Polymer supported iminodipropylene glycol functions for removal of boron

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Abstract

Polymer supported iminodipropylene glycol functions have been shown to be efficient in chelation with boric acid and can be used for removal of boric acid at ppm levels. Glycidyl methacrylate (GMA)–methyl methacrylate (MMA)–DVB (divinyl benzene) terpolymer beads have been prepared and used as support. The polymer support with 3.4 mmol g^{-1} oxirane content can be readily modified by reacting with an excess of ethylene diamine, in high conversion yields (99.1%). Reaction of the latter with glycidol gives corresponding resin with aminopropylene glycol functions. The resulting resin has been demonstrated to be an efficient sorbent for removal of boron. The resin has 3 mmol g^{-1} of boron loading capacity and shows reasonably rapid sorption ability so that boron in 10 ml of H$_3$BO$_3$ solution (50 ppm) can be removed almost completely in less than 12 min of contact time by 0.5 g of polymer sample. Splitting of sorbed boron can be achieved by simple acid leaching (4 M HCl) and regenerated by NaOH solution (0.1 M).

1. Introduction

Boric acid and borates are environmentally hazardous chemicals owing to their plant stunting effect, especially when present at levels of more than 4 ppm in irrigation water.

The most important boron source in the world is located in West Anatolia and the region around the boron mines suffers from boron pollution. Wastes from the boron mines and boric acid plants are the main sources of the pollution.

Unfortunately there is as yet no economical method of boron removal from water. Perhaps the only commercial boron specific sorbent is polystyrene-based resin with *N*-methyl-D-glucamine functions, which emerged in the mid 1960s [1]. This resin has proven to be a powerful sorbent for removal of boron at ppm levels. However, during regeneration by acid treatment, an average 14% of activity loss has been reported [2].

The chemistry of boron indicates that molecules with vic-diols are capable of forming

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neutral boron esters or tetra alkyl borate type of compounds, even in aqueous solutions. Design of new boron-specific sorbents are based mostly on this key principle. Having many vicinal diol functions, sugar derivatives such as sorbitol and mannitol are preferred as chelating agents on polymer supports for boron uptake.

In our previous study, crosslinked polystyrene sulfonamide with sorbitol functions has been proven to be regenerable without activity loss in boron sorptions [3]. This material has high boron loading capacities in buffered solutions whereas in non-buffered conditions its capacity is somewhat less.

In a recent study, it has been demonstrated that the presence of a tertiary amine function is essential for an efficient chelation with boric acid [4]. The role of the tert-amine function must be neutralisation of the proton brought about by formation of tetra borate complex. Based on this principle, in our recent studies, we have developed two glycidyl methacrylate-based polymers with *N*-methyl-D-glucamine functions starting either from monomer [5] or crosslinked polymer [6]. Both polymers are efficient and regenerable in boron sorption. All the useful materials developed so far seem to be confined only to polymer supported *N*-methyl-D-glucamine functions.

In searching for new functions for chelation with boric acid, we have noticed that iminodipropylene glycol functions have suitable structure matching with prerequisites for chelation with boric acid.

The boron chelating ability of iminodipropylene glycol function has been tested in our previous study, using the low-molecular weight compound, *N*-hexadecyl iminodipropylene glycol. In that study, its solution in 2-ethyl hexanole has been demonstrated to be an efficient chelating agent for selective extraction of boric acid from aqueous solutions [7].

In the present study, this analogy has been extended to polymer supported iminopropylene glycols as boron specific sorbent. In this study, the kinetics of boron sorption and regeneration conditions for the sorbent has been 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), ethylene diamine (Merck), glycidol (Fluka). They were used as supplied.

2.1. Preparation of GMA–MMA–DVB terpolymer beads

The terpolymer beads were prepared by suspension polymerisation of GMA (0.4 mol), MMA (0.5 mol), DVB (0.1 mol) mixture in 120 ml toluene with 350 ml of distilled water as continuous phase.

The stabilizer used was 0.8 g styrene–maleic acid copolymer as described before [6]. The vacuum dried bead product was sieved and the 210–420 µm size fraction was used in the next modification.

Epoxide content of this fraction was determined as 3.40 ± 0.08 mmol g^{-1}, by the pyridine–HCl method given in the literature [8].

2.2. Modification of the bead polymer by ethylene diamine

Ten grams of the bead polymer were added portion wise to the stirred solution of 20 ml (0.3 mol) ethylene diamine in 40 ml 2-methyl pyrrolidone at 0 °C. The mixture was placed on a continuous shaker and shaken for 24 h at room temperature. The reaction content was 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 washed several times with water (5×200 ml) and dried under vacuum at room temperature for 48 h. The dry product weighed 12.3 g.

2.3. 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 un-reacted 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; 18.1 ml of the NaOH consumption indicates 5.52 mmol g^{-1} of total amine content.

2.4. Modification of the amino groups with glycidol

Then, 10.2 g of the above product was dispersed in 15 ml of 2-methyl pyrrolidone. The mixture was stirred mechanically and 6 ml (0.0904 mol) of glycidole (3.1 equivalent of amine content) was added dropwise to the mixture.

Stirring was continued for another 6 h at room temperature and 1 h at 50 °C in a silicone oil bath. The mixture was filtered and washed five times with water (200 ml). The product was dried at 50 °C under vacuum for 24 h. The yield was 16.2 g.

2.5. Determination of the boron loading capacity

Polymer sample (1 g) was wetted with 10 ml of distilled water in a conical flask. To the flask, 40 ml of 0.54 M H_3BO_3 solution was added, so its final concentration was 0.43 M. No buffer solution was used in the experiments to avoid possible interference of the buffer components. The flask was closed and shaken with a continuous shaker, at room temperature for 24 h. Thus, 5 ml of the filtrate was mixed with 10 ml of 0.5 M sorbitol solution and titrated with 0.1 M NaOH solution using phenolphthalein as color indicator, as described before [9].

A titer consumption of 19 ml indicates 0.38 M concentration of the residual boric acid. The mixture was filtered and residual boron in the filtrate was assayed. Based on the difference in the initial and final H_3BO_3 concentrations, the capacity was found to be 3.0±0.1 mmol g^{-1}.

2.6. pH-Dependent boron sorption

A series of buffer solutions was prepared (100 ml of each) using appropriate combination of 0.2 M NaOH and 0.2 M CH_3COOH solutions (pH.2.7, 3.4, 4.0, 6.8). In each buffer solution, 1.7 g (27.5 mmol) H_3BO_3 was dissolved and made up to 50 ml, so the final concentration was 0.43 M.

The boron loading experiments were repeated using those buffered H_3BO_3 solutions, as described above. The data collected are listed 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 the concentration of the foreign ion was 0.14 M. Ion sources of the foreign ions were $CaCl_2$, $MgSO_4.7H_2O$ and $Fe(NO_3)_3.9H_2O$. 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 complexometric titration with EDTA solutions. The boric acid concentration was assayed by the titrimetric method, as given above. These experiments were also repeated in the absence of boric acid to determine the extractability of the

Table 1
Boron sorption and desorption characteristics of the resin at room temperatures

$[H_3BO_3]$ (M)	Buffer	Capacity (mmol g^{-1})	Recovered $[H_3BO_3]$[a] (mmol g^{-1})
	Non-buffered		
0.43	(pH 6–6.5)	3±0.1	2.84±0.05
0.43	6.8	3.1	–
0.43	4.05	3.0	2.9±0.05
0.43	3.4	2.7	–
0.43	2.7	1.8	–

[a] By analysis of the acid leaching solution with carminic acid.

Table 2
Effect of foreign ions on boron sorption in non-buffered conditions

$[H_3BO_3]$ (M)	Foreign ion	Foreign ion sorbed (mmol g^{-1})	Boron uptake
–	Mg(II), 0.2 M	0.2	–
–	Fe(III), 0.2 M	0.8	–
–	Ca(II), 0.2 M	0.3	–
0.41	Mg(II), 0.14 M	0.2	3.1 ± 0.05
0.41	Ca(II), 0.14 M	0.34	3.0 ± 0.07

foreign ions alone. 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 5.34×10^{-3} M H_3BO_3 solution as follows:

Resin (1 g) was wetted with 5 ml of water for 3 h prior to addition of 100 ml of H_3BO_3 solution (5.6×10^{-3} M). The mixture was stirred with a magnetic stirring bar. Five-milliliter aliquots were taken at appropriate time intervals and filtered. Residual boron contents of the filtrates were determined colorimetrically ($\lambda = 585$ nm) by the carminic acid method [10]. The data derived were used to build up the concentration–time plots in Fig. 1.

2.9. Desorption of boron from loaded samples

Boron contents of the loaded polymer samples (approximately 0.5 g of each) were desorbed by treating with 4 M HCl solution (20 ml per g of the loaded samples), for 24 h, at room temperature.

Desorbed boron in the filtered acid solution was assayed by the titrimetric method as described above. This analysis gave 7.1×10^{-2} mol l^{-1} boron concentration in the acid solution, which corresponds to 2.84 mmol per g of the loaded polymer. The analytical results for the samples loaded with boron from boric acid solutions with different pH values are given in Table 1.
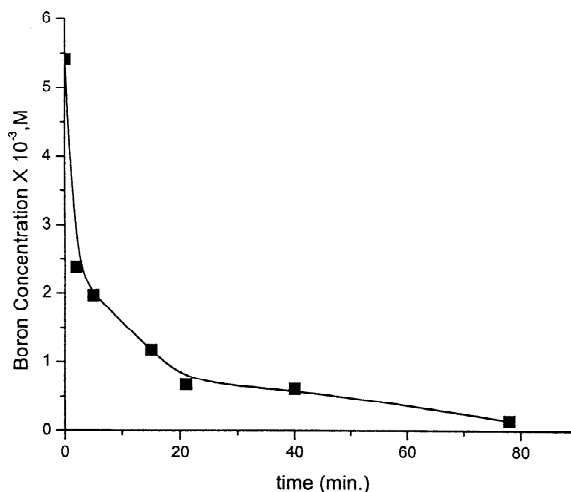

Fig. 1. Concentration–time plots for 105 ml of 5.34×10^{-3} M $[H_3BO_3]$ solutions (containing 57.7 ppm boron) interacted with 1 g dry resin.

The filtered polymer samples were washed with an excess of water, treated with 20 ml of 0.1 M NaOH solution and washed again with distilled water. This procedure gives almost boron-free samples, which are reusable.

3. Results and discussion

In the present work, an alternative boron specific resin has been developed according to the reaction pathways as depicted in Scheme 1.

In the first step, a polymeric support with reactive epoxy groups was prepared by cross-linking terpolymerization of DVB (0.1 mol)–MMA (0.5 mol)–GMA (0.4 mol) mixture. The polymerization was carried out by suspension polymerization methodology using toluene as diluent and water as continuous phase. 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. This might be due to the small reactivity differences of GMA compared with MMA [11]. Another reason may be due to the location of GMA segments on the outer parts of the particles, during the polymerization.

Scheme 1.
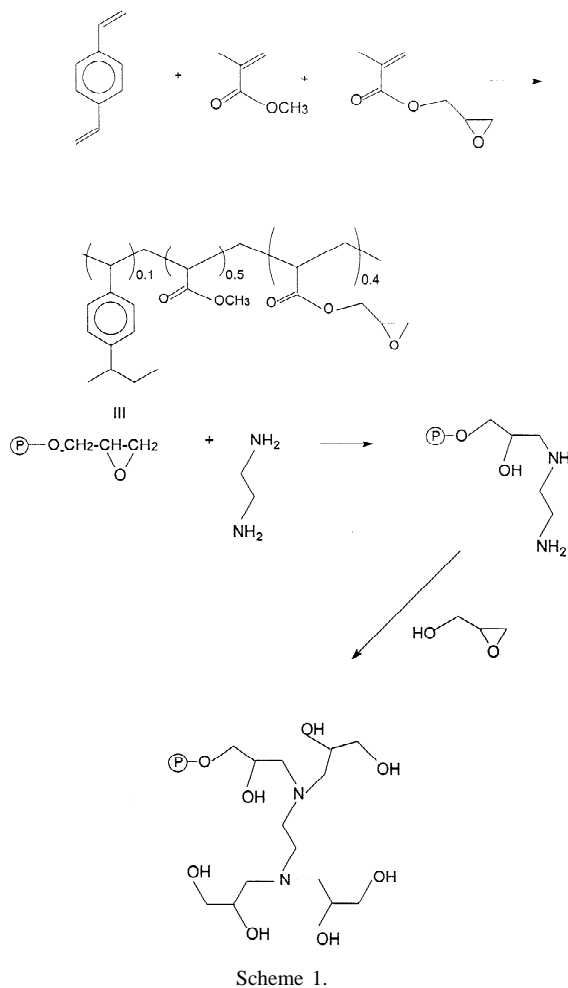
This material, when treated with excess ethylenediamine, gives corresponding polymer with diamino groups. The amine content of this polymer (5.52 mmol g^{-1}) implies a high conversion of the oxirane functions (99.1%). Obviously, the use of excess ethylene diamine minimizes the reaction of the second amino group with other oxirane function. Also the oxirane functions are isolated from each other by the co-monomer segments, which provide a kind of sterical hindrance to react an attached ethylene diamine function with another GMA segment in the crosslinked matrix. Further modification of the amino groups with equivalent amount of glycidol, yield iminopropylene

glycol functions. The mass increase (63%) in this step implies almost quantitative conversion of the amine functions.

3.1. Boron uptake

Vicinal diol functions incorporated into the polymer structure act as chelating agent for basic acid, by forming cyclic boron esters. Boron loading capacity of the sorbent is about 3.0 mmol g^{-1}, in non-buffered conditions.

There are two sites available for boron binding. Since the molecular weight of the segment possessing iminopropylene glycol functions is 424 Da, the average molecular weight of 10 repeating units of the polymer would be 2432.6 Da then, the theoretical boron sorption capacity would be $(0.4 \times 2 \times 1000)/232.69 = 3.44$ mmol. Practical capacity, 3 mmol g^{-1} accounts for 87.2% of the theoretical capacity.

Interestingly, no appreciable change occurs in the pH of the aqueous solutions during boron sorption, and the pH values lie in the 6–6.5 range. Reaction of glycidol with amino groups of the polymer should give trans diol functions by ring opening of the oxirane functions. Since the vicinal diols are in *trans* form, anionic borate ester formation seems to be less favorable. However, anionic borate ester formation is not completely avoidable and boron binding may occur in both structures.

In the case of anionic borate ester formation, strong acidity of the cyclic borate is being compensated by the amino group which drives chelation of the boric acid. pH-dependent boron loading experiments indicate that boron ester on the sorbent is stable at pH values above 4.0. This result is inconsistent with those observed in boron–sugar complex [12] functions.

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 which are most common ions in

water sources. Beforehand, the extractability of those ions was studied in the absence of boron. The ethylenediamine unit in the resin structure is expected to impart some chelating effect for the transition metal ions, especially for Fe(III) ions.

Fortunately, extracted amounts of Fe(III) are around 0.8 mmol g^{-1} in non-buffered solutions. In the present case, tetracoordination of Fe(III) through two ethylenediamine functions has been avoided by isolation with the MMA co-monomer segments.

This is reminiscent of the ammonia–Fe(III) reaction yielding ferric hydroxide in aqueous solutions. Therefore the Fe(III) ion sorption observed must be due to precipitation of ferric hydroxide on polymer particles, rather than true coordination.

This explanation also holds for Ca(II) and Mg(II) ions, i.e. minor sorptions (0.2 mmol g^{-1}) detected are due to precipitation of their hydroxides. As a result, the presence of Ca(II) or Mg(II) ions does not bring any significant interference on boron uptake.

About 0.2 mmol g^{-1} capacity loss in the presence of 0.2 M Fe(III) may not be significant because its presence, in such a high concentration, is not common in water sources.

3.3. Boron uptake kinetics

Since the extraction of boric acid by solid supported diol functions is a heterogeneous reaction in nature, the kinetics of boron uptake must depend also on the stirring rate. Batch kinetic experiments, therefore, provide a rough estimation of the profile of the sorption kinetics. In the batch kinetic experiments, very dilute (57.7 ppm of boron) solutions were used to examine the efficiency of the resin material for boric acid in low concentrations.

Concentration–time plots in Fig. 1 show that boric acid in 105 ml of H_3BO_3 solution (5.34×10^{-3} M, 57.7 ppm boron) can be extracted by 1 g of resin in about 20 min of contact time at moderate stirring rates (350–400 rpm). This result reveals the applicability of the material

for very low boron concentrations. The concentration–time profile in Fig. 1 indicates a second-order kinetics, $k = 0.67$ M^{-1} s^{-1} (with a correlation factor of 0.989) with respect to the boric acid concentration. The rate constant found can be considered as satisfactory from an application view point. In the sorption kinetics, the validity of the particle diffusion model has been tested using the mathematical procedure proposed by Native et al. [13]. Thus $1 - 3(1 - x)^{2/3} + 2(1 - x)$ versus time plot (where x denotes the ratio of sorbed amount to the capacity) gives a linear plot for the earlier stage (up to 20 min) of the process. This result can be ascribed to a 'shell progressive mechanism' controlled by film diffusion. However, the plot deviates greatly from linearity after 20 min. As a result, the kinetics data do not match well with the above mechanism, and this is most probably due to low porosity of the bead particles.

3.4. Recovery of boric acid

Loaded polymer samples, when treated with 4 M HCl become almost boron-free (Table 1). In this way, 2.84 mmol boric acid is recovered per g of loaded sample, which accounts for about 95% of the capacity. However, repeated acid treatment results in quantitative stripping of the boron.

In conclusion, the polymer resin with iminopropylene glycol functions exhibits reasonable efficiency in extraction of boric acid from aqueous solutions. Its characteristics, such as high boron sorption capacity, regenerability and appreciable selectivity are comparable with those of polymer supported sugar derivatives. Since the material described is readily obtainable from simple reagents, it can be considered as an alternative potential candidate in large-scale boron removal.

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