Adsorption of Boron from Aqueous Solutions by Fly Ash*

D. Kavak, N. Öztiirk
Osmangazi University, Faculty of Engineering and Architecture, Department of Chemical Engineering, 26480, Eskişehir

ABSTRACT: Adsorption studies for boron removal from aqueous solutions on fly ash were carried out under varying experimental conditions of pH, contact time, temperature, adsorbent dose and initial boron concentration. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms at different initial boron concentrations and isotherm constants were determined. The Langmuir model agrees very well with experimental data. Maximum adsorbent capacity *(q„)* was calculated from Langmuir isotherm as 20.88 mgB/g at pH 2 and 25°C. Thermodynamic parameters such as change in free energy (AG °), enthalpy (AH °), entropy (AS °) were also determined. The desorption data shows that the removal percent of from the fly ash is 42% in 2 M H_2S0_4 solution at original pH and 25°C.

1. INTRODUCTION

Boron minerals occurring in nature in more than 200 compounds are known variously as tincal, colemanite, ulexite and kernite, depending on the ratios of calcium, sodium, magnesium, etc., and water content present in the mineral. Turkey has the largest boron reserve, which is approximately 90 million tons in the world. It was estimated that Turkey has about 60% 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 (Okay et al., 1985). During the production of boron compounds, many of these are introduced into the environment in the form of waste.

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 (Nadav, 1999; Bayar, 2001; Badruk et al., 1999; Hatcher and Bower, 1958). Referring to Nable et al., (1997), safe concentrations of boron in irrigation water are 0.3 mg/L for sensitive plants,

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

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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, mam 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) (Öztürk and Kavak, 2003; Recepoglu and Beker, 1991; Simonnot et al., 1999; Balkı, 1982; Goldberg et al., 1996).

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. Various workers have exploited substances such as fly ash, slag, wool, rice straw, coconut husk, sawdust, peat moss rice husk, sugar cane dusk, dried animal bones, sawdust, bagasse fly ash, clays, soils, and so on for this purpose.

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 (Janos et al., 2003).

In this work, boron removal from aqueous solutions by batch adsorption method was investigated by a low cost and abundantly available adsorbent (fly ash). Factors affecting sorption, such as pH, contact time, temperature, adsorbent dosage, initial boron concentration were also investigated. Batch capacity was calculated.

2. EXPERIMENTAL WORK

Fly ash used in this study was obtained from a textile plant where Soma coals were used. Adsorbent particle sizes used in adsorption experiments were between 40-60 mesh. The fly ash samples were dried at 105°C for 2 h before each set of experiments.

The aqueous solution of H3BO3 was prepared by using the analytical grade Merck product. The solution was prepared in such a manner that the initial boron concentration adsorption experiments were 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 and shaken at 140 rpm in a temperature-controlled water bath (NUVE) with shaker (MEMMERT). Adsorbent and solution mixtures were shaken for 48 h (equilibrium time). 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 on boron adsorption by fly ash was studied by adjusting the pH of boron solutions using dilute HCl and NaOH solutions at three different temperatures. The effect of temperature was examined by studying at 25, 35 and 45 °C in the temperature-controlled water bath with shaker. Different adsorbent doses (100-5000 mg) were applied to 50 mL of the solution containing 600mg/L boron at pH 2 and at three different temperatures in order to find out the effect of adsorbent dosage to boron removal. Langmuir and Freundlich isotherms were employed to study the adsorption capacity of the adsorbent.

3. RESULTS AND DISCUSSION

3.1. Effect of pH

The adsorption of boron was studied over the pH range 2-11 at three different temperatures (Fig. 1). The maximum uptake of boron takes place at pH 2 for fly ash at all temperatures.

3.2 Effect of contact time

Removal of boron by fly ash with time was examined at pH 2 and three different temperatures

(Fig. 2). The amount of boron adsorbed increases with agitation time and attains equilibrium at about 24 hours at 25 °C for an initial concentration of 600 mg/L. The boron removals versus time curves are single, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of boron on the surface of the adsorbent.

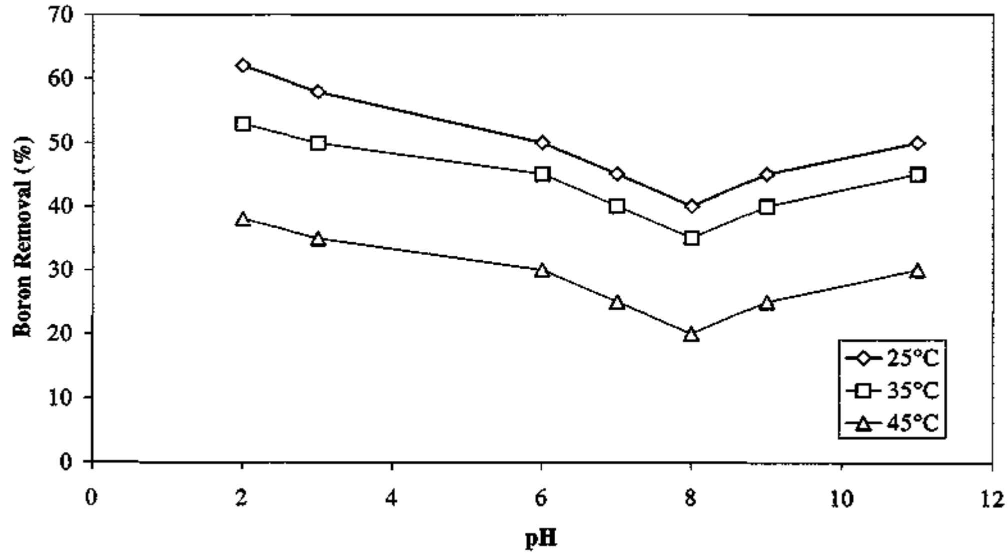

Figure 1. Effect of pH on the boron removal by adsorption at three different temperatures.

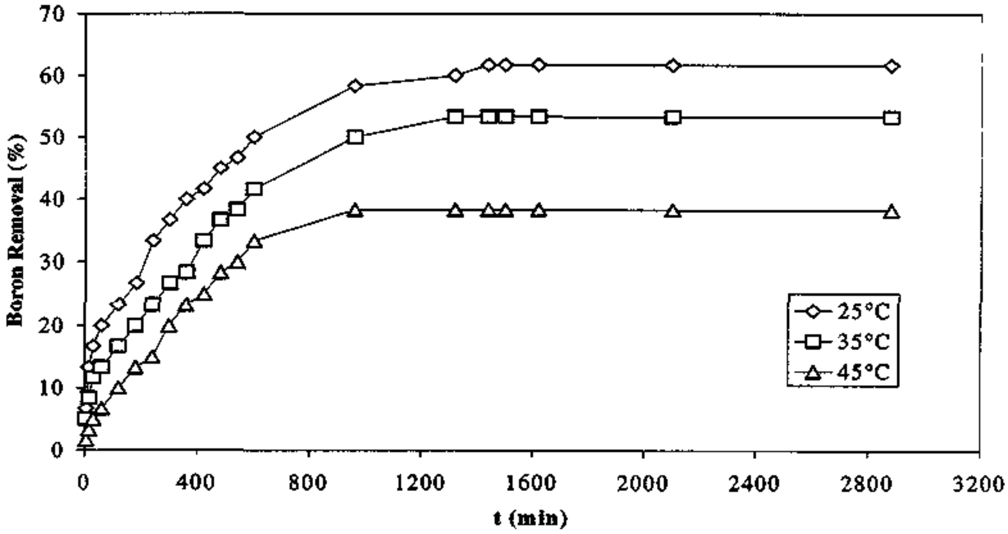

Figure 2. Effect of contact time on boron removal at different temperatures and pH 2.

3.3. Effect of Temperature

The effect of temperature on the adsorption of boron on fly ash is shown in (Fig. 3). 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^{0}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:

$$AG" = RT\ hi\ K \qquad (1)$$

where R is gas constant and K is the equilibrium constant and T is the temperature in K.
According to the van't Hoff equation,

$$\mathrm{lntf} = \frac{AS"}{R} \quad \frac{AH^0}{RT} \qquad (2)$$

where AS^0 and *AW* are change in entropy and entalphy of adsorption, respectively. A plot of InK vs 1/T is linear (Fig. 4). Values of AH^0 and AS^0 were evaluated from the slope and intercept of van't Hoff plots (Table 1). The negative values of *Alf* confirm the exothermic nature of adsorption. The negative values of *AS?* suggest the system exhibits random behavior. The positive values of *AG°* at 45°C indicate spontaneity is not favoured at high temperatures.

Table 1. Thermodynamic parameters

Temperature (°C)	*K*	AG^0 (kcal/mol)	*Alf* (kcal/mol)	<dS°(kcal/molK)
25	1.609	-0.2814	-8.92	-0.029

35	1.143	-0.082
45	0.622	0.300

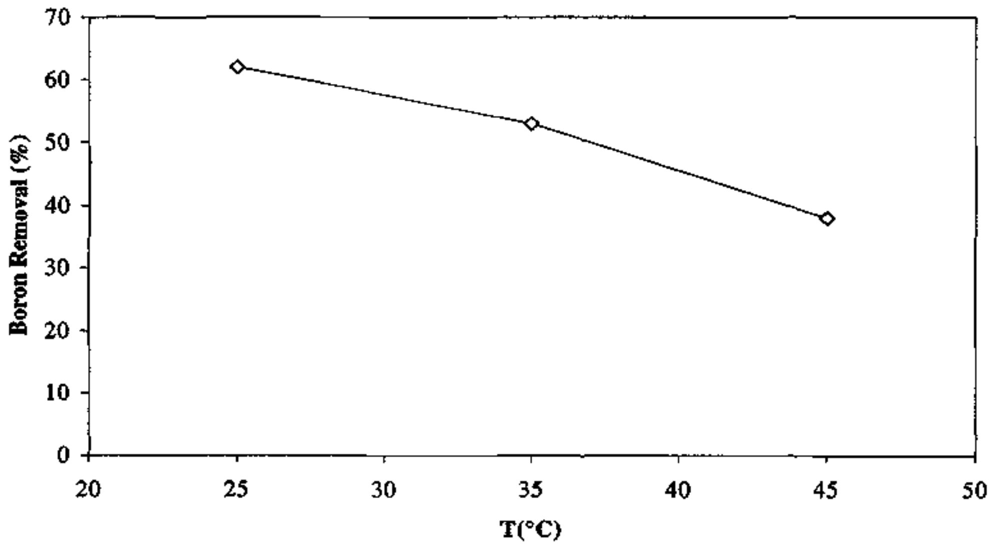

Figure 3. Effect of temperature on the boron removal by adsorption using fly ash (at pH 5.75)

3.4. Effect of Adsorbent Dosage

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

3.5. Initial boron concentration

Figure 6 indicates the .effect of initial boron concentration on the adsorption of boron by fly ash. When the initial boron concentration of sample was increased from 10 to 1500 mg/L, the removal decreased from 90 to 27% for fly ash at 25°C

3.6. 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 (Banat et al., 2000). 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 (Namasivayam and Kavifha, 2002):

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \quad *(3)$$

where C_e is the concentration of the boron solution (mg/L) at equilibrium and $q_e$is the amount adsorbed at equilibrium (mg/g). 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. 7). Values of q_0 and b were calculated from the slope and intercept of the linear plots and are presented in Table 2. The applicability of the Langmuir isotherm suggests the monolayer coverage of the boron adsorption onto fly ash (Demirbaş et al., 2002).

The Freundlich isotherm was also applied for the boron removal by adsorption. Freundlich isotherm model is given by the following equation (Namasivayam and Kavitha, 2002):

$$\log q_e = \log K_f + (1/n)\log C_e \quad (4)$$

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 logg,, versus $\log C_e$ (Fig. 8). In general, as the K_s value increases, the adsorption capacity of the adsorbent increases. The isotherm data are given in Table 2. It has been shown using mathematical calculations that n was between 1 and 10 representing beneficial adsorption (Sivaraj et al., 2001). So fly ash adsorbent used in the study provide beneficial adsorption.

3.7. Desorption Studies

Desorption tests performed with 2M H2SO4 gave 42% desorption value.

Table 2. Langmuir and Freundlich constants at different temperatures

Temperature (K)	Langmuir Constansts			Freundlich Constants		
	qo (mg/g)	b (L/mg)	R^2	*Kf* (mg/g)	n	R^2
298	20.88	0.014	0.9931	0.559	1.774	0.9528
308	16.39	0.012	0.9913	0.337	1.666	0.9445
318	10.80	0.014	0.9903	0.250	1.726	0.9254

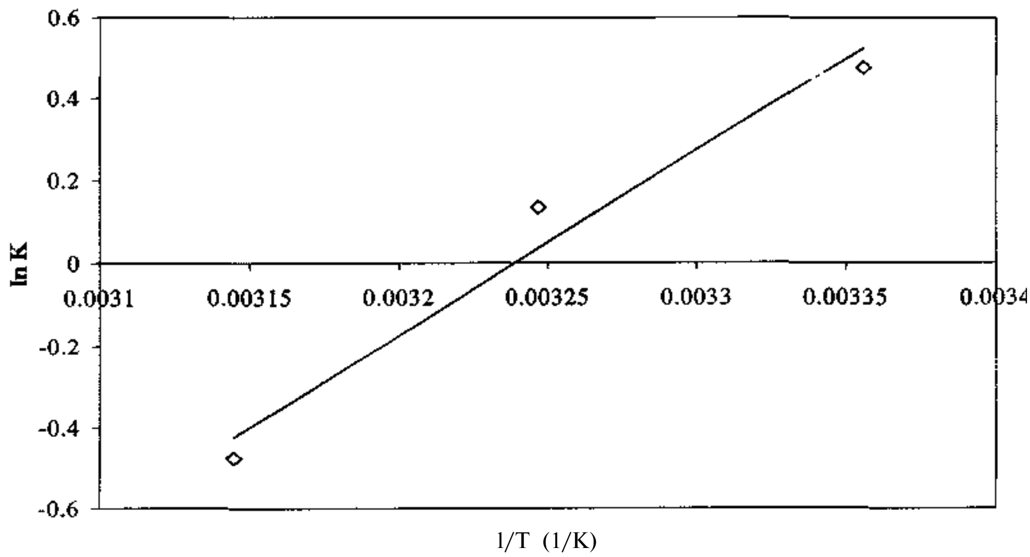

Figure 4. van't Hoff plot for boron adsorption.

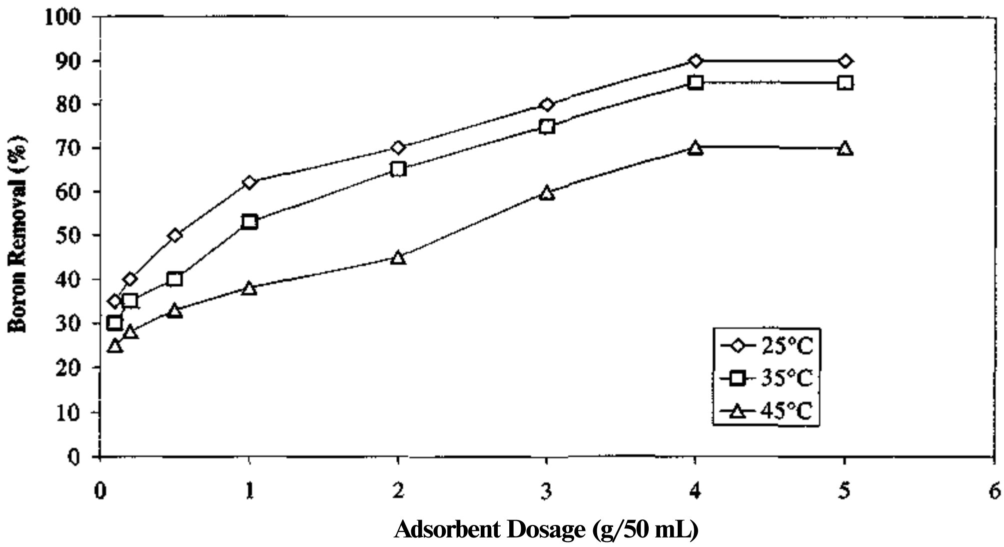

Figure 5. Effect of adsorbent dosage on the boron removal (at pH 2 and three different temperatures)

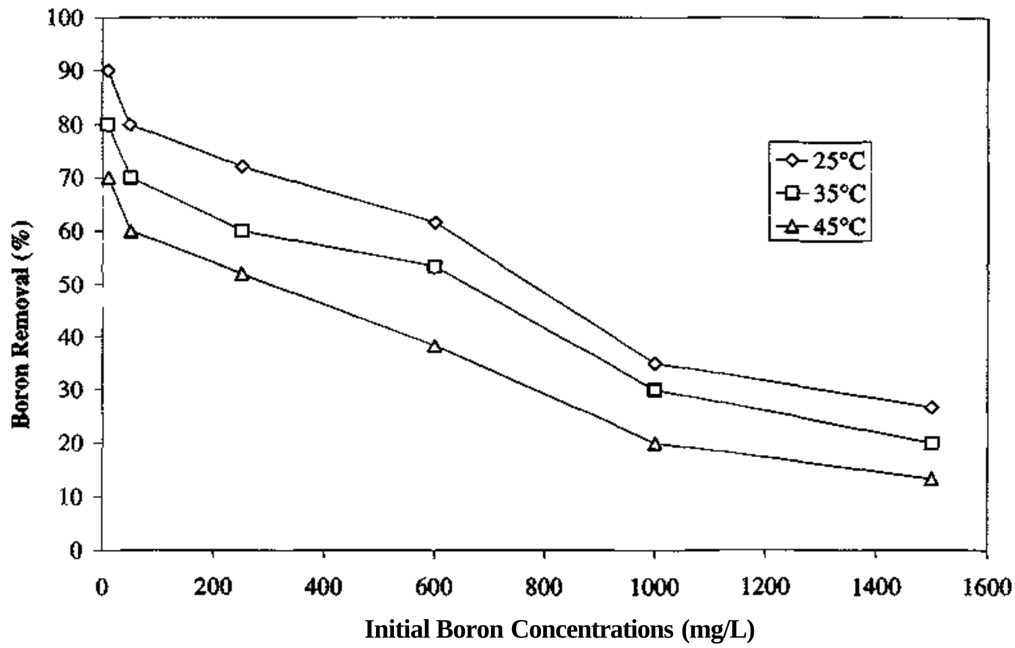

Figure 6 Effect of initial boron concentration on boron removal at three different temperatures and pH 2

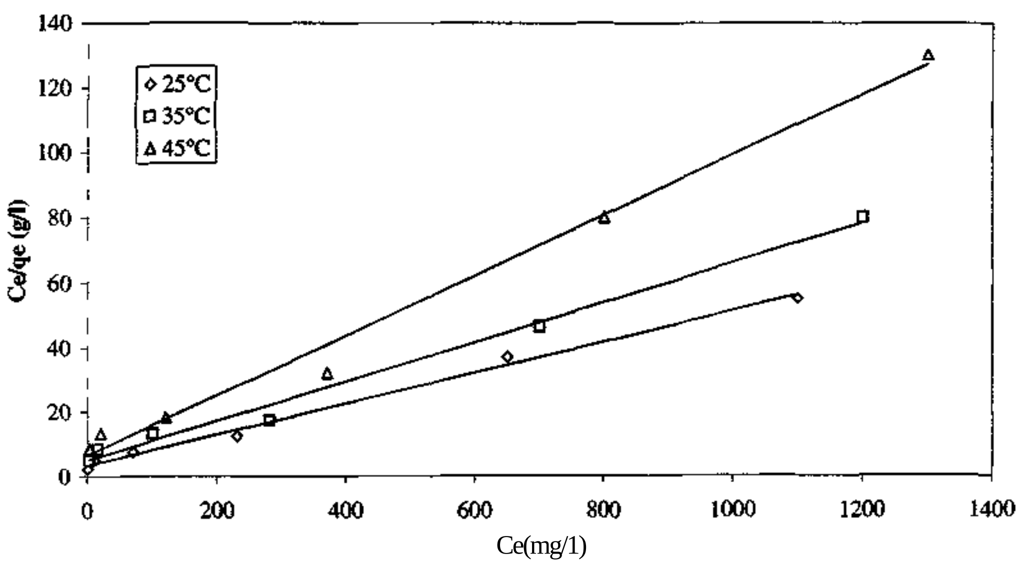

Figure 7 Langmuir plots for boron removal by adsorption at three different temperatures and pH 2

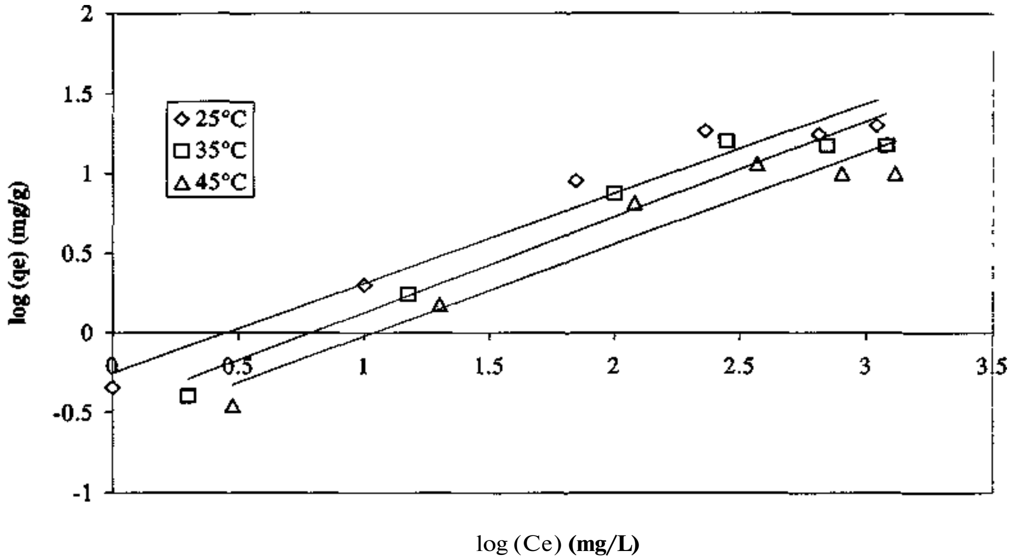

Figure 8. FreundUch plots for boron removal by adsorption at three different temperatures.

4. CONCLUSIONS

Maximum boron removal was obtained at 25°C and pH 2 for fly ash. The adsorption was found to be exothermic in nature. The Langmuir isotherm is obeyed better than the Freundlich isotherm, as is evident from the values of regression coefficients.

REFERENCES

Badruk, M., N. Kabay, M. Demircioglu, H.

Mordogan, Ipekoglu, U. 1999. *Removal of boron from wastewater of geothermal power plant by selective Ion-Exchange Resins. II. Column sorption- Elution studies,* Separation Science and Technology, No.34(15), 2981-2995.

Balkı, N., 1982. *Examining of Simav River for Boron Pollution and Investigation of Treatment Wastewater Polluted River by Adsorption,* Ph.D.Thesis, Uludağ University, Bursa, Turkey.

Banat, F.A., Al-Bashir. B., Al-Asheh, S., Hayaajneh.O., 2000. *Adsorption of phenol by bentonite,* Environmental Pollution, No. 107, 391-398.

Bayar, D., 2001. *Boron Removal From Aqueous Solution By Adsorption And Experimental Design,* M.Sc. Thesis, Osmangazi University, Chemical Engineering Department, Eskişehir, Turkey.

Demirbaş, E., Kobya, M., Öncel.S., Şencan,S.2002. *Removal of Ni(II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies,* Bioresource Technology, No: 84,291-293.

Goldberg, S., Forster,H.S., Lesch, S.M.,Heick, E.L. 1996. *Influence of anion competition on boron adsorption by clays and soils,* Soil Science, No:161(2), 99-103.

Hatcher, J.T., Bower, C.A. 1958. *Equilibria and dynamics of boron adsorption by soils,* Soil Science, No. 85(6), 319-323.

Janos, P., Buchtova, H., Ryznarova, M. 2003. Sorption of dyes from aqueous solutions onto fly ash, Water Research, No. 37,4938-4944.

Nable, R.O., Banuelos, G.S. Pauli, J.G. 1997. *Plant and Soil,* Kluwer Academic Publishers, Netherlands, 181-198.

Nadav N., 1999. *Boron removal from seawater reverse osmosis permeate utilizing selective ion exchange resin,* Desalination, No.124,131-135.

Namasivayam C, Kavitha, D. 2002 *Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste,* Dyes and Pigments, No.54,47-58.

Okay, O., Güçlü, H. Soner, E. Balkaş, T. 1985. *Boron pollution in the Simav River, Turkey and various methods of boron removal,* Water Research, No.l9(7), 857-862.

Öztürk, N., Kavak, D. 2003. *Boron removalfrom aqueous solutions by adsorption using full factorial design,* Fresenius Environmental Bulletin, No.l2(12), 1450-1456.

Recepoğlu, O., Beker, Ü. 1991. A *preliminary study on boron removal from Kizildere/Turkey geothermal waste water.* Geothermics, No.20(l/2), 83-89.

Simonnot, M.O., Castel, C, Nicolai, M., Rosin, C, Sardin, M., Jauffret, H., 1999. *Boron removal from drinking water with a boron selective resin. Is the treatment really selective?,* Water Research, No.34(l), 109-116.

Sivaraj, R., Namasivayam, C, Kadirvelu, K., 2001. *Orange peel as an adsorbent in the removal of Acid Violet 17 (acid dye) from aqueous solutions,* Waste Management, No.21,105-110.