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Modelling of boron removal from solutions by ion exchange for column reactor design in boron mine wastewater treatment

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ABSTRACT

In this study, the performance of Purolite S 108 resin for boron removal from solutions and boron mine wastewater in a column reactor was investigated. The investigated experimental parameters for synthetic solutions were initial pH, temperature, concentration, resin amount, solution flow rate and regeneration number. When the maximum adsorption capacity values of the resin were compared, the optimum removal conditions were determined as pH (9.5), concentration (1,000 mg/L), temperature (15°C), resin amount (20 g) and solution flow rate (2.976 mL/min). The resin boron exchange capacity did not change significantly up to fifth resin use. Maximum capacity was calculated as 10.67 mg/g at 1,000 mg/L concentration. The boron exchange reaction of the Purolite S 108 resin was a slow process. The kinetics of boron removal by the resin was analyzed using the Adams–Bohart, Yoon–Nelson and Thomas models. The kinetic data showed fitness for two models except Adams–Bohart model. Also, an empirical kinetic model was developed for operation of resin column. The developed model from synthetic solution experiments was applied to the boron mine wastewater to estimate 4.55%, 45.5% and 83.33% breakthrough times for removal and recovery. The developed empirical model could estimated the these breakthrough times correctly. Resin was effective for boron.

Keywords: Boron removal; Column reactor; Empirical model; Kinetics; N-methylglucamine type chelating resin

1. Introduction

Boron does not exist as pure element in nature [1] and it is only found as metal borates with 230 different formulas [2]. The big borate deposites in the world are mainly located in Turkey (72.2%), Russia (8.5%) and the USA (6.8%) [3]. Some usage fields of boron are glass, glass objects, soap, detergent, porcelain, enameled, agriculture and metal production [3]. The wastewater of boric acid production plant (1,600 mgB/L), nickel plating plant (160 mgB/L), borate mine (382 mgB/L) and geothermal establishments (1–63 mgB/L) contains toxic levels of boron for the living creatures in the environment [4]. During the production of borax, boron oxide and boric acid, the solid wastes with toxic concentration of boron are formed [5]. Boron accumulation in the soils is very fast due to difficulty of washing it and boron forms complexes with the heavy metals in the soils that are more toxic than heavy metals [6,7]. The useful and toxic effects of boron for plants, humans and animals have narrow concentration range [8]. When boron deficiency is encountered in plant at serious degree, plant growth reduces, yield losses occur and even the plant dies [9]. Generally, boron toxicity in plants appears as yellowing, spotting or drying of leaf [9]. The adverse effects of boron on humans are dependent on concentration and exposure time. The boron exposure at high concentration in humans causes diseases in cardio-vascular,

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nervous, alimentary and sexual systems and exposure at low concentration results in reduced growth, potential neurotoxicity, hematological effects on children and newborns [10]. For humans, daily intake of boron by drinking water is expected in the range of 0.2–0.6 mg/d and by diet is expected as 1.2 mg/d [10]. Therefore, the contamination of drinking water sources and agricultural lands with boron causes big concerns. To protect the health of humans, boron limit value in drinking water is proposed as 2.4 mg/L by the WHO. The discharge value of boron in most developed countries is about 1 ppm [11].

Boron can be removed from wastewater by physicochemical methods. Boron removal by adsorption occurs by either physical or chemical adsorption or complexation reaction with the adsorbents. For instance, boron fixation by illite clay was proposed as chemical reaction occurring between frayed edge of the illite clay and tetrahedral borate $B(OH)_4^-$ anion [12]. Boron adsorption mechanism onto Mg–Al (NO_3) layered double hydroxide was reported to be physical adsorption and ion exchange [13]. Demey-Cedeño et al. [14] reported that the presence of OH^- groups in alginate was the reason of the formation of complexes with borate ions. So far, a few adsorbents have been tested for boron treatment. The limited adsorbents have been reported to be having appropriate capacity for boron removal from wastewater containing high boron concentration and some of them are sepiolite [15], fly ash [16] and calcium hydroxide [17]. It has been proposed that when boron concentration is in the range of 1–3 g/L as B_2O_3, the inorganic sorbents such as (M(OH)n), M = Al, Fe, Sn, Ti, Mn, Ni, Mg, Zn, Zr, etc., are being applied [18]. The electrocoagulation (EC) removes boron from diluted and concentrated solutions successfully based on the used electrode type [18,19]. When the end point operation pH of EC process is adequately high, the residual cation concentration arising from spent anode can prove the discharge standards due to formation metal hydroxide flocs from electrodes such as iron, aluminium and zinc. Boron removal in the electrocoagulation process is materialized by formation of inner-sphere and outer-sphere adsorption between surface of metal hydroxide and boron ions based on operation pH and boron concentration [20]. The reverse osmosis is an effective technology for deboration of wastewater and seawater but the biofouling and silicon in operation of reverse osmosis membranes are some of the major handicaps [21,22]. Solvent extraction of boron is a rapid process and resulted in a borated organic phase that should be treated with stripping base solution for boron recovery [23]. The electrodialysis is sensitive to co-existing anions for boron removal from wastewater. Briefly, these mentioned processes have their own advantages and drawbacks.

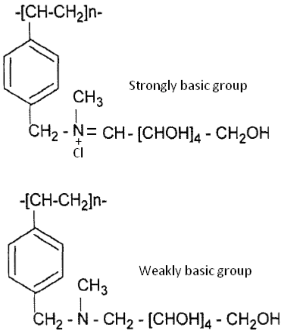
When the recovery of boron from wastewater is necessary, the application of boron selective resins, produced by functionalization of styrene-divinylbenzene beads with N-methyl glucamine chelating groups [24], is an appropriate choice and in the body of the boron resins, boron forms complex with vis-diols [25]. Determination of optimum removal conditions and kinetics for boron resins can set a light to encounter operational problems such as 10% and 90% breakthrough times and the capacity in the industrial application of column reactor for boron removal. The usage of column reactor is the most practical and efficient way for ion exchange application [26]. Kinetic models have been successfully applied to the kinetic data obtained from the boron removal in a column reactor [5,26]. So far, the Purolite S 108 resin has been applied to synthetic solutions (20–108 mgB/L) and Kızıldere geothermal power plant wastewater (30 mgB/L) (in Turkey) for boron removal in a column reactor [25,27,28]. The performed literature survey has showed that there is no study showing the performance of Purolite S 108 resin to remove boron in a column reactor under various experimental conditions. For this reason, boron removal from synthetic solutions containing high boron concentration using Purolite S 108 resin was investigated under changing solution conditions. The kinetics of boron removal in a column reactor was analyzed by applying the Adams–Bohart, Yoon–Nelson and Thomas models. Also, the resin was regenerated four times using 1 M HCl solution to determine the capacity variation of the resin after regeneration. Also, boron removal from boron mine wastewater with about 611.11 mg/L concentration was studied. The 4.55%, 45.5% and 83.33% breakthrough times of boron for boron mine wastewater was tried to estimate by the developed model which is based on Yoon–Nelson model. In this study, we aimed to the boron recovery from Çam Köy boron mine wastewater and therefore, the resin usage is operated up to maximum capacity values (~90% breakthrough). On the other hand, the resins generally lose their performance by time and the resin gets converted to waste material, therefore, maximum recovery of boron is to be achieved at one time and low acid leaching number. Therefore, the data were obtained from first point to exhaustion point. The Çamköy waste boron dam uses 520 m^3/h wastewater recycle and its dam body volume is too high. The exit concentration of resin column can be recycled to the dam and then dam water can be reused for boron recovery. The complete capacity of the resin under experimental conditions must be known.

2. Materials and methods

2.1. Column kinetics and regeneration experiments

The investigated resin was Purolite S 108 with chloride form. The resin has N-methyl glucamine type functional groups. The physico-chemical properties of the resin are given in Table 1 [7]. Boron solution was synthetically prepared using solid boric acid (Merck, Germany, assay 99.5%–100.5%). Boron removal experiments were continued in a jacketed column reactor connected with a temperature controlling water circulator. The column reactor had 1.78 cm inner diameter and 25 cm length. The experimental setup is given in Fig. 1. Before transferring the studied solution to the reservoir reactor, concentration and pH of the solution was regulated, respectively. Solution pH levels were adjusted using 0.5 HCl or NaOH solutions by using a pH meter (WTW, Inolab, Germany). At basic pHs, solid NaOH granules were used for pH adjustment. Then, the prepared solution was spilled to the reservoir reactor for heating or cooling of the solution. When the desired temperature was reached, the boron solution was transferred from the reservoir reactor to the column reactor in down-flow mode using a peristaltic pump. The operation temperature of the

Table 1
Chemical and physical characteristics of Purolite S 108

Property	Description
Polymer structure	Macroporous polystyrene cross-linked with divinylbenzene
Optical appearance	Spherical beads
Functional groups	Complex amino
Ionic form, as shipped	Cl
Total capacity (Cl_ form) (eq L^{-1})	0.6 (min)
Total boron capacity (Cl_ form) (eq L^{-1})	0.35
Selective boron capacity (Cl_ form) (eq L^{-1})	0.20 (min)
Moisture retention (Cl_ form) (%)	45–55
Reversible swelling FB → Cl (%)	10 (max)
Specific gravity (Cl_ form)	1.1
Temperature limit (Cl_ form) (°C)	60
pH limits (operating)	1–13
Structure	

jacketed column reactor was kept as constant at same working temperature with the reservoir. A sample volume of 8 mL was taken at predetermined time intervals from down side of the column reactor. Boron determination for the taken solutions was done by titrimetric method as follows [29]. A sample volume of 5 mL was spilled to 100 mL beaker and 50 mL pure water was appended and solution pH was fixed to 7.6. Then, mannitol was added to the solution up to pH decrease of the stirring solution stopped. The mannitol added solution was titrated with 0.02 N KOH solution up to solution pH became again 7.6. The 5 g mannitol addition approach and more mannitol addition up to constant pH values for determination of 100, 500 and 1,000 mg/L boron concentrations gave exactly same base consumptions for 0.05 N KOH. These comparison was done because a general procedure is the addition of 5 g mannitol approximately up to 8.33 mg/100 mL pure water boron concentrations [9,29]. For this comparison, the end point equilibrium pH values for 5 g mannitol addition and mannitol addition up to constant pH value are given in Table 2. The pH raise at constant pH approach for titration with 0.05 N KOH was rapid than 5 g mannitol addition, therefore, the pH difference for two approach was rapidly closed by KOH addition [29]. Because pH raise at high mannitol amounts is fast than low mannitol amounts [29]. The potassium hydroxide solution was standardized with 500 mg/L boron solution and the correction factor was recorded. A volume of 1 mL 0.02 N KOH solution is equal to 0.6964 mg B_2O_3. In the regeneration studies, after exhaustion of the resin in the column reactor, the boron was eluded from the resin using 1 M HCl solution at acid flow rate range of 2.901–3.03 mL/min. During the elution studies, a sample volume of 2 mL was taken from the down side of the column reactor and boron analysis was done. Then, acid-treated resin was neutralized by 100 g/1,000 mL NaOH solution at flow rate range of 2.901–3.03 mL/min. The neutralized resin was washed with 1 L pure water at the same solution flow rate with elution and neutralization. After this, the reconditioned resin particles became ready for further usage. The total volume of neutralization solution (sodium

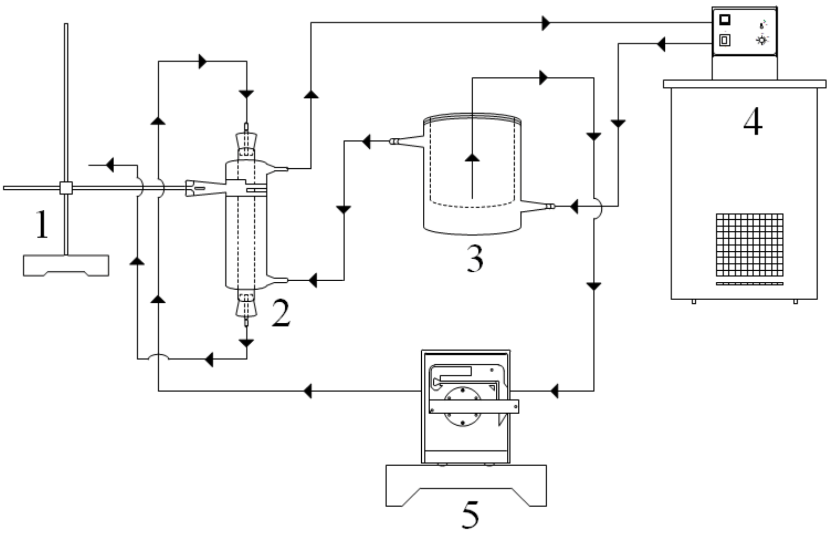


Fig. 1. Experimental setup (1-potholder, 2-column reactor, 3-reservoir, 4-temperature-controlled water circulator, 5-peristaltic pump).

Table 2
Comparison of boron determination methodologies for 0.05 N KOH

According to constant equilibrium pH value for mannitol addition			According to 5 g mannitol addition		
Boron conc. (mg/L)	Eq. pH value	KOH consumption (mL)	Boron conc. (mg/L)	Eq. pH value	KOH consumption (mL)
100	3.65	1.05	100	3.88	1.05
500	3.18	5.35	500	3.60	5.25
1,000	3.05	10.75	1,000	3.44	10.70

hydroxide solution) and rinse water volume had 1,000 mL volume and this value is equal to 46.62 bed volume number. Resin capacity was calculated by the following differential equation.

$$q_0 = \int_0^{V_t} \frac{\left(C_0 - C\right)dV}{m} \tag{1}$$

where q_0 is the resin capacity (mg/g), V_t is the solution volume passing from the column reactor (L) at time t (min), C and C_0 are the concentration of an outward solution and its inlet concentration (mg/L), respectively, m is resin amount in the column reactor (g). The effects of 10, 15 and 20 g resin amounts were studied and column heights belonging to these resin amounts were 5.75, 8.625 and 11.5 cm, respectively.

The developed empirical model was applied to the colemanite mine wastewater to estimate different breakthrough times. The boron mine wastewater was supplied from Bigadiç district boron mine in Balıkesir city in Turkey. Boron removal experiments from boron mine wastewater was studied at natural pH (8.50) value of solution and the studied experimental parameters were flow rate (1.863 mL/min), 15 g resin amount, 30°C ± 2°C solution temperature. The characterization of the boron mine wastewater is given as follows: pH (8.50), conductivity 2,137 μS/cm, total hardness 658.784 mgCaCO$_3$/L, boron (611.11 mg/L), sulphate (713 mg/L), nitrate (1.36 mg/L), silicon (8.8 mg/L) and suspended solids (9 mg/L). Boron removal was analyzed from first breakthrough point to exhaustion point because we aimed maximum boron recovery at minimum regeneration number.

The effect of sulphate concentration on boron removal was investigated at pH = 8.5, 25°C, 1.5 g, 200 rpm, 50 mL, 4.5 h, 500 mg/L boron concentration, and 0, 50, 100, 500, 750 mg/L sulphate concentrations. These experiments were carried out in an incubator shaker.

3. Results and discussion

3.1. Effect of pH on boron removal

The formation of monoborate and polyborate ions in solution phase from boric acid is based on solution pH and concentration [30,31]. Boric acid starts to convert to monoborate anion at pHs above 7 and completely turns into monoborate anion at pH above 11 for boron concentration of 1,000 mg/L [31]. In this study, pH effect on boron removal by Purolite S 108 resin was studied at pH range of 4.5–10.5 and other parameters were as follows: concentration (500 mg/L), temperature (30°C), resin amount (15 g) and solution flow rate (1.982–2.083 mL/min). The obtained results are given in Figs. 2a and b. The full trend of breakthrough curves is given in Figs. 2a and b shows the exit concentrations for any wastewater discharge state at 1 mg/L boron concentration. As can be seen from Fig. 2a, the exhaustion time of the resin increased with increasing pH value and optimum initial solution pH was determined as 9.5. This result can be related with the increasing monoborate anions and low hydroxyl competition in solution phase with pH raise from 4.5 to 9.5 at 500 mg/L boron concentration. At pH 10.5, the dominant boron species was monoborate anion [32]. The capacity values of the resin for 4.5, 6.5, 8.5, 9.5 and 10.5 pH values were calculated as 8.18, 8.79, 8.78, 9.94 and 9.47 mg/g, respectively. At pHs below 6, boron is present as boric acid; at pH value around 8, boric acid, monoborate and polyborate anions exist and at pH value of 10.5, only monoborate and boric acid exist at around 500 mg/L concentration [32]. The polyborate ion fraction reaches maximum at pH 8, on contrary to this, polyborate fraction is almost zero at pH 10.5 for boron concentration of around 500 mg/L [32]. The increasing capacity trend of the resin at pH 9.5 in the present study was also reported similarly for other several boron selective resins such as Amberlite IRA-743 at pH 9 [6] and Diaion CRB 02 at pH 8 [5]. The reason of high capacity of pH 9.5 than 10.5 was due to the hydroxyl ion competition on boron removal.

3.2. Effect of concentration on boron removal

Boron ion types in the aqueous solutions have been identified as boric acid ($B(OH)_3$), monoborate $B(OH)_4^-$, diborate $B_2O(OH)_5^-$, triborate $B_3O_3(OH)_4^-$, tetraborate $B_4O_5(OH)_4^{2-}$ and pentaborate $B_5O_6(OH)_4^-$ ions at boric acid concentration of 0.4 M [30]. It has been reported that while monoborate ion is present at boron concentration below 0.025 M, triborate ion begins to originate for boron concentration above 0.025 M and polyborate ions fraction increases at higher concentrations above 0.1 M at pH range of 7–10.5 [31]. The concentration effect on boron removal by Purolite S 108 resin was studied at concentration range of 250–1,000 mg/L and the other parameters were as follows: pH (8.5), temperature (30°C), resin amount (15 g) and flow rate (2.069–2.083 mL/min). The obtained results are given in Figs. 3a and b. The full trend of breakthrough curves is given in Figs. 3a and b. The Fig. 3b shows the exit concentrations for any wastewater discharge state at 1 mg/L boron concentration. It can be seen from Fig. 3a, the exhaustion time for the resin decreased with raising concentration. The reason of this trend was the limited complexing site number against

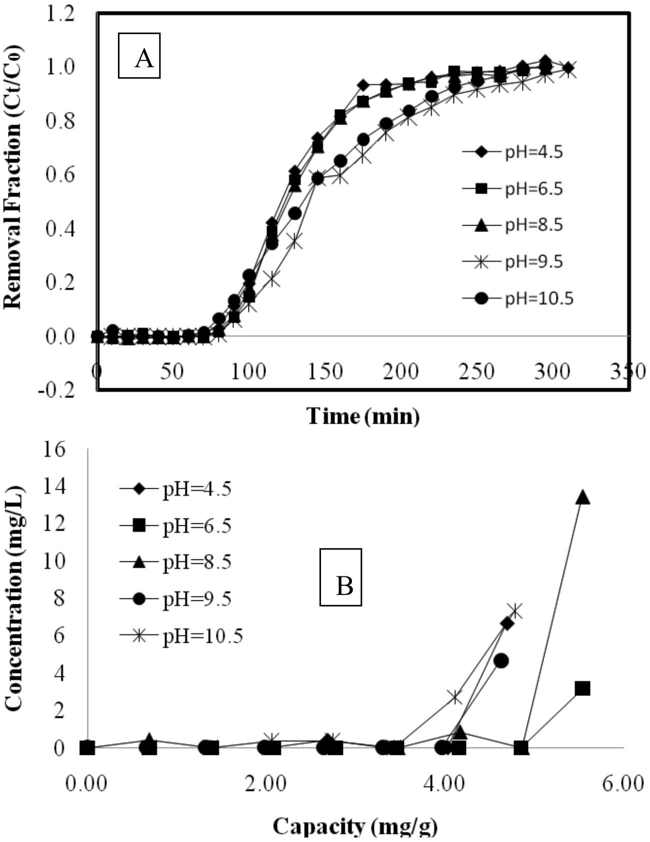


Fig. 2. (a) pH effect on boron removal for exhaustion and (b) exit concentration vs. capacity for pH effect.

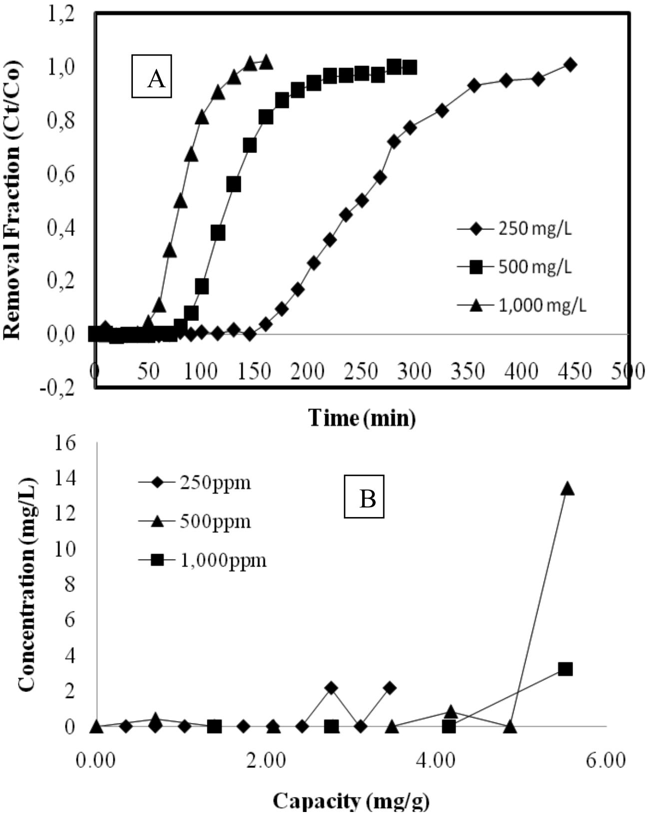


Fig. 3. (a) Concentration effect on boron removal for exhaustion and (b) exit concentration vs. capacity for concentration effect.

high boron concentration. The resin exchange capacities were calculated as 8.45, 8.78 and 10.67 mg/g for 250, 500 and 1,000 mg/L solution concentrations, respectively. The decrease of exhaustion time with concentration increase is a routine trend for the fixed bed reactors and similar trend was reported for Amberlite IRA-743, an N-methyl glucamine type chelating boron resin [33]. The capacity of the Purolite S 108 resin increased as a result of driving force of high concentration and formation of polyborate–resin complex for pH value of 8.5 at 1,000 mg/L concentration [31]. The macroporous resins pores have a diameter above 50 nm and polyborates have maximum 1–2 nm molecular size. It was thought that while polyborates were increasing the capacity, they might retarded the boron diffusion and might caused to early breakthrough.

3.3. *Effect of temperature on boron removal*

The molar fraction of polyborate anions increases with temperature decrease at above 0.025 M boron concentration for pH range of 7–10.5 [31]. While the increasing effect of high temperature on the ion exchange rate shows endothermic process, the increasing effect of low temperature on the ion exchange rate indicates exothermic process. Also, the liquid film layer thickness around the resin decreases with the temperature increase because the viscosity of the solution decreases at high temperatures [34]. In this study, temperature effect was studied at temperature range of 7.5°C–45°C and other parameters were kept as constant: pH (8.5), concentration (500 mg/L), resin amount (15 g) and flow rate (2–2.083 mL/min). The obtained results are given in Figs. 4a and b. The full trend of breakthrough curves is given in Fig. 4a. The Fig. 4b shows the exit concentrations for any wastewater discharge state at 1 mg/L boron concentration. the exit concentrations for any wastewater discharge state at 1 mg/L boron concentration. The exhaustion time of the resin increased with decreasing temperature and it was difficult to saturate the resin at 7.5°C temperature. The resin could be saturated at 94% extent at 7.5°C. The capacity values were calculated as 9.84, 10.26, 8.78 and 9.42 mg/g for 7.5°C, 15°C, 30°C and 45°C solution temperatures, respectively. The high capacity at low temperatures was due to increasing molar fraction of polyborate anions at pH 8.5. The reason of high value of capacity at 40°C than 30°C can be related with the swelling of resin particles. It was reported the same results for capacity increase at low temperatures in batch reactor [35] and the resin used in the study was Purolite S 108 with chlorine form [35]. But the decrease of boron removal rate at low temperatures showed the endothermic nature of the process and it may be also due to shrink of the resin. At low temperatures, the boron breakthrough was faster than high temperature.

3.4. *Effect of resin amount on boron removal*

Boron removal from synthetic solutions was studied at resin amounts of 10, 15 and 20 g. The other experimental parameters were kept as constant: pH (8.5), concentration

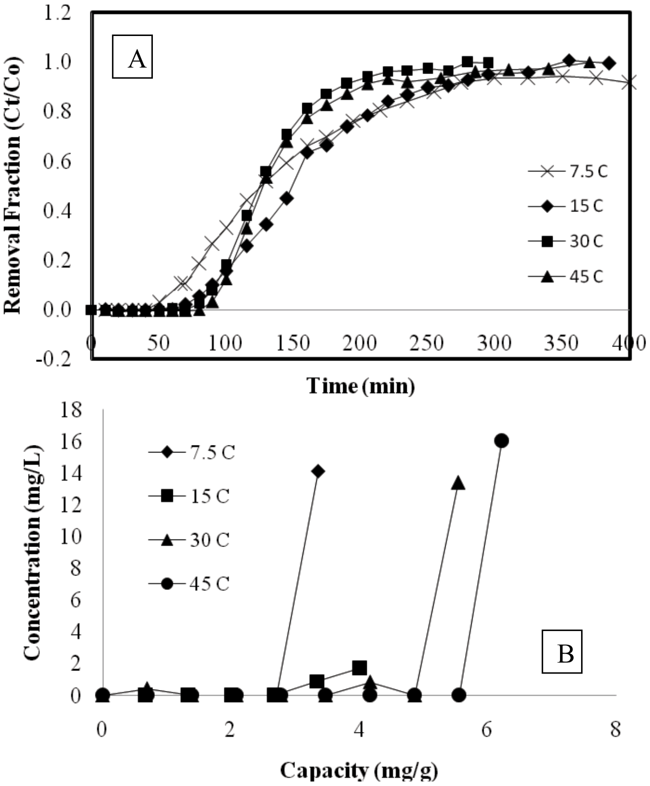


Fig. 4. (a) Temperature effect on boron removal for exhaustion and (b) exit concentration vs. capacity for temperature effect.

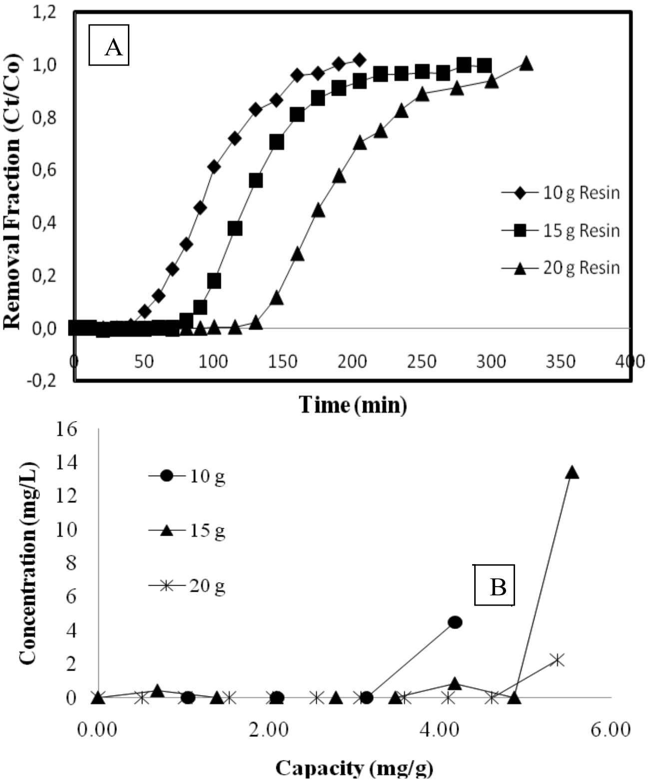


Fig. 5. (a) Dosage effect on boron removal for exhaustion and (b) exit concentration vs. capacity for dosage effect.

(500 mg/L), and temperature (30°C) and flow rate (2.046–2.089 mL/min). The obtained results are given in Figs. 5a and b. The full trend of breakthrough curves is given in Figs. 5a and b shows the exit concentrations for any wastewater discharge state at 1 mg/L boron concentration. As can be seen from the results given in Fig. 5a, the exhaustion time for boron removal increased with increasing resin amount. The increasing resin amount increased the effective site number for boron complexation and therefore breakthrough time increased at high resin amounts. Resin capacities were calculated as 9.59, 8.78 and 9.87 mg/g for 10, 15 and 20 g resin amounts. These results can be related with equilibrium between liquid and resin phase.

3.5. Effect of flow rate on boron removal

Boron removal by Purolite S 108 resin was studied at flow rate range of 2.083–2.976 mL/min. The other parameters were kept as constant and were as follows: pH (8.5), concentration (500 mg/L), temperature (30°C), resin amount (15 g). The obtained results are given in Figs. 6a and b. The full trends of breakthrough curves are given in Figs. 6a and b, which shows the exit concentrations for any wastewater discharge state at 1 mg/L boron concentration. The breakthrough time decreased with increasing flow rate. This was due to decreasing contact time of boron solution with the resin at high flow rates. Capacity values were calculated as 8.78, 9.12 and 9.53 mg/g for 2.083, 2.61 and 2.976 mL/min solution flow rates, respectively. The reason of capacity increase at high flow rates was thought to become due to increasing mass transfer rate at high flow rates. Similarly, the decrease of breakthrough time with increasing flow rate was reported for Amberlite IRA-743 resin [33].

3.6. Effect of resin regeneration on boron removal

Four consecutive complexation–elution–neutralization–washing cycles were applied to the resin to determine the capacity variation of the resin with regeneration. The applied experimental parameters were as follows: pH (8.5), concentration (500 mg/L), resin amount (15 g), temperature (30°C), and flow rate (2.901–3.03 mL/min). The obtained results are given in Figs. 7a and b. The full trends of breakthrough curves are given in Figs. 7a and b, which shows the exit concentrations for any wastewater discharge state at 1 mg/L boron concentration. Resin capacity values were calculated as 9.53, 9.71, 9.89, 9.90 and 9.67 for the first five resin uses, respectively. Similar effect for resin regeneration was reported for Diaion CRB 02, a N-glucamine type chelating resin [25]. The resin regeneration with 100 g/1,000 mL NaOH solution after elution to converted the resin to hydroxyl form (free base form or exchange chloride with hydroxyl ions) did not have any important effect on capacity. Boron elution profile from the resin is given in Fig. 7b. The outward boron concentration reached maximum value (3,651.59 mg/L) by acid treatment (1 M HCl).

3.7. Kinetic analysis for boron removal

The equilibrium zone in the column reactor is advanced by the counter ions to the mass transfer zone and thus the

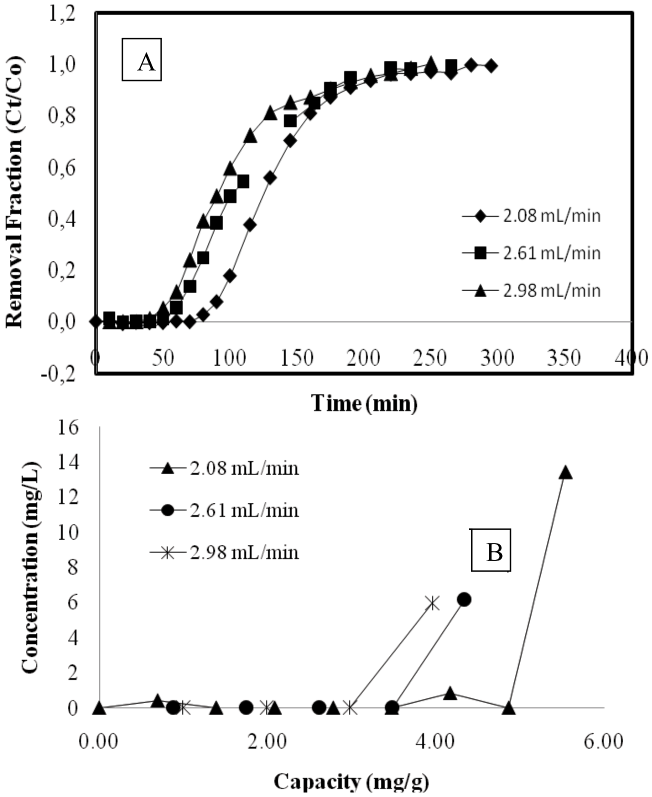


Fig. 6. (a) Flow rate effect on boron removal for exhaustion and (b) exit concentration vs. capacity for flow rate effect.

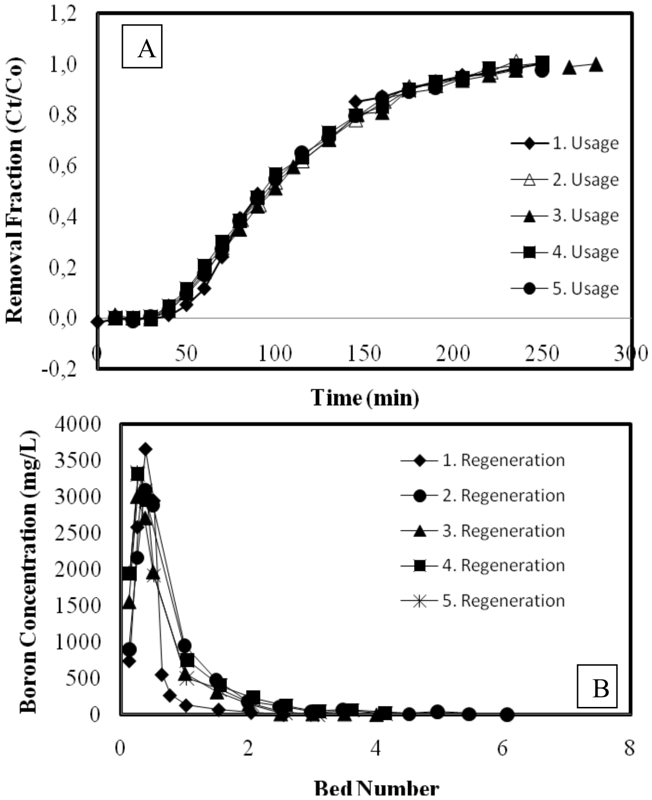


Fig. 7. (a) Regeneration effect on boron removal for exhaustion and (b) boron stripping from resin by 1 M HCl.

concentration of counter ions decreases through the column [36]. Generally, operation of the column reactor is continued up to the 0.9 outlet-to-inlet concentration ratio which is the maximum limit value for operation. However, the exchange material is determined to be exhausted when the inlet and outlet concentrations are equal to each other [37]. In favourable equilibrium for the column reactor, the slopes of the curves do not change and are in parallel with each other at changing column heights. In unfavourable equilibrium, the breakthrough curves do not demonstrate a parallel profile and show separated pattern with changing column heights [36]. As boron concentration changes from top of the column reactor to the down side, the borate ion types show differences throughout the column and this affects the boron exchange mechanism and adsorbed boron ion type. Also, the pH of solution changes throughout the column and this affects the adsorbed boron type. While the only monoborate and boric acid exist at below 270 mg/L, polyborates start to form above 270 mg/L boron concentration. In the literature, the most widely used kinetic models for description breakthrough curves of column reactors are Adams–Bohart, Thomas and Yoon–Nelson models.

The Thomas model assumes the plug flow behaviour in the bed, and uses Langmuir isotherm for equilibrium, and second-order reversible reaction kinetics. This model is suitable for adsorption process where the external and internal diffusion limitations are absent [38]. The Thomas model can be given as follows [39]:

$$\ln\left(\frac{C_0}{C}-1\right)=\frac{K_T q_0 m}{Q}-\frac{K_T C_0}{Q}V \tag{2}$$

where K_T is the overall reaction rate for the Thomas model (L/min mg), Q is the volumetric flow rate (L/min), C and C_0 are concentration of the outward solution and its inlet concentration (mg/L), respectively, m is the weight of ion exchange resin (g), q_0 is equilibrium boron capacity (mg/g), and V is the volume of solution passing from the column reactor (L) at time t.

The Yoon–Nelson model is not only less complicated than other models but also requires no detailed data concerning the characteristics of the adsorbate, the type of the adsorbent, and the physical properties of the adsorption bed. The Yoon–Nelson model assumes that the reduction in the possibility of adsorbate adsorption on the adsorbent is proportional with the possibility of its adsorption and breakthrough on the adsorbent [39]. The Yoon–Nelson model is expressed as follows [39]:

$$\ln\left(\frac{C}{C_0-C}\right)=K_{\mathrm{YN}}t-\tau K_{\mathrm{YN}} \tag{3}$$

where K_{YN} is the overall reaction rate of the Yoon–Nelson model (1/min), τ is the time for 50% outward-to-inlet boron concentration ratio (min). C is boron concentration for column exit at any time t and C_0 is initial concentration (mg/L), respectively. t is time (min).

The Adams–Bohart sorption model was developed for sorption of chlorine onto activated carbon and its rate constant is assumed to be proportional with the remaining adsorbent capacity and concentration of adsorbate. This model is used for the initial part of the breakthrough curves [40]. The Adams–Bohart model is given as follows:

$$\ln\frac{C}{C_0} = kC_0t - kN_0\frac{Z}{U_0} \tag{4}$$

Here, k is kinetic constant (L mg^{-1} min^{-1}), U_0 is linear flow rate (cm min^{-1}), N_0 is the saturation capacity of the adsorbent (mg/L), Z is the column depth (cm), C is the outward boron concentration (mg/L) and C_0 is the initial concentration of boron (mg/L).

The kinetic analyses were performed between first breakthrough and first exhaustion points. The analysis of kinetic models is given in Table 3. As can be seen in Table 3, boron removal data fitted to the Yoon–Nelson and Thomas models. According to resin amount effect curves, the boron adsorption onto resin was determined as unfavourable because the pattern of the curves was not parallel with each other for increasing resin amounts. The coefficient of determination values for the Thomas model were in the range of 0.806–0.970. The fitness of kinetic data to the Thomas model indicates Langmuir isotherm mechanism for boron adsorption and boron adsorbed onto resin by monolayer coverage. The isotherm data between boron and Purolite S 108 resin was reported as to be fitted the Langmuir isotherm in our previous study [7]. Also, it was reported that the boron removal mechanism by Purolite S 108 resin in a batch reactor was controlled by particle diffusion and by ash layer diffusion at high concentrations than 700 mg/L boron [41]. But the fitness of kinetic data to the Thomas model assumes that the external and internal diffusion limitations are absent, therefore it can be said that particle diffusion and ash layer diffusion limitations are no or low in boron removal by Purolite S 108 resin in the column reactor. This may be due to the mechanism and ion transport differences in the batch and column reactors and very low flow rate of the solution. The adsorption capacity values of the Purolite S 108 could almost be estimated by the Thomas model (Table 3). The fitness of the Thomas model to the data decreased with increasing resin amount and temperature. The coefficient of determination values for Yoon–Nelson model were in the range of 0.806–0.970. The Yoon–Nelson model could be estimated the 50% breakthrough times (τ) correctly for boron removal in the column reactor (Table 3). From the assumption of Yoon–Nelson model, the rate of boron adsorption onto the resin can be evaluated as proportional with the free active sites in the Purolite S 108 resin and the remaining concentration of the boron. The coefficient of determination values for Adams–Bohart model were in the range of 0.472–0.728. The low coefficient of determination values of Adams–Bohart model was due to application of analysis to full time interval between first breakthrough point and first exhaustion point because this model is suitable for the first stage of breakthrough lines. The rate constants of Thomas, Yoon–Nelson and Adams–Bohart models showed random trend for pH

Table 3
Coefficient of determination values and model parameters for kinetic models

Parameters						Thomas Model			Yoon–Nelson Model			Adams–Bohart Model		
T (°C)	C ppm	pH	RA (g)	FR (mL/min)	RN	$K_T \times 10^{-5}$	q_0 (mg/g)	R^2	K_{YN}	T	R^2	$k \times 10^{-5}$	N_0	R^2
30	500	4.5	15	2.013	1	8.14	9.29	0.917	0.0407	138.40	0.917	3.44	40,374	0.637
30	500	6.5	15	2.078	1	9.62	8.03	0.898	0.0481	115.96	0.898	4.62	38,381	0.615
30	500	8.5	15	2.083	1	7.29	9.67	0.909	0.0365	139.08	0.909	2.92	42,717	0.636
30	500	9.5	15	1.982	1	6.19	11.01	0.922	0.031	166.29	0.922	2.6	48,314	0.613
30	500	10.5	15	2.055	1	7.17	10.66	0.915	0.0358	155.83	0.915	3.88	41,707	0.674
30	250	8.5	15	2.069	1	9.56	8.86	0.958	0.02	256.74	0.958	4.72	34,144	0.722
30	1,000	8.5	15	2.069	1	9.1	11.93	0.935	0.09	86.50	0.935	5	40,627	0.725
30	500	8.5	10	2.089	1	10.6	10.60	0.946	0.05	101.51	0.946	5.38	40,677	0.705
30	500	8.5	20	2.046	1	8.14	10.35	0.873	0.04	202.28	0.873	4.76	34,610	0.656
7.5	500	8.5	15	2.027	1	3.75	10.45	0.904	0.018	161.17	0.904	1.6	54,497	0.644
15	500	8.5	15	2	1	6.17	11.93	0.874	0.0309	178.74	0.874	3.62	46,678	0.649
45	500	8.5	15	2.078	1	4.72	9.81	0.806	0.0236	141.68	0.806	1.72	49,090	0.472
30	500	8.5	15	2.61	1	8.5	10.26	0.938	0.04	117.91	0.938	4	41,734	0.660
30	500	8.5	15	2.976	1	7.4	10.90	0.894	0.0369	109.78	0.894	3.48	46,941	0.619
30	500	8.5	15	2.901	2	6.4	10.51	0.950	0.03	108.83	0.950	2.78	47,409	0.69
30	500	8.5	15	2.924	3	6.01	10.64	0.974	0.03	109.36	0.974	2.12	54,114	0.683
30	500	8.5	15	3.03	4	10	10.53	0.970	0.03	104.35	0.970	2.32	54,351	0.703
30	500	8.5	15	3	5	7.94	10.84	0.933	0.04	108.45	0.933	3.64	46,684	0.648

increase. The rate constant of Yoon–Nelson model showed increasing trend for concentration increase and other models showed no trend for increasing concentration. All the models showed no trend for increasing resin amount. The rate constant of Adams–Bohart decreased with temperature increase and other models showed random trend. The rate constant of Adams–Bohart, Thomas and Yoon–Nelson exhibited random trend for increasing solution flow rate. All the models showed random pattern for rate constant at increasing resin regeneration number. A column sorption study was carried out using calcium alginate gel beads as adsorbent for the removal of boron from aqueous solutions. Rate constant of Adams–Bohart model increased with pH decrease, concentration decrease, alginate mass decrease, flow rate increase and diameter decrease [14]. Boron adsorption from solutions was studied by Dowex 2 × 8 resin in a column reactor and rate constant of Thomas and Yoon–Nelson model increased with flow rate increase [26]. A two-step process for boron recovery from clay waste is proposed in the study of Kıpçak and Özdemir [5]. The Yoon–Nelson model rate constant increased with concentration and flow rate increase. Thomas model rate constant decreased with concentration increase and increased with flow rate increase.

3.8. Empirical model and sulphate effect

To help the simulation of column reactor for boron removal and to determine the 50% and 90% breakthrough times for practical boron removal from waters, an empirical kinetic model was developed based on Yoon–Nelson model using Statistica 10.0 programme. Based on trial and error method, the $\ln(C/C_0–C)$ term in the Yoon–Nelson model was changed with $\ln(C_0/(C_0–C))$ as this approach gives the opportunity of analysis of data set with the programme and gives the high coefficient of determination values according to single parameter analysis. This change was done because the negative values in $\ln(C/C_0–C)$ caused problem when exponential of the term was being developed. Therefore, the developed model developed model is mentioned empirical model rather than mathematical. In the analysis, 273 items of boron analysis results were used in development of the empirical model. The developed model had 0.91 coefficient of determination value and is given as follows:

$$t = 73.95997 + \left(\begin{array}{l} \mathrm{pH}^{1.01805} \times T^{-0.16324} \times R^{2.50827} \times \mathrm{FR}^{-0.69957} \times \\ C^{-0.58876} \times \mathrm{RN}^{-0.09757} \times \left(\ln\left(\dfrac{C_0}{\left(C_0 - C\right)} \right) \right)^{0.82883} \end{array} \right) \tag{5}$$

Here, t is time (min), pH is solution pH, T is temperature (degree), R is resin amount (g), FR is solution flow rate (mL/min), C is concentration (mg/L), RN is regeneration number, C_0 is initial boron concentration (mg/L). The experimentally obtained and statistically estimated 50% and 90% breakthrough times are given in Table 4. The model was distorted

Table 4
Experimentally obtained and statistically estimated 50% and 90% breakthrough times

Parameters						Exp. 50% breakthrough time (min)	50% model breakthrough time (min)	Exp. 90% breakthrough time (min)	90% model breakthrough time (min)
T (°C)	C (mg/L)	pH	RA (g)	FR (mL/min)	RN				
30	500	4.5	15	2.013	1	115–130	102.11	160–175	150.09
30	500	6.5	15	2.078	1	115–130	114.02	190	182.33
30	500	8.5	15	2.083	1	115–130	126.52	190	216.13
30	500	9.5	15	1.982	1	130–145	134.81	235	238.56
30	500	10.5	15	2.055	1	130–145	139.73	220	251.86
30	250	8.5	15	2.069	1	250	153.37	325	288.75
30	1,000	8.5	15	2.069	1	80	109.1	115	168.92
30	500	8.5	10	2.089	1	90	92.93	145	125.28
30	500	8.5	20	2.046	1	175	183.42	275	370.03
7.5	500	8.5	15	2.027	1	130	141.08	255–275	255.51
15	500	8.5	15	2	1	145-	134.44	250	237.56
45	500	8.5	15	2.078	1	115–130	123.23	205	207.24
30	500	8.5	15	2.61	1	100–110	119.15	175	196.2
30	500	8.5	15	2.976	1	90–100	115.35	175	185.2
30	500	8.5	15	2.901	2	90–100	113.31	175	180.40
30	500	8.5	15	2.924	3	100	111.6	175	175.7
30	500	8.5	15	3.03	4	90–100	109.7	175	170.6
30	500	8.5	15	3	5	90–100	109.15	175	169.14

from estimation the 50% and 90% breakthrough times for 250, 1,000 mg/L concentrations and 20 g resin amount. Also, the developed empirical model could estimated the 50% breakthrough times well than 90% breakthrough times (Table 4). The analysis was performed for the 50% and 90% breakthrough times because boron removal and recovery was aimed from colemanite mine wastewater. Thus, maximum boron recovery can be supplied at one time.

The effect of sulphate concentration on boron removal from synthetically prepared solution was studied at 0–750 mg/L sulphate concentrations and results are given in Fig. 8b. The results showed that sulphate has no important effect on boron removal by the resin and the resin has high selectivity. The difference between removal efficiencies were about maximum 4.63%. This difference contains probably the standard deviation of the boron recovery as well. In an other article, it has been reported that the glucamine type selective boron resins (such as Amberlite IR-743) have high selectivity under complex wastewater conditions [42].

3.9. Application of model to the boron mine wastewater

The boron mine wastewater with 611.11 mg/L concentration was applied to the model for estimation of 4.55%, 45.5% and 83.33% breakthrough times. The experimental operation times for these breakthrough values were 90, 120 and 180 min and the model estimated these times as 79.33, 119.04 and 184.52 min. As can be seen from these results, the developed model for borate mine wastewater is suitable for industrial application in mine field. The figure belonging to the boron mine wastewater treatment is given in Fig. 8a. The selectivity of the resin eliminated the sulphate effect on boron removal by the resin. The vis-diols in the resin are selective for boron. The empty bed contact time (EBCT) and various empty bed velocity (EBV) values for technical operation of the resin column are given in Table 5.

$$\text{EBV} = \frac{Q}{A} \tag{6}$$

$$\text{EBCT} = \frac{V}{Q} \tag{7}$$

Here, Q is solution flow rate (m^3/hr), A is the cross sectional area (m^2) and V is the resin bed volume (m^3).

The major anthropogenic boron sources in the ecosystem are coal mining and combustion, oil exploration or geothermal waters, and mining and processing of boron ores [43] and selective ion exchange resins are the major method for boron removal and recovery [44]. Therefore, the developed model can be applied to some of these wastewaters based on concentration interval.

3.10. Thermodynamic analysis

The Eyring equation enables the calculation of enthalpy, entropy and Gibbs free energy change of the ion exchange reaction. In calculation of these thermodynamic parameters, the Thomas model rate constants were used and its clear from the temperature effect results (Table 3), the boron

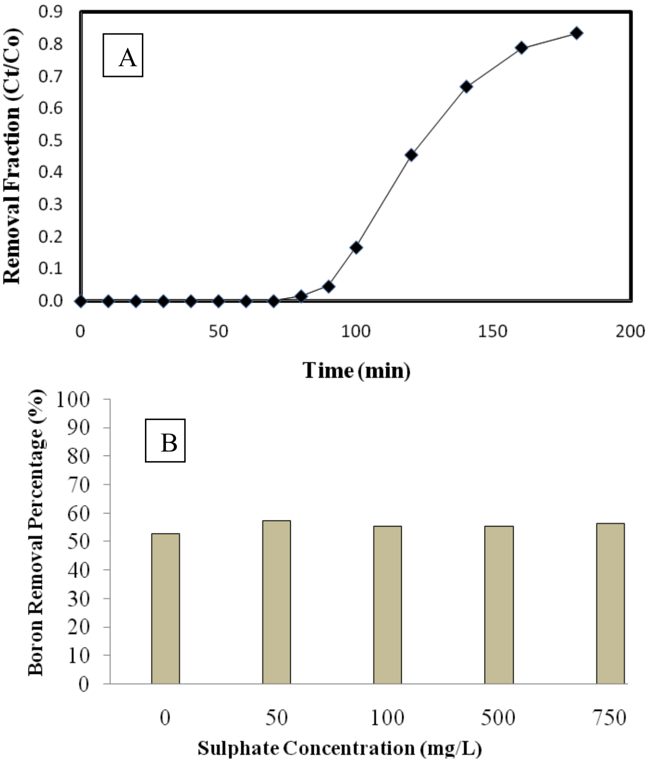


Fig. 8. (a) Boron removal for exhaustion from Çam Köy boron waste dam and (b) sulphate effect on boron removal.

Table 5
EBV and EBCT values of resin column

Parameters	Value	Q (m^3/h)	Cross sectional area (m^2)	Column height (m)	V (m^3)	EBV (m/h)	EBCT (h)
Resin Amount (g)	10	0.126×10^{-3}	2.49×10^{-4}	0.0575	0.143×10^{-4}	0.506	0.113
	15	0.125×10^{-3}	2.49×10^{-4}	0.08625	0.214×10^{-4}	0.502	0.171
	20	0.123×10^{-3}	2.49×10^{-4}	0.115	0.286×10^{-4}	0.494	0.233
Flow rate (mL/min)	2.08	0.125×10^{-3}	2.49×10^{-4}	0.08625	0.214×10^{-4}	0.502	0.171
	2.61	0.157×10^{-3}	2.49×10^{-4}	0.08625	0.214×10^{-4}	0.631	0.136
	2.98	0.179×10^{-3}	2.49×10^{-4}	0.08625	0.214×10^{-4}	0.719	0.120
Mine water flow rate (mL/min)	1.863	0.112×10^{-3}	2.49×10^{-4}	0.08625	0.214×10^{-4}	0.450	0.191

removal rate decreased with temperature decrease. The temperatures 7.5°C, 15°C, 30°C were used for calculation of these parameters.

$$\ln\left(\frac{k}{T}\right)=\left[\frac{k_b}{h}+\frac{\Delta S}{R}\right]-\frac{\Delta H}{R}\times\frac{1}{T} \tag{8}$$

where k_b and h are Boltzmann's (1.3807×10^{-16} cm^2 gs^{-2} K^{-1}) and Planck's constants (6.6261×10^{-27} cm^2 gs^{-1}), respectively. ΔH (enthalpy change) and ΔS (entropy change) were calculated from slope and intercept of line, respectively. k is the Thomas model rate constant and R is the gas constant (8.314 J/mol K). The enthalpy value of boron exchange was calculated as 16.852 kJ/mol and this value showed the endothermic nature of the boron exchange with the resin.

4. Conclusion

The performance of Purolite S 108 resin for boron removal in a column reactor was investigated in this study. Experimental parameters were initial solution pH, temperature, concentration, resin amount, solution flow rate and regeneration number. For the present study, the conclusions can be summarized as follows. Optimum solution pH and temperature were determined as 9.5 and 15°C, respectively. Resin exhaustion time increased with increasing resin amount and decreasing concentration and decreasing solution flow rate. The capacity of the resin did not significantly change with regeneration up to 5th resin uses and resin capacity values were 9.53, 9.71, 9.89, 9.90 and 9.67 for the first five resin uses. Kinetic analysis of boron removal was done by applying Yoon–Nelson, Thomas, and Adams–Bohart models. All the models are suitable for description of data except Adams–Bohart model. Although the resin was an effective material for boron removal from concentrated boron solutions, the boron removal by the resin was a slow process. An empirical kinetic model was developed based on Yoon–Nelson model and the model could almost estimated the 50% and 90% breakthrough times for all the parameter intervals. Maximum capacity was calculated as 10.67 mg/g at 1,000 mg/L concentration. The developed model could estimate successfully the 4.55%, 45.5% and 83.33% boron removal breakthrough times for colemanite mine wastewater.

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