

Boron Removal by Glucamine-Functionalized Hydrogel Beads in Batch Fashion

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ABSTRACT: In this study, poly(hydroxypropyl methacrylate) gel beads were synthesized, then it was functionalized to yield glucamine carrying hydrogel beads as a sorbent for boron uptake. The batch-mode sorption studies were performed to obtain the optimum resin concentration and pH for boron removal. The results showed that percent of boron removal increased with increasing amount of resin and reached 98% at 12 mg-resin/mL-solution. The boron removal did not effected much with the change of pH between 4 and 9. The boron adsorption isotherm is in good accordance with the Langmuir and Freundlich equations. The equilibrium adsorption amount

of boron is 13.5 mmol g⁻¹ at optimum conditions which is 5 to 50 times higher than the other boron selective adsorbents recorded in literature. Desorption studies showed that 100% elution is possible with HCl. As a conclusion the glucamine carrying hydrogel beads can be effectively used for uptake of boron from aqueous solutions because of their high boron adsorption capacity and reusability. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1610–1615, 2011

Key words: boron; glucamine; adsorption; hydrogel bead; environmental pollution

INTRODUCTION

Boron is widely distributed in the environment, occurring naturally (seawater, geothermal waters) or from anthropogenic pollution, mainly in the form of boric acid or borate salts. Although it is an important micronutrient for plants, animals, and humans, it can also be toxic at certain levels. Boron can cause disease in the nervous systems of animals¹ and high concentrations in drinking water can be toxic to human being.² A few ppm of boron present in irrigation water can be toxic for some crops.¹ In addition to boron mines, the main anthropogenic sources of water soluble boron compounds in aqueous environment are wastewater containing detergents, fertilizer and insecticide productions, and other industrial effluents.^{2,3} There are several processes stated for boron removal from aqueous solutions. Among these methods, advanced treatment method such as adsorption process is most extensively used to obtain low-boron concentrations.

Various types of materials have been used as sorbents including several minerals and polymer-based chelating resins. The development of chelating resins, containing functional groups for boron removal and recovery from natural waters and wastewaters,

is a prerequisite for improving the capacity, selectivity, and sorption rates. Several studies were performed to obtain boron selective resins, and it was reported that the most promising boron adsorbents are containing hydroxyl groups.^{1,4–6} Polymer supported chelating resins with vicinal diol groups are reported as efficient for boron removal, but these resins are instable in harsh chemical environments.⁷ An adsorption capacity of 1.15 mmol g⁻¹ was reported for a hybrid gel with boron-chelating groups prepared using (3-glycidoxypropyl)trimethoxysilane and *N*-methylglucamine (MG).² Maximum boron adsorption capacity obtained with *N*-MG-type cellulose derivative (1.1 mmol g⁻¹) were same as the commercially available *N*-MG-type polystyrene resin.⁸ Other investigators obtained maximum boron adsorption capacities as 3.39, 6.8, 16.98, 23.5, and 32.4 mg g⁻¹ with calcinated alumina; amine and polyol groups grafted organic-inorganic hybrid mesoporous material; Dowex 2 × 8; cross-linked polymer gels derived from *N*-glucitol-*N*-methyl-2-hydroxypropyl methacrylate; and glycidyl methacrylate-methyl methacrylate-divinyl benzene terpolymer beads with aminopropylene glycol functions, respectively.^{1,9–12} Because investigations on new sorbents to obtain high boron removal capacities are still attractive, in this study, poly(hydroxypropyl methacrylate) [poly(HPMA-Cl)] gel beads were synthesized and then functionalized to yield poly(HPMA-Cl)-*N*-methyl-D-glucamine as a sorbent for high level of boron uptake.

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EXPERIMENTAL

Reagents and equipment

The boron solutions used in this study were prepared with boric acid (H_3BO_3). All reagents used in this study were supplied by Sigma-Aldrich. The pH of the solutions was adjusted with dilute HCl and NaOH solutions. All the solutions in the study were prepared using distilled water. The monomer, HPMA-Cl and the crosslinking agent, ethylene dimethacrylate were used without further purification. Benzoyl peroxide (BPO) recrystallized from methanol and polyvinyl alcohol (87–89% hydrolyzed, MW:85.000–146.000) was used as the initiator and the stabilizer, respectively, in the preparation of hydrogel beads.

Boron concentrations were determined by ICP-MS (Perkin Elmer SCIEX). pH measurements were performed by CyberScan 1000 pH meter. Electron micrographs of crosslinked poly(HPMA-Cl) gel beads were obtained by SEM (Phillips, XL-30S FEG, Germany). FTIR spectra of the nanospheres were obtained by using FTIR spectrophotometer (Varian FTS 7000).

Preparation of boron selective sorbent

Crosslinked poly(HPMA-Cl) gel beads were prepared according to the polymerization procedure reported elsewhere.¹³ The stabilizer poly(vinyl alcohol) (0.2 g) was dissolved in deionized water (50 mL) for the preparation of a continuous phase. The dispersed phase was prepared by mixing cyclohexanol (4 mL), HPMA-Cl (2.5 mL), and EGDMA (2.5 mL). Then, benzoyl peroxide (0.1 g) as an initiator was dissolved in the organic phase. The dispersed phase and the continuous medium were mixed within a glass-sealed polymerization reactor placed in a water bath equipped with a thermoregulator. The polymerization was performed at 90°C for 4 h. Poly(HPMA-Cl-co-EGDMA) beads were washed two times with ethanol and then two times with water before being dried. Then, *N*-methyl-D-glucamine (NMG) (1 g) was linked to the poly(HPMA-Cl-co-EGDMA) beads (1.0 g) in 1,4-dioxane/water (10 mL/40 mL) medium via the direct reaction between chloropropyl and amine groups. The reaction was performed at 80°C for 6 h. After the completion of reaction, the beads were washed two times with ethanol and two times with water before being dried.

Batch-mode sorption studies

To obtain the optimum amount of resin concentration various amounts of resins (0.005, 0.01, 0.02, 0.05, 0.1, 0.2, and 0.3 g) were added into 25 mL of 10 mg-B/L solution. Adsorption was performed at 30°C for 24 h

with continuous shaking. Boron concentrations were measured before and after the adsorption.

The adsorption capacity, Q (mg boron/g resin) was calculated by following equation:

$$Q = V(C_o/C)/W \quad (1)$$

where, C_o and C are the boron concentrations in the solution before and after adsorption ($mg\ L^{-1}$), V is the volume of the solution (L), and W is the weight of the adsorbent (g). The equilibrium adsorption capacity, Q_e , was obtained when C_e is used instead of C in eq. (1).

To investigate the effect of solution pH on boron uptake, the equilibrium adsorption amounts were determined at different pH values (4; 5; 6; 7; 8.5; 9). In all run, 0.1 g resin was added to 25 mL of 10 mg-B/L solution before pH adjustment and boron concentrations were measured after continuous shaking for 1 h at 30°C.

For adsorption isotherm study, 0.1 g of resin was contacted with 25 mL of boron solution at initial concentrations of 2, 5, 10, 20, 50, 100, 150, 200, 500, 750, and 1000 mg-B/L at 30°C for 24 h with continuous shaking. The experimental data were compared with Langmuir and Freundlich isotherm models.

Langmuir equation was applied to calculate adsorption capacity and is expressed as:

$$C_e/Q_e = 1/Q_o K_L + C_e/Q_o \quad (2)$$

where C_e is the equilibrium concentration ($mg\ L^{-1}$), Q_e is the equilibrium adsorption capacity ($mg\ g^{-1}$), Q_o and K_L are Langmuir constants representing adsorption capacity ($mg\ g^{-1}$) and energy of adsorption ($L\ mg^{-1}$), respectively.

The Langmuir separation factor, R_L , which indicates the type of isotherm, is defined as:

$$R_L = 1/(1 + K_L C_o) \quad (3)$$

where K_L is the Langmuir constant, and C_o is the initial boron concentration ($mg\ L^{-1}$).

The Freundlich equation is illustrated as:

$$\log Q_e = \log K_F + (1/n) \log C_e \quad (4)$$

where K_F and n are Freundlich constants representing adsorption capacity ($mg\ g^{-1}$) ($L\ mg^{-1}$)^{1/n} and adsorption intensity, respectively, Q_e is the equilibrium adsorption capacity ($mg\ g$), and C_e is the equilibrium concentration ($mg\ L^{-1}$).

For the boron adsorption kinetic experiments, 0.1 g of the resin was added into 25 mL of 10 $mg\ L^{-1}$ boron solution, and the residual boron at different times (3, 5, 10, 15, 20, 30, 60, and 90 min) were determined. To analyze the adsorption kinetics pseudo-second

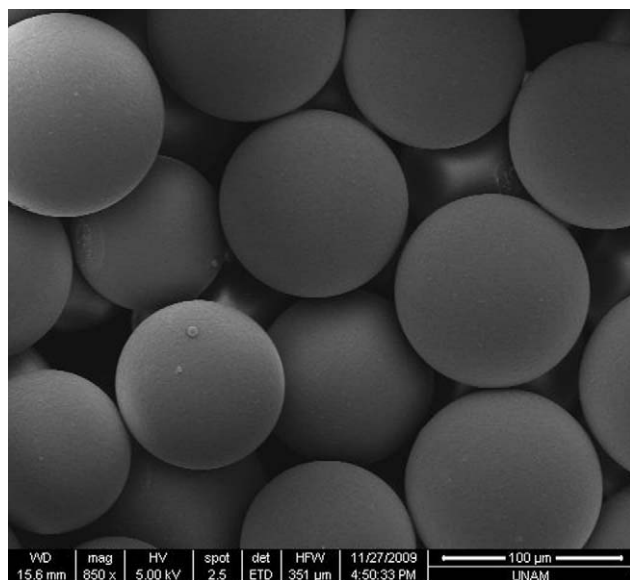


Figure 1 SEM micrograph of the large size polydisperse hydrogel spheres (Mag: 100X).

order model was used. According to Fuenta and Camacho,¹⁴ the pseudo-second order rate equation is defined as:

$$dq/dt = k(q_e - q)^2 \quad (5)$$

where q and q_e are the sorption capacity at time t and at equilibrium (mg g^{-1}), k is the pseudo-second-order rate constant of sorption (g/mg min). Integrating eq. (5) for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q$, the following linear form can be obtained:

$$t/q = 1/(kq_e^2) + t/q_e$$

The desorption of boron from the resin was performed with 0.5 M HCl solution.

RESULTS AND DISCUSSIONS

HPMA-Cl-based beads were selected as a new starting material for the preparation of a diol functionalized sorbent that could be used for boron isolation. For the synthesis of the sorbent, a diol carrying ligand, NMG was covalently attached onto the beads via the direct reaction between secondary amine groups of NMG and chloropropyl group of HPMA-Cl units. Therefore, the selection of highly reactive structure like poly(HPMA-Cl-co-EGDMA) beads and a direct attachment reaction for ligand binding should probably allow the attachment of more amount of diol carrying ligand onto the beads with respect to the conventional binding procedures

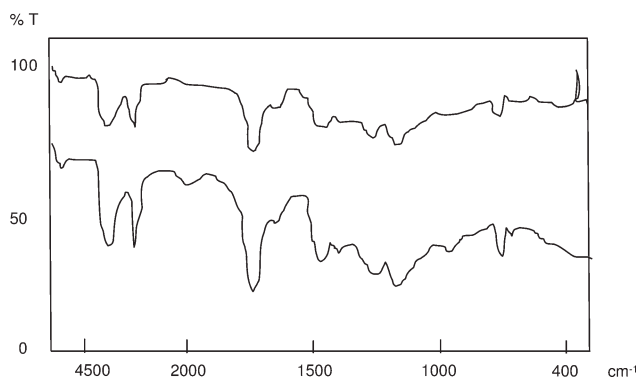


Figure 2 FTIR spectrum of (a) plain and (b) NMG functionalized poly(HPMA-Cl) beads.

involving the use of various activation agents. The beads carrying higher amount of diol carrying ligand should provide higher boron adsorption with respect to these sorbents.

Boron adsorption-desorption behavior

A representative electron micrograph of gel beads is given in Figure 1. Based on the electron micrograph given here, the average bead size and the coefficient of variation for size distribution were determined as 124 μm and 11.2%, respectively. FTIR spectra of NMG attached and plain poly(HPMA-Cl) beads are given in Figure 2. For modified and plain particles, the ratios of the areas of hydroxyl (3500 cm^{-1}) to carbonyl (1730 cm^{-1}) bands were calculated as 2.89 and 2.01, respectively. According to these ratios, there is a 44.5% increase in OH peak intensity due to the attachment of NMG onto the terminal chlorine moiety of poly(HPMA-Cl) beads. A detailed characterization of gel beads is given elsewhere.¹³

As shown in Figure 3, boron removal was strongly influenced by the added quantity of resin, showing a highly positive slope at the beginning due to the increase in sorbent surface area and, after the added resin amount of 0.05 g, the curve tends to stabilize with 93% of boron removal. High-boron removal with

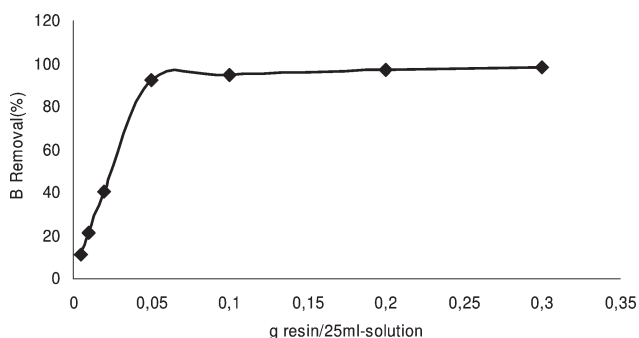


Figure 3 Effect of resin amount on the removal of boron by poly(HPMA-Cl)-NMG beads.

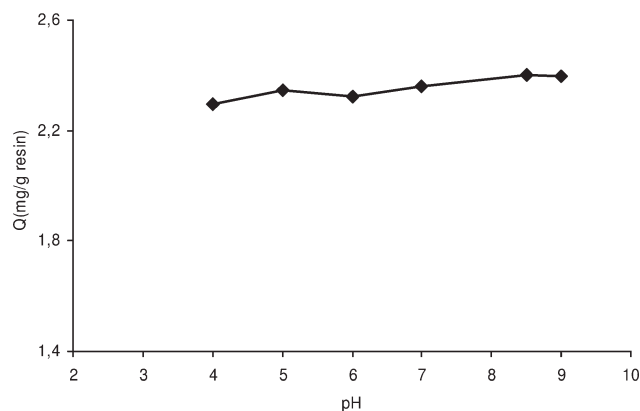


Figure 4 Effect of pH on the removal of boron by poly(HPMA-Cl)-NMG beads.

a maximum of 98% was observed with the addition of 0.3-g resin into 25-mL solution of 10 mg-B/L.

Figure 4 shows the equilibrium adsorption amounts obtained at different pH values. As can be seen from this figure that the equilibrium adsorption amounts stay unchanged between pH 4 and 9. Although several pH values were reported as optimal, the maximum adsorption amounts can be obtained near neutral pH values (4–10) in general, and it decreases at high- and low-pH values.^{2,8,11,15–17} Maximum boron removal is expected around pH 9 because the $B(OH)^{4-}$ ions in solution which is the primary anion at pH > 8–9 being exchanged with the OH^- ions on the resin at this pH¹¹. A sharp decrease was noted after pH 9 by other investigators due to the competitiveness of borate ions and high amount of hydroxyl ions for same adsorption sites.^{2,9,11,18} For the sorbent synthesized in this study, the removal was relatively high in the pH range examined, and there was not a specific optima. This should be related to the relatively higher adsorption capability of our sorbent for both boric acid and borate ions. Relatively higher ligand (i.e., NMG) concentration can be obtained due to the direct binding of boron selective ligand to the chloropropyl functionality of the gel beads. Higher ligand concentra-

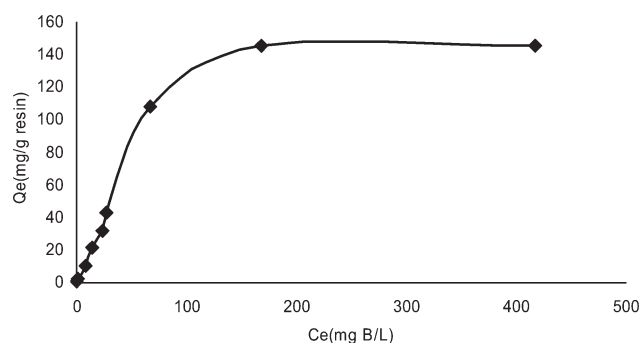


Figure 5 Isotherm for the removal of boron by poly(HPMA-Cl)-NMG beads (30°C and pH 9). All relative errors are smaller than 5%.

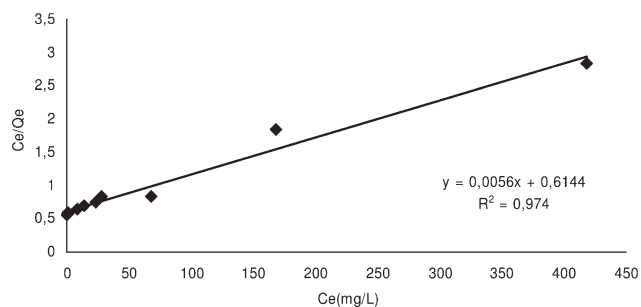


Figure 6 The Langmuir isotherm for the removal of boron by poly(HPMA-Cl)-NMG beads (30°C and pH 9).

tion then may lead to the higher boron adsorption in all pH values examined.

The plot of adsorption isotherm is given in Figure 5. An ascending convex isotherm indicates that the adsorption process is favorable. As seen in Figure 5, the equilibrium boron adsorption capacity increased with increasing the initial boron content in solution, and it leveled off at approximately 145 mg boron/g dry beads. The increase in boron adsorption with increase in the initial boron concentration is due to the increase in the driving force of the concentration gradient as expected. The plateau value obtained with (HPMA-Cl)-NMG beads corresponds to 13.5 mmol boron/g beads, which is enormously higher with respect to the boron adsorption capacities of the sorbents reported in the literature (i.e., 2.18 mmol g^{-1}).¹⁹ Higher ligand concentration within the gel beads and gel-type microporosity of the beads providing relatively higher surface area in the water-swollen form should be the factors responsible for relatively higher equilibrium boron adsorption. The presence of gel-type microporosity was previously shown for the polyacrylate-based beads with very similar structure [i.e., poly(2-hydroxyethyl methacrylate-co-ethylene glycol dimethacrylate, poly(HEMA-co-EGDMA) beads] obtained by also a very similar suspension polymerization procedure.²⁰

The plot of linear Langmuir and Freundlich equations for boron removal by poly(HPMA-Cl)-NMG beads were given in Figures 6 and 7. These graphs

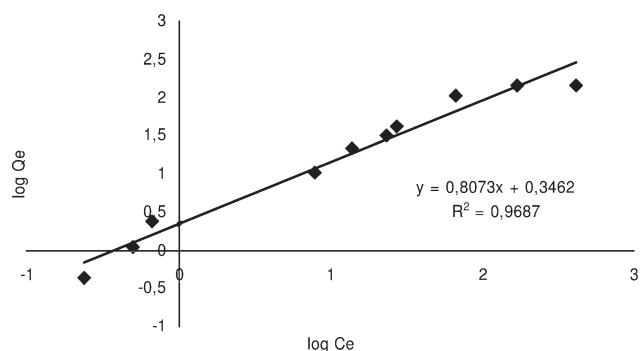


Figure 7 The Freundlich isotherm for the removal of boron by poly(HPMA-Cl)-NMG beads (30°C and pH 9).

TABLE I
 R_L Values for Poly(HPMA-Cl)-NMG Beads

C_o (mg/L)	2	10	50	100	200	500	750	1000
R_L	0.98	0.92	0.69	0.53	0.36	0.18	0.13	0.10

show a satisfactory correlation coefficient of 0.974 and 0.969 for each isotherm, respectively.

The Langmuir separation factors for boron removal by poly(HPMA-Cl)-NMG beads were shown in Table I. Because R_L values are less than 1 the sorption process is favorable.

The adsorption kinetics data indicated a rapid binding of boron by poly(HPMA-Cl)-NMG beads as shown in Figure 8. Boron concentrations of solutions go down to almost zero within less than 15 min at the conditions studied. The short adsorption equilibrium time observed in our experiments suggests that there is no internal diffusion; hence, the adsorption equilibrium is reached within several minutes.²¹ Bicak and Senkal²² reported that sorption of boron from aqueous solutions with sorbitol-modified poly(*N*-glycidyl styrene sulfonamide) is reasonably fast, and the equilibrium is established in about 30 min. It was also reported that more than 95% of boron is extracted by polymer supported 2-hydroxyethylamino propylene glycol functions in less than 30 min.²³

Second-order boron sorption was obtained with $k = 5.95 \times 10^{-3}$ g/mg min for 0.1 g of hydrogel beads. The correlation coefficient was obtained as 0.99 indicating a good agreement of experimental data with the second-order kinetic model (Figure 9).

As can be seen in Table II, the elution experiments showed that 0.5 M HCl solution is able to strip all absorbed boron from the hydrogel beads by the first contact with the HCl. Where the desorption yield defined as the percent-ratio of desorbed amount of boron from the gel beads to the adsorbed amount of

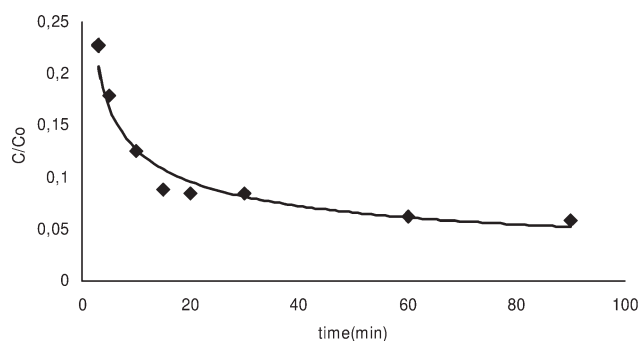


Figure 8 Adsorption rate of boron on the poly(HPMA-Cl)-NMG beads (0.1 g dry gel in 25 mL of 10 mg L⁻¹ boron solution).

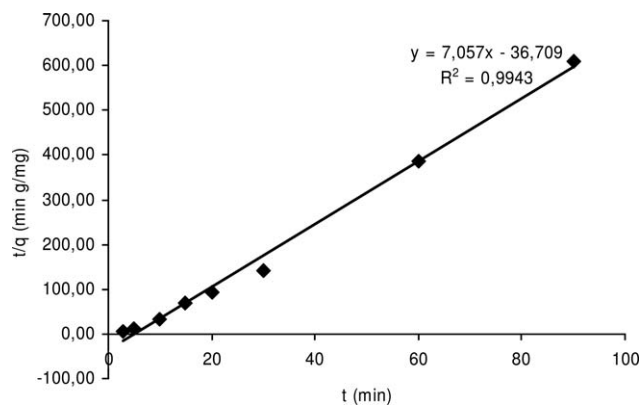


Figure 9 Pseudo-second-order boron sorption kinetics of poly(HPMA-Cl)-NMG beads.

boron onto the beads. The results indicated that the gel beads synthesized were good candidates as a potential sorbent for either boron removal or recovery.

CONCLUSIONS

Novel polydisperse hydrogel spheres with functional groups have been developed for boron adsorption from aqueous environment. It was found that the equilibrium boron adsorption capacity increases with increasing the initial boron content in solution, and it leveled off at approximately 145 mg boron/g dry bead, which is higher than the other resins reported for boron removal. Because of this high-boron adsorption capacity, the poly(HPMA-Cl)-NMG beads are promising in removal of boron from aqueous solutions.

Desorption studies illustrated that the adsorbed boron can easily be stripped off from hydrogel beads by HCl indicating that the resin can be reused after an alkaline treatment.

According to kinetic studies, second-order boron sorption was obtained and boron concentrations of solutions reached to almost zero within less than 15 min, which suggests that there is no internal diffusion.

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TABLE II
 Desorption Values Obtained for Poly(HPMA-Cl)-NMG Beads

	mg-B adsorbed	mg-B eluted	% Elution
10 mg-B/L	0.25	0.22	88
100 mg-B/L	2.15	2.20	100

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