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Removal of Boron from Wastewater of Geothermal Power Plant by Selective Ion-Exchange Resins. II. Column Sorption–Elution Studies

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ABSTRACT

Column sorption-elution studies for boron removal were performed using *N*-glucamine-type chelating ion-exchange resins Diaion CRB 02 Purolite S 108. The breakthrough curves were obtained as a function of resin type and feed flow rate. Boron was effectively removed from the wastewater of Kizildere, Turkey, geothermal power plant by passing it through the resins Diaion CRB 02 and Purolite S 108 at a space velocity of 25 bed volumes per hour. The boron on the resins was quantitatively eluted with 0.25 M H_2SO_4 solution. The resin Diaion CRB 02 was used to study the recycle use of resin for boron removal from the wastewater of Kizildere geothermal power plant. The capacity of Diaion CRB 02 remained constant after three sorption–elution–washing–regeneration cycles.

Key Words. Boron; Ion-exchange; Chelating resin; Water pollution; Water treatment; Geothermal wastewater

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INTRODUCTION

Boron contamination of natural waters is a concern around the world. Boron is needed for plant growth but in relatively small amounts. However, if it is present in amounts larger than required, it becomes toxic (1).

There are several physicochemical treatment processes typically used to remove boron from water and wastewater. These are adsorption with inorganic adsorbents (2–5), ion exchange (5–18), solvent extraction (19), and a combination of adsorption and solvent extraction (20), membrane processes (21), and ultrafiltration (22).

Chelating resins containing functional groups in which hydroxyl groups are in the *cis*-position show high selectivity for boron removal through the formation of borate–diol complexes (5–17). The wastewater disposed of from the Kizildere, Turkey, geothermal power plant has a flow rate of 1500 tons/h and contains boron at a concentration of approximately 30 mg/dm^3. The concentration of boron in this wastewater is very high for it to be used for irrigation in agriculture. The results of preliminary tests on boron removal from wastewater of the Kizildere geothermal power plant using the ion-exchange resin Amberlite IRA 743 were described by Recepoglu et al. (23). The regeneration conditions for Amberlite IRA 743 were recently reported by Beker et al. (24).

The chelating resins Diaion CRB 01 and CRB 02 were developed to remove boron selectively from solutions which also contain large quantities of other ions (25). It is thought that the oxygen atom of the hydroxyl group in the resin interacts with boron atoms to form a chelate compound, and so it can selectively adsorb the borate ion. These resins were used for the manufacture of high purity magnesia from brine on an industrial scale (25). The purity of the magnesia affects the fire resistance of bricks, and a need has emerged in recent years to remove boron from the brine order to increase this purity still further. It has been reported that the boron concentration in brine can be reduced to a level of about 1 mg B/dm^3, which is the permitted level (25).

Boron isotopic fractionation was recently carried out using boron-specific *N*-methyl glucamine-type resins Diaion CRB 02 and Amberlite IRA 743 by the method of Oi et al. (26).

In our previous study we gave the results of batch sorption of boron by *N*-glucamine-type resins Diaion CRB 02 and Purolite S 108 (27). We reported that boron in wastewater of the Kizildere geothermal power plant was effectively removed by both Diaion CRB 02 and Purolite S 108 resins (27). The present study describes the column performances of these resins for boron removal from the wastewater of the Kizildere geothermal power plant.

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EXPERIMENTAL

Chelating Ion-Exchange Resins

N-Glucamine type resin Diaion CRB 02 was kindly supplied by Mitsubishi Chemical Co., Japan, and Purolite S 108 by Purolite International Ltd., UK. The properties and structures of these resins are reported in Tables 1 and 2, respectively.

Wastewater of Kizildere-Turkey Geothermal Power Plant

The wastewater of the Kizildere geothermal field (pH 9.30–9.50) is disposed of from the power plant at a flow rate of 1500 tons per hour and contains boron at a concentration of approximately 30 mg/dm^3. The concentrations of other ionic species in the wastewater are: K, 145; Na, 1300; NH_4, 3.5; Ca, 0.39; Mg, 0.08; Fe (total), $<$0.05; As (total), 0.58; Li, 4.8; Al, 0.71; SiO_2, 415; Cl, 134; I, 4.6; F, 15; Br, 0.53; NO_2, 0.01; NO_3, $<$1; HCO_3, 1037; CO_3, 780; SO_4, 695 mg/dm^3.

TABLE 1
Characteristics and Structure of Diaion CRB 02

Constitutional type	Highly porous type
Ion form as shipped	OH form
Shipping density (g/dm^3) (approx.)	635
Moisture content (%)	50–60
Exchange capacity	Acid 0.6 meq/cm^3 (min.)
Screen grading	1180–300 μm (through 300 μm, max. 1%)
Effective size (mm)	0.35–0.55
Uniformity coefficient (max.)	1.6
Operating temperature (°C) (max.)	100°C max. (OH form)
Effective pH range	6–10
Specific surface area (m^2/g)	27
Structure:	

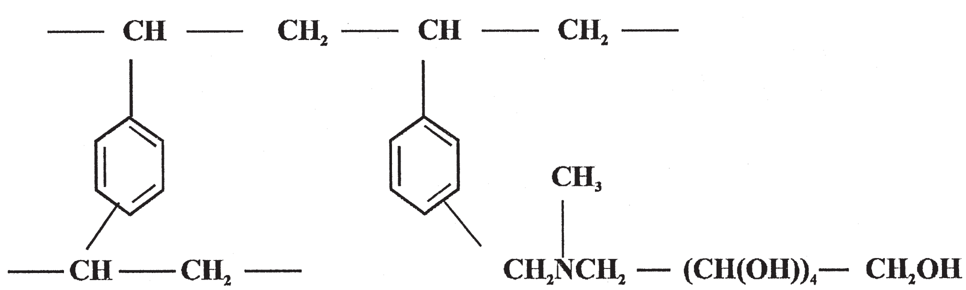
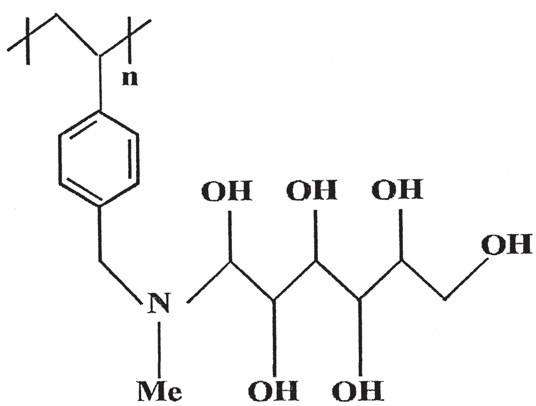


TABLE 2
Characteristics and Structure of Purolite S 108

Polymer matrix structure	Macroporous styrene–divinylbenzene
Physical form and appearance	Opaque cream spheres
Whole bead count	>95%
Functional group	Complex amino
Ionic form (as shipped)	Cl
Shipping weight, g/dm^3 (lb/ft)	650 (41)
Screen size range:	
British Standard Screen	16–52 mesh, wet
US Standard Screen	18–50 mesh, wet
Moisture retention, Cl^- form	52–58%
Reversible swelling (Fe → Cl)	<6%
Specific gravity, moist Cl^- form	1.06
Boron-exchange capacity, Cl^- form (wet, volumetric)	0.35 eq/L
Maximum operating temperature, Cl^- borate forms	60°C (140°F)
Operating pH range	1–13
Specific surface area (m^2/g)	17.1
Structure:	



Column Sorption–Elution of Boron

The resins in the 0.355–0.500 mm particle size range were selected for the column tests. The resin beads were immersed in deionized water for 24 hours before being packed into the column. The columns were made of glass and had an internal diameter of 0.7 cm. Each column was packed with a 3.0-cm^3 wet-settled volume of resin. A solution of 0.01 M H_3BO_3 (pH 5.6) solution was delivered by downflow to the column using a peristaltic pump (Atto SJ-1211 H Model) capable of delivering flow rates of 5, 10, and 15 bed volumes per hour. 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 collecting 3 cm^3 fractions of the column elutions of the resin loaded with boron using 1 M HCl at a space velocity (SV: bed volumes per hour) of 5 h^{-1}.

The recycle tests were conducted using the resin Diaion CRB 02 (3 cm^3) and by passing 0.01 M H_3BO_3 solution at SV 15 h^{-1}. After the elution step performed with 1 M HCl solution at SV 5 h^{-1} and the washing step with deionized water, the resins were regenerated using 2 M NaOH and then washed with deionized water before sending them to the following cycle.

The column sorption studies for boron removal from the wastewater of the Kizildere geothermal power plant were carried out by using both Diaion CRB 02 and Purolite S 108 resins (3 cm^3) at a 0.500–0.710 mm particle size range. The wastewater (600 cm^3) was passed through the column at SV 25 h^{-1}. The boron-loaded resins were eluted with 0.25 M H_2SO_4 at SV 5 h^{-1}. The recycle use of Diaion CRB 02 was also tested by using wastewater obtained from the Kizildere geothermal power plant.

The analysis of boron in the solution was carried out spectrophotometrically using the Carmine Method.

RESULTS AND DISCUSSION

Column Removal of Boron from Boric Acid Solution

In our previous study it was reported that *N*-glucamine-type resins Diaion CRB 02 and Purolite S 108 could be effectively used for boron removal from boric acid solution (27). Boron removal by Diaion CRB 02 increased versus an increase in pH. Boron uptake almost leveled off between pH 5–6. A similar pH dependency was observed with the resin Purolite S 108 (27). The results of the preliminary column tests with boric acid solution showed that the resin Diaion CRB 02 was promising for boron removal from wastewater of the Kizildere geothermal power plant (27). Therefore, further column tests were conducted on the removal of boron by selective chelating resins Diaion CRB 02 and Purolite S 108. First, tests with 0.01 M boric acid solution (pH 5.6) were performed with these resins in the 0.355–0.500 mm particle diameter range. Figure 1 shows the breakthrough curves of boron obtained at SV 10 h^{-1}. Boron concentration in the effluent was very low up to 30 bed volumes (BV) for Diaion CRB 02 and up to 20 BV for Purolite S108. Then the concentration of boron increased gradually. The resin Diaion CRB 02 was exhausted at about 50 BV while Purolite S108 was exhausted at 30 BV. The breakthrough and total capacity values of the resins are summarized in Table

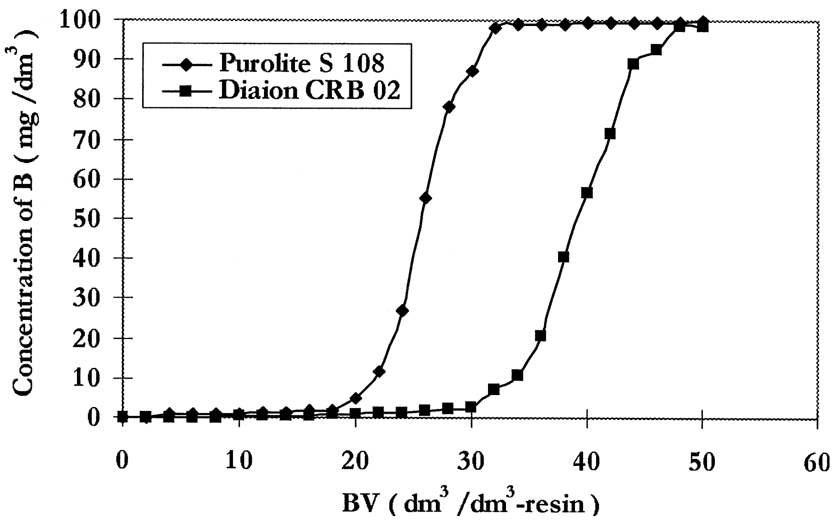


FIG. 1 Breakthrough curves of boron.

3. The elution profiles are given in Fig. 2. Boron loaded on the resins Diaion CRB 02 and Purolite S108 was quantitatively eluted with 1 M HCl solution with elution efficiencies of about 100 and 86%, respectively. The boron concentration in the eluate reached 1.3 g B/dm^3 for resin Purolite S 108. This value is 13 times higher than that of the boron concentration in the feed solution; the concentration value for Diaion CRB 02 is 24 times higher with a boron concentration of 2.4 g B/dm^3.

Resin Diaion CRB 02 was used to study the effect of SV (space velocity) on breakthrough capacity and recycle use of resin for boron removal. The tests were conducted by passing 0.01 M H_3BO_3 solution through the column (downflow) at SV 5, 10, and 15 h^{-1}. As shown in Fig. 3, the breakthrough point shifted to a larger value with a decrease in SV. The loaded resins were

TABLE 3
Column Performances of Diaion CRB 02 and Purolite S 108 for Boron Removal from 0.1 M Boric Acid Solution

Resin	Breakthrough capacity (mg B/cm^3-resin)	Total capacity (mg B/cm^3-resin)	Elution (%)
Diaion CRB 02	3.13	4.15	100.0
Purolite S 108	2.20	2.73	85.6

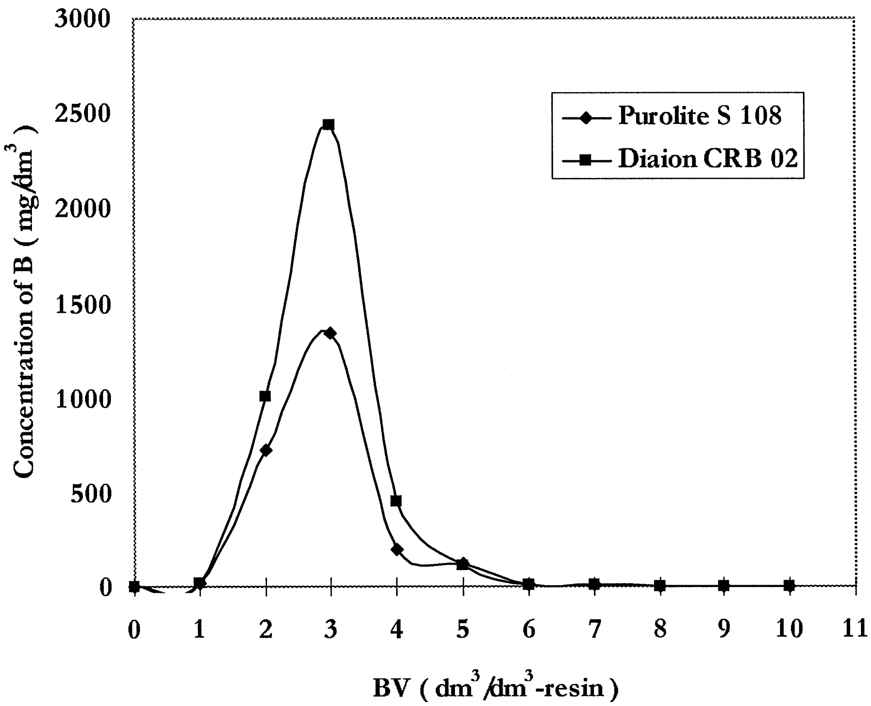


FIG. 2 Elution profiles of boron.

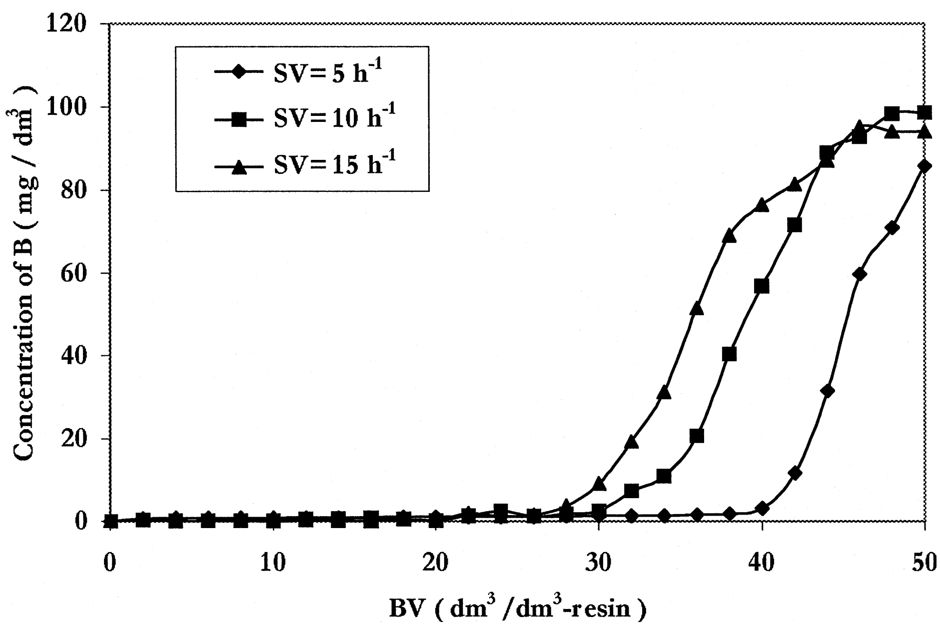


FIG. 3 Effect of SV on breakthrough capacity of Diaion CRB 02.

quantitatively eluted with 1 M HCl at SV 5 h^{-1}. The resulting elution profiles are shown in Fig. 4. Recycle use of Diaion CRB 02 was studied at SV 15 h^{-1} by the use of three sorption–elution–washing–regeneration–washing cycles. The resulting breakthrough curves are given in Fig. 5. Elution profiles of each cycle are exhibited in Fig. 6. The breakthrough capacity of the resin increased to some extent during the second and third cycles. This could be due to activation of functional sites on the resin by reconditioning with 2 M NaOH during the regeneration step. On the other hand, total capacity values remained almost the same after three sorption–elution–regeneration cycles.

Column Removal of Boron from Wastewater of Geothermal Power Plant

According to our previous report, resin Diaion CRB 02 showed good performance for column removal of boron from boric acid solution containing 30 mg B/dm^3 at pH 5.6 (27). In the present study the resins Diaion CRB 02 and Purolite S 108 were used for column removal of boron from wastewater of the Kizildere geothermal power plant. As was summarized in the Experimental section, the wastewater contains other inorganic species such as Na, Ca, K, SiO_2, HCO_3, CO_3, etc. Figure 7 shows the breakthrough curves of boron obtained by using Diaion CRB 02 and Purolite S 108. Both resins exhibited a selective removal of boron from wastewater containing various inorganic species. The column capacity values of the resins are given in

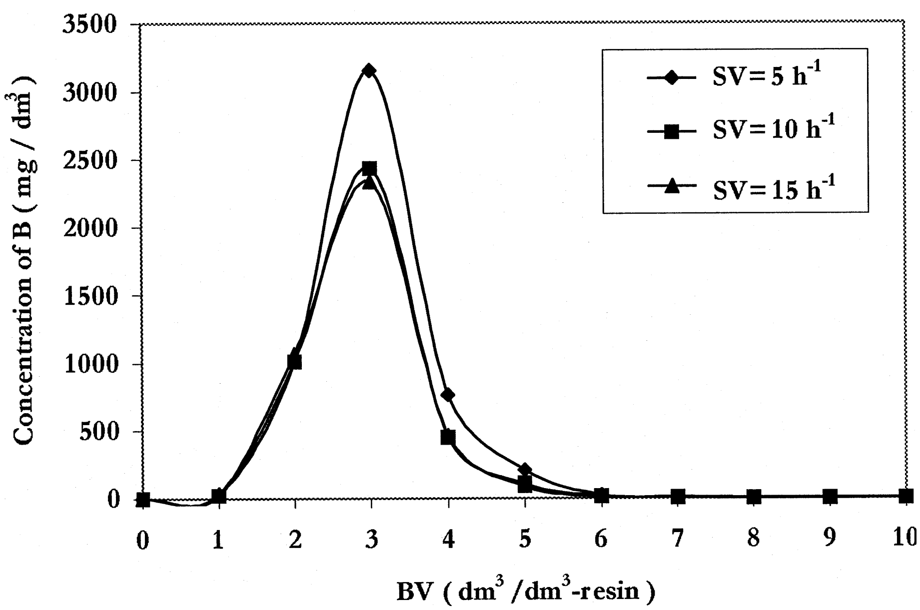


FIG. 4 Elution profiles of boron.

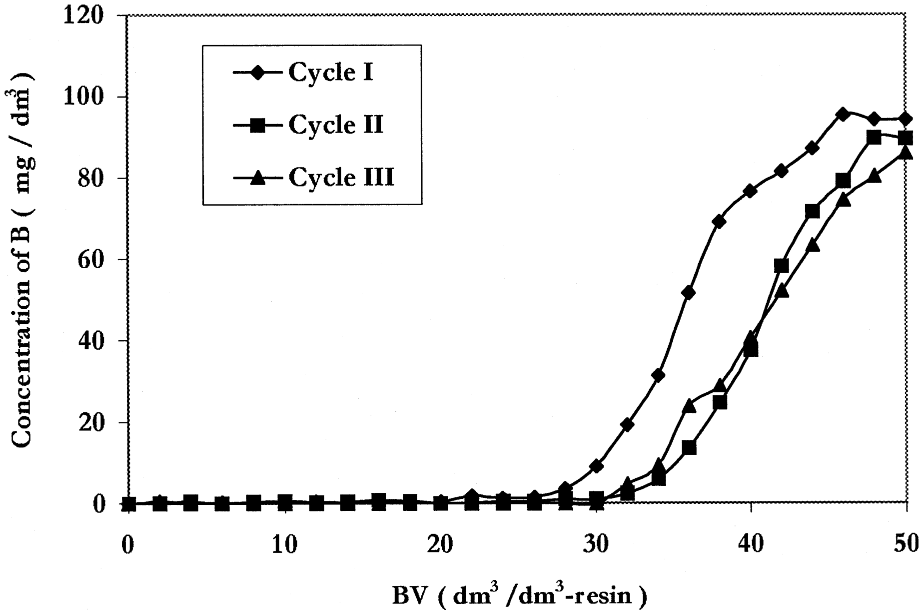


FIG. 5 Recycle use of Diaion CRB 02 for boron removal.

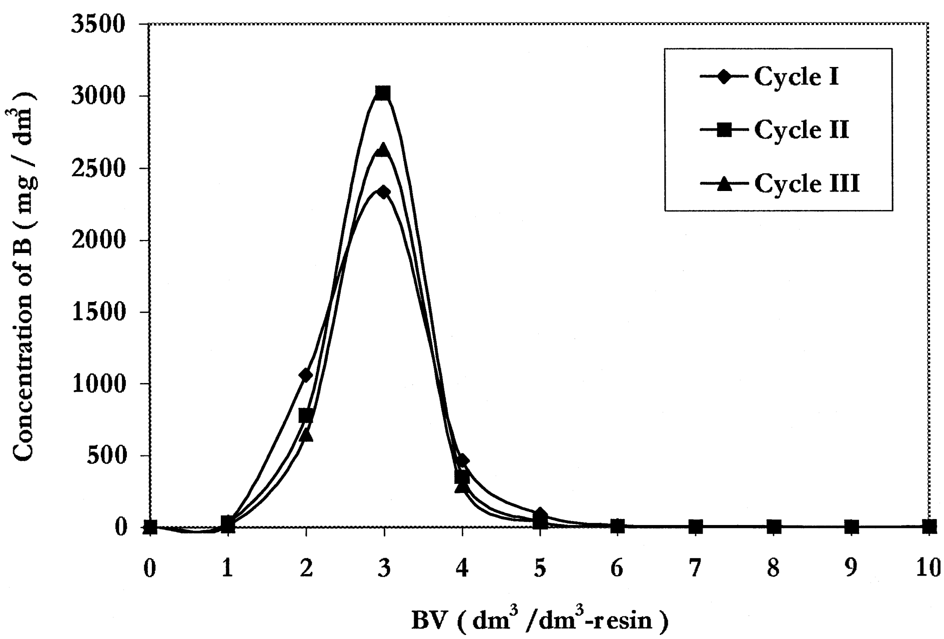


FIG. 6 Elution profiles of boron during each cycle.

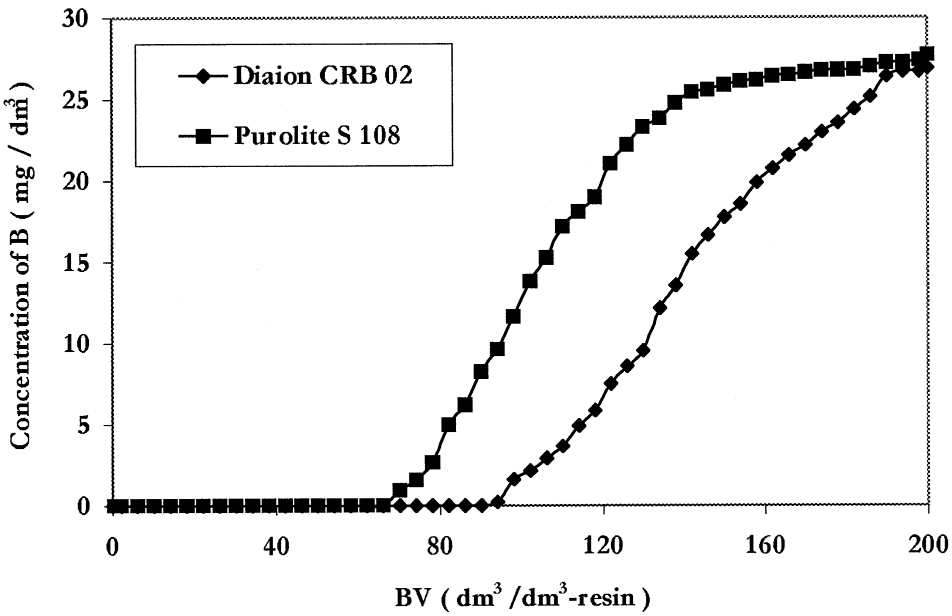


FIG. 7 Breakthrough curves of boron obtained using Kizildere geothermal wastewater.

Table 4. Resin Diaion CRB 02 showed better performance than Purolite S 108 as was expected from the results obtained with 0.01 M H_3BO_3 solution in the previous part. The batch removal of dissolved silica by Diaion CRB 02 and Purolite S 108 have been reported as 3.28 and 12.2 mg Si/g-resin, respectively (28). These results also show that dissolved silica in wastewater causes more interference for boron removal with Purolite S 108 than with Diaion CRB 02. Geothermal wastewater has a high temperature and contains dissolved silica. The effect of temperature on batch removal of boron was investigated by Badruk (28). It was reported that boron removal by Diaion CRB 02 resin decreased with an increase in temperature from 40 to 50°C. Oi et al. also explained that for resin Diaion CRB 02, a lower temperature resulted in a larger amount of boron adsorbed per 1 g of resin, although

TABLE 4
Column Performances of Diaion CRB 02 and Purolite S 108 for Boron Removal from Kizildere Geothermal Wastewater

Resin	Breakthrough capacity (mg B/cm^3-resin)	Total capacity (mg B/cm^3-resin)	Elution (%)
Diaion CRB 02	2.74	3.80	88.1
Purolite S 108	2.08	2.94	75.7

this trend was not clear for Amberlite IRA 743 resin, which has the same structure as Diaion CRB 02 (26). This should be taken into consideration in applications for boron removal from the wastewater of geothermal power plants.

In our previous report we explained that quantitative batch stripping of boron is obtained not only with HCl solution but also with H_2SO_4 solution in the 0.05–0.5 M concentration range. Bearing this in mind, H_2SO_4 solution (0.25 M) was used as an eluting agent for boron because of its cost-effectiveness for an elution process in an industrial application. The resulting elution profiles are given in Fig. 8. Boron was quantitatively eluted from the resins as summarized in Table 4. The concentration of boron in the eluate solution reached 2.2 g/dm^3, about 83 times higher than that of wastewater when Diaion CRB 02 was used. The respective value for Purolite S 108 was about 40 times higher. The eluted boron could be precipitated as boric acid crystals by a further concentration process. From an economic viewpoint, the same eluant solution could be used several times for the elution process. This will also help to concentrate boron in the eluate for further crystallization. Further tests on developing more economical elution and concentration processes are now under investigation.

In order to see the influence of ionic species which exist in wastewater, a separate column test with Diaion CRB 02 resin was carried out using an aqueous solution containing boron at a concentration of 30 mg/dm^3 (pH 5.6). As

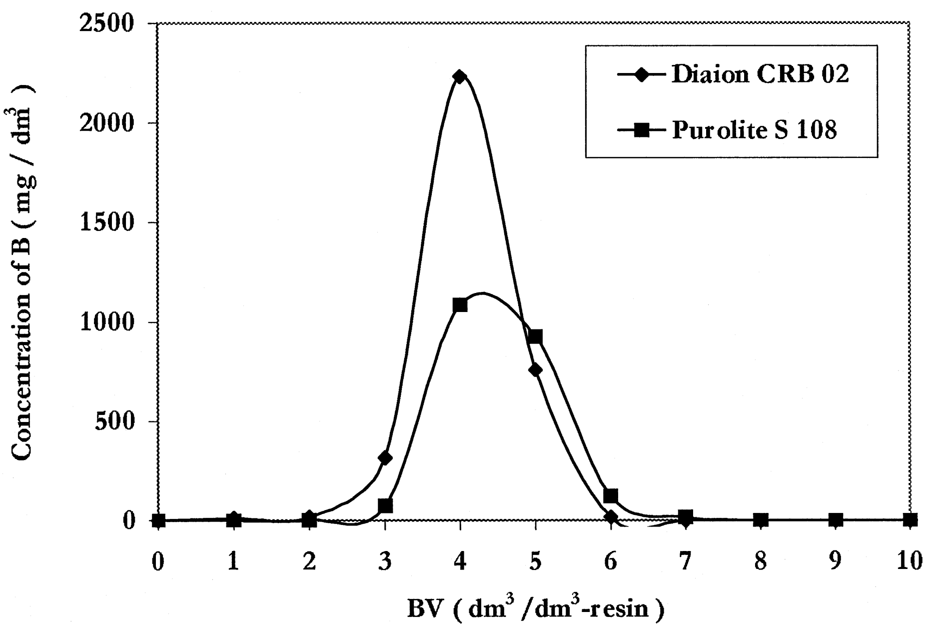


FIG. 8 Elution profiles of boron.

was pointed out previously, boron removal by Diaion CRB 02 is pH-dependent, and boron uptake almost leveled off between pH 5–6. For comparison, the breakthrough curves obtained with both aqueous solutions of boron and wastewater are plotted in Figure 9. The breakthrough points show good agreement, as seen in Fig. 9. This result show that boron can be selectively and effectively removed by Diaion CRB 02 resin from wastewater containing many ionic species. The resulting elution curves are shown in Fig. 10. The loaded boron was effectively eluted in both cases.

Recycle use of Diaion CRB 02 for boron removal from the wastewater of the Kizildere geothermal Power Plant was performed by following three sorption–elution–washing–regeneration–washing cycles. The wastewater (600 cm^3) was passed through the column at SV 25 h^{-1}. The breakthrough curves obtained at each cycle are presented in Fig. 11. The breakthrough capacity of the resin remained almost the same after three cycles. The elution profiles of each cycle are shown in Fig. 12. A chelating resin will be of real value if it can be recycled many times after the regeneration process. Although the results performed with the resin Diaion CRB 02 showed that the total capacity of the resin for boron remained almost the same after three sorption–elution–regeneration cycles, the resin capacity should be monitored after more than three cycles in order to evaluate its potential for industrial-scale application. Also, the long-term influence of dissolved silica should be determined. Work in this direction is continuing.

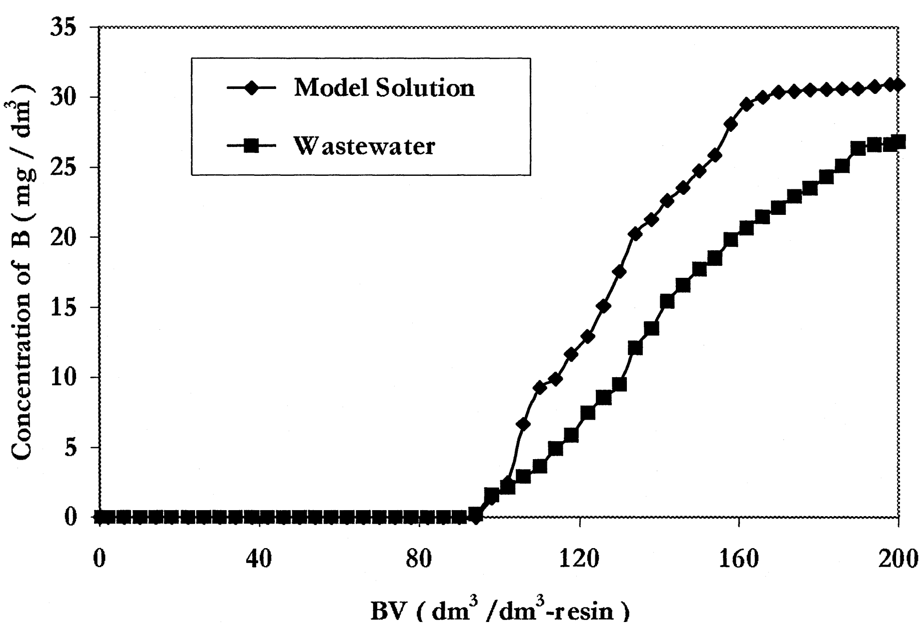


FIG. 9 Effect of ionic species in wastewater on breakthrough curves of boron.

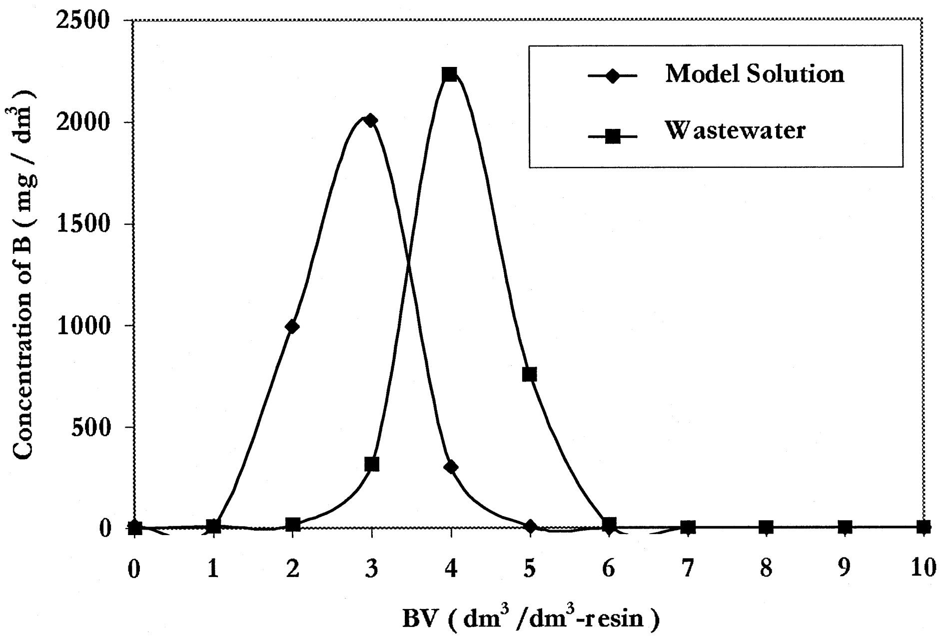


FIG. 10 Elution profiles of boron.

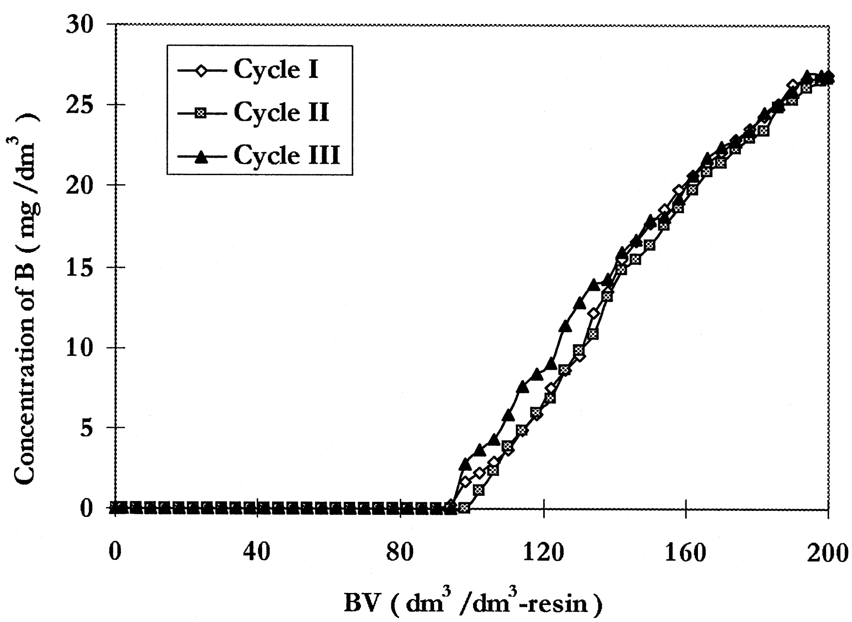


FIG. 11 Recycle use of Diaion CRB 02 for boron removal from Kizildere geothermal wastewater.

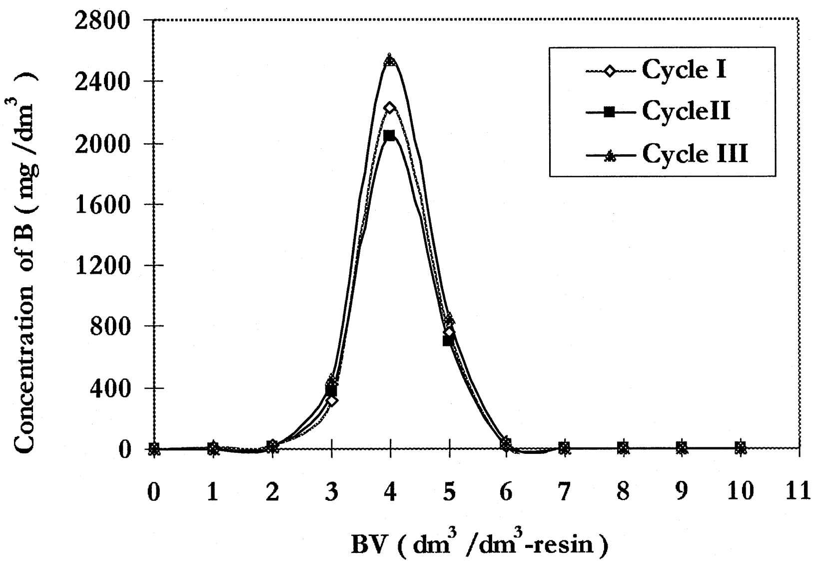


FIG. 12 Elution profiles of boron.

CONCLUSIONS

The concentration of boron in wastewater of the Kizildere geothermal power plant (about 30 mg B/dm^3), and the flow rate of wastewater disposed of from the power plant (1500 tons/h) into the B. Menderes River, and the accumulation of boron in the river are worthwhile problems to be tackled. The level of boron in the wastewater should be decreased to 1 mg B/dm^3 for it to be utilized for irrigation in agricultural areas.

N-Glucamine-type resins Diaion CRB 02 and Purolite S 108 were found to be promising for column removal of boron from wastewater of the geothermal power plant. The treatment costs should be minimized when the technical objectives are met.

Emphasis should be on cheaper ion-exchange resins with a higher capacity than the resins employed in this work for the development of a cost-effective process in which the technical objectives are obtained.

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