

Behavior of Chelating Fibers Having Polyol Groups in Column Mode Adsorption of Boric Acid

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Tris(hydroxymethyl)aminomethane (Tris) or N-methylglucamine (Nmgl) was introduced into poly(glycidyl methacrylate) chains, which were grafted onto polyethylene coated polypropylene fiber and nonwoven cloth by means of electron beam irradiation induced graft polymerization technique. The grafted fiber and cloth were functionalized by heating them in ethanol solution of Tris or Nmgl. Amount of the introduced Tris or Nmgl was nearly equal to each other (ca. 2 mmol/g-fiber). Performances of Tris fixed cloth were studied by batchwise methods. Although equilibrium capacity of this cloth for boric acid was less than that of Diaion CRB02, its other performances, such as the selectivity and adsorption rate, were nearly equal to or higher than those of Diaion CRB02. In addition, behavior of both Tris and Nmgl fixed fibers in column mode adsorption of boric acid was examined by using glass columns packed with respective fibers. Capacities of Tris and Nmgl fixed fibers were ca. 1.0 and 1.3 mmol of B/g-fiber, respectively. Breakthrough capacities of both fibers for boric acid decreased with an increase in flow rates. However, those of Tris and Nmgl fixed fibers were as high as 0.57 and 0.92 mmol of B/g-fiber, respectively even at an hourly flow rate of 50 bed volumes, indicating that they can take up boric acid much faster than does a boric acid specific resin Diaion CRB02.

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Some surface waters contain boron as boric acid. For instance, boron more than 10 mg/l frequently occurs in hot spring waters. In addition, industrial wastewaters also contain boron at unacceptable concentrations.¹ Although a lot of technologies for removal of boron have been proposed so far, much attention has been paid to boron specific adsorption resins, such as Amberlite IRA 743, Diaion CRB02, Puralite S 108 and so on. These resins have macroreticular crosslinked polystyrene matrices, on which N-methylglucamine (Nmgl) is chemically fixed. However, their main disadvantages are high costs and slow kinetics in the adsorption of boric acid, although they have high specificity to boric acid in neutral pH region.^{1,2} Thus, it is necessary to develop cheaper boric acid specific adsorbents with rapid adsorption rates. In this connection, we have proposed a new type of boric acid adsorbent, which was prepared by addition of tris(hydroxymethyl)aminomethane (Tris) to epoxy groups in macroreticular glycidyl methacrylate-divinylbenzene copolymer beads.³ However, this resin showed slow kinetics in column mode adsorption of boric acid; breakthrough points were less than 20 bed volumes for a feed containing 5 mM boric acid at flow rates of ca. 10 h⁻¹ in space velocity.³

Fibrous ion exchangers or adsorbents take up much more rapidly a target species than granular ones.^{4,5} In particular, Saito and Sugo have developed routes to attain fibrous adsorbents having extremely high adsorption rates to various species by means of radiation induced graft polymerization technique. In this work, Tris and Nmgl were fixed to epoxy groups of poly(glycidyl methacrylate) chains, which were chemically bound to polyethylene coated polypropylene fiber (PPPE) by means of electron beam irradiation induced graft polymerization method. In this work, two different forms of PPPE fibers were

used; one was nonwoven PPPE cloth and the other short cut PPPE fiber itself. Boric acid adsorption abilities of the resulting fibers having fixed Tris or Nmgl were investigated by both batchwise and columnar methods.

Experimental

Electron beam irradiation to trunk fibers

Nonwoven cloth of PPPE (1.5 denier) and short cut PPPE (0.9 denier, length ca. 5 cm) as trunk polymers for graft polymerization were provided by Kurashiki Textile MFG Co., Osaka, Japan. The cloth was used after cutting into pertinent pieces (usually 10 cm x 15 cm). After a trunk polymer (fiber or cloth) was dried in a vacuum oven at 40 °C for a day, it was put into polyethylene bags. After air in the bags was displaced by nitrogen, the bags containing the trunk polymer were irradiated with electron beam (2 MeV, 1 mA) for 10 min (total dose 100 kGy), and the irradiated fiber and cloth were stored in an electric refrigerator at -60 °C. The electron accelerator used was a cascade type one (Dynamitron, named Accelerator No. 2) at Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute.

Graft polymerization of glycidyl methacrylate

Glycidyl methacrylate (GMA) of chemical grade was purchased from Kanto Chemical Co. It was used without purification. The electron beam irradiated PPPE fiber (or nonwoven cloth of PPPE) was taken into a glass ampule (500 ml). Then, the ampule was connected to a vacuum line, and air in the ampule was eliminated by a vacuum pump. Then, dimethyl sulfoxide solution of GMA (400 ml) was introduced into the ampule. After sealing the ampule, it was maintained at 40 °C for a

given time. The resulting GMA grafted PPPE fiber and cloth were washed with *N,N*-dimethylformamide and then with methanol. After air-drying, they were dried in vacuum at 40 °C. From weight difference (W_{in}) before and after the grafting, a degree of grafting (dg) was calculated. The dg in % is designated by $100(W_{in}/W_0)$. Here, W_0 is the weight of the trunk polymer before grafting.

Because of heterogeneous nature of radical generation on trunk polymer by electron beam irradiation as well as the followed liquid phase graft polymerization, GMA concentration and reaction time to give a given dg value are different between fiber and cloth. For instance, the reaction for 2 h with 5 wt% GMA in dimethyl sulfoxide was adopted in the case of the PPPE cloth; dg values of the GMA grafted clothes (20 pieces) were from 94 to 103 %. For short cut PPPE fiber (6 g), the reaction for 2 h with 10 wt% GMA in methanol gave the dg of 93 %.

Functionalization of GMA grafted PPPE cloth and fiber

GMA grafted PPPE cloth (or fiber), Tris (or Nmgl), and ethanol were taken into a stainless steel autoclave. After sealing the autoclave, it was heated in oil bath. Detailed conditions will be given in a later section with results. The functionalized cloth and fiber were washed with water and then with ethanol. After air-drying, they were dried in vacuum at 40 °C for a day. The functionalized cloth and fiber were characterized by measuring their IR spectra and by CHN analysis.

In this work three types of fibrous adsorbents were prepared. Table 1 summarizes their symbols.

Table 1 Symbols for fibrous boric acid adsorbents

Symbol	Precursor	Ligand for fixation
FTris-c	GMA-grafted PPPE cloth	Tris
FTris-f	GMA-grafted PPPE fiber	Tris
FNmg-f	GMA-grafted PPPE fiber	Nmgl

Batchwise study

Equilibrium uptake of boric acid. After each adsorbent was equilibrated with aqueous boric acid at 40 °C for 24 h, the concentration of boron in the aqueous phase was determined by means of ICP-AES. Equilibrium uptake was calculated from the decrease of the boron concentration in the aqueous phase. The pH of aqueous phase was adjusted with hydrochloric acid and/or sodium hydroxide.

Adsorption rate. Into a three necked flask (200 ml) equipped with a mechanical stirrer, FTris-c (or Diaion CRB02) and water were taken, and the resulting mixture was allowed to stand overnight. Then, a boric acid solution was added to the flask, and immediately the resulting solution was stirred at 400 rpm for the first 2 min, and then at 170 rpm. At pertinent intervals, an aliquot (0.2 ml) of the aqueous phase was sampled, and the concentration of boron in the sample was determined. From the decrease in the concentration of boric acid in the aqueous phase, the uptake of boric acid at the sampled time was calculated. Detailed conditions will be given with results in a later section.

Column mode study

Each adsorbent in free amine form was swollen with water. Then, it was packed into a glass column (i. d. 0.7 cm); its bed volume was 1.5 ml. As feed, a solution of boric acid was down flow supplied to the column at various flow rates. After the adsorption operation, the column was washed with water and then 0.5 M sulfuric acid was supplied to the column to elute boric acid adsorbed. All column effluents including washing were collected on a fraction collector, and the concentration of boric acid in each fraction was measured. Total uptake of boric acid was determined by elution of boric acid adsorbed on each column with 0.5 M sulfuric acid.

After the elution operation, the column was washed with water and then with 1 M sodium hydroxide to change the adsorbent into free amine form. Finally the column was washed with water, and then next adsorption-elution cycle was started.

Results and Discussion

Functionalization of GMA grafted PPPE cloth

Maeda et al.³ reported that even macroporous poly(glycidyl methacrylate) beads should be treated in refluxed 1,4-dioxane solution (ca. 101 °C) of Tris (14 wt%) for 5 h. Since it is expected that epoxy groups on grafted poly(glycidyl methacrylate) chains are more reactive, much milder conditions were surveyed. First, less toxic ethanol was used as solvent instead of 1,4-dioxane, and results are given in Fig. 1. At 80 °C, it took at least 3 h to complete the functionalization with Tris. At 100 °C, on the other hand, the reaction completed within 2 h in both cases of Tris and Nmgl. Thus, the further functionalization was conducted at 100 °C for 2 h. Ligand contents of FTris-c, FTris-f and FNmg-f were nearly equal (1.9–2.1 mmol/g).

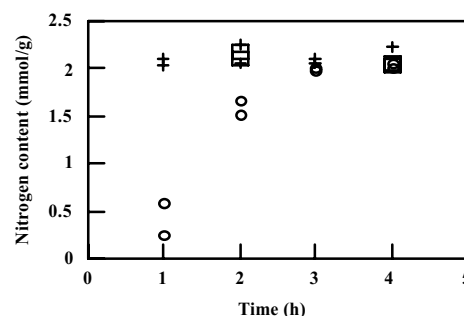


Fig.1 Functionalization with Tris and Nmgl. Conditions: ethanol 3 ml, GMA grafted PPPE cloth 0.2 g, Tris or Nmgl 1 g. ○ 80 °C and + 100 °C for Tris; □ 100 °C for Nmgl.

Properties of FTris-c evaluated by batchwise method

Batchwise study was limited to FTris-c. Diaion CRB02 (32–60 mesh) was also used for the sake of comparison. This resin has a macroreticular crosslinked polystyrene matrix, to which Nmgl is chemically fixed. Fig. 2 shows the dependence of uptake of boric acid by FTris-c on the initial concentration of boric acid. At the low concentration level of boric acid less than 0.0025 M, both exhibit nearly equal uptake. However, Diaion CRB02 exhibits higher uptake than FTris-c in the concentration level higher than 0.0025 M. This is probably due to its higher ligand content.

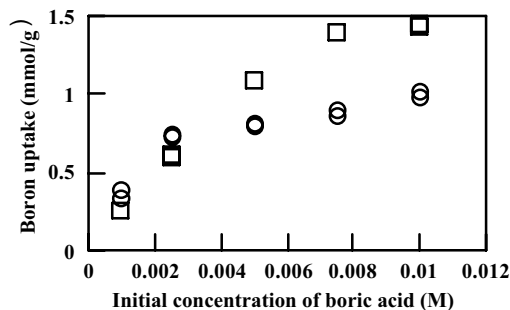


Fig. 2 Dependence of uptake of boric acid on its initial concentration. ○ FTris-c (0.05 g), □ Diaion CRB02 0.1g. Boric acid solution 25 ml. Equilibrium pH 5.86–6.39.

Dependence of boric acid uptake on pH

Figure 3 shows pH profile of boric acid uptake by FTris-c. The maximum uptake is observed between pH 6 and 8 as in the case of the Tris fixed resin.³ This pH profile predicts that boric acid adsorbed on FTris-c will be able to elute quantitatively with 1 M solutions of strong acids.

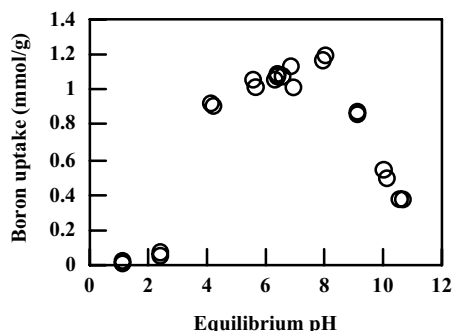


Fig. 3. Dependence of boric acid uptake by FTris-c on pH. FTris-c : 0.05 g (pH > 2), 0.08 g at pH 1.1. Solution 0.01 M boric acid. The pH was adjusted with HCl and/or NaOH.

Effect of common inorganic anions

Boric acid occurring in seawater, hot spring water, and so on are accompanied by common inorganic anions, such as bromide, chloride, sulfate and in some case nitrate. Then, the effect of these anion was tested. Table 2 summarizes results. As judged from Table 2, any tested anion did not essentially interfere with the adsorption of boric acid. At 0.1 M of each anion, however, the uptake is slightly lowered. It seems that this can not be ascribed to direct interference by these anions, since all anions give the very similar tendency. Probably, this may come from an indirect effect of electrolytes, e.g. ionic strength effect on activity coefficients.

Table 2 Effect of common inorganic anions on boric acid uptake by FTris-c.

Anion	Concn. of anion (M)	Equilibrium pH ^{a)}	Boric acid uptake ^{a)} (%)
Chloride	0.1	7.04	69.2
	0.005	6.78	72.5
	0.0005	6.45	73.9
Nitrate	0.1	7.70	69.4
	0.005	6.85	70.8
	0.0005	6.55	72.7
Bromide	0.1	6.97	70.4
	0.005	6.95	73.3
	0.0005	6.84	75.0
Sulfate	0.1	6.95	69.6
	0.005	7.09	73.5
	0.0005	7.10	73.0

FTris-c: 0.05 g. Concentration of boric acid in solution: 0.0005 M (25ml).

^{a)}Averages of duplicated runs.

Adsorption rate

Generally resins with fixed polyol groups thermodynamically exhibit high selectivity to boric acid, as shown in Table 2. However, kinetic performances are much more important from practical viewpoints. Indeed, the most serious defect on boric acid specific adsorbents is slow kinetics in the boric acid adsorption.

Figure 4 compares time course in the adsorption of boric acid between FTris-c and Diaion CRB02. The equilibrium uptake under conditions shown in Fig. 4 was 1.2 mmol/g for Diaion CRB02 and 0.71 mmol/g for FTris-c. In the case of FTris-c, the

equilibrium was established at 30 – 40 min, whereas it took ca. 24 h to attain the equilibrium in the case of Diaion CRB02. Thus, the fiber based boric acid adsorbent having polyol groups exhibit much higher adsorption rates, compare with those of crosslinked copolymer based ones. In ion exchange between solutions and crosslinked copolymer based granular resins, rates of the adsorption of ionic species are usually particle diffusion controlled. We are studying kinetic aspects of fibrous cation exchangers having oxy acid groups of phosphorus. These fibers exhibit much higher adsorption rates than does FTris-c in the adsorption of boric acid. Thus, it seems that rates of reaction of boric acid with polyol groups fixed on polymeric matrices are not fast. Boric acid is adsorbed through multiple condensation reactions of hydroxyl groups of boric acids with those of polyols fixed on polymer chains. Then, the reaction rates are much slower because of restricted freedoms of hydroxyl groups fixed to polymer matrices, resulting in slow overall rates in the adsorption of boric acid.

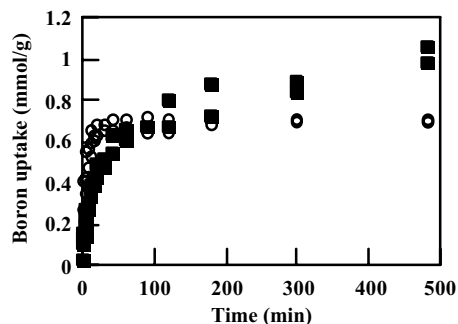


Fig. 4 Time course of uptake of boric acid with FTris-c (O) and Diaion CRB02 (■). FTris-c 0.5 g. Diaion CRB02 0.3 g. Solution 0.005 M boric acid 150 ml.

Column mode study

As described in the preceding section, FTris-c takes up boric acid much faster than Diaion CRB02. Since FTris-c is inconvenient to use in column mode experiment, FTris-f was used here. Results are shown in Fig. 5. With an increase in flow rate, the breakthrough point of boric acid decreased.

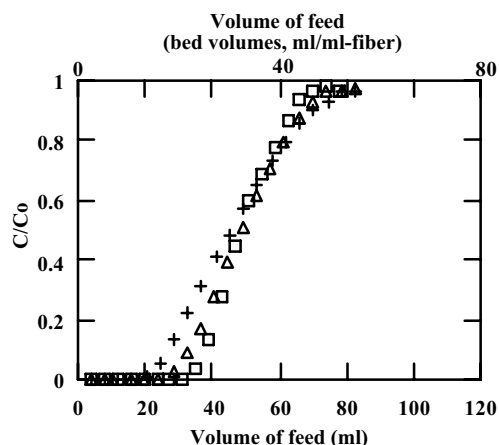


Fig. 5 Column mode adsorption of boric acid with FTris-f. Column: 1.5 ml of wet FTris-f (0.4 g). Feed: 0.01 M boric acid. Flow rate: □ 10 h⁻¹, Δ 20 h⁻¹, + 50 h⁻¹. For detailed conditions, refer to Table 3.

The functional group of commercially available boric acid selective resins, such as Diaion CRB02 and Amberlite 743, is NmgI. Thus, of interest is the removal of boric acid with FNmgI-

f column, and Fig. 6 shows the results. Up to flow rate of 20 h^{-1} , breakthrough profiles are little affected by flow rates. With a further increase in flow rate, breakthrough points became smaller. In column mode uptake of boric acid with fibers having polyol groups, therefore, breakthrough profiles depend on flow rates of feeds different from cases of metal ion uptake by fibrous cation exchangers having oxy acid groups of phosphorus. In cases of these cation exchange fibers, breakthrough profiles of cations are independent of flow rates up to extremely high flow rates of 1000 h^{-1} .

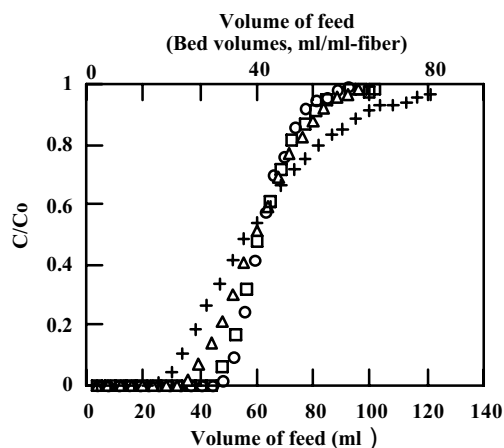


Fig. 6 Column mode adsorption of boric acid with FNmgl-f column: 1.5 ml of wet FNmgl-f (0.4 g). Feed: 0.01 M boric acid. Flow rate: \circ 10 h^{-1} , \square 20 h^{-1} , \triangle 50 h^{-1} , $+$ 100 h^{-1} . For detailed conditions, refer to Table 3.

Thus, adsorption rates of boric acid by the fibrous adsorbents proposed in this work are not so extremely fast as those of other fibrous adsorbents. However, FNmgl-f can take up boric acid much faster than commercially available resins having Nmgl as shown in Fig. 7, which shows breakthrough curves of boric acid during its adsorption from a boric acid spiked seawater sample with Diaion CRB02 and FNmgl-f columns.

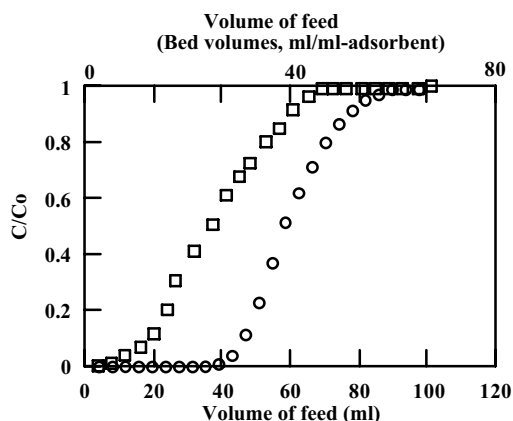


Fig. 7 Adsorption of boric acid from seawater containing ca. 10 mM of boric acid. \square Diaion CRB02, \circ FNmgl-f. Flow rates of feed were 20 h^{-1} for Diaion CRB02 and 40 h^{-1} for FNmgl-f. For detailed conditions, refer to Table 4.

The feed was supplied to Diaion CRB02 and FNmgl-f columns at flow rates of 20 h^{-1} and 40 h^{-1} , respectively. In spite of the faster flow rate of feed, FNmgl-f column gives a much larger breakthrough capacity for boric acid than Diaion CRB02 one as shown in Table 4.

The present work gives fibers having grafted polymer chains to which Tris or Nmgl is fixed. Nmgl based fiber showed higher uptake of boric acid than Tris based one. This seems to be natural, because Nmgl has 5 hydroxyl groups but Tris only 3 ones. Compared with a commercially available resin Diaion CRB02, both Tris and Nmgl based fibers exhibit much faster kinetics in the adsorption of boric acid. Thus, the method proposed by this work is one of promising approaches to improve rates of boric acid specific adsorbents.

Table 3 Performances of FTris-f and FNmgl-f columns

Flow rate (h^{-1})	Volume of feed supplied (BV^{a})	C_0^{b} (mM)	Total uptake of B (mmol/g)	BP $^{\text{c}}$ (BV^{a})
FTris-f column				
10	51.9	9.80	1.0	23(0.86) $^{\text{d}}$
20	54.9	10.2	1.0	20(0.75)
50	55.3	9.76	0.98	16(0.57)
FNmgl-f column				
10	61.3	10.1	1.5	32(1.2)
20	67.4	9.94	1.3	31(1.2)
50	64.0	9.74	1.4	25(0.92)
100	80.8	10.1	1.4	19(0.73)

$^{\text{a}}$ Bed volumes. $^{\text{b}}$ Concentration of boric acid in feed.

$^{\text{c}}$ Breakthrough point. $^{\text{d}}$ Figures in parentheses are breakthrough capacity in mmol/g.

Table 4 Removal of boric acid from seawater.

Flow Rate (h^{-1})	Volume of feed supplied (BV^{a})	C_0^{b} (mM)	Total uptake of B (mmol/g)	BP $^{\text{c}}$ (BV^{a})
FNmgl column				
40	64.7	9.95	1.2	28 (1.1) $^{\text{d}}$
Diaion CRB02 column				
20	67.7	9.75	0.72	9(0.3)

$^{\text{a}}$ Bed volumes. $^{\text{b}}$ Concentration of boric acid in feed.

$^{\text{c}}$ Breakthrough point. $^{\text{d}}$ Figures in parentheses are breakthrough capacity in mmol/g.

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