Boron Removal from Aqueous Solution by Ion-Exchange Resin*

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ABSTRACT: Boron removal was studied using Dowex 2x8 anion exchange resin. The sorption behaviour of resin was investigated as a function of pH, contact-time, temperature, initial boron concentration and resin dosage. The maximum sorption value for boron was observed at pH 9. The equilibrium time was found to be 15 min. The sorption of boron decreased as temperature and initial boron concentration increased. This result exhibited that sorption process is exothermic. Thermodynamic parameters of the process such as free energy change, enthalpy change and entropy change were calculated. Increase in adsorbent dosage increases the removal efficiency up to optimum dosage beyond which the removal efficiency is negligible. The Langmuir isotherm was used to describe observed sorption phenomena. It was observed that the maximum adsorption capacity of 22.27 mg B/g for Dowex 2x8 was achieved at pH of 9 and 25°C. The quantitative stripping of boron from Dowex 2x8 was obtained with 0.5M H_2SO_4 and 0.5 M HCl solutions at 25°C.

1. INTRODUCTION

Boron is an important material for Turkish economy. Turkey possesses over 60 percent of the world's boron reserves. The known boron reserves in Turkey are located in four main districts, namely Emet, Bigadiç, Kırka and Mustafakemalpaşa (Okay, 1985; Şener, 1988).

Boron minerals occuring İn nature in more than 200 compounds are known variously as tincal, colemanite, ulexite, and kernit, depending on the ratios of calcium, sodium, magnesium, etc., and water content present in the mineral (Şahin, 2002). Boron compounds are used in a wide range of industrial applications. The production of boron compounds has increased in recent years, due to increasing demands for these compounds İn nuclear technology, the production of heat-resistant materials such as refractories and ceramics; high quality steel, heat-resistant polymers, catalysts, leather, carpets, cosmetics and photographic chemicals, borosilicate glass and agricultural products (Morales et. al., 2000).

In underground waters and streams boron might be found a lot especially waters with soda. Some thermal waters and volcanic sources bear boron abundantly. In general volcanic gases and precipitates are rich in boron content. Between 4-36 mg/L boron can be traced in such waters. Boron in seawater (4.45 mg/L in average) is fed by rivers and volcanoes, clay minerals and biological activities cause its precipitation (Badruk, 1998).

Boron is biologically an essential nutrient for many plants but high boron concentrations (typical! y>0.75 mg/L) in irrigation water cause toxic effects (e.g., for oranges, lemons and apples) whereas low abundances

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(<0.25 mg/L) require boron addition to maximize crop yields. High boron levels in drinking water can be also toxic to humans (Vengosh et. al., 1999).

There are several methods suggested for boron removal from aqueous solutions. The main processes that have been studied are: (1) precipitation-coagulation (Badruk, 1998) (2) adsorption on oxides (Okay et.al., 1985) (3) adsorption on active carbon or cellulose (Öztürk and Kavak, 2003) (4) ion exchange (Recepoğlu and Beker, 1991; Jyo et. al., 2001; Simonnot et. ai., 2000) (5) solvent extraction (Hoşgören, 1997) (6) membran filtration (Pastor, 2001). Among these methods, the ion exchange process is most extensively used.

In this study, batch sorption tests were performed using Dowex 2x8 resin for boron removal from aqueous solution. The sorption behaviour of resin was investigated as a function of pH, contact time temperature, initial boron concentration and resin dosage.

2. EXPERIMENTAL WORK

2. I.Materials

A strong basic anion exchange resin, Dowex 2x8, was supplied from Supelco. The resin particle size is between 100 and 200 mesh. Moisture content of resin is 37%. The functional group in resin is benzyl-dimethylethanolamine.The resin was washed several times using distilled water then immersed in 2N NaOH solution for 48 h and washed again distilled water. Finally, the resin was dried at 40°C under vacuum for 24 h before being used.

Boric acid solutions were prepared by using the analytical grade Merc product.

2.2. Batch Sorption of Boron

A fixed amount of dry resin (lg) and 50 mL of H3BO3 solution which contain 600 mg B/L were placed in capped polyethylene bottle and shaken at 130 rpm using a temperature controlled water bath (NUVE) with shaker (MEMMERT). The boron concentration in the supernatant was determined spectrophotometrically (HACH DR-2000) using Carmine Method.

In order to investigate pH effects on boron sorption, pH of the H3BO3 solutions (600 mg B/L) were adjusted to different values (3, 5, 7, 9 and 10) by using dilute NaOH or HCl solutions. pH was measured using a pH-meter (Consort P903). Kinetic tests were carried out by contacting 10 g resin with 500 mL H3BO3 (600 mg B/L) solution at constant temperature and optimum pH in water bath with shaker. The concentration of boron in supernatant was determined at different time intervals. Kinetic tests were carried out at three different temperatures (25, 35 and 45°C). For adsorption isotherm study, lg of resin was contacted with 50 mL of H1BO3 solution at concentrations of 100, 250, 600, 1000 and 1500 mg B/L at 25°C and optimum pH for 24 h with continuous shaking. Sorption of 600 mg B/L of H3BO3 solution by different resin doses (0.25-3 g/50mL) was carried out at the optimum pH. The adsorbed boron was eluted using either HCl or H2SO4 solution (25 mL) at 0.5 M concentration. The elution experiment was carried out at 25°C, for 2h mixing in a shaker.

3. RESULTS AND DISCUSSION

3.1.EffectofpH

The effect of pH on the sorption of boron is shown Fig. 1. The most effective pH value was 9. The dominant aqueous species of boron are undissociated boric acid, B(OH)3° and the borate anion, $B(OH)4^{-}$, whose relative abundances are a sensitive function of pH. While at low pH B(OH)i° predominates, at high pH (>8-9) $B(OH)_4$ is the primary anion (Barth, 2000; Badruk, 1999). Due to Off ions on the resin was exchanged $B(OH)_4$ ions in solution maximum boron removal was obtained atpH9.

3.2. Effect of Contact Time

The effect of contact time on boron removal is shown in Fig.2. Equilibrium was obtained by 15 min of sorption time.

3.3. Effect of Temperature

The effect of temperature on the boron removal by Dowex 2x8 was examined at 25, 35 and 45°C. The results are presented in Fig.3. The sorption of boron decreased as temperature increased. This result exhibited that process is exothermic. Thermodynamic parameters of the process were calculated and given in Table 1. The changes in the standard free energy, enthalpy and entropy of the sorption processes were calculated using the following equations (Khattri and Singh, 1999):

$$\Delta G^\circ = -RT \ln K \quad (1)$$

$$\Delta H^0 = R[T_2T_1/(T_2-T_1)] \ln (K''/K') \quad (2)$$

$$\Delta S^0 = (\Delta H^0 - \Delta G^0) / T \quad (3)$$

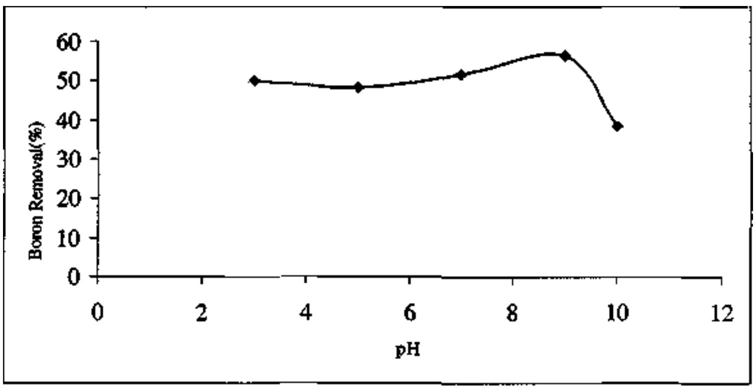
Where R is the gas constant and K, IC and K" are the equilibrium constants at temperatures of T, Ti and T_2, respectively. The equilibrium constant can be determined as:

$$K = \frac{\text{concentration of boron present on the resin}}{\text{remaining concentration of boron in solution}} \quad (4)$$

Table 1. Thermodynamic parameters of process

Temp. (°C)	AG^0 (kJ/mol)	AH^0 (kJ/mol)	AS^0 (j/K mol)
25	-0.492	-46.9	-155.6
35	1.026	-22.578	-76.6
45	1.833		

The negative values of the enthalpy changes confirm the sorption process is exothermic and the negative values of the entropy changes suggest that the system exhibits random behavior. The negative value of AG^0 indicates spontaneous nature of boron sorption at 25 °C. Positive AG^0 values were observed at 35 and 45 °C, indicating that spontaneity is not favoured at high temperatures.



Figurel. Effect of pH on the boron removal by Dowex 2x8 at 25°C

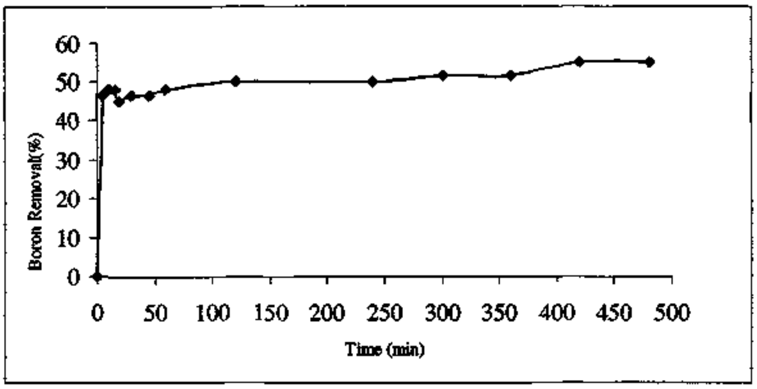


Figure 2. Effect of contact time on boron removal by Dowex 2x8 at pH 9

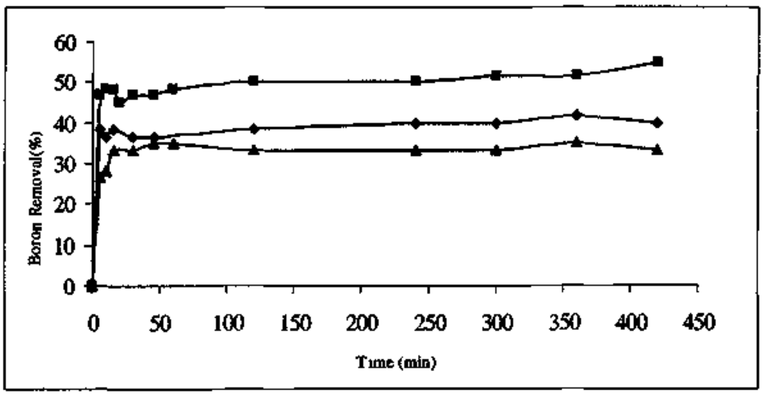


Figure3. Effect of temperature on boron removal by Dowex 2x8 (• 25°C, ^ " C , A45°C) at pH 9

3.4. Effect of Concentration

The Langmuir equation (5) was applied for the sorption equilibrium of resin (Walter and Weber, 1972)

$$C_e/q_e = 1/(Q_0b) + C_e/Q_0 \quad (5)$$

Where C_e is the equilibrium concentration (mg/L), q_e is the amount of boron adsorbed at equilibrium (mg/g), Qo and b are Langmuir constants related to sorption capacity and energy of sorption, respectively. The lineer plots Ce/q_e versus C_e (Fig.4) show that adsorption obeys the Langmuir isotherm model. Q_0 and b were determined from Langmuir plots and found to be 22.27 mg B/g resin and 0.008 L/mg.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless seperation factor, RL defined by

$$R_L=1/(1+bC_0) \quad (6)$$

where b is the langmuir constant and C_0 is the initial boron concentration (mg/L), RL values indicate the type of isotherm. An R_L value between 0 and 1 indicates favorable adsorption. The RL values were found to be between 0 and 1 for boron concentrations of 100, 250, 600, 1000, 1500 mg/L (Table 2)

Table 2. Langmuir constants

Boron conc. (mg/L)	Qo (mg/g)	b (L/mg)	RL
100	22.27	0.008	0.55
250			0.33
600			0.17
1000			0.11
1500			0.07

3.5. Effect of Resin Dosage

Fig. 5 shows the removal of boron as a function of resin dosage. Increase in resin dosage increased the percent removal of boron because of increase in number of exchangeable ions on resin.

3.6. Batch Elution of Boron

In order to obtain elution efficiency, either H2SO4 or HCl solutions at 0.5 M concentrations were used as eluants for stopping of boron from Dowex 2x8. The results are given in Table 3.

Table 3. Batch stripping of boron from Dowex 2x8

Stripping agent	Stripping (%)
H_2SO_4 (0.5 M)	88.3
HCl (0.5 M)	100

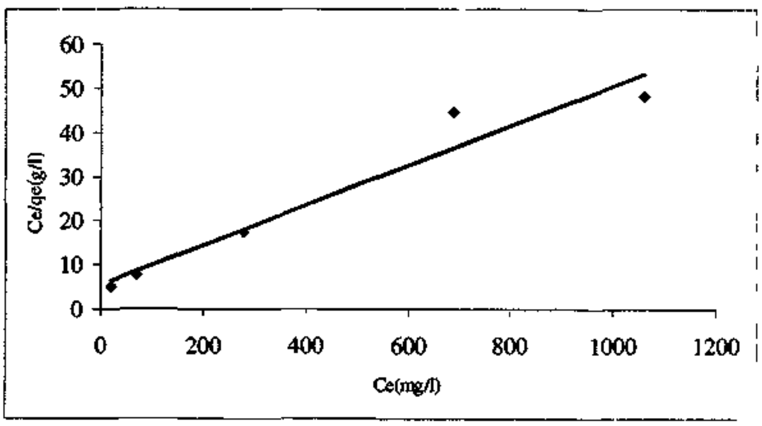


Figure 4. Langmuir plots for the boron removal by Dowex 2x8 at 25°C and pH 9

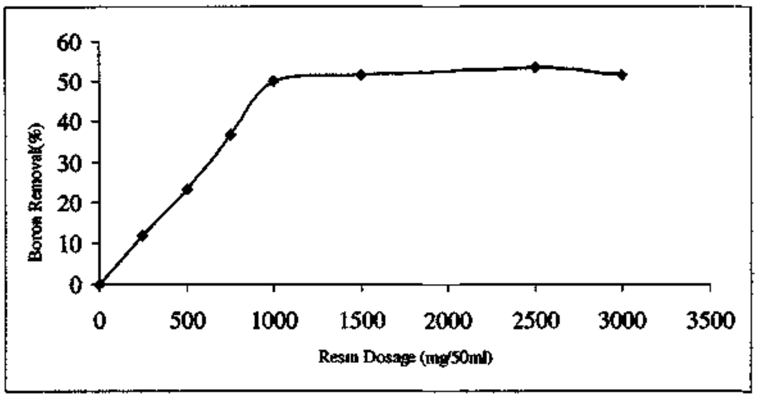


Figure 5. Effect of resin dosage on boron removal by Dowex 2x8 at 25°C and pH 9

4. CONCLUSIONS

The use of the Dowex 2x8 for boron removal from aqueous solutions was investigated. The experimental results indicated that the most effective pH value was 9. The percent removal of boron from aqueous solution increased with time, with equilibrium being achieved within 15 min. at 25°C and a pH value of 9. The maximum boron removal at pH 9 was 55%. The empirical Langmuir isotherm was found to adequately describe the equilibrium relation between the resin and liquid phases of the ion exchange process. Elution studies showed that the boron can be easily eluted by HCl indicating that the resin can be reused but special efforts have to be made in the seperation of the eluted boron from the acid eluants.

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