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Adsorption of boron from boron-containing wastewaters by ion exchange in a continuous reactor

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Abstract

In this study, boron removal from boron-containing wastewaters prepared synthetically was investigated. The experiments in which Amberlite IRA 743, boron specific resin was used were carried out in a column reactor. The bed volume of resin, boron concentration, flow rate and temperature were selected as experimental parameters.

The experimental results showed that percent of boron removal increased with increasing amount of resin and with decreasing boron concentration in the solution. Boron removal decreased with increasing of flow rate and the effect of temperature on the percent of total boron removal increased the boron removal rate. As a result, it was seen that about 99% of boron in the wastewater could be removed at optimum conditions.

Keywords: Boron removal; Ion exchange; Amberlite IRA 743; Wastewater; Adsorption

1. Introduction

Boron has a number of minerals, in nature, mostly calcium and/or sodium borates, such as colemanite ($2CaO\cdot3B_2O_3\cdot5H_2O$), ulexite ($Na_2O\cdot2CaO\cdot5B_2O_3\cdot16H_2O$) and tinkal ($Na_2O\cdot2B_2O_3\cdot10H_2O$), etc. There is a variety of application including various boron fertilizers, insecticides, corrosion inhibitors in anti-freeze formulations for motor vehicle and other cooling system, buffers in pharmaceutical and dyestuff production, and the use of boron compounds for moderator in nuclear reactor, where anthropogenic water-soluble boron compounds are discharged to aqueous environment [1,2].

Boron is normally in very low amounts in soil and irrigation waters, but it accumulates very fast in soils irrigated with boron-containing wastewaters because of difficulty of washing it. 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 heavy metals forming them. Although little amount of boron is a nutrient for some plants, its excessive amount affects badly the growth of many agricultural products. Also, the maximum boron level in drinking water for human health is given as 0.3 mg/L in WHO standards [3].

Because inorganic boron compounds are antiseptics, conventional biological treatment methods cannot be used for boron removal from wastewaters. Also, coagulation–precipitation methods are not effective and not feasible for this purpose. So, ion exchange methods are applied in boron removal from wastewater as an advanced method [4,5].

Numerous researchers studied boron removal and/or recovery from wastewaters. Amberlite IRA 743, a boron specific resin, was used in boron removal from geothermal waters containing 19 mg/L boron and it was found that 99% of boron from geothermal water could be removed [6]. Also, the effects of pH on boron removal from industrial wastewaters were investigated with this resin and it was found that 99% of boron from industrial wastewaters could be removed at pH

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9.50 [7]. Amberlite XE 243 was used in boron removal in wastewaters from borax and boric acid factories and it was found that 95% of boron in wastewater can be removed [8]. Amberlite IRN-78 LC in OH^- form, a strong basic anion exchange resin, also, was used to remove boron from water containing boron up to 1500 mg/L and characteristics of boron adsorption on it was determined [9].

In a study carried out to obtain a specific boron resin by which boron is removed from irrigated waters, chloro metylated styrene-divinyl benzene copolymer was aminated by 1-deoxy-1-(methyl amino)-glucitol[10]. WOFATIT MK 51, which is characterized by a methyl aminoglucitol group, was used to remove boric acid from brines containing high concentrations of alkali and alkali earth salts [11].

The removal of boron in the wastewater from ceramic tiles processes was studied and appropriate results were obtained for solution of boron pollution [12]. Diaion San-1, a strong-base anion exchange resin, was used to investigate the effects of temperature on the boron adsorption and reported that boron is adsorbed on the resin in forms of monoborate, tetraborate and pentaborate ions [13].

Since boric acid and borates dissolve in water to form various borate ions, the composition of borate ions should be found out to understand the solution behavior, which depends on a number of factors, including the concentration of boric acid, the temperature and pH.

2. Experimental

In this study, boron concentration was chosen high because boron concentration from boron industry wastewater was quite high. The boric acid employed in this study was 99.99%. Wastewater samples used in the experiments were prepared synthetically. The solution with boron concentration of 250 mg/L was prepared by dissolving 1429 mg H_3BO_3 dried at 105 °C in distilled water. The same operations were repeated for the solutions with boron concentrations of 500 and 1000 mg/L at different weights. In the run employed Amberlite IRA 743 resin, optimum pH was observed at 9.5 although initial pH of solution was about 6.20 [7]. Therefore, in this study, pH was adjusted desired value by used 0.1 N NaOH. The samples were used for the ion exchange experiments. The parameters chosen in the experiments were temperature, boron concentration, the bed volume of resin and flow rate and their ranges were given in Table 1.

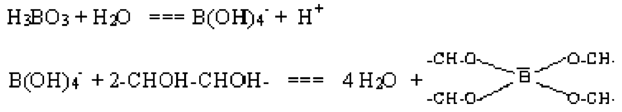
Amberlite IRA 743, which is a weak-base anion exchange resin, was used as an anion-exchanger throughout the experiments; its characteristics are listed in Table 2. This resin has a macroporous polystyrene matrix, on which *N*-methylglucamine functional groups are attached as seen in Fig. 1. It is commonly known that boron is retained according to the following reaction scheme; borate ion is complexed by sorbitol groups and a part of it is retained by a tertiary amine site that behaves as a weakly basic anion exchange [14]. The reactions can be expressed as follows

Table 1
Experimental parameters

Parameters	Range
The bed volume of resin (cm^3)	71.6, 107.5 and 143.2
Flow rate (mL/min)	10, 20 and 30
Boron concentration (mg/L)	250, 500 and 1000
Temperature (K)	283, 293, 303 and 313

Table 2
Characteristics of Amberlite IRA-743 resin

Properties	Value
Exchange capacity (mequiv./mL)	0.60
Particle size (mm)	0.40–0.60
Effective size (mm)	0.52
Moisture content (%)	56
pH range	0–14
Uniformity coefficient	1.40
Maximum operation temperature (K)	373
Ionic form	OH^-
True density (wet; g/cm^3)	0.68



$$H_3BO_3 + H_2O === B(OH)_4^- + H^+ \quad \text{(Boric acid dissociation)} \quad (1)$$

$$B(OH)_4^- + 2\text{-}CHOH\text{-}CHOH\text{-} === 4H_2O + \begin{matrix}\text{-}CH\text{-}O \\ \text{-}CH\text{-}O\end{matrix} > B < \begin{matrix}O\text{-}CH\text{-} \\ O\text{-}CH\text{-}\end{matrix} \quad \text{(Boron complexation)} \quad (2)$$

$$\text{-}CH_2\text{-}N(CH_3)\text{-}CH_2\text{-} + H^+ \longrightarrow \text{-}CH_2\text{-}N^+H(CH_3)\text{-}CH_2\text{-} \quad \text{(Amine protonation)} \quad (3)$$

A continuous system was used for removing of boron by the exchange reaction from wastewater. The temperature of the reactor was controlled with a HAAKE D8 thermostat connected to reactor. Experimental set-up is seen in Fig. 2. The ranges of experimental parameters were 250, 500 and 1000 mg/L for boron concentration, 71.6, 107.5 and 143.2 cm^3 for the bed volume of resin, 283, 293, 303 and 313 K for temperature and 10, 20 and 30 mL/min for flow rate, respectively. In the experiments, a weighted amount of the resin was put into the reactor. The desired temperature was maintained within ±0.5 °C. The solution was given at desired flow rate. The samples were accepted in desired volumes. The amount of boron adsorbed on the resin was calculated from the solution-phase concentration of boron. The

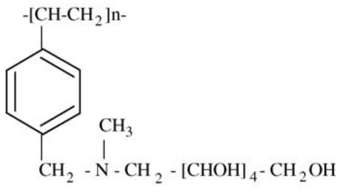


Fig. 1. Chemical structure of the Amberlite IRA 743 resin.

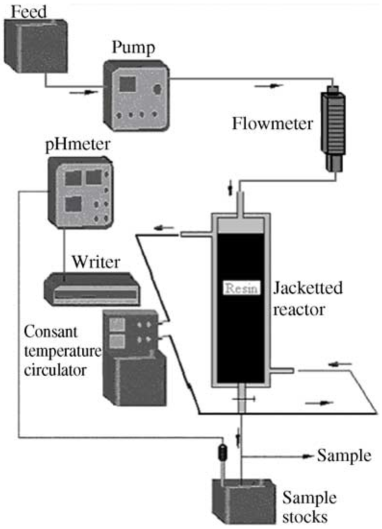


Fig. 2. Schematic view of the experimental system.

analytical determination of boric acid was done spectrophotometrically by means of carmine, which forms a complex compound with boric acid [15]. Boron analyses were performed at 585 nm of wavelength using a SHIMADZU 160 Model spectrophotometer.

3. Results and discussion

3.1. Equilibrium adsorption of boron

Fig. 3 demonstrates the amount of boron adsorbed by the Amberlite IRA-743 resin (Q) as a function of adsorption time (t). The amount of boron adsorption Q increases with an increase in the initial boron concentration. This is due to the increased concentration gradient of boron across the liquid–solid interface at higher initial boron concentration that facilitates overall mass transfer of boron from the liquid phase to the solid (resin) phase. The increase in the initial boron concentration also significantly shortens the time to reach adsorption equilibrium (Q_e) in this figure. For example, these times are 25 min for 1000 mg/L, 50 min for 500 mg/L and a longer time for 250 mg/L. The results obtained were shown graphically in Figs. 3 and 4.

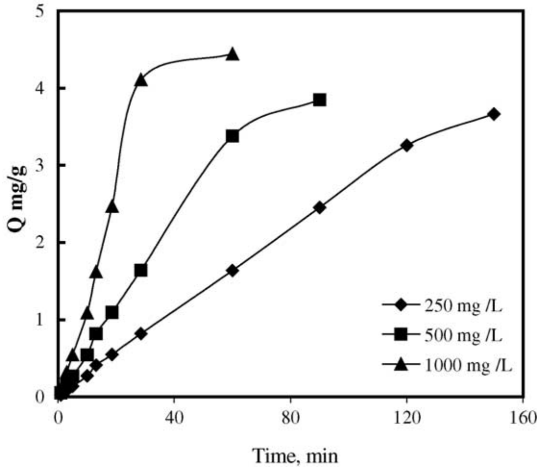


Fig. 3. The amount of boron adsorbed per unit weight of resin as a function of time with 15 g (107.5 cm^3) of resin and 293 K.

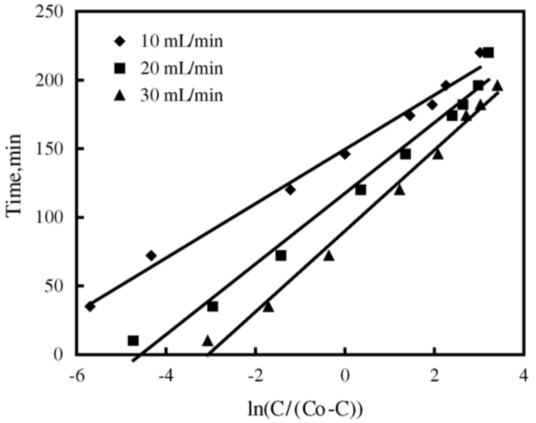


Fig. 4. Linear plot of t vs. $\ln[C/(C_0 - C)]$ for various flow rates with 500 mg/L initial boron concentration.

In the literature, various resins were used for boron removal from wastewater and geothermal water. It was seen that Amberlite IRA 743 employed in this study could be removed, about 99% of boron in the wastewater under optimum conditions.

3.2. The effects of parameters

In the runs, the effects of parameters such as the bed volume of resin, boron concentration, temperature and flow rate in the same reaction time were investigated and summarized as follows:

1. The effect of bed volume of resin: the effects of bed volume of resin were examined in the resin volume of 71.6, 107.5 and 143.2 cm^3. In the experiments, temperature at 293 K, boron concentration of 500 mg/L, and flow rate of 10 mL/min were kept constant and as shown graphically in Fig. 5, boron removal increased with increasing the resin volume.
2. The effect of boron concentration: the effect of boron concentration was examined at 250, 500 and 1000 mg/L. In the experiments, temperature at 293 K, bed volume of resin of 107.5 cm^3, and flow rate of 10 mL/min were kept constant. The results obtained graphically in Fig. 6 show that boron removal decreased with increasing boron concentration in wastewater. Finally, boron concentrations were decreased to 0.3 mg/L for 250 mg/L, 2 mg/L for 500 mg/L and 9 mg/L for 1000 mg/L.
3. The effect of flow rate: the effect of flow rate on boron removal was determined at 10, 20 and 30 mL/min. In the experiments, boron concentration of 500 mg/L, temperature at 293 K and bed volume of resin of 143.2 cm^3 were

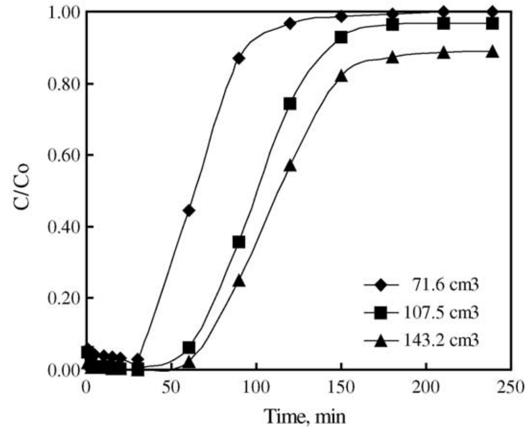


Fig. 5. The effect of bed volume of resin on the removal of boron.

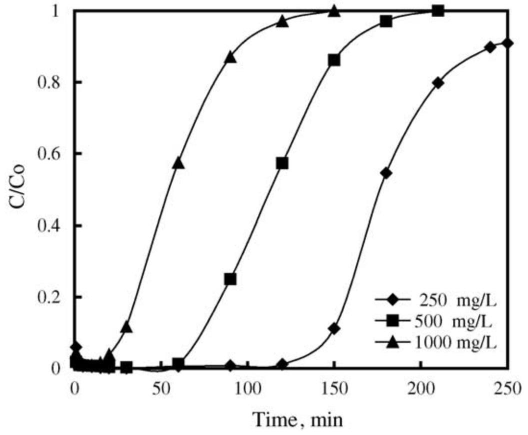


Fig. 6. The breakthrough curves for boron concentrations with 10 mL/min flow rates.

kept constant. Results given in Fig. 7 graphically show that flow rate affected boron removal inversely.

4. The effect of temperature: the effect of temperature on the boron removal was examined at 283, 298, 303 and 313 K.

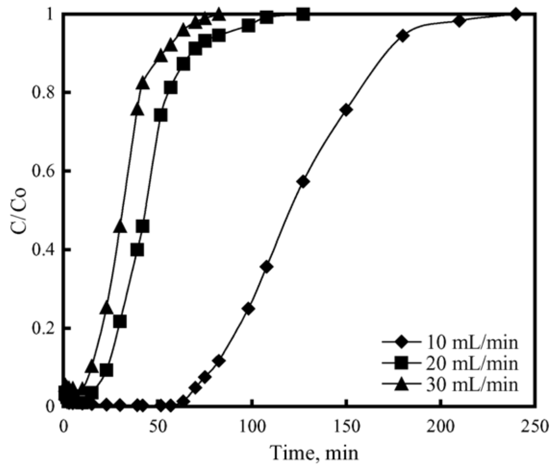


Fig. 7. The breakthrough curves for flow rates with 500 mg/L initial boron concentration.

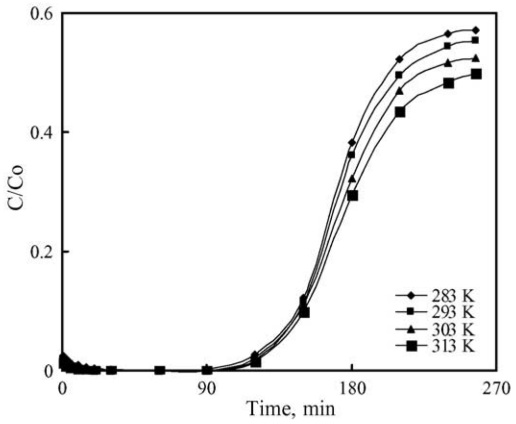


Fig. 8. The breakthrough curves for temperatures with 250 mg/L initial boron concentration.

The bed volume of resin of 143.2 cm^3, boron concentration of 250 mg/L and flow rate of 10 mL/min were kept constant in the experiments. As were shown graphically in Fig. 8, boron removal increased with increasing the temperature up to 313 K.

3.3. Process kinetics

A theoretical model was adopted in the present study for describing the change in the boron concentration at the column exit. In the adsorption column, the entering aqueous solution flows through the stationary bed of Amberlite IRA 743 resin and a portion of boron in the aqueous solution is retained within the resin bed. Let the fraction of boron adsorbed is A, and the fraction of that remaining in the aqueous solution and passing through the stationary resin bed is P. It is reasonable to assume that the rate of decrease in the adsorption fraction (A) is proportional to A and P as represented by

$$-\frac{dA}{dt} \propto AP \tag{4}$$

$$-\frac{dA}{dt} = kAP \tag{5}$$

It is noted in the above equation that $P = 1 - A$. Although Eq. (5) is nonlinear, it can be integrated with an initial condition of $A = A_a$ at $t = t_a$.

$$\ln\left|\frac{A(1-A_a)}{A_a(1-A)}\right| = k(t_a - t) \tag{6}$$

Noting that $P = 1 - A$, the above equation can be rewritten as

$$\ln\left|\frac{P_a(1-P)}{P(1-P_a)}\right| = k(t_a - t) \tag{7}$$

By defining t_a as the adsorption time, as denoted by τ, when $P = 0.5$ (one-half of the adsorption capacity), Eq. (8) becomes

$$P = \frac{1}{1 + \exp|k(\tau - t)|} \tag{8}$$

$$t = \tau + \frac{1}{k}\ln\left(\frac{P}{1-P}\right) \tag{9}$$

The boron fraction (P) that passes through the Amberlite IRA-743 resin column is equal to C/C_0 with C being the boron concentration in the aqueous solution exiting the adsorption column at time t and C_0 is the inlet boron concentration. According to Eq. (9), a plot of adsorption time (t) versus $\ln[C/(C_0 - C)]$ yields a straight line with the intercept and slope of the straight line equal to τ and $1/k$, respectively. Alternatively, τ can also be obtained at the adsorption time when $\ln[C/(C_0 - C)] = 0$, because of the fact that by definition, τ is the adsorption time, when C is one-half of C_0. With k and τ determined in this fashion, Eq. (9) can be used to construct the entire breakthrough curve. Since, only two model parameters are involved in Eq. (9), two accurate experimental data points of C as a function of adsorption time (t) would be theoretically sufficient to establish those two parameters. However, for accurate estimates of the model parameters, a complete breakthrough curve would be necessary.

The derivation for Eq. (9) was based on the definition that 50% breakthrough of the adsorption process occurs at τ. Accordingly, the resin bed should be completely saturated at 2τ due to the sigmoid nature of the breakthrough curve. The amount of boron adsorbed by the resin is one-half of the total boron entering the adsorption column within the 2τ period. Hence, the following equation can be written

$$W_e = \tfrac{1}{2} C_e F(2\tau) = C_e F\tau \tag{10}$$

The above equation establishes the relation among the adsorption capacity of the column (W_e), inlet boron concentration (C_0), liquid flow rate (F) and the 50% breakthrough time (τ).

Fig. 4 shows a plot of adsorption time (t) versus $\ln[C/(C_0 - C)]$ for boron adsorption in a column for three flow rates. This figure reveals that for all flow rates, the observed data follow the linear relationship of t versus $\ln[C/(C_0 - C)]$ reasonably well. The model parameters of the breakthrough curves (τ and k) obtained from this figure are listed in Table 3 for various flow rates. The breakthrough curves constructed using the model parameters listed in Table 3 (solid lines) are compared with the observed data in Fig. 5. It is apparent that the model predictions are quite good. The excellent model fit at the low C/C_0 is particularly important because it allows accurate prediction of the breakthrough point for safe boron discharge.

The lower portion of Table 3 lists the model parameters of adsorption column for three initial boron concentrations of 250, 500 and 1000 mg/L and they were obtained in the same fashion by plotting t against $\ln[C/(C_0 - C)]$ as shown in Fig. 4.

Table 3
Model parameters of the breakthrough curves

	k (min^{-1})	τ (min)	r^2
Flow rate (mL/min)			
10	0.05	149.5	0.990
20	0.039	117.4	0.980
30	0.034	90.0	0.991
Initial concentration (mg/L)			
250	0.045	190.0	0.997
500	0.042	138.0	0.985
1000	0.038	77.0	0.978

4. Conclusions

The following results are determined with the evaluation of obtained data:

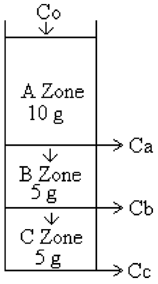
1. The removal of boron increased with increasing bed volume of resin. This is an expected result because of increasing of resin–solution contact surface.
2. The removal rate of boron increases with decreasing the boron concentration in the wastewater. But, although the total rates in the high concentrations were slower than those in smaller concentrations, the amounts of boron in higher concentrations were bigger than those in smaller concentrations removed. Since Amberlite IRA 743 lost rapidly ion exchange capacity in high-boron wastewater, the resin must be regenerated frequently.
3. That the difference of boron removal between 10 and 20 mL/min is bigger than the difference between 20 and 30 mL/min can be connected with residence time of solution. The residence time of solutions with flow rates of 10, 20 and 30 mL/min equal 14.32, 7.16 and 4.77 min, respectively. Thus, this states that residence time differences between 10 and 20 mL/min and between 20 and 30 mL/min are 7.16 and 2.39 min, respectively. As residence time differences decrease, corresponding curves approach each other.
4. The removal of boron from wastewater increased with increasing temperature up to 313 K. But, it was determined that more effective results were obtained in removal of boron for first 60 min.
5. When the feeding solution of 500 mg/L initial boron concentration and of 10 mL/min flow rate arrives at the end of the A zone, the boron concentration of the solution equals to C_a, so it can be written as follows:

   $C_0 > C_a$

   When the solution with C_a arrives at the beginning of the B zone, due to lower boron concentration than initial boron concentration, removal rate within this zone decreases and at the end of B zone, concentration of boron drops to C_b, so it can be written as follows:

   $C_a > C_b$

   Adsorption rate in C zone is relatively lower due to lower boron concentration than that of B zone. Thus, that the change in breakthrough curves between column heights of 15–20 cm is lower than that of column heights 10–15 cm can be attributed this behavior.



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