

Monodisperse-Porous *N*-Methyl-D-Glucamine Functionalized Poly(vinylbenzyl Chloride-*co*-Divinylbenzene) Beads as Boron Selective Sorbent

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ABSTRACT: To generate a new sorbent with high boron adsorption capacity, we synthesized monodisperse-porous poly(vinylbenzyl chloride-*co*-divinylbenzene), poly(VBC-*co*-DVB), beads 8.5 μm in size by a new "modified seeded polymerization" technique. By using their chloromethyl functionality, the beads were derivatized by a simple, direct reaction with a boron-selective ligand, *N*-methyl-D-glucamine (NMDG). The selection of poly(VBC-*co*-DVB) beads as a starting material allowed to obtain high boron sensitive-ligand density on the beads depending on their high chloromethyl content. In the batch adsorption runs performed using NMDG-attached poly(VBC-*co*-DVB) beads as sorbent, boron removal was efficiently performed in a wide pH range between 4 and 11. Quantitative boron removal was observed with the sorbent concentration of 4 g/L. In the same runs, plateau value of equilibrium adsorption isotherm was obtained as 14 mg boron/g beads. Relatively

higher boron adsorption was explained by high ligand density and high specific surface area of the sorbent. Boron adsorption isotherms were analyzed using Langmuir and Freundlich models. In the kinetic runs performed for boron removal, the equilibrium was attained within 10 min at a value of 98%. The fast kinetic behavior was explained by the smaller particle size and enhanced porosity of the new sorbent. Infinite solution volume model and unreacted core model were used to evaluate boron adsorption onto the NMDG-attached poly(VBC-*co*-DVB) beads. The results indicated that the adsorption process is controlled by the particle-diffusion step. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: boron-selective sorbent; *N*-methyl-D-glucamine; modified seeded polymerization; monodisperse porous beads; poly(vinylbenzyl chloride-*co*-divinylbenzene)

INTRODUCTION

Boron is one of the essential micronutrient elements dissolved in natural water and required for the normal growth of various plants. There is a noticeable effect on plants in terms of both nutrition and toxicity. Boron is also an important micronutrient for animals and human, but deficiency and excess of boron concentration has very narrow concentration range.¹ Long-term consumption of water and food products with increased boron content results in malfunctioning of cardiac-vascular, nervous, alimentary, and sexual systems of humans and animals. Blood composition undergoes changes, physical and intellectual progress of children decelerates and risk of pathological birth increases. Low-dose boron exposure has been shown to cause reduced growth, potential neurotoxic and

hematological effects owing to delta-aminolevulinic acid dehydratase inhibition on newborns and children and suppression of male reproductive system function. Intake of boron for humans is expected to be 0.2–0.6 mg/day from drinking water and 1.2 mg from diet. Boron compounds belong to second class of toxicological danger.^{2–5} In this connection, boron content in drinking and irrigating water as well as waste water is regulated in different countries throughout the world. There is a mandatory limit in the USA for boron in drinking water as 0.6 mg/L.⁶ In Commonwealth of Independent States countries, the maximum permissible concentration of boron in drinking water is 0.5 mg/L.⁷ The World Health Organization and several European countries have adopted or recommended drinking water limit for boron equal to 0.3 mg/L as the nonobserved effect level.⁸ In Japan, the permissible boron level is even lower and equals 0.2 mg/L.⁹ Also, the existence of trace amounts of boron in ultrapure water for cleaning and etching processes can seriously influence the characteristics of semiconductor at microelectronic industries. Therefore, the removal of ultra-trace, trace or large amount of boron is still a very important problem.^{10,11}

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There is no easy method available for the removal of boron from water and wastewater. The main processes applied according to the boron concentration in the medium are precipitation–coagulation, reverse osmosis, electrodialysis, solvent extraction, membrane filtration, and ion exchange.^{12–17} Among these methods, the use of boron selective beads is more promising owing to their high selectivity and reusability. Vicinal diol groups on the beads are regarded as the most efficient ligands for the chelation of boron. In accordance with this principle, the polymer beads with *N*-methyl-*D*-glucamine (NMDG) functionality were reported as boron-specific sorbents.^{18–20}

Monodisperse polymer beads have been of great interests in many applications, including standard calibrations, biomedical examinations, chromatographic fillers, spacers, ink additives, and catalytic substrates.^{21–24} Sophisticated techniques have been developed to create monodisperse polymer beads in micrometer size range. One of the techniques with a high production yield is “seeded polymerization.”^{25,26} This technique demonstrates that submicron-sized seeded beads can be grown to hundreds of micrometers by using a successive monomer swelling and polymerization processes.^{27,28}

Alexandratos made a significant contribution on the synthesis of diol carrying sorbents for the removal of heavy metals from water.^{29–31} In the present study, a diol-functionalized sorbent was also prepared for boron removal. For this purpose, monodisperse-porous poly(VBC-*co*-DVB) beads were obtained by a modified seeded polymerization procedure. A boron-selective ligand, NMDG was directly attached onto the poly(VBC-*co*-DVB) beads via a simple and single-stage reaction protocol. The boron uptake properties of NMDG-attached poly(VBC-*co*-DVB) were investigated in batch fashion.

EXPERIMENTAL

Materials

2,2'-Azobisisobutyronitrile (AIBN, Merck AG, Darmstadt, Germany) recrystallized from methanol and polyvinylpyrrolidone (PVP K-30, M_n : 40,000, Sigma Chemical, St. Louis, MO) were the initiators and the stabilizers in the preparation of seed latex. Styrene (Yarpet AS, Turkey) was distilled under vacuum. The monomers, vinylbenzyl chloride (VBC), and divinylbenzene (DVB) were supplied from Aldrich Chemical, WI, USA, and used without further purification. Sodium dodecyl sulfate (SDS, Sigma) was used as an emulsifier in the preparation of aqueous emulsion medium for the swelling of polystyrene (PS) seed beads. Poly(vinyl alcohol) (PVA, 87–89% hydrolyzed, M_n : 85,000–146,000, Aldrich) was the

stabilizer in the seeded polymerization. Dodecanol (Fluka Chem., WI), and dibutyl phthalate (DBP; Aldrich), toluene (Riedel-de Haën, Seelze, Germany) were the porogen components in the synthesis of monodisperse porous poly(VBC-*co*-DVB) beads. Tetrahydrofuran (THF; Aldrich) was used for the extraction of poly(VBC-*co*-DVB) beads. NMDG (Sigma), 1,4-dioxan (Lab-Scan, Gliwice, Poland) were of analytical grade and they were used as supplied.

Synthesis of seed latex

Monodisperse PS seed latex (2.2 μm in size) was prepared by dispersion polymerization of styrene (10 mL) in ethanol (100 mL). First, the steric stabilizer, PVP (K-30) (1.0 g) was dissolved in ethanol. After adding styrene (10 mL), AIBN (0.12 g) was dissolved in the resulting medium by sonication. Dispersion polymerization was performed in a sealed Pyrex cylindrical reactor shaken at 120 rev/min for 24 h at 70°C. After polymerization, seed latex was washed with distilled water several times by successive centrifugation and decantation.

Synthesis of monodisperse porous poly(VBC-*co*-DVB)

The monodisperse porous poly(VBC-*co*-DVB) beads were synthesized by a “modified seeded polymerization” as described elsewhere.³² Typically, 0.5 g of PVA was dissolved in distilled water (90 mL) and 0.15 g of SDS was added as emulsifier. Then, an organic phase containing VBC (2.0 mL), DVB (2 mL), AIBN (0.08 g), and diluents, toluene (2.0 mL), DBP (2.0 mL), and dodecanol (0.5 mL) was added to the mixture. The mixture was sonicated for 25 min to disperse the organic phase within water. PS seed latex (0.35 g) was then added to this emulsion and resulting medium was stirred at room temperature for 24 h at 400 rpm for swelling of seed latex within the aqueous emulsion. Polymerization was performed at 70°C in a sealed reactor with a shaking rate of 120 rev/min for 24 h. The resulting polymer beads were washed with ethanol and extracted twice with THF (50 mL) at 60°C for 1 h and then extensively washed with ethanol.

Synthesis of monodisperse porous poly(VBC-*co*-DVB) beads containing NMDG

To prepare NMDG-attached poly(VBC-*co*-DVB) beads, poly(VBC-*co*-DVB) beads (1.0 g) were treated with 1.0 g NMDG in water : 1,4-dioxan (5:15 v/v) mixture (20 mL) at 80°C for 8 h in a pyrex batch reactor. NMDG-attached poly(VBC-*co*-DVB) beads were extensively washed with distilled water by applying a centrifugation–decantation procedure.

Batch-mode sorption studies for boron removal from aqueous solutions

To find the appropriate concentration of NMDG-attached poly(VBC-co-DVB) beads for boron removal from aqueous medium, various amounts of beads (0.005, 0.01, 0.02, 0.05, 0.1, 0.2, and 0.3 g) were contacted with boron solutions (25 mL, pH 8.5) with an initial boron concentration of 10 mg/L. The beads were equilibrated for 24 h at 30°C with continuous shaking. Effect of pH on boron uptake by NMDG-attached poly(VBC-co-DVB) beads was investigated under similar conditions. In these runs, the amount of sorbent was fixed to 0.1 g and pH was adjusted to desired value by using 0.1M HCl or 0.1M NaOH solution. For equilibrium adsorption isotherm, 0.1 g of beads was contacted with boron solution (25 mL) with boron concentrations of 2, 5, 20, 50, 100, 150, and 200 mg/L at 30°C for 24 h under continuous shaking.

Kinetic runs were carried out in plastic bottles at room temperature. The boron solution (25 mL, initial boron concentration: 10 mg/L) was contacted with NMDG-attached poly(VBC-co-DVB) beads (0.1 g) at different times. The medium was magnetically stirred at 300–350 rev/min. The boron concentration in the solution was monitored at 5, 10, 15, 20, 30, 45, 60, 90, and 120 min. Boron concentration in the sample was determined by ICP-MS (ELAN 9000 model, AJ 12700901, Perkin Elmer, Massachusetts, USA).

The desorption of boron from NMDG-attached poly(VBC-co-DVB) beads was investigated using different media (0.5M HCl; 0.1M HCl or 0.1M CH₃COOH, 25 mL) at room temperature. The adsorption–desorption cycles were repeated three times to test the reusability of NMDG-attached poly(VBC-co-DVB) beads.

Characterization of NMDG-attached poly(VBC-co-DVB) beads

Size distribution properties and surface morphology of poly(VBC-co-DVB) beads were examined by a Scanning Electron Microscope (SEM, JEM 1200 EX, JEOL, Japan). The average bead size and the coefficient of variation for size distribution were calculated according to the expressions described elsewhere.³³ The pore size distribution and the average pore size of plain poly(VBC-co-DVB) beads were determined by inverse size exclusion chromatography (ISEC) according to the procedure discussed elsewhere.³³ ISEC study was performed in THF using stainless steel HPLC columns (50 mm long × 7.8 mm id) packed with poly(VBC-co-DVB) beads. PS standards with different average molecular weights (i.e., 2,000,000, 5,50,000, 2,12,000, 1,14,200, 44,000, 18,000, 3680, and 770 Da) and toluene were

injected into the HPLC column packed with the poly(VBC-co-DVB) beads. The specific surface area of poly(VBC-co-DVB) beads was determined using Brunauer–Emmett–Teller apparatus (Quantachrome, Nova 2200E, Florida, USA). FTIR spectra of plain poly(VBC-co-DVB) and NMDG-attached poly(VBC-co-DVB) beads were recorded using KBr pellets in an FTIR spectrometer (FTIR-8101, Shimadzu, Japan).

RESULTS AND DISCUSSION

A new boron selective sorbent was prepared using monodisperse-porous poly(VBC-co-DVB) beads and NMDG as the support material and the boron-selective ligand, respectively. Chloromethyl functionality allowed direct, covalent attachment of boron-selective ligand onto the beads by a simple and single-stage reaction. Poly(VBC-co-DVB) beads were obtained using a monomer mixture containing 50% (v/v) VBC and 50% (v/v) DVB. The results of our previous studies indicated that final VBC content of the beads was very close to that of the initial monomer mixture. Hence, high chloromethyl content of the selected beads allowed high boron selective ligand density on the sorbent beads because NMDG was attached via the chemical reaction between amine and chloromethyl groups. In addition to these factors, low-sized sorbent beads allowed to work with an extremely short-diffusion path for the adsorption of boron within the sorbent beads. This property was evaluated as a factor accelerating the diffusion rate within the beads and reducing the internal mass-transfer resistance during the boron adsorption. Hence, a fast adsorption kinetics was expected by the use of low-sized sorbent. The monodisperse character of the sorbent beads also contributed positively to the intraparticle diffusion process during boron adsorption. In addition to all these factors, high specific surface area of the selected beads is also another factor causing an increase in the amount of boron adsorbed onto the sorbent. Hence, based on all these reasons, poly(VBC-co-DVB) beads were selected as the base material for the synthesis of a boron selective sorbent.

Synthesis of monodisperse porous (VBC-co-DVB) beads with NMDG functionality

Particle size distribution and surface morphology of poly(VBC-co-DVB) beads are shown in the SEM images given in Figure 1. The average size and the coefficient of variation for size distribution were determined as 8.5 μm and 5.0%, respectively, for the plain poly(VBC-co-DVB) beads, using the SEM image shown in Figure 1(a). No significant change was observed in the size distribution properties after NMDG attachment. The SEM image shown in

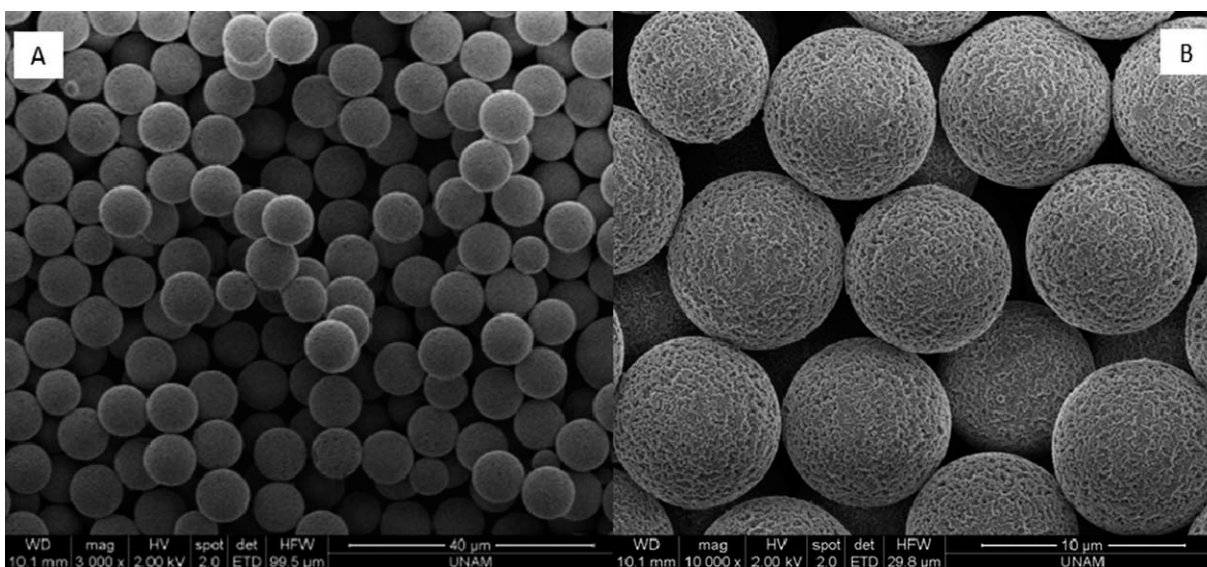


Figure 1 A representative SEM image of poly(VBC-*co*-DVB) beads.

Figure 1(b) indicates that poly(VBC-*co*-DVB) beads had a highly porous-surface predominantly containing macropores. A typical pore-size distribution curve of poly(VBC-*co*-DVB) beads determined by inverse-size exclusion chromatography is shown in Figure 2. As it can be observed, most of the pores were collected in the range of 40–250 Å. Based on this distribution, the median pore size was determined as 90 Å. An appreciable micropore fraction was also observed at 10 Å. The specific surface area of plain poly(VBC-*co*-DVB) beads was determined as 35 m²/g according to nitrogen adsorption–desorption method.

NMDG was covalently attached onto the beads according to the chemical reaction shown in Figure 3. Poly(VBC-*co*-DVB) beads carrying covalently attached NMDG are desirable for the synthesis of a boron-selective sorbent because only this form can give a cyclic borate ester with boric acid in the aqueous medium. FTIR spectra of plain poly(VBC-

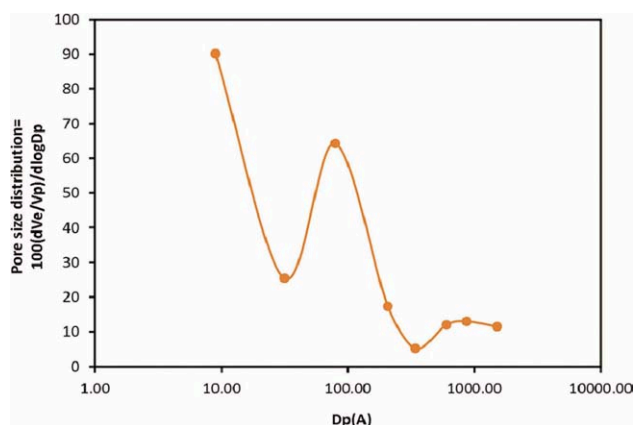


Figure 2 Pore size distribution curve of poly(VBC-*co*-DVB) beads. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

co-DVB) and NMDG-attached poly(VBC-*co*-DVB) beads are shown in Figure 4. The relative intensity of broad band in the range of 3300–3500 cm⁻¹, indicating –OH stretching vibration was much higher in the FTIR spectrum of the NMDG-attached beads compared to the spectrum of plain poly(VBC-*co*-DVB) beads. For NMDG-attached beads, the relative intensity of hydroxyl band with respect to the aliphatic band at 2800 cm⁻¹ was calculated as 2.4. The same value was determined as 1.2 for the plain poly(VBC-*co*-DVB) beads. Twofold higher relative intensity observed for NMDG-attached poly(VBC-*co*-DVB) beads clearly showed the covalent attachment of NMDG onto the beads and approximately twofold increase in the concentration of hydroxyl functionality in the particle structure after functionalization. In the FTIR spectrum of plain poly(VBC-*co*-DVB) beads, the hydroxyl band in the range of 3300–3500 cm⁻¹ should be related to the possible partial hydrolysis of chloromethyl functionality during polymerization. Nitrogen content of NMDG-attached poly(VBC-*co*-DVB) beads was determined as 0.97% (w/w), by elemental analysis. Nitrogen content of the plain poly(VBC-*co*-DVB) beads was also checked to consider

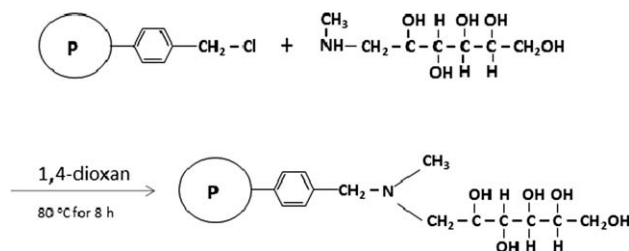


Figure 3 Schematic illustration of the functionalization of poly(VBC-*co*-DVB) with NMDG.

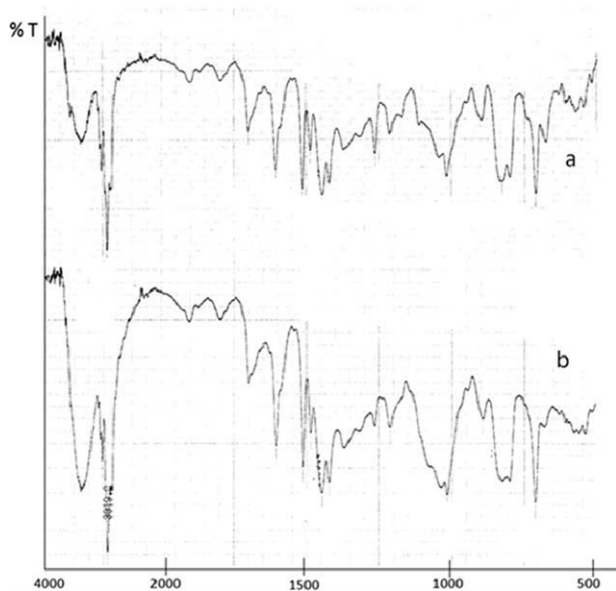


Figure 4 FTIR spectra of plain poly(VBC-co-DVB) beads (a) and after functionalization with NMDG (b).

any possible nitrogen obtained from the initiator (i.e., AIBN). However, this value could not be determined as it was lower than 0.1% (w/w). By using the nitrogen content of NMDG-attached poly(VBC-co-DVB) beads, its NMDG content was calculated as 135.2 mg NMDG/g dry beads or 0.69 mmol NMDG/g beads. Each NMDG molecule contains five hydroxyl functionalities and free boron in solution uses diol functionality to interact with NMDG.³⁴ Different diol–boron binding combinations are possible based on the five hydroxyl functionalities of each ligand molecule. However, based on the interaction of boron and NMDG defined in the literature³⁴ one can conclude that the equivalent amount of boron adsorbed onto the sorbent should be higher than the NMDG molar content of the sorbent designed.

Poly(VBC-co-DVB) copolymer in the beaded form is a highly stable structure. According to the results obtained in the previous studies, the decomposition temperature should be higher than at least 300°C.³⁵ Melting point of the ligand attached, NMDG is 129–131.5°C. Then, no significant decomposition is anticipated for the sorbent obtained by attaching NMDG onto poly(CMS-co-DVB) beads, in the temperature range that can be used for studying with geothermal waters.

Effect of sorbent concentration on boron sorption

To find an appropriate sorbent concentration for complete removal of boron from aqueous solution, a batch-mode sorption study was performed by varying the amount of sorbent. Figure 5 shows the removal of boron as a function of sorbent concentration. The percent removal of boron increased with increasing sorbent concentration. This behavior

should be related to the increase in the specific surface area of the sorbent. To remove boron quantitatively from aqueous solution (>95%), the concentration of NMDG-attached poly(VBC-co-DVB) beads was determined as 4.00 g/L. Here, 10 mg/L of boron concentration was selected as a representative value commonly observed in geothermal waters in Turkey. Note that the anions like $\text{SO}_4^{=}$, NO_3^{-} , HCO_3^{-} , and Cl^{-} can be found in geothermal waters. These anions can interfere with the boron adsorbed onto the sorbent designed. For investigating possible interferences, the sorbent proposed has been still tested for boron adsorption using Balçova geothermal water.

Effect of pH on boron sorption

To have an idea about the performance of NMDG-attached poly(VBC-co-DVB) beads at different pHs; the sorption of boron was investigated as a function of pH. Figure 6 shows the results of boron sorption by the NMDG-attached poly(VBC-co-DVB) beads at a pH range of 4–11. The beads can remove boron from aqueous solution efficiently at each pH. The boron uptake almost leveled off in the pH range of 4–7. Above pH 7, the uptake increased slightly with increasing pH. It should be noted that the boron sorption behavior of NMDG-attached poly(VBC-co-DVB) beads against pH was similar to that obtained with commercially available boron-selective ion exchange beads.^{36–38}

Sorption isotherms by NMDG-attached poly(VBC-co-DVB) beads

The most commonly used equations for modeling sorption equilibrium data are Langmuir and

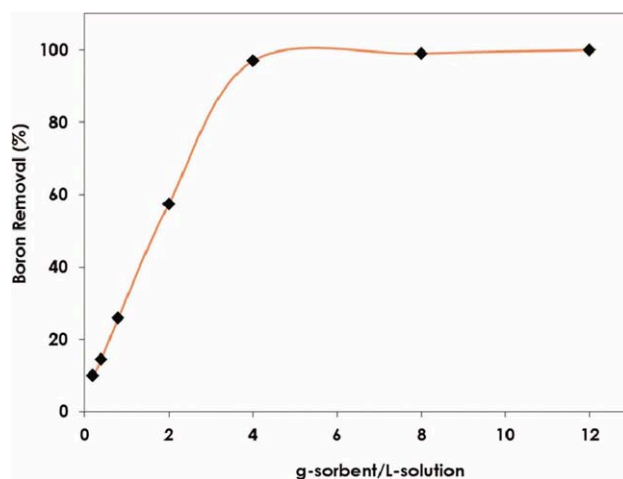


Figure 5 Effect of sorbent concentration on boron removal from aqueous solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

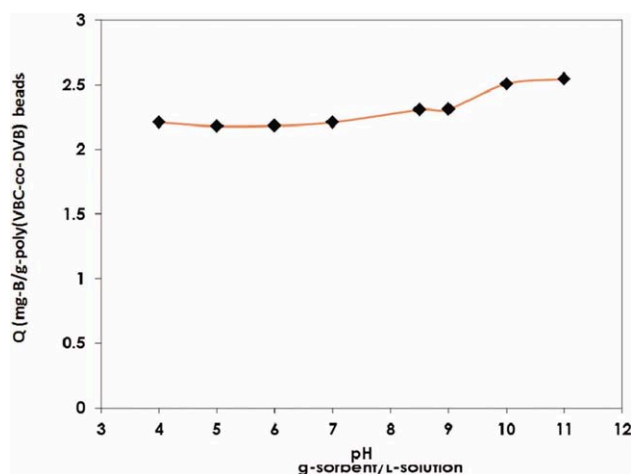


Figure 6 Effect of pH on boron removal from aqueous solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Freundlich isotherms.^{39,40} Both models were used to describe the relationship between the amount of boron sorbed and its equilibrium concentration in the solution.

The Langmuir isotherm is given by eq. (1)

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (1)$$

where Q_e (mg/g) is the amount of boron adsorbed per gram of NMDG-attached poly(VBC-co-DVB) beads at equilibrium, C_e is the equilibrium concentration of boron in the solution (mg/L), Q_0 (mg/g), and b (L/mg) are the Langmuir constants related to the capacity and energy of sorption, respectively. It is found that the sorption capacity of the beads for boron increases with increasing the initial boron concentration in the solution. The maximum boron uptake value (Q_0) and the energy of sorption value (b) were determined as 14.4 mg boron per gram-dry beads and 0.6 L/mg, respectively. These values were obtained by least square estimation with the correlation coefficient of 0.999. Note that the equivalent amount of NMDG attached onto the poly(VBC-co-DVB) beads was determined as 0.69 mmol/g dry beads. The maximum boron uptake (i.e., 14.4 mg boron per gram-dry beads) corresponds to 1.33 mmol boron per gram of dry beads. This value is approximately two times higher with respect to NMDG content of the beads. Theoretically, one diol functionality on each NMDG molecule interacts with one boron atom. Higher equivalent boron adsorption with respect to NMDG attached onto the beads should be explained by the number of possible diol combinations (i.e., more than one) on each NMDG molecule that can potentially interact with the boron in the solution.

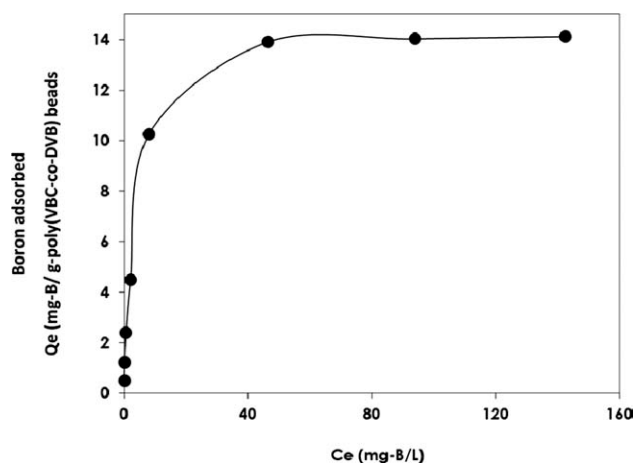


Figure 7 Equilibrium isotherm for boron removal from aqueous solution.

The Freundlich isotherm is derived to model the multilayer sorption and relates the uptake of solute onto the sorbent with the solution concentration. This isotherm is expressed as given in eq. (2)

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

where K_f and n are the Freundlich constants, indicating relative capacity and adsorption intensity, respectively. The values of K_f and n were determined as 3.4 mg/g and 2.9, respectively, for Freundlich isotherm model. Value of $n > 1$ represents favorable sorption.⁴¹ This isotherm with high n -values is classified as the L-type isotherm, reflecting relatively high affinity between boron and poly(VBC-co-DVB) beads with NMDG functionality (Fig. 7). The correlation coefficient for fitting to Freundlich equation was found to be 0.951 (Table I). According to the correlation coefficient obtained, we can consider that sorption isotherm could be better explained with Langmuir model.

Boron sorption kinetics of NMDG-attached poly(VBC-co-DVB) beads

To have an idea about the kinetic performance of NMDG-attached poly(VBC-co-DVB) beads, boron uptake was monitored with time. As shown in Figure 8, the removal of boron increased with time

TABLE I
Isotherm Constants for Boron Sorption by NMDG-Attached Poly(VBC-co-DVB) Beads

Langmuir isotherm constants			Freundlich isotherm constants		
Q_0 (mg/g)	b (L/mg)	r^2	K_f (mg/g)	n	r^2
14.4	0.6	0.999	3.4	2.9	0.951

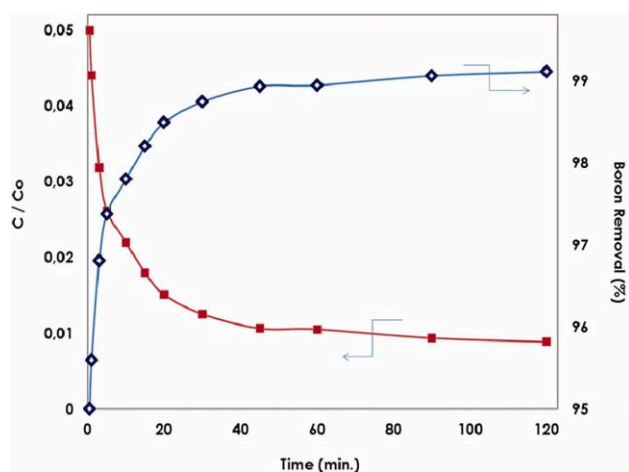


Figure 8 Kinetic performance of NMDG-attached poly(VBC-co-DVB) beads for boron removal. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and reached equilibrium within 10 min with the boron removal of 98%.

Batch kinetic runs were evaluated using some mathematical models. The ion exchange between the counter ion in the solution and the exchangeable ion on the beads is well described by a heterogeneous process. The models for process dynamics cover both the diffusional steps (bulk solution, a film layer at the external surface of the particle, and through the pores of the beads) and the exchange reaction on the active sites. As the resistance in bulk solution is easily controlled and negligible, the overall rate of ion-exchange process is usually determined by three resistances that is, film diffusion, particle diffusion, and chemical reaction. In the first approach, two separate diffusional cases, namely, particle diffusion and film diffusion, are considered. The solution is obtained by the integration of the material balance for the infinite solution volume (ISV) model based on Fick's Law. Another approach uses the unreacted core model (UCM) where the ion exchange is treated

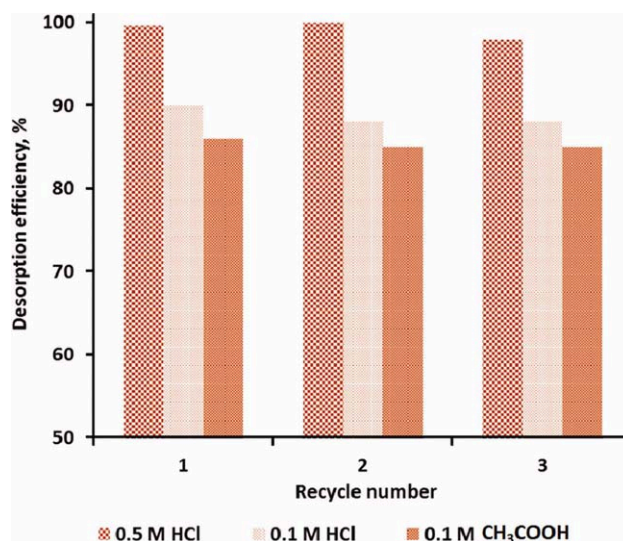


Figure 9 Percentage of boron desorbed from NMDG-attached poly(VBC-co-DVB) beads with different eluent solutions over three cycles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as a heterogeneous reaction in which the reaction occurs first at the outer skin of the particle and then within a zone moving into the particle through the unreacted core.^{41,42} These kinetic models were developed for spherical beads by considering different rate-determining steps summarized in Table II. The value of X is the fractional attainment of adsorption equilibrium. It was calculated according to equilibrium time (2 h) by the following equation. Where q_e and q_t (both in mg boron/g beads) are the amount of boron sorbed per unit mass of the beads at equilibrium and time t , respectively.

$$X = \frac{q_t}{q_e} \quad (3)$$

These models were investigated to fit the kinetic data of boron sorption onto the NMDG-attached

TABLE II
Evaluation of Kinetic Models for NMDG-Attached Poly(VBC-co-DVB) Beads^a

Method	Equation	k	Rate-controlling step	Linear correlation coefficient, r^2
ISV	$-\ln(1 - X) = k_{if}t$	$k = 3DC/r_o\delta C_r$	Film diffusion	0.9840
ISV	$-\ln(1 - X^2) = kt$	$k = D_r\pi^2/r_o^2$	Particle diffusion	0.9853
UCM	$X = kt$	$k = 3C_{A0}K_{mA}/ar_oC_{S0}$	Liquid film	0.9505
UCM	$3 - 3(1 - X)^{2/3} - 2X = kt$	$k = 6D_{eR}C_{A0}/ar_o^2C_{S0}$	Reacted layer	0.9754
UCM	$1 - (1 - X)^{1/3} = kt$	$k = K_sC_{A0}/r_o$	Chemical reaction	0.9690

^a X , fractional attainment of equilibrium or extent of resin conversion; k , rate constant (L/s); t , time (s); D_r , diffusion coefficient in solid phase (m^2/s); r_o , average particle radius (mm); k_{if} , rate constant for film diffusion (infinite solution volume condition (L/s)); D , diffusion coefficient in solution phase (m^2/s); δ , film thickness (mm); C , total concentration of both exchanging species (M); C_r , total concentration of both exchanging species in the ion exchanger (M); C_{A0} , concentration of species A in bulk solution (M); K_{mA} , mass transfer coefficient of species through the liquid film (m/s); a , stoichiometric coefficient; C_{S0} , concentration of solid reactant at the bead's unreacted core (M); D_{eR} , effective diffusion coefficient in solid phase (m^2/s); K_s , reaction constant based on surface (m/s).

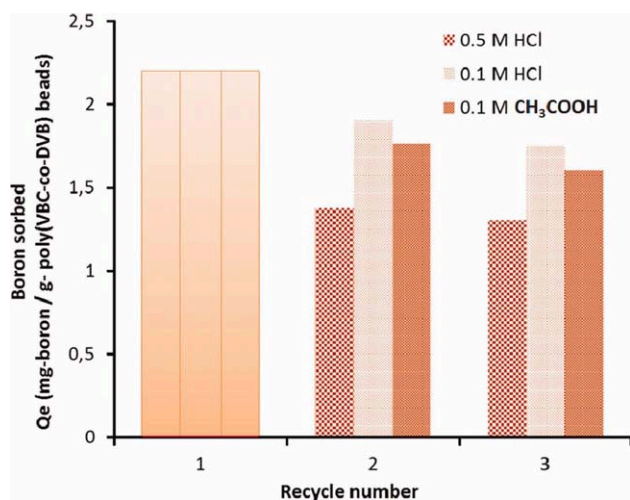


Figure 10 Reusability of NMDG-attached poly(VBC-co-DVB) beads on boron removal after three adsorption-desorption cycles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

poly(VBC-co-DVB) beads. As the equilibrium was attained in 10 min, the data obtained at contact times larger than 10 min were neglected. Linear correlation coefficients for five models for boron adsorption kinetics with the NMDG-attached poly(VBC-co-DVB) beads are listed in Table II. Linear correlation coefficients help to decide the rate-determining step. According to ISV models, one can conclude that the boron adsorption onto the NMDG-attached poly(VBC-co-DVB) beads is a particle diffusion-controlled process. As summarized in Table II, the highest correlation coefficient was also found for particle diffusion step using UCM.^{43–45} Hence, the application of both models gave the same result for the determination of rate-limiting step in the adsorption process.

Desorption tests

HCl (0.1 and 0.5M) and CH₃COOH (0.1M) solutions were used as eluent for desorbing boron from NMDG-attached poly(VBC-co-DVB) beads. Figure 9 shows the desorption efficiency of boron with different eluents. Quantitative desorption yields were obtained with 0.5M HCl solution in each cycle. No significant decrease was observed in the desorption yield with increasing cycle number. However, lower desorption yields were obtained with 0.1N HCl and 0.1M CH₃COOH solutions. To determine the reusability of NMDG-attached poly(VBC-co-DVB) beads, adsorption-desorption cycles were repeated sequentially three times. Boron adsorbed at equilibrium versus cycle number is shown in Figure 10. As shown in Figure 10, boron desorptions were also performed using three different eluents. For each eluent, a slight decrease in boron adsorption was

observed after the first cycle. However, no significant decrease occurred for the boron adsorptions obtained at 2nd and 3rd cycles.

CONCLUSIONS

Monodisperse NMDG-attached poly(VBC-co-DVB) beads could be effectively used as sorbent for the removal of boron from aqueous solutions in the pH range of 4–11. It was possible to obtain high adsorption capacity between pHs 8.5 and 10. For quantitative removal of boron from a model solution, a particle concentration of 4 g/L is needed. The equilibrium adsorption of boron onto the NMDG-attached poly(VBC-co-DVB) beads was adequately described by Langmuir isotherm. The adsorption rate was controlled by the particle diffusion process. Desorption of boron from the NMDG-attached poly(VBC-co-DVB) beads was achieved using acidic eluent solutions.

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