

Modification of crosslinked glycidyl methacrylate-based polymers for boron-specific column extraction

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Abstract

Terpolymers of glycidyl methacrylate (0.4 mol) with methyl methacrylate (0.5 mol) and divinyl benzene (0.1 mol) in spherical beads form have been modified with *N*-methyl-*D*-glucamine in *N*-methyl pyrrolidone solvent. Polymers with (2.05 mmol g⁻¹) functionality have moderate swelling ability (1.81 v/v_0) and show excellent boron uptake ability (2.15 mmol g⁻¹) for extraction of trace quantities of H₃BO₃ from aqueous solutions. The resinous polymer with 110–210 µm size has a reasonable breakthrough capacity (0.835 mmol g⁻¹) and a sharp elution profile in the column extractions. No interferences come from Ca(II), Mg(II) and Fe(III) ions (0.1 M), though slightly in the presence of these ions due to coprecipitation of borates by the metal hydroxides formed on the resin particles. The capacity of the resin and flow rate do not change even after 20 recyclings in the column extractions. The method has been shown to be promising for large-scale boron extractions from aqueous solutions. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Extraction of trace boric acid or borates using crosslinked polymer resins is of special importance due to the plant-stunting effect of boron when present in irrigation water even in trace quantities as low as 4 ppm. The effect is extremely drastic in the regions of boron-mining in west Anatolia [1]. Although successful reports of liquid–liquid extraction of boric acid using organic soluble vic-diols have appeared [2–4] these methods are applicable only for

relatively concentrated boric acid solutions. Removal of trace quantities of boric acid is a great problem and more important is that increasing trends in boron levels in rivers have become alarming owing to the extensive use of various perborate formulations as detergent additives.

Removal of boron by chelation is based on the use of vic-diols which form stable chelates with boric acid and its salts in ordinary conditions.

Molecules with three or more hydroxyl functions tend to bind boric acid tightly by forming either neutral boron ester or borate complex anion with a proton as counter ion. Since

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hydroxyl functions are non-reactive for common metal ions and other species in ordinary conditions, complexation of these type of compounds produce a means of specific boron binding. Having six hydroxyl functions, sugar derivatives such as sorbitol and mannitol have exceptionally high boron binding abilities.

In accordance with this key principle, a boron-specific resin, polystyrene based resin with *N*-methyl-D-glucamine functions, emerged in the mid 1960s [5]. This commercial resin shows excellent efficiencies in boron uptake although some activity loss is observed in regeneration steps [6]. On the basis of boron chelation with vic-diols, in our previous studies we have developed a polystyrene sulfonamide resin with sorbitol functions which is effective when used together with buffer solutions [7]. In a related study, Japanese workers demonstrated that amine functionality is essential for high levels of boron chelation with polyols [8]. Apparently the role of the amine function is the capture of proton formed by diol complexes by boron. More recently we have prepared a vinyl monomer by reacting *N*-methyl-D-glucamine with glycidyl methacrylate. Its crosslinked polymers show perfect chelating ability specifically towards boric acid [9]. The only drawback of this material was its high swelling ability.

In the light of the previous studies we come to the following conclusions to prepare a perfect chelating resin for boron extraction from aqueous solutions.

- (i) The chelating group must have two or more hydroxyl functions which are on the adjacent carbon atoms.
- (ii) An amine function per one mole of boric acid is essential for a high chelation.
- (iii) The sorbent must not have hydrolysable linkages thus it must be regenerable by acid–base treatments.
- (iv) Preferably, the backbone of polymer sorbent must be as inert as possible and it must not contain electron-rich substituents on phenyl rings.

- (v) The polymer sorbent must have moderate swelling ability for continuous column extractions.

On the basis of the above criteria to prepare a perfect resin, in the present study we have obtained glycidyl methacrylate-based terpolymers in bead form. Its modification by *N*-methyl-D-glucamine gives a boron chelating polymer resin. In the study boron uptake ability and regeneration conditions of the resulting polymer sorbent have been investigated in column extraction conditions.

2. Experimental

Glycidyl methacrylate (GMA) (Fluka) and methyl methacrylate (MMA) (Fluka) were distilled before use. Divinyl benzene (DVB) (Aldrich), *N*-methyl-D-glucamine (Fluka), styrene (Fluka), maleic anhydride (Aldrich), boric acid (E.Merck), azobisisobutyronitrile (AIBN) (Fluka) and other chemicals were analytical grade chemicals, they were used as supplied.

2.1. Preparation of sodium salt of maleic acid–styrene copolymer

The styrene–maleic anhydride alternating copolymer (STMA) was prepared according to the procedure given in the literature [10].

2.2. Preparation of GMA-MMA-DVB terpolymer beads

A 1-l three-necked flask was equipped with a mechanical stirrer, nitrogen inlet and reflux condenser. The flask was placed in a thermostated silicon bath at 65°C. To the flask 4 g Na_2SO_4 and 0.8 g hydrolysed styrene–maleic anhydride copolymer in 300 ml water were added, while stirring nitrogen was purged through the mixture. Monomers, 26.4 ml (0.2 mol) of glycidyl methacrylate, 26.5 ml (0.25 mol) of methyl methacrylate and 7.1 ml (0.05 mol) of divinyl benzene (DVB) were mixed

together with 1 g of AIBN (azobisisobutyronitrile) in 60 ml of toluene. The organic mixture was added dropwise, through a dropping funnel to the flask in about 30 min.

The mixture was stirred for 10 h (350–400 rev./min). Then the reaction content was poured into 1 l of cold water. The spherical beads formed were decanted simply and washed with excess of water and methanol (50 ml), respectively. The product was dried under vacuum for 24 h at room temperature, the yield 58.3 g. The product in perfect spherical beads form was sieved and 105–210 μm size of fraction was used for further reactions. It was observed that most of the product (94%) was in the 105–420 μm size range. Surface area of the 105–210 μm fraction was measured as $0.674 \text{ m}^2 \text{ g}^{-1}$ (BET method).

2.3. Determination of the oxirane content

Oxirane content of the terpolymer beads was determined by pyridine-HCl method as described in the literature [11]. Titration of the filtered pyridine-HCl solution with NaOH (0.1 M) gave $3.40 \pm 0.08 \text{ mmol g}^{-1}$ of oxirane content.

2.4. Modification of the terpolymer beads by *N*-methyl-D-glucamine

N-methyl-D-glucamine (15 g; 78.68 mmol) was dissolved in 110 ml of *N*-methyl pyrrolidone by heating at 80°C in silicone-oil bath. While stirring with a mechanical stirrer, 17.1 g of GMA + MMA + DVB resin were added to the hot solution, portionwise.

Reaction was continued for 4 h at 80°C . Then the mixture was cooled and poured into 1 l of distilled water, filtered and washed with excess of water and methanol, respectively.

Modified beads were dried under vacuum overnight at room temperature (yield 24 g). The surface area of the product was found to be $0.368 \text{ m}^2 \text{ g}^{-1}$ (BET method).

2.5. Determination of the glucamine functionality

Degree of functionalization with *N*-methyl-D-glucamine was followed simply by acid titration of the amine function. To do that, 0.5 g of the modified resin sample was soaked in 20 ml 0.1 M HCl solution and the mixture was stirred for 2 h at room temperature.

The mixture was filtered and 10 ml of the filtrate were titrated with 0.1 M NaOH solution using phenolphthalein color indicator. From the differences in acid contents of the initial and final solutions, the amine content of the modified polymer resin was calculated as 2.05 mmol/g of the resin sample.

2.6. Boron loading capacity of the resin

The capacity of the resin was determined by batch method as follows: 1 g of the resin sample was mixed with 30 ml of artificial H_3BO_3 solution (0.246 M) and stirred for 6 h. The mixture was filtered and unreacted boric acid in the filtrate was assayed based on NaOH titration (using a microburette) in the presence of phenolphthalein as color indicator as described in the literature [12].

For the determination of residual boric acid content of the filtrate 4 ml of the filtrate were mixed with 10 ml of 0.2 M D-sorbitol solution and titrated with 0.1 M NaOH solution. By the difference in initial and final boric acid contents of the filtrate, the capacity was calculated as 2.15 mmol/g of the resin sample.

2.7. Boron sorption kinetics of the resin

Batch kinetic experiments were performed using $9.06 \times 10^{-3} \text{ M H}_3\text{BO}_3$ solutions (98 ppm in terms of boron) as follows: 1 g of the resin sample was interacted with 100 ml of the above boric acid solution. The mixture was stirred with a magnetic stirring bar (400–450 rev./min). Ten-ml aliquots were taken at appropriate time intervals and residual boron contents were

analysed to obtain concentration–time plots in Fig. 2.

2.8. Column extraction of boric acid

For column extraction experiments a glass column with 2.2 cm of internal diameter, 40 cm height and with sintered glass filter at the bottom was employed. Ten grams of the resin sample (105–210 μm size) were mixed with 50 ml of water. The slurry was charged at the top of the column cautiously for a homogenous column-packing.

A Mariotte Vessel was used to provide constant flow rates. Boric acid solution (8 l) containing 50 ppm boron was charged to the vessel. The column was filled with water and the Mariotte Vessel was connected through a suitable delivery tube at the top of the column.

Flow rate was adjusted to 44 ml/min and effluent was collected in volumetric cylinders (50 ml) successively.

By analysis of the effluent fractions, boron loading profile of the resin was obtained as shown in Fig. 3. The dead volume was 34 ml.

2.9. Determination of the swelling ratio

Swelling ratio of the bead sample was determined by measuring volume expansion of 10 g dry sample. The sample was put in a burette and dry volume was measured as 15.4 ml. Then the sample was transferred into a beaker and 50 ml water were added into it. Wet resin was charged to the burette by means of water. Excess of water was drained off and wet-settled volume was measured as 28.2 ml. The ratio of the two gave the equilibrium swelling ratio, 1.81 (v/v_0).

2.10. Determination of boron loading capacity in competitive conditions

In order to investigate any probable interference coming from common metal ions, the loading experiments were repeated as follows:

the column was charged with fresh resin as described above and washed twice with 200 ml of distilled water.

Solutions of CaCl_2 (0.454 M), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.456 M), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.4 M) and H_3BO_3 (0.4 M) were prepared in four separated bottles. Fifty ml of the metal ion solutions were mixed separately with 50 ml of the H_3BO_3 solution. Fifty ml of the final solutions were charged to the column. After 6 h 10 ml of effluents were collected and titrated with 0.1 M NaOH as described above. Boron sorption capacities of the resin samples were assigned by analysis of boric acid in the metal ion solutions.

2.11. Reaction of the resin with the foreign ions

To examine any probable reaction of the resin with the foreign ions the resin samples were reacted separately with CaCl_2 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solutions (0.2 M).

For this purpose 20 ml of each solution were interacted with 1 g resin samples. Analysis of filtered solutions by EDTA titration [13] gave 0.16 and 0.18 M concentrations for Ca(II) and Mg(II) ions, respectively. From the difference of metal contents of the initial and final solutions sorbet Ca(II) and Mg(II) ions were found to be 0.95 and 1.1 mmol g^{-1} , respectively.

2.12. Leakage test of the resin

In order to test any functionality lost from the resin, in a separate experiment 2.5 g of fresh resin sample were soaked in 1 l of distilled water and heated to boil for 30 min and filtered. The filtrate was evaporated to a volume of 64 ml. To impart conductivity 100 mg of H_3BO_3 were dissolved in the filtrate. Conductivity of the solution was 3.15 μS . When compared to that of blank solution (H_3BO_3 in the same concentration) (3.12 μS) conductivities are almost the same. This indicates that no *N*-methyl-D-glucamine linkage occurs from the resin. If any

NMG linkage had happened this would have resulted in remarkable rise in the conductivity, due to complexation of NMG with boric acid.

3. Results and discussion

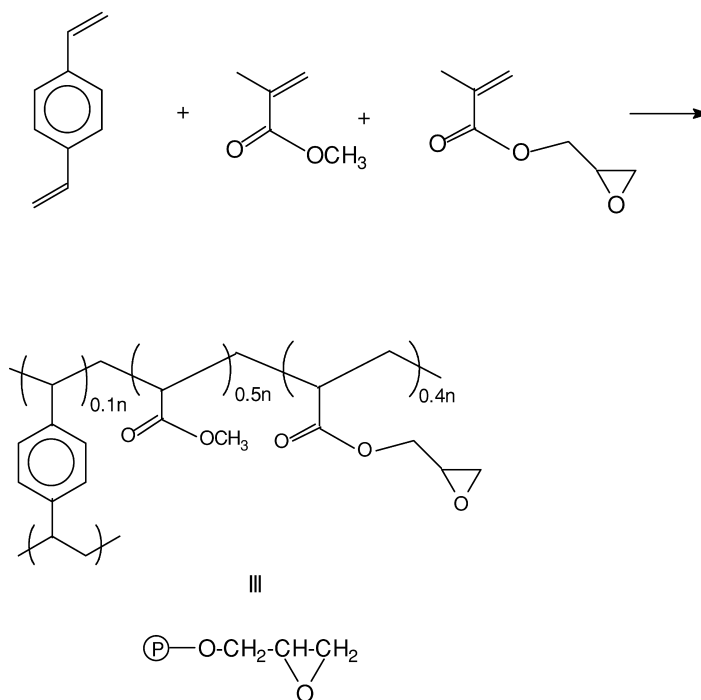
Suspension polymerization of the mixture containing GMA (0.4 mol), MMA (0.5 mol) and DVB (0.1 mol) yields crosslinked polymer resin in bead form (Scheme 1). Using sodium salt of styrene–maleic acid alternating copolymer as stabilizer, in a lab-scale reactor the polymerization (initiated with AIBN at 65°C) gives a bead form of polymer with relatively narrow size distribution (105–420 μm).

Analysis of the epoxide content of the resulting polymer beads gives $3.44 \pm 0.05 \text{ mmol g}^{-1}$ which is somewhat higher than the value predicted (3.33 mmol g^{-1}) by the feed composition. The small deviation can be attributed to differences in reactivity ratios of GMA and MMA [14].

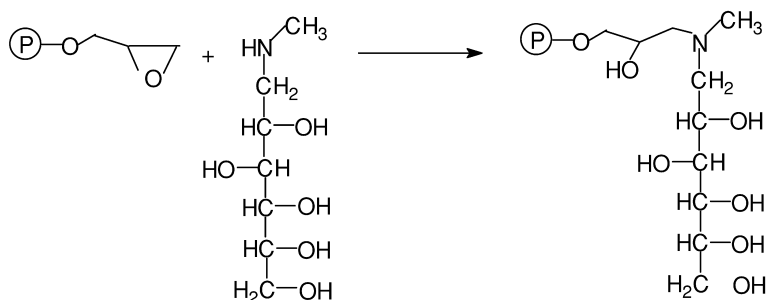
Portionwise addition of the resin beads to concentrated solution of *N*-methyl-D-glucamine in *N*-methyl pyrrolidone at 80°C (constant temperature) gives rise to a resin having *N*-methyl-D-glucamine functions (Scheme 2) by ring opening of the epoxide functions.

Additional catalyst is not necessary for the reaction because the amine function of *N*-methyl-D-glucamine serves as catalyst. With the catalytic effect of the amine, reaction through hydroxyl functions is also possible. However, the reaction is believed to occur mostly via amine functions due to higher reactivity of the latter with oxirane groups. Percentage weight increase (62.5%) implies a very high degree of functionalization (DF) 2.02 mmol g^{-1} . Functionalization degree based on acid titration of the amine functions gives 2.05 mmol g^{-1} of the NMG content. This indicates almost quantitative conversion. In other words each epoxy group has been reacted with one NMG molecule.

FT-IR spectra (Fig. 1a and b) of the epoxide bearing resin and its modified form do not differ



Scheme 1.



Scheme 2.

very much from each other. There are two important differences in the patterns of the two spectra. The broad band in the $3300\text{--}3500\text{ cm}^{-1}$ range indicates OH stretching vibrations in the structure of the modified resin. Also increasing intensity of C–O stretching vibration of the band at 1150 cm^{-1} must be due to the five carbinols of the NMG function of the resin. Moreover, two peaks associated with bending of the epoxy ring at $750\text{--}950\text{ cm}^{-1}$ range disappears in Fig. 1b.

After modification, the resin gains hydrophilicity and shows 81.0% volume expansion ($1.81 v/v_0$) in water, while retaining the shapes of the resin microspheres. This is a moderate swelling degree and suitable to use as column packing material for large scale boron extractions.

3.1. Boron extractions

Batch and column extraction experiments have been carried out to investigate the boron uptake ability of the polymer resin. In all experiments $105\text{--}210\text{ }\mu\text{m}$ size of fraction has been used. In the batch experiment wet resin sample was simply soaked into $0.1\text{ M H}_3\text{BO}_3$ solution. By analysis of unreacted boric acid in the solution, the capacity was calculated as 2.15 mmol/g of the resin. This amount is slightly higher than the NMG content of the resin which implies additional contribution of the latter two hydroxyl functions remaining in boron uptake.

In these experiments we have used non-buffered solutions deliberately to obey the practical conditions of applications.

In order to test the efficiency of the resin for trace quantities the resin sample was interacted with an aqueous solution containing 50 ppm of starting boron concentration and boron sorption was followed kinetically. By analysis of the aliquots taken at appropriate time intervals, concentration–time plots in Fig. 2 were prepared.

Although the stirring rate is of great importance in boron uptake kinetics, the figure shows that at moderate stirring rates ($350\text{--}400\text{ rev./min}$) boron concentration goes down to zero in about 12 min of contact time. In other words the boron sorption of the resin is rapid enough to use in column extractions.

3.2. Column extraction

Column experiments have been performed using a small scale extraction column. Constant flow rates were provided using a pressure equalising system, the so-called Mariotte Vessel. From the loading curve in Fig. 3 the breakthrough capacity was found to be 1.2 mmol g^{-1} . Breakthrough was assumed as the volume of feeding solution passed through the column until the concentration of boric acid in effluent reached 10% of feed concentration. A breakthrough volume of 1670 ml gives $0.835\text{ mol H}_3\text{BO}_3/\text{kg}$ of breakthrough capacity.

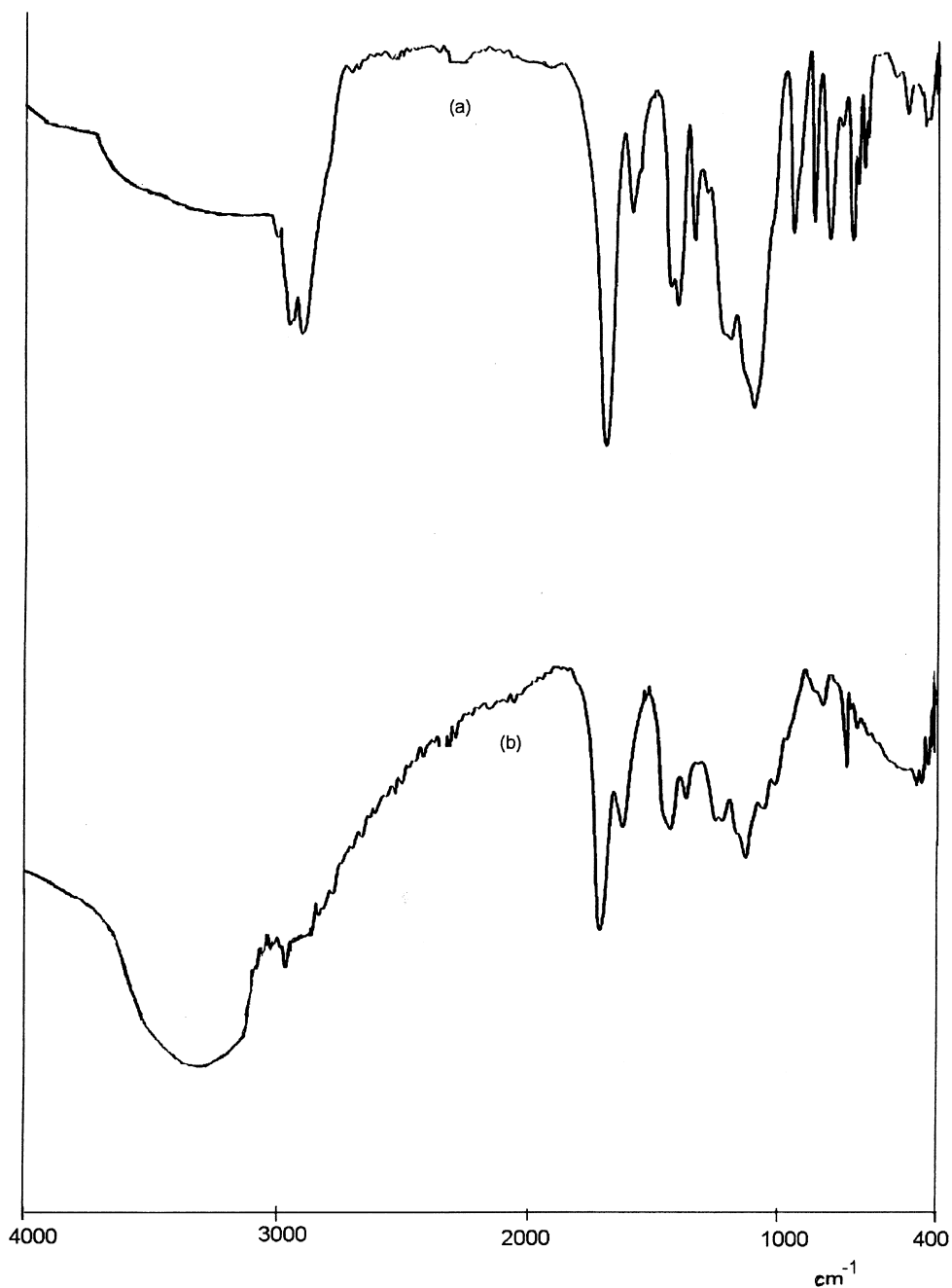


Fig. 1. FT-IR spectra of the polymer (a), and its modification product with *N*-methyl-D-glucamine functions (b).

Elution tests were carried out by washing out of the loaded resin with 2 M HCl solution. The column produces a sharp elution profile as shown in Fig. 4. The figure clearly indicates that

all the boron sorbed is eluted by about 200 ml of the acid solution. In other words, 200 ml of 2 M HCl is enough for a complete elution of the sorbed boron.

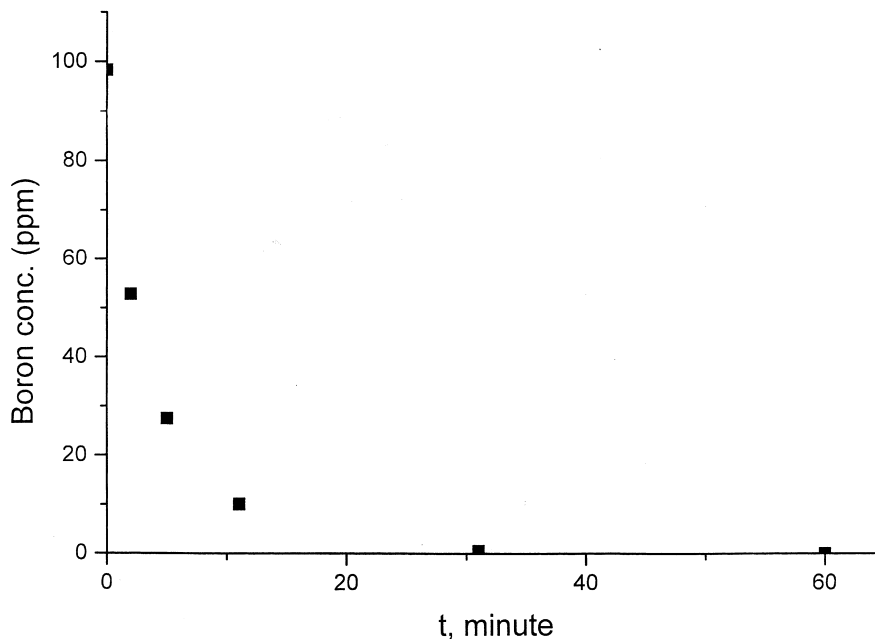


Fig. 2. Boron uptake kinetics of resin (1 g) using artificial boric acid solution with 98 ppm initial boron concentration.

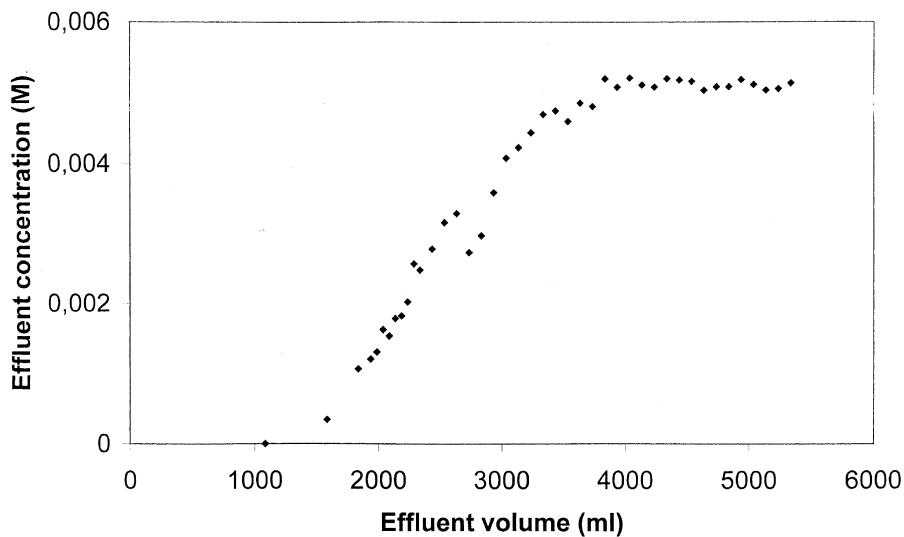


Fig. 3. Column loading profile of the resin sample (10 g), using 50 ppm initial boron concentration (flow rate: 44 ml/min).

3.3. Test of interferences

In order to examine effects of common metal ions, capacity measurements were repeated in the presence of Ca(II), Mg(II) and Fe(III) ions. However, surprisingly boron loading capacities were substantially higher than even before.

Repeated experiments gave the same results. In other words the effect of those ions were positive rather than a negative interference effect (Table 1).

A number of mechanisms can be considered for this unexpected result. Interestingly as far as we know no reports have been published on the

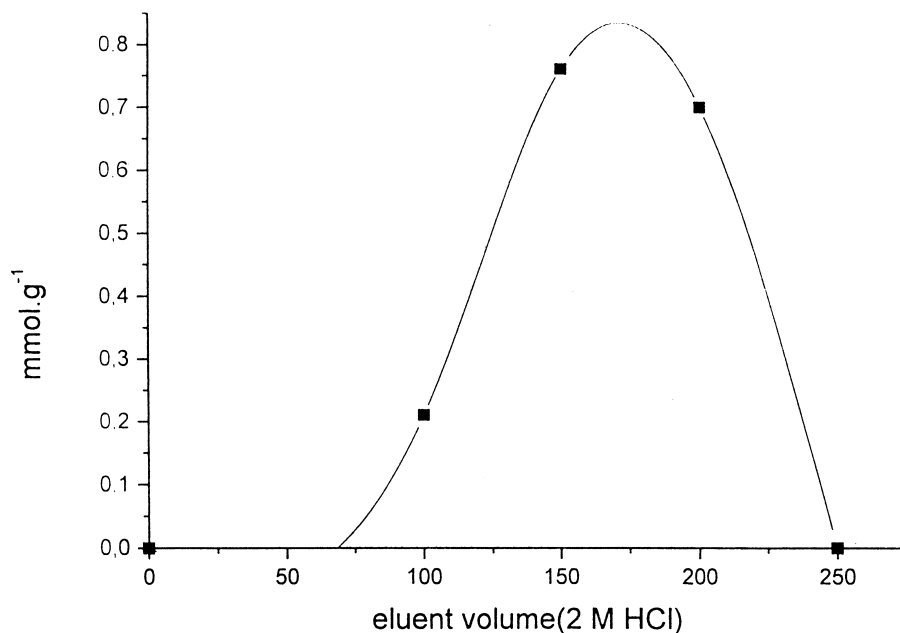


Fig. 4. Column elution profile of the loaded resin (10 g) eluted with 2 M HCl (flow rate: 44 ml/min).

Table 1

Boron uptake characteristics of the resin

Initial H ₃ BO ₃ conc., (volume)	Foreign ion (concentration)	Capacity ^a (mmol g ⁻¹) (method)	Desorbed boron (mmol g ⁻¹)
0.246 M (30 ml)	–	2.15 mmol g ⁻¹ (batch)	2.10 mmol g ⁻¹ (with 2 M HCl)
5 × 10 ⁻³ M (1.67 l, breakthrough volume)	–	Breakthrough capacity 0.835 mol/kg dry resin (column)	–
0.2 M (100 ml)	Ca(II) (0.227 M)	2.7 mmol g ⁻¹ (batch)	–
0.2 M (100 ml)	Mg(II) (0.228 M)	2.81 mmol g ⁻¹ (batch)	–
0.2 M (100 ml)	Fe(III) (0.2 M)	2.64 mmol g ⁻¹ (batch)	–

^a After 20 recyclings, the capacity was 2.14 mmol g⁻¹ (batch method).

enhancement of boron sorption in the presence of foreign ions. The most plausible explanation of the fact is precipitation of those ions in hydroxide form in the microenvironment of the resin phase. Apparently hydroxide ions are produced by tertiary amine function of the resin and hydroxide ions cause precipitation of Ca(OH)₂, Mg(OH)₂ and Fe(OH)₃ on resin particles. Thereafter those metal hydroxides

form corresponding borates which are insoluble in water. In the literature there are some reports associated with these metal hydroxides which have some effectivities on boron sorbents for relatively high concentrations of boric acid [15]. To prove this assumption CaCl₂ and MgSO₄·7H₂O and solutions (0.2 M) were separately interacted with the resin in the absence of boric acid. Concentrations of the final

solutions were less than the initial concentrations. This result is evidence of the metal hydroxide precipitation proposed.

3.4. Recyclability of the resin

The resin can be regenerated by washing with dilute NaOH solution (1 M). This is essential to restore the free amino group which was transformed into ammonium cation by acid treatment. Also acid contaminants are simply washed out by the NaOH solution. After final washing with distilled water the resin becomes regenerated and ready for the next use. The regenerated resin gives almost exactly the same loading profile (down-flow) with that obtained in the first loading.

In order to inspect any probable activity lost in the following steps, loading and desorbing processes were repeated 18 times more without measuring boron in the effluents in the intermediate steps. After 20 regenerations the capacity of the resin was examined by batch method and was found to be 2.14 mmol g^{-1} which is almost the same as that of the original resin. It is important to note that no change in flow rate was observed even after 20 regenerations, which implies a constant particle size throughout the regeneration cycles. This has been evidenced by sieving the dry sample used. The fraction of smaller than $105 \mu\text{m}$ size was 6 mg per 10 g of used resin which corresponds to 0.06% of mechanical disintegration of the resin particles. This amount can be neglected in comparison to polystyrene-based resins which suffer greatly from mechanical cracking in long term uses. Obviously mechanical stability of the resin arises from relatively low glass transition temperature of the methacrylic ester backbone.

In conclusion, the resin presented has the following advantages over common polymeric boron sorbent.

- (i) The resin shows a reasonably high activity in specific boron sorption.
- (ii) It can be regenerable more than 20 times without any activity loss.

(iii) No interferences come from Ca(II), Mg(II) and Fe(III) ions. Instead the capacity of the resin rises in the presence of these ions, due to additional contributions of the metal hydroxides in precipitating their borates.

(iv) No particle disintegration is observed in long term uses. Because of the above advantages of the resin it has potential for large scale applications as column packing material for boric acid uptake from aqueous solutions.

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