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THE REMOVAL OF FLUORIDE ION FROM AQUEOUS SOLUTION BY A CATION SYNTHETIC RESIN

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ABSTRACT

The removal of fluoride ion in aqueous solution by using an aluminum-formed synthetic resin, Amberlite IR-120 (MERCK, USA), was studied in this research. The experimental results indicated that the removal efficiency was influenced significantly by solution pH and the optimum operating pH was found to be in the range of 5–7. The removal of fluoride by Amberlite IR-120 resin was increased with the presence of sulfate ions in aqueous solution. The Langmuir and Freundlich isotherms can adequately describe the equilibrium behaviors of the adsorption processes. The surface reaction-limiting kinetic model can adequately describe the removal behaviors of fluoride ion by Amberlite IR-120 in batch systems. Results for column experiments indicate that the utilization of contact bed and the removal capacities improved with increasing empty bed contact time (EBCT). The Bed-Depth-Service-Time (BDST) model can describe the removal behavior of fluoride in the column adequately, indicating that the removal rate was possibly determined by the surface reaction step.

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Key Words: Cation Exchanger; Resin; Fluoride

INTRODUCTION

Fluoride ions present in aqueous environment are of great concern because of their possible accumulation and damage to the human tissues (1). The average fluoride concentration in seawater is about 1.4 mg/L, but the fluoride concentrations in surface and ground water vary with different regions. It was reported that as high as 67 mg/L of fluoride was found in some natural waters (2). The World Health Organization suggested a limiting concentration of 1.5 mg/L for fluoride present in drinking water (3). Therefore, several technologies have been developed for reducing the concentrations of fluoride from water sources. Currently, the most widely used technique is precipitation, which is usually carried out by adding calcium compounds to fluoride-containing waters to form calcium fluoride precipitates. The major problem associated with precipitation process is the generation of massive amounts of sludge (4). Researches on the removal of fluoride by various synthetic resins were reported. Popat et al. (3) used an aluminum-formed cation resin, Indion 225 (ACROS, Belgium), to study the removal of fluoride and the formation of aluminum-fluoride complexes on the resin surface was assumed to be the primary mechanism. However, Chikuma and Nishimura (5) studied the fluoride removals by a chloride-formed anion exchanger, Amberlite IRA-400 (MERCK, USA). The chloride ions held on the surface of anion resin are exchanged for fluoride ions in aqueous solution. Comparing the application of cationic and anionic resins, we found that the application of anionic resin was more easily interfered by the presence of foreign ions and more difficult to be regenerated. Therefore, in this particular study, aluminum-formed Amberlite IR-120, a strongly acidic cation exchanger, was used for the removal of fluoride from aqueous solution. The equilibrium models were established based on the results obtained from batch experiments to understand the adsorption behavior of fluoride in aqueous solutions. Moreover, the above studies focused primarily on batch experimental systems, and few works have been carried out on the kinetic behavior of this process for column tests. The primary research interest was in the effects of several operational factors on fluoride removal in adsorption columns in order to obtain more practical design data.

EXPERIMENTAL PROCEDURE AND ANALYSIS

The stock solutions used in this investigation were prepared with reagent-grade chemicals and RO-deionized water. Standard acid and base solutions

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(H_2SO_4 and NaOH) were prepared weekly for pH adjustment. The surface area of the resin, Amberlite IR-120, was measured by BET method using a Micromeritics ASAP 2000 analyzer (Varian, USA) and the zeta potential (pH_{zpc}) of resin was determined by direct titration method (6,7). In this research, the surface area and pH_{zpc} of Amberlite IR-120 resin was determined to be about 1.2 m^2/g and 8.5, respectively (aluminum form). The resin used in this research was transformed into aluminum form by adding the resin into 0.1 *N* aluminum nitrate solution for more than 24 hr, then rinsed with double-distilled water, filtered with a 0.45×10^{-6} m filter, and dried in a 70°C incubator. The amount of aluminum transformation can be calculated by the difference of initial and final aluminum concentrations of the aluminum nitrate solution (0.16∼0.86 mmol/g).

Batch kinetic studies were performed in a 2-L reaction vessel filled with fluoride solution of known concentration and the solution pH was maintained at the desired level using a Kyoto AT-210 automatic pH controller (Kyoto Elec., Japan). An Ika-Werk RW20 DZM mixing device (Ika Co. Ltd., Japan) was used at constant mixing speed of 210 rpm after a series of tests was performed to minimize the effect of bulk mass transfer on the reaction rate. A predetermined amount of resin was then added to the vessel and appropriate temperature control was maintained by containing the entire apparatus setup in a constant temperature water bath. Typical reaction runs lasted for at least 24 hr. At intermittent contact time periods, aliquots of the solution were transferred manually, filtered, and analyzed for fluoride and aluminum concentrations. Total sampling volumes were kept below 5% of the total solution volume.

Up-flow column exchange experiments were performed for continuous kinetic studies. The laboratory apparatus shown in Fig. 1 consisted of two vertical fixed-bed columns having an inner diameter of 2.0 cm, 16-cm height, and the two columns were operated simultaneously. Each column could be charged with predetermined amounts of resin. Solution flow rates were maintained steady with a Cole–Palmer creeping pump (Cole-Parmer, USA). The solution temperature was maintained at 30°C for all column experiments. Samples were taken by an Advantec SF-2120 fractional collector (Advantec Toyo Kaishai Ltd., Japan) at different time intervals and then filtered for pH determination and fluoride and aluminum concentration analysis. The concentrations of fluoride and aluminum were determined with a Dionex DX-120 ion chromatograph (Dionex, USA) and a Varian Spectra AA-20 spectrophotometer (Varian, USA), respectively.

RESULTS AND DISCUSSIONS

A series of batch experiments was carried out to study the effect of solution pH on the removal of fluoride by Amberlite IR-120 resin and the results are shown in Fig. 2. In most cases, the adsorption equilibrium seemed to be reached

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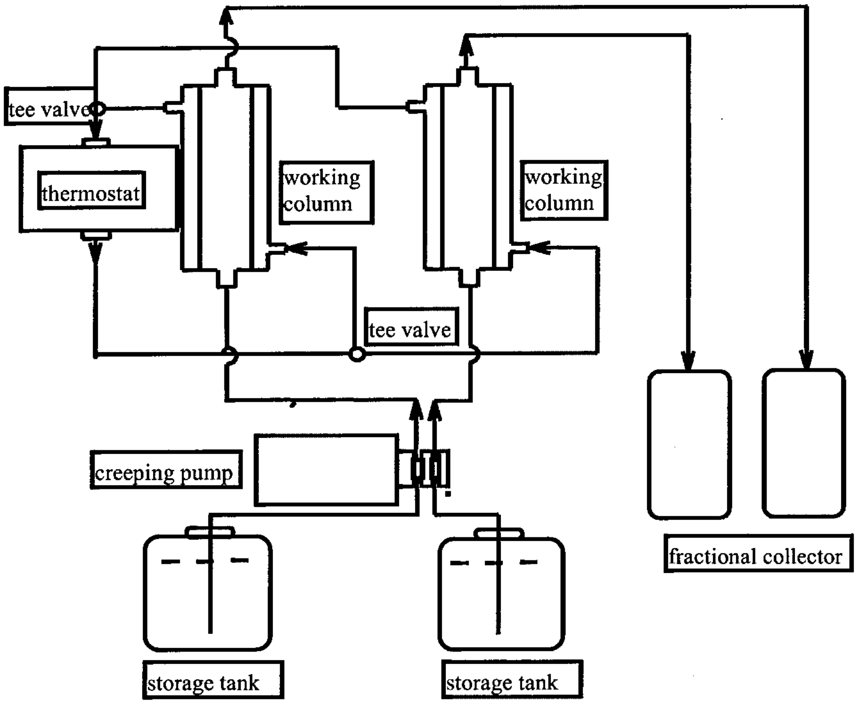

Figure 1. The schematic representation of the experimental apparatus in this work.

within 8–10 hr of contact time. For acidic solutions, the capacities of resin were relatively constant. The adsorption of fluoride is favorable for acidic solutions, possibly because of the electrostatic attraction that occurs when the negatively-charged fluoride ions present in aqueous solutions are attracted by the positively-charged surface of Amberlite IR-120 (the pH of acidic solutions are less than the pH_{zpc} of Amberlite IR-120).

The exchange capacities of Amberlite IR-120 resin for fluoride decreased rapidly for solution pH greater than 7.0, as shown in Fig. 2. The aluminum concentrations in aqueous solutions were also detected for the experiments. The results shown in Fig. 3 indicate that the amount of aluminum ions released is increased with the concentration of fluoride for solution of pH 4.0. Therefore, the reduction of fluoride removal by Amberlite IR-120 for alkaline solutions may be contributed by two factors: the repulsion of fluoride ion by the negatively-charged surface of resin; and the presence of excessive amounts of hydroxide ion, which competes for active sites on the resin surface. The adsorption rates were also found to decrease with increasing solution pH levels.

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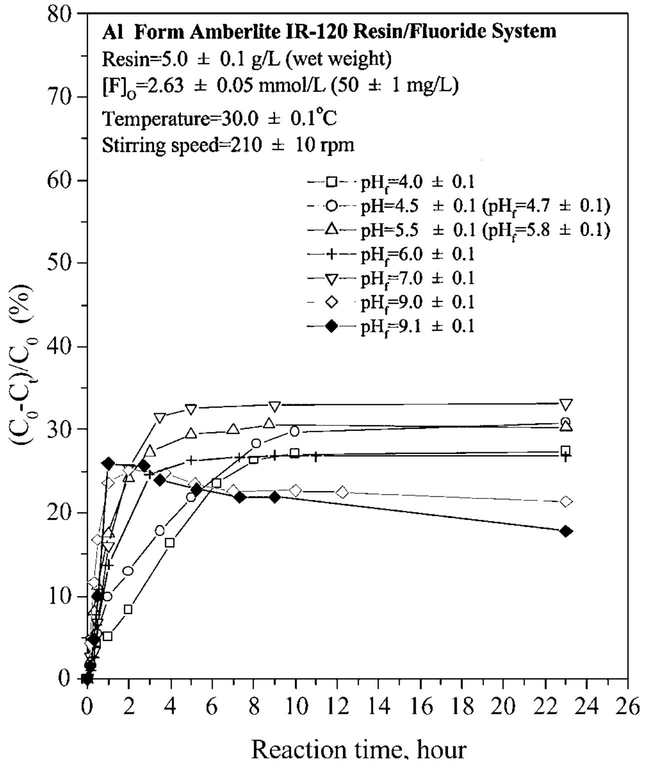

Figure 2. The removal of fluoride ion by Al-form Amberlite IR-120 resin under various solution pH values.

A series of batch experiments was conducted for various initial fluoride concentrations at pH 4.0 and 30°C to establish the adsorption isotherms. Both Freundlich and Langmuir models were fitted with the experimental data with relatively good applicability. The fitted parameters for these two models summarized in Table 1 indicate the removal of fluoride by Amberlite IR-120 and is assumed to be favorable and single-layered.

The change of solution pH was recorded for certain experiments conducted without pH control, for instance, results as shown in Fig. 4 for experiments conducted at pH 4.0. The solution pH was found to increase during the course of experiments, possibly because of the exchange of hydroxide and fluoride ions on the surface of the resin. The simplified removal mechanism is shown below.

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Table 1. Fitting Parameters of Two Adsorption Isotherm

	Isotherm Model	
Fitting Parameters	Freundlich Isotherm	Langmuir Isotherm
n	$0 < 0.4625 < 1$	—
Q_m (mmol/g)	—	0.244
K_{abs} (l/mmol)	—	0.848
r^2	0.992	0.999

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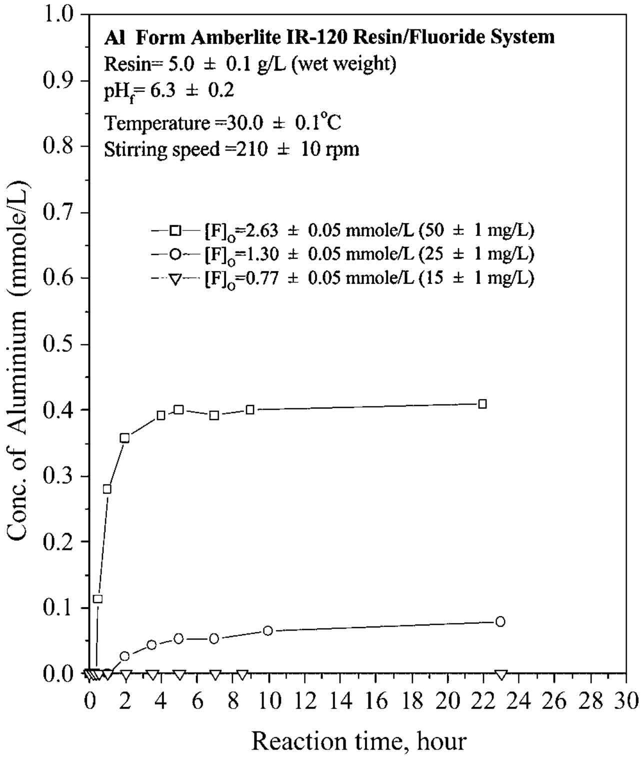

Figure 3. The release of dissolved aluminum ion during the fluoride removal by Al-form Amberlite IR-120 resin at various initial fluoride concentrations.

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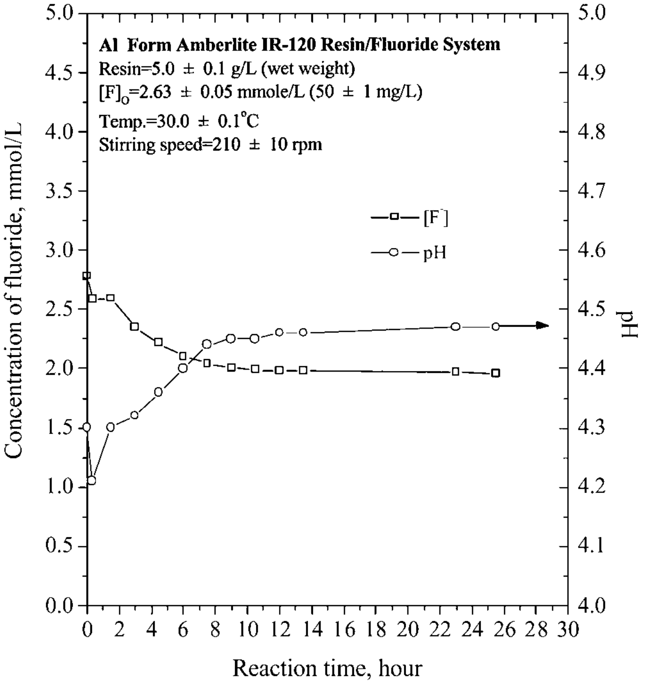

Figure 4. The temporal variation of solution pH value during the fluoride removal by Al-form Amberlite IR-120 resin.

For pH_i less than 6.0:

$$R\text{—}Al + F^- \rightleftarrows (R\text{—}Al\text{—}F)_{ad}$$

$$(R\text{—}Al\text{—}OH)_{ad} + F^- \rightleftarrows (R\text{—}Al\text{—}F)_{ad} + OH^-$$

For pH_i greater than 6.0:

$$R\text{—}Al + F^- \rightleftarrows (R\text{—}Al\text{—}F)_{ad}$$

where pH_i is initial pH value.

The kinetic studies on the removal of fluoride by Amberlite IR-120 resin were also conducted by analyzing the temporal variations of fluoride concentration for experiments conducted at different solution pH, as shown in Fig. 2. Mixing in the batch systems was kept well enough to minimize the effect of bulk diffusion control on the exchange rate. Therefore, the removal of fluoride by resin is assumed to be surface-reaction controlled. The calculated global

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Table 2. The Calculated Rate Constants and Exchange Capacity for Fluoride Removed by Al-form Amberlite IR-120 Resin at Various Solution pH_f

pH_f	4.0 ± 0.1	4.7 ± 0.1	5.8 ± 0.1	6.0 ± 0.1	7.0 ± 0.1
k(g/min mol)	10.53	12.38	31.65	31.45	23.72
q_0(mol/g)	1.52×10^{-4}	1.62×10^{-4}	1.56×10^{-4}	1.42×10^{-4}	1.71×10^{-4}

exchange rates based on the experimental results were found to be approximately first order with the fluoride concentration and could be expressed by the following second-ordered rate equation:

$$-r_A = -kC_fS \tag{1}$$

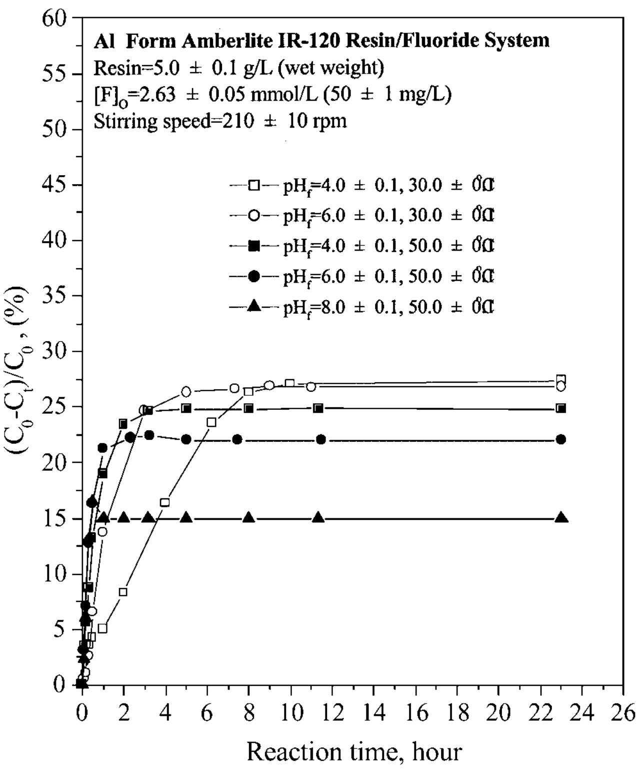

Figure 5. The temporal variation of fluoride removal by Al-form Amberlite IR-120 resin at different solution temperature and pH_f.

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Table 3. The Removal Amount of Fluoride in Al-form Amberlite IR-120 Resin Column System Under Various Resin Dosages and Flow Rates

Resin Dosage (g)	Flow Rate (mL/hr)	EBCT (min)	$t_{0.5}$ (min)	Removal Amount (mmol/g)
30	280	5.72	240	0.079
30	370	4.59	140	0.056
30	460	3.48	50	0.038
30	700	2.42	35	0.044
20	280	10.43	90	0.066
30	280	10.43	190	0.061
40	280	10.43	450	0.072
50	420	6.06	120	0.046

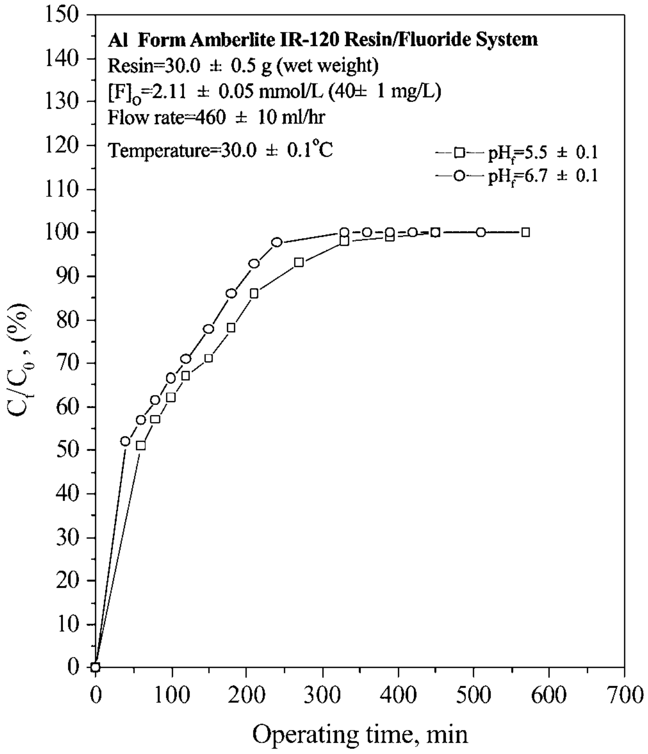

Figure 6. The breakthrough behaviors of fluoride ion by Al-form Amberlite IR-120 resin in column system at different solution pH_f.

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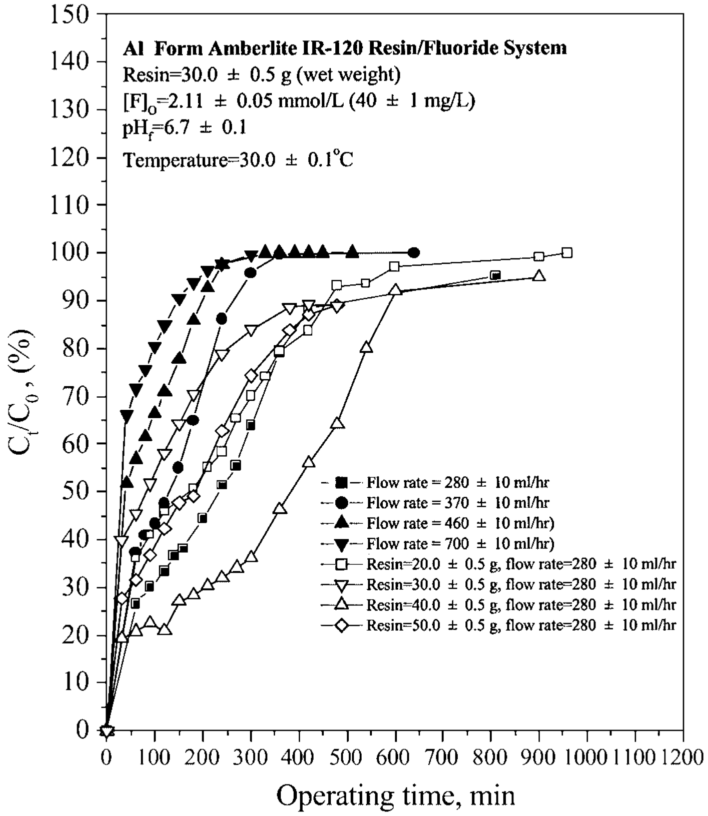

Figure 7. The breakthrough behaviors of fluoride ion by Al-form Amberlite IR-120 resin in column system at various flow rates and resin dosages.

where C_f and S are the concentrations of fluoride in aqueous solution and the active sites on the surface of resin, respectively. By establishing the fluoride and site balances, the second-ordered rate equation is found satisfactory to describe the exchange behavior of fluoride in batch systems. The calculated K and q_o (exchange capacity, mol/g) values are summarized in Table 2. The exchange capacity of resin is relatively constant for experiments conducted at different pH conditions. However, the rate of exchange varies because the surface charge of resin is strongly dependent on solution pH.

The removal of fluoride ions by Amberlite IR-120 resin was studied at 50°C for different solution pH_f (final pH) levels, the experimental results are also shown in Fig. 5. Exchange capacities of resin are decreased by the elevation of solution temperature, while exchange rates are much faster at 50°C compared

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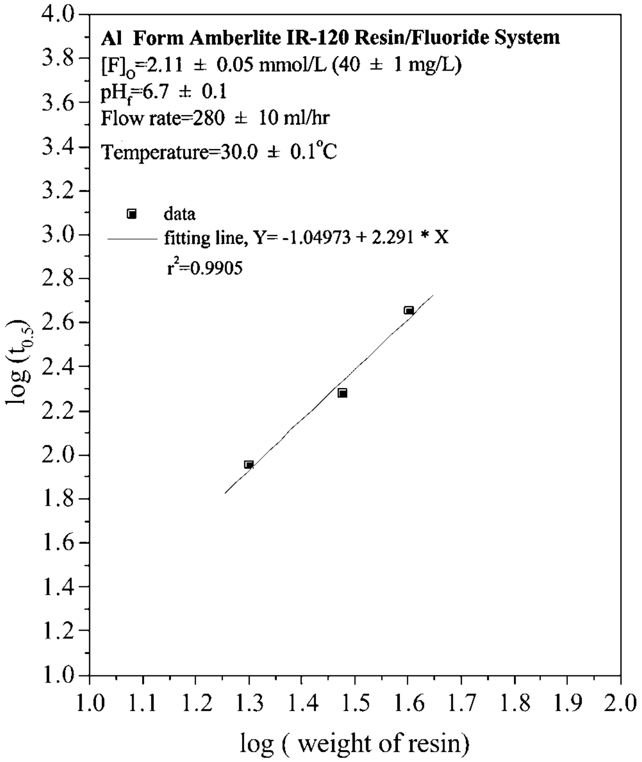

Figure 8. The power law correlation of $t_{0.5}$ to ETBC for column systems.

with the rates at 30°C, especially for acidic solutions. The calculated activation energies at different solution pH levels are determined to be 7–15 kcal/mol using Arrhenius relationship.

Up-flow column experiments were conducted in this study to examine exchange behavior under various conditions. For instance, Fig. 6 indicates the fluoride removal by Amberlite IR-120 at two different pH_f values. The exchange capacities of resin were calculated to be 0.059 and 0.038 mmol/g for solution pH_f of 5.5 and 6.7, respectively. As the contact time of liquid and resin for a column system is much less than that for a batch system, the calculated values of exchange capacity of column systems are consequently much smaller than the values for batch systems. Results for experiments conducted at different flow rates and resin dosages are summarized as shown in Fig. 7. The temporal behavior shown in Fig. 7 is studied by using two parameters. One is the $t_{0.5}$, which

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Table 4. The Adsorption Rate Constants in Al-form Amberlite IR-120 Resin Column System Under Fixed Removal Amount (q_0) Under Various Flow Rate via BDST Model

Resin Dosage (g)	Flow Rate (mL/hr)	EBCT (min)	K (l/min mmole)
30	280	5.72	0.00196
30	370	4.59	0.00516
30	460	3.48	0.0092
30	700	2.42	0.01441

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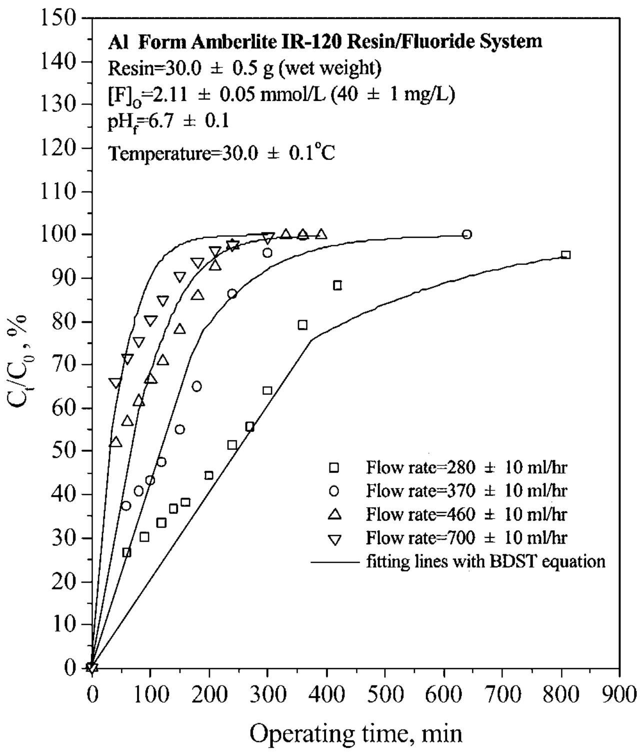

Figure 9. The modeling of column experimental results conducted at different flow rates by BDST model.

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is defined as the operating time of the column, to reach a 50% breakthrough concentration. The other is empty bed contact time (EBCT), which is directly proportional to either bed depth or flow rate. Table 3 shows the calculated $t_{0.5}$ and EBCT values for the breakthrough curves shown in Fig. 7. Increasing flow rate or decreasing resin dosage accelerated the breakthrough of the column. A power law correlation, $T_{0.5} = 3.75 \times \mathrm{EBCT}^{2.33}$, was obtained as shown in Fig. 8.

The key issue in designing ion exchange columns is to accurately predict the service time of the column before regeneration or replacement of resins. Efforts have been made by various previous researchers (8–10) to correlate the process variables and to develop comprehensive methods of calculating process performance. The Bed-Depth-Service-Time (BDST) model is utilized in this research, which relates the service time of a column to the height of resin in the column. As the resin mass is directly proportional to the height of fixed-bed cylindrical column, the resin mass is more frequently used in the BDST model. Thus, the model is expressed as:

$$t = \frac{q_0}{C_0 v} M - \frac{1}{kC_0} \ln\left(\frac{C_0}{C_t} - 1\right) \tag{2}$$

where t is the service time (min); q_0 is the exchange capacity (mol/g); C_0 is the initial concentration of solute (M); v is the volumetric flow rate (l/min); M is the mass of resin in the column (g); k is the rate constant (l/min–mol); C_t is the effluent concentration of solute (M).

From the slope and the intercept of the linear plot of t vs. M, the adsorption capacity (q_0) and the rate constant (k) were calculated for each set of experiments. In this research, the value of q_0 is chosen to be 0.0333 mmol/g based on the average exchange capacity of resin for many column experiments conducted at pH 6.7 and 30°C. The k values are therefore calculated for experiments carried out at different flow rates as shown in Table 4. The experimental results were fitted with relatively good accuracy as shown in Fig. 9, indicating that the removal rate of fluoride by Amberlite IR-120 is mainly determined by the surface reaction step. The k values are found to decrease with increasing EBCT values and a linear decay correlation of k and EBCT was obtained and is shown in Fig. 10. This phenomenon might have resulted from the following reasons: (1) the assumption of uniform energy for surface sites in BDST model is not adequate in this study; (2) the effect of diffusion is ignored in BDST model, which might not be applicable in this study. Therefore, further improvement of the adequate modeling equation is necessary.

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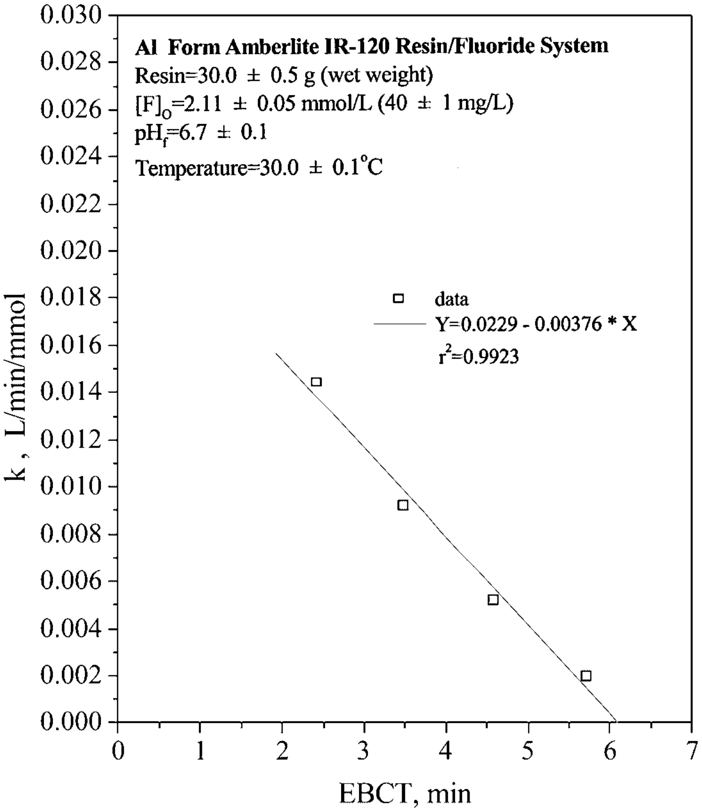

Figure 10. The correlation of EBCT and rate constant for column system.

SUMMARY

The removal of fluoride by aluminum-formed Amberlite IR-120 resin was found to vary over the entire solution pH, possibly because of electrostatic interactions between the surface of Amberlite IR-120 resin and the dominant fluoride species in solution. It is feasible to achieve relatively good removal for solution of pH less than 7.0 with the application of sufficient amounts of Amberlite IR-120 resin. The developed equilibrium model based on coordination chemistry can describe adequately, the equilibrium behavior of the investigated systems. A second-ordered kinetic model based on surface-reaction consideration fits the temporal data with fairly good accuracy. The effect of solution temperature was found to have minimum impact on the exchange capacity of resin, but the exchange rates were much faster at higher solution temperature. For

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experiments conducted in a column, it was shown that increasing the flow rate or decreasing the resin dosage accelerated the breakthrough of fluoride through the resin column. The BDST model was used to describe the exchange behavior of an exchange column. Even though experimental results indicated that further modification of the BDST model is necessary, this model still offers an alternative to estimate the exhaust time of an exchange column.

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