Removal of boron from Kizildere-Denizli geothermal brines using ion-exchange method

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Abstract

The first geothermal power plant of 20 MW in Turkey was installed in Denizli-Kizildere geothermal field located in the Western Anatolia. The water disposed of from the power plant is about 800-1000 tons/h, and its boron content of approximately 30 mg/dm^3 is on the high side to use for irrigation in agricultural areas. It is particularly detrimental to citrus fruits. In order to be able to utilize this brine wastewater for irrigation, the maximum content of boron need to be reduced to less than 1 mg/dm^3. This paper describes research work, investigates optimum conditions for utilizing ion-exchange methods to remove boron from Denizli-Kizildere Geothermal wastewater.

Keywords: *boron removal, ion exchange, geothermal brine, boron*

1 General information

1.1 Introduction

Borates are defined as salts or esters of boric acid, a compound containing the radical B_2O_3 (Bates, 1987). Boron is found in the earth's crust at an average concentration of about 10 ppm (Smith, 1958). Boron is not found free in nature but is always bound to oxygen (Baudis and Fichte). Boric acid borate buffer mixtures serve as pH standard and occur in natural aqueous systems. From the results it is clear that, in addition to the mononuclear boric acid and orthoboric ion to be trigonal ($B(OH)^3$) and ($B(OH)^{-4}$) species, a number of polyborate ions are also formed (Mesmer et al., 1972).

$$B(OH)^3 + H_2O \rightarrow B(OH)^{-4} + H^{+1} \text{(Xiao et al., 1991)} \quad (1)$$

The occurrence of boron varies depending on the pH of the water. In acidic waters (pH<6) orthoboric acid is dominant. Tetra-pentha-hexa and other polyborates are common in neutral and alkaline natural waters. Dissolution of alkaline metallic borates in aqueous media is faster than the others and dissolution rate of borates in general increases with increasing temperature. Therefore in hydrothermal media boron migrates quickly. Boric acid dissolves faster in hot waters than cold waters. There are two kinds of boron species, $B(OH)^3$ and $B(OH)^{-4}$, in a diluted aqueous solution. The predominant boron species (above 90%) in the brine (pH 7.7) is neutral $B(OH)_3$ according to above equation. Therefore, the following surface chelation mechanism is suggested in literature (Ooi et al., 1996) on boron adsorption

$$X\text{-}OH + B(OH)^3 \rightarrow X\text{-}O\text{-} B(OH)^2 + H_2O \quad (2)$$

1.2 Toxicology of boron

Boron is needed in relatively small amounts, however and it becomes toxic, if present in amounts appreciably greater than needed. For some crops 1 to 2 mg/l may be toxic, if 0.2 mg/l boron in water is essential (Ayers, 1994). Experimental laboratory data indicate that this compound is only slightly toxic for animals and humans.

1.3 Ion exchange resins

Ion exchange process is becoming more extensively used in water and wastewater treatment (Dorfner, 1991). Ion exchange resins are polymers carrying fixed functional groups. Functional groups are charged acidic or basic or chelating group attaching to the polymer matrix. The charge of the group is normally compensated by an exchangeable ion. All cyclic ion exchange process includes sorption, elution and regeneration stages. Elution and regeneration can be integrated in one step. Washing steps (if needed) can be incomplete (Zagarodni, 1997).

2 Experiments

2.1 Materials

The characteristics of the Kizildere geothermal brine are summarized in Table 1. All resins were dried at 40°C under vacuum prior to their use. Boric acid solutions were prepared from an analytical grade H_3BO_3 and deionized water obtained from a water purification system. All other materials were reagent grade and used as received.

Table 1: The properties of Kizildere geothermal brine.

pH	: 9.30	Total hardness (AS°)	: 0.06
Specific Conductivity (µmho/cm)	: 4120	Temporary Hardness(AS°)	: 0.06
Evaporation Residual (180°C)(mg/dm^3)	: 4108	Permanent Hardness (AS°)	: 0
K^+ (mg/dm^3)	: 145	HCO_3^- (mg/ dm^3)	: 1037
Na^+ (mg/dm^3)	: 1300	CO_3^{2-} (mg/ dm^3)	: 780
NH_4^+ (mg/ dm^3)	: 3.5	SO_4^{2-} (mg/ dm^3)	: 695
Ca^{2+}(mg/ dm^3)	: 0.39	Cl^- (mg/ dm^3)	: 134
Mg^{2+} (mg/ dm^3)	: 0.08	I^- (mg/ dm^3)	: 4.6
Fe (total) (mg/ dm^3)	: <0.05	I^- (mg/ dm^3)	: 4.6
As (total)(mg/ dm^3)	: 0.58	F^- (mg/ dm^3)	: 15
B(total)(mg/ dm^3)	: 30.2	NO_2^- (mg/ dm^3)	: < 0.01
Li^+ (mg/ dm^3)	: 4.8	NO_3^- (mg/ dm^3)	: < 1
Al^{3+}(mg/ dm^3)	: 0.71	PO_4^{3-} (mg/ dm^3)	: < 0.1
SiO_2 (mg/ dm^3)	: 415	Br^- (mg/ dm^3)	: 0.53

2.2 Batch sorption

In the experiment 0.25 g of different resins was contacted with 50 cm^3 of 0.01 M H_3BO_3 solution and Kizildere geothermal brine (pH 9) for 48 h at 30°C with continuous shaking. The supernatant (2 cm^3) was taken and analyzed spectrophotometrically using a Carmen method.

2.2.1 Effect of Ca(II) and Na(I) ions on boron sorption

The effect of Na(I) and Ca(II) ions on sorption behaviour of boron has been studied using 0.00125 M $CaCl_2$, 0.0025 M $CaCl_2$, 0.00375 M $CaCl_2$, 0.0075 M $CaCl_2$, 0.5 M $CaCl_2$, 1 M $CaCl_2$, 0.5 M NaCl, 1 M NaCl and 2 M NaCl. For this 0.25 g Diaion CRB 02 Glucamine resin (1-0.250 mm) was contacted with 50 cm^3 of 0.01 M H_3BO_3 solution containing Ca(II) and Na(I) ions at various concentrations. The sorption experiments were performed at 30°C with a continuous shaking for 48 h.

2.3 Column sorption

The chelating resin Diaion CRB 02 was used in column sorption of boron. The columns employed were made of glass of internal diameter ~0.7 cm. Each column was packed with 3.0 cm^3 wet-settled volume of resin. The solution of 0.01 M H_3BO_3 solution and Kizildere geothermal brine was delivered as downflow to the column using a peristaltic pump (Atto SJ-1211 H Model) capable of delivering various flow rates of SV (space velocity: bed volume/h). The breakthrough curves were obtained by analysis of successive 6 cm^3 fractions of the effluent. The fractions were collected using a fraction collector (Advantec SF 2120 Model). The column elution profiles were obtained by the column elution of the resin loaded with boron ions using 1 M HCl for 0.01 M H_3BO_3 solution and 0.25 M H_2SO_4 for Kizildere geothermal brine at SV $5h^{-1}$, collecting 3 cm^3 fractions of effluent.

3 Results and discussion

3.1 Batchwise extraction of boron by different resins

For comparison, various chelating ion exchange resins have been used for batch sorption of boron. The results are presented in Table 2. As shown in Table 2, among the resins tested, Diaion CRB 02, RGB gave the most promising results for boron removal from H_3BO_3 solution and Kizildere geothermal brine. The resins Diaion CRB 02 gave the largest removal (49% for 0.01 M H_3BO_3 and 98% for Kizildere geothermal brine) for boron in the geothermal brine.

3.1.1 Effect of Ca(II) and Na(I) ions on boron sorption

Kizildere geothermal brine contains other ionic impurities such as Na, Ca, Si, K. The effect of Ca(II) and Na(I) ions on sorption of boron was studied using the resins Diaion CRB 02. The results are summarized in Table 3.

3.2 Columnar sorption of boron from 0.01 M H_3BO_3 solution

3.2.1 Effect of SV

Columnar sorption of boron from 0.01 M H_3BO_3 solution was studied at SV 5,10,15 h^{-1} using Diaion CRB 02 (Figure 1). The loaded columns with boron were eluted with 1 M HCl at SV 5 h^{-1} (Figure 2).

Columnar sorption of boron from Kizildere geothermal brine was studied at SV 15 and 25 h^{-1} using Diaion CRB 02 (Figure 3). Breakthrough capacity increased some extent with a decrease in SV. The loaded columns with boron were eluted with 0.25 M H_2SO_4 at SV $5h^{-1}$ (Figure 4).

Table 2: Boron removal by various ion exchange resins from 0.01 M H_3BO_3 solution and Kizildere geothermal brine by various resins.

RESIN	Removal of Boron			
	(%)[1)]	mgB/g-resin[1)]	(%)[2)]	mgB/g-resin[2)]
Diaion CRB 02	49.3	9.68	98.1	6.69
RGB	42.3	8.42	71.6	4.88
Purolite S 108	28.4	5.58	93.6	6.38
Diaion C 200	6.2	1.22	4.2	0.29
Purolite S 940 (0.5-0.355	5.5	1.08	5.5	0.38
Dowex 50W	4.9	0.96	0.0	0.0
Purolite A 103	4.9	0.96	17.3	1.18
RSPO	4.0	0.78	0.0	0.0
Purolite C 106	3.9	0.76	0.0	0.0
Purolite A 500	3.6	0.71	2.2	0.15
Purolite CT 175(0.6-	2.7	0.52	3.9	0.27
Purolite C 150(0.6-0.355	2.3	0.45	3.1	0.21
Diphonix(100-200 mesh)	1.9	0.37	6.6	0.45

1): For 0.01 M H_3BO_3, 2): For Kizildere geothermal brine; Sorption : 0.25 g resin, 50 cm^3 solution, 30°C, 48 h

Table 3: Effect of Ca(II) and Na(I) ions boron sorption by Diaion CRB 02(1-0.25 mm).

Solution	Removal (%)	mgB/g-R[1)]
0.00125 M $CaCl_2$ in 0.01 M H_3BO_3	40.9	7.74
0.0025 M $CaCl_2$ in 0.01 M H_3BO_3	43.1	7.95
0.00375 M $CaCl_2$ in 0.01 M H_3BO_3	42.1	8.54
0.0075 M $CaCl_2$ in 0.01 M H_3BO_3	46.9	8.59
0.5 M $CaCl_2$ in 0.01 M H_3BO_3	42.6	8.22
1 M $CaCl_2$ in 0.01 M H_3BO_3	42.6	8.20
0.5 M NaCl in 0.01 M H_3BO_3	42.4	7.67
1 M NaCl in 0.01 M H_3BO_3	41.2	7.39
2 M NaCl in 0.01 M H_3BO_3	42.5	8.09

R[1)]: Resin, Sorption: 0.25 g resin, 50 cm^3 0.01 M H_3BO_3, 30°,48 h

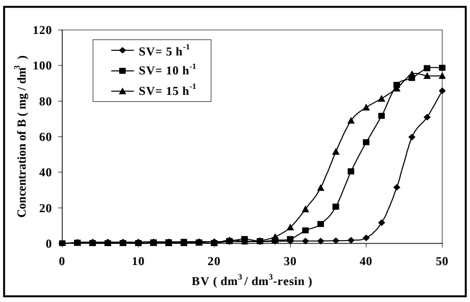


Figure 1: Effect of SV on breakthrough volume of Diaion CRB 02.

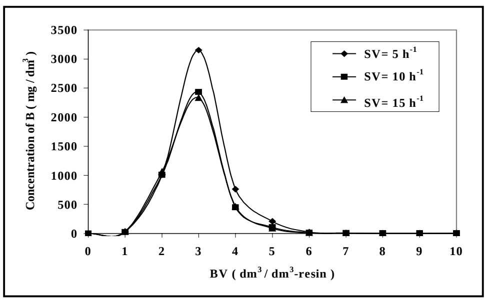
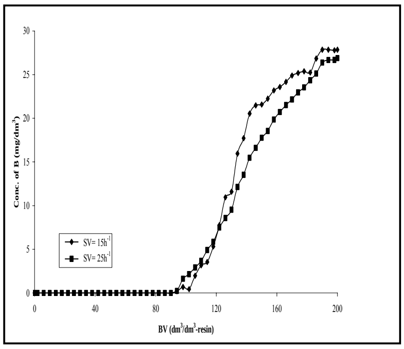


Figure 2: Elution profiles.



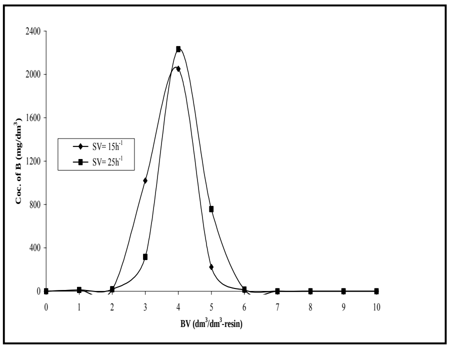
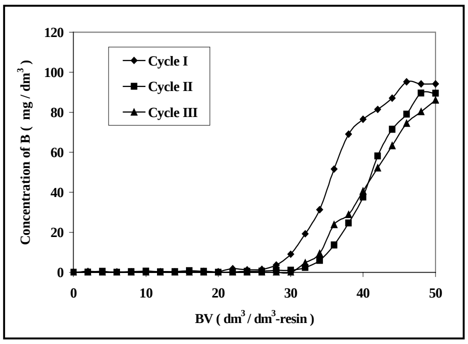


Figure 3: Effect of SV on column sorption of boron from Kizildere geothermal brine.

Figure 4: Elution curves of boron.

3.2.2 Recycle use of diaion CRB 02

Diaion CRB 02 was used to study the recycle use of resin for boron removal from 0.01 M H_3BO_3 solution (Figures 5 and 6). During the third cycle, the breakthrough point remained almost at the same position.



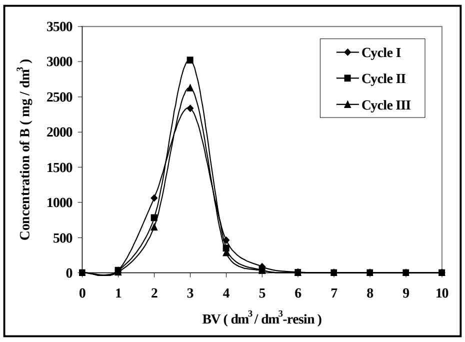
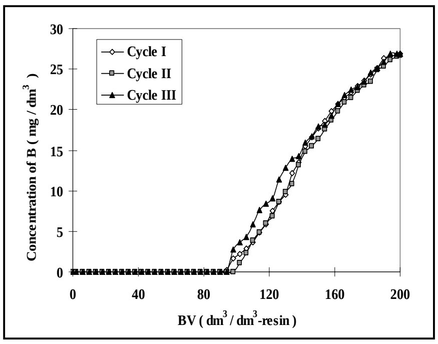


Figure 5: Recycle use of Diaion CRB 02 for boron removal.

Figure 6: Elution profiles.

Diaion CRB 02 was used to study recycle use of resin for boron removal from Kizildere geothermal brine at SV 25 h^{-1} (Figures 7 and 8).



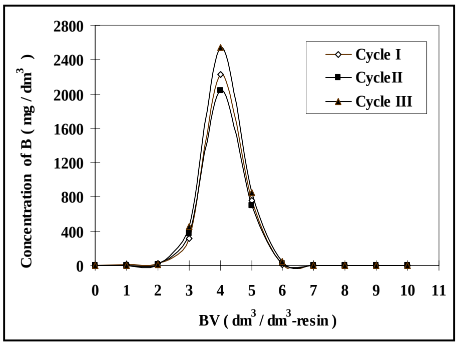


Figure 7: Recycle use of Diaion CRB 02 for boron removal from Kizildere brine.

Figure 8: Elution profiles of boron.

4 Conclusions and recommendations

The geothermal brine from the Kizildere geothermal area contains approximately 30 mgB/dm^3. In order to be able to utilize this brine for irrigation, the maximum content of boron needs to be reduced to below 1 mg/dm^3. N-Glucamine type resin Diaion CRB 02 was found to be the most promising as a sorbent for boron removal from Kizildere geothermal brine.

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