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Adsorption of boron from aqueous solutions using fly ash: Batch and column studies

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Abstract

In the present paper, boron removal from aqueous solutions by adsorption was investigated. Fly ash particle size used in adsorption experiments was between 250 and 400 μm. During the experimental part of this study, the effect of parameters such as pH, agitation time, initial boron concentration, temperature, adsorbent dosage and foreign ion on boron removal were observed. In addition, adsorption kinetics, adsorption isotherm studies and column studies were made. Maximum boron removal was obtained at pH 2 and 25 °C. Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°), entropy (ΔS°) were also determined. As a result of the kinetic studies, it was observed that the adsorption data conforms to the second degree kinetics model. In the isotherm studies, Langmuir and Freundlich isotherm models were applied and it was determined that the experimental data conformed to Langmuir isotherm model. Batch adsorbent capacity (q_o) was calculated as 20.9 mg/g. The capacity value for column study was obtained by graphical integration as 46.2 mg/g. The Thomas and the Yoon–Nelson models were applied to experimental data to predict the breakthrough curves and to determine the characteristics parameters of the column useful for process design.

Keywords: Boron removal; Adsorption; Fly ash; Batch study; Column study

1. Introduction

Boric acid and boron salts have extensive industrial use in the manufacture of glass and porcelain, in wire drawing, the production of leather, carpets, cosmetics and photographic chemicals, for fireproofing fabrics, and weatherproofing wood. Boron compounds are used in certain fertilisers for the treatment of boron deficient soils. Boric acid, which has mild bactericidal and fungicidal properties, is used as disinfectant and as food preservative. Borax is widely used in welding and brazing of metals, and more recently, boron compounds have found applications for hand cleansing, high-energy fuels, cutting fluids and catalysts [1].

Turkey has the largest boron reserve which is approximately 90 million tons in the world. It was estimated that Turkey has about 70% of the known reserves of the world. The known borate reserves in Turkey are located in four main districts, namely Emet, Bigadiç, Kırka and Mustafakemalpaşa [2].

There is no easy method for the removal of boron from waters and wastewaters. One or more methods may be applied according to boron concentration in medium. For boron removal, main processes that have been studied are: (1) precipitation–coagulation, (2) adsorption on oxides, (3) adsorption on active carbon, cellulose or clay minerals, (4) ion exchange with basic exchanger, (5) solvent extraction, (6) membrane filtration, (7) use of boron selective resins (Amberlite XE 243, Amberlite IRA 743) [3–7].

A very low boron content is required in irrigation water for certain metabolic activities, but if its concentration is only slightly higher, plant growth will exhibit effects of boron poisoning, which are yellowish spots on the leaves and fruits, accelerated decay and ultimately plant expiration [8–10]. Referring to Nable et al. [11], safe concentrations of boron in irrigation water are 0.3 mg/L for sensitive plants,

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Nomenclature

b	Langmuir isotherm constant which related to energy of adsorbent (L/mg)
C_{ad}	adsorbed boron concentration in the column (mg/L)
C_0	initial boron concentration (mg/L)
C_e	concentration of boron solution at equilibrium (mg/L)
K	adsorption equilibrium constant
K_f	Freundlich adsorption isotherm constant (mg/g)
k	kinetic constant in the Yoon and Nelson model (L/min)
K_T	kinetic constant in the Thomas model (L/(mg min))
k_2	rate constant for the pseudo-second-order model (g/(mg min))
m	adsorbent amount (g)
n	Freundlich adsorption isotherm constant
R	gas constant
R_L	dimensionless separation constant
R^2	Correlation coefficient
T	temperature (°C, K)
t	time (min)
q_o	monolayer capacity of the adsorbent (mg/g)
q_e	amount of boron adsorbed at equilibrium (mg/g)
q_t	the amount of boron adsorbed at t time (mg/g)
V	throughput volume (L)
ΔG°	standard free energy (kcal/mol)
ΔH°	standard enthalpy change (kcal/mol)
ΔS°	standard entropy change (kcal/(mol K))

Greek letters

θ	volumetric flow rate (L/min)
τ	time required for 50% adsorbate breakthrough (min)

1–2 mg/L for semi tolerant plants, and 2–4 mg/L for tolerant plants.

Adsorption is one of the techniques, which is comparatively more useful and economical at low pollutant concentration. The application of low cost and easily available materials in wastewater treatment has been widely investigated during recent years. Activated carbon is currently the most widely used adsorbent for wastewater treatment, but recognizing the high cost of activated carbon, many investigators have studied the feasibility of cheap, commercially available materials as its possible replacements.

Fly ash is a waste material originating in great amounts in combustion process. The use of fly ash in wastewater treatment has been studied extensively in recent years and the results of laboratory investigations showed that fly ash is a good adsorbent for the removal of hazardous materials from wastewater [12].

In this study, boron removal from aqueous solutions by batch and column adsorption methods was investigated by a low cost and abundantly available adsorbent (fly ash). Factors affecting sorption, such as pH, agitation time, temperature, adsorbent dosage, initial boron concentration and the presence of inorganic salts were investigated. Kinetic and isotherm studies were made. Thermodynamic parameters, batch and column capacities were calculated. The Thomas and Yoon–Nelson models were applied to experimental data obtained from column study.

2. Experimental

Fly ash used in this study was obtained from a textile plant where Soma coals were used. Fly ash was analyzed in the Eskişehir Anadolu University. Chemical analysis result is given in Table 1. Fly ash was screened before being used. The particle size of the fly ash was between 250 and 400 μm. The fly ash samples were dried at 105 °C for 2 h before each set of experiments. The aqueous solution of H_3BO_3 was prepared by using the analytical grade Merck product. The solution was prepared in such a manner that the initial boron concentration in adsorption experiments was held at 600 mg/L. pH was measured with pH meter (Consort P903).

In batch adsorption experiments, known weights of adsorbents (1 g) were added to capped volumetric flasks each of which containing 50 mL solution (600 mg/L boron) and shaken at 140 rpm in a temperature-controlled water bath with shaker (MEMMERT) for 48 h. After adsorption, samples were centrifuged and boron in supernatants was analysed. Boron was determined using HACH DR-2000 Spectrophotometer by carmine method. All of the tests were duplicated. The effect of pH was studied by adjusting the pH of boron solutions using dilute HCl and NaOH solutions at 25, 35 and 45 °C. In kinetic studies, batch experiment was repeated at different periods using 1 g of adsorbents and 50 mL solution at pH 2 and 25, 35 and 45 °C. Boron concentration

Table 1
Chemical composition of the used fly ash

Constituents	Contents (%, w/w)
SiO_2	31.90
Al_2O_3	23.50
CaO	6.29
Fe_2O_3	4.76
SO_4	1.62
MgO	1.35
K_2O	0.99
TiO_2	0.54
Na_2O	0.35
P_2O_5	0.17
BaO	0.05
Cr_2O_3	0.02
MnO	0.01
Ignition loss	29.5

in supernatant have been constant after a time period. This period has accepted as equilibrium time for fly ash. The effect of temperature was carried out by fly ash at 25, 35 and 45 °C. Different adsorbent doses (100–5000 mg) were applied to 50 mL of the solution containing 600 mg/L boron at pH 2 and 25, 35 and 45 °C in order to find out the effect of adsorbent dosage on boron removal. Effect of initial boron concentration was investigated at three different temperatures and pH 2. Langmuir and Freundlich isotherms were employed to study the adsorption capacity of the adsorbent. Boron plant wastewaters can contain various ions such as sulphate, sodium, calcium, magnesium, etc. The effects of Na_2SO_4 and $CaCl_2$ on boron removal by adsorption were studied.

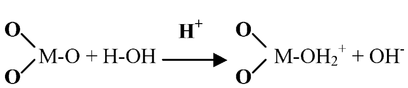
In column experiment a glass column (0.7 cm i.d. and 15 cm length) was filled with 1.2 g of fly ash on glass wool support. Boron solution (600 mg/L boron) at 25 °C and pH 2 was delivered downflow to the column using a peristaltic pump (ATTO SJ 1211 model) at 3 mL/min flow rate. To obtain breakthrough curve the effluent was collected as 1.5 mL fractions with a fraction collector (Spectra/chrom CF-1) and analysed. Column studies were terminated when the column reached exhaustion. The desorption studies carried out after the column adsorption studies were conducted at 25 °C and 3 mL/min flow rate. The adsorbed boron was desorbed from fly ash by using 2 M H_2SO_4 solution.

3. Results and discussion

3.1. Effect of pH

The adsorption of boron was studied over the pH range 2–11 (Fig. 1). The maximum uptake of boron takes place at pH 2.

The chief constituents of fly ash are oxides. As can be seen from Eq. (1) at acidic pH values the oxides in solution tends to form an aqua complex to yield a positively charged surface.



(1)

where M is mainly Si, Al, Ca, Fe, etc.

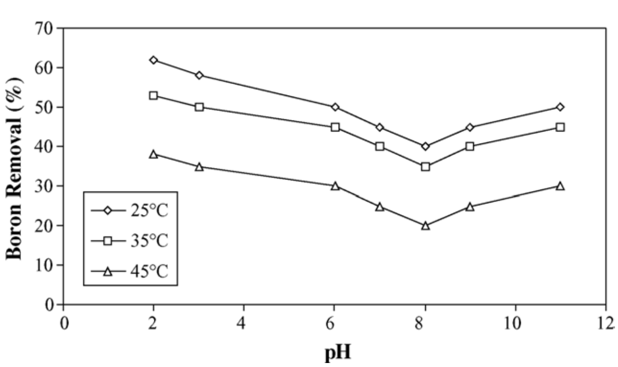
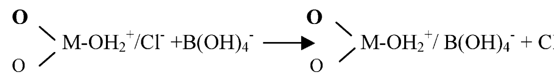


Fig. 1. Effect of pH on the removal of boron.

The positive charged hydroxilated oxide surfaces is suitable for adsorption of borate anions. In addition if hydrochloric acid was used for acidification, the positively charged surface might be associated with chloride ions, which would subsequently be exchanged for borate anions, as shown in Eq. (2). As a result, maximum sorption of borate anion occurred at the most acidic pH tested.



(2)

According to Eq. (3), at high pH values borate anions is dominant.

$$B(OH)_3 + OH^- \rightarrow B(OH)_4{}^- + H^+ \tag{3}$$

So, precipitation may occurs by calcium and aluminium oxides at high pH values.

3.2. Effect of agitation time

Removal of boron by fly ash with time was carried out at pH 2 and a temperature of 25, 35 and 45 °C (Fig. 2). The amount of boron adsorbed increases with agitation time and attain equilibrium at about 24 h for fly ash for an initial concentration of 600 mg/L at 25 °C.

3.3. Sorption kinetics

In order to examine the controlling mechanisms of adsorption process pseudo-first-order kinetics model and pseudo-second-order kinetics model are used to test the experimental data.

The rate constant of adsorption is determined from the following pseudo-first-order rate expression given by Lagergreen [13] and Ho [14]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{4}$$

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

If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetics rate equation is

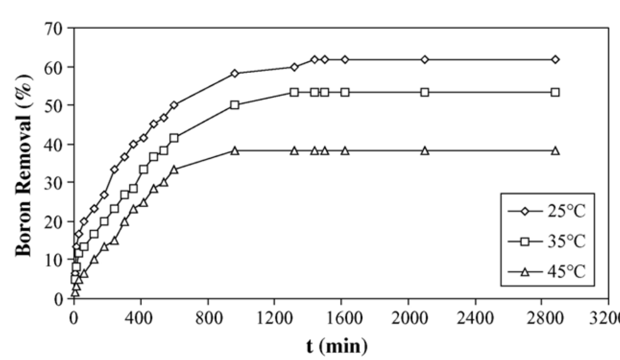


Fig. 2. Effect of agitation time on the removal of boron (at pH 2).

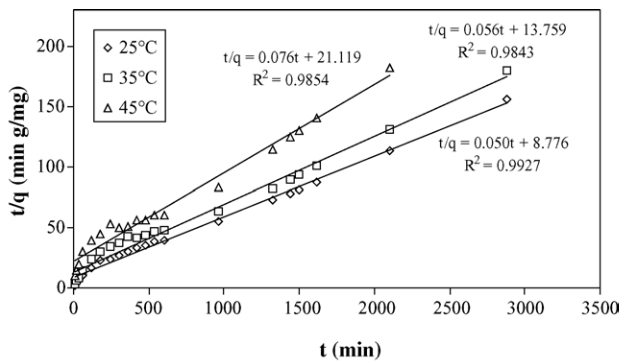


Fig. 3. Plots of pseudo-second-order model for boron removal (at pH 2).

expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where k_2 is the rate constant of pseudo-second-order chemisorption (g/(mg min)). For boundary conditions ($t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$), pseudo-second-order kinetic model of Ho and McKay [15] is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

The fit of these models was checked by each linear plot of log ($q_e - q_t$) versus t, t/q_t versus t, respectively, and by comparing to the regression coefficient for each expression. The result showed that such pseudo-first-order rate expression is not fully valid for the present system. Due to low correlation coefficients figures not shown. A good agreement of the experimental data with the pseudo-second-order kinetic model (Fig. 3) was observed. Second-order sorption rate constant (k_2) and q_e values were determined from the slopes and intercepts of the plots (Fig. 3). The values of these parameters are presented in Table 2. The correlation coefficients (R^2) for the second-order-kinetic model are higher than 0.98. The theoretical q_e values agree perfectly with the experimental q_e values (Table 2). These indicate that the adsorption of boron obeys pseudo-second-order kinetic model.

3.4. Effect of temperature

The effect of temperature on the adsorption of boron on fly ash is shown in (Fig. 2). The uptake of boron was found to decrease with increasing temperature, indicating that boron adsorption on the adsorbent surface was favoured at lower temperatures. The boron removal percent followed the order 25 °C > 35 °C > 45 °C. The decrease in adsorption with increasing temperature indicated exothermic nature of the adsorption process.

The change in standard free energy, enthalpy and entropy of adsorption were calculated using the following equations:

$$\Delta G^\circ = -RT \ln K \quad (7)$$

where R is gas constant and K is the equilibrium constant (concentration of adsorbed boron/concentration of boron remained at solution) and T is the temperature in K.

According to the van't Hoff equation:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

where ΔS° and ΔH° are change in entropy and enthalpy of adsorption, respectively. A plot of $\ln K$ versus $1/T$ is linear (Fig. 4). Values of ΔH° and ΔS° were evaluated from the slope and intercept of van't Hoff plots (Table 3). The negative values of ΔH° confirm the exothermic nature of adsorption. The negative values of ΔS° suggest the system exhibits random behavior. The positive values of ΔG° at 45 °C indicate spontaneity is not favoured at high temperatures.

3.5. Effect of adsorbent dosage

Fig. 5 gives the removal percentage of boron as a function of adsorbent dosage. In general, the increase in adsorbent

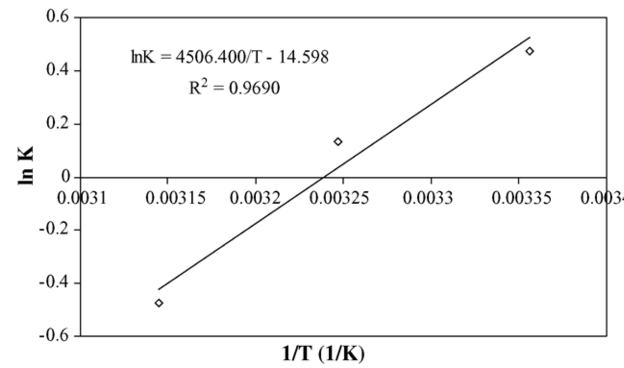


Fig. 4. van't Hoff plot for the removal of boron (at pH 2).

Table 3
Thermodynamic parameters for the removal of bxoron

Temperature (°C)	K	ΔG° (kcal/mol)	ΔH° (kcal/mol)	ΔS°(kcal/(mol K))
25	1.609	−0.310	−8.950	−0.029
35	1.143	−0.020		
45	0.622	0.270		

Table 2
Pseudo-second-order kinetic parameters for the removal of boron

Adsorbent	$k_2 \times 10^4$ (g/(mg min))			q_e (Experimental) (mg/g)			q_e (Calculated) (mg/g)		
	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
Fly ash	2.85	2.27	2.72	18.50	16.00	11.50	20.00	17.90	13.20

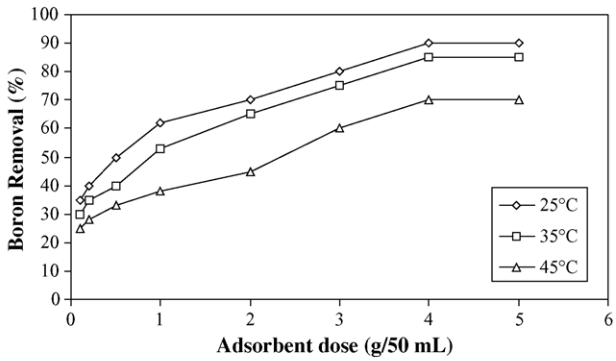


Fig. 5. Effect of adsorbent dose on the removal of boron (at pH 2).

dosage increased the percent removal of boron, which is due to the increase in adsorbent surface area. The results obtained in the study are in agreement with this. Adsorbent dosage was varied from 2 to 100 g/L. The results also clearly indicate that the removal efficiency increases up to optimum dosage beyond which the removal efficiency is negligible. Because at equilibrium concentration difference which driving force for adsorption decreases for 4 g/50 mL solution and 5 g/50 mL solution adsorbent dosages.

3.6. Effect of initial boron concentration

Solutions of different initial boron concentrations (10, 50, 250, 600, 1000, 1500 mgB/L) were used to investigate the effect of concentration on the removal of boron by 1 g adsorbent at pH 2. Adsorption yield values were calculated from following equation:

$$\text{Adsorption yield (\%)} = \left[\frac{C_0 - C_e}{C_0}\right] \times 100 \quad (9)$$

where C_e is the concentration of the boron solution (mg/L) at equilibrium and C_0 is the initial boron concentration (mg/L). Effect of initial boron concentration on boron adsorption was given in Fig. 6. The adsorption yields (%) were decreased by increasing of initial boron concentration.

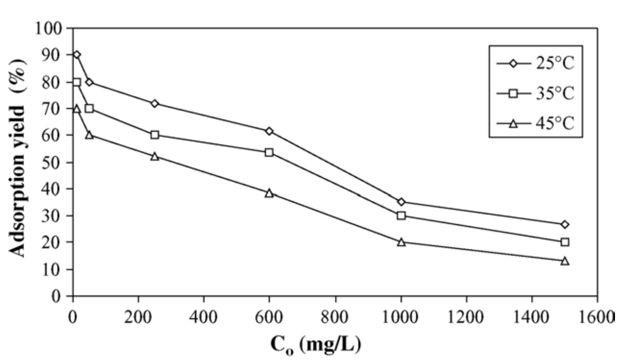


Fig. 6. Effect of initial boron concentration on the removal of boron (at pH 2).

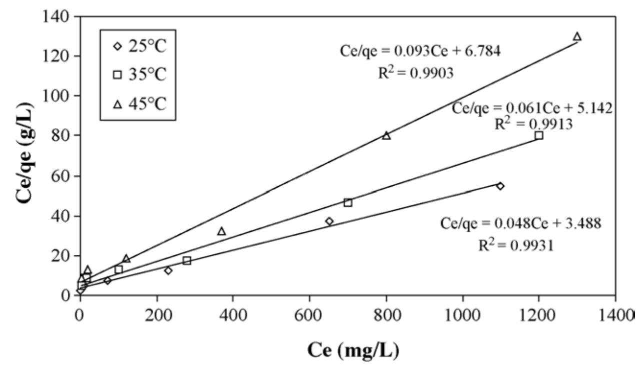


Fig. 7. Langmuir plots for the removal of boron (at pH 2).

Table 4
Langmuir and Freundlich constants at different temperatures

Temperature (°C)	Langmuir constants			Freundlich constants	
	q_0 (mg/g)	b (L/mg)	R_L	K_f (mg/g)	n
25	20.880	0.014	0.106	0.559	1.774
35	16.390	0.012	0.122	0.337	1.666
45	10.800	0.014	0.106	0.250	1.726

3.7. Adsorption isotherms

Several models have been published in the literature to describe experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently employed models. In this work, both models were used to describe the relationship between the adsorbed amount of boron and its equilibrium concentration in solution.

Langmuir isotherm is represented by the following equation [16]:

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \quad (10)$$

where the constant q_o signifies the adsorption capacity (mg/g) and b is related to the energy of adsorption (L/mg). The linear plot of C_e/q_e versus C_e shows that adsorption follows a Langmuir isotherm (Fig. 7). Values of q_o and b were calculated from the slope and intercept of the linear plots and are presented in Table 4. The applicability of the Langmuir isotherm suggests the monolayer coverage of the boron adsorption onto fly ash [16].

To determine if the boron adsorption process by fly ash is favourable or unfavourable for the Langmuir type adsorption process, the isotherm shape can be classified by a term "R_L", a dimensionless constant separation factor, which is defined below [17]:

$$R_L = \frac{1}{1 + bC_0} \quad (11)$$

where R_L is a dimensionless separation factor and b is Langmuir constant (L/mg). The parameter R_L indicates the shape of the isotherm accordingly:

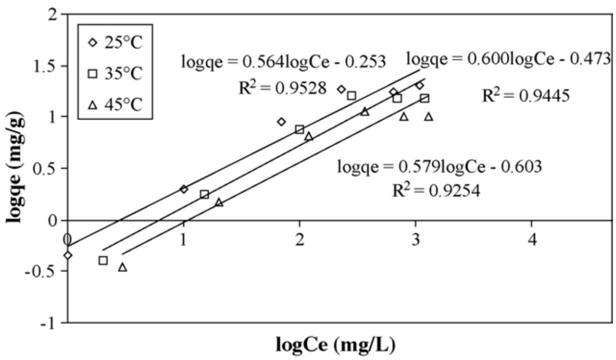


Fig. 8. Freundlich plots for the removal of boron (at pH 2).

$R_L > 1$, unfavourable;
$R_L = 1$, linear;
$0 < R_L < 1$, favourable;
$R_L = 0$, irreversible.

Calculated R_L values (Table 4) indicated that adsorption of boron on fly ash was favourable at 600 mg/L initial boron concentration, 25, 35 and 45 °C temperatures and pH 2.

The Freundlich isotherm was also applied for the boron removal by adsorption. Freundlich isotherm model is given by the following equation [16]:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \qquad (12)$$

where K_f and n are Freundlich adsorption isotherm constants, being indicative of the adsorption capacity and intensity of adsorption. Values of K_f and n were calculated from the intercept and slope of the plots of $\log q_e$ versus $\log C_e$ (Fig. 8). In general, as the K_f value increases, the adsorption capacity of the adsorbent increases. The isotherm data are given in Table 4. It has been shown using mathematical calculations that n was between 1 and 10 representing beneficial adsorption [18]. So fly ash adsorbent used in the study provide beneficial adsorption at 25, 35 and 45 °C and pH 2.

3.8. Effects of other ions

In the present study all of the tests were done with H_3BO_3 solution. However in real boron plant wastewaters contain various species. The effect of presence of two salts, i.e. Na_2SO_4 and $CaCl_2$ on boron adsorption was studied (Fig. 9). Tests were conducted in the presence of 1 M Na_2SO_4 and 2.5 M $CaCl_2$ solutions. It was observed that the decrease in the adsorption is about 3–4%.

3.9. Column studies

The performance of packed beds is described through the concept of the breakthrough curve. The breakthrough curve shows the loading behaviour of boron to be removed from solution in a fixed bed and is usually expressed in terms of adsorbed boron concentration (C_{ad} = inlet boron concentration (C_0) − outlet boron concentration (C_e)) or normalised concentration defined as the ratio of effluent boron concentration to inlet boron concentration (C_e/C_0) as a function of time or volume of effluent for a given bed height [19]. The area under the breakthrough curve obtained by integrating the adsorbed concentration (C_{ad}; mg/L) versus the throughput volume (V; L) plot can be used to find the total adsorbed boron quantity (maximum column capacity). Total adsorbed boron quantity (q_o; mg/g) in the column for a given feed concentration and flow rate is calculated from Eq. (13):

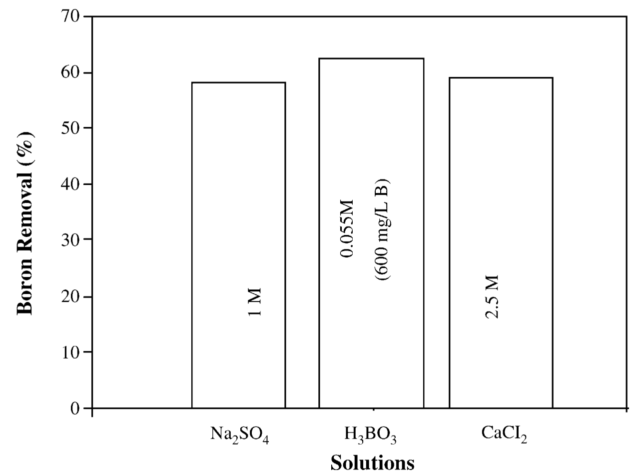


Fig. 9. Effect of added salts on the removal of boron (at pH 2).

$$q_o = \int_0^{V_T} \frac{(C_0 - C_e)\,dV}{m} \qquad (13)$$

where m is the mass of the adsorbent (g). The capacity value q_o was obtained by graphical integration as 46.2 mg/g.

3.9.1. Application of the Thomas model

Successful design of a column adsorption process requires prediction of the concentration–time profile or breakthrough curve for the effluent. The maximum adsorption capacity of an adsorbent is also needed in design. Traditionally, the Thomas model is used to fulfil the purpose. The model has the following form [20]:

$$\frac{C_e}{C_0} = \frac{1}{1 + \exp[K_T(q_o m - C_0 V)/\theta]} \qquad (14)$$

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

$$\ln\left(\frac{C_0}{C_e} - 1\right) = \frac{K_T q_o m}{\theta} - \frac{K_T C_0}{\theta} V \qquad (15)$$

The kinetic coefficient K_T and the adsorption capacity of the bed q_o can be determined from a plot of $\ln[(C_0/C_e) - 1]$ against t at a given flow rate (Fig. 10).

The Thomas equation coefficients for boron adsorption were $K_T = 4.62 \times 10^{-4}$ L/(min mg) and $q_o = 45.8$ mg/g. The value of q_o is a measure of the adsorption capacity at the fly

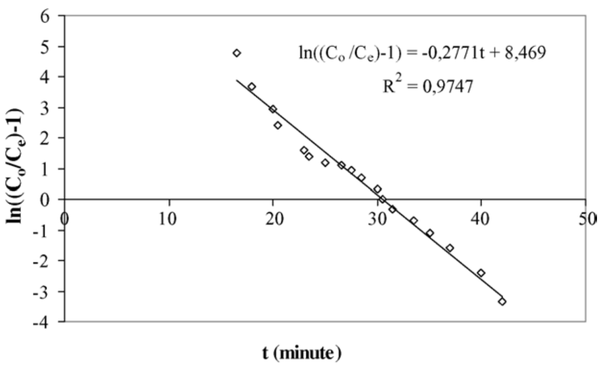


Fig. 10. Plot of t vs. $\ln[(C_0/C_e) - 1]$.

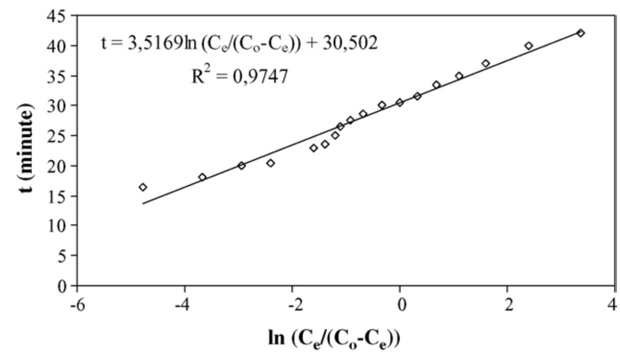


Fig. 12. Plot of $\ln[C_e/(C_0 - C_e)]$ vs. t.

ash for boron. The theoretical predictions based on the model parameters are compared in Fig. 11 with the observed data.

3.9.2. Application of the Yoon and Nelson model

This model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. The Yoon and Nelson model not only is less complicated than other models, but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent, and the physical properties of adsorption bed.

The Yoon and Nelson equation regarding to a single component system is expressed as [19]:

$$\frac{C_e}{C_0} = \frac{1}{1 + \exp[k(\tau - t)]} \tag{16}$$

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

$$t = \tau + \frac{1}{k}\ \ln\frac{C_e}{C_0 - C_e} \tag{17}$$

The calculation of theoretical breakthrough curves for a single-component system requires the determination of the parameters k and τ for the adsorbate of interest. These values may be determined from available experimental data. The approach involves a plot of sampling time (t) versus $\ln[C_e/(C_0 - C_e)]$ according to Eq. (17) (Fig. 12). The model parameters for boron adsorption by fly ash were $k = 0.284$ L/min and $\tau = 30.5$ min. Alternatively, τ can also be obtained at the adsorption time when $\ln[C_e/(C_0 - C_e)]$ is zero because of the fact that by definition τ is the adsorption time when C_e is the one-half of C_0.

These values were used to calculate the breakthrough curve. The theoretical curves were compared with the corresponding experimental data in Fig. 13.

The derivation for Eq. (16) was based on the definition that 50% breakthrough of the adsorption process occurs at τ. Accordingly, the bed should be completely saturated at 2τ. Due to the symmetrical nature of breakthrough curve, the amount of boron adsorbed by the fly ash is one half of the total boron entering the adsorption column within the 2τ period. Hence, the following equation can be written [21]:

$$q_o = \frac{1}{2}C_0\theta(2\tau) = C_0\theta\tau \tag{18}$$

The above equation establishes the relation among the adsorption capacity of the column (q_o), inlet concentration (C_0), liquid flow rate (θ) and the 50% breakthrough time (τ). q_o was calculated as 45.7 mg/g using Yoon and Nelson model.

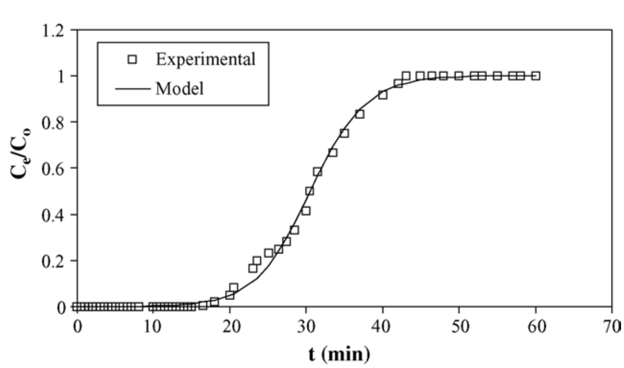


Fig. 11. Comparison of the experimental and predicted breakthrough curves according to Thomas model (at 25 °C, pH 2 and C_0 600 mg/L).

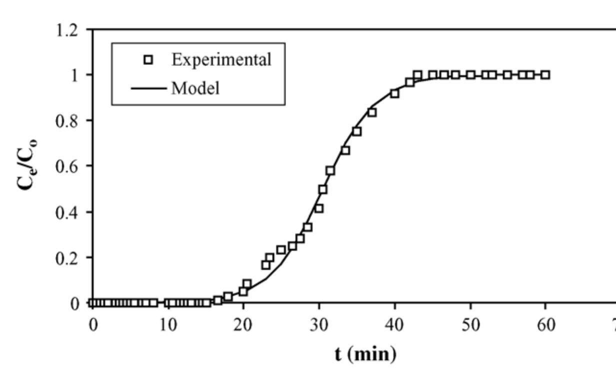


Fig. 13. Comparison of the experimental and predicted breakthrough curves according to Yoon–Nelson model (at 25 °C, pH 2 and C_0 600 mg/L).

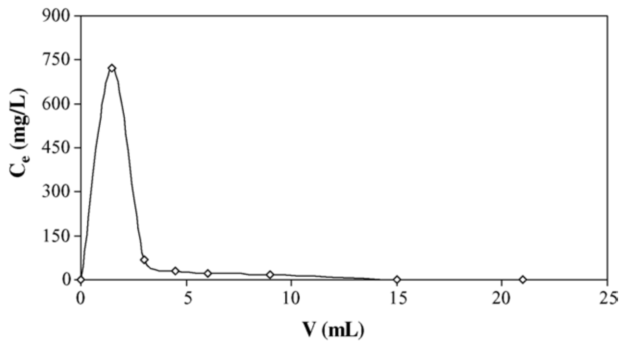


Fig. 14. Desorption of boron.

3.10. Desorption studies

Fig. 14 shows the desorption behaviour of boron. Desorption tests performed with 2 M H_2SO_4 gave 4% desorption value. Because the fly ash samples used in this study is a waste material and boron desorption value is very low, the regeneration of adsorbent was not investigated.

4. Conclusions

- Fly ash is an effective adsorbent for the removal of boron. Fly ash is waste material so regeneration is not necessary.
- Maximum boron removal was obtained at 25 °C and pH 2 for fly ash.
- The adsorption was found to be exothermic in nature.
- The adsorption yield was decreased by increasing of initial boron concentration.
- Equilibrium adsorption data followed Langmuir isotherm for fly ash.
- The pseudo-second-order equation gives a best fit to the equilibrium data.
- The batch adsorption capacity was found 20.9 mg/g.
- The column capacity value was obtained by graphical integration as 46.2 mg/g.
- The Thomas and the Yoon–Nelson models were applied to data obtained from experimental studies performed on fixed column to predict the breakthrough curves and to determine the column kinetic parameters. The capacity values were obtained as 45.8 and 45.7 mg/g using the Thomas and the Yoon–Nelson models, respectively, for fly ash.

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References

[1] S. Şahin, A mathematical relationship for the explanation of ion exchange for boron adsorption, Desalination 143 (2002) 35–43.
[2] O. Okay, H. Güçlü, E. Soner, T. Balkaş, Boron pollution in the Simav River, Turkey and various methods of boron removal, Water Res. 19 (7) (1985) 857–862.
[3] N. Öztürk, D. Kavak, Boron removal from aqueous solutions by adsorption using full factorial design, Fresenius Environ. Bull. 12 (12) (2003) 1450–1456.
[4] N. Öztürk, D. Kavak, Boron removal from aqueous solutions by adsorption on waste sepiolite and activated waste sepiolite using full factorial design, Adsorption 10 (2004) 245–257.
[5] O. Recepoğlu, Ü. Beker, A preliminary study on boron removal from Kızıldere/Turkey geothermal waste water, Geothermics 20 (1/2) (1991) 83–89.
[6] N. Balkı, Examining of Simav River for boron pollution and investigation of treatment wastewater polluted river by adsorption, Ph.D. Thesis, Uludağ University, Bursa, Turkey, 1982 (in Turkish).
[7] S. Goldberg, H.S. Forster, S.M. Lesch, E.L. Heick, Influence of anion competition on boron adsorption by clays and soils, Soil Sci. 161 (2) (1996) 99–103.
[8] D. Bayar, Boron removal from aqueous solution by adsorption and experimental design, M.Sc. Thesis, Osmangazi University, Chemical Engineering Department, Eskişehir, Turkey, 2001 (in Turkish).
[9] M. Badruk, N. Kabay, M. Demircioglu, H. Mordogan, U. Ipekoglu, Removal of boron from wastewater of geothermal power plant by selective ion-exchange resins. II. Column sorption–elution studies, Sep. Sci. Technol. 34 (15) (1999) 2981–2995.
[10] J.T. Hatcher, C.A. Bower, Equilibria and dynamics of boron adsorption by soils, Soil Sci. 85 (6) (1958) 319–323.
[11] R.O. Nable, G.S. Banuelos, J.G. Paull, Plant and Soil, Kluwer Academic Publishers, Netherlands, 1997, pp. 181–198.
[12] P. Janos, H. Buchtova, M. Ryznarova, Sorption of dyes from aqueous solutions onto fly ash, Water Res. 37 (2003) 4938–4944.
[13] S. Lagergreen, About the theory of so called adsorption of soluble substances, K. Sven. Vetenskapsakad. Handl. 24 (4) (1898) 1–39.
[14] Y.S. Ho, Citation review of Lagergreen kinetic rate equation on adsorption reaction, Scientometrics 59 (1) (2004) 171–177.
[15] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (2) (1998) 115–124.
[16] W.J. Weber, Physicochemical Processes for Water Quality Control, John Wiley and Sons Inc., New York, 1972.
[17] M. Rao, A.V. Parwate, A.G. Bhole, Removal of Cr and Ni from aqueous solution using bagasse and fly ash, Waste Manage. 22 (2002) 821–830.
[18] R. Sivaraj, C. Namasivayam, K. Kadirvelu, Orange peel as an adsorbent in the removal of Acid Violet 17 (acid dye) from aqueous solutions, Waste Manage. 21 (2001) 105–110.
[19] Z. Aksu, F. Gönen, Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves, Process Biochem. 39 (2004) 599–613.
[20] T. Mathialagan, T. Viraraghavan, Adsorption of cadmium from aqueous solutions by perlite, J. Hazard. Mater. 94 (2002) 291–303.
[21] S.H. Lin, C.S. Wang, Treatment of high-strength phenolic wastewater by a new two-step method, J. Hazard. Mater. 90 (2002) 205–216.