Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation of Boron from Geothermal Water Using a Boron Selective Macroporous Weak Base Anion Exchange Resin

Idil Yilmaz-Ipek[a]; Pelin Koseoglu[b]; Umran Yuksel[b]; Nazlı Yasar[a]; Gözde Yolseven[a]; Mithat Yuksel[a]; Nalan Kabay[a]
[a] Ege University, Chemical Engineering Department, Izmir, Turkey [b] Ege University, Chemistry Department, Izmir, Turkey

Online publication date: 22 March 2010

To cite this Article Yilmaz-Ipek, Idil , Koseoglu, Pelin , Yuksel, Umran , Yasar, Nazlı , Yolseven, Gözde , Yuksel, Mithat and Kabay, Nalan(2010) 'Separation of Boron from Geothermal Water Using a Boron Selective Macroporous Weak Base Anion Exchange Resin', Separation Science and Technology, 45: 6, 809 — 813

To link to this Article: DOI: 10.1080/01496391003607357
URL: http://dx.doi.org/10.1080/01496391003607357

Separation Science and Technology, 45: 809–813, 2010

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496391003607357

Separation of Boron from Geothermal Water Using a Boron Selective Macroporous Weak Base Anion Exchange Resin

Idil Yilmaz-Ipek,[1] Pelin Koseoglu,[2] Umran Yuksel,[2] Nazlı Yasar,[1] Gözde Yolseven,[1] Mithat Yuksel,[1] and Nalan Kabay[1]
[1]*Ege University, Chemical Engineering Department, Izmir, Turkey*
[2]*Ege University, Chemistry Department, Izmir, Turkey*

In this study, batch and column mode tests were performed to evaluate the efficiency of boron removal from geothermal water containing 10-11 mg B/L using Lewatit MK 51 which is a macroporous weak base anion exchange resin with polyhydroxyl groups showing a very high selectivity and capacity for boron. The optimum resin amount for boron removal from geothermal water was determined as 4.0 g resin/L-geothermal water. It was found that the sorption kinetics was influenced by particle size of the resin and temperature. The stirring rate had almost no effect on kinetic performance of the resin. According to the results of column-mode study performed, breakthrough and total capacities of the resin were obtained as 2.75 and 4.98 mg/mL-resin, respectively.

Keywords boron; geothermal water; ion exchange resin; water treatment

INTRODUCTION

Geothermal waters may contain high concentration of boron and other species. In many of the geothermal fields and boron-rich thermal springs, boron presents as undissociated boric acid (H_3BO_3) and borate ions [$B(OH)_4^-$]. H_3BO_3 is dominant at low pH values while [$B(OH)_4^-$] is dominant at high pHs (1).

Thermal waters are generally used as irrigation water for agricultural areas. Their boron contents accumulate in the soil and this may cause the change in characteristics of it. Also, these waters could mix with underground waters by passing through the soil and constitute complexes with Pb, Cu, Cd, and Ni ions. The toxicities of these complexes are higher than those of the heavy metals alone (2). A minimum of boron concentration in the irrigation water is required for some metabolic activities of plants, such as cellular multiplication, the metabolism of nucleic acids and the metabolism of sugars (3). However, if boron concentration in irrigation water is only slightly higher than minimum, this will negatively affect the plant growth and signs of boron toxicity will be observed. Regular use of irrigation water with more than 1 mg/L of boron is harmful for most plants. Sensitive plants, including most citrus species, have a boron tolerance of only 0.40–0.75 mg/L, while vegetables are more boron tolerant with maximum thresholds of 1–4 mg/L. As a result, it is obvious that although boron is a vital micronutrient for plants, it can be detrimental at higher concentrations and boron levels in drinking and irrigation waters are required to be lowered under permissible limits (1,4). WHO has recommended a limit of 0.3 mg/L for drinking water (5).

There are several methods for boron removal from water that contains a high concentration of boron, even though most of them are inefficient to obtain the desired concentration and too difficult to utilize (5). Among those methods, the ion exchange process is the most extensively used one. The comparative results were obtained using different N-glucamine type resins and column performances of these resins for boron removal from geothermal wastewater were investigated by Kabay et al. (6). A column-mode removal of boron from geothermal wastewaters using Diaion CRB 02 N-glucamine-type chelating resin for 10 sorption – washing – elution – washing – regeneration – washing cycles was also studied 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 (7). Elsewhere, the efficiency of boron removal from geothermal water was investigated using boron-selective ion exchange resins Diaion CRB 02 and Dowex (XUS 43594.00) by batch and column methods (8). The effect of the ionic strength of the solution on boron removal by boron selective ion exchange resins were reported elsewhere (5).

In this study, the batch and column mode experiments were performed to evaluate the efficiency of boron removal from geothermal water using the commercial weak base anion exchange resin Lewatit MK 51 which is a macroporous

Received 18 July 2009; accepted 6 December 2009.
Address correspondence to Nalan Kabay, Ege University, Chemical Department, Faculty of Engineering, Izmir 35100, Turkey. Tel.: 90-232-3887600; Fax: 90-232-3887776. E-mail: nalan.kabay@ege.edu.tr

weak base anion exchange resin with polyhydroxyl groups showing a very high selectivity for the removal of boric acid/borates from aqueous solutions. The high selectivity of Lewatit MK 51 resin for boron allows for the selective removal of boron from water and aqueous solutions containing high levels of salt. In addition to the experimental tests, kinetic data were evaluated using some model equations.

MATHEMATICAL MODELLING OF SORPTION KINETICS

Conventional Kinetic Modelling of Sorption

Pseudo First-Order Equations

A simple kinetic of sorption is the pseudo first-order equation in the form of (9):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

Integrating Eq. (1) and applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives Eq. (2):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2}$$

where q_e and q_t are the amounts of boron sorbed at equilibrium and at time t (mg/g), respectively, and k_1 is the rate constant of pseudo first-order sorption, ($\min^{-1}$).

Pseudo Second-Order Equations

A pseudo second-order equation based on sorption equilibrium capacity may be expressed in the form (9):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

After define integration by applying the initial conditions, Eq. (3) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{4}$$

Eq. (4) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where k_2 is the rate constant of pseudo second-order sorption (g/mg min).

Diffusional and Reaction Models

Batch kinetic studies were evaluated using diffusional and reaction models. The models for process dynamics include 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 the other method prefers the unreacted core model (UCM) to describe the rate determining steps in ion exchange process (10). These two kinetic models developed for spherical particles to specify the rate-determining steps are given in Table 1.

EXPERIMENTAL

Materials

Weak base anion exchange resin, Lewatit MK 51, was kindly provided by LANXESS Deutschland GmbH and ÖKOTEK. Properties of this resin are given in Table 2. Some characteristics of the geothermal water used are shown in Table 3.

Batch-Mode Studies

To determine the optimum resin amount for boron removal from geothermal water, 100 mL of geothermal water was contacted with weak base anion exchange resin Lewatit MK 51 at a particle size range of 0.500–0.710 mm using different resin amounts (0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 g) with continuous shaking at 30°C for 24 hours.

Kinetic Tests

Batch kinetic tests were performed by contacting 2 g of Lewatit MK 51 resin at a particle size range of 0.500–0.710 mm with 500 mL of geothermal water at 25°C and at a stirring rate of 250 rpm to investigate the effects

TABLE 1
Diffusional and reaction models

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

TABLE 2
Properties of Lewatit MK 51

Properties	
Functional group	Polyalcohol
Ionic form as shipped	FB/Cl^-
Bead size, mm	0.3–1.25
Effective bead size, mm	0.44–0.54
Shipping weight (+/−5%), g/L	710
Density, g/mL	1.1
Water retention, %	48–55
Total capacity (min.), eq/l	0.8
Recommended operating temperature (max.), °C	30
Recommended operating pH range	0–7

of resin particle size range (0.355–0.500, 0.500–0.710, 0.710–1.000 mm), temperature (15, 25, 35, 45°C), and at various stirring rates (200, 250, 300 rpm) for boron removal from geothermal water.

Column-Mode Studies

In column-mode studies, a glass column with an internal diameter of 0.7 cm was used. 0.5 mL of wet-settled volume of the resin at a particle size range of 0.355–0.500 mm was packed into the column. Geothermal water was passed through the column by down-flow at SV 20 h^{-1} by a peristaltic pump. Each successive 3 mL (6 BV) fractions of the effluent were collected using a fraction collector. Breakthrough curves were obtained by analysis of these successive fractions. Resin packed into the column was washed with deionized water after sorption step. The boron loaded resin was eluted with 5% H_2SO_4 at SV 10 h^{-1}. The column elution profiles were obtained by analysis of each successive 2 mL (4 BV) fractions of eluates.

Boron Analysis

The analysis of boron was performed spectrophotometrically using Azomethine-H and Curcumine methods at λ_{max}: 415 and 543 nm, respectively.

TABLE 3
Characteristics of geothermal water

Cations	C (mg/L)	Anions	C (mg/L)
Na^+	358.2	Cl^-	189.2
K^+	29.9	SO_4^{2-}	138.4
Ca^{2+}	36.2	F^-	6.8
Mg^{2+}	2.8	HCO_3^-	771.0
B = 10.7 mg/L (pH 7.4, EC 1747 (μS/cm)			

RESULTS AND DISCUSSION

Batch-Mode Study

Optimum resin amount for boron removal from geothermal water was determined using Lewatit MK 51 resin at a particle size range of 0.500–0.710 mm. Figure 1 shows that optimum resin amount for boron removal from geothermal water is 4.0 g resin/L-geothermal water.

Kinetic Tests

The kinetic behavior of Lewatit MK 51 resin was examined in order to get a measure of the relative kinetic performance of this resin as a function of resin particle size, temperature, and stirring rate. Figures 2–4 present plots

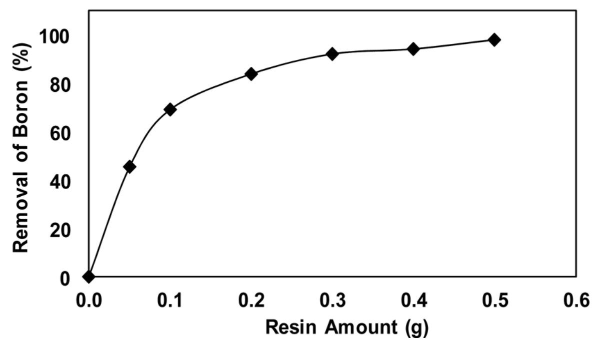

FIG. 1. Effect of resin amount on boron removal from geothermal water.

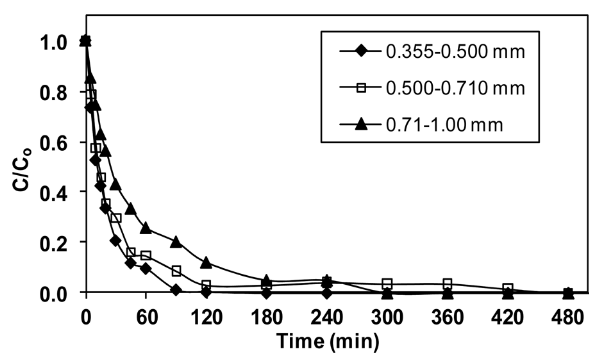

FIG. 2. Effect of resin particle size on sorption kinetics.

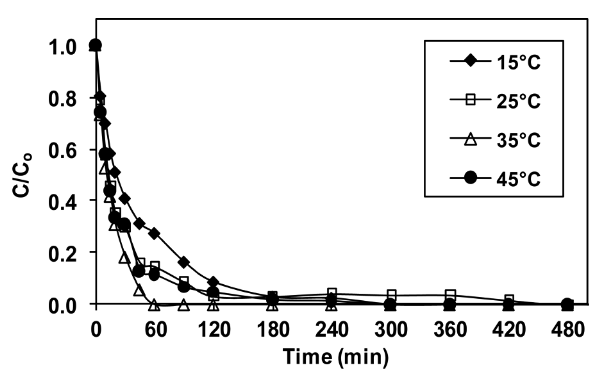

FIG. 3. Effect of temperature on sorption kinetics.

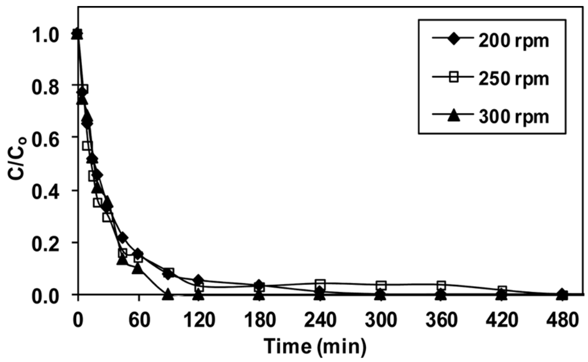

FIG. 4. Effect of stirring rate on sorption kinetics.

of the change in concentration at any time to initial concentration versus time. As shown in Fig. 2, at a moderate stirring rate, the boron removal rate was high at a small particle size range (0.355–0.500 mm) than those of particle size ranges of 0.500–0.710 and 0.710–1.000 mm since the ability of boron to reach the binding sites of the resin increased due to increased effective surface area.

The kinetic studies were evaluated using pseudo-first-order and pseudo-second-order kinetics models as described before. To obtain the correlation coefficients, $\log(q_e - q_t)$ versus t and t/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 equations for boron sorption on the resin. Since the correlation coefficients of pseudo-second-order kinetics (R^2) (Table 4) are greater than those of pseudo-first-order kinetics, it can be concluded that the sorption of boron by Lewatit MK 51 resin obeys the pseudo-second-order kinetic model for all resin particle size ranges.

The linear correlation coefficients obtained by plotting the related equations in Table 1 versus time were summarized in Tables 5 and 6. The maximum correlation coefficients for the linear models show that the rate determining step for boron sorption is controlled by particle diffusion for all resin particle size ranges.

Additionally, Fig. 3 shows that the boron removal rate was found to be greater at temperatures of 25 and 35°C than at 15°C. It can be concluded that the diffusion of boron through the functional groups of the resin was improved due to the increase in temperature. Besides, because the maximum operating temperature for this resin was given as 30°C (Table 2), the boron removal rate was decreased at 45°C.

Finally, Fig. 4 shows that the stirring rate has almost no effect on the kinetic performance of the resin for boron removal from geothermal water, especially in the initial 1 h.

TABLE 4
Evaluation of batch kinetic studies according to conventional kinetic modelling

Resin particle size (mm)	R^2 (first order kinetics)	R^2 (second order kinetics)
0.355–0.500	0.9885	0.9989
0.500–0.710	0.9709	0.9968
0.710–1.000	0.9840	0.9987

TABLE 5
Evaluation of sorption kinetics according to ISV model

	R^2 (ISV)	
Resin particle size (mm)	$-\ln(1-X)$	$-\ln(1-X^2)$
0.355–0.500	0.9955	0.9965
0.500–0.710	0.9952	0.9958
0.710–1.000	0.9860	0.9955

TABLE 6
Evaluation of sorption kinetics according to UCM model

	R^2 (UCM)		
Resin particle size (mm)	X	$3-3(1-X)^{2/3}-2X$	$1-(1-X)^{1/3}$
0.355–0.500	0.9333	0.9989	0.9838
0.500–0.710	0.9671	0.9964	0.9891
0.710–1.000	0.9400	0.9948	0.9743

Column-Mode Study

In order to get some information about column performance of weak base anion exchange resin on boron removal from geothermal water, Lewatit MK 51 resin was used for column-mode study.

As seen from the breakthrough curve of boron (Fig. 5), this resin was found to be effective for boron removal from

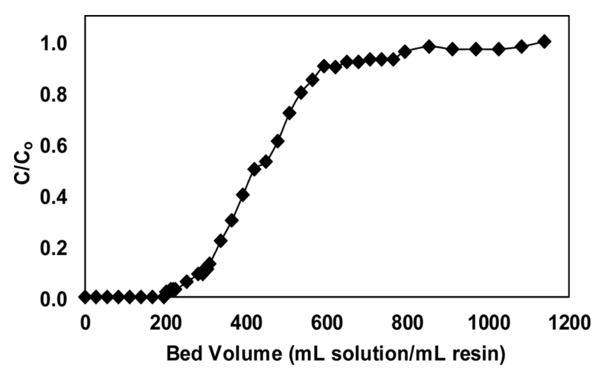

FIG. 5. Breakthrough curve of boron (SV: $20\,h^{-1}$).

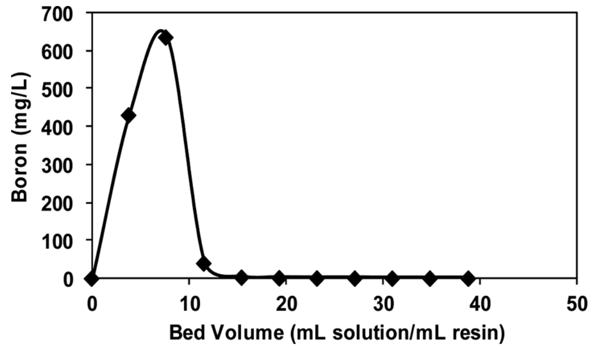

FIG. 6. Elution profile of boron (SV: $10\,h^{-1}$).

geothermal water. The breakthrough capacity was calculated by accepting the breakthrough point as 0.64 mg B/L, which is the highest concentration just before 1.0 mg/L above which boron concentration in irrigation water is harmful for most of the plants (4). The breakthrough and total capacities were calculated as 2.75 and 4.98 mg B/mL, respectively. Boron loaded resin was eluted effectively using 5% H_2SO_4 as shown in Fig. 6.

CONCLUSIONS

In the present study, batch and column mode tests for boron removal from geothermal water were conducted using weak base ion exchange resin Lewatit MK 51. The optimum resin amount for boron removal from geothermal water was found as 4.0 g resin/L-geothermal water. The sorption kinetic rate was higher at a smaller particle size range (0.355–0.500 mm). According to the results of the kinetic tests, boron sorption using Lewatit MK 51 resin obeys the pseudo-second-order kinetic model, which gives the best correlation coefficient. The rate determining step for boron sorption is found to be particle diffusion controlled for all resin particle size ranges. The breakthrough and the total capacities were calculated as 2.75 and 4.98 mg/mL, respectively. Boron loaded resin was eluted effectively using 5% H_2SO_4.

ACKNOWLEDGEMENTS

This study was supported by the National Boron Research Institute, BOREN (Project Number 2008-G-0192). We thank to LANXESS Deutschland GmbH and OKOTEK for providing us the boron selective resin sample. We are also grateful to Izmir Geothermal Energy Co. for the support to provide with the geothermal samples.

NOMENCLATURE

a: stoichiometric coefficient
C: total concentration of both exchanging species, M
C_{Ao}: concentration of species A in bulk solution, M
D: diffusion coefficient in solution phase, m^2/s
D_{eR}: effective diffusion coefficient in solid phase, m^2/s
D_r: diffusion coefficient in solid phase, m^2/s
K_{li}: rate constant for film diffusion (infinite solution volume condition), L/s
K_{mA}: mass transfer coefficient of species A through the liquid film, m/s
k: rate constant, L/s
k_s: reaction constant based on surface, m/s
r_o: average particle radius, mm
t: time, s
X: fractional attainment of equilibrium or extent of resin conversion
δ: film thickness, mm

REFERENCES

1. Yilmaz, A.E.; Boncukcuoglu, R.; Kocakerim, M.M.; Yilmaz, M.T.; Paluluoglu, C. (2007a) Boron removal from geothermal waters by electrocoagulation. *Journal of Hazardous Materials*, 153: 146–151.
2. Cengeloglu, Y.; Tor, A.; Arslan, G.; Ersoz, M.; Gezgin, S. (2007) Removal of boron from aqueous solution by using neutralized red mud. *Journal of Hazardous Materials*, 142: 412–417.
3. Nadav, N. (1999) Boron removal from seawater reverse osmosis permeate utilizing selective ion exchange resin. *Desalination*, 124: 131–135.
4. Koseoglu, H.; Kabay, N.; Yüksel, M.; Sarp, S.; Arar, O.; Kitis, M. (2008) Boron removal from seawater using high rejection SWRO membranes-impact of pH, feed concentration, pressure, and cross-flow velocity. *Desalination*, 227: 253–263.
5. Yilmaz, I.; Kabay, N.; Yuksel, M.; Holdich, R.; Bryjak, M. (2007b) Effect of ionic strength of solution on boron mass transfer by ion exchange separation. *Separation Science and Technology*, 42 (5): 1013–1029.
6. Kabay, N.; Yilmaz, I.; Yamac, S.; Samatya, S.; Yuksel, M.; Yuksel, U.; Arda, M.; Saglam, M.; Iwanaga, T.; Hirowatari, K. (2004a) Removal and recovery of boron from geothermal wastewater by selective ion exchange resins: I. Laboratory tests. *Reactive & Functional Polymers*, 60: 163–170.
7. Kabay, N.; Yılmaz, I.; Yamac, S.; Yuksel, M.; Yuksel, U.; Yildirim, N.; Aydogdu, O.; Iwanaga, T.; Hirowatari, K. (2004b) Removal and recovery of boron from geothermal wastewater by selective ion-exchange resins – II. *Field tests. Desalination*, 167: 427–438.
8. Yilmaz-Ipek, I.; Kabay, N.; Yuksel, M.; Kirmizisakal, O.; Bryjak, M. (2009). Removal of boron from Balcova-Izmir geothermal water by ion exchange process: Batch and column studies. *Chemical. Engineering. Communications*, 196: 277–289.
9. Ozcaar, M.; 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.
10. Badruk, M.; Kabay, N.; Demircioğlu, M.; Mordoğan, H.; İpekoglu, Ü. (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.