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Selective boron extraction by polymer supported 2-hydroxylethylamino propylene glycol functions

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Abstract

Boron sorption ability of polymer supported 2-hydroxyethylamino propylene glycol functions was investigated. 2-hydroxyethylamino propylene glycol was prepared by reaction of glycidol with excess ethanolamine in *N*-methyl, 2-pyr-rolidone (NMP). This was reacted with terpolymer of glycidyl metacrylate (0.4 mol) with methyl metacrylate (0.5 mol) and divinylbenzene (0.1 mol) which was prepared in spherical beads form $(210-422 \ \mu m)$ by suspension polymerization.

The resulting terpolymer having hydroxyethylamino propylene glycol functions (1.82 mmol g⁻¹) was found to be as efficient as previously reported iminodipropylene glycol functional resins in removal of trace boron from water. The resin showed a boron loading capacity of 1.6 mmol g⁻¹. Nearly second-order kinetics, with respect to the boric acid ($k = 1.65 \text{ mol } l^{-1} \text{ s}^{-1}$, with a correlation factor of 0.99129) was determined in non-buffered conditions.

It was observed that, more than 95% of boron is extracted by this resin from very dilute H_3BO_3 solution (100 ppm initial concentration) in less than 30 min of contact time. Splitting of sorbed boron can be achieved by simple acid leaching (4 M HCl) and regenerated by NaOH (0.1 M) solution.

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1. Introduction

Boron is widely distributed on the earth, mainly in the form of boric acid or borate salts. Presence of boron in irrigation water, as low as 4 ppm, induces marked plant stunting effect. Although no any harmful effect of boron on living organism has been reported, World Health Organization (WHO) recommends a maximum boron concentra-

* Corresponding author. *E-mail address:* bicak@itu.edu.tr (N. Bicak). tion of 0.3 mg l^{-1} for drinking water. The same norms are recommended when seawater is used as a source of water.

Boron mines and detergent wastes are considered as the main origins of boron contaminants in water. Among various methods studied, such as adsorption on magnesium oxide [1] and ion exchange resins [2], polymeric boron chelating resins have proven to be more efficient sorbents when trace boron is to be removed. Polymer bound sugar derivatives such as *N*-methyl D-glucamine [3], sorbitol [4] and mannitol have been employed successfully in removal of trace

boron. However regenerabilities of those materials are limited. For instance boron specific resin Amberlite IRA-743 with sorbitol functional groups [that is, $R-CH_2-N(CH_3)-C_6H_8(OH)_5$] forms complexes with boron and is highly specific. Using this resin, it is possible to reduce water's boron concentration below 1 ppm [5]. Despite a boron removal efficiency of 90%, this process is unsatisfactory because of expensive resin regeneration and capacity loss in each regeneration step [6].

Recently we have introduced polymer supported imino-bis-propyleneglycol function as boron selective chelating group. It was demonstrated that, these materials are also very efficient in sorption of trace boron from water [7]. In a detailed study, Smith et al described modification of branched polyethyleneimines with suitable epoxy compounds to give monool, diol and triol functions on each amino group. They proved that polymers possessing more hydroxyl groups around the amine nitrogen are better boron chelators. It was demonstrated that, more than 99.5% of boron can be removed from dilute boric acid solution by the polymers with triol chelating units on each amine group [8].

Since bis-propyleneglycols are formed by ring opening of the oxirane functions in those studies, the resulting *vic*-diols created on polymeric supports must be *trans*- to each other.

Although some authors suggest *cis*-diol behavior in *vic*-diols formed by ring opening of the epoxy moiety [9], easy recovery of loaded boron in the present case (see following section) implies boron chelating mostly via *trans*-propanediol. Both isomers may form boron complex, but the *cis*-isomer is expected to form more stable complex. In this configuration a neutral boron ester formation seems to be favor. But tetra coordinated borate formation is still possible with the helps of additional hydroxy group formed during ring opening of the epoxy function on the GMA component of resin. In other words boron binding by this chelating group occurs either by neutral boron ester formation or by formation of negatively charged borate.

In the following studies, we have also investigated boron binding properties of polymer supported imino-bis-(2,3-cis-propanediol) functions. This resin with cis-diol functionality was found to be rapid in boron uptake while the capacity per chelating group was retaining almost the same [10]. However the recovery of sorbed boron by acid leaching, in that case, was very slow due to formation of highly stable tetra coordinated borate esters. This result revealed that, recovery of boric acid by acid treatment is easy when hydroxy groups of *vic*-diols are in *trans*-configuration and three of four newly introduced hydroxy groups take part in chelating with boron as mentioned above. We have concluded that, if three of the hydroxy groups are employed, the fourth hydroxyl group might not be necessary in boron binding.

In order to prove this assumption, in this work we have studied boron binding efficiency of 2-hydroxylethylamino propylene glycol functions having one hydroxyl group less than the formers. It was concluded that, three hydroxy groups of 2-hydroxylethylamino propylene glycol, together with additional hydroxy group formed by the ring opening of the epoxy group might be satisfactory for the boron binding. For this purpose 2-hydroxylethylamino propylene glycol was prepared by reacting glycidol with ethanolamine. Then it was reacted with GMA (0.4 mol) based terpolymer beads with 3.4 mmol g^{-1} of oxirane group density. Characterization and boron uptake ability of the resulting polymer was investigated. In this study, the kinetics of boron sorption, effect of foreign ions and regeneration conditions of the sorbent were investigated.

2. Experimental

All the chemicals used were analytical grade: glycidyl methacrylate (Fluka), methyl methacrylate (Fluka), divinyl benzene (Aldrich, 55% mixtures of *m* and *p* isomers, the remainder is 3- and 4-ethylvinyl benzene). They were used as supplied. Ethanolamine (Merck) was purified by vacuum distillation (70–73/0.5 mm) prior to use. Commercial glycidol partially polymerizes spontaneously upon standing especially when stored at room temperature. It was purified by distillation under reduced pressure (67–69 °C/0.5 mm), before use.

2.1. Preparation of GMA–MMA–DVB terpolymer beads

The terpolymer beads were prepared by suspension polymerization of GMA (0.4 mol), MMA (0.5 mol), DVB (0.1 mol) mixture as described before [3]. The vacuum dried bead product was sieved and the 210–422 μ m size of fraction was used in the next modification. Epoxide content of this fraction was determined as $3.40 \pm 0.03 \text{ mmol g}^{-1}$, by the pyridine–HCl method given in the literature [11].

2.2. Preparation of 2-hydroxylethylamino propylene glyscol

(IUPAC naming: 1-[2-hydroxylethylamino] 2, 3-propanediol).

Glycidol (32.8 ml, 0.5 mol) was added drop wise to excess ethanolamine (107 g, 1.5 mol) in a 250 ml of two-necked canonical flask equipped with a reflux condenser and a dropping funnel, while stirring at room temperature. The reaction was exothermic. After completion of the addition, the flask was placed in an oil bath at 120 °C and excess of ethanolamine was distilled of at 70–73 °C/0.5 mm. The residual viscous liquid, 2-hydroxyethylamino propylene glycol was colorless and pure enough for the next reaction. The yield was 52.5 g (76.6%). Purity of the product was checked by TLC (with basic alumina using dimethoxy ethane as solvent).

2.3. Modification of the bead polymer by 2-Hydroxylethylamino propylene Glycol

Five grams of the bead polymer was added portion wise to the stirred solution of 7.3 g 2-hydroxyethylamino propylene glycol at room temperature. The mixture was placed on a continuous shaker and shaken for 24 h at room temperature. The reaction content was heated to 70 °C for 15 min, filtered and washed with 250 ml of water. The product was transferred to a beaker with 250 ml water and left in contact overnight. The filtered product was filtered, washed several times with water (5 × 200 ml) and dried under vacuum at 45 °C for 48 h. The dry product weighed 6.627 g.

2.4. Determination of the amine content

A sample of the above product (0.5 g) was mixed with 10 ml of 1 M HCl solution and stirred with a stirring bar for 24 h at room temperature. The mixture was filtered and unreacted acid content was determined by titration of 2.5 ml of the filtrate with 0.1 M NaOH solution in the presence of phenolphthalein color indicator. Thus 5.96 ml of the NaOH consumption against the blanck indicates 1.82 mmol g⁻¹ of total amine content.

2.5. Determination of the boron loading capacity

Maximum boron loading capacity of the resin was determined by interaction of 0.25 g of the polymer sample with artificial boric acid solution. The sample was wetted with 5 ml of distilled water for 4 h. Three grams of H₃BO₃ (4.852 × 10⁻² mol) was dissolved in water and diluted to 100 ml. Twenty five milliliter of this solution was added to the above mixture and the mixture was shaken on a shaker for 24 h at room temperature. After filtration, the residual boron content of the solution was determined by titration 2 ml of the filtrate in the presence of 10 ml of 0.5 M sorbitol solution using phenolphthalein as color indicator, as described in the literature [12]. Thus 13.44 ml of 0.06 M NaOH (F = 0.97) consumption (13.9 ml for the blank) indicated a H₃BO₃ loading capacity of 1.6 ± 0.1 mmol g⁻¹ of the polymer sample.

2.6. pH-Dependent boron sorption

A series of buffer solution was prepared (100 ml of each) by using appropriate combination of 0.2 M sodium acetate and 0.2 M acetic acid solutions for pH 2, 4.05, 5 and 0.06 M sodium hydrogen phosphate and 0.06 M potassium dihydrogen phosphate for pH 8, respectively. In each buffer solution, 1.5 g (24.3 mmol) H_3BO_3 was dissolved and made up 50 ml, so that the final concentration to be 0.485 M.

The resin samples (0.5 g of each) were interacted with 20 ml of these buffered solutions for 24 h. Then, the solutions were filtered and residual boron contents of the filtrates were assigned colorimetrically ($\lambda = 585$ nm) by carminic acid method [13]. The data collected are given in Table 1.

2.7. Boron sorption in the presence of foreign ions

The above experiments were repeated in the presence of some common ions such as Ca(II), Mg(II) and Fe(III). For this purpose, binary mixtures of H_3BO_3 with one of the foreign ions were prepared so that the concentrations of the foreign ion were adjusted to 0.14 M. The foreign ion sources were

Table 1				
pH-Dependent boron	sorption	capacity	of the	resin

[H ₃ BO ₃] (M)	Buffer (pH)	Capacity (mmol g ⁻¹)	Recovered $[H_3BO_3]^a$ (mmol g ⁻¹)
0.485	2.0	0.86	Nd
0.485	4.05	0.98	0.94 ± 0.03
0.485	5.0	1.54	Nd
0.485	7.4 (non- buffered)	1.60	1.52 ± 0.03
0.485	8.0	1.68	1.54 ± 0.05

Nd: Not determined.

^a By analysis of the acid leaching solution with carminic acid.

CaCl₂, MgSO₄ · 7H₂O and Fe (NO₃)₃ · 9H₂O. The polymer sample (0.5 g) was interacted with 20 ml of the solutions for 24 h at room temperature. Non-absorbed boric acid and the metal ion were assayed separately by analysis of each component. Ca(II), Mg(II) and Fe(III) ions were determined by titration with disodium salt of ethylenediamine tetraacetic acid (EDTA) solution (0.1 M). The boric acid concentrations were assayed by the carminic acid method, as described above. These experiments were repeated also in the absence of boric acid to determine the extracted amounts were calculated and are collected in Table 2.

2.8. Boron sorption kinetics of the resin

Batch kinetics experiments were carried out using highly dilute boric acid solutions as follows: The resin (1 g) was wetted with 5 mL distilled water for 30 min. To this mixture there was added 100 mL of boric acid solution (0.6 g H₃BO₃ l⁻¹), so as boron concentration of the initial solution to be 100 ppm (9.24 × 10⁻³ M). While stirring with a magnetic bar, aliquots (2 ml) were taken at appropriate time intervals and filtered. Residual boron contents of the filtrates were determined colorimetrically as described above. The data derived were used to build up of the concentration–time plots in Fig. 3.

2.9. Desorption of boron from loaded samples

Acid leaching method was used for desorption of the boron as follows: Loaded resin sample (0.25 g) was left in contact with 5 ml of water for 4 h. Then 20 ml of 4 M HCl solution was added and stirred at room temperature for 24 h. It was filtered and 2 ml

Table 2

Effect of foreign ions on boron sorption in non-buffered conditions

[H3BO3] (M)	Foreign ion	Foreign ion sorbed (mmol g^{-1})	Boron uptake (mmol g^{-1})
0.41	0.14 M,	0.10	1.62 ± 0.03
	Mg(II)		
0.41	0.14 M,	0.13	1.60 ± 0.03
	Ca(II)		
_	0.20 M,	0.11	_
	Mg(II)		
_	0.20 M,	0.13	_
	Ca(II)		
0.41	0.20 M,	0.34	1.55 ± 0.04
	Fe(III)		

of the filtrate was titrated with 0.05 M KOH solution in the presence of phenolphthalein indicator. At the end of neutralization of the excess hydrochloric acid, 10 ml of 0.5 M D-sorbitol solution was added to the mixture. Consumption of 0.38 ml additional KOH solution reveals a 1.52 mmol of desorbed boron per gram of loaded sample.

Desorbed quantities of boron from the samples loaded at different pH's are given in Table 1.

After the acid treatment the polymer samples were filtered, washed with 20 ml of 0.1 M NaOH solution and excess of distilled of water (3×50 mL). Boron-free polymer samples so obtained are reusable.

3. Results and discussion

In the present work, GMA based resin was modified with 2-hydroxyethylamino propylene glycol for selective boron extraction as depicted in Scheme 1. The GMA based resin beads (210–422 μ m) was prepared by crosslinking terpolymerization of DVB (0.1 mol)–MMA (0.5 mol)–GMA (0.4 mol) mixture in aqueous suspension. MMA was selected as diluting co-monomer, to avoid additional crosslinking by reaction with two reacting sites of modifying molecule.

Analysis of the epoxy content of the spherical bead product gave 3.4 mmol g^{-1} , which is slightly higher than calculated (3.33 mmol g^{-1}) from the feed composition, presumably due to the small reactivity differences of GMA compared with MMA [14]. The resulting beaded resin with 3.4 mmol g^{-1} oxirane content was modified with 2-hydroxyethylamino propylene glycol in NMP.

2-Hydroxyethylamino propylene glycol was prepared by reaction of glycidol with 3-fold excess of ethanolamine without solvent. The reaction was exothermic. After removal of excess ethanolamine under vacuum, the product was obtained as viscous clear liquid which is pure enough as evidenced by NMR spectra.

In its ¹H NMR spectrum (Fig. 1) five protons on the methylol carbons represent the signal at 4.8 ppm. The broad signal in 3.4–4.0 ppm range is associated with the replaceable protons together with those of CH_2 –N group of the ethanolamine component. Whereas, proton signals of the CH_2 –N group of the propylene glycol component is observed as separate peak at 2.7 ppm.

¹³C NMR spectrum of the product (Fig. 2) shows five different types of carbon signals having nearly equal intensities. The down field signals appearing



Scheme 1. Preparation 2-hydroxyethylamino propylene glycol functional resin and its boron uptake.



Fig. 1. ¹H NMR spectrum of 2-hydroxyethylamino 2,3-propanediol in DMSO-d₆.

at 61.5, 65.5 and 70 ppm are associated with the carbons bearing hydroxyl groups. The other two signals at 51.3 and 52 ppm represent the carbons attached to nitrogen atom. This result clearly indicates formation of 2-hydroxyethylamino 2,3-propanediol with reasonaly high purity.



Fig. 2. 13 C NMR spectrum of 2-hydroxyethylamino 2,3-propanediol in CDCl₃.

2-Hydroxyethylamino propylene glycol so obtained was reacted with the GMA resin in NMP. Acid titration of the modified resin revealed 1.82 mmol g⁻¹ of amine content. Considering with the mass increase in the modification, this corresponds to 73.5% of conversion yield. This amount is relatively lower than the theoretical conversion, most probably due to the bulkiness of hydroxyethylamino propylene glycol group.

3.1. The Boron uptake

Hydroxyethylamino propylene glycol functions incorporated into the polymer structure act as boron chelating agent. Maximum boron loading capacity of the resin was found to be 1.60 mmol g^{-1} , in non-buffered conditions.

Four hydroxy groups around nitrogen of the amino group can be considered as unit binding site for sorption of each boric acid molecule. Then, the boron uptake capacity found $(1.6 \text{ mmol g}^{-1})$ accounts for 87.9% of the theoretical capacity. Interestingly, no appreciable change occurs in the pH of the solution during boron sorption, and the pH values lie in the 6-6.5 range. Since the vicinal diols of hydroxyethylamino propylene glycol in are in *trans*- form, boron uptake by anionic borate ester formation seems to be less favorable. However, anionic borate ester formation is not completely avoidable due to presence of new formed hydroxy function by ring opening of the epoxy group on the polymer and boron binding may occur by forming both structures.

But in the case of anionic borate ester formation, strong acidity of the cyclic borate is being compensated by the amino group and non-changing pH during interaction with the boric acid solution can not ascribed to only neutral boron ester formation.

pH-dependent boron loading experiments indicate that boron uptake sharply rises above pH 4.0 due to greater stability of the supported boron complex at high pH levels (Table 1). Boron sorption capacity of the resin slightly increases by increasing pH and reaches 1.68 mmol g^{-1} at pH 8. This implies that, basidity of the amino group of the resin provides additional contribution in boron binding. This result is consistent with those observed in boron–*N*methylglucamine complexes [15].

3.2. Effect of foreign ions

In order to examine the possible interference of foreign ions, boron uptake experiments were carried out in the presence of Ca(II), Mg(II) and Fe(III) ions. The experiments showed that, these foreign ions are also absorbed in appreciable quantities in the presence or absence of boric acid. The highest sorption is observed for Fe(III) ions $(0.34 \text{ mmol g}^{-1})$. Sorption of the foreign ions observed must be due to precipitation of their hydroxides on the polymer particles. Weak basidity of the tertiary amino group on the polymer is responsible for the metal hydroxide precipitations as it was demonstrated on imino-bis-propyleneglycol functional resins [7]. Fortunately sorption of those ions does not reduce the boron sorption capacity. This must be due to boron sorption ability of those metal hydroxides.

As a result, the presence of the foreign ions studied does not reduce the boron uptake capacity of the resin.

3.3. Boron uptake kinetics

Batch kinetic method was employed for estimation of the boron sorption kinetics. The batch kinetic experiments were conducted using highly diluted boric acid solutions (with 100 ppm of initial boron concentrations) in order to examine efficiency of the resin material for removal trace boron.

Concentration-time plots in Fig. 3 indicate that, the boron sorption is reasonably fast. One gram of the resin sample is able to extract boric acid almost completely from 105 ml of H_3BO_3 solution with 100 ppm of initial boron concentration These results



Fig. 3. Concentration-time plots of boric acid solution (105 ml) with 100 ppm of initial boron concentration while contacting with 1 g resin sample.

obey nearly second-order kinetics with a rate constant of $k = 1.65 \text{ mol } 1^{-1} \text{ s}^{-1}$ (correlation factor: 0.99129), with respect to the boric acid.

3.4. Recovery of boric acid

Loaded polymer samples, when treated with 4 M HCl become almost boron-free (Table 1). In this way, 1.52 mmol boric acid is recovered per g of loaded sample. This accounts for about 95% of the charged. However, repeated acid treatment results in quantitative stripping of the boron.

Although, in this work, we have not tested recycling ability of the regenerated polymer samples, since 2-hydroxyethlamino propylene glycol functions are structurally similar to those previously studied polymer supported imino-bis-propylene glycols, it is more likely that this resin too is reusable in many cycles.

4. Conclusion

GMA based bead polymer with 2-hydroxylethylamino propylene glycol functions was determined to be efficient sorbent for selective removal of boric acid from aqueous solutions. Its characteristics, such as capacity per chelating unit, selectivity and regenerability are comparable with those of polymer supported imino-bis-propylene glycols and sugar derivatives which were reported in the literature.

Since 2-hydroxylethylamino propylene glycol is readily obtainable in sufficient purity, the reaction of the GMA based polymer with this compound gives boron selective resin. Although each of boron chelating units of this resin has one hydroxy group less than those reported iminodipropylene glycol functional resin, it shows reasonably selective boron sorption ability.

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