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Boron Removal by Anion Exchangers Impregnated with Citric and Tartaric Acids

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ABSTRACT

The separation of boron compounds, boric acid and borax, with anion-exchange resins, before and after impregnation with citric and tartaric acids, has been studied. Three different commercially available anion exchangers were selected for this study. The results indicate that ion-exchanging on the examined resins is not quite effective for the removal of boron from boric acid and borax water solution. The presence of citric or tartaric acid is essential for the enhancement of the sorption capacity above that observed for the untreated resins. Sorption data show that citric acid is a more effective impregnant than tartaric acid.

Key Words. Boron; Anion exchangers; Impregnation; Separation; Citric acid; Tartaric acid

INTRODUCTION

Boric acid and borax have a wide variety of applications in both industrial and consumer products (1). They are used in many fused products, including textile fiberglass, optical and sealing glasses, ceramic glazes, and porcelain enamels. Boron is a necessary trace nutrient for plants and is added in small quantities to a number of fertilizers (2). Borates, when applied at a relatively high concentration, act as nonselective herbicides.

Boron may occur naturally in some waters or its presence may originate from industrial waste discharges or agricultural use of boron pesticides and fertilizers. Its concentration in wastewater should not exceed 10 mg/dm^3.

Investigations on boron removal from water by ion exchange have been reported (3–5). Ion-exchange resins containing polyols have been developed that are highly specific for removing borates from solution (6, 7). Boron separation from water by electrodialysis was investigated by Pilipenko (8) and Song (9).

The use of citric and tartaric acids as impregnants of activated carbon has been studied previously in this laboratory (10). It was shown that the impregnation generally increases the ability of carbon to sorb boron. It is possible that impregnation of anion-exchange resins with citric and tartaric acids acids could lead to a modification of their affinity toward boron. This paper presents laboratory data on the effect of impregnation of three different anion-exchange resins on the kinetics of boron removal from solution.

EXPERIMENTAL

Materials

All chemicals were of analytical reagent grade and used without further purification. The stock solutions of boron were made by adding appropriate amounts of boric acid or borax to 1 dm^3 of distilled water to give a boron concentration of 1 g/dm^3. Boron influent concentrations examined, ranging from 0.0092 mol/dm^3 (100 mg/dm^3) to 0.0026 mol/dm^3 (28 mg/dm^3), were prepared from a stock solution. These values correspond to the actual values in some wastewaters in Yugoslavia. The ionic strength of all the water solutions investigated was about 0.001 mol/dm^3. IRA 93, IRA 400 and WOFATIT L 150, three commercially available anion-exchange resins, were selected for this study.

Analysis

Three analytical methods for the determination of boron in water were used. Titrations of boric acid with sodium hydroxide in the presence of mannitol were performed conductometrically (11). This procedure was used for samples containing more than 50 mg/dm^3 of boron. Boron was also determined by atomic absorption utilizing a nitrous oxide-acetylene flame. Using the 249.7-nm line, the limit of detection was 15 mg/dm^3. A SP9 Series Atomic Absorption Spectrometer (Pye Unicam) was used in this study. A spectrophotometric method was used for the determination of boron in the range of 0.1 to 10 mg/dm^3. In the presence of boron, a solution of carminic acid in concentrated sulfuric acid changes from bright red to a blush blue depending on the amount of boron presence (12). The absorbance was measured at 590 nm with a spectrophotometer (Specol 10, Carl Zeiss) with a 1-cm cuvette. A calibration curve was prepared using standard solutions of boron in the 0.1–10 mg/dm^3 range.

Procedure

The sorption of boron was investigated by flowing a sample solution containing boron at a flow rate of 100 cm^3/min through a chromatographic column with a diameter of 2 cm. The experiments were conducted at room temperature (21 ± 2°C). Samples were taken after each 100 cm^3 of eluted effluent and analyzed for boron. The sample size was 5 cm^3.

Impregnation of untreated resins was carried out using a method previously described (13, 14) with aqueous solutions of tartaric and citric acids. It was accomplished by a standard column chromatography procedure using the corresponding influent. The impregnant contents were determined by titration with a strong base. The capacities of impregnated resins for citric and tartaric acids are given in Table 1.

RESULTS AND DISCUSSION

The results of the laboratory studies are presented in two sections: the first includes work on boron from boric acid water solution separation; the second covers separation of borate ion from borax water solution.

Boric Acid Water Solution

The separation studies were begun by conducting experiments with unimpregnated resins to determine their efficiency in the applied system. A sample containing 100 mg/dm^3 of boron was passed through a column loaded with anion-exchange resin. Figure 1 shows the breakthrough curves for boron separation using different kinds of resin.

TABLE 1
The Amount of Applied Impregnant on Various Resins

Anion exchanger	Content of impregnant (mg/g) Citric acid	Content of impregnant (mg/g) Tartaric acid
IRA 93	225	50
IRA 400	256	50.4
WOFATIT L 150	244	174

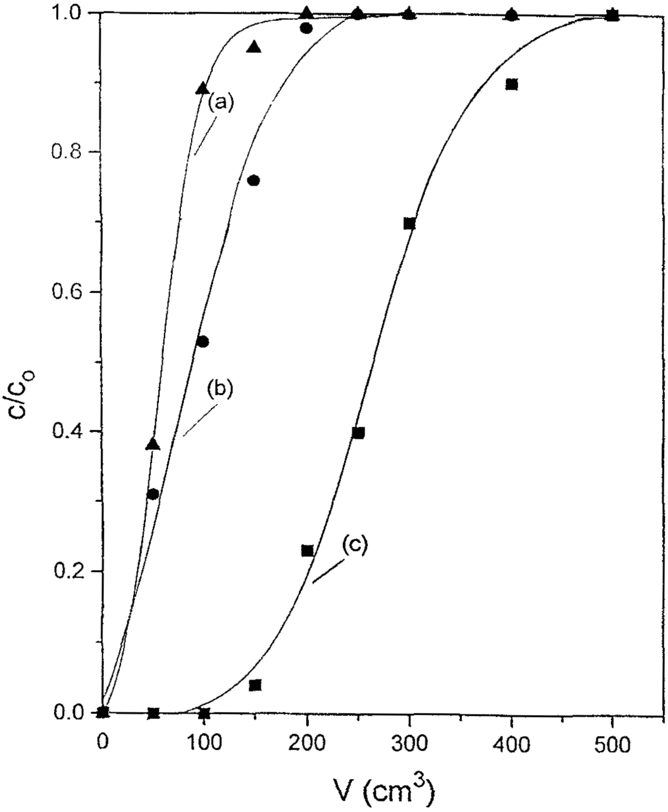


FIG. 1 The effectiveness of examined resins to remove boron from a boric acid water solution. Breakthrough curves (C_0 = 0.0092 mmol/dm^3, pH 6, I = 0.001 mol/dm^3). (a) IRA 93. (b) IRA 400. (c) WOFATIT L 150.

It is obvious that the rate of uptake is closely related to the type of resin. IRA 93 is a weakly basic anion resin and only a small quantity of weak boric acid is removed. IRA 400 and WOFATIT L 150 are strongly basic anion resins and can more effectively remove boric acid. Partial results of these experiments, presented in Table 2, indicate that WOFATIT L 150 exhibits a significant uptake of boron.

Removal of boron from water was also accomplished using impregnated resins. The calculated sorption capacities of impregnated and unimpregnated resins are given in Table 2. The data clearly show that the application of citric and tartaric acids generally increases the ability of the resins to sorb boron. It suggests a major role of impregnation.

TABLE 2
The Effectiveness of Sorbents Used to Remove Boron from *Boric Acid* Water Solution in a Continuous Flow System

Examined sorbent	Capacity (mg/g)
IRA 93	0.39
IRA 93 + citric acid	0.55
IRA 93 + tartaric acid	0.50
IRA 400	0.60
IRA 400 + citric acid	1.19
IRA 400 + tartaric acid	0.98
WOFATIT L 150	1.69
WOF + citric acid	2.60
WOF + tartaric acid	2.12

The results also indicate that boron removal is dependent on the type of resin and the applied impregnant. For a given concentration of boron, citric acid is a more effective impregnant than tartaric acid. It is evident from data recorded in Table 1 that the amounts of citric acid were much higher than the corresponding values of tartaric acid. This suggests that the capacity of impregnated resins depends on the impregnant content. Since WOFATIT L 150 showed the best separation characteristics, this study focused on this treatment process. Therefore, Fig. 2 shows the breakthrough curves for boron separation by WOFATIT L 150 before and after impregnation.

The position of the breakthrough curves indicate that WOFATIT L 150 impregnated with citric acid is an effective sorbent of boron and capable of sorbing at least 2.60 mg/g. The first appearance of boron in the effluent was detected after 300 cm^3 of solution had passed through the column.

Borax Water Solution

In order to predict adequately the effect of impregnation on a subsequent adsorption process, it is first necessary to determine the capacities of the unimpregnated materials. Thus, in this part of our investigation, experiments with unimpregnated resins were also performed. Figure 3 shows the breakthrough curves for boron. The curves in this figure were obtained for a system with an influent concentration of 28 mg/dm^3 of boron. Partial results of these experiments indicate that WOFATIT L 150 and IRA 400 performed better than IRA 93 which has a faster breakthrough curve.

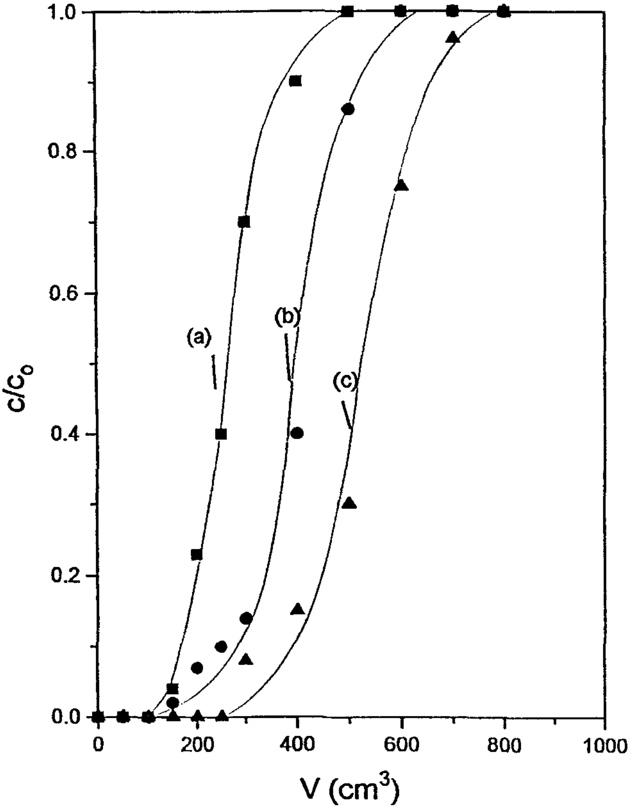


FIG. 2 Breakthrough curves for boron separation from boric acid water solution by WOFATIT L 150, impregnated and unimpregnated (C_0 = 0.0092 mmol/dm^3, pH 6, I = 0.001 mol/dm^3). (a) WOFATIT L 150. (b) WOFATIT L 150 + tartaric acid. (c) WOFATIT L 150 + citric acid.

In order to compare the results of treatment by various impregnated resins, the weight of boron removed per gram of each sorbent was calculated. The results are summarized in Table 3. In the systems studied, the capacity to sorb boron also increases with impregnation. The data for boron capacity indicate a consistent pattern: the resins impregnated with citric acid are more efficient than the same resins impregnated with tartaric acid. However, the amount of boron retained by IRA 400 impregnated with citric acid was lower than that found for the resin impregnated with tartaric acid. The enhanced removal of boron by this sorbent can indicate that either equilibrium capacity was not attained or some transformation occurred within the bed.

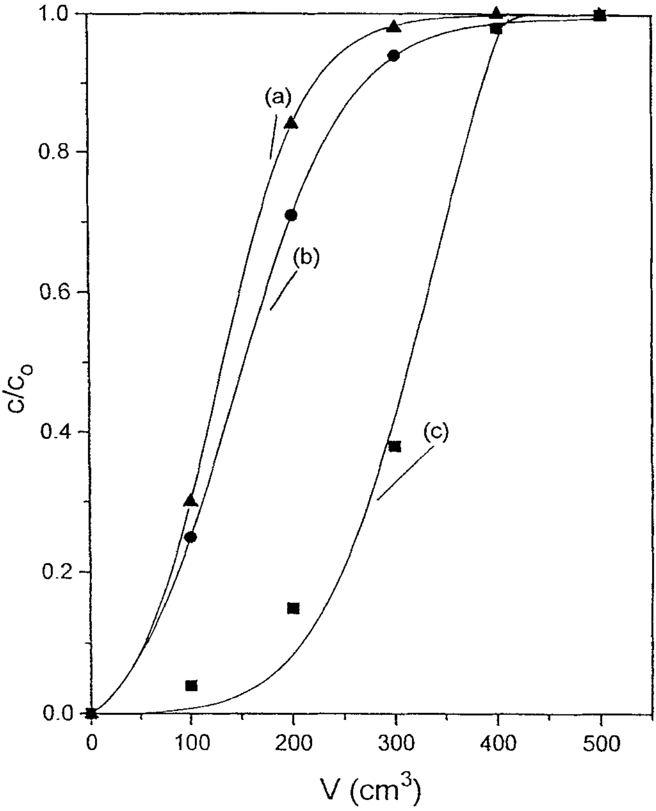


FIG. 3 Breakthrough curves for the separation of boron from borax water solution by different anion exchangers (C_0 = 0.0026 mmol/dm^3, pH 9.4, I = 0.001 mol/dm^3). (a) IRA 93. (b) IRA 400. (c) WOFATIT L 150.

TABLE 3
The Effectiveness of Sorbents Used to Remove Boron from *Borax* Water Solution in a Continuous Flow System

Examined sorbent	Capacity (mg/g)
IRA 93	0.39
IRA 93 + citric acid	1.00
IRA 93 + tartaric acid	0.76
IRA 400	0.46
IRA 400 + citric acid	0.67
IRA 400 + tartaric acid	0.89
WOFATIT L 150	0.83
WOF + citric acid	1.52
WOF + tartaric acid	1.30

It has been shown in this work that WOFATIT L 150 impregnated with citric acid is the most effective for removing boron from water. The same resin impregnated with tartaric acid also successfully removed boron. Figure 4 shows the breakthrough curves for boron for WOFATIT L 150 impregnated with citric and tartaric acids and also for the unimpregnated resin.

According to Fig. 4, WOFATIT L 150 impregnated with citric and tartaric acids performed better than the unimpregnated resin. The breakthrough curves exhibit a characteristic S shape, but with varying degrees of steepness and position of the saturation point. This indicates a different sorption mechanism in the examined systems.

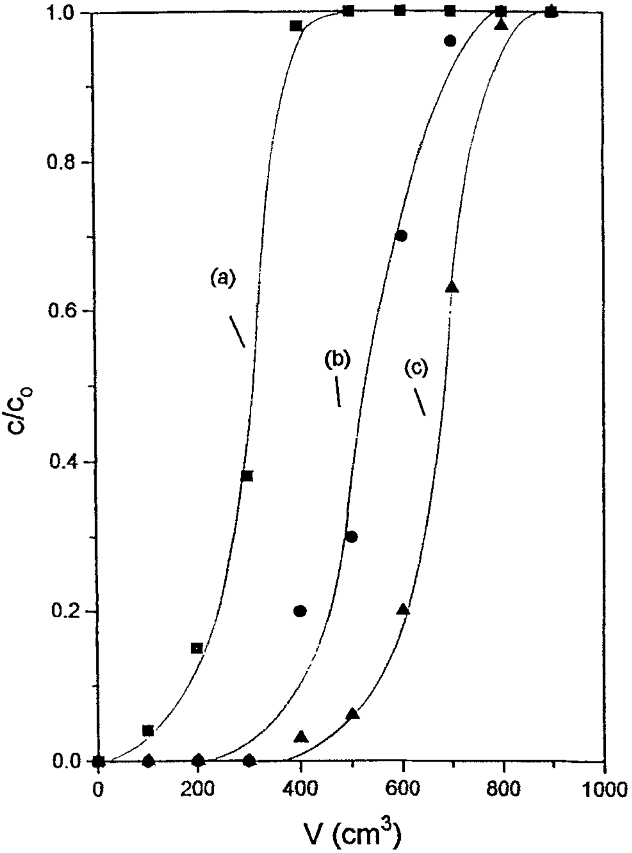
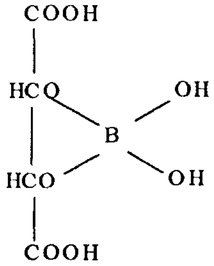
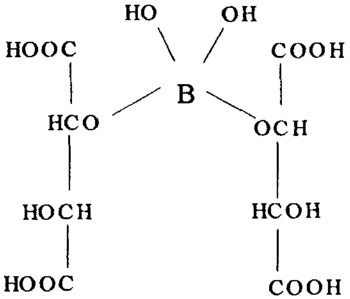


FIG. 4 Removal of boron from borax water solution by WOFATIT L 150. The influence of impregnation on the separation characteristics (C_0 = 0.0026 mmol/dm^3, pH 9.4, I = 0.001 mol/dm^3). (a) WOFATIT L 150. (b) WOFATIT L 150 + tartaric acid. (c) WOFATIT L 150 + citric acid.

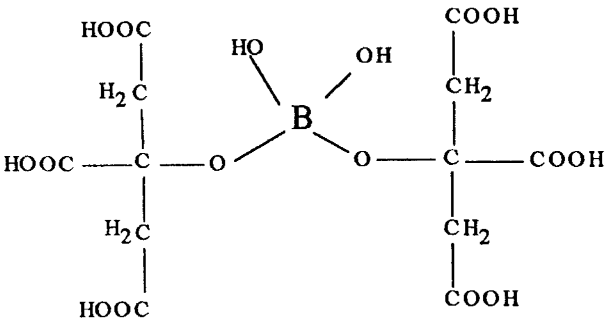
On the basis of the experimental investigations, a possible mechanism of the reaction of boric acid and borax with citric and tartaric acids can be proposed. During impregnation the large molecules of citric and tartaric acid enter the resins and are trapped in the most highly crosslinked regions, their chains becoming entangled with the resin matrix. This could eventually reduce the capacity of the anion exchangers (15). In all cases the sorption capacities of the impregnated resins were much higher than those of the unimpregnated resins. Therefore, the observed increases in sorptive capacity associated with impregnation of the resins are probably caused by interactions between the organic molecules and boron species on the resin surface or inside the resin. It is known that some organic compounds with adjacent hydroxyl groups show an appreciable tendency to form complexes with boric acid and borate ions (16). Under the conditions of this investigation, the predominant mechanism for the removal of boron appears to be the formation of organoboron complexes. It seems that the complexes of boric acid and borax with tartaric acid have the structure



but also complexes containing two tartaric acids per boric acid could be formed with the structure



Similarly, the complex of citric acid and boric acid or borate ion could involve two molecules of citric acid:



Further investigation will be required to describe precisely the mechanism responsible for the observed increases in capacity. Also, some of the borate ions are removed by ion exchange on available sites free after impregnation. Under the examined conditions it is not possible to determine how much of the removal can be attribute to complexation and how much to ion exchange.

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