Mathematical Model for Adsorption of Boric Acid on a Boron-Specific Ion Exchanger

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The present study was undertaken to investigate boron removal from the waste waters of borax and boric acid producing plants. A boron-specific resin, Amberlite XE 243, was selected for the present work. Experimental results show that the ion-exchange operations are effective in removing boron from the waste waters.

The variation of boron concentrations in the effluents has been observed to depend, for various initial boron concentrations, C_0, on the ratio of the filtrate volume to the volume occupied by resin.

An empirical equation has been developed relating boron concentration, C, to filtrate and resin volumes V_1 and V, respectively, as

$$C = 2.34 \times 10^{-6} \cdot C_0 (V)^{-0.043} (V_1)^{2.80}$$

Turkey possesses approximately 60% of the world's boron reserves. Boron occurs as a trace element in most soils. It is present in sea water to the extent of a few parts per million and is estimated to constitute about 10 ppm of the earth's crust. The abundance of boron in geological materials is often used as an indicator of paleosalinity.[1] On the other hand, boron is readily adsorbed in clay minerals, especially illite, and its low mobility after deposition is a common assumption in paleosalinity characterizations. As well as the importance of total boron abundance in geological materials, boron isotopic composition and fractionation studies are of paramount geochemical significance. A recent extensive survey of geothermal fluids exhibited that the boron concentration varies widely.

The concentration of boron in water used for irrigation of crops has long been recognized as an important toxic factor. Although boron is an essential trace element for the nutrution of higher plants, boron concentrations exceeding 0.5 mg dm^{-3} in irrigation water may be harmful to certain crops.

It is doubtful whether continuous application of more than 0.5 mg dm^{-3} will eventually produce toxic effects on plants.[2,3] Many varieties of fruit, e.g. apples, plums, and pears, are listed among the most sensitive crops which can tolerate no more than 0.5—1 mg dm^{-3} boron. However, sugar bees, onions, cabbages, and carrots can tolerate boron concentrations of 2—4 mg dm^{-3} while potatoes, peas, wheat, and oats are among the crops listed as being able to withstand 1—2 mg dm^{-3} of boron.[2,3]

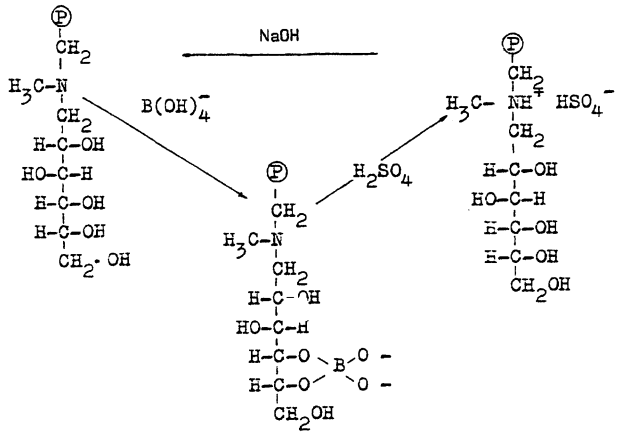
There is currently no simple method of boron removal from waste water. Boron removal by conventional biological treatment, chemical coagulation with lime, addition of iron(II) or aluminum salts have proved to be ineffective.[4] The adsorption of boron on clay, soil and other minerals has been extensively studied by many investigators.[5] However, the ion-exchange method is applied as the most suitable removal method.[6—8] A synthetic polymer (known as Amberlite XE-243 boron-selective resin), which contains a hydrophobic styrene backbone and also a tertiary amine group, is more suitable as a column-packing material.[6,9]

Experimental

Boric acid (reagent grade) in distilled water and the waste waters of a borax and boric acid producing plant were used as the source of boron throughout the study. An aqueous suspension of the resin was poured into an ion-exchange column, taking care to remove trapped air bubbles. Glass wool and glass beads were placed in the bottom of the column. The liquid sample was transported to the column by means of a peristaltic pump. The liquid sample having a concentration of 1600 mg B dm^{-3} was diluted with distilled water. Samples containing 500 and 50 mg B dm^{-3} were also prepared.

The above three samples are first treated with resins at different pH values to establish the optimum pH at which the maximum adsorption is attained. The maximum adsorption was observed to take place at pH 8. Then the adsorption of boron was observed at this pH by applying boron-containing samples at flow rates of 1,2,3,4,6, 7, and 10 cm^3 min^{-1} through columns of 2, 5 and 10 cm diameter. Initial boron concentrations were 1600, 500, and 50 mg B dm^{-3}. Boron concentrations were determined by the carminic acid and atomic absorption methods.[10—12] Experiments were conducted at room temperature under 21∓2 °C. Water depth above the top of the resin was kept constant and was equal to about 2 cm without pressure.

Regeneration. The exhausted beds were backwashed for 10 min at a column expansion of 100%. Conventionally, exhausted boron-specific resin is regenerated with 10% sulfuric acid solution (Scheme 1). Regeneration was done at a flow rate of 1 cm^3 min^{-1}. Since the amine residue of the resin is neutralized during acid regeneration to form the acid sulfate, hydrolysis of the amine acid sulfate during the subsequent exhaustion cycle results in a very acidic effluent. To avoid this, the resin is then converted back to the free amine form with 4% NaOH solution. The resin was then



Scheme 1.

washed with distilled water. The following scheme expresses the loading and elution of the boron-specific resin:

Results and Discussion

The optimum pH value was observed to be 8. On basis of different diameter values of adsorption columns, similar tables are presented for other sets of initial boron concentrations. However, because of space limitations, these experiments are not described in this paper.

Figures 1, 2, and 3 indicate the dimensionless boron concentration (C/C_0) change with the ratio of filtrate volume to bed volume (V_1/V) for inlet concentrations and column diameters as (C_0=1600, 500, 50 mg dm^{-3} and D=2 cm), (C_0=1600, 500, 50 mg dm^{-3} and, 5 cm), and (C_0=1600, 500, 50 mg dm^{-3} and, 10 cm), respectively. In these figures, V_1 signifies the volume of filtrate collected over a period of t_1 ; A corresponds to the cross-sectional area of the column, and finally, L is the resin depth.

The ratios of concentrations (C/C_0) and (V_1/AL) were treated through regression analysis after the scatter plots on double logarithmic graph paper as already shown in Figs. 1, 2, and 3. On the basis of these scatter diagrams, it became clear that the C/C_0 ratio is almost independent of the flow rates for

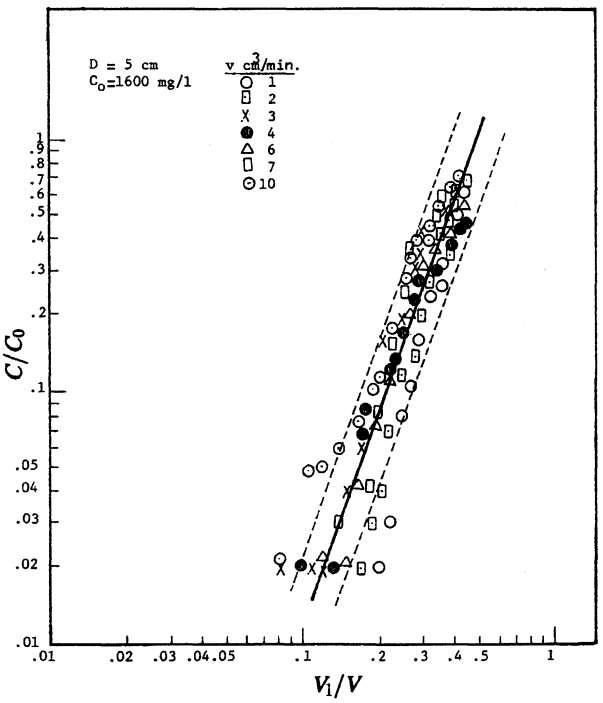
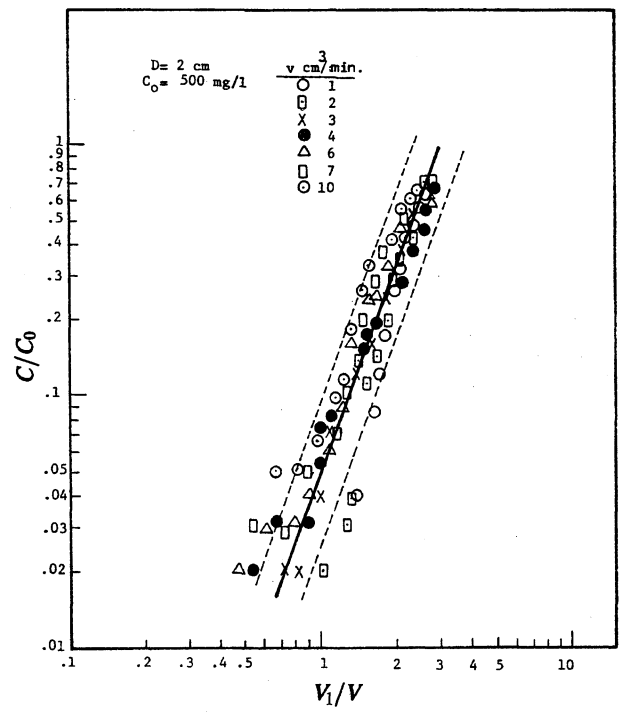


Fig. 2. Graph showing variations of V_1/V versus C/C_0.



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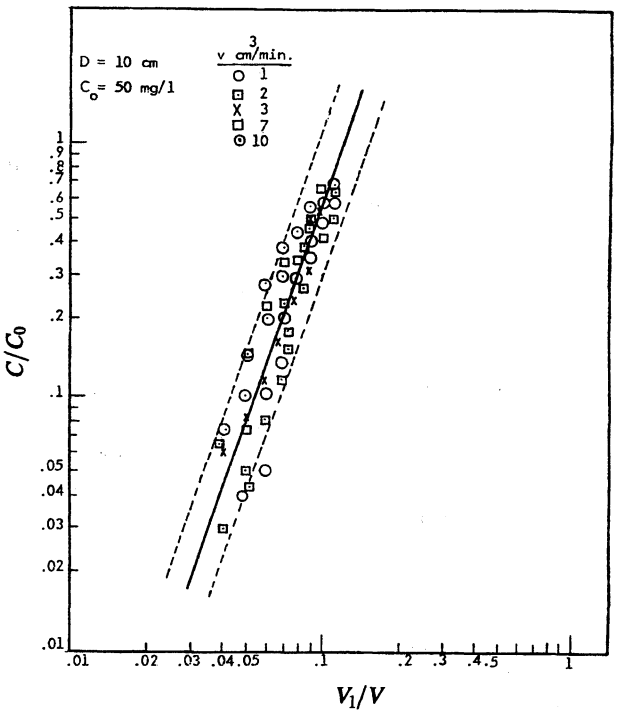

Fig. 3. Graph showing variations of V_1/V versus C/C_0.

Table 1. Values of the Coefficients a and b

Column diameter (cm)	Coefficient a	Coefficient b	R	s.d.(%)
2	0.050	2.80	0.9932	1.0
5	8.33	2.80	0.9869	1.0
10	345.00	2.80	0.9851	0.7

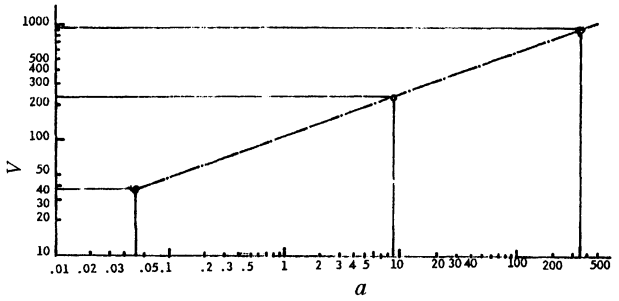

Fig. 4. Relation between a and V.

a given column diameter. Since on double logarithmic paper, the scatter diagram revealed a linear trend, it is concluded that the general form of the relationship is in the following power form as

$$\frac{C}{C_0} = a\cdot\left(\frac{V_1}{V}\right)^b \quad (1)$$

It is also obvious from Figs. 1, 2, and 3 that the scatter diagram is confined within a relatively narrow band. The main reason for this narrow scatter may be attributable to unavoidable experimental errors in the chemical analysis. Use of the classical least squares technique gave rise to the coefficient estimates in Table 1.

An inspection of this table shows that whatever the value of the column diameter, the coefficient b assumes almost a constant value equal to 2.80. However, a proportional relationship appears between the coefficient "a" and the column diameter indicating that "a" is a function of bed volume, V. In order to depict this relationship, the values of "a" were plotted versus volume, V, on double logarithmic paper as in Fig. 4. The result is a straight line which again by the least squares technique leads to the least squares techniques leads to

$$a = 2.34\times10^{-6}\cdot(V)^{2.747} \quad (2)$$

The coefficient of determination for this expression is R= 0.999. Substitution of this expression and the value of b=2.80 into Eq. 1 yields:

$$C = 2.34\times10^{-6}\cdot C_0\cdot(V_1)^{2.80}\cdot(V)^{-0.043} \quad (3)$$

This final formulation provides an estimation of effluent boron concentration provided that the column dimensions, inlet concentration, and the flow rates are given. Although it is not directly obvious from Eq. 3, the effluent boron concentration from an ion-exchange column is a function of the volumetric boron loading rate (L_v) because the same equation, considering that $L_v=C_0\ (V_1/V)$, can be rewritten as

$$C = 2.34\times10^{-6}\cdot L_v\cdot(V)^{0.957}\cdot(V_1)^{1.80} \quad (4)$$

As is already stated in Eq. 1, the dimensionless effluent boron concentration C/C_0 is only a function of the bed volume (V) and the filtrate volume (V_1).

The experimental results together with the estimated effluent boron concentrations from Eq. 3 are presented in Table 2. In the same table, the relative error percentages are shown for the sake of comparison. A close inspection of this table indicates that the relative errors remain between 1.40 and 3.10 percent for most of the values.

Conclusions

Laboratory tests showed that boron can be removed from the waste waters of a borax and boric acid producing plant by ion-exchange. As expected, the boron-specific resin Amberlite XE 243 with 95% boron removal efficiency can be applied for boron removal from the waste waters.

The influent boron solution in these experiments exhibited a pH of 8. The strongest boron adsorption capacity was observed at pH=8. The effluent boron concentrations at

Table 2. Comparison of Effluent Boron Concentrations Calculated from Eq. 3 with Experimental Results

Column diameter	Initial boron concn	Effluent boron concn/mg dm^{-3}			Relative error
cm	mg dm^{-3}	Exper. results	Calcd values	Difference	%
2	1600	755.33	772.99	−17.66	2.33
	500	262.28	269.25	−6.97	2.66
	50	26.28	26.92	−0.64	2.43
5	1600	787.42	811.50	−24.08	3.06
	500	245.40	253.59	−8.19	3.34
	50	25.00	25.35	−0.35	1.40
10	1600	931.50	918.44	+13.06	1.40
	500	253.80	242.30	+11.50	4.53
	50	23.5	24.23	−0.73	3.10

the optimum pH value were subjected to mathematical and graphical analysis.

Consequently, a regresion equation relating the effluent boron concentration to bed volume and to effluent volume was presented. The developed equation can be used with an acceptable accuracy in predicting the effluent boron concentrations. Results of this work may form a basis for similar studies with resins other than Amberlite XE 243. Last but not least, although the experiments in this paper were carried out for a certain circular cross-sectional column under specified conditions, and accordingly, the parameters of the model are determined, the author states that the form of the model is suitable for different columns, velocities, and temperatures, however, the parameters will assume different values.

Nomenclature

The following symbols are used in this paper.

a,b=coefficients in developed equation
A=crossectional area of the column (cm^2)
C=effluent boron concentration ($mg\,dm^{-3}$)
C_0=initial boron concentration ($mg\,dm^{-3}$)
D=column diameter (cm)
L=height of the resin in the column (cm)
R=correlation coefficient
t_1=ion exchange time (s)
v=flow rate (cm^3min^{-1})
V=bed volume (cm^3)
V_1=total volume of water (cm^3)

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