



Removal of boron from aqueous solutions by batch adsorption on calcined alunite using experimental design

Duygu Kavak*

Department of Chemical Engineering, Faculty of Engineering and Architecture, Eskişehir Osmangazi University, 26480, Meşelik, Eskişehir, Turkey

ARTICLE INFO

Article history:

Received 8 December 2007

Received in revised form 20 April 2008

Accepted 24 June 2008

Available online 3 July 2008

Keywords:

Boron
Boron removal
Adsorption
Calcined alunite
Experimental design

ABSTRACT

In the present paper, boron removal from aqueous solutions by batch adsorption was investigated and 2^3 full factorial design was applied. Calcined alunite was used as adsorbent. In the study, three parameters affected the performance and two levels of these parameters were investigated. The chosen parameters were temperature (25 and 45 °C, respectively), pH (3 and 10) and mass of adsorbent (0.5 g adsorbent per 25 mL solution and 1 g adsorbent per 25 mL solution). The significance of the effects was checked by analysis of variance (statistical software, MINITAB-Version 15). The model-function equation for boron adsorption on calcined alunite was obtained. The results showed that temperature, pH and mass of adsorbent affected boron removal by adsorption. Boron removal increased with increasing pH and adsorbent dosage, but decreased with increasing temperature. The optimum conditions were found as pH 10, adsorbent dosage = 1 g of calcined alunite per 25 mL solution and temperature = 25 °C by using factorial design. In addition, the effects of parameters such as calcination temperature, pH, temperature, adsorbent dosage and initial boron concentration on boron removal were investigated. The adsorption isotherm studies were also performed. Maximum adsorbent capacity (q_0) was calculated as 3.39 mg/g. Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also determined.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

High levels of boron are obtained in groundwater in some Mediterranean countries, such as Turkey, which has the largest boron reserves in the world. Boron pollution is a severe problem for Turkey. Wastes from the boron mines and boric acid plants are the main sources of the pollution. In addition to this, geothermal waters contain high levels of boron concentration in west Anatolia in Turkey. The recent European Union (EU) drinking water directive defines an upper limit of 1 mg B/L. A minimum of boron in irrigation water is required for certain metabolic activities, but at only slightly higher concentration, plant growth will exhibit effects of boron poisoning, which are yellowish spots on the leaves and fruits, accelerated decay, and ultimately plant expiration [1–5].

There is no universal method for the removal of boron from water. One or more methods may be applied according to the boron concentration in the medium. The main removal processes studied so far involve some of the following methods: precipitation–coagulation, adsorption, ion exchange, solvent extraction after boron complexation, ultrafiltration and the use of boron selective resins, particularly Amberlite XE243 (Evaluation of

boron removal from water by hydrotalcite-like compounds) [6,7]. These investigations have shown that treatments using selective resins are suitable for drinking water despite their high application and regeneration costs. In recent years, some sorption (adsorption, biosorption and ion exchange) processes have gained importance as effective purification and separation techniques for removal of toxic substances from water due to the preparation of some innovative materials.

Up to now, many different materials such as modified or unmodified clay minerals, oxides, polymeric gels and active carbon were used for the removal of boron from waters and wastewaters by adsorption technique. Certain clays having mostly SiO_2 and Al_2O_3 such as sepiolite [7], neutralized red mud [5], magnesium oxide [8], hydrotalcite-like compounds [6], modified bentonite [2], siral samples [1], and siral-30 and pural [9] have been used in the application of boron sorption.

The application of low cost and easily available materials in wastewater treatment has been widely investigated during recent years. Adsorption is a comparatively more useful and economical technique at low pollutant concentrations. Activated carbon is currently the most widely used adsorbent for wastewater treatment, but recognizing its high cost, many investigators have studied the feasibility of cheaper and commercially available materials as its possible replacements [10–12]. Alunite ore, $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{Al}(\text{OH})_3$, is one of the minerals of the jarosite

* Tel.: +90 222 2393750/3284; fax: +90 222 2393613.

E-mail address: dbayar@ogu.edu.tr.

Nomenclature

b	Langmuir isotherm constant related to the energy of adsorbent (L/mg)
C_0	initial boron concentration (mg/L)
C_e	concentration of boron solution at equilibrium (mg/L)
F	Fisher test value
K	adsorption equilibrium constant
K_F	Freundlich adsorption isotherm constant (mg/g)
n	Freundlich adsorption isotherm constant
p	probability value
R_L	dimensionless separation constant
t	Student's test value
T	temperature ($^{\circ}\text{C}$, K)
q_0	monolayer capacity of the adsorbent (mg/g)
q_e	amount of boron adsorbed at equilibrium (mg/g)
ΔG°	standard free energy (kJ/mol)
ΔH°	standard enthalpy change (kJ/mol)
ΔS°	standard entropy change (kJ/mol K)

group and it is insoluble in water. It forms when volcanic rocks are changed hydrothermally and occurs with SiO_2 minerals and contains approximately 50% SiO_2 . Alunite exists in substantial deposits in Giresun-Şebinkarahisar, Kütahya-Şaphane and İzmir-Foça in Turkey. The deposits in Turkey are estimated as about 37 million tonnes [13].

The application of statistical experimental design techniques in adsorption process development can result in improved product yields, reduced process variability, closer confirmation of the output response to nominal and target requirements, and reduced development time and overall costs. It is also possible to reduce the number of experiments [4].

In this study, boron removal from aqueous solutions using calcined alunite by batch adsorption methods was investigated. Factors affecting adsorption, such as calcination temperature, pH, temperature, adsorbent dosage and initial boron concentration were also investigated. The experimental work is carried out using a 2^3 factorial design in order to examine the main factors affecting the adsorption and their interactions.

2. Materials and methods

Alunite was provided from Kütahya (Şaphane), Turkey and used as adsorbent for all experiments. It was crushed and sieved between 90 and 150 μm range and the samples taken from this range were calcined in a furnace (Heraeus) at various temperatures between 100 and 900 $^{\circ}\text{C}$, respectively for 3 h. The samples were then preserved in a desiccator for further use. The BET surface area of calcined alunite was determined from N_2 adsorption isotherm with a surface area analyzer (Quantachrome Instruments, Nova 2200e), and the result was 12.28 m^2/g . The chemical analysis of natural alunite was determined by using XRF instrument (ARL FISON 8400/60). The chemical composition of alunite, given in Table 1. Silica, alumina, sulphur trioxide and potassium oxide were found as major constituents along with other compounds in the form of impurities. It is, thus, expected that the adsorbate species will be removed mainly by SiO_2 and Al_2O_3 [13].

In batch adsorption experiments, adsorbents were put onto capped volumetric flasks each of which contains 10 mg/L boron solution. The flasks were shaken at 140 rpm for 48 h in a temperature-controlled water bath with shaker (MEMMERT). After adsorption, the samples were centrifuged at 6000 rpm for 15 min

Table 1
Chemical composition of alunite [13]

Constituents	Percentage by weight
SiO_2	43.47
Al_2O_3	27.12
SO_3	23.50
K_2O	5.50
Other compounds	0.41

and the boron amounts in supernatant solutions were determined spectrophotometrically using Hach-DR/2000 Spectrophotometer by carmine method [14]. The pH was measured with pH meter (Consort P903). The effect of calcination temperature on the adsorption of boron onto various alunite samples was also investigated. The optimum calcination temperature was found as 700 $^{\circ}\text{C}$ and applied throughout all adsorption experiments. Further experiments were carried out at various pH values between 3 and 12. The solution pH was carefully adjusted by adding a small amount of dilute HCl or NaOH solution. The optimum pH was determined as 10 and applied throughout all of the adsorption experiments. The experiments performed to investigate the effect of temperature were carried out by using calcined alunite at three different temperatures of 25, 35 and 45 $^{\circ}\text{C}$. Various adsorbent doses (0.5–1.5 g) were applied to 25 mL of the solution containing 10 mg/L boron at pH 10 and 25 $^{\circ}\text{C}$ in order to investigate the effect of adsorbent dosage on boron removal. The effect of initial boron concentration was investigated at 25 $^{\circ}\text{C}$ and pH 10. Langmuir and Freundlich adsorption isotherms were examined to fit the experimental data.

Factorial design is employed to reduce the total number of experiments in order to achieve the best overall optimization of the system. The design determines which factors have important effects on a response as well as how the effect of one factor varies with the level of the other factors. The principal steps of the statistically designed experiments are determination of response variables, factors and factor levels, choice of the experimental design, and statistical analysis of the data. Today, the most widely used kind of experimental design, to estimate main effects as well as interaction effects, is the 2^n factorial design in which each variable is investigated at two levels. Research can be designed for multiple factors and treatments, but data analysis and treatment establishment becomes more complex and time consuming as the numbers of factors and treatments increase [15–17].

3. Results and discussion

3.1. Statistical design of experiments

The parameters involved in the adsorption experiments were optimized by full factorial design (2^3) using statistical software MINITAB (Version 15) of Minitab, Inc., USA. The levels (–) and (+) in the adsorption of boron for temperature (T), pH and mass of adsorbent (m) are given in Table 2. All the experiments were carried out in random order in duplicates using 10 mg B/L.

In this investigation for quantification of the effects of the three variables on the boron removal, a two-level factorial design of

Table 2
Factors and levels used in factorial design

Factor	Level	
	(–)	(+)
Temperature (T , $^{\circ}\text{C}$)	25	45
pH	3	10
Mass of adsorbent (m , g)	0.5	1

Table 3

Design of trial runs for boron removal from aqueous solution in two replicate experiments

Trial	T	pH	m	Adsorbed B (%)	
				(1)	(2)
1	+	–	–	10	10
2	+	–	+	12	13
3	+	+	–	13	12
4	–	+	–	14	14
5	–	–	–	13	12
6	+	+	+	28	29
7	–	–	+	14	14
8	–	+	+	48	50

experiments was adopted. The variables studied are temperature (25 and 45 °C, respectively), pH of solution (3 and 10) and mass of adsorbent (0.5 and 1 g, respectively). The number of experiments required for understanding all the effects is given by $a^k = 2^3 = 8$ where a is the number of levels and k is the number of factors. The two levels assigned to each variable are expressed in coded forms as (+) and (–) [18,19].

The regression equation developed from different sets of experiments shows the dependence of yield on individual parameters as well as interactions for simultaneous variations of parameters.

For three variables with two levels for each variable experimental design matrix, 8 possible combinations (totally 16 combinations were performed because each experiment was done two times) with the adsorption of boron were tabulated in Table 3. For treatment of data, Minitab Statistical Software release (Version 15) was employed in order to investigate the effects, coefficients, standard deviation of coefficients, and other statistical parameters of the fitted models, besides the statistical plots (normal probability of the standardized effects, Pareto). Analyses were done by means of Fisher's 'F' test and Student's 't' test. The Student's t -test was used to determine the significance of the regression coefficients of the parameters. The p -values were used as tools to check the significance of each of the interaction among the variables, which in turn may indicate the patterns of the interactions among the variables. In general, larger the magnitude of t and smaller the value of p , the more significant is the corresponding coefficient term [20].

Main factor, interaction effect, coefficients of the model, standard deviation of each coefficient, and probability for the full 2^3 factorial design are presented in Table 4 ($R^2 = 99.74\%$). As can be seen, all main factors and their interactions are significant at 5% of probability level ($p < 0.05$). The analysis of variance for the full 2^3 factorial design is presented in Table 5. As can be seen from Table 5, the p value is 0.000. The p values for main effect (0.000), two-way interaction (0.000) and three-way interaction (0.000) are very small.

The Pareto chart of standardized effects at $p = 0.05$ is presented in Fig. 1. All the values presented an absolute value higher than 2.3 ($p = 0.05$), which were located at right of the dash line, were significant. A p -value less than 0.05 (95% confidence) indicates that

Table 5

Analysis of variance for boron adsorption (%)

Source	Degree of freedom (d.f.)	Sum of squares (seq. SS)	Adjusted sum of squares (adj. SS)	Adjusted mean square (adj. MS)	F-value	p-Value
Main effects	3	1930.19	1930.19	643.40	1143.81	0.000
Two-way interactions	3	543.19	543.19	181.063	321.89	0.000
Three-way interactions	1	18.06	18.06	18.063	32.11	0.000
Residual error	8	4.5	4.5	0.563		
Pure error	8	4.5	4.5	0.7563		
Total	15	2495.94				

F: Fisher's test value.

Table 4

Full factorial fit for the boron adsorption (%)

Term	Effect	Coefficient	t-Value	p-Value
Constant		20.56	109.67	0.000
T	–9.37	–4.69	–25.00	0.000
pH	10.87	5.44	29.00	0.000
m	16.62	8.31	44.33	0.000
T pH	–1.62	–0.81	–4.33	0.003
T m	–7.37	–3.69	–19.67	0.000
pH m	8.88	4.44	23.67	0.000
T pH m	–2.12	–1.06	–5.67	0.000

S.E. of coefficient = 0.1875, t -value: Student's test value, p : probability.

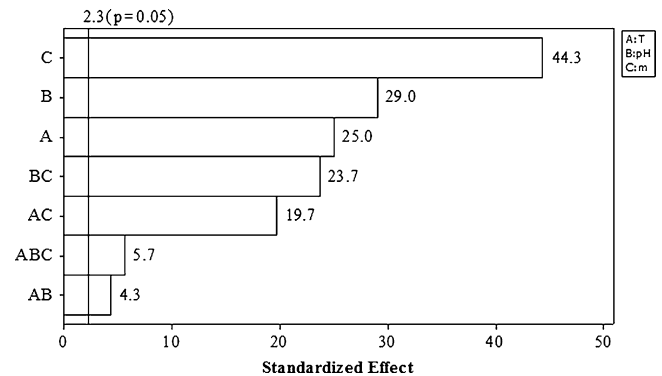


Fig. 1. Pareto chart of standardized effects for boron adsorption onto calcined alunite. (A) temperature (T), (B) pH, (C) mass of adsorbent (m).

the model is considered to be statistically significant. The absolute standardized value of the effect of each factor and its interaction appeared at the right of each bar (Fig. 1).

Regression equation for boron adsorption (%) on calcined alunite is:

$$\text{Boron adsorption (\%)} = 20.56 + 8.31m + 5.44pH - 4.69T + 4.44pHm - 3.69Tm - 1.06TpHm - 0.81TpH. \quad (1)$$

The effects of individual variables and interactional effects can be estimated from the above equation. According to this equation, pH of the solution and mass of the adsorbent have a positive effect, while temperature has a negative effect, on the boron removal by adsorption in the variation range of each variable selected for the present study. On the other hand, mass of adsorbent has the greatest effect on boron removal, which is followed by pH of solution and temperature, respectively.

3.2. Thermal analysis

Thermogravimetric (TGA) and differential thermal analysis (DTA) of alunite were carried out by a Linseis-L81 Model equipment

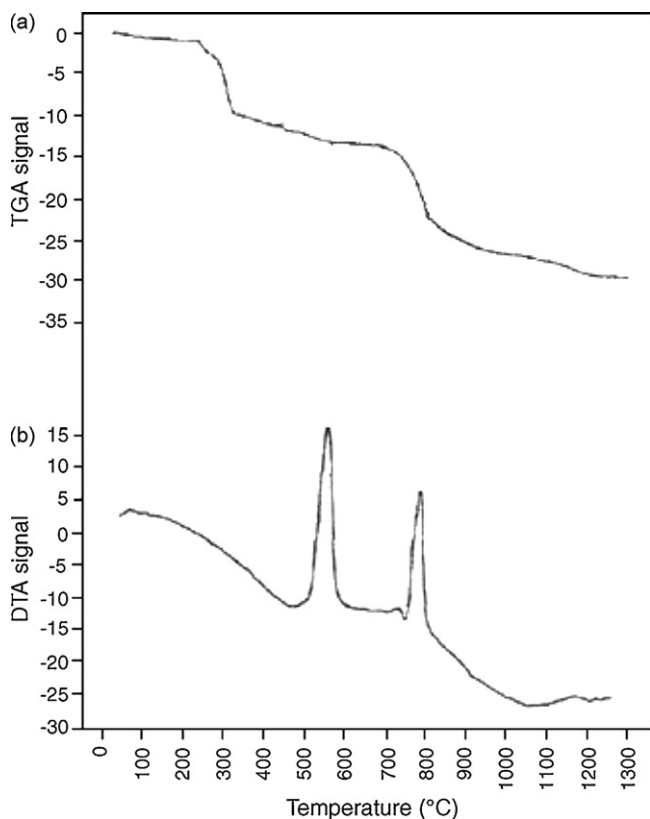
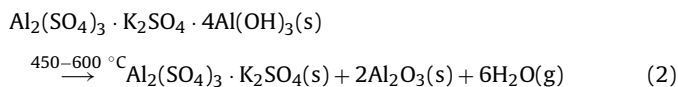
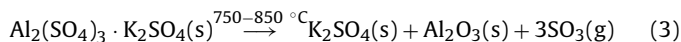


Fig. 2. (a) TGA and (b) DTA thermograms of alunite.

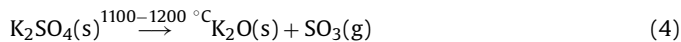
[13]. TGA and DTA thermograms of alunite are illustrated in Fig. 2. This figure exhibits an endothermic peak at 450–600 °C, accompanied by complete dehydroxilation of alunite. In this stage, mineral was transformed into crystalline $KAl(SO_4)_2$ (alum) and amorphous Al_2O_3 . In these temperature ranges, alunite decomposed by losing its structural water according to the following reaction:



The other endothermic peak was observed between 750 and 850 °C, respectively in Fig. 2, which refers to the partial desulphatization of alunite by decomposition of alum and loss of 3/4 sulphate as SO_3 as following reaction:



In the temperature range of 1100–1200 °C, it is observed that a final endothermic peak is present, according to the following reaction:



3.3. The effect of calcination temperature

The alunite was calcined at temperatures ranging from 100 to 900 °C for 3 h. The adsorption experiments with these calcined alunites were carried out using aqueous solutions with a boron concentration of 10 mg/L. The results are shown in Fig. 3. It can be seen on Fig. 3 that the adsorption of boron on calcined alunite changes with alunite calcination temperature and is highest at 700 °C.

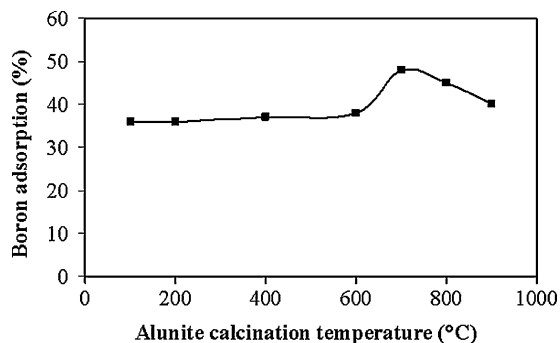


Fig. 3. Effect of calcination temperature on adsorption of boron by alunite.

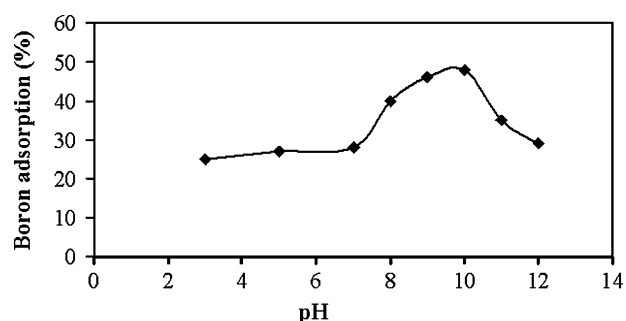


Fig. 4. Effect of pH on adsorption of boron. Conditions: 1 g/25 mL dose, 25 °C, 10 mg/L concentration.

3.4. The effect of initial pH

The pH value of the H_3BO_3 solution plays an important role in the whole adsorption process and particularly on the amount of adsorbed. Fig. 4 shows the effect of pH on the boron removal by calcined alunite. The maximum uptake of boron takes place at pH 10. As expected, when the pH increases, to an identical pH to the pK value (9.2), the adsorption process is more effective. It reaches a maximum. The borate ion concentration rises quickly and the adsorbed boron concentration increases to a maximum of pH 10. Later, the pH increases raising the concentration of hydroxyl ions in relation to the concentration of borate ions and, owing to the competitiveness of these two species for adsorption sites, the adsorbed boron decreases [8].

3.5. The effect of temperature

The effect of temperature on the adsorption of boron on calcined alunite is shown in Fig. 5. The uptake of boron was found to decrease

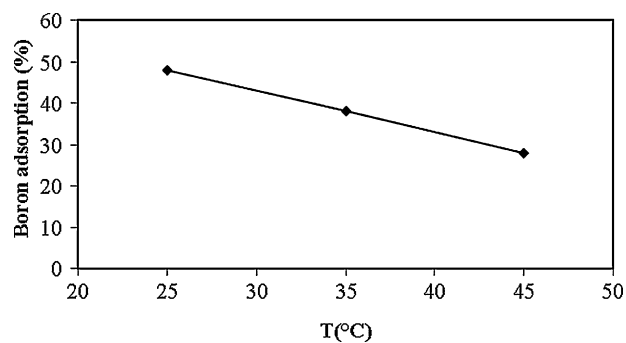


Fig. 5. Effect of temperature on adsorption of boron. Conditions: 1 g/25 mL dose, pH 10, 10 mg/L concentration.

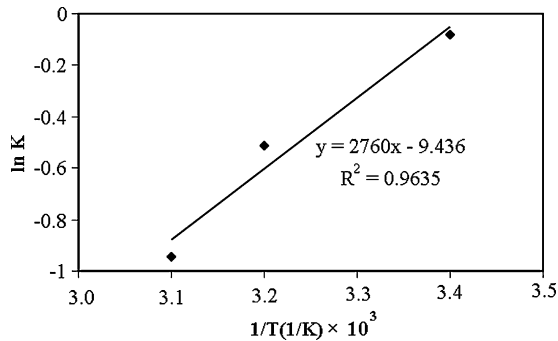


Fig. 6. van't Hoff plot for adsorption of boron. Conditions: 1 g/25 mL dose, pH 10, 10 mg/L concentration, 25 °C.

with increasing temperature, indicating that boron adsorption on the adsorbent surface was favoured at lower temperatures. The boron removal percentage level followed the order of at 25 °C > at 35 °C > at 45 °C. The decrease in adsorption with increasing temperature indicated exothermic nature of the adsorption process.

The molar free energy change of the adsorption process is related to the equilibrium constant (K) and calculated from the equation:

$$\Delta G^{\circ} = -RT \ln K \quad (5)$$

where R is gas constant, T is the absolute temperature in K. K values were estimated as

$$K = \frac{C_s}{C_e} \quad (6)$$

where C_s is the equilibrium concentration of boron on adsorbent (mg/L), C_e is the equilibrium concentration of boron in solution (mg/L).

Standard enthalpy change (ΔH°) and standard entropy change (ΔS°) of adsorption can be estimated using the following equation:

$$\ln K = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (7)$$

A plot of $\ln K$ against $1/T$ renders a straight line, as shown in Fig. 6. The slope of the plot is equal to $-\Delta H^{\circ}/R$ and its intercept value is equal to $\Delta S^{\circ}/R$. These thermodynamic parameters are presented in Table 6. Generally, the change of free energy for physisorption is between -20 and 0 kJ/mol, but chemisorption is in between range of -80 to -400 kJ/mol. The negative value of the enthalpy change (-22.95 kJ/mol) indicates that the adsorption is physical in nature involving weak forces of attraction and is also exothermic, thereby demonstrating that the process is stable energetically. The negative entropy change (ΔS°) value (-0.07845 J/molK) corresponds to a decrease in the degree of freedom of the adsorbed species [21]. The positive values of ΔG° at 25, 35 and 45 °C, respectively indicate that spontaneity is not favoured at these temperatures.

3.6. The effect of adsorbent dosage

Adsorbent dosage was varied from 0.02 to 0.06 g/L. The effect of the amount of calcined alunite on the boron removal is presented

Table 6
Thermodynamic parameters for the boron adsorption

Temperature (°C)	K	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/molK)
25	0.92	0.423	-22.94	-0.0784
35	0.60	1.207		
45	0.39	1.991		

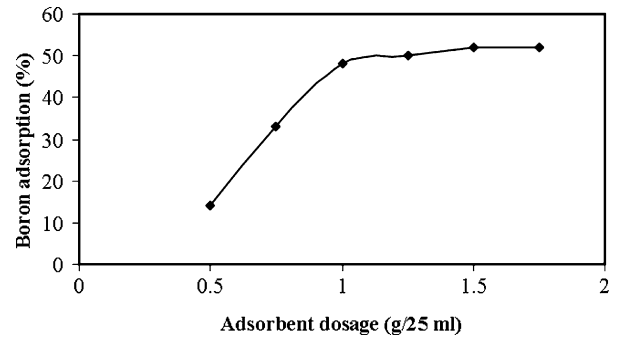


Fig. 7. Effect of adsorbent dosage on adsorption of boron. Conditions: pH 10, 10 mg/L concentration, 25 °C.

Fig. 7. As expected, the removal of boron is increased with increasing calcined alunite dosage, which is due to the increase in surface area of the calcined alunite. Boron removal is not changed importantly after 1 g/25 mL adsorbent dosage because loading capacity decreased since the unit of q is mg boron/g calcined alunite.

3.7. The effect of initial boron concentration

Solutions of various initial boron concentrations (5, 10, 25, 50, 100, 150, 250 mg B/L) were used to investigate the effect of concentration on the removal of boron by 1 g calcined alunite per 25 mL solution at pH 10 and 25 °C. Adsorption yield values were calculated from the following equation:

$$\text{Adsorption yield (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (8)$$

where C_e is the equilibrium concentration of the boron solution (mg/L) at equilibrium and C_0 is the initial boron concentration (mg/L). The effect of initial boron concentration on boron adsorption is given in Fig. 8. The efficiency of boron removal is affected by the initial concentration, with decreasing removal percentages as the concentration increases from 5 to 250 mg B/L. These effects can be explained as follows: there are number of exchangeable sites in alunite structure at low B/calcined alunite ratios. As B/calcined alunite ratio increases, exchangeable sites are saturated, resulting in a decrease in the adsorption efficiency.

3.8. Adsorption isotherms

Several adsorption isotherm models have been used to describe the experimental adsorption data [22]. The Langmuir and Freundlich models are the most frequently employed models. In this work, both models were used to describe the relationship between

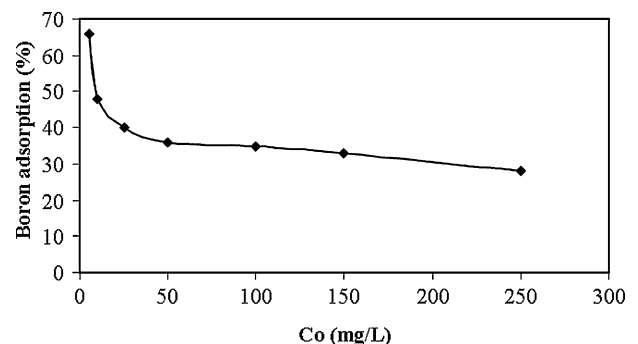


Fig. 8. Effect of initial boron concentration on adsorption of boron. Conditions: 1 g/25 mL dose, pH 10, 25 °C.

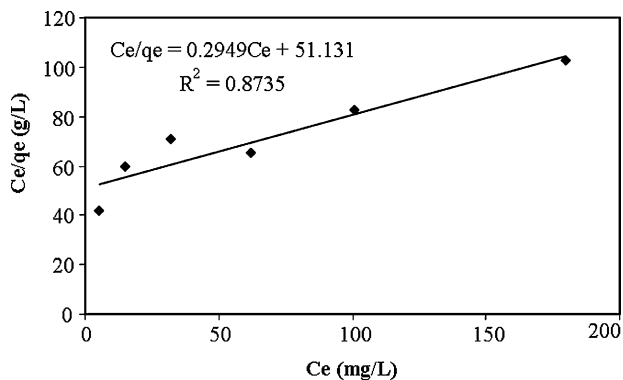


Fig. 9. Langmuir plots for adsorption of boron. Conditions: 1 g/25 mL dose, pH 10, 10 mg/L concentration, 25 °C.

the adsorbed amount of boron and its equilibrium concentration in solution.

Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \quad (9)$$

where the constant q_0 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. 9). Values of q_0 and b were calculated respectively from the slope and intercept of the linear plots and are presented in Table 7. The applicability of the Langmuir isotherm suggests the monolayer coverage of the boron adsorption onto calcined alunite [23].

To determine if the boron adsorption process by calcined alunite 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 [24]:

$$R_L = \frac{1}{1 + bC_0} \quad (10)$$

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:

- $R_L > 1$ unfavourable
- $R_L = 1$ linear
- $0 < R_L < 1$ favourable
- $R_L = 0$ irreversible

The calculated R_L value (Table 7) indicated that the adsorption of boron on calcined alunite was favourable at 10 mg/L initial boron concentration, 25 °C temperature and pH 10.

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

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (11)$$

where K_F and n are Freundlich adsorption isotherm constants indicative of the adsorption capacity and intensity of adsorption,

Table 7
Langmuir and Freundlich constants at 25 °C

Langmuir constants		Freundlich constants		
q_0 (mg/g)	b (L/mg)	R_L	K_F (mg/g)	n
3.39	0.0058	0.9452	0.033	1.287

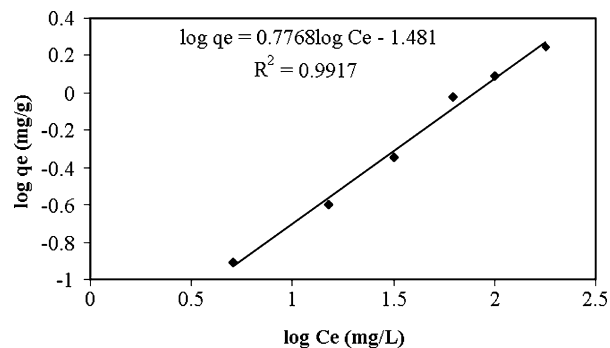


Fig. 10. Freundlich plots for adsorption of boron. Conditions: 1 g/25 mL dose, pH 10, 10 mg/L concentration, 25 °C.

Table 8
Adsorption capacity of various adsorbents as reported in literature

Adsorbent	Maximum adsorption capacity (mg/g)	References
Fly ash	20.9	[8]
Neutralized red mud	5.99	[5]
Sepiolite (activated)	178.6	[7]
Sepiolite (non activated)	96.1	[7]
Mg–Fe hydrotalcite	3.6	[6]
Mg–Al hydrotalcite	14.0	[6]
Siral 5	1.12	[1]
Siral 40	0.97	[1]
Siral 80	0.94	[1]
Calcined alunite	3.39	Present study
Çamlica Bentonite 1(CB1)	2.53	[12]
Çamlica Bentonite 2(CB2)	0.12	[12]

respectively. The values of K_F and n were calculated respectively from the intercept and slope of the plots of $\log q_e$ versus $\log C_e$ (Fig. 10). The isotherm data are given in Table 7. It has been shown using mathematical calculations that the n values representing beneficial adsorption is between 1 and 10 [24]. Thus, according to the data given in Table 7, the calcined alunite adsorbent used in the study provided a beneficial adsorption at 25 °C and pH 10.

3.9. Comparison of the present study with other adsorbents

Comparison of adsorption capacity (3.39 mg/g) observed in this study with other adsorption capacities in the literature is given in Table 8.

4. Conclusions

- From the factorial experimental design, the optimum conditions for the best adsorption results of 10 mg/L of boron were found as 25 °C pH 10 and 1 g of calcined alunite per 25 mL solution. At these conditions, boron adsorption percentage was approximately 49%.
- The adsorption was found to be exothermic in nature.
- The experimental data fit the Freundlich isotherm better than the Langmuir isotherm. The linearized Freundlich isotherm is indicating a physical adsorption.
- The batch adsorption capacity was found as 3.39 mg/g.

References

- [1] M. Yurdakoç, Y. Seki, S. Karahan, K. Yurdakoç, Kinetic and thermodynamic studies of boron removal by Siral 5, Siral 40, Siral 80, J. Colloid Interface Sci. 286 (2005) 440–446.
- [2] S. Karahan, M. Yurdakoç, Y. Seki, K. Yurdakoç, Removal of boron from aqueous solution by clays and modified clays, J. Colloid Interface Sci. 293 (1) (2006) 36–42.

- [3] A.E. Yilmaz, R. Boncukcuoğlu, M.M. Kocakerim, An empirical model for parameters affecting energy consumption in boron removal from boron-containing wastewaters by electrocoagulation, *J. Hazard. Mater.* 144 (1–2) (2007) 101–107.
- [4] S. Seyhan, Y. Seki, M. Yurdakoc, M. Merdivan, Application of iron-rich natural clays in Çamlıca, Turkey for boron sorption from water and its determination by fluometric-azomethine-H method, *J. Hazard. Mater.* 146 (2007) 180–185.
- [5] Y. Cengeloglu, A. Tor, G. Arslan, M. Ersoz, S. Gezgin, Removal of boron from aqueous solution by using neutralized red mud, *J. Hazard. Mater.* 142 (2007) 412–417.
- [6] O.P. Ferreira, S.G. Moraes, N. Durán, L. Cornejo, O.L. Alves, Evaluation of boron removal from water by hydrotalcite-like compounds, *Chemosphere* 62 (1) (2006) 80–88.
- [7] 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.
- [8] M.M.F.G. Soto, E.M. Camacho, Boron removal by means of adsorption with magnesium oxide, *Sep. Purif. Technol.* (2006) 36–44.
- [9] Y. Seki, S. Seyhan, M. Yurdakoc, Removal of boron from aqueous solution by adsorption on Al_2O_3 based materials using full factorial design, *J. Hazard. Mater.* 138 (2006) 60–66.
- [10] N. Öztürk, D. Kavak, Adsorption of boron from aqueous solutions using fly ash: batch and column studies, *J. Hazard. Mater. B* 127 (2005) 81–88.
- [11] N. Öztürk, D. Kavak, Boron removal from aqueous solutions by adsorption using full factorial design, *Presen. Environ. Bull.* 12 (12) (2003) 1450–1456.
- [12] N. Öztürk, D. Kavak, Boron removal from aqueous solutions by batch adsorption onto cerium oxide using full factorial design, *Desalination* 223 (2008) 106–112.
- [13] S. Tunalı, A.S. Özcan, A. Özcan, T. Gedikbey, Kinetics and equilibrium studies for the adsorption of Acid Red 57 from aqueous solutions onto calcined-alunite, *J. Hazard. Mater.* B135 (2006) 141–148.
- [14] Standard Methods for the Examination of Water and Wastewater, 16th ed., APHA INC., New York, 1985.
- [15] A. Gürses, M. Yalçın, Ç. Doğan, Electrocoagulation of some reactive dyes: a statistical investigation of some electrochemical variables, *Waste Manage.* 22 (2002) 491–499.
- [16] S. Chegrouche, A. Bensmaili, Removal of Ga(III) from aqueous solution by adsorption on activated bentonite using a factorial design, *Water Res.* 36 (2002) 2898–2904.
- [17] S. Al-Asheh, N. Abdel-Jabar, F. Banat, Packed-bed sorption of copper using spent animal bones: factorial experimental design desorption and column regeneration, *Adv. Environ. Res.* 6 (2002) 221–227.
- [18] R. Ragonese, M. Mulholland, J. Kalman, Full and fractionated experimental designs for robustness testing in the high-performance liquid chromatographic analysis of codeine phosphate, pseudoephedrine hydrochloride and chlorpheniramine maleate in pharmaceutical preparation, *J. Chromatogr. A* 870 (2000) 45–51.
- [19] A. Massumi, N.M. Najafi, H. Barzegari, Speciation of Cr(VI)/Cr(III) in environmental waters by fluorimetric method using central composite, full and fractional factorial design, *Microchem. J.* 72 (2002) 93–101.
- [20] D.C. Montgomery, *Design and Analysis of Experiments*, 3rd ed., Wiley, New York, 1991.
- [21] M.J. Jaycock, G.D. Parfitt, *Chemistry of Interfaces*, Ellis Horwood Ltd., Chichester, 1981.
- [22] 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.
- [23] W.J. Weber, J.C. Morris, Removal of biologically-resistant pollutants from waste waters by adsorption, in: *Advances in Water Pollution Research*, Pergamon Press, New York, 1962, pp. 231–266.
- [24] 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.