrite can react in the body with secondary amines, amides, and carbamates to form N-nitroso compounds, several of which are potential human carcinogens, causing cancer of the nasopharynx, esophagus and stomach [Pontius, 1993; Kalagiri, 1994]. Hill et al. [1973] reported that the death rate of an English town with water containing 20 mg NO_3^--N/L from gastrointestinal cancer was higher than that of other towns. Epidemiological studies in China, Iran, Canada and Southern Australia have shown an increased incident of esophageal cancer and birth defects associated with several dietary factors, from drinking water and food which are high in nitrate and nitrite [Yang, 1980; Pontius, 1993; Bouchard et al., 1992]. Nitrate also is a nutrient source for the growth-limiting factor to the causes of eutrophication. This causes serious damage to sea food industries.

The problem of nitrate contamination requires that appropriate water treatment and purification technologies be developed. Several methods have been utilized in reducing nitrate contamination from water supplies. The denitrification process should be selected depending upon the quality of water sources, degree of treatment required, climate conditions, operational capacity, economical feasibility and availability of technology. In terms of efficiency, cost and relative ease of operation, ion exchange, reverse osmosis, electrodialysis, bio-denitrification methods have been found effective in nitrate removal.

Reverse osmosis and electrodialysis are considered to be very effective technically, but too expensive for routine nitrate removal unless desalting is also required to reduce the total dissolved solids level or to remove additional contaminants [Clifford and Liu, 1993].

Biodenitrification is an effective, efficient and easy method of nitrate reduction and removal from water supplies. But this denitrification process has the possibility of imparting residual organics and suspended solids to the distribution system, thereby increasing the oxygen demand and potentially encouraging undesirable bacterial growth in the water. This problem should be solved before the process can be adopted in potable water treatment.

Nitrate removal from drinking water using ion exchange is economical and convenient and provides a suitable solution for small or medium-sized water treatment plants containing comparably low nitrate levels [Kim et al., 1999]. Ion exchange is the most common process for public water supplies in the United States. Approximately 15 of these plants were operating in the United States during 1992 [Clifford and Liu, 1993]. Ion exchange systems are operated on demand, and utilize the beneficial selective reversal which common-

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ly occurs upon regeneration [AWWA, 1990].

This paper presents the nitrate removal performance of anion exchange resins, which is a part of the denitrogenation process development by mixed-bed ion exchange. This study also includes the effects of important system parameters such as resin type, initial nitrate concentration, volumetric flow rate, column diameter, and height, and temperature using batch and continuous experimental systems.

THEORY

Ion exchange is a physicochemical process in which ions in the water are exchanged for a chemically equivalent number of ions associated with the exchange material. This ion-exchange material includes naturally occurring clays and synthetic resins. The resins are in the form of gel or macroporous granules. The resin structure consists of an interconnected network of hydrocarbons where soluble ionic functional groups are attached. In this process, raw water contacts with ion exchange resin, and nitrates in water are exchanged for similarly charged chloride ions. The process is continuous until the resin bed is exhausted and then regenerated before the process is continued. The process is described as:

$$R-Cl+NO_3^- \leftrightarrow R-NO_3+Cl^- \tag{1}$$

where the selectivity coefficient is defined as:

$$K=\frac{[R-NO_3][Cl^-]}{[R-Cl][NO_3^-]} \tag{2}$$

and the regeneration process is:

$$R-NO_3+NaCl \rightarrow R-Cl+Na^++NO_3^- \tag{3}$$

Ion exchange is an exothermic process, and the temperature adversely affects the ion-exchange equilibrium and hence the selectivity coefficient. The selectivity coefficient can conveniently describe ion-exchange equilibria, and selectivity is the preference of the particular ion exchanger for one ion over the other ion. Resin selectivity toward the exchanging ions is used to determine the sharpness of the exchange wave [Helfferich, 1962]. The selectivity coefficient is greater than unity when ion in the solution phase is preferred by the resin phase. In this case, the equilibrium is said to be favorable.

Many methods of correlating the temperature dependency of selectivity coefficient were proposed, but Kraus-Raridon method provided a convenient and practical method for determining the effect of temperature on equilibria [Divekar et al., 1987]. Using the Debye-Hückel theory of electrolytes, Kraus and Raridon [1959] developed a method for expressing selectivity coefficients as a function of temperature. The expression for the selectivity coefficient is

$$\log K=\log K_t+C'\log(T/T_t)+C''(1-T_t/T) \tag{4}$$

where C', C'' and K_t are constants and subscript t refers to a reference temperature. By fitting experimental data to Eq. (4), Kraus et al. [1960], determined parameters C', C'' and K_t by the least squares method. Divekar et al. [1987], verified the deviations between observed and calculated values of the selectivity coefficient within limits of experimental error. Divekar et al. [1987], also developed an equation for the cation- and anion-exchange selectivity coefficients by using experimental results especially reported on Dowex resins, and applied it to the mixed-bed ion exchange model for ultralow concentration. Their equation is easy to use but not practically proposed.

Selectivity of ion-exchange resins is enhanced by increasing the degree of crosslinking and by decreasing the solution concentration. Ions with higher valence, smaller equivalent volume, and greater polarizability are preferred. The effect of the degree of crosslinking on the selectivity is illustrated by Myers and Boyd [1956]. The selectivity sequence for anions is $PO_4^{3-}>SO_4^{2-}>HPO_4^{2-}>NO_3^->HCO_3^-$ [Dahab, 1993]. This sequence shows that sulfates are preferred to nitrates. This resin selectivity for sulfate over nitrate is a major disadvantage associated with ion exchange.

EXPERIMENTAL

The anion exchange process has been successfully used in removing nitrate from both groundwater and surface water. In this study, both batch and continuous operation systems were used to show the nitrate removal characteristics of anion resins.

For the present study, Cl^--type anion exchange resin of PA408 provided by the Samyang Company, Limited, and OH^--type of Dowex Monosphere 550A by the Dow Chemical Company, were used. These are grouped into Type II of strong basic resins. The physicochemical properties of the resin are shown in Table 1. The resins were rinsed with high purity water and stored in plastic containers until they were used for the experimental runs. Sodium nitrate ($NaNO_3$) of analytical reagent grade was the nitrate source in the experiments.

The batch system has been performed to investigate the effects of resin type, feed solution concentration, and temperature on the equilibrium data of nitrate. The system simply consists of flask, a magnetic stirrer and bar, and a thermometer. Table 2 shows the experimental conditions of the system. Ion exchange resin and nitrate solution of the known weight and concentration, respectively, were added to the pure water in a 1-liter flask container, and vigorously agitated. Water bath with magnetic stirrer was used to maintain the constant temperature in the system. Water samples were collected periodically by hand using sample bottles. To avoid any leaching from the bottle itself, the samples were analyzed within at most 6 hours by using ion chromatography (IC).

The continuous operation system has been used to study the ef-

Table 1. Characteristic values of anion exchange resins*

Parameter	Values	
	PA 408	Monosphere 550A
Resin type	Cl^- Type	OH^- type
Appearance	Hard, Yellow, Sphere, Opacity	Hard, White, Spherical beads
Bulk density (g/L)	655.0	640.7
Water retention capacity (%)	54-64	44-50
Capacity (meq/ml)	≥0.9	1.10
Diameter (mm)	0.35-0.55	0.59
Specific weight	1.06-1.12	-

*From the vendors.

Table 2. Experimental conditions of the batch reactor

Parameter	Values
Resin weight (g)	0.1
pH	7.0-9.4
Temperature (°C)	15, 25, 35
Feed concentration [NO_3^--N] (mg/L)	1.64, 3.29, 4.94
Agitation rate (rpm)	≥1000

Table 3. Experimental conditions of the column reactor

Parameter	Values
Feed concentration [NO_3^--N] (mg/L)	1.64, 3.29, 4.94
Feed flow rate (L/hr)	7.2, 10.8
Temperature (°C)	20, 30, 40
Column diameter (cm)	1.2
Resin depth (cm)	2.0-6.0
Resin weight (g)	2.0, 4.0

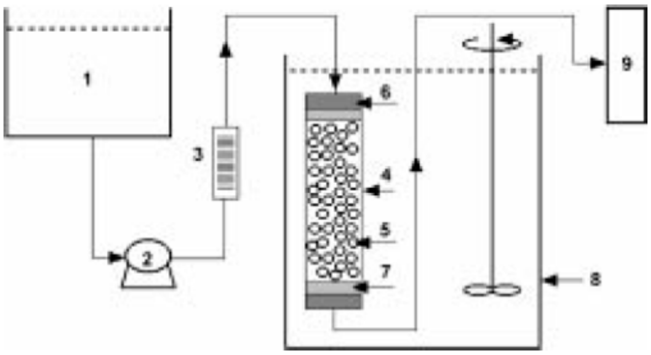

Fig. 1. Schematic diagram of the continuous operation system.

1. Feed storage
2. Pump
3. Flow meter
4. Glass column
5. Anion resin
6. Silicone stopper
7. Glass wool
8. Water bath
9. Ion chromatography

fects of resin type, initial feed concentration, temperature, volumetric flow rate, column diameter and height on the breakthrough curves of nitrate. Table 3 shows the experimental conditions of the continuous system, and Fig. 1 shows the schematic diagram of the system. The experimental system consisted mainly of a packed-bed column, its accessory for feeding, water bath, feed storage, and ion chromatography for measuring effluent concentrations. The ion-exchange column used for the experiment was made from Pyrex glass to see the resin loaded inside the column. Glass wool with stainless steel screens was used to support the resin and to ensure uniform flow distribution. A water bath was used to maintain the desired temperature inside the column. Feed solution was distributed from a 50-liter Nalgene carboy to the column through a peristaltic pump. The pump drive was equipped with a speed controller for adjusting the flow rate to the design conditions. The feed solution was designed to simulate groundwater with the concentration of 10 mg NO_3^--N/L, but lower nitrate concentrations were also made to study the effect of feed solution concentration.

A Dionex IC (model DX-300) and Standard Methods were used to analyze the water samples for both batch and continuous operation systems. These two methods verified mutually the accuracy of the data.

RESULTS AND DISCUSSION

The experiments were performed by using both batch and continuous operation systems under various conditions. The results of water sample analysis were described as the ratio of the effluent concentration (C) to the feed concentration (C_o) vs. run time or solution volume passing through the experimental column. The results from each experiment separately discussed the effects of the experimental variables such as resin type, temperature, feed concentration, flow rate, column diameter, and height.

1. Batch Operation System

The results of the batch experiments were used to study the ion exchange reaction equilibrium between chloride or hydroxide ions in the resin phase and nitrate in the solution. Fig. 2 compares the performance of ion exchange resins, activated carbon, and zeolite, which are known to be effective for removing nitrate in the solution. At 30 °C, 2 g of each solid particles was added to the 25 mg/L nitrate concentration of 1 liter solution. In this figure, the ion exchange resins show better performance than activated carbon or zeolite, regardless of the resin type. These Samyang ion-exchange resins of PA408, porous type II resin, and SA 10AP, gel type I resin, show similar nitrate removal performance of more than 80% while activated carbon and zeolite show a rate of 40% or less. This means that the ion exchange mechanism is more efficient than the adsorption mechanism of activated carbon or zeolite to remove nitrate. From this figure, it can be concluded that adsorption is not as a good method as ion exchange reaction to remove nitrate in the solution.

Fig. 3 shows the effect of resin weight on the removal efficiency of the PA408 resin. Although SA10AP showed better performance for the removal of nitrate than PA408 in Fig. 2, PA408 was chosen in the experiment because of its physical strength. Fig. 3, as expected, shows better removal performance when the resin weight increases, but the efficiency reduces with the increased resin weight. The weight of nitrate removed in the solution per the unit weight of resin

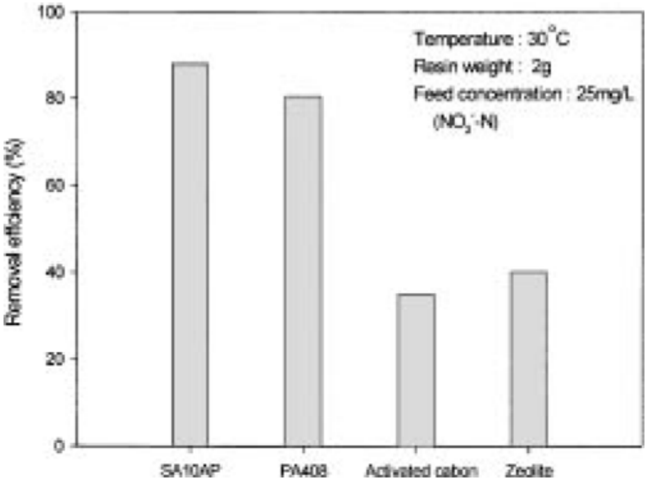

Fig. 2. Comparison of nitrate removal efficiencies at equilibrium of activated carbon, natural zeolite, and anion resins.

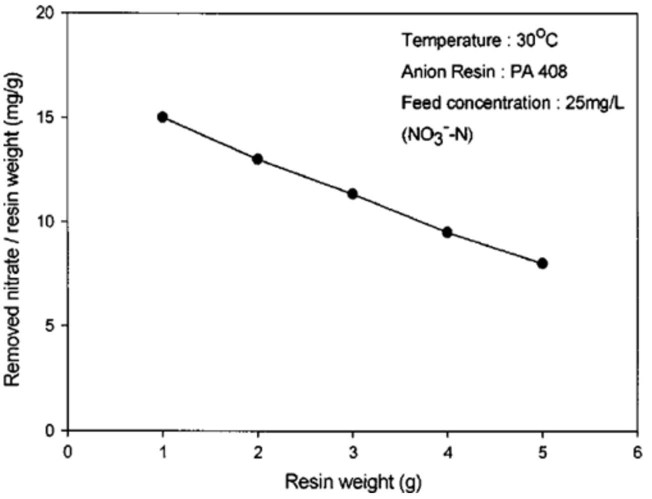

Fig. 3. Nitrate removal efficiency as a function of resin weight.

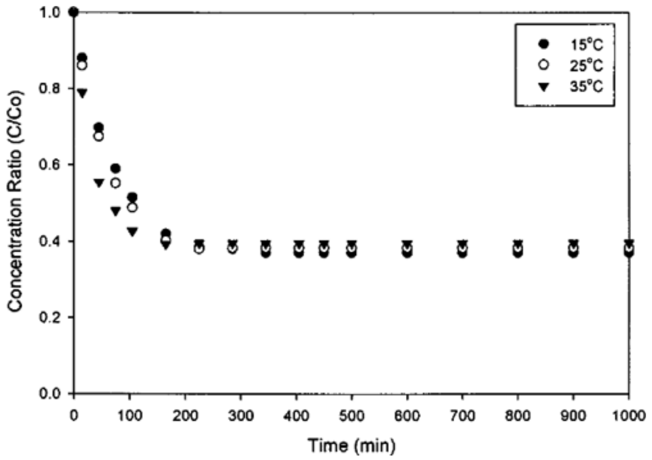

Fig. 4. Effect of temperature on nitrate concentration profile in the batch system with NO_3^--N 4.94 mg/L and PA408.

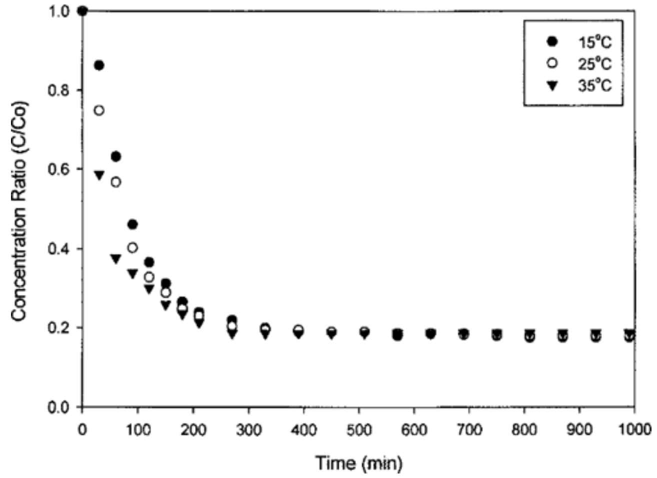

Fig. 5. Effect of temperature on nitrate concentration profile in the batch system with NO_3^--N 4.94 mg/L and 550A

is about 15 mg with 1 g of the ion exchange resin, but reduces to about 8 mg with 5 g of the resin. In this figure, the nitrate concentration at equilibrium in the batch reactor shows better nitrate removal efficiency with the smaller resin weight.

Figs. 4 and 5 show the effect of temperature on the equilibrium curve of nitrate with PA408 and 550A, respectively. A close investigation of these figures reveals that as the temperature increases, the concentration profile of nitrate has sharper slope and reaches the equilibrium state faster. This trend well agrees with the model simulation of Divekar et al. [1987], who evaluated the temperature effect on the performance of the mixed-bed ion exchange at concentrations approaching the dissociation of water. With increasing temperature, the selectivity coefficient and solution viscosity decrease, while the ionization constant of water and ionic diffusion coefficient increase. They believed that the selectivity coefficient and viscosity change to a much smaller extent than the other parameters, and that this change is overridden by the other two factors to improve the performance of the mixed-bed ion exchange. Figs. 4 and 5 also show that the equilibrium concentration increases as the temperature increases. This means that the operation capacity of the resin is not likely changed significantly by temperature. Therefore, it can be said that temperature affects the ion exchange rate more than the capacity of resin.

Fig. 6 contains the same data as Figs. 4 and 5 at 35 °C and shows the difference between the performance of PA408 and 550A. The 550A resin, which is OH^- type, shows a sharper slope of the curve than the PA408 resin, which is Cl^- type. The slope of the curve implies that the exchange rate of nitrate with hydroxide is higher than that with chloride, which means the selectivity of the 550A resin for nitrate over hydroxide is bigger than that of PA408 for nitrate

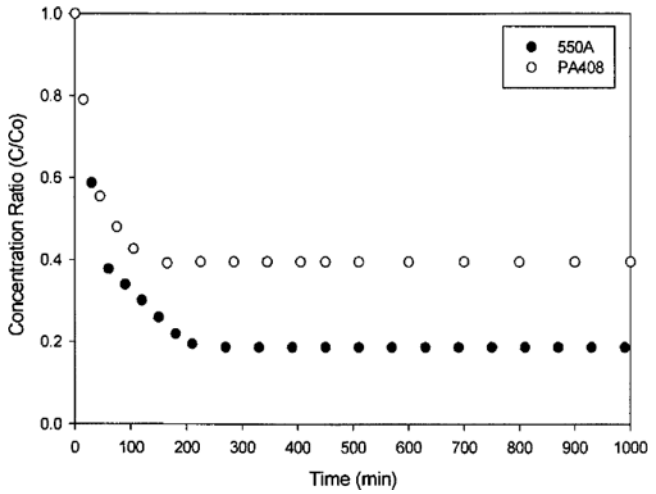

Fig. 6. Effect of resin type on nitrate concentration profile in the batch system with NO_3^--N 4.94 mg/L at 35 °C.

Table 4. Selectivity coefficients of anion exchange resins with NO_3^--N 4.94 mg/L

Temperature (°C)	Selectivity coefficient (K)	
	PA408 (Cl^--NO_3^-)	Monosphere 550A (OH^--NO_3^-)
15	4.88	64.70
25	4.27	56.49
35	3.78	49.50

over chloride. The equilibrium concentration of 550A is lower than that of PA408, and this is because 550A has a bigger total capacity than PA408.

Selectivity coefficients of nitrate over chloride or hydroxide were obtained from the equilibrium data and given in Table 4. These data were applied to the equation of Kraus-Raridon [1959] based on Debye-Hückel theory. Using selectivity coefficient values of 15, 25, and 35 °C, the equation for PA408 was correlated as:

$$\log K_{Cl^-}^{NO_3^-} = 4.2678 - 0.5367\log\left(\frac{T}{25}\right) + 0.0915\left(1 - \frac{25}{T}\right) \quad \text{at } 4.94 \text{ mg/L} \quad (5)$$

and for 550A:

$$\log K_{OH^-}^{NO_3^-} = 56.4891 - 0.6291\log\left(\frac{T}{25}\right) + 0.1209\left(1 - \frac{25}{T}\right) \quad \text{at } 4.94 \text{ mg/L} \quad (6)$$

Fig. 7 shows how the variation of initial nitrate concentration affects the ion-exchange performance. The figure shows higher equilibrium concentration and worse performance as the initial concentration increases. Based on the figure, it is possible to suggest that a low initial concentration needs longer reaction time to reach equilibrium.

Although highly nitrate-selective resins were used in the experiment, the performance of these ion exchange resins was affected by the existence of the other anions, especially sulfate. To study the fates of anions existing in the solution, the solution of ion mixture of SO_4^{2-}, NO_3^-, NO_2^-, and HCO_3^- of the same equivalent amount was used as an influent solution. These ions are easily found in natural water sources. The resulting concentration profiles of the ions are shown in Fig. 8. As is shown in this figure, the selectivity sequence of the anion exchange resin in the experiment was found as $SO_4^{2-} > NO_3^- > NO_2^- > HCO_3^-$. This result coincides well with the result of Dahab [1991] except NO_2^- ion, but the order of nitrite was found as expected.

2. Continuous Operation System

The results of the continuous column experiments are given in Figs. 9-14, from which one can see that different levels of initial leakage of nitrate appear in the effluent of the exchange process. The initial leakages might be due to the insufficient contact time between the solution and the resin, which results from the high flow rate and the relatively short bed depth. These conditions were selected for a reasonable duration of the experimental runs.

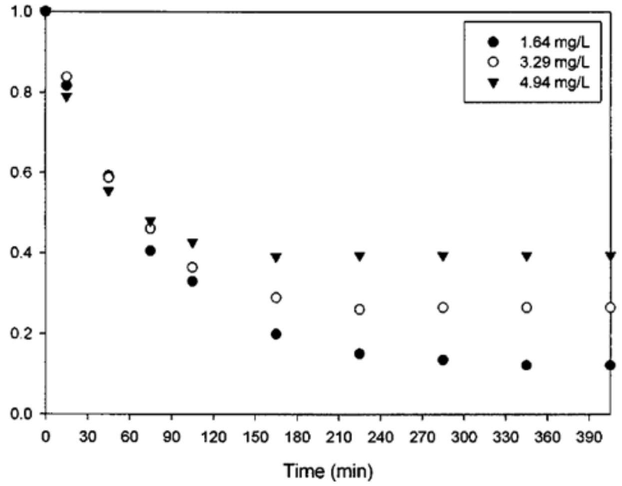

Fig. 7. Effect of initial feed concentration on nitrate concentration profile in the batch system at 35 °C (PA408).

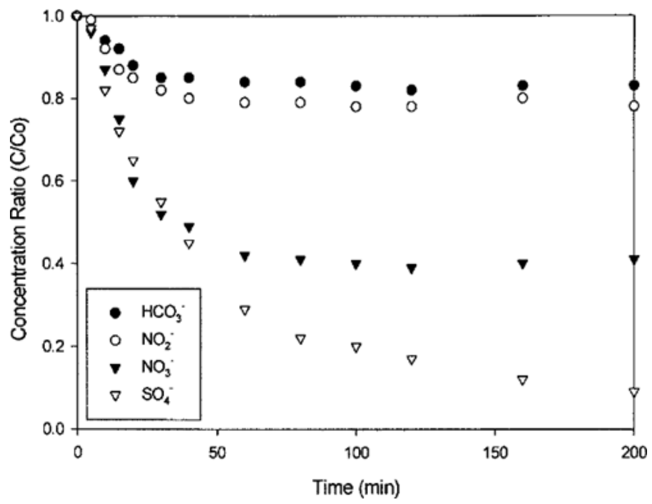

Fig. 8. Concentration profiles of various anions in the batch system at 35 °C.

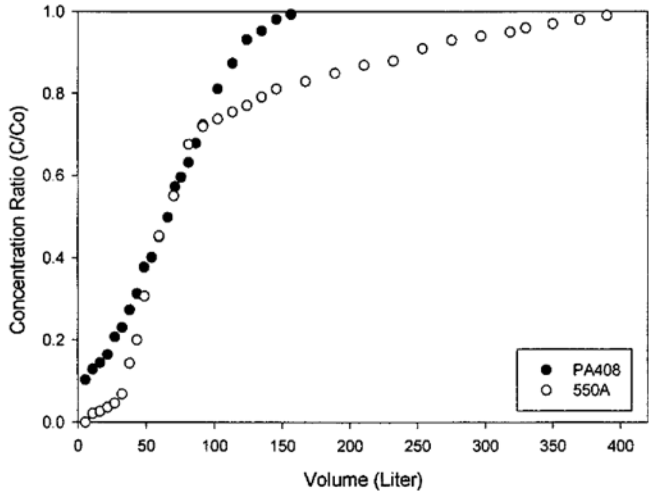

Fig. 9. Nitrate breakthrough curves with PA408 and 550A at 30 °C (NO_3^--N 1.64 mg/L).

The performance of two anion exchange resins, 550A and PA408, for the removal of nitrate was compared in Fig. 9. It is observed in this figure that 550A shows a lower level of initial leakage and much longer time to reach the equilibrium state than PA408. This can be explained by the differences in the selectivity coefficients and the capacities of those resins. The selectivity coefficient directly relates to the ability of the resin to remove an ion over another. Considering the results obtained through the batch experiments (see Fig. 6), it could be expected that 550A showed much better performance for the removal of nitrate in the continuous system than PA408, resulting in the lower initial leakage. The capacity of the resin is defined as the net number of ionic sites utilized in a given weight of the resin in a given process. As shown in Table 1, the capacity of PA408 is lower than that of 550A, and as a result, PA408 is ex-

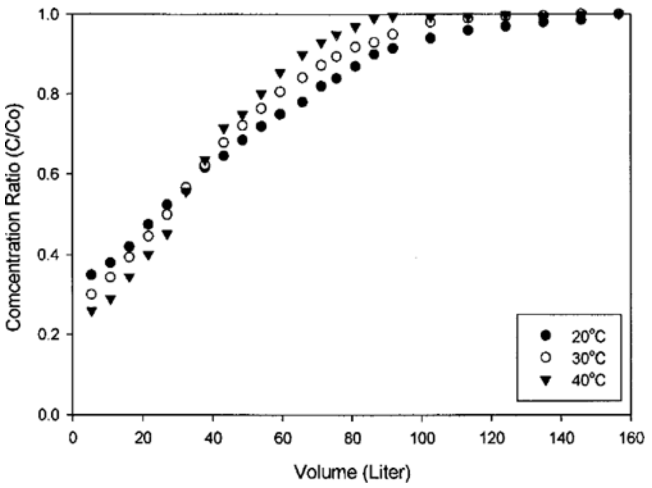

Fig. 10. Effect of temperature on nitrate breakthrough curves with NO_3^--N 1.64 mg/L (PA408).

hausted and reaches the equilibrium state faster than 550A. It is obvious from the figure that the selectivity coefficient and the capacity of resin influence the shape of the breakthrough curve significantly.

Fig. 10 shows the effect of temperature on the effluent concentration profile of nitrate. The figure indicates that the differences among the curves with different temperatures are more obvious than those in the batch experiments. With the higher temperature, the breakthrough curve shows lower initial leakage and steeper slope. This results in two distinct zones in the curve. In one zone, the higher temperature gives better removal performance; in the other, the reverse effect is noticed. Thus, it can be concluded that temperature enhances the exchange rate below the resin capacity and causes faster exhaustion to the equilibrium state.

The effect of the volumetric flow rate on the breakthrough curve of nitrate is shown in Fig. 11. The figure indicates that the initial leakage increases and the slope becomes broader as the flow rate increases. This might be because the contact time between the solution and the resin decreases with the increased flow rate. As the same as temperature, the flow rate also appears not to affect the capacity of the resin significantly. An interesting point observed in the figure is that the slope of breakthrough curves is broad compared with the results of Yoon et al. [1995], who studied the effect of cation to anion resin ratio on the mixed-bed ion exchange performance at ultralow NaCl solution concentration. They used the Ambersep 900OH of Rohm and Haas Company, especially manufactured for the mixed-bed ion exchange. The resin selectivity coefficient of 900OH was 15-18 for Cl^--OH^- exchange, much bigger than the resin used in this experiment. The lower selectivity coefficient makes a broader slope of the breakthrough curve.

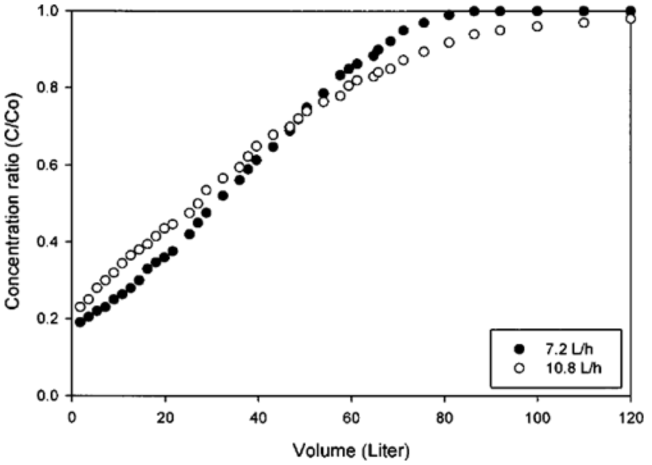

Fig. 11. Effect of volumetric flow rate on nitrate breakthrough curves with NO_3^--N 1.64 mg/L at 30 °C (PA408).

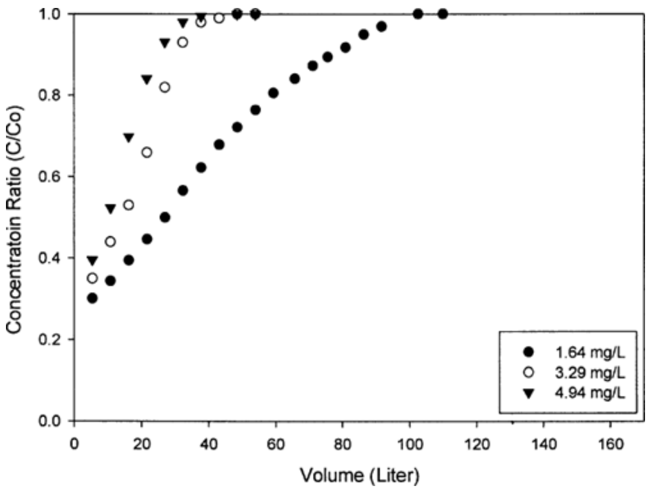

Fig. 12. Effect of feed concentration on nitrate breakthrough curves with 2 g of PA408 at 30 °C.

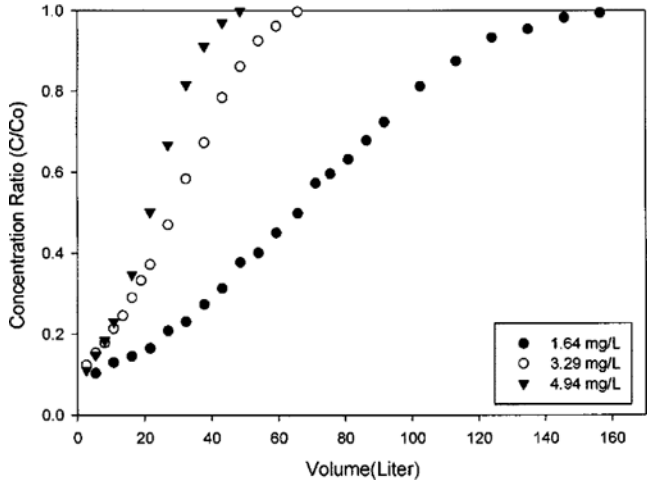

Fig. 13. Effect of feed concentration on nitrate breakthrough curves with 4 g of PA408 at 30 °C.

Figs. 12 and 13 show the effect of feed concentration on the nitrate breakthrough curve with the different weight of the resin. As expected, the curves in both figures indicate a steeper slope and faster breakthrough when the concentration increases. While the initial leakage also increases with the feed concentration when the weight of the resin is 2 g in Fig. 12, it is almost constant regardless of the concentration with 4 g of the resin in Fig. 13. These weights correspond to 3 cm and 6 cm of bed height of the continuous column, respectively. The ratio of the treated solution volume, which is the

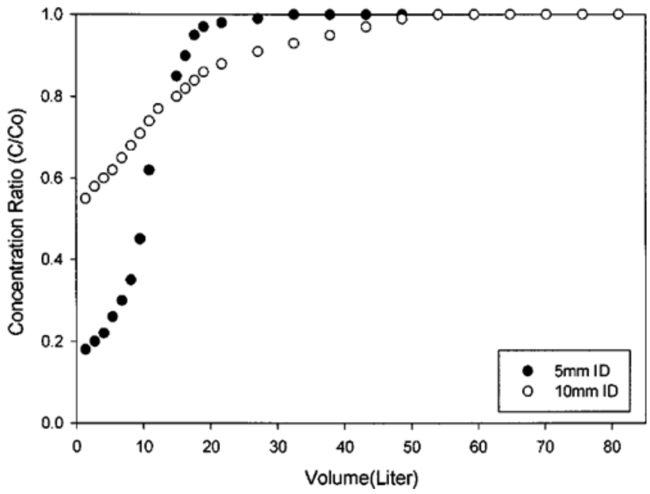

Fig. 14. Effect of column diameter on nitrate breakthrough curves with NO$_3^-$-N 3.29 mg/L at 30 °C (PA408).

left-hand side area of the breakthrough curves, agrees with the ratio of the resin weights. Therefore, it can be said that the capacity of the resin is likely not to be changed by the variation of the initial feed concentration.

The initial leakage depends on the bed height for the favorable equilibrium. 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 broad breakthrough curve [Vermeulen and Hiester, 1959]. As a function of bed height, anion breakthrough curves in Figs. 12 and 13 show different levels of initial leakage. This is because of the relatively short bed of the system and thus, insufficient contact between the solution and the resin for the favorable equilibrium. The results in this experiment coincide with the results of Yoon et al. [1999], who studied the temperature effects on the mixed-bed ion exchange performance at ultralow NaCl solution concentration. They used the Dowex Monosphere 550A with selectivity coefficient of 22.0 manufactured by Dow Chemical Company, and showed a steeper anion breakthrough curve than cation breakthrough curve and different levels of breakthrough as a function of cation to anion resin ratio.

Column diameter with a constant flow rate influences the performance of the continuous column, especially at an early stage of the process. Fig. 14 shows the effect of column diameter with the same weight of the resin on the nitrate breakthrough curve. The serious increase of initial leakage for 10 mm inside diameter might be due to the short bed. The ratio of 10 to 5 mm inside diameter corresponds to the bed height ratio of 4 to 1. The effect of bed height was described previously in Figs. 12 and 13.

CONCLUSIONS

The effects of the system parameters, such as resin type, feed concentration, temperature, flow rate, column diameter and height, on the performance of an ion exchange unit for the removal of nitrate were experimentally evaluated. Through both batch and continuous column experiments, the following conclusions are drawn:

1. The selectivity coefficient and the total capacity of resin directly affect the ability of the ion exchange unit to remove nitrate. The OH$^-$ type anion resin shows better results for the removal of nitrate than the Cl$^-$ type resin. This is because the selectivity of the former resin for nitrate over hydroxide is bigger than that of the latter for nitrate over chloride. The equilibrium concentration of nitrate decreases as the resin capacity increases.

2. Temperature affects positively the performance of ion exchange for the removal of nitrate below the resin capacity. As temperature increases, the exchange rate increases and the equilibrium is more favorable.

3. As the initial feed concentration increases, the equilibrium concentration decreases and the breakthrough time is shorter. However, the total amount of nitrate removed is not changed.

4. With the increased volumetric flow rate and column diameter, the contact time between the solution and the resin decreases, resulting in the increased initial leakage and the steeper slope of the curve. The operation capacity of the resin does not appear to be affected significantly by these parameters.

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