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### Effect of Ionic Strength of Solution on Boron Mass Transfer by Ion Exchange Separation

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## Effect of Ionic Strength of Solution on Boron Mass Transfer by Ion Exchange Separation

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**Abstract:** In the present study, batch kinetic tests have been performed for boron removal from model solutions using boron selective ion exchange resins Diaion CRB 02, Dowex (XUS 43594.00) and Purolite S 108. Several kinetic models have been used to evaluate the sorption kinetics of boron by means of a well mixed stirred system, diffusional models, pseudo-first-order, and pseudo-second-order kinetic models. The mass transfer model, based on a well stirred system including maximum capacity ( $Q_m$ , mg/g) and Langmuir constant ( $b$ , L/mg) values obtained from Langmuir isotherms, has been used to obtain predictive concentration changes against time. The experimental results have been used to compare with the modelling data for different ionic strength media.

**Keywords:** Boron, ionic strength, ion exchange, mass transfer, water

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## INTRODUCTION

In many regions, water resources suffer from several salinization problems. One of the inorganic constituents that is problematic and difficult to get rid of is boron. Boron, is an essential micronutrient for plants to complete certain metabolic activities, however, higher boron levels accelerate plant decay and expiration. Different plants can withstand different boron levels. For example, the optimal boron concentration range is 0.3–0.5 mg/L for citrus and grapes and 0.50–0.75 mg/L for corn (1). Boron compounds passing to soil, surface waters, and ground waters form many complexes with heavy metals such as Pb, Cd, Cu, Ni, etc. and these complexes are more toxic than the heavy metals within them (2). Boron removal is also a critical issue in the production of ultra-pure water in the electronics industry (3).

The World Health Organization has given a recommended maximum limit of 0.3 mg/L of boron in drinking water because boron may have a harmful effect on humans. It has been demonstrated that boron produces harmful effects on the masculine reproductive organs in laboratory animals such as mice, rats, and rabbits, which is an indicator of some teratogenic effects in humans (3). So, there is a need for removal of boron from water and wastewater to obtain the concentration limit for environmental pollution control.

There are several methods of boron removal from the water that contains a high concentration of boron, even though most of them are inefficient in obtaining the desired concentration and too difficult to utilize.

The coprecipitation method using metal hydroxide is an inefficient and environmentally ineffective process due to low removal rate, requirement of a large amount of metal hydroxide, and disposal of large amount of unrecyclable wastes. The evaporation–crystallization process is sufficient only in the case of very high boron concentrations, especially more than several thousand ppm. Likewise, solvent extraction needs expensive extractants which are toxic (4). Besides, a new hydrothermal treatment technique was developed to recover boron as recyclable precipitate  $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$  from aqueous solutions (4). There are conventional adsorption methods worked on by several researchers. Treatment wetlands are one method that could be used to remove boron, but the inability of *S. polyrrhiza* to remove even low levels of boron from the test solutions indicates this species is not suitable for treating boron-containing wastewater (5). G. Pieruz et al. investigated a process based on liquid-liquid electrochemistry to transfer selectively borate anions present in produced water to an immiscible phase (6). Removal of silicon and boron from ultra-pure water using EDI (electrodeionization) was worked by R. Wen et al. (7). There are also some membrane processes such as reverse osmosis and electrodialysis for boron removal. However, these techniques require a high cost for manufacturing and maintenance. Often these methods are efficient only in the case of high pH values. For example, the removal efficiency using reverse osmosis

was about 40–80% and in some cases (pH 10–11) over 90% (1). In electrodialysis, the removal efficiency is 40–75%; and the process was found to be expensive (8).

Besides the prementioned methods, there are hybrid processes that combine two or more process to remove elements from water and wastewater such as membrane-ion exchange etc (9). The membrane-ion exchange hybrid process integrates sorption processes with membrane separation of sorbents. Combination of sorbents with their separation on membranes reveals many advantages comparing with conventionally used fixed bed systems (10).

The classical method for eliminating boron is ion exchange which has been also used in the present study. In the case of ion exchangers, the boron removal efficiency is 90–98%, but the regeneration costs can be very high (8). Batch and column-mode studies for boron removal from geothermal wastewaters using N-glucamine type resins were performed by Badruk et al. (11, 12). Kabay et al. studied column-mode removal of boron from geothermal wastewaters using Diaion CRB 02 N-glucamine-type chelating resin for ten sorption-washing-elution-washing-regeneration-washing cycles in Kizildere geothermal field, Denizli. Column-mode recovery of boron from acidic eluate solution was performed using Diaion WA 30, a weak base anion exchange resin (13). Also, the comparative results were obtained using different N-glucamine type resins (Purolite S108, Diaion CRB 01, Diaion CRB 02) and column performances of these resins for boron removal from geothermal wastewater were studied (14).

This paper presents the effect of ionic strength of the solution on kinetic performance for boron removal from water by ion exchange. Also, different kinds of kinetic models have been used to evaluate the kinetic studies and some conclusions drawn regarding the optimum design for the ion exchange resin bead.

### Modelling of Sorption Kinetics

In order to compare the mass transfer coefficients of the sorption processes, several kinetic models such as well-known pseudo first and second order kinetic equations and stirred cell models can be used to evaluate the kinetic studies.

#### Seeded Microfiltration Cell Kinetic Modelling

The kinetics of the process have been modelled by a mass transfer model based on a well mixed stirred system as explained by Holdich et al. (15) for boron removal using a seeded microfiltration system. Mass balance for boron in a stirred cell with well mixing provides:

$$V \frac{dC}{dt} = F(C_{feed} - C) - m \frac{dq}{dt} \quad (1)$$

where

$V$  = the liquid volume in the cell

$C$  = the concentration in the solution (both in the cell and the exit)

$C_{feed}$  = the concentration in the feed to the cell

$F$  = feed flow rate

$m$  = mass of the resin in the cell

$q$  = average mass of boron per mass of resin.

The system of equations can be solved simultaneously in an equation solver capable of solving partial differential equations such as PDESOL (Numerica, Dallas, USA) (15). The related equations are given below:

$$\begin{aligned}
 q(t = 0, 0 \leq r \leq R) &= 0 \\
 C(t = 0) &= 0 \\
 C^* &= \frac{q|_r = R}{b(q_m - q|_{r=R})} \\
 q - x &= dx(q) \\
 \frac{\partial q(t \geq 0)}{\partial r} \Big|_{r=0} &= 0 \\
 \frac{\partial q(t \geq 0)}{\partial r} \Big|_{r=R} &= \frac{K}{D_{eff} \rho_s} (C - C^*) \\
 V \frac{dC}{dt} &= F(C_{feed} - C) - \frac{3}{R} m D_{eff} \frac{\partial q}{\partial r} \Big|_{r=R} \\
 \frac{\partial q}{\partial t} &= \frac{1}{r^2} \frac{\partial}{\partial r} \left( D_{eff} r^2 \frac{\partial q}{\partial r} \right)
 \end{aligned}$$

### Diffusional and Reactional Models

Alternative kinetic studies have been evaluated using diffusional and reaction models. The models for process dynamics includes both the diffusional steps (bulk solution, a film layer at the external surface of the particle, pores) and the exchange reaction on the active sites. Since the resistance in bulk solution is easily controlled and negligible, three resistances, such as film diffusion, particle diffusion, and chemical reaction, usually determine the overall rate of the ion-exchange process. One approach uses the infinite solution volume

(ISV) model, whereas another method uses the unreacted core model (UCM) to describe the rate determining steps in ion exchange process (11). These two kinetic models developed for spherical particles to specify the rate-determining steps are given in Table 1.

## EXPERIMENTAL

### Materials

Diaion CRB 02 and Purolite S 108 ion exchange resins were kindly provided by Mitsubishi Co., Japan and Purolite International Ltd., UK, respectively and Dowex (XUS 43594.00) resin was kindly sent by Dow Chem., Germany. In the experiments, the functional group of Purolite S 108 resin was converted from  $\text{Cl}^-$  form into  $\text{OH}^-$  form. The conversion was achieved by washing 16 g of the resin with 100 mL of 1M sodium hydroxide solution for 24 h at room temperature with continuous shaking.

The model solution containing 20 mgB/L (pH of this solution was adjusted with sodium hydroxide up to pH = 9.0–9.2) was used in the experiments.

The ionic strength of Kizildere geothermal wastewater has been calculated as 0.07 mol/L but in the experiments the ionic strength of the solutions has been adjusted to 0.1 mol/L (Table 2).

### Equilibrium Uptake of Boric Acid

Adsorption isotherms studies were conducted using 0.1 g of Dowex (XUS 43594.00) and Purolite S 108 resins at a particle size of 0.250–1.000 mm and 50 mL of solutions containing different boron concentrations (4, 8, 10, 15, 20, 30, 40 mg B/L, pH 9.0) at 30°C and for 48 hours with continuous

**Table 1.** Diffusional and reaction models

Model	Equation	Rate-determining step
ISV	$F(X) = -\ln(1 - X) = kt$ where $k = D_r \pi^2 / r_0^2$	Film diffusion
ISV	$F(X) = -\ln(1 - X^2) = K_{1i}t$ where $K_{1i} = 3DC / r_0 \delta C_r$	Particle diffusion
UCM	$F(X) = X = (3C_{A0}K_{mA} / a_{r0}C_{s0})t$	Liquid film
UCM	$F(X) = 3 - 3(1 - X)^{2/3} - 2X = (6D_{eR}C_{A0} / a_{r0}2C_{s0})t$	Reacted layer
UCM	$F(X) = 1 - (1 - X)^{1/3} = (k_s C_{A0} / r_0)t$	Chemical reaction

**Table 2.** Chemical composition and ionic strength of the Kizildere geothermal wastewater

Ionic species	C (mg/L)	MW (g/mol)	Charge	C (mol/L)	C · z <sup>2</sup>	I.S. = (C · z <sup>2</sup> ) / 2 (Total)
Na <sup>+</sup>	1190.00	23.00	1	0.05174	0.05174	
K <sup>+</sup>	142.00	39.00	1	0.00364	0.00364	0.02769
Li <sup>+</sup>	3.78	6.94	1	0.00054	0.00054	0.02796
Ca <sup>2+</sup>	0.51	40.00	2	0.00001	0.00005	0.02799
Mg <sup>2+</sup>	0.42	24.30	2	0.00002	0.00007	0.02802
F <sup>-</sup>	15.36	19.00	1	0.00081	0.00081	0.02843
Cl <sup>-</sup>	94.20	35.50	1	0.00265	0.00265	0.02975
SO <sub>4</sub> <sup>2-</sup>	646.00	96.00	2	0.00673	0.02692	0.04321
HCO <sub>3</sub> <sup>-</sup>	1660.00	61.00	1	0.02721	0.02721	0.05682
CO <sub>3</sub> <sup>2-</sup>	224.00	60.00	2	0.00373	0.01493	0.06429
As <sup>3+</sup>	0.85	74.92	3	0.00001	0.00010	0.06434
B <sup>3+</sup>	19.00	10.81	3	0.00176	0.01582	0.07225

Note: T-SiO<sub>2</sub> and S-SiO<sub>2</sub> have not been included in the I.S. calculation (T-SiO<sub>2</sub> = 330 mg/L and S-SiO<sub>2</sub> = 287 mg/L) (T: total, S: soluble).

shaking. To investigate the effect of the ionic strength on equilibrium uptake of boron, the following solutions were prepared:

1. [Boric acid + NaOH] (pH = 9)
2. [Boric acid + NaOH + 0.1 M NaHCO<sub>3</sub>] (pH = 9)
3. [Boric acid + NaOH + 0.1 M NaNO<sub>3</sub>] (pH = 9)

Because the ionic strength of Kizildere geothermal wastewater (Table 2) is about 0.1 M, in the experiments related to conditions 2 and 3, this concentration value was maintained in addition to boric acid and NaOH.

### Kinetic Tests with Ion Exchange Resins using Model Boron Solution

The effect of ionic strength on kinetic performance of boron removal was studied by contacting 2 g of Dowex (XUS 43594.00) and Purolite S 108 resins (0.250–1.000 mm) with 500 mL of 20 mg B/L (pH = 9) solution prepared at the following conditions on a magnetic stirrer and at room temperature:

1. [Boric acid + NaOH] (pH = 9)
2. [Boric acid + NaOH + 0.1 M NaHCO<sub>3</sub>] (pH = 9)
3. [Boric acid + NaOH + 0.1 M NaNO<sub>3</sub>] (pH = 9)

The boron concentrations of the samples were monitored by taking the samples from the solution at defined time.

### Analytical Procedure

The analysis of boron was performed spectrophotometrically using the Azomethine-H method ( $\lambda_{\text{max}}$ : 415 nm).

## RESULTS AND DISCUSSION

### Adsorption Isotherms of Boron

In models of ion exchange or adsorption, the equilibrium concentration of the species transferring from the liquid to the solid phase can be modelled using an adsorption isotherm. The widely used Langmuir isotherm is expressed as (16):

$$q_e = \frac{bC_e q_m}{1 + bC_e} \quad (2)$$

A linear form of this expression is:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (3)$$

where  $q_e$  (mg/g) and  $C_e$  (mg/L) are the amount of boron adsorbed per unit weight of sorbent and remained boron concentration in solution at equilibrium, respectively. The value of  $b$  is the Langmuir equilibrium constant which has the unit of L/mg. A plot of  $C_e/q_e$  versus  $C_e$  gives a straight line with a slope of  $1/q_m$  and intercept of  $1/bq_m$ .

In the present study, equilibrium uptake of boron was investigated using different kinds of ion exchange resins and model boron solutions having different ionic species. The Langmuir isotherms have been used to describe the sorption of boron onto the resins. Linear plots of  $C_e/q_e$  versus  $C_e$  show that sorption isotherms obey the Langmuir isotherm model for Dowex (XUS 43594.00) and Purolite S 108 resins for all solutions used as shown in Table 3.

Calculated Langmuir equilibrium constant,  $b$ , L/mg and the theoretical monolayer saturation capacity,  $Q_m$ , mg/g values are given in Table 3. As seen from Table 3, increase in ionic strength led to an improvement of  $Q_m$ . It was considered that an increase in ionic strength leads to the increase in diffusion of  $\text{B}(\text{OH})_4^-$  ions to the binding sites of the resin. In addition, the kind of electrolyte species that are used for adjusting the ionic strength of the solution did not affect the  $Q_m$  values for both Dowex (XUS 43594.00) and Purolite S 108 resins. Also,  $Q_m$  values for Dowex (XUS 43594.00) are found to be higher than those for Purolite S 108. Besides, as tabulated in Table 3, calculated  $b$  values changed as a function of resin type and ionic strength.

**Table 3.** Evaluation of boron adsorption isotherms of Dowex (XUS 43594.00) and Purolite S 108 resins

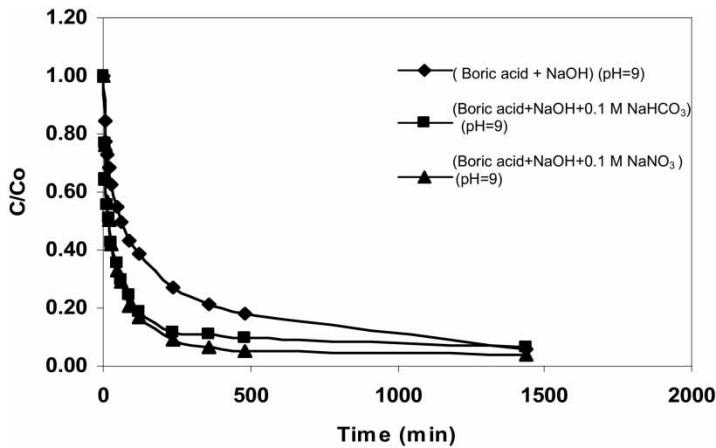
Ion exchange resins/model solution	R <sup>2</sup>	Q <sub>m</sub> (mg/g)	b (L/mg)
Dowex [Boric acid + NaOH] (pH = 9)	0.9830	8.51	0.59
Dowex [Boric acid + NaOH + 0.1 M NaHCO <sub>3</sub> ] (pH = 9)	0.9864	13.61	1.51
Dowex [Boric acid + NaOH + 0.1 M NaNO <sub>3</sub> ] (pH = 9)	0.9972	13.42	5.78
Purolite S 108 [Boric acid + NaOH] (pH = 9)	0.9944	4.25	1.05
Purolite S 108 [Boric acid + NaOH + 0.1 M NaHCO <sub>3</sub> ] (pH = 9)	0.9986	6.30	1.53
Purolite S 108 [Boric acid + NaOH + 0.1 M NaNO <sub>3</sub> ] (pH = 9)	0.9952	6.28	0.89

### Investigation of Sorption Kinetics

All the kinetics studies were evaluated using pseudo-first-order and pseudo-second-order kinetics models. To obtain the correlation coefficients,  $\log(q_e - q_t)$  versus  $t$  and  $1/(q_e - q_t)$  versus  $t$  were plotted for first-order and second-order kinetic models, respectively. The linearity of the plots shows the empirical applicability of the pseudo-first-order or pseudo-second-order kinetic equation for boron sorption on the resins. Since the correlation coefficients of pseudo-second-order kinetics ( $R^2$ ) (Table 4) are greater than those of

**Table 4.** Evaluation of batch kinetic studies with respect to conventional kinetic modelling of sorption

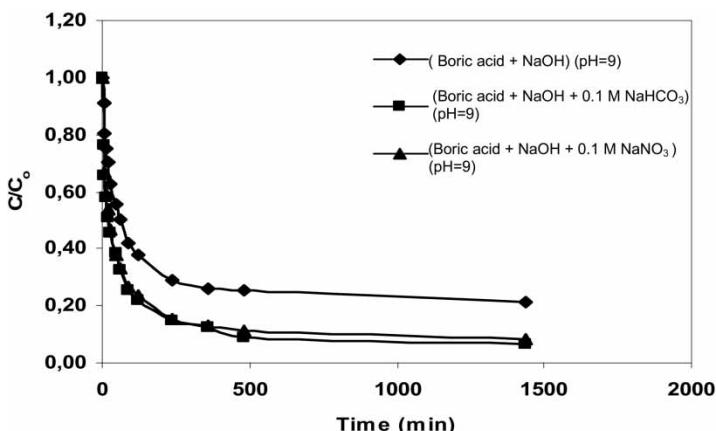
Ion exchange resin and experimental conditions	R <sup>2</sup> (First order kinetics)	R <sup>2</sup> (Second order kinetics)
Dowex (XUS 43594.00) [Boric acid + NaOH] (pH = 9)	0.9828	0.9937
Dowex (XUS 43594.00) [Boric acid + NaOH + 0.1 M NaHCO <sub>3</sub> ] (pH = 9)	0.9745	0.9968
Dowex (XUS 43594.00) [Boric acid + NaOH + 0.1 M NaNO <sub>3</sub> ] (pH = 9)	0.9862	0.9996
Purolite S 108 [Boric acid + NaOH] (pH = 9)	0.9802	0.9959
Purolite S 108 [Boric acid + NaOH + 0.1 M NaHCO <sub>3</sub> ] (pH = 9)	0.9546	0.9770
Purolite S 108 [Boric acid + NaOH + 0.1 M NaNO <sub>3</sub> ] (pH = 9)	0.9815	0.9981



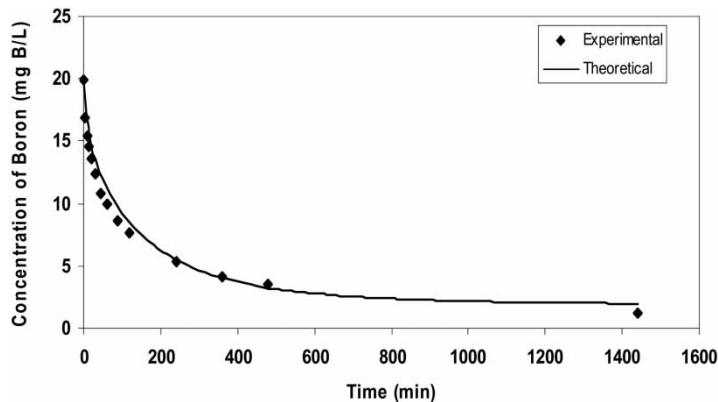
**Figure 1.** Effect of ionic strength on boron removal by batch kinetic study using Dowex (XUS 43594.00).

pseudo-first-order kinetics for all experimental conditions, it can be concluded that the sorption of boron by both resins obeys the pseudo-second-order kinetic model.

Also, the kinetic behaviors of Dowex (XUS 43594.00) and Purolite S 108 resins were examined and compared in order to get a measure of the relative kinetic performance of the resins in the presence of other ionic species in the solution. Figures 1 and 2 show that the ratio of boron concentration to initial

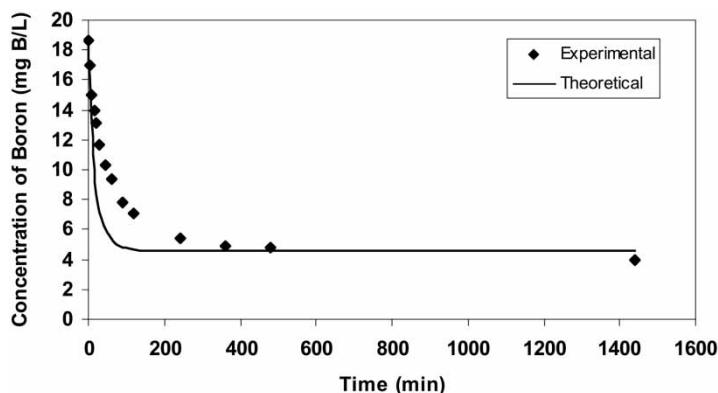


**Figure 2.** Effect of ionic strength on removal of boron by batch kinetic study using Purolite S 108.

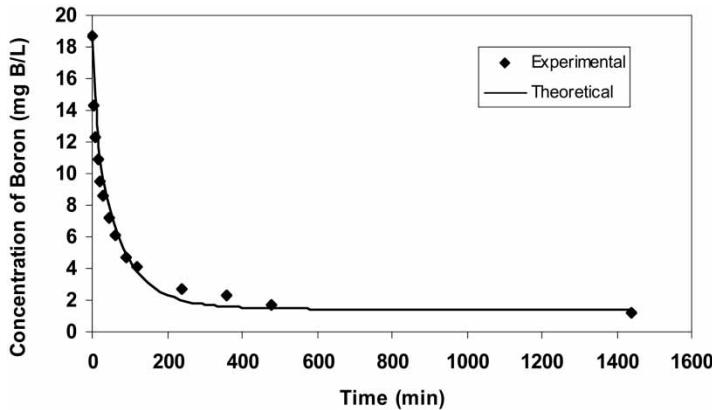


**Figure 3.** Model and experimental data of batch kinetic study using Dowex (XUS 43594.00) and [Boric acid + NaOH] (pH = 9) solution ( $D_{\text{eff}} = 1.50\text{E-}13 \text{ m}^2/\text{s}$ ).

concentration decreased to almost 0.50 at about 60, 20, and 20 min of contact time with only boric acid solution (pH = 9) and with boric acid in 0.1 M  $\text{NaHCO}_3$  and in 0.1 M  $\text{NaNO}_3$  solutions, respectively for both resins at moderate stirring rates. In terms of contact time, the ionic strength of the solution affects the kinetic performance of the resin although the kind of the electrolyte species did not influence the kinetic performance of the resin. It can be considered that an increase in ionic strength leads to an improvement in diffusion of  $\text{B(OH)}_4^-$  ions to the binding sites of the resin due to the facilitated transport phenomenon. The mobility of  $\text{B(OH)}_4^-$  ions through the ion exchange resin is enhanced with the aid of ionic species increased by ionic strength in the bulk solution.



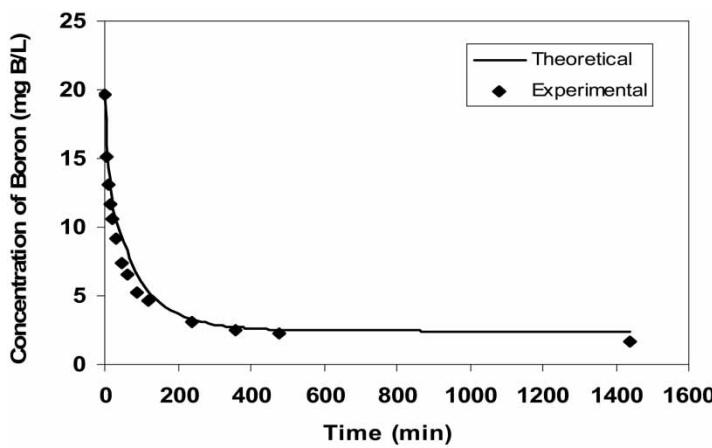
**Figure 4.** Model and experimental data of batch kinetic study using Purolite S 108 and [Boric acid + NaOH] (pH = 9) solution ( $D_{\text{eff}} = 4.00\text{E-}12 \text{ m}^2/\text{s}$ ).



**Figure 5.** Model and experimental data of batch kinetic study using Purolite S 108 [Boric acid + NaOH + 0.1 M NaHCO<sub>3</sub>] (pH = 9) solution ( $D_{eff}$  = 7.00E-13 m<sup>2</sup>/s).

As shown in Figures 3–6, the experimental data were evaluated using a seeded microfiltration cell kinetic model. Effective diffusion coefficients of boron inside the particle, m<sup>2</sup>/s ( $D_{eff}$ ) which give the best fitting for theoretical and experimental results are  $1.50 \times 10^{-13}$  m<sup>2</sup>/s for Dowex (XUS 43594.00) in the case of only the boric acid solution and  $4.00 \times 10^{-12}$ ,  $7.00 \times 10^{-13}$ , and  $7.00 \times 10^{-13}$  m<sup>2</sup>/s for Purolite S 108 for only boric acid solution, boric acid in 0.1 M NaHCO<sub>3</sub>, and in 0.1 M NaNO<sub>3</sub> solutions, respectively.

Finally, Table 5 summarizes the calculated mass transfer coefficient values using seeded microfiltration cell kinetic modelling method. As seen



**Figure 6.** Model and experimental data of batch kinetic study using Purolite S 108 and [Boric acid + NaOH + 0.1 M NaNO<sub>3</sub>] (pH = 9) solution ( $D_{eff}$  = 7.00E-13 m<sup>2</sup>/s).

**Table 5.** Evaluation of batch kinetic studies by means of mass transfer coefficients

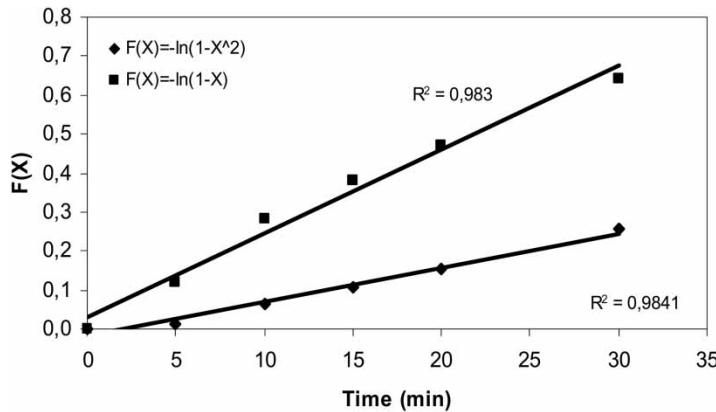
Ion exchange resin and solution	Modelling data K (m/s)
Dowex (XUS 43594.00) [Boric acid + NaOH] (pH = 9)	1.34 · E-4
Dowex (XUS 43594.00) [Boric acid + NaOH + 0.1 M NaHCO <sub>3</sub> ] (pH = 9)	1.34 · E-4
Dowex (XUS 43594.00) [Boric acid + NaOH + 0.1 M NaNO <sub>3</sub> ] (pH = 9)	1.34 · E-4
Purolite S 108 [Boric acid + NaOH] (pH = 9)	1.33 · E-4
Purolite S 108 [Boric acid + NaOH + 0.1 M NaHCO <sub>3</sub> ] (pH = 9)	1.33 · E-4
Purolite S 108 [Boric acid + NaOH + 0.1 M NaNO <sub>3</sub> ] (pH = 9)	1.33 · E-4

**Table 6.** Evaluation of diffusional and reaction models for Purolite S 108

Solution	R <sup>2</sup>				
	− ln (1 − X)	− ln (1 − X <sup>2</sup> )	X	3 − 3 (1 − X) <sup>2/3</sup> − 2X	1 − (1 − X) <sup>1/3</sup>
[Boric acid + NaOH] (pH = 9)	0.9830	0.9841	0.9507	0.9813	0.9740
[Boric acid + NaOH + NaHCO <sub>3</sub> ] (pH = 9)	0.9280	0.9834	0.8521	0.9833	0.9053
[Boric acid + NaOH + NaNO <sub>3</sub> ] (pH = 9)	0.9440	0.9981	0.8650	0.9981	0.9206

**Table 7.** Evaluation of diffusional and reaction models for Dowex (XUS 43594.00)

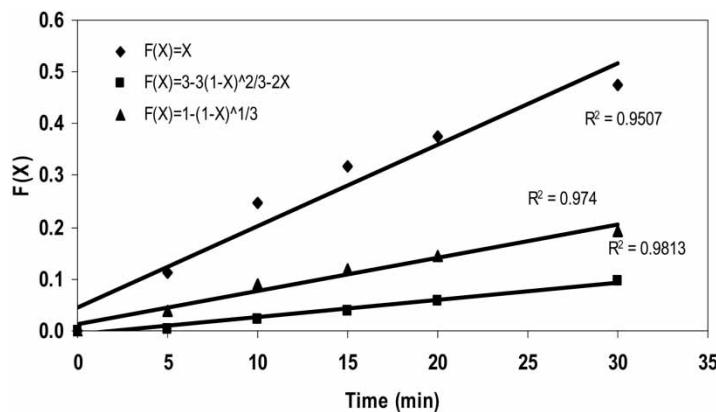
Solution	R <sup>2</sup>				
	− ln (1 − X)	− ln (1 − X <sup>2</sup> )	X	3 − 3 (1 − X) <sup>2/3</sup> − 2X	1 − (1 − X) <sup>1/3</sup>
[Boric acid + NaOH] (pH = 9)	0.9352	0.9993	0.8895	0.9992	0.9211
[Boric acid + NaOH + NaHCO <sub>3</sub> ] (pH = 9)	0.9524	0.9965	0.8727	0.9961	0.9291
[Boric acid + NaOH + NaNO <sub>3</sub> ] (pH = 9)	0.9571	0.9988	0.8808	0.9983	0.9352



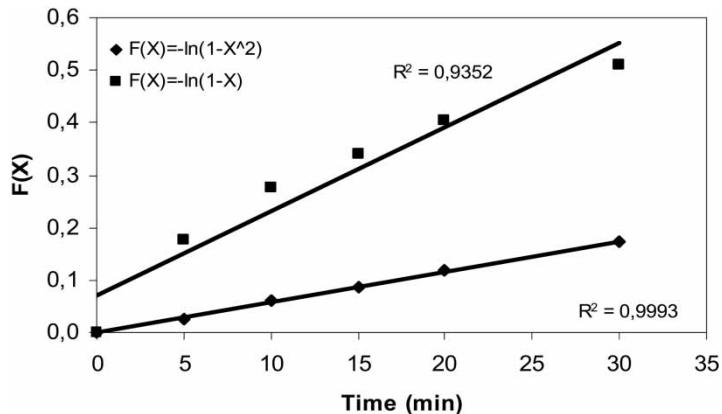
**Figure 7.** Kinetic behavior of Purolite S 108 and [Boric acid + NaOH] (pH = 9) solution based on infinite solution volume models.

in Table 5, the calculated mass transfer coefficients for all experimental conditions are found to be almost the same.

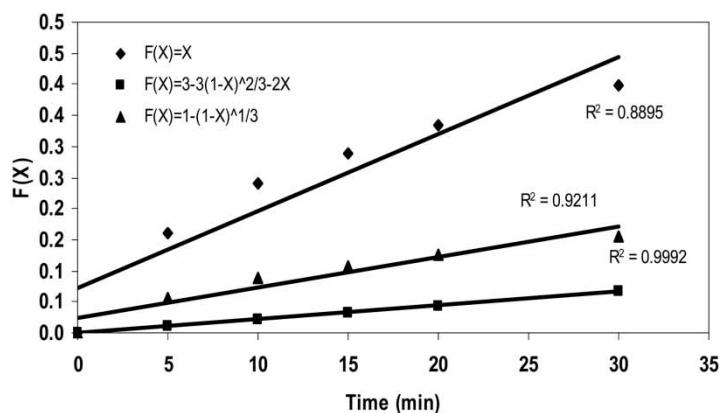
Tables 6 and 7 give the linear correlation coefficients obtained from the plots of  $F(X)$  function versus time. The plots given in Figures 7–10 were obtained using the solution of boric acid and NaOH mixture (pH = 9) only. As seen in Tables 6 and 7, the maximum correlation coefficients for the linear models show that the boron sorption by both resins is controlled by particle diffusion at various conditions.



**Figure 8.** Kinetic behavior of Purolite S 108 and [Boric acid + NaOH] (pH = 9) solution based on unreacted core models.



**Figure 9.** Kinetic behavior of Dowex (XUS 43594.00) and [Boric acid + NaOH] (pH = 9) solution based on infinite solution volume models.



**Figure 10.** Kinetic behavior of Dowex (XUS 43594.00) and [Boric acid + NaOH] (pH = 9) solution based on unreacted core models.

## CONCLUSIONS

Ionic strength of the solution affected the kinetic performance of the resin although kind of the electrolyte species did not influence the kinetic performance of the resin. It was obtained that the sorption of boron by both resins obeyed the pseudo-second-order kinetic model. According to the linear diffusion models it was obtained that boron sorption by both resins is controlled by the particle diffusion.

## APPENDIX

An example of the model for a “*Batch Process*” using “*PDESOL*” program is given in Appendix:

### Constants

$q_m = 8.51e-3'$  Langmuir maximum  $q$  value g/g

$b = 0.59'$  Langmuir parameter  $b$   $m^3/g$  of boron

$m = 2'$  mass resin used g

$V = 5e-3'$  volume of cell in  $m^3$

$radius = 250e-6'$  m

$\mu = 0.001'$  viscosity of liquid

$\rho_{sol} = 1.1'$  specific gravity of solid

$\rho_{liq} = 1'$  specific gravity of liquid

$diff = 0.8e-8'$   $m^2/s$  Diffusivity of transferring species in water

$D_{eff} = 1.3e-13'$   $m^2/s$  Internal diffusivity of transferring species in bead

$c_{feed} = 19.88'$   $g/m^3$  Concentration of species in feed (also ppm)

$vel_{ter} = 9.329e-3'$  Terminal settling velocity—Manual

### Calculated Constants

$\rho = \rho_{sol} \cdot 1e + 6'$   $g/m^3$

$\Delta\rho = (\rho_{sol}-\rho_{liq}) \cdot 1000'$  density difference in  $kg/m^3$

$Re = 2 \cdot radius \cdot \rho_{liq} \cdot 1000 \cdot vel_{ter}/\mu'$  Particle Reynolds number

$Sc = \mu/(\rho_{liq} \cdot 1000 \cdot diff)'$  Scmidt number

$Sh = 2 + .6 \cdot Re^{.5} \cdot Sc^{.33}'$  Sherwood number

$K = Sh \cdot diff/(2 \cdot radius)'$  Mass transfer coefficient

$V2 = Re$

$V3 = K$

### Initial Conditions

$q@t0 = 0$

$C@t0 = c_{feed}$

### Boundary Conditions and Equations

$$\begin{aligned}
 C_{equ} &= q@xU/b/(qm-q@xU) \\
 q_x &= dx(q) \\
 q_x@xL &= 0 \\
 q_x@xU &= (K \cdot (C - C_{equ}))/(\rho \cdot D_{eff}) \\
 C_t &= -m \cdot 3/V \cdot D_{eff}/radius \cdot q_x@xU \\
 q_t &= 1/(x > 1e-6)^2 \cdot dx(D_{eff} \cdot x^2 \cdot q_x)
 \end{aligned}$$

### NOMENCLATURE

X	fractional attainment of equilibrium or extent of resin conversion
k	rate constant (L/s)
t	time (s)
D <sub>r</sub>	diffusion coefficient in solid phase (m <sup>2</sup> /s)
r <sub>o</sub>	average particle radius (mm)
K <sub>li</sub>	rate constant for film diffusion (infinite solution volume condition (L/s))
D	diffusion coefficient in solution phase (m <sup>2</sup> /s)
δ	film thickness (mm)
C	total concentration of both exchanging species (M)
C <sub>A0</sub>	concentration of species A in bulk solution (M)
K <sub>mA</sub>	mass transfer coefficient of species A through the liquid film (m/s)
a	stoichiometric coefficient
C <sub>S0</sub>	concentration of solid reactant at the bead's unreacted core (M)
D <sub>eR</sub>	effective diffusion coefficient in solid phase (m <sup>2</sup> /s)
k <sub>s</sub>	reaction constant based on surface (m/s)

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## REFERENCES

1. Sagiv, A. and Semiat, R. (2004) Analysis of parameters affecting boron permeation through reverse osmosis membranes. *Journal of Membrane Science*, 243: 79–87.
2. Boncukcuoglu, R., Yilmaz, A.E., Kocakerim, M.M., and Copur, M. (2004) An empirical model for kinetics of boron removal from boron containing wastewaters by ion exchange in a batch reactor. *Desalination*, 160: 159–166.
3. Qin, J.J., Oo, M.H., Wai, M.N., and Cao, Y.M. (2005) Enhancement of boron removal in treatment of spent rinse from a plating operation using RO. *Desalination*, 172: 151–156.
4. Itakura, T., Sasai, R., and Itoh, H. (2005) Precipitation recovery of boron from wastewater by hydrothermalmineralization. *Water Research*, 39: 2543–2548.
5. Davis, S.M., Drake, K.D., and Maier, K.J. (2002) Toxicity of boron to the duckweed, *Spirodella polyrrhiza*. *Chemosphere*, 48: 615–620.
6. Pieruz, G., Grassia, E., and Dryfe, R.A.W. (2004) Boron removal from produced water by facilitated ion transfer. *Desalination*, 167: 417.
7. Wen, R., Deng, S., and Zhang, Y. (2005) The removal of silicon and boron from ultra-pure water by electrodeionization. *Desalination*, 181: 153–159.
8. Yurdakoc, M., Seki, Y., Karahan, S., and Yurdakoc, K. (2005) Kinetic and thermodynamic studies of boron removal by Siral 5, Siral 40, and Siral 80. *Journal of Colloid and Interface Science*, 286: 440–446.
9. Matisa, K.A., Lazaridisa, N.K., Zouboulisa, A.I., Galliosa, G.P., and Mavrovb, V. (2005) A hybrid flotation—microfiltration process for metal ions recovery. *Journal of Membrane Science*, 247: 29–35.
10. Koltuniewicz, A., Witek, A., and Bezak, K. (2004) Efficiency of membrane-sorption integrated processes. *Journal of Membrane Science*, 239: 129–141.
11. Badruk, M., Kabay, N., Demircioglu, M., Mordogan, H., and Ipekoglu, U. (1999) Removal of boron from wastewater of geothermal power plant by selective ion-exchange resins. I. Batch-sorption-elution studies. *Separation Science and Technology*, 34 (13): 2553–2569.
12. Badruk, M., Kabay, N., Demircioglu, M., Mordogan, H., and Ipekoglu, U. (1999) Removal of boron from wastewater of geothermal power plant by selective ion-exchange resins. II. column-sorption-elution studies. *Separation Science and Technology*, 34 (15): 2981–2995.
13. Kabay, N., Yilmaz, I., Yamac, S., Yuksel, M., Yuksel, U., Yildirim, N., Aydogdu, O., Iwanaga, T., and Hirowatari, K. (2004) Removal and recovery of boron from geothermal wastewater by selective ion—exchange resins - II. Field tests. *Desalination*, 167: 427–438.
14. Kabay, N., Yilmaz, I., Yamac, S., Samatya, S., Yuksel, M., Yuksel, U., Arda, M., Saglam, M., Iwanaga, T., and Hirowatari, K. (2004) Removal and recovery of boron from geothermal wastewater by selective ion exchange resins. I. Laboratory tests. *Reactive and Functional Polymers*, 60: 163–170.
15. Holdich, R.G., Cumming, I.W., and Perni, S. (2005) Boron mass transfer during seeded microfiltration. *Chemical Engineering Research and Design*, 83 (A12): 1–9.
16. Ozcaar, M. and Sengil, I.A. (2004) Two-stage batch sorber design using second-order kinetic model for the sorption of metal complex dyes onto pine sawdust. *Biochemical Engineering Journal*, 21: 39–45.