Polymer Networks Based in (4-Vinylbenzyl)-*N*-methyl-D-glucamine Supported on Microporous Polypropylene Layers with Retention Boron Capacity

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ABSTRACT: New cellulose porous layers, with capacity to transport and retain boron from aqueous solution, were developed via interpenetrating polymer network (IPNs). These polymer systems were made to assemble mimetic systems of plant root tissue for the study of available boron transport. For that cellulose porous layers supported on polypropylene matrix were used as primary network for the formation of IPN. A vinyl monomer, (4-vinylbenzyl)-*N*-methyl-D-glucamine (VbNMDG), was synthesized at three concentration levels and cellulose ultrafiltration membranes were modified by *in situ* polymerization in the inside of the pores. Change of hydrophilicity, percent of secondary network, permeability and retention properties were studied. The formation of IPNs in the inside of the pores decreased the permeabilities of polymer layers. In addition, a decrease of hydrophilicity was seen. A linear increase of boron retention in function of VbNMDG concentrations was observed for the different boron concentrations and a negative effect on retention capability was evidenced for several charge and discharge cycles. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40653.

INTRODUCTION

Boron is an essential micronutrient associated with the growth and development of the plants and productivity of the crops. Boron has been found to play a role in the lignification processes, membrane transport, enzyme interactions, nucleic acid synthesis, and carbohydrate metabolism.[1–3] However, there is a small range between boron deficiency and boron toxicity in plants, and in consequence, the boron concentration in irrigation water or in soils plays an important role in both crop yields and the quality of products.[3] At the present time, it is accepted that boron is essential for the growth of plants in many ways. However, it becomes toxic for the plants when the amount of boron is slightly greater than required since the range of boron concentration between deficiency and excess is narrow.[1,4] In the plants, the physiological negative effect of boron involves the decrease of root cell division, retarded shoot and root growth, inhibition of photosynthesis, deposition of lignin, reduction in leaf chlorophyll etc.[1–3]

The main form of B, which is available in the natural environment, is in the form of undissociated boric acid; in consequence, boron is absorbed from the soil solution by plant roots mainly as H_3BO_3.[5] At the present time, the mechanism of boron uptake by plant roots is a controversial subject; there is evidence supporting an active uptake and by passive entry into cells. Thus, under deficiency conditions several proteins have been associated to transport of boron, but at normal nutritional levels, mediated transport of boron is not clear. However, it is generally accepted that boric acid moves passively through the lipid bilayer and that the internal complexation of boron is one of the driving forces of boron uptake.[5,6]

Between main technologies used for boron removal are reverse osmosis (RO), ion exchange methods, adsorption on membrane filtration, solvent extraction and inorganic adsorbents.[4,7–11] Recently, Kabay et al., Hilal et al., and Wolska and Bryjak reviewed the technologies for boron removal from aqueous systems.[4,9,10] At the present time, RO, boron selective resins and adsorption on membrane filtration have been the focus of much research.[4]

RO is a membrane technology used for seawater desalination. Thus, boron in the form of negatively charged borate ion, $B(OH)_4^-$, is easily removed by RO membranes like other dissolved ionic substances.[4] However, it is difficult to eliminate

non-dissociated neutrally charged boric acid in seawater by this technique.[4,9–11] On the other hand, the principle of boron selective resins is the use of complexation reactions. Boric acid reacts with compounds possessing multi hydroxyl groups (polyols) to form a variety of borate esters.[4,12,13] In relation with this point, it have been reported that the stability of the borate complex formed strongly depends on the type of diol used. Thus, a strong complex is formed when the diol used involves the hydroxyl groups oriented in such a way that they accurately match the structural parameters required by tetrahedrally coordinated boron. For example, a stable complex is formed by the reaction of boron with compounds possessing cis-diol system such as D-mannitol, D-sorbitol, and D-ribose.[12] Adsorption on membrane filtration has been considered as an alternative for separation process. This technique is based in the concept of the hybrid process which combines a sorption process with membrane separation. In this hybrid process, solutes are absorbed by sorbents followed by a membrane separation of the saturated sorbents (i.e., complexing resin based in D-sorbitol).[4,9,14]

The production of new polymer materials is very useful in the development of new technologies for removal, retention and recovery of boron from aqueous solution. Works recently published are based in the modification by surface reactions for the introduction of NMDG groups,[15] by blending semi-interpenetrating network polymeric nanoparticle,[16] and by surface adsorption of linear polymers.[17] Another alternative for the modification of porous materials is by interpenetrating polymer networks (IPNs). These are a fast and versatile route for many polymer systems.

IPNs are polymeric structures formed when two distinct multi-functional polymers become entangled at the molecular level.[18–21] IPNs are formed when at least one of the multi-functional monomers is reacted in the presence of the other polymer. IPNs are classified depending of network configuration as sequential IPN (SIPN), simultaneous IPN (SIPN), and semi-IPNs. Thus, IPNs are formed when one of the monomers is added and polymerized in an existing polymer, SIPN are produced by two non-interfering polymerizations from a mixture of the monomers and semi-IPNs are SIPNs in which only one of the polymers is crosslinked while the other is linear.[15] The distinctive properties of IPNs have attracted considerable attention, and continue to be of interest in both fundamental and applied investigations. A main objective in the production of IPNs is the combination of chemical and physical properties of individual polymers in a same material (i.e., boron retention properties, membrane properties, chemical and mechanical resistance). In addition, in some cases a synergistic effect is expected. Some applications of IPNs are fuel cell membranes, drug delivery, and tissue engineering.[21–23]

The objective of this work was to develop, via IPNs, polymer porous layers with capacity to transport and retain boron from aqueous solution to assemble mimetic systems of plant root tissue for the study of available boron transport in the soil-plant system. Thus, cellulose layers with nanoporous supported on polypropylene matrix were used as primary network for in situ polymerization of a boron selective monomer: (4-vinylbenzyl)-N-methyl-D-glucamine.

EXPERIMENTAL

Reagents and Materials

Vinylbenzyl chloride (VBCl, Aldrich) and N-methyl-D-glucamine (NMDG, Aldrich) were used in the synthesis of (4-vinylbenzyl)-N-methyl-D-glucamine (VbNMDG); VbNMDG is a vinyl monomer with hydroxyl groups capable to link boron from aqueous solution. N,N-Methylene-bis-acrylamide (MBA, 98 %, Aldrich) and ammonium persulphate (Aldrich) were used for polymerizing of VbNMDG via free radical. 1,4-Dioxane (Aldrich) and bi-distilled water were used as solvents. Cellulose disk-shaped membranes with 100 kDa molecular weight cut-off (biomax PBGC, manufactured by Millipore) were used as primary network for the formation of IPNs. Boron aqueous solutions were prepared from boric acid (H_3BO_3, Aldrich) using bi-distilled water. Nitric acids (HNO_3, Aldrich) and sodium hydroxide (NaOH, Aldrich) were used to control the pH. A stirred-cell filtration unit (Millipore, model 8050) was used in experiment diafiltration; components and operation modes of the filtration system have been described in previous publications.[24,25]

Synthesis of VbNMDG

NMDG was dissolved in a dioxane-water solvent mixture (2 : 1 volume ratio). The solution was added to the reactor and heated for 20 minutes until NMDG was completely dissolved. Later, 3.20 mL (21.9 mmol) of VBCl was dissolved in 10 mL of dioxane and 10 mL of 1.0 mol L^{-1} NaOH solution was added to the reactor. The reaction was kept under reflux with constant stirring for 5 hours. By extraction with ethyl ether the unreacted VBCl was removed remaining in the aqueous phase functionalized monomer (VbNMDG). This reaction was performed using three level of VBCl concentration (21.9, 43.8, and 65.7 mmoles). Functionalizing of VBCl with NMDG was evaluated by Fourier-transformed infrared spectroscopy (FT-IR) and by polymerization test of aqueous phase (this test is based in the polymerization reaction of aqueous phase in presence of initiator and crosslinker; double bound C=C associated to the VBCl only can be in aqueous phase when functionalization was satisfactorily performed).

Formation of IPNs in the Inside of Cellulose Layers

The modification of cellulose layer (or membrane) was performed by injection of functionalized monomer in the inside of the material pores in presence of radical initiator (2.0% mol of ammonium persulphate with respect to the monomer) and crosslinker reagent (8.0% of MBA). For that, 20 mL of reactive mixture was added to the stirred-cell ultrafiltration unit and introduced in the membrane pores by pressure (100 kPa using N_2). When a volume equal to 10 mL of solution was identified in the permeate, filtration system was stopped and the membrane was placed in a parallel plate system designed for avoiding the contact with active layer. Later, this plate system was heated by 1 h using an airflow oven at 30°C to carry out the polymerization of poly[(4-vinylbenzyl)-N-methyl-D-glucamine)], P(VbNMDG). Notation used to describe the IPNs formed

Table I. Sample Identification, Amount of VBCl Added in the Synthesis of VbNMDG, Percent of VbNMDG Calculated from Eq. (1) and Changes of Contact Angle with Three Different Solvents for the Samples CM_0 and MM_1

Sample	Sample identification	Amount of VBCl (mmoles)	Percent of VbNMDG (%)	Angle contact measures		
				Water	Ethylene glycol	1,3-propanediol
Unmodified cellulose	CM_0	0.0	0.0	72.1 ± 0.3	79.5 ± 0.4	69.0 ± 0.1
Modified cellulose	MM_1	21.9	2.9	51.8 ± 0.2	50.2 ± 0.5	68.3 ± 0.2
	MM_2	43.8	23.8			
	MM_3	65.7	47.5			

according to the amount of VbNMDG is shown in the Table I ("Results and discussion" section).

Characterization Experiments

Percent of P(VbNMDG) in the IPNs. Modified membrane were washed with bi-distilled water using a stirred-cell filtration unit (100 mL of water at 100 kPa) and dried using an airflow oven at 30°C until constant mass. Unmodified membrane masses were measured previously to the formation of IPNs. Mass percent of P(VbNMDG) was determined respect to total mass of IPNs by eq. (1).

$$Percent\ of\ P(VbNMDG) = \frac{w_{IPN} - w_0}{w_{IPN}} \times 100 \qquad (1)$$

where w_0 and w_{IPN} are the mass of unmodified and modified membranes, respectively.

Surface Analysis. Unmodified and modified membrane surfaces were analyzed by scanning electron microscopy (SEM) and diffuse reflectance infrared Fourier transform (DRIFT) to identify the main functional groups.

Contact Angle. Changes of membrane hydrophilicity were analyzed by contact angle by drop deposition method. ± 3 μL drops of three liquids with different polarities (water, ethylene glycol, and 1,3-propanediol) were deposited one by one on the membrane surface and the process was captured on video format to be analyzed. This experiment was performed for one single modified membrane (MM_1) and for unmodified cellulose layer (CM_0). A description of this procedure has been previously published.[20]

Permeability Analysis. Permeability test was performed to the all membranes and consisted in the measurement of the permeated bi-distilled water mass and the permeated time at different applied pressures (100, 200, 300, and 400 kPa). The mass was measured with a high precision balance with errors lower than $\pm 1 \times 10^{-7}$ kg (Sartorius Analytic A120S).

Retention Experiments

Batch Experiments. Batch experiments at pH 7.0 were performed to determine the boron retention capacity of IPNs. Samples of IPNs were weighed and placed in batch of polypropylene to avoid mistakes on determination of boron concentration. A boron solution was added to the system and filtered to measure the boron concentration remains in the solution. Contact effect was evaluated for two times (30 and 60 min) and two boron concentration levels (0.15 and 3.00 mg L^{-1}). These

experiments are denoted to be Exp-1 (30 min and 0.15 mg L^{-1}) and Exp-2 (60 min and 3.00 mg L^{-1}). Boron concentrations were analyzed using azomethine-H method.[21] The experimental blanks were performed using unmodified membranes. Boron retention (R_B) was calculated by

$$R_B = 1 - \frac{C_2}{C_1} \qquad (2)$$

where C_2 and C_1 are final and initial boron concentration, respectively. In addition, molar ratio of boron to NMDG units (r_B), was calculated by

$$r_B = \frac{n_B}{n_{NMDG}} \qquad (3)$$

where n_B and n_{NMDG} are the moles of boron and NMDG, respectively.

Charge and Discharge Experiments. To determine the reuse capability of IPNs and its effect on the boron retention capacity, charge and discharge cycles were performed at pHs 7.0 and 11.0, respectively. Procedure was similar to that described in the "Batch Experiments" section. Discharge was carried out using NaOH solutions.

Diafiltration Experiments. To determine the maximum retention capacity (MRC) diafiltration experiments were performed using the washing method.[22,23] In this case, a boron solution was placed in the inside of a stirred-cell filtration unit (amicon 3050) at pH 5.0 and, from reservoir, water at the same pH was continuously added (applied pressure was 300 kPa); boron concentration was 8.5 mg/L to assure an excess of boron. Permeate was collected and quantified by azomethine-H method.

RESULTS AND DISCUSSION

Formation and Characterization of IPNs

A description of functionalization reaction is shown in the Figure 1. Synthesis of VbNMDG consisted in the insertion of one polyol chain on VBCl to obtain a monomer with boron retention capability and, in consequence, a polymer with the same capability. IR-FT spectra of precursors (VBCl and NMDG), reaction product (VbNMDG), modified and unmodified cellulose layers are shown in the Figure 2. Typical vibrations of the NMDG and VBCl structures were observed. For NMDG, the main signals were at $\sim$3331, 1075, and 1045 cm^{-1} which are characteristic bands of the —OH, C—O, and C—N bonds, respectively; for VBCl, the main signals were at 1629 and 843 cm^{-1} which are characteristic bands of the C=C and C—Cl
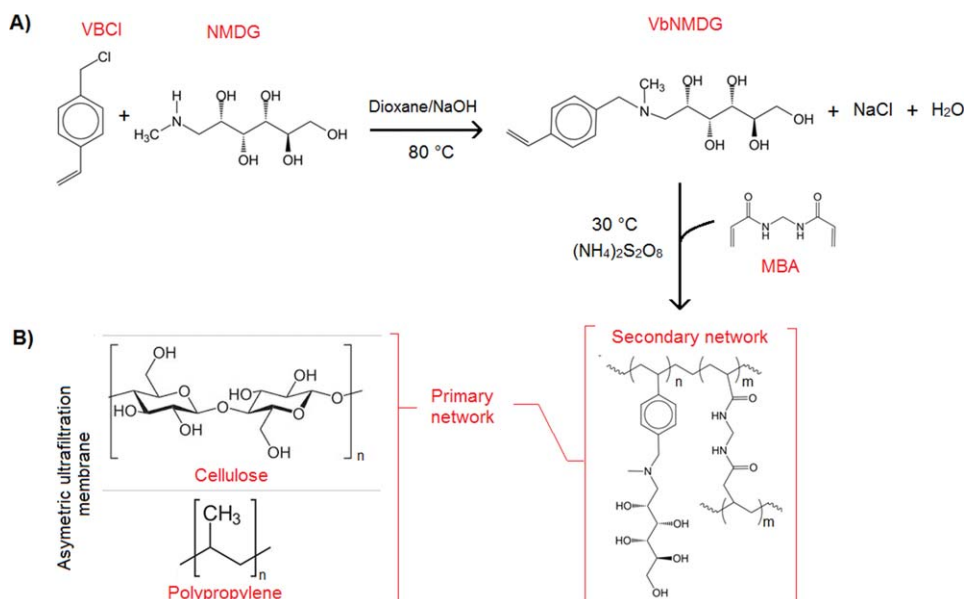
Figure 1. Sequence of reactions for producing the IPNs: (A) synthesis of VbNMDG and formation of IPN and (B) structure of primary network (cellulose supported on polypropylene). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bonds, respectively. On the other hand, from VbNMDG spectrum can be seen a sign at ~3400 cm^{-1} associated with —OH groups of NMDG and another at 1640 cm^{-1} associated with C=C bonds. In addition, the band around 843 cm^{-1} associated with C—Cl bond disappeared and a new typical bands associated to C—N of tertiary amines can be clearly identified (1080 and 1041 cm^{-1}). On the other hand, polymerization test of aqueous phase was positive indicating that double bonds of

VBCl are present in the aqueous phase. The presence of C=C bonds in aqueous phase is a result of hydrophilic nature of NMDG chains.

Also, in the Figure 2 can be seen the DRIFT spectra of unmodified and modified cellulose layers. An intense band around 3700 and 3000 cm^{-1} is characteristic of stretching vibration of —OH bonds of cellulose and glucamine groups, this band was identified both for unmodified and modified membranes. For unmodified membrane, signals around of 1653 and 1176 cm^{-1} were attributed to the C=O and C—O stretching vibrations, respectively. In addition, a band near of 2909 cm^{-1} was identified and assigned to asymmetric and symmetric stretching vibration of methylene and methyl groups. The modified membrane spectrum showed a band about 1662 cm^{-1} was attributed to C=O stretching vibration. In addition, two news bands can be identified in the modified membrane spectrum at 1167 and 1129 cm^{-1} associated to the stretching vibration of N—H bonds of tertiary amines. N—H bonds can be associated directly with the secondary network formed by polymerization of VbNMDG.

In addition, from Figure 2 can be seen that the unmodified cellulose layer seems to have more peaks than the modified cellulose layer. This can be explained as a result of surface analysis technique used (DRIFT). In this technique the IR-FT spectrum is obtained from surface analysis. Some experimental variables associated with the analytical response (i.e., penetration depth) depend of nature of material and density of polymer fibers. For unmodified membrane, material is formed by two layers (cellulose deposited on polypropylene) and pore diameter is large in comparison with modified membrane with a small pore diameter. When IPN is formed, density is increased and penetration depth is decreased, in consequence, a mayor number of signs in the modified membrane could be associated to a weak interaction of incident radiation with deeper polymer layers.
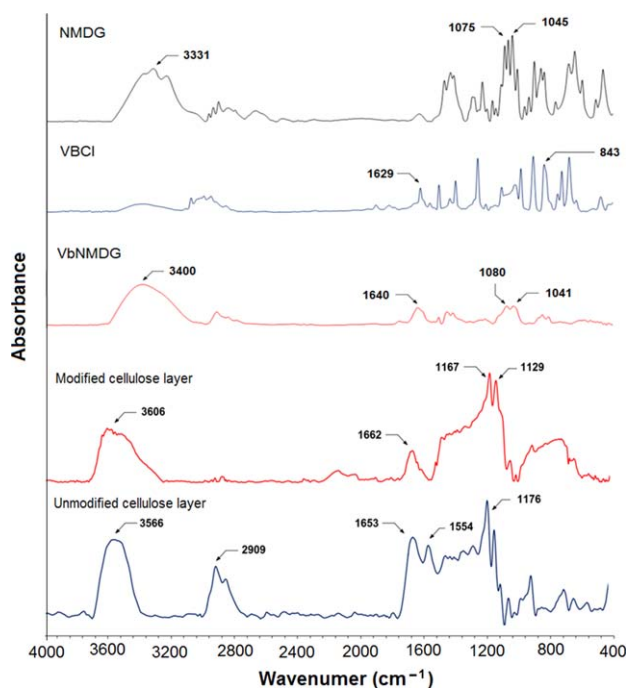

Figure 2. FT-IR spectra of VBCl, NMDG and VbNMDG and DRIFT spectra of unmodified and modified cellulose layers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
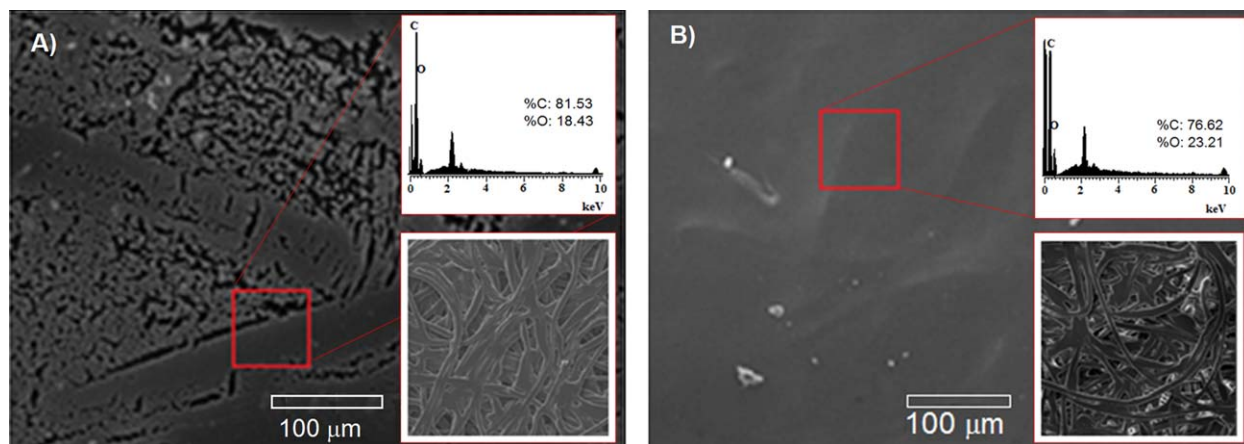
Figure 3. Images of SEM for unmodified and modified cellulose layers (A and C, respectively) and their corresponding elemental analysis by EDS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A decrease of the surface heterogeneity was seen from SEM images (see Figure 3). The decrease of surface heterogeneity can be explained as a result of the pore size decrease since the secondary network was mainly formed in the inside of the pores. This result is congruent with decrease of hydraulic permeability of IPN in comparison with unmodified cellulose layers. Permeabilities were 2.46×10^{-10}, 4.43×10^{-10}, and 4.65×10^{-10} $m^3 \ m^{-2} \ s^{-1} \ Pa^{-1}$ for MM_1, MM_2, and MM_3, respectively. Initial permeability of cellulose layers was $7.4 \pm 0.4 \times 10^{-10}$ m^3 $m^{-2} \ s^{-1} \ Pa^{-1}$. The decrease of permeability indicates that by formation of IPN in the inside of the pores, the porosity surface, pore diameter and hydration properties of cellulose were modified; however, it was evidenced that by this procedure the porous nature of material was maintained.

Percents of VbNMDG in the IPNs were calculated from the increase in mass using the eq. (1) (see Table I). It can be seen that the percent of VbNMDG is larger as the amount of VBCl

is increased. Clearly this is a result of a larger concentration of VbNMDG in the reactive solution used to produce the IPNs. In addition, angle contact measures indicate that hydrophilicity of the surface is increased by modification of the cellulose (see Table I). The increase in the surface hydrophilicity can be explained as a result of hydrophilic groups of glucamine chains (mainly groups —OH). Thus, a greater amount of —OH groups permits a stronger interaction between the surface and polar molecules via hydrogen bonds.

Boron Retention Experiments

A linear increase of R_B in function of VbNMDG concentration is observed for the different boron concentrations evaluated (0.15 and 3.00 mg L^{-1}) (see Figure 4). In addition, when boron concentration was 3.00 mg L^{-1} and contact time was 60 min (Exp-2), values of R_B were approximately 10 times larger than R_B for a boron concentration of 0.15 mg L^{-1} and a contact time of 30 min (Exp-1). This difference is clearly related with the boron concentration and contact time at the same pH. A larger boron concentration favors the diffusion of boron from aqueous phase to the inner of the material. On the other hand, a larger contact time promotes a mayor interaction between boric acid molecules and NMDG groups. Therefore, it is expected that boron retention for Exp-2 is larger than boron retention for Exp-1.

From previous results, charge and discharge cycles were performed for 3.00 mg L^{-1} boron concentration for a contact time of 60 min (pH 7.0). Boron selective adsorption process by NMDG groups is driven by the formation of tetradentate complex and by the dissociation process from H_3BO_3 into tetrahydroxyborate anion $B(OH)_4^-$, which produce an adverse effect on boron adsorption capacity. In consequence, at pH < pKa boron is found to be a neutral specie (pKa $\sim$ 9.2), however, when pH > pK_a, tetrahydroxyborate anion is formed and the formation of tetradentate complex is disfavored.[22]

For different charge cycles, six in total, a decrease of boron retention capacity was evidenced in all cases (see Figure 5). This decrease can be explained from an incomplete discharge when NaOH solution at pH 12 is used and a decrease of active sites
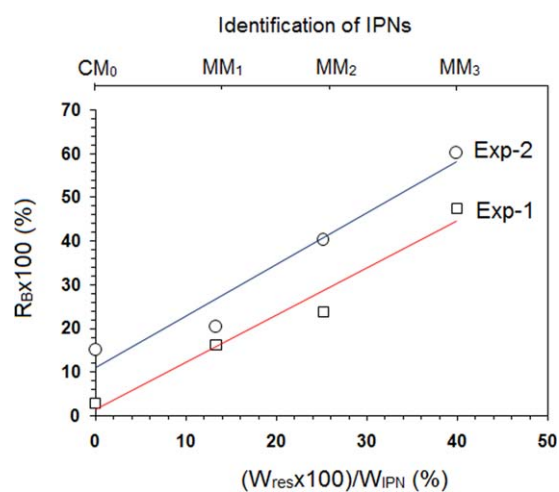

Figure 4. Boron retention for IPNs (MM_1, MM_2 and MM_3) and unmodified cellulose (CM_0). Exp 1: boron concentration of 0.15 mg L^{-1} and contact time of 30 minutes, and Exp 2: boron concentration of 0.30 mg L^{-1} and contact time of 60 minutes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
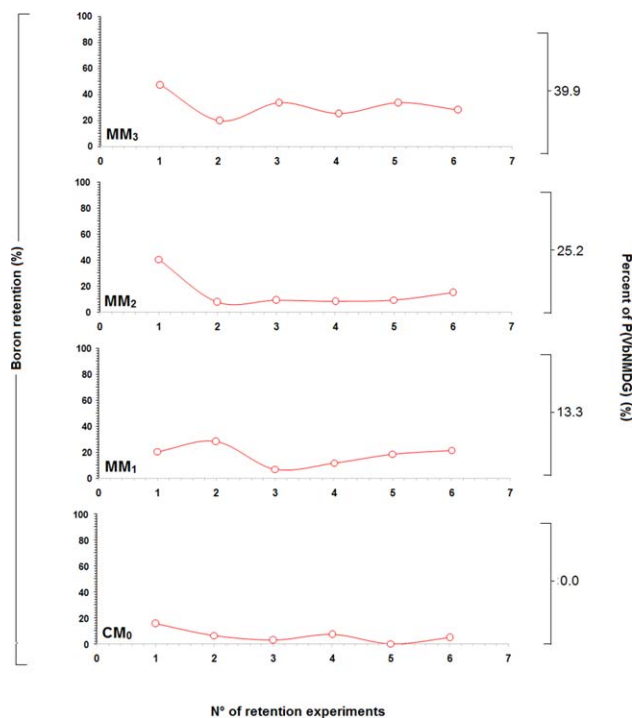
Figure 5. Boron retention experiments by six cycles of charge for IPNs (MM_1, MM_2 and MM_3) and unmodified cellulose (CM_0). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

in the IPNs. Percent of discharged boron was ∼80% for a contact time of 24 h. Since R_B for CM_0 decreases progressively with the increase on the discharge cycles, it is suggested that alkaline hydrolysis of cellulose layer can be associated to the decrease of boron retention capacity.

Values of r_B are shown are shown in the Table II for three values of pH. These data evidence the decrease of r_B as a function of pH and incorporation grade of NMDG chains. In addition, for a higher incorporation of resin a lower r_B was observed at pH 5.0, whereas an inverse tendency was evidenced at pH 7.0. Thus, when pH is acid (pH = 5.0) values of r_B are larger than 1.0 suggesting that under this conditions the intrachain interactions are favored according as number of NMDG chains is increased. However, at pH 7.0 r_B is increased but from values lower than 1.0 and in consequence is suggested that this result could be consequence of the decrease of intrachain interactions. Additional experiments are required to explain these observa-

Table II. Molar Ratio of Boron to NMDG Units for Three pH Values (5.0, 7.0, and 9.0) and Three Grade of Incorporation of Resin: MM_1, MM_2, and MM_3 With 0.0096, 0.0277, and 0.0414 mg of IPN

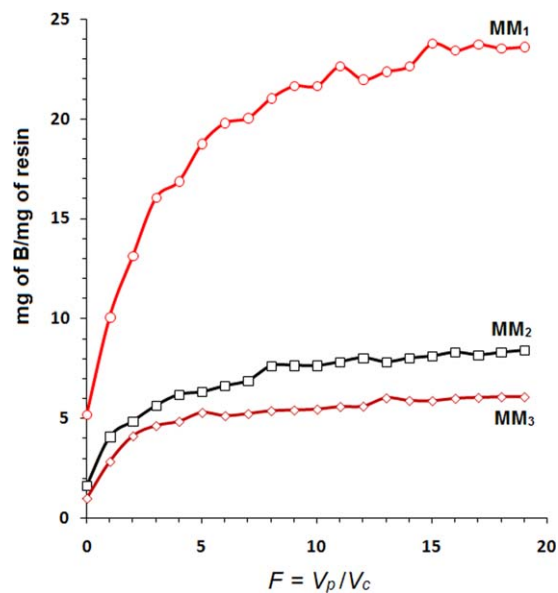| Sample	Sample identification	r_B		
		pH: 5.0	pH: 7.0	pH: 9.0
Modified cellulose	MM_1	2.6	0.2	0.5
	MM_2	1.5	0.6	0.4
	MM_3	1.1	1.0	0.3

Figure 6. Boron milligrams per incorporated resin milligrams at pH 5.0 for MM_1, MM_2 and MM_3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tions. On the other hand, at pH 9.0 no tendency for r_B in function of incorporated resin was identified. In this case, values of r_B can be averaged to be 0.4 ± 0.1 (i.e., five moles of boron per two chains of NMDG). This result indicates that, at pH 9.0, boron is retained preferably by interchain interactions maybe by formation of the formation of tetradentate complex.[22]

In the Figure 6 is shown the change of boron milligrams per incorporated resin milligrams in function of filtration factor, F = permeate volume (V_p)/volume of solution in the inside of ultrafiltration cell (V_c).

When $F = 13$ (i.e., $V_p = 390$ mL) the saturation point was achieved. In this point can be assumed that MRC was obtained. Values of MRC were 22.3, 7.8, and 6.0 mg of B per mg of resin incorporated for MM_1, MM_2 and MM_3, respectively. These results suggest that amount of NMDG units incorporated to the IPN is an important factor for retention properties of material.

By comparison of permeability values with RMC values can be seen that the permeability increased in the following order $L_{MM1} < L_{MM1} < L_{MM3}$, whereas than the RMC values decreased in the inverse order ($MRC_{MM1} > MRC_{MM2} > MRC_{MM3}$). These results can be explained by considering that a low permeability implies a longer contact time and in consequence a better interaction between boron and NMDG chains is obtained.

CONCLUSIONS

Porous membranes based in N-methyl-D-glucamine and cellulose with boron retention capacity, hydrophilic surface and adequate water permeability were developed via IPNs. By procedure here described, cellulose porous layer can be modified by *in situ* polymerization of vinyl monomers in the inside of porous material, and in consequence, a decrease of permeability is produced by pore size reduction. In addition, a linear increase of R_B in function of VbNMDG concentrations was observed for

the different boron concentrations (0.15 and 3.00 mg L^{-1}) and different insertion grade of N-methyl-D-glucamine groups. A negative effect on retention capability was evidenced for several charge and discharge cycles. Values of MRC were 22.3, 7.8, and 6.0 mg of B per mg of resin incorporated for MM_1, MM_2, and MM_3, respectively.

ACKNOWLEDGMENTS

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