

## Boron Removal by Liquid-Phase Polymer-Based Retention Technique Using Poly(glycidyl methacrylate *N*-methyl D-glucamine)

Julio Sánchez,<sup>1</sup> Bernabé L. Rivas,<sup>1</sup> Eliza Nazar,<sup>2</sup> Marek Bryjak,<sup>2</sup> Nalan Kabay<sup>3</sup>

<sup>1</sup>Polymer Department, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile

<sup>2</sup>Department Polymer and Carbon Materials, Wrocław University of Technology, Wrocław, Poland

<sup>3</sup>Chemical Engineering Department, Faculty of Engineering, Ege University, Izmir, 35100 Turkey

Correspondence to: B. L. Rivas (E-mail: brivas@udec.cl)

**ABSTRACT:** The removal of boron was analyzed by liquid-phase polymer based retention (LPR) technique using washing and enrichment method. The extracting reagents were water-soluble polymers (WSPs) containing quaternary ammonium salts and *N*-methyl-D-glucamine (NMG) groups. The removal experiments of boron using the washing method were conducted at 1 bar of pressure by varying pH, polymer:boron molar ratio, and concentrations of interfering ions (chloride and sulfate). The results showed higher retention capacity for boron (60%) at pH 10 with the polymer containing NMG group. The optimal polymer:boron molar ratio was 40 : 1. Selectivity experiments showed that the presence of interfering ions did not affect the boron removal capacity. The maximal boron retention capacity was determined by the enrichment method, obtaining a value of 12 mg B/g-polymer. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1541–1545, 2013

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### INTRODUCTION

Boron is widely distributed in the environment and the presence of this element concerned to the scientific community due to the effect of boron on living organisms, especially in the case of plants.<sup>1</sup> A low concentration of boron is necessary for the growth of plants while its excessive amount can be toxic. Boron is an essential element in the human diet, but the specific biochemical function is not yet identified.<sup>2</sup>

Boron at certain concentrations has been considered as a water contaminant, which has to be regulated.<sup>3</sup> Excessive intake of boron can cause nausea, headache, diarrhea, kidney damage, and even death from circulatory collapse.<sup>4</sup> The World Health Organization (WHO) had originally suggested a maximal permissible limit of 0.5 mg boron/L in drinking water; however, this value was revised lately and new limit was set at 2.4 mg/L.<sup>5</sup>

Boron in water comes from natural and anthropogenic sources. It is found in sediments and rocks and also used for production of glass, enamel, cosmetics, leather, textiles, paints, detergents, pesticides, and others.<sup>6</sup> In Northern Chile, it is possible to find water containing high concentrations of boron, arsenic along with sulfates and chlorides. This affects the quality of irrigation water.<sup>7–9</sup>

Chemistry of boron should be taken into account to develop new alternative methods for its removal from aqueous environments efficiently. The boron appears in water mostly as boric acid- a weak acid with a  $pK_a$  of 9.2. At pH below 9.2, boron is found mostly as boric acid  $[B(OH)_3]$  while at pH above 9.2 it is found as borate ion  $[B(OH)_4^-]$ .<sup>10,11</sup>

Different technologies have been used to remove boron from natural or industrial wastewater. Some researchers have studied clays and other minerals for boron adsorption.<sup>12,13</sup> Magnesium oxide has been used for removal of boron; however, this material is inefficient and expensive.<sup>14</sup> Solvent extraction has also been used in the removal of boron but the method is effective for high concentrations only.<sup>15</sup> Ion exchange is the most widely used technique for removal of boron.<sup>16–19</sup> The boron selective chelating ion exchange resins are effective for removal of boron but their use generates high cost and complexity of their regeneration.<sup>16</sup> Membrane separation is an useful method for removal of boron. Supported liquid membranes, reverse osmosis and electrodialysis were studied for the retention of boron.<sup>20–22</sup> However, removal using membrane processes, especially reverse osmosis, is pH dependent and requests to use high pressure.<sup>23</sup>

Recently, the separation of toxic inorganic species has been investigated by a hybrid method using membranes coupled to

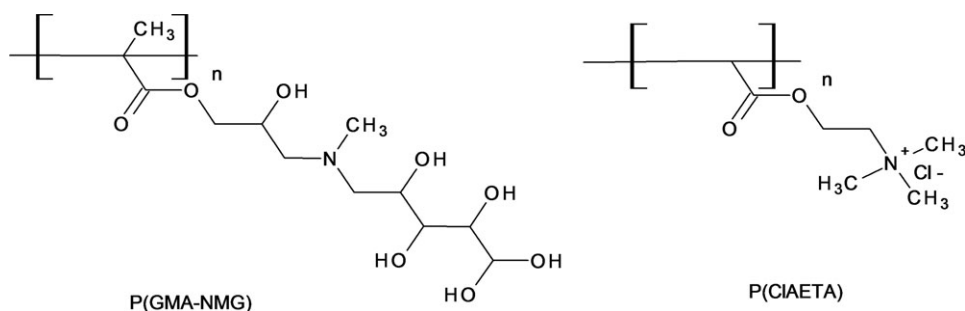


Figure 1. Chemical structure of the water-soluble polymers.

water-soluble functional polymers. This method is known as polymer enhanced ultrafiltration (PEUF) or liquid-phase polymer-based retention (LPR).<sup>24,25</sup> The process involves the simultaneous use of a ultrafiltration membrane and water-soluble polymers having functional groups which interact with the ionic species of low molecular weight, form complexes which cannot pass through the membrane. Through LPR, it is possible to separate a series of metal cations, as well as toxic inorganic anions such as arsenates and chromates from aqueous solution.<sup>24–27</sup> LPR presents a number of advantages compared with other separation systems because the process runs in homogeneous medium that eliminates problems with diffusion into sorbent particles and interface mass transfer restrictions are avoided. It is also possible to perform the selective interaction of the polymer towards certain species of interest. Currently, in the literature just a few examples are related to boron removal using LPR.<sup>28–33</sup> Dilek et al. used poly(vinyl alcohol) as the chelating agent using a constant boron concentration of 10 mg/L at different contents of polymer and various pH values for boron removal. Maximum boron retention was obtained as 28% at pH 10.<sup>28</sup> Doganay et al. showed 54–57% of boron retention for hydroxyethylaminoglycerol functionalized poly(glycidylmethacrylate) or poly(4-vinyl-1,3-dioxalan-2-one-co-vinyl acetate) as polychelators.<sup>29</sup> Hence, it seems that PEUF can be employed effectively for boron removal using the specifically tailored polymers.

This study shows the removal of boron from aqueous solutions by LPR through washing and enrichment methods. For this, the following water-soluble polymers were used: poly[2-(acryloyloxy)ethyl] trimethylammonium chloride, P(CIAETA), and poly[glycidyl methacrylate *N*-methyl *D*-glucamine], P(GMA-NMG). These polymers were synthesized by radical polymerization and fractionated by ultrafiltration membranes. The studies on removal of boron using the washing method were conducted at 1 bar of pressure by varying pH, boron concentration, polymer:boron molar ratio and the presence of interfering ions such as chloride and sulfate. The maximum boron retention capacity was determined by the enrichment method.

## EXPERIMENTAL

### Materials

The 2-[(acryloyloxy)ethyl] trimethylammonium chloride, CIAETA, 80 wt % aqueous solution and *N*-methyl-*D*-glucamine, NMG, and glycidyl methacrylate, GMA, were purchased from Sigma-Aldrich and used as delivered. Ammonium persulfate,

AP, (Sigma-Aldrich) was used as initiator. Other chemicals were purchased from Sigma-Aldrich.

Ultrafiltration membrane of 50 kDa molecular weight cut-off served for water soluble polymer fractionation and cellulose membrane (Millipore) of 10 kDa molecular weight cut-off was used for running the LPR processes.

### Synthesis of Water-Soluble Polymers

Poly[2-[(acryloyloxy)ethyl]trimethylammonium chloride], P(CIAETA), was prepared by free-radical polymerization. Approximately, 5 g of monomer and 1 mol % AP were dissolved in 40 mL of water under N<sub>2</sub> atmosphere. The reaction was conducted at 70°C for 24 h.

Poly(glycidylmethacrylate-*N*-methyl-*D*-glucamine), P(GMA-NMG) was prepared as follows: A 60 mL of an aqueous solution of NMG was placed into a three-neck round bottom flask. Then, 6.8 mL (50.0 mmol) of GMA was slowly added to the solution. The reaction mixture was incubated for 5 h at 70°C with vigorous stirring. The product was washed with diethyl ether to remove the excess of GMA. The detailed procedure was described elsewhere.<sup>34</sup> Reaction solution containing GMA-NMG monomer was subjected to radical polymerization. The solution was transferred to a polymerization reactor and 1 mol-% of AP was added. The reaction mixture was degassed with N<sub>2</sub> gas for 20 min, and the reactor was placed in a thermostated bath at 70°C for 24 h and kept under N<sub>2</sub> atmosphere. The obtained polymer was dissolved in distilled water and fractionated by ultrafiltration membranes with a molecular weight cut-off of 50,000 Da. Collected retentate was lyophilized. The structures of P(CIAETA) and P(GMA-NMG) are shown in Figure 1.

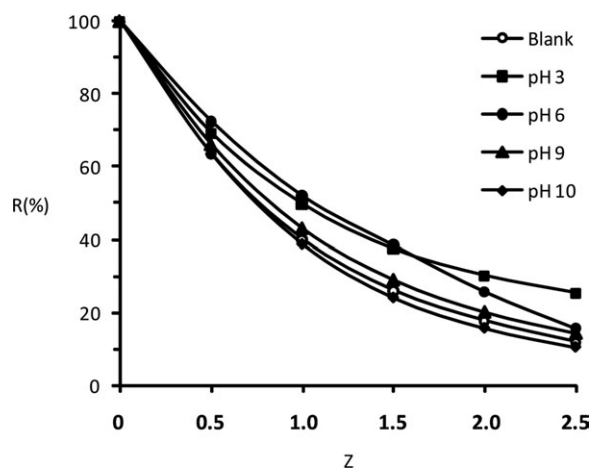
### LPR Technique

The ability of P(CIAETA) and P(GMA-NMG) to remove boron by means of the LPR technique has been studied by washing and enrichment methods.

The main components of a LPR system are: filtration unit (Amicon 8050 stirred cell of 50 mL volume), membrane filter with a known cut-off, reservoir and pressure source, e.g., pressurized nitrogen gas. The detailed description of the system was presented previously.<sup>25</sup> In the ideal case, the system may be considered as a mixed flow reactor.

### Washing Method

The washing method is method where a liquid sample containing water-soluble polymer and boron to be separated are placed in the ultrafiltration cell at a given pH and ionic strength. This



**Figure 2.** Retention profile of boron as a function of pH using polymer P(CIAETA).

mixture is then washed with boron-free solution that reproduces the same pH and ionic strength values. For the test, a solution of 2 mg/L of boric acid was used. The pH value was adjusted by adding 0.1M NaOH or 0.1M HNO<sub>3</sub> and the ionic strength was adjusted by NaCl and Na<sub>2</sub>SO<sub>4</sub>.

The solutions were brought to 20 mL of total volume, and the pH was adjusted to 3, 6, 9, and 10 by adding 0.1M HNO<sub>3</sub> or 0.1M NaOH in separate experiments. The pH value was measured by a pH meter (H. Jürgen and Co). All ultrafiltration studies were performed under a total pressure of 1 bar at room temperature using an ultrafiltration membrane of regenerated cellulose with a MWCO of 10,000 Da. The total volume (20 mL) in the cell was kept constant and fractions of 10 mL were collected by filtration. Results of the boron uptake are systematically presented as the percentage of retention *R* (%) versus the filtration factor *Z* (volume of filtrate/volume of the cell).

#### Enrichment Method

The second mode presented in this work is the enrichment method which determines the maximum retention capacity (MRC) of the water-soluble polymer. A boron containing solution passes from the reservoir through the ultrafiltration cell filled with polymer solution. Both cell and reservoir solutions are adjusted to the same values of pH and ionic strength. In this study, reservoir solution contained 2 mg/L of boron while the cell solution –30 mg of water-soluble polymers. Total permeate volume of the LPR system was set to 200 mL.

In both, washing and enrichment methods, blank experiments (in the absence of the water-soluble polymer) were done to evaluate the interaction of the ultrafiltration membrane with boron. Boron concentration was measured by Azomethine H method ( $\lambda_{\text{max}} = 415 \text{ nm}$ )<sup>35</sup> and its quantity retained by the system was calculated from the mass balance.

To study the removal of boron from aqueous solution using the washing method, two factors should be defined: (1) retention (*R*) that shows the fraction of boron remaining in the cell, and (2) filtering factor (*Z*) showing the volume exchange ratio.

$$R = [B_{\text{cell}}]/[B_i] \quad (1)$$

where  $[B_{\text{cell}}]$  is the amount of boron that are retained in the cell and  $[B_i]$  is the initial amount of boron.

The filtration factor (*Z*) is the ratio between the total permeate volume ( $V_p$ ) and the retentate volume ( $V_r$ ):

$$Z = V_p/V_r \quad (2)$$

The maximum retention capacity (MRC) of water-soluble polymers was determined by the enrichment method. It is defined as follows:

$$C = (MV)/P_m \quad (3)$$

where  $P_m$  is the amount of polymer (g),  $M$  is initial concentration of boron (mg/L), and  $V$  is the volume of permeate (mL) that passes through the membrane. The maximum boron retention capacity was calculated when 200 mL of permeate was collected.

## RESULTS AND DISCUSSION

### Effect of pH on Boron Removal

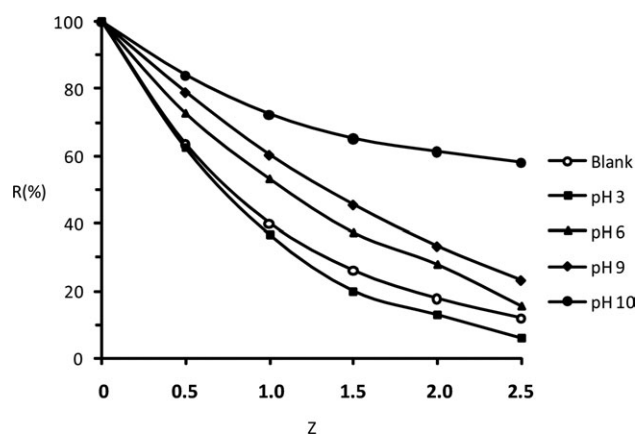
Our previous studies showed that P(CIAETA) was able to remove chromate and arsenates.<sup>25–27</sup> In this article, the performance of P(CIAETA) and P(GMA-NMG) to remove boron from the solution by the LPR washing method was investigated. As mentioned before, the borate anion  $B(\text{OH})_4^-$  dominates at higher pH while nonionized boric acid  $B(\text{OH})_3$  at lower pH.<sup>2</sup> Considering the speciation of boron, the removal by means of P(CIAETA) is expected to be higher at high pH where borate anion is present. However, the results showed lower boron retention capacities in a wide range of pH (see Figure 2) and the boron removal did not exceed 30% in the pH range studied.

The blank runs without water-soluble polymers were conducted to determine the effect of the membrane material on boron removal. It was shown that the membrane sorbed boron. However, the extent of sorption was not so high because the removal of boron was below 20%.

On the other hand, polymers containing hydroxyl groups are capable to interact with borate anion. The presence of borate ion is enhanced in the basic medium, therefore the chelation of borate with –OH functional groups are favored at higher pH values.<sup>2,29</sup> The boron retention capacity of P(GMA-NMG) was higher when compared with P(CIAETA) in the same experimental conditions and reached 60% at pH 10 (see Figure 3).

### Optimum Polymer: Boron Molar Ratio

The removal of boron was optimized by changing the polymer:boron ratio. The influence of the polymer concentration on boron removal was studied using the washing method. Different polymer:boron molar ratios, such as 100 : 1, 40 : 1, and 5 : 1, were prepared at pH 10. The change in boron retention *R*(%) versus *Z* is shown in Figure 4. The experimental data indicated that a polymer:boron molar ratio of 40 : 1 for P(GMA-NMG) was needed to reach a maximum boron removal (60%). In the



**Figure 3.** Retention profile of boron as a function of pH using polymer P(GMA-NMG).

case of P(CIAETA), the boron retention for the same polymer: boron molar ratio was lower than that of P(GMA-NMG).

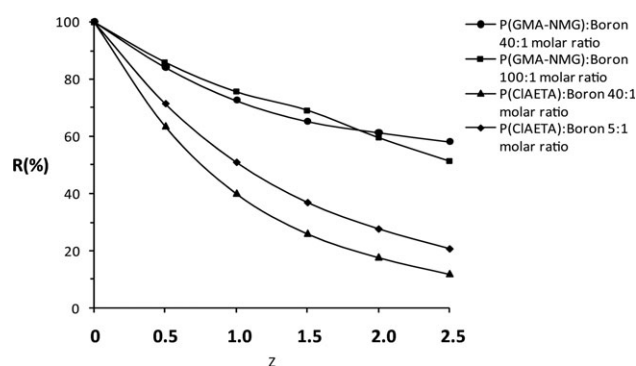
#### Effect of Boron Concentration

The effect of boron concentration on its percent removal was studied for P(GMA-NMG) using polymer:boron molar ratio of 40 : 1 at pH 10. The boron concentration in the feed was changed from 2 mg/L to 20 mg/L. The retention capacity took the maximal value when the concentration of boron was lowest. At 20 mg/L of boron concentration retention capacity by P(GMA-NMG) was 18% and increased gradually up to 60% when the boron concentration was lowered to 2 mg/L (see Figure 5).

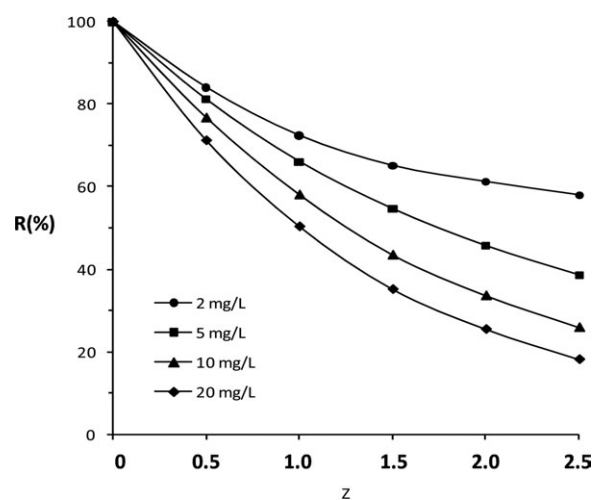
#### Effect of Interfering Ions on Boron Removal

P(GMA-NMG) presents the highest retention of boron in comparison to P(CIAETA) by the LPR technique when no other anions present in the solution. In order to determine the effect of other anions on boron separation, sulfate and chloride containing solutions were employed. In this study, we used the washing method at variable ionic strength using 20 to 200 mg/L of  $\text{Na}_2\text{SO}_4$  and NaCl with a P(GMA-NMG):B mole ratio of 40 : 1 at pH 10.

The results showed that the boron retention did not decrease dramatically with the increasing concentration of interfering



**Figure 4.** Retention profile of boron at different polymer:boron molar ratio.



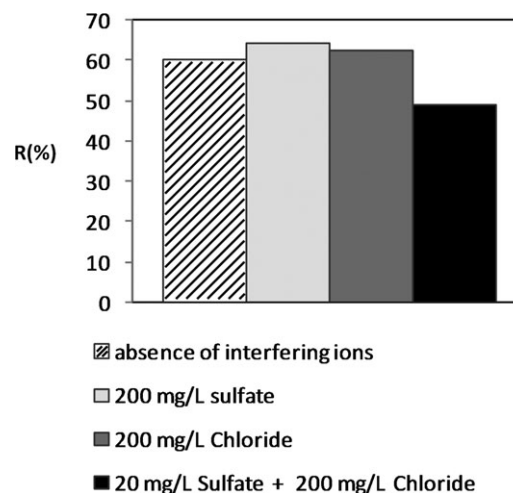
**Figure 5.** Retention profile of boron at different boron concentrations in the feed using P(GMA-NMG).

ions (see Figure 6). P(GMA-NMG) retains boron around to 60% in the presence of 20 mg/L of  $\text{SO}_4^{2-}$  or in presence of 200 mg/L of  $\text{Cl}^-$ . In the presence of both interfering anions (20 mg/L sulfate and 200 mg/L chloride) the maximal retention was 48%.

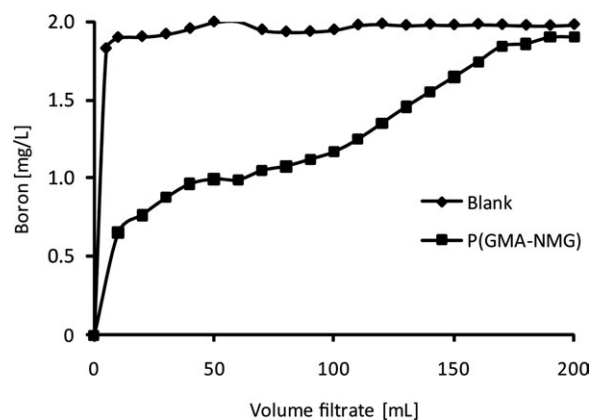
#### Maximum Boron Retention Capacity

The polymer maximum retention capacity (MRC) was evaluated at pH 10 using 30 mg of water-soluble polymer in the ultrafiltration cell. Figure 7 shows the concentration of boron in the permeate versus volume of permeate. In order to calculate the MRC value, the blank run without water-soluble polymers was performed. From the difference in the slopes, the amounts of boron bound to the polymer and being uncomplexed as well as the maximum retention capacity can be calculated.

According to the data obtained from blank test, it is possible to say that boron concentration reached to 2 mg/L in the first fraction of permeate so there was almost no retention of boron by



**Figure 6.** Retention of boron by P(GMA-NMG) in the absence and presence interfering ions in the feed.



**Figure 7.** Boron concentration in the filtrate versus volume of filtrate using P(GMA-NMG) and P(CIAETA) as an extracting reagent at pH 10. The blank is the experiment without polymer.

the membrane itself. The maximum retention capacity of P(GMA-NMG) was 12.4 mg B/g-polymer.

## CONCLUSIONS

The results showed that 60% of retention capacity for boron was obtained at pH 10 with the polymer containing NMG group. The optimum polymer:boron molar ratio was 40 : 1. The retention capacity took the maximal value when the concentration of boron was lowest. Selectivity experiments showed that the presence of interfering ions did not affect the boron removal capacity dramatically. The cellulose membrane did not affect separation also. The maximum boron retention capacity was determined to be 12 mg B/g P(GMA-NMG). It is considered that the LPR method is a potential alternative for the removal of boron from aqueous solutions.

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