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Boron removal from aqueous solutions by ion-exchange resin: Column sorption–elution studies

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Abstract

A column sorption–elution study was carried out by using a strong base anion-exchange resin (Dowex 2 × 8) for the removal of boron from aqueous solutions. The breakthrough curve was obtained as a function of feed flow rate and the total and breakthrough capacity values of the resin were calculated. The boron on the resin was quantitatively eluted with 0.5 M HCl solution at different flow rates. Three consecutive sorption–elution–washing–regeneration–washing cycles were applied to the resin in order to investigate the reusability of the ion-exchange resin. Total capacity values remained almost the same after three sorption–elution–regeneration cycles. The Thomas and the Yoon–Nelson models were applied to experimental data to predict the breakthrough curves and to determine the characteristic column parameters required for process design. The results proved that the models would describe the breakthrough curves well.

Keywords: Boron; Ion-exchange; Dowex 2 × 8; Column study; Breakthrough curve

1. Introduction

Boron is widely distributed in the environment mainly in the form of boric acid or borate salts. The main sources of boron in surface and ground waters are urban wastewater with detergents and cleaning products, industrial effluents from a great number of industrial activities and diverse chemical products used in agriculture [1].

Boron contamination of water is a serious environmental problem. In aqueous solutions boron exist as boric acid, $B(OH)_3$ or borate anion, $B(OH)^-{}_4$ depending upon solution pH. Removing boron from water is difficult and can be prohibitively expensive and impractical.

Treatment concerning boron removal processes includes several categories. The first is in the precipitate processes group (including coagulation and lime softening). The next two categories are adsorption processes and ion exchange. The last category includes the membrane processes (reverse osmosis and electrodialysis reversal) [2].

Numerous works have been done for boron removal and/or recovery from wastewaters. Amberlite IRA 743, a boron-specific resin, was used in boron removal from drinking waters, boron-containing wastewaters or geothermal wastewaters [3–5]. *N*-Glucamine-type chelating resins such as Diaion CRB 01, Diaion CRB 02, Purolite S 108(1) and Purolite S 108(2) were used in boron removal from wastewaters of geothermal plants, and their column capacities were obtained as 3.43, 3.23, 2.32 and 2.44 mg B/mL resin, respectively by Kabay et al. [6]. Total column capacity of Diaion CRB 02 was obtained as 4.2 mg B/mL resin by Badruk et al. [7]. Amberlite XE 243 was also used to remove boron from wastewaters from boric acid and borax plants [8]. Amberlite IRN-78LC resins were investigated both experimentally and theoretically for boron thermal regeneration system [9]. Okay et al. [10] studied boron removal from the drainage waters of Bigadiç boron mines of Turkey by adsorption by using α-cellulose, magnesium oxide and ion exchange by Amberlite IRA743. Polat et al. [11] presented an alternative methodology for boron removal by using coal and fly ash as adsorbents. In another study, adsorption studies for boron removal from aqueous solutions on sepiolite were carried out [12]. Boron adsorption onto activated sludge was investigated using bench-scale reactors under simulated wastewater treatment conditions [13]. Layered double hydroxides (LDHs) or

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hydrotalcite (HT)-like compounds with different kinds of metal ions (Mg–Al and Mg–Fe) in the brucite-like sheets were prepared and their adsorption properties were studied in the boron removal from aqueous solutions under laboratory conditions [14]. Boron removal from wastewaters by electrocoagulation using aluminum electrode material was investigated recently [15]. The electrodialytic treatment of boron-containing wastewater, of 63.5–76.5 mg/L of B concentration, was examined by Turek et al. [16]. Dydo et al. [17] studied on boron removal from chemical landfill leachate by nanofiltration and reverse osmosis by using BW-30, TW-30, NF-90 and NF-45 (Filmtec) membranes. Boron removal from aqueous solutions was studied through Neosepta-AHA membrane by Donnan dialysis method [18].

The removal of boron from aqueous solutions by using red mud was investigated by Cengeloglu et al. [19], who reported that the Freundlich sorption capacity is 5.996 mg/g. In the study of Seyhan et al. [20], the maximum adsorption capacities were reported as 2.534 and 0.1184 mg/g for Çamlıca Bentonite 1 and Çamlıca Bentonite 2, respectively. Cotton cellulose was used as the biosorbent for boron removal by Liu et al. [21] and they found maximum boron uptake as 11.3 mg/g at pH 7. Wang et al. [22] developed a chelating polymeric sorbent for removal or recovery of boron from aqueous solutions and column total capacity of this resin was given as 1.26 mmol/g and also the reusability of the sorbent was as high as 10 cycles without obvious loss in its sorption behaviour.

Among these methods, the ion-exchange process is most extensively used. Ion exchangers are solid and suitably insolubilized high molecular weight polyelectrolytes which can exchange their mobile ions for ions of equal charge from the surrounding medium. The resulting ion exchange is reversible and stoichiometric with the displacement of one ionic species by another on the exchanger. The column process is the most common and efficient ion-exchange method [23]. Strongly basic anion-exchange resins derive their functionality from quaternary ammonium exchange sites. The two main groups of strong basic anion-exchange resins are Type I and Type II, depending on the type of the amine used during the chemical activation process. Type I sites have three methyl groups; in Type II an ethanol group replaces one of the methyl groups. Dowex 2 × 8 is a Type II resin. Type II resin feature removal of all anions and give best results on waters and wastewaters that predominantly contain free mineral acid (chlorides and sulfates) [24,25]. In real boron plant wastewaters contain these components.

The present study describes the column performances of Dowex 2 × 8 for boron removal from the aqueous solutions. Thomas and Yoon–Nelson models were applied to the results obtained from the column study. Column capacities were also calculated.

2. Experimental

Dowex 2 × 8 is a strong basic anion-exchange resin. It was purchased from Supelco. The characteristics of the resin are given in Table 1 and the structure of the resin is given in Fig. 1.

Table 1
Typical chemical and physical characteristics of Dowex 2 × 8

Constitutional type	Microporous
Ionic form	Cl^-
Mesh (particle size)	100–200 mesh (0.149–0.074 mm)
Moisture content (%)	37
Functional group	Benzyl-dimethylethanolamine
Density (g/mL)	0.7
Total exchange capacity (meq/mL resin)	1.33
(meq/g resin)	3.5
Maximum operating temperature (°C)	66
pH range	0–14

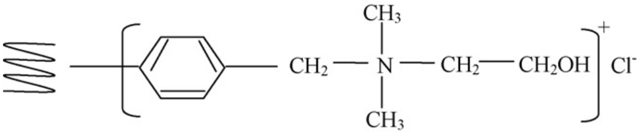

Fig. 1. Structure of Dowex 2 × 8.

Before the ion-exchange resin was used in the experiments, it was pretreated. It was first washed by distilled water several times. Then the resin was immersed in 2N NaOH solution for 48 h and finally washed again by distilled water. The aqueous solution (600 mg B/L at original pH (5.8)) to be used in the experiments was prepared by dissolving an appropriate amount of boric acid (Merck product) in the distilled water. A high boron concentration was chosen in this study because boron concentration in boron industry wastewater was quite high. The other solutions used in the experiments were freshly prepared for each experimental run.

The column experiments were performed in a glass column (0.7 cm internal diameter and 15 cm length). Glass wool was placed in the bottom of the column and then packed with 3 mL wet-settled volume of resin. The aqueous solution was delivered down-flow to the column at 39 and 45 mL/h flow rates using a peristaltic pump (ATTO SJ 1211 Model). Experimental system is given in Fig. 2. From the outlet of the column, each successive 1.5 mL fractions of the effluent were collected using a fraction collector (Spectra/chrom CF-1). Breakthrough curves were obtained by analysis of each fraction by the spectrophotometer (HACH DR-2000) using Carmine method [26]. Column studies were terminated when the column reached exhaustion. The column elution experiments were performed at 39 and 45 mL/h flow rates by using 0.5 M HCl solution. The elution profile was

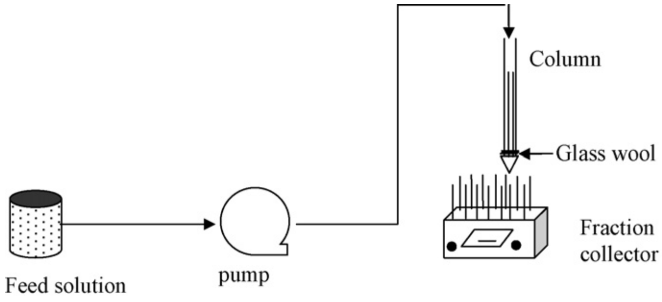

Fig. 2. Experimental system.

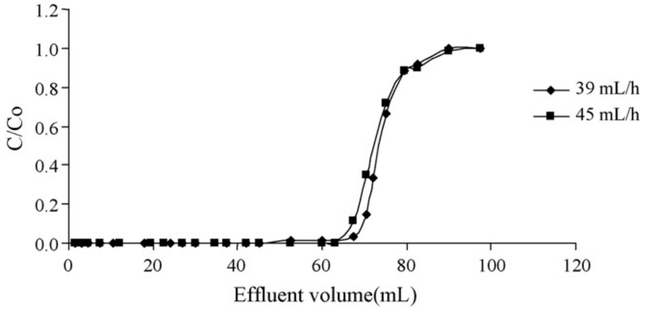

Fig. 3. Effect of flow rate on breakthrough capacity of Dowex 2 × 8.

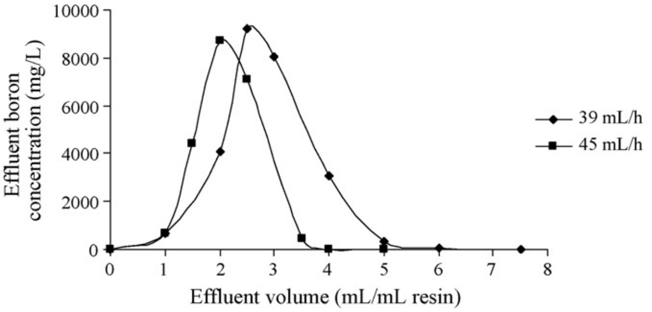

Fig. 4. Elution profiles of boron at different flow rates.

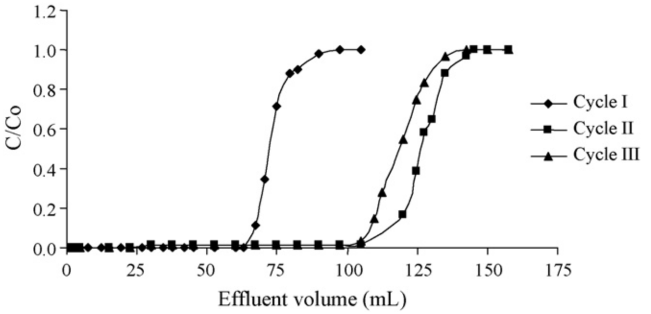

Fig. 5. Recycle use of Dowex 2 × 8 for boron removal.

obtained by analysing the 1.5 mL fractions collected by a fraction collector. The absence of boron in the effluent indicated the completion of elution.

The recycle tests were conducted using the Dowex 2 × 8 (3 mL) and by passing 600 mg B/L H_3BO_3 solution through the column at 45 mL/h. After the elution step performed by using 0.5 M HCl solution at 45 mL/h and the washing step with distilled water, the resin was regenerated using 2N NaOH and finally washed with distilled water. Another loading cycle was then carried out.

3. Results and discussion

Breakthrough curves generally permit a good description of the process in ion-exchange columns since a breakthrough capacity characteristic for a column under given conditions can be assigned to these curves.

The breakthrough curves show the loading behaviour of boron to be removed from solution in a fixed bed and is usually expressed in terms of sorbed boron concentration (C_{sor} = inlet boron concentration (C_0) − effluent boron concentration (C)) or normalized concentration defined as the ratio of effluent boron concentration to inlet boron concentration (C/C_0) as a function of time (t) or volume of effluent (V) for a given bed height. The area under the breakthrough curve obtained by integrating the sorbed concentration versus the throughput volume plot can be used to find the total sorbed boron quantity (maximum column capacity). Sorption capacity of the bed (q_0; mg/g) is calculated from Eq. (1) [27]:

$$q_0 = \int_0^{V_T} \frac{(C_0 - C)\mathrm{d}V}{m} \tag{1}$$

where m is the mass of the ion-exchange resin (g).

Fig. 3 shows the results of the column experiments with various flow rates. The experiments were conducted by passing H_3BO_3 solution (600 mg B/L) through the column at 39 and 45 mL/h. If the flow rate is higher, the H_3BO_3 solution does not have enough time to react with the ion-exchange resin, which consequently results in less volume of effluent. Obtained results for different flow rates (Fig. 3) are in accordance with previous literature [28]. The loaded resin was quantitatively eluted with 0.5 M HCl at 39 and 45 mL/h. The resulting elution profile is shown in Fig. 4. The column capacity values of the resin are given in Table 2.

In order to demonstrate the reusability of the Dowex 2 × 8 resin, the sorption–elution–washing–regeneration–washing cycle was repeated three times. Recycle use of Dowex 2 × 8 was studied at 45 mL/h. The resulting breakthrough curves are given in Fig. 5. The column capacity values of the resin for each cycle were given in Table 3. According to Table 3, the breakthrough capacity of the resin increased to some extent during the second and third cycles. This could be due to activation of functional sites on the resin by reconditioning with NaOH during the regeneration step [28]. At the same time, flow rate decreased at the second and third cycles because resin bed settled down. Total capacity values remained almost the same after three cycles. So recycle number was not increased more than three. Elution profiles of each cycle are shown in Fig. 6.

Table 2
Column performance of Dowex 2 × 8 at different flow rates

Flow rate (mL/h)		Sorption capacity		Breakthrough capacity		Column utilization (%)	Elution efficiency (%)
Sorption	Elution	mg B/(mL resin)	mmol B/(mL resin)	mg B/(mL resin)	mmol B/(mL resin)		
39	39	15	1.98	13.94	1.84	93	97
45	45	14.93	1.97	13.13	1.73	88	71

Table 3
Column performance of Dowex 2 × 8 for each cycle

Cycle		Sorption capacity		Breakthrough capacity		Column utilization (%)	Elution efficiency (%)
Sorption	Elution	mg B/(mL resin)	mmol B/(mL resin)	mg B/(mL resin)	mmol B/(mL resin)		
1	1	14.93	1.97	13.13	1.73	88	71
2	2	25.79	3.4	22.95	3.03	89	88
3	3	24.49	3.2	21.79	2.88	89	82

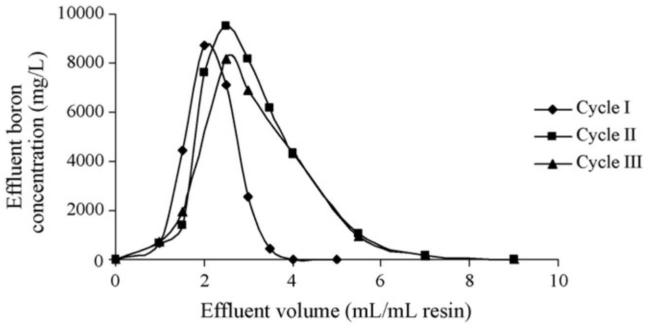

Fig. 6. Elution profiles of boron.

3.1. The Thomas model

The sorption data from column studies were analyzed using the Thomas model. The main advantages of this model are its simplicity and reasonable accuracy in predicting the breakthrough curves under various operating conditions [29]. The model is represented by [27,30]

$$\frac{C}{C_0}=\frac{1}{1+\exp[K_T(q_0m-C_0V)/Q]} \tag{2}$$

where K_T is the Thomas rate constant (mL/(min mg)) and Q is the volumetric flow rate (L/min). The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_o}{C}-1\right)=\frac{K_Tq_0m}{Q}-\frac{K_TC_0}{Q}V \tag{3}$$

The kinetic coefficient K_T and sorption capacity of the bed q_0 can be determined from a plot of $\ln[(C_0/C)-1]$ against time at a given flow rate (Figs. 7 and 8).

The Thomas equation coefficients for boron sorption were given in Table 4. As flow rate increased, the values of K_T increased and the values of q_0 decreased. The data in Table 4 also showed a negligible difference between the experimental and predicted values of the bed capacity (q_0) obtained at 39 and 45 mL/h flow rates.

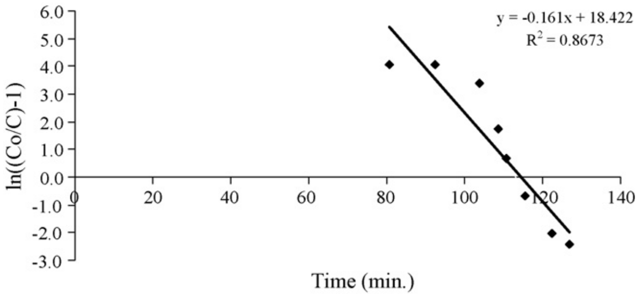

Fig. 7. Plot of $\ln[(C_0/C)-1]$ vs. t for 39 mL/h flow rate.

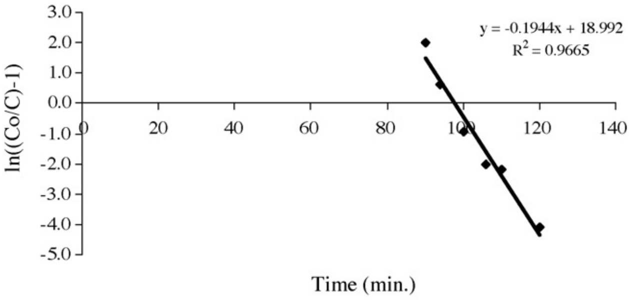

Fig. 8. Plot of $\ln[(C_0/C)-1]$ vs. t for 45 mL/h flow rate.

The theoretical predictions based on the model parameters are compared with the observed data in Figs. 9 and 10.

3.2. The Yoon and Nelson model

The Yoon and Nelson model is not only less complicated than other models, but also requires no detailed data concerning the characteristics of the sorbate, the type of the sorbent, and the physical properties of the sorption bed.

The Yoon and Nelson equation regarding to a single-component system is expressed as [27]

$$\frac{C}{C_0}=\frac{\exp(K_{YN}t-\tau K_{YN})}{1+\exp(K_{YN}t-\tau K_{YN})} \tag{4}$$

Table 4
The Thomas equation coefficients for boron sorption by Dowex 2 × 8

Flow rate (mL/h)	Thomas model			
	K_T (mL/(min mg))	$q_{0,\mathrm{cal.}}$ (mg/g)	$q_{0,\mathrm{exp.}}$ (mg/g)	R^2
39	0.268	21.276	21.428	0.8673
45	0.324	20.93	21.33	0.9665

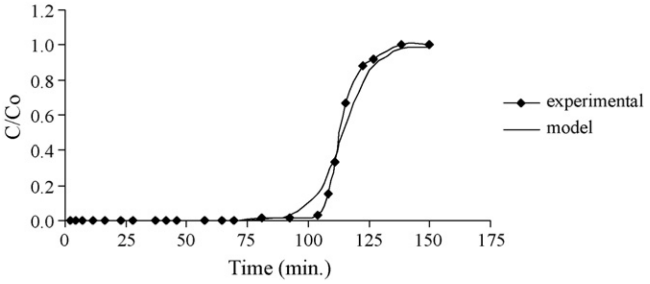

Fig. 9. Comparison of the experimental and predicted breakthrough curves according to Thomas model for 39 mL/h flow rate (at 25 °C, C_0 = 600 mg B/L).

Table 5
The Yoon and Nelson equation coefficients for boron sorption by Dowex 2 × 8

Flow rate (mL/h)	Yoon–Nelson model					
	K_{YN} (min^{-1})	$\tau_{cal.}$ (min)	$\tau_{exp.}$ (min)	$q_{0,cal.}$ (mg/g)	$q_{0,exp}$ (mg/g)	R^2
39	0.161	114.42	113.8	21.24	21.428	0.8673
45	0.1944	97.69	93.3	20.93	21.33	0.9665

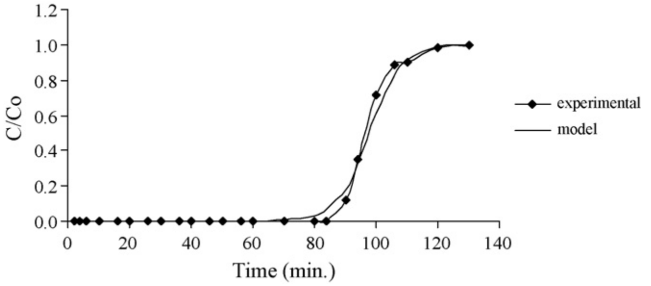

Fig. 10. Comparison of the experimental and predicted breakthrough curves according to Thomas model for 45 mL/h flow rate (at 25 °C, $C_0 = 600$ mg B/L).

where K_{YN} is the rate constant (min^{-1}); τ, the time required for 50% adsorbate breakthrough (min). The linearized form of the Yoon and Nelson model is as follows:

$$\ln\frac{C}{C_o - C} = K_{YN}t - \tau K_{YN} \qquad (5)$$

The values of K_{YN} and τ were determined from $\ln(C/(C_0 - C))$ against t plots at different flow rates (Figs. 11 and 12). Due to the symmetrical nature of the breakthrough curve, the amount of boron sorbed by the Dowex 2 × 8 is one half of the total boron entering the sorption column within the 2τ period. Hence the following equation can be written [31]:

$$q_0 = \frac{1}{2}C_0Q(2\tau) = C_0Q\tau \qquad (6)$$

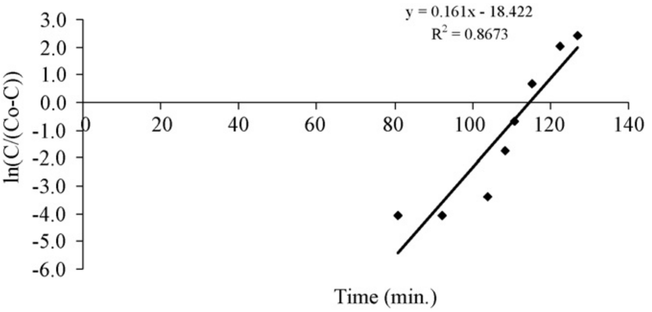

Fig. 11. Plot of. ln($C/(C_0 - C)$) vs. t for 39 mL/h flow rate.

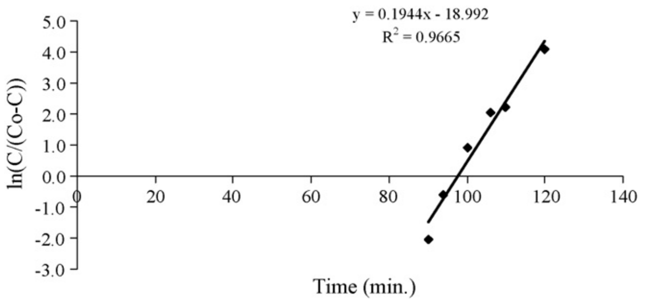

Fig. 12. . Plot of ln($C/(C_0 - C)$) vs. t for 45 mL/h flow rate.

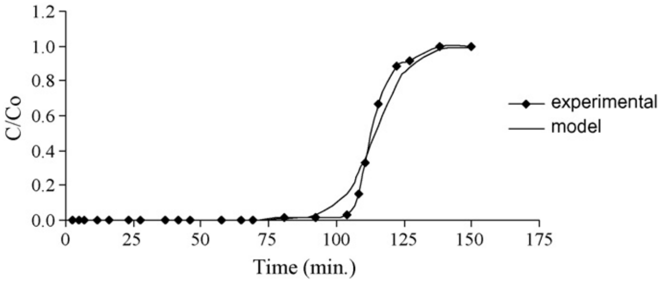

Fig. 13. Comparison of the experimental and predicted breakthrough curves according to the Yoon and Nelson model for 39 mL/h flow rate (at 25 °C, $C_0 = 600$ mg B/L).

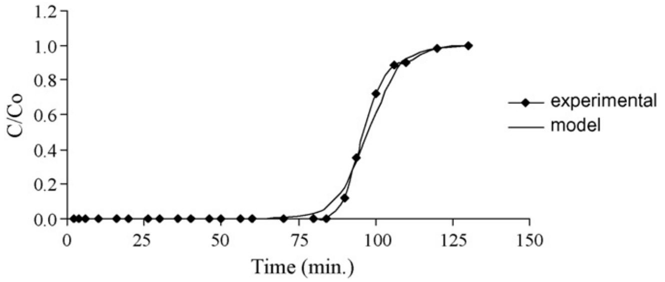

Fig. 14. Comparison of the experimental and predicted breakthrough curves according to the Yoon and Nelson model for 45 mL/h flow rate (at 25 °C, $C_0 = 600$ mg B/L).

The values of K_{YN}, τ and q_0 are also listed in Table 5. From Table 5 the rate constant K_{YN} increased and the 50% breakthrough time τ decreased with increasing flow rate. The data in Table 5 indicated that τ and q_0 values are very similar to the experimental results. The theoretical curves were compared with the corresponding experimental data in Figs. 13 and 14.

4. Conclusions

For the column ion-exchange experiments, Dowex 2 × 8 anionic ion-exchange resin was used. The following results are obtained:

1) Columnar sorption of boron from H_3BO_3 solution was studied at 39 and 45 mL/h flow rates and the breakthrough capacities were obtained as 13.94 and 13.13 mg B/mL resin, respectively. The breakthrough point shifted to right more with a decrease in the flow rate.

2) Column utilization values were 93% and 88%, elution efficiency values were 97% and 71% for 39 and 45 mL/h flow rates, respectively. So recovery of boron may be considerable.
3) The capacity increases with the first cycle. The capacity did not noticeably change after the 2nd and 3rd cycles. The results showed that Dowex 2 × 8 could be repeatedly used in boron sorption studies.
4) The Thomas and the Yoon–Nelson models were adopted for representing the column breakthrough. The capacity values were obtained as 21.276 and 21.24 mg/g using the Thomas and the Yoon–Nelson models, respectively. The theoretical models and their parameters fitted the experimental breakthrough curves well.

Acknowledgement

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