

Removal of boron from refined brine by using selective ion exchange resins

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Abstract

Boron removal by ion exchange resin from refined brine which was used to produce low-boron lithium salts was studied. A new boron-specific resin, XSC-800 was used in the experiments for the separation of boron. The column-mode and batch-mode sorption studies were both performed so as to obtain the optimum conditions for boron removal from refined brine. Parameters such as flow rate of brine, boron concentration, temperature, pH, height/diameter (*H/D*) ratio of the column, anion concentration, stirring speed and diameter of the resin were investigated. The results showed that the removal effect of boron by XSC-800 improved with increasing temperature, pH, *H/D* ratio, and with decreasing the flow rate of brine, boron concentration, chloride anion concentration and diameter of the resin. While the stirring speed and the recycles of the resin had no significant effects on boron removal. As a result, boron can be removed from refined brine much completely by the resin at the optimum conditions. On the other hand, kinetics of the exchange process was studied by using the moving boundary model. In order to describe the kinetics more accurately, the model was modified by introducing a time correction factor. The results showed that the rate-determining step of this process under the conditions studied was controlled by particle diffusion. In addition, the apparent activation energy E_a of the process was found to be 20.38 kJ/mol. © 2007 Elsevier B.V. All rights reserved.

Keywords: Boron removal; Ion exchange; XSC-800; Kinetics; Moving boundary model

1. Introduction

Boron is widely distributed in the environment, occurring naturally or from anthropogenic contamination, mainly in the form of boric acid and borate salts. Boric acid and borates have extensive industrial use in the manufacture of glass and porcelain; in wire drawing; in the production of leather, carpets, cosmetics and photographic chemicals; for fireproofing fabrics and weatherproofing wood. During the production of boron compounds, many of which are introduced into the environment in the form of waste.

Although boron is a micronutrient for some plants, animals and humans, the range between deficiency and excess is narrow. The acceptable daily intake of boron is $0.3 \text{ mg kg}^{-1} \text{ day}^{-1}$,

which is well above the normal exposure levels. Yet WHO has recommended a limit of 0.3 mg/L for drinking water [1].

There are many methods suggested for boron removal from aqueous solutions. Adsorption by magnesium, ferrous and aluminum oxides and adsorption by fly ash, clay and red mud are reported to be useful only for concentrated boron solutions and not for trace quantities [2–7]. Solvent extraction, reverse osmosis (RO) and electro-deionization have been demonstrated to be effective for removal of boron in rather low concentrations [8–10]. Besides, ion exchange technique which is now most extensively used has been proven to be an effective method for removing micro-amount of boron from aqueous solutions.

For the most common anions, the following retention order on resin can be established, the borate being the first eluted ion: $\text{SO}_4^{2-} > \text{NO}_3^- > \text{PO}_4^{3-} > \text{C}_2\text{O}_4^{2-} > \text{Cl}^- > \text{B}(\text{OH})_4^-$. Consequently, it is the worst retained because of its low affinity to resin. Therefore, it is very necessary to use specific resins for boron removal. It was reported that Amberlite IRA 743, a

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Table 1
Properties of the resin XSC-800

Matrix	Macro-porous cross-linked polystyrene-DVB
Functional groups	<i>N</i> -Methylglucamine
Appearance	Spherical beads
Screen size range	0.315–1.25 mm
Ionic form as shipped	Free base
Theoretical boron capacity	≥5 g/L
Total capacity	≥2.6 mmol/(g day)
Moisture retention	45–55%
Temperature limit	373 K

boron-specific resin, had been used for boron removal from geothermal waters containing boron with 19 mg/L and with 99% of which removed [11].

In the west of China, there exist abundant boron resources in salt lakes which cover about 40% of the total reserves in China. In this work, a boron-specific resin, XSC-800 was investigated to remove micro-amount of boron from the refined brine from which most of boron had been separated and Li_2CO_3 to be produced. The presence of boron, even in a very low concentration, is frequently a major problem in the production of Li_2CO_3 , for it will affect the purity of the product and pollute the tail stripper to be drained seriously. Therefore, it is very necessary to remove this part of boron firstly. The resin XSC-800 characterized by unique *N*-methylglucamine functional groups was used to remove micro-amount of boron from said brine containing high concentrations of alkali salts. Extensive investigations were carried out so as to better know the effects of parameters on boron removal and the kinetics of the boron adsorption process.

2. Experimental

2.1. Materials and chemicals

The resin XSC-800 was kindly sent by Sian power resin factory, China. The chemical and physical properties of the chelating resin are given in Table 1. The refined brine whose composition summarized in Table 2 was provided by Qinghai Lithium Co. Ltd., China.

The resin was sieved by a vibro-lab sieving machine. After sieving, each mesh size fraction was collected for later use.

High purity water having a boron blank of lower than 0.4 ng/mL, produced by sub-boiling distillation and passage through boron-specific resin, was used.

Table 2
Main chemical composition of refined brine

Ionic species	Concentration (g/L)
Cl^-	50.0
Na^+	18.0
Li^+	10.0
Mg^{2+}	0.0006
Ca^{2+}	0.0100
Boron	0.0400–0.4000

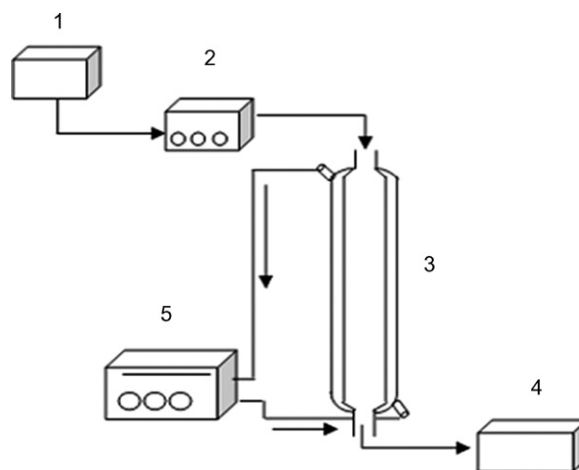


Fig. 1. Schematic diagram of column-mode experimental system. (1) Feed tank; (2) peristaltic pump; (3) ion exchange column; (4) sample tank; (5) thermostat.

2.2. Column-mode sorption-elution studies

The column was made of glass and had an internal diameter of 2 cm. The refined brine was delivered down-flow to the column using a peristaltic pump. The temperature was controlled by a thermostat connected to the column. From the outlet of the column, samples were taken per 2 bed volume (BV) fractions of the effluent. Breakthrough curves of boron were obtained by analysis of each sample. After the sorption, the resin was washed with 1 BV deionized water. The elution of boron from the resin was performed with 10% H_2SO_4 solution passed through the column at a flow rate of 5 bed volume per hour (BV/h). And then, the resin was regenerated with 4% NaOH solution. Both flow rates of elution and regeneration were controlled by a peristaltic pump. The experimental setup was given in Fig. 1.

In this work, the most important aspect is not to obtain eluted concentrations of boron below the detection limit of the analytical method selected and used, but rather to determine the moment in which the concentration of the effluent reaches the permitted value of 1 mg/L. This is known as the breakthrough point, from which the discharge through the column must be interrupted and the resin must be regenerated. This can also be defined as the breakthrough capacity as the mass of solute separated by the exchanger at the breakthrough point.

2.3. Batch-mode sorption studies

A batch reactor was used for boron removal from refined brine by the exchange reaction. The temperature was controlled with a 501 model thermostat (Shanghai Experimental Apparatus Co. Ltd., China) linked to the reactor. The stirring speed was controlled by a precise electro-motion stirrer. The experimental setup for this study was given in Fig. 2.

2.4. Boron analysis

The concentrations of boron in solutions were examined using the Azomethine-H spectrophotometric method which was in common use due to its sensitivity, selectivity, accuracy and

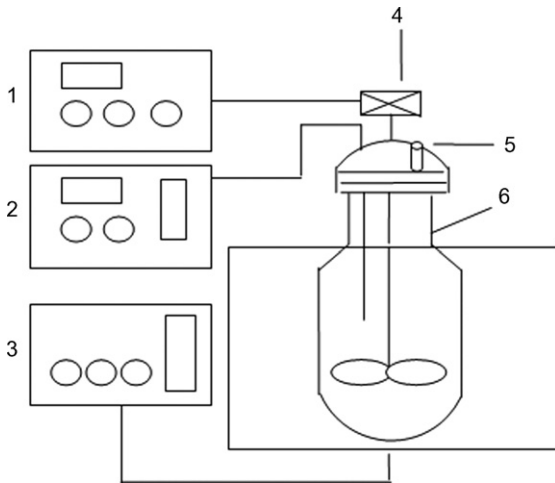


Fig. 2. Schematic diagram of batch-mode experimental system. (1) Stirring controller; (2) pH meter; (3) thermostat; (4) stirrer; (5) discharge port; (6) reactor.

also due to the fact that it was simpler than other methods [12]. The absorbance of the boron-Azomethine-H complex at the wavelength of 410 nm was measured using 7230G model spectrophotometer (Shanghai Precise Scientific Apparatus Co. Ltd., China). The precision of this method was $\pm 2.0\%$.

3. Results and discussion

3.1. Effects of parameters

The effects of parameters such as brine flow rate, concentration of boron, temperature, pH, H/D ratio of the column and anion concentration were investigated intensively by column-mode operation.

3.1.1. Effect of brine flow rate

The effect of brine flow rate on boron removal was examined at 5, 16 and 30 BV/h. Boron concentration of 40 mg/L, temperature at 293 K, pH at 10 and H/D ratio of 15 were kept constant in the experiments. The breakthrough curves of boron obtained at different flow rates were given in Fig. 3. As shown in Fig. 3, the faster the flow rate, the sooner the breakthrough, i.e. the removal rate of boron decreased with increasing brine flow rate. And the removal rate can be calculated by the following formula:

$$Q = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

where Q (%) is the removal rate of boron, C_0 the initial concentration of the boron, and C is the concentration of boron in the effluent. On condition that C_0 is constant, Q will be in inverse proportion to C .

The reason for the phenomenon might be as follows: as the flow rate of the refined brine increased, the contact time for it with the resin was shortened. Therefore, there was not enough time for the resin to adsorb boron at high brine flow rate, and the breakthrough point reached ahead with low removal rate of boron.

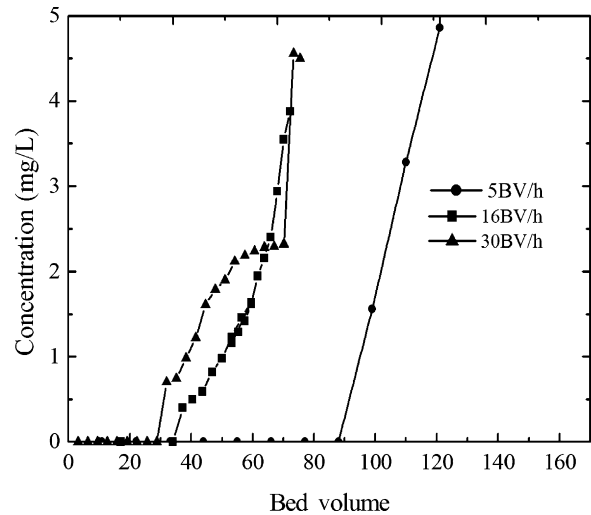


Fig. 3. Effect of brine flow rate on boron removal.

3.1.2. Effect of boron concentration

Various boron concentrations can be reached by pretreatment of the brine. The effect of boron concentration on boron removal was examined at 40, 50 and 100 mg/L. Brine flow rate of 16 BV/h, temperature at 293 K, pH at 10 and H/D ratio of 15 were kept constant in the experiments. The breakthrough curves of boron obtained at different boron concentrations were given in Fig. 4.

The results showed that the time to reach the breakthrough point was significantly shortened with increasing the initial boron concentration as shown in Fig. 4, which indicated that high boron concentration was not favorable to the removal of boron. This might be because there were not enough active sites on the resin to adsorb so much boron with high initial concentrations.

3.1.3. Effect of temperature

The effect of temperature on boron removal was examined at 293, 303, 313, and 323 K. Brine flow rate of 16 BV/h, boron concentration of 40 mg/L, pH at 10 and H/D ratio of 15 were kept constant. The results obtained were given graphically in

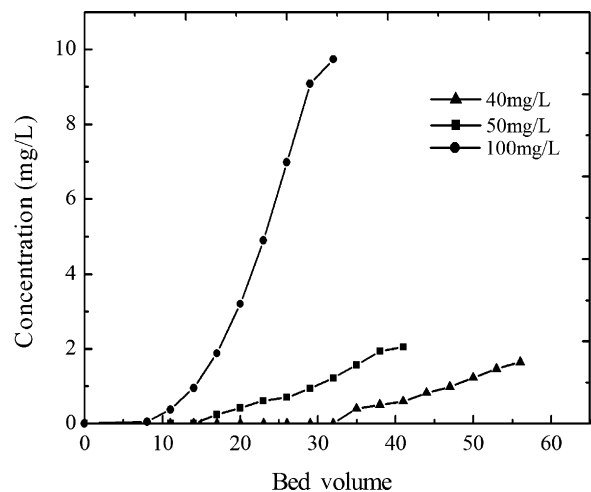


Fig. 4. Effect of boron concentration on boron removal.

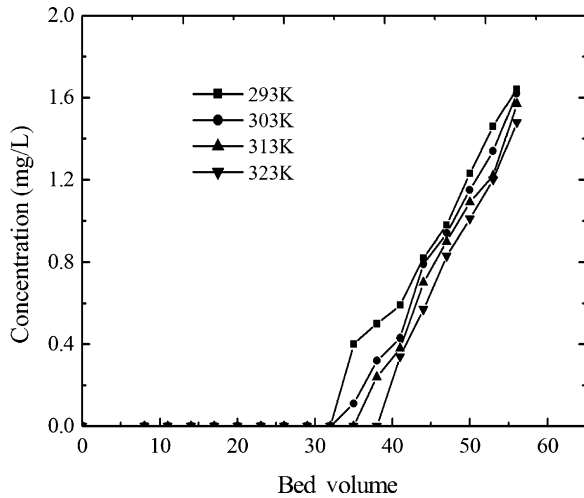


Fig. 5. Effect of temperature on boron removal.

Fig. 5 which showed that the boron removal rate increased with increasing temperature. This can be explained as follows: as the temperature rose, the random motion of boron was accelerated which meanwhile promoted the exchange process. Consequently, the adsorption rate of boron increased.

3.1.4. Effect of pH

The effect of pH on boron removal was examined at the pH range of 4–12. In the experiments, brine flow rate of 16 BV/h, boron concentration of 40 mg/L and *H/D* ratio of 15 were kept constant. The adsorption capacities (q , mg/g) obtained at different pH values were given in Fig. 6. The adsorption capacity of q can be defined as the formula below:

$$q = \frac{(C_0 - C)V}{M} \quad (2)$$

where C_0 is the initial concentration of boron in the brine, C the concentration of boron in the effluent, V the volume of the effluent, and M is the mass of the resin.

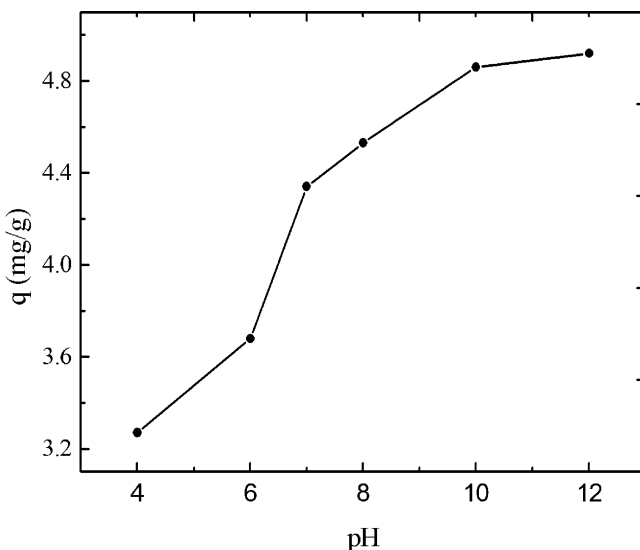


Fig. 6. Effect of pH on removal of boron.

As shown in Fig. 6, adsorption capacity of boron on the resin increased with increasing pH. Actually, the resin only extracts the $B(OH)_4^-$ species from neutral or alkaline solutions. The $B(OH)_4^-$ species, which can be adsorbed by the resin, is the main boron species when the pH value of the loaded solution in the column is high. When the pH value is lower than 7, the resin containing aminated chloromethylated styrene-divinylbenzene copolymer functional group can adsorb Cl^- and release OH^- . The release of OH^- leads to the increase in the pH value of solution in the column, hence the formation of $B(OH)_4^-$ species and the removal of boron.

3.1.5. Effect of *H/D* ratio of the column

The effect of *H/D* ratio of the column on boron removal was examined at 10, 12 and 15. In the experiments, brine flow rate of 16 BV/h, boron concentration of 40 mg/L, pH at 10 were kept constant. The breakthrough curves of boron obtained were given in Fig. 7. An increase of boron adsorption capacity with the increase of *H/D* ratio was observed. As the *H/D* ratio increases, the liquid distribution can be improved and the contact time of liquid–solid phase increases, so does the boron removal rate.

3.1.6. Effect of chloride anion concentration

The effect of anion concentration with Cl^- as example on boron removal was examined at 50, 75 and 100 g/L. The Cl^- concentration over 50 g/L can be obtained by adding NaCl to the brine. In the experiments, brine flow rate of 16 BV/h, boron concentration of 40 mg/L, pH at 10 and *H/D* ratio of 15 were kept constant. The breakthrough curves of boron obtained were given in Fig. 8. It was shown that the new boron-specific resin had higher capacity in lower ionic strength solutions. This may be because that the resin XSC-800 not only adsorbs $B(OH)_4^-$ but also Cl^- in the solution. When the concentration of Cl^- is much higher than $B(OH)_4^-$, an adsorption competition occurs between Cl^- and $B(OH)_4^-$. Thus, the anion concentrations in the refined brine should be controlled as low as possible so as to remove the boron completely.

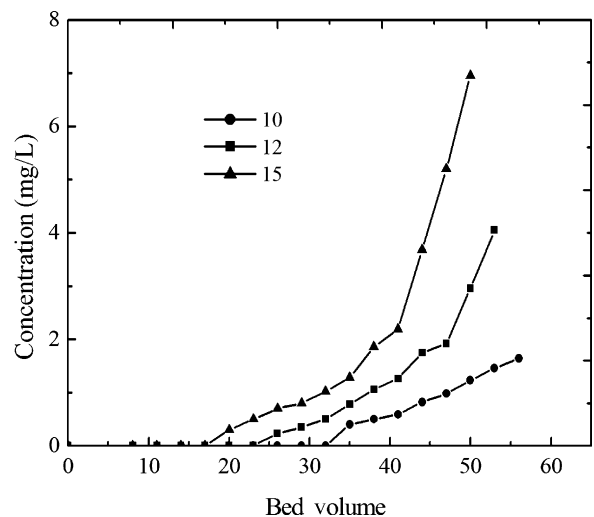


Fig. 7. Effect of *H/D* ratio.

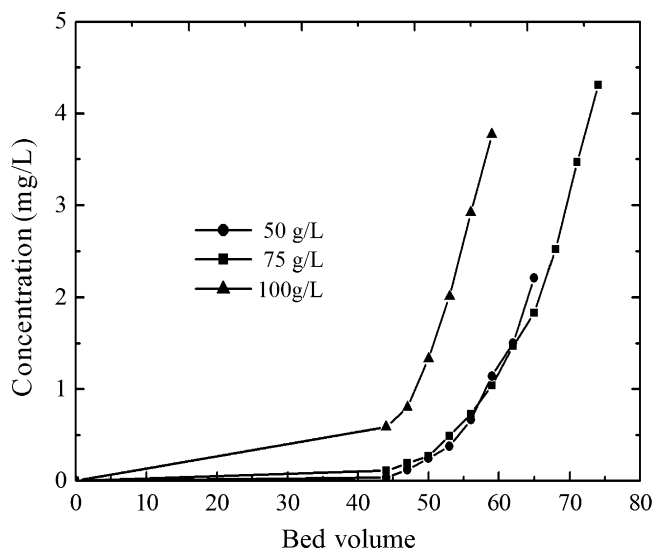


Fig. 8. Effect of chloride anion concentration on boron removal.

3.1.7. Column-mode recycle test

Resin life is one of the important parameters for determining a kind of resin to be applied in industrial production or not. The resin life was tested by resin adsorption–regeneration cycles. As shown in Fig. 9, there was no obvious difference for the resin exchange capacity after recycles which indicated that the boron-specific resin XSC-800 had good stability and service life.

Under the optimal conditions mentioned above, the boron can be removed much completely by selective ion exchange resin XSC-800. The treated refined brine with boron concentration of 1 mg/L can meet the requirement for producing low-boron Li_2CO_3 .

3.2. Kinetic analysis

3.2.1. Theoretical model

In order to get insight into the reaction mechanisms and to determine kinetic parameters, moving boundary model was chosen to fit the data for boron removal by ion exchange resins as a

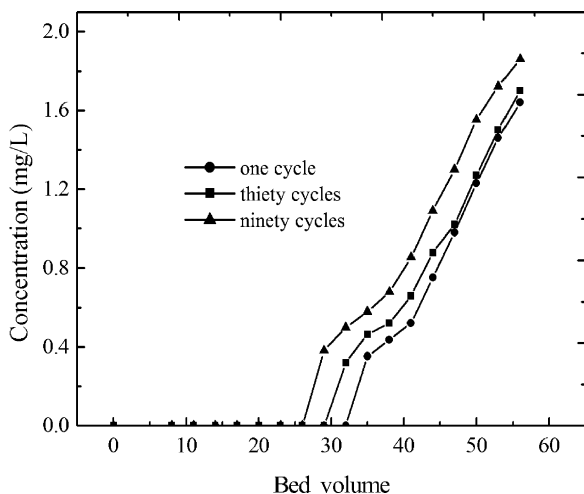


Fig. 9. Effect of recycles on exchange capacity of the resin.

first approximation in this paper. The model proposed by Helfferich in 1965 supposed that some ion-exchange reactions were advanced from surface to the center of the spherical particles layer by layer and there existed a specific boundary between the reacted and un-reacted zones. For spherical particles, the relationships between time and fractional conversion were as follows [13]:

- when fluid film diffusion controls

$$t = \frac{aQr_0}{3C_0K_f} F = \frac{1}{k_F} F \quad (3)$$

- when particle diffusion controls

$$t = \frac{aQr_0^2}{6\bar{D}C_0} [1 - 3(1 - F)^{2/3} + 2(1 - F)] = \frac{1}{k_D} P(F) \quad (4)$$

- when chemical reaction controls

$$t = \frac{r_0}{K_c C_0} [1 - (1 - F)^{1/3}] = \frac{1}{k_C} G(F) \quad (5)$$

- there into,

$$F = \frac{C_0 V_0 - (C_n V_n + \sum_{i=1}^{n-1} C_i V_i)}{MQ}, \quad n \geq 2 \quad (6)$$

where F is the exchange degree of boron, t the time, C_0 the initial concentration, V_0 the initial volume, C_n the boron concentration at the time required, V_n the volume at the time required, C_i the boron concentration of solution extracted, V_i the volume of extracted solution, M the mass of resin, Q the exchange capacity of resin, \bar{D} the effective diffusion coefficient of counter-ion, r_0 the diameter of resin, a the proportional coefficient, K_f the coefficient of film diffusion, K_c the reaction constant, k_F the rate constant for fluid film diffusion control, k_D the rate constant for particle diffusion control and k_C is the rate constant for chemical reaction control.

The success of this model has led it to be routinely used in the analysis of ion exchange kinetics. Although it has been used to describe the rate of uptake of water-soluble species on biopolymers, some doubts have been raised as to its applicability in some instances. So, different modified moving boundary models were proposed later so as to describe the kinetics of different systems properly [14–18].

3.2.2. Fitting of the data

To determine the nature of the control, the experimental data obtained by batch-mode operation under high stirring speed were fitted using the said equations, respectively, to determine which was applicable to the boron adsorption process by the resin. Generally, the influence of the fluid film diffusion can be neglected under high stirring speed. Figs. 10 and 11 represented linear fitting of the data to the moving boundary model described by Eqs. (5) and (4) at different temperatures as an example. Initially, $G(F)$ showed a linear dependence with time, while deviated later, which indicated that at the beginning of the reaction the chemical reaction determined the reaction rate shown in Fig. 10. Late, while the product layer was developed,

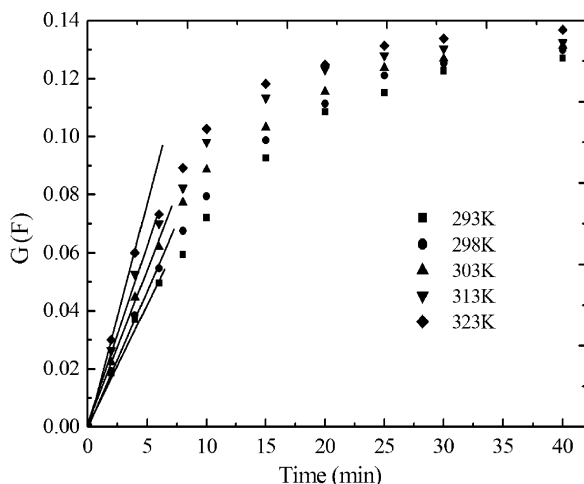


Fig. 10. Linear fitting of the data to the moving boundary model described by Eq. (4).

it was the particle diffusion mechanism that controlled the reaction, as suggested by the linearity of $P(F)$ at the late time of reaction shown in Fig. 11.

For the period of chemical reaction control was very short compared with the particle diffusion mechanism, it can be seen that the boron adsorption process by the resin was mostly controlled by particle diffusion. And it can be believed roughly that the kinetics of the particle diffusion mechanism can represent the kinetics of the whole process. So, the exchange kinetics of the particle diffusion control was mainly studied in this paper.

The apparent reaction rate constant k_D of the exchange process at different temperatures, i.e. slope of the lines, can be obtained from Fig. 11.

The plot of $\ln k_D$ versus $1/T$ was given in Fig. 12 according to the Arrhenius equation as below:

$$\ln k_D = A - \frac{E_a}{RT} \quad (7)$$

where k_D is the reaction rate constant for particle diffusion control, A the pre-exponential factor, E_a the apparent activation energy, R the gas constant and T is the temperature.

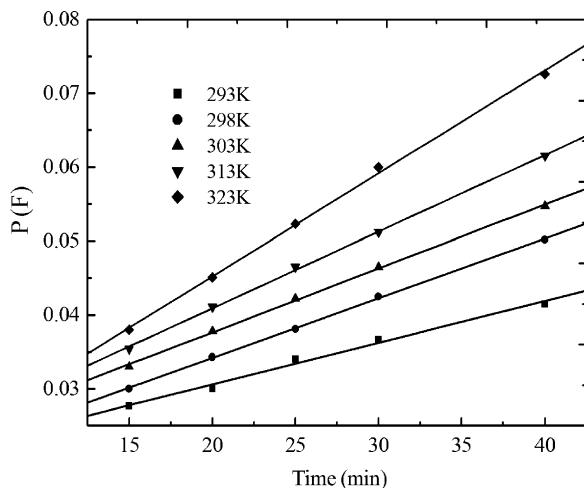


Fig. 11. Exchange kinetics of boron at different temperatures.

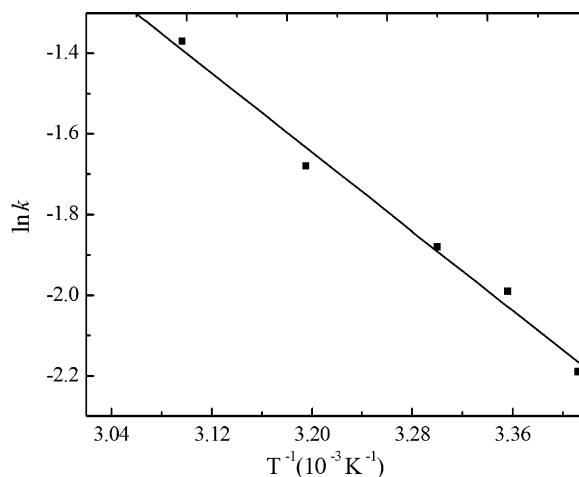


Fig. 12. Diagram of Arrhenius.

Fitting the data in Fig. 12, and the results were obtained as shown in Eq. (8) with correlation coefficient of 0.9979.

$$\ln k_D = 6.199 - \frac{2.452}{T} \quad (8)$$

The apparent activation energy E_a of the exchange process was found to be 20.38 kJ/mol by comparison of Eqs. (7) and (8).

The effect of stirring speed on boron removal was examined at 100, 500 and 750 rotation per minute (r/min) in a batch reactor. The results given in Fig. 13 showed that the stirring speed had no significant effect on boron removal under the conditions of this experiment. And this meant that there was nearly no fluid film diffusion resistance and boron removal rate was controlled by particle diffusion in this process.

The resin with 0.75 and 0.45 mm particle size was selected and investigated in the experiments to see the influence of resin diameter on boron adsorption. And the results were given in Fig. 14, from which an increase of the boron adsorption with the decrease of resin diameter was observed. This might be because bigger particles had smaller total specific surface area and fewer reaction active spots than smaller ones, hence the low-boron exchange rate.

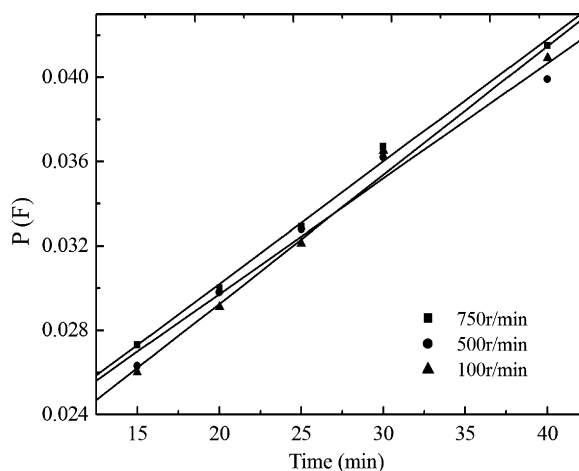


Fig. 13. Exchange kinetics of boron at different stirring speed.

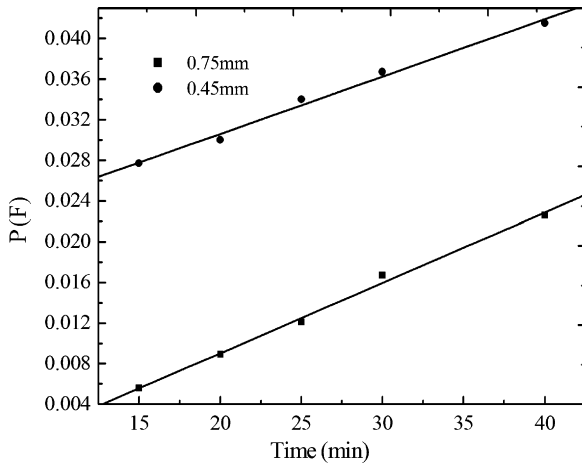


Fig. 14. Exchange kinetics of boron in different resin diameters.

It was found that there existed a linear relationship between removal rate and $1/r_0^2$ after calculation which further indicated that the adsorption process was controlled by particle diffusion.

Good linear relationship was found between $P(F)$ and t at different boron concentrations with correlation coefficients of 0.9900 (50 mg/L), 0.9974 (100 mg/L), 0.9990 (200 mg/L), 0.9981 (250 mg/L) and 0.9979 (400 mg/L), respectively, as shown in Fig. 15. From Fig. 15, straight slope, i.e. the apparent rate constant of the boron exchange process can be obtained, and they are 0.0002, 0.0006, 0.0026, 0.0037 and 0.0051, respectively.

3.2.3. Model modification

The testing whether or not Eq. (4) should be applicable requests two facts, linearity of the data and the convergence of the lines to the origin. Interestingly, the linear relationship between $P(F)$ and t was established during almost the whole process under the conditions studied, but the straight line did not go through the origin of the graphs. This deviation may be caused by the foregoing assumption. The similar problem was encountered by Li et al. when they dealt with the kinetics for desulfurization by ZnO with this model [19,20]. It seems that

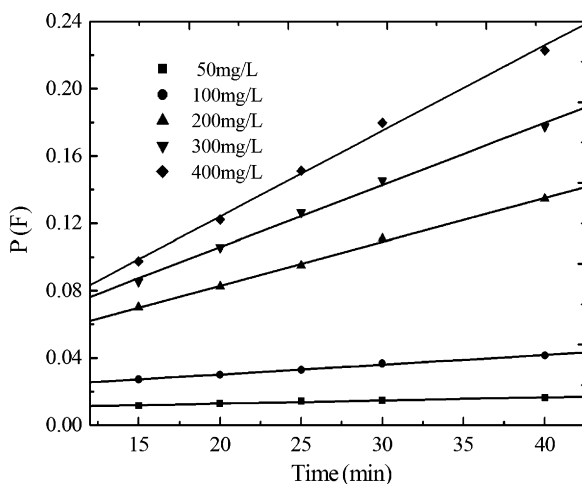


Fig. 15. Exchange kinetics of boron at different concentrations.

the original moving boundary model could not describe satisfactorily the exchange process in this paper, which suggests that some necessary modifications are needed in order to reduce the deviations and to better explain the process. For the liquid film diffusion resistance can be neglected, so the modified model can be expressed as below.

When it is chemical reaction control at the beginning of the reaction with short period, and then transferred to diffusion control later lasted almost the whole process, Eq. (4) can be modified in the form as below:

$$t = \theta + \frac{aQr_0^2}{6\bar{D}C_0} [1 - 3(1-F)^{2/3} + 2(1-F)] = \theta + \frac{1}{k_D} P(F) \quad (9)$$

where θ is the correction factor with units of minutes indicating the contribution of chemical reaction, which can be seen as the time from the beginning of the reaction to the point that the particle diffusion control starts from.

In fact, as early as 1970s, similar modification of the model for the reactions with a moving boundary had been made by Szekely et al. to fit the kinetic lines which did not go through the origin [21–23].

Clearly, the modified model can express the exchange process more accurately as shown in Figs. 11 and 13–15, and can explain why the straight lines did not go through the origin of the graphs.

4. Conclusions

The following results were determined with the evaluation of the obtained data.

- (1) The boron-specific resin XSC-800 has been used to remove boron from refined brine with satisfactory result.
- (2) Parameters influencing boron removal from the refined brine were investigated with the results as below: boron removal decreased with increasing brine flow rate, boron concentration, anion concentration and diameter of resin; and increased with increasing temperature, pH and H/D ratio of the column; while stirring speed and the recycles of the resin had no significant effects on boron removal.
- (3) The adsorption process kinetics was carried out with the moving boundary model for boron removal by ion exchange resin by batch-mode operation. It was found that the original model could not satisfactorily describe the process under the conditions studied, and it was modified by introducing a time correction factor so as to express the exchange process more accurately. As a result, it was found that the adsorption process was controlled by particle diffusion under the conditions studied; and the apparent activation energy E_a of this process was 20.38 kJ/mol after calculation.

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