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Modification of ultrafiltration membranes via interpenetrating polymer networks for removal of boron from aqueous solution

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ABSTRACT

Interpenetrating polymer networks (IPNs) are polymeric structures formed when two distinct multi-functional polymers become entangled at the molecular level. Thus, an IPN permits the combination of chemical and physical properties of individual polymers in the same material. The objective of this work was to develop new ultrafiltration membranes with the capacity of boron retention via IPNs. Cellulose ultrafiltration membranes were used as substrate resin (or primary network) for in situ polymerization of a boron selective monomer based on *N*-methyl-*D*-glucamine. Structural properties, percent of secondary network, change of hydrophilicity, permeability and boron retention properties were studied. Results suggest that surface porosity is not affected by the formation of IPN. In addition, pore radius was decreased at 40.9% whereas the pore number was increased at 202.1% and values of boron retention were 20.5%, 17.8% and 14.8% for pHs 5.0, 7.0, and 9.0, respectively. It was concluded that new ultrafiltration membranes could be produced by in situ polymerization of vinyl monomer in order to improve their retention, surface, and permeability properties.

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1. Introduction

Boron is an essential micronutrient related with the growth and development of plants. In addition, boron is a structural component of cell walls which has been connected with the lignification processes, membrane transport, enzyme interactions, nucleic acid synthesis, and carbohydrate metabolism [1–3]. The boron concentration in irrigation water or in soils plays an important role in both crop yields and the quality of products [1]. Currently, it is accepted that boron is essential for the growth of plants in many ways; however, it becomes toxic for plants when the amount of boron is slightly greater than required since the range of boron concentration between deficiency and excess is narrow (0.5–0.75 and 4.0–6.0 for orange and tomato, respectively) [1–4]. In plants, the physiological adverse effect of boron involves the reduction of root cell division, retarded shoot and root growth, inhibition of photosynthesis, deposition of lignin and suberin, decrease in leaf chlorophyll, etc. [1–3]. These symptoms are highly dependent on the amount of boron excess and the tolerance of the plant [1]. On the other hand, the toxic effects of boron in animals and humans remain largely unknown. It is known that boron toxicity depends on the length, frequency, and level of exposure and therefore it is difficult

to quantify. A chronic exposure of boron may cause cutaneous disorders, retarded growth and have an adverse impact on the male reproductive system in rats and mice [4].

Several technologies have been used for boron removal (i.e., reverse osmosis, solvent extraction, inorganic adsorbents, ion exchange methods, adsorption on membrane filtration) [4–9]. Recently, Kabay et al., Hilal et al., and Wolska and Bryjak reviewed the technologies for boron removal from aqueous systems [4,7,8]. Currently, reverse osmosis, boron selective resins and adsorption on membrane filtration have been the center of many researches related to boron removal [4]. Reverse osmosis 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 reverse osmosis membranes like other dissolved ionic substances [4]. However, it is difficult to eliminate non-dissociated neutrally charged boric acid in seawater by this technique [4,7,8]. 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 [10,11]. In relation with this point, it has 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

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is formed by the reaction of boron with compounds possessing *cis*-diol system such as *D*-mannitol, *D*-sorbitol, and *D*-ribose [4,10,11].

The process of adsorption on membrane filtration has been considered as an alternative separation process. This technique is based on the concept of the hybrid process that combines a sorption process with membrane separation. In this process, solutes are absorbed by sorbents followed (i.e., complexing resin based on *D*-sorbitol) by a membrane separation of the saturated sorbents [7,12].

Interpenetrating polymer networks (IPNs) are polymeric structures formed when two distinct multi-functional polymers become entangled at the molecular level [13–16]. 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 on network configuration as sequential IPN (one of the monomers is added and polymerized in an existing polymer), simultaneous IPN (which is produced by two non-interfering polymerizations from a mixture of the monomers) and semi-IPNs (only one of the polymers is crosslinked while the other is linear) [13].

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 the same material. In addition, in some cases a synergistic effect is expected. Some applications of IPNs are fuel cell membranes, drug delivery and tissue engineering [16–18].

In a broader context, we are working on the development of “artificial root” functionally analogous to plant roots. As a consequence, cellulose material was identified to be the most appropriate material; however, this has no boron retention capacity. On the other hand, poly(*N*-methyl-*D*-glucamine), Poly(NMDG), is a versatile polymer used for boron removal. Poly(NMDG) is mainly used as ligand in complexing resins or as linear water-soluble polymer by liquid-phase polymer-based retention technique (LPR) [19–22].

The objective of this work was to develop new ultrafiltration membranes, by IPNs, with capacity of boron retention from aqueous solution. Thus, cellulose ultrafiltration membranes were used as substrate resin (or primary network) for in situ polymerization of a boron-selective monomer based on *N*-methyl-*D*-glucamine in the inside of the membrane pores. This is a non-commercial monomer which permits one to develop, by insertion of functional chains, a wide group of new monomers with new properties which could be incorporated to the active layer of ultrafiltration membranes via IPNs. Here, we describe the modification of cellulose membrane and their structural, morphological and retention properties. In addition, monomer synthesis is shown in order to illustrate the sequential procedure for membrane modification.

2. Materials and methods

2.1. 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). *N,N*-methylene-*bis*-acrylamide (MBA, 98%, Aldrich) and ammonium persulphate (Aldrich) were used for free radical polymerizing reaction of VbNMDG. 1,4-dioxane (Aldrich) and bi-distilled water were used as solvents. Cellulose disk-shaped membranes with 100 kDa molecular weight cut-off, MWCO (Biomax PBGC, manufactured by Millipore Co.), were used as primary network for the formation of IPNs. Boron aqueous solutions were prepared from boric acid (H₃BO₃, Aldrich) using bi-distilled water. Nitric acid (HNO₃, 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 [19,23].

2.2. Synthesis of VbNMDG and modification of ultrafiltration membrane

Functionalizing reaction was performed using three levels of VBCl concentration (21.9, 43.8, and 65.7 mmole) with a 1:2 M ratio (VBCl:NMDG). Thus, NMDG was dissolved in a dioxane–water solvent mixture (2:1 volume ratio), added to the reactor and heated for 20 min until NMDG was completely dissolved. Later, VBCl was dissolved in 10 mL of dioxane and slowly added to the reactor. 10 mL of 1.0 mol/L NaOH solution was added and the reaction was kept under reflux with constant stirring for 5 h. By extraction with ethyl ether the unreacted VBCl was removed remaining in the aqueous phase functionalized monomer (VbNMDG). Functionalization reaction is shown in Fig. 1. Modified membranes were identified as MM₁, MM₂, and MM₃, respectively. In addition, the first concentration level of VBCl was used for subsequent modifications; these replicates were identified to be MM₁₁, MM₁₂, and MM₁₃. Unmodified membranes were identified as MM₀₁, MM₀₂, and MM₀₃.

The modification of ultrafiltration membranes was performed by the injection of functionalized monomer in the inside of the membrane pores in the presence of radical initiator (2.0% mol of ammonium persulphate with respect to the monomer) and cross-linker 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 N₂). When a volume equal to 10 mL of solution was identified in the permeate, the filtration system was stopped and the membrane was placed in a parallel plate system designed for avoiding contact with the active layer. Later, this plate system was heated for 12 h using an airflow oven at 30 °C in order to carry out the polymerization. Functionalizing of VBCl with NMDG was evaluated by Fourier-transform infrared spectroscopy (FT-IR) using an OMNIC 5.2a (Nicolet Instrument Corp.) and by polymerization test of aqueous phase (this test is based on the polymerization reaction of aqueous phase in the presence of initiator and crosslinker reagents; the presence in the aqueous phase of double bond C=C associated with the VBCl is possible only when the functionalization was performed satisfactorily).

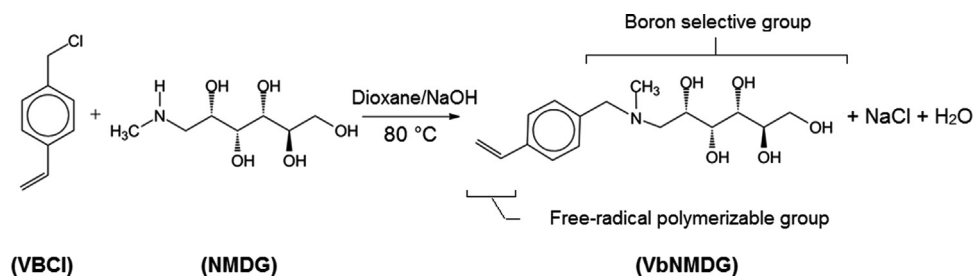


Fig. 1. Reaction scheme for synthesis of VbNMDG.

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