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Ceren Oktar Doğanay[a]; H. Önder Özbelge[b]; Niyazi Bıçak[c]; Nihal Aydoğan[d]; Levent Yılmaz[b]
[a] Department of Advanced Technologies, Gazi University, Ankara, Turkey [b] Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey [c] Department of Chemistry, Istanbul Technical University, İstanbul, Turkey [d] Department of Chemical Engineering, Hacettepe University, Ankara, Turkey

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Use of Specifically Tailored Chelating Polymers for Boron Removal from Aqueous Solutions by Polymer Enhanced Ultrafiltration

Ceren Oktar Doğanay,[1] H. Önder Özbelge,[2] Niyazi Bıçak,[3] Nihal Aydoğan,[4] and Levent Yılmaz[2]

[1]*Department of Advanced Technologies, Gazi University, Ankara, Turkey*
[2]*Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey*
[3]*Department of Chemistry, Istanbul Technical University, İstanbul, Turkey*
[4]*Department of Chemical Engineering, Hacettepe University, Ankara, Turkey*

Two selective functional polychelatogens, namely hydroxyethylaminoglycerol functioned poly(glycidylmethacrylate (PNS) and Poly(4-Vinyl-1,3-dioxalan-2-one-co-vinyl acetate) (COP) were synthesized and utilized in polymer-enhanced ultrafiltration (PEUF) to remove boron from the aqueous solution. The effect of operating parameters on boron retention was investigated. PNS was synthesized in three molecular weights to observe the effect of molecular weight in borate retention. Increase in pH increased boron retention for all of the synthesized polymers. Decrease in loading resulted in an enhancement in retention values when COP, medium (PNSM) and the low molecular weight of PNS (PNSL) were used. No significant change was observed in the permeate flux with COP (41 L/$m^2 \cdot h$), PNSL (48 L/$m^2 \cdot h$) and PNSM (47 L/$m^2 \cdot h$). However, a decrease in the loading led to a decrease in the permeate flux for high molecular weight PNS (PNSH). Conformational changes in the polymer structure were examined using dynamic and static light-scattering. Retention results for all of the polymers were found to be remarkably higher than the literature, when polyvinyl alcohol was used as the chelating agent. Satisfactory retention results were obtained using both PNSL (R: ~54%) and PNSM (R: ~57%), showing that PEUF can be employed effectively for borate removal using the specifically tailored polymers.

Keywords boron removal; membrane separation techniques; polychelatogen; ultrafiltration

INTRODUCTION

Water contamination by boron is a widespread environmental problem, since even a few mg/L concentration of boron may result in deleterious effects in plant growth (1). Turkey possesses approximately 60% of the world's boron reserves. Boron concentration can reach values as high as 30–40 mg/L in geothermal waste waters and drainage waters discharged from boron mines which causes a threat of boron pollution to the receiving rivers (2). Therefore there is an imperative need for on effective separation method for boron removal.

There are several physicochemical treatment processes typically used to remove boron from water and wastewater. Adsorption of boron by clays, soils, and other minerals were extensively studied by many investigators (3–7). Magnesium oxide was reviewed as a potential adsorbent for the removal of boron from aqueous solutions (8). However, a large number of stages were required to decrease the boron content to under 1 mg/L, which makes this method inefficient and uneconomical (9). Solvent extraction was another widely used process for removing boron which was stated to be effective in high concentration streams and utilized more for production of boric acid rather than removal from aqueous streams (10,11). The most extensively used technique for boron removal is ion exchange with strong base anion exchange resins (9,12–16). These resins are effective for boron removal, but besides boron, all other species are removed, resulting in a very high regeneration cost (9). A promising method for removing boron from aqueous solutions is the use of membrane processes. Supported liquid membrane (SLM), reverse osmosis, and electrodialysis are the most commonly studied membrane processes in the literature for boron retention (17–19). Liquid membranes containing specific carrier molecules such as diols, immobilized in a thin, inert, microporous film were used selectively to make complex with boron than transported across the membrane. However, applications of SLM are limited due to the instability of the membrane (17). Reverse osmosis was another membrane technique applied for boron removal (20–24). In RO applications for boron removal, it was found that the rejection of boron highly depended on pH and it tended to rise with increasing driving pressure (20). Although rejection values could be improved by increasing driving

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Address correspondence to Dr. Ceren Oktar Doğanay, Department of Advanced Technologies, Gazi University, Ankara, Turkey. E-mail: ceren.doganay@gazi.edu.tr

pressure and adjusting pH, the filtrate was not able to meet WHO Drinking Water Quality Guideline. Studies about boron transport through ionic membranes are limited (18,19). It was stated that in the processes the use of electrotransport through an anionic membrane would provide an interesting way to recover boron. However, even with the optimum conditions, the boron concentration in dialyzate could not be reduced to permissible levels. Conventional membrane methods alone are not capable of reducing boron content down to a permissible level even in seawater (25). Therefore, an additional removal of boron from desalinated water at the finishing stage is needed.

Polymer-enhanced ultrafiltration can be a promising method based on the complexation between a water-soluble polymeric binding agent and the target component, which is desired to be separated from the aqueous solution. Upon ultrafiltration (UF), the complexes are retained; thus the target component is removed from the solution (2).

There are several advantages inherent to polymer-enhanced ultrafiltration compared to other conventional water-treatment techniques. Complexation can be made selective for any target compound based on the knowledge of complexation chemistries. Theoretically, the same functional groups used in the preparation of insoluble resins can be incorporated to the water-soluble polymers, thus diffusion limitations observed in resins can be eliminated (23). Besides, the UF process requires lower energy for operation which makes the PEUF process a promising technique for metal ion retention. In a majority of the previous PEUF studies, batch systems were employed, mostly for the retention of cations (26–29). This mode shows some disadvantages like feasibility only for small-scale processes and existence of dead-operation times. Since, in most of the previous studies batch mode of PEUF was employed, the feed concentrations were not constant throughout the experiments; therefore the effect of operating parameters were not investigated. In the literature, very few studies used PEUF for boron removal from aqueous solutions (2,26,30–32) and most of these studies utilized batch mode of PEUF in which the feed concentration keeps changing throughout the process (30–32). The purpose of those studies was to mainly select specific polymeric agents for boron removal and to study the boron-binding properties of these special chelating groups (1,19,31).

In PEUF studies, the selection of the polymer to be used for complexation with the target metal ion plays an important role in the efficiency and the selectivity of the process. Therefore, it is crucial to find a suitable polymer to achieve complexation with the target metal. Boric acid is known to make complexes with polymers containing favorably-oriented hydroxyl pairs. Polymers that are selective to boron binding have most often been prepared by the attachment of sugar-like polyol ligands to polymeric backbones of both resins and soluble polymers (33). The complexation of boron using sugar derivatives like D-glucose, D-sorbitol, and D-mannitol accompanies the formation of protons that lowers the pH. Hence, the proton itself liberated during the complexation limits the complexation of boron. In order to overcome this drawback, it was suggested that sugars comprising amine functions, such as N-methyl-D-glucamine (MG), should be used. The role of the amine groups in the polymer structure is to capture the proton released during the complexation reaction (34). In the afore-mentioned studies, in which batch mode of PEUF was utilized, N-methyl-D-glucamine (NMG) grafted poly(epichlorohydrin) (30), glucoheptanonamide derivatives of poly(amido amine) and poly(ethylene imine) (32) and alkyl monool, 1,2-diol, 1,2,3-triol containing polyethylene imine (PEI) were used as chelating agents. Since they were batch studies, the feed concentrations were not constant throughout the experiments, so the loading effects of the polymers could not be investigated. A few recent studies have concentrated on the operating parameters that have included the selection of an optimum pH and concentration of metal to polymer ratio, (loading) (2).

In the previous investigation of our group, continuous PEUF was performed for the removal of boron from water and the effects of operating parameters on boron removal were investigated with a constant boron concentration of 10 mg/L at different loadings (metal/polymer) and pH values. A commercial polymer, poly(vinyl alcohol) (PVA) was used as the chelating agent. Maximum boron retention was observed as 28% at a pH of 10 and a loading of 0.01 which was the minimum loading corresponding to maximum polymer concentration (2). In that study it was shown that PEUF can be employed for boron removal from aqueous solutions and it was concluded that in order to increase the removal performance of the process, polymers having high boron affinity consisting of more active OH-groups should be used.

In the literature, it was reported that polymer-bound sugar derivatives such as N-methyl-D-glucamine, sorbitol, and mannitol have been employed successfully in the removal of trace boron. However, regeneration of those materials in order to reuse in the process is limited due to acid hydrolysis (35).

Therefore, in this study two boron selective functional polychelatogens, namely, hydroxyethylamino-glycerol functioned polyglycidyl methacrylate (PNS) and a copolymer of 4-Vinyl-1,3-dioxalan-2-one and vinyl acetate (COP), which are much more stable than sugar derivatives, were synthesized and continuous PEUF was employed to investigate the effect of operating parameters (pH and loading) on the retention of boron using these selective polymers. PNS was synthesized in three different molecular weights to observe the effect of molecular weight on boron retention. Dynamic and static light scattering measurements were also performed to examine the conformational changes in the structure of

the synthesized polymers at different pH values as well as in the presence of boron in the solution.

EXPERIMENTAL

Materials

In the synthesis of the functional polymers, ethanolamine (Merck) was distilled before use. All the other chemicals were analytical grade commercial products; glycidyl methacrylate (Aldrich), glycidol (Aldrich), morpholine (Aldrich), allyl chloride (Aldrich), allyl bromide (Aldrich), divinyl benzene (Aldrich), 4-Vinyl-1, 3-dioxalan-2-one (Aldrich), and vinyl acetate (Aldrich). They were used as recieved.

In the ultrafiltration experiments and in atomic-absorption spectrometry analysis, boric acid (H_3BO_3, Merck), sodium chromate (Na_2CrO_4, Merck), sodium hydroxide (NaOH, Merck), nitric acid (HNO_3, Merck), sodium sulfate anhydrous (Na_2SO_4, J. T. Baker), sodium chloride (NaCl, Merck), and ultrapure water having a specific conductance of $18.3\,\mu\Omega \cdot cm^{-1}$ obtained from water purification system (Human Reverse Osmosis(RO)-UltraPure (UP) water purification systems) were used. All chemicals in this study were used without further purification.

Synthesis of Hydroxyethylamino Glycerol Functioned Poly(glycidylmethacrylate) (PNS)

A water-soluble glycidyl methacrylate (GMA) based polymer with hydroxyethylamino glycerol functions was synthesized, as boron-selective functional polymer according to the reaction scheme given in Fig. 1.

In the first step glycidol was added dropwise to the solution of ethanolamine in toluene at 0°C and the mixture was heated at 150°C. Toluene and the excess of ethanolamine were removed under vacuum at 150°C. The resulting pale yellow viscous liquid (1-[2-hydroxyethylamino] glycerol) (HEG) was used in the next step without any further purification.

In the second step, 7.1 g of Poly(GMA), which was prepared before, was dissolved in tetrahydrofuran (THF). This solution was added dropwise to the stirring solution of HEG in THF at 55°C. The resulting mixture was precipitated in ether. By changing the monomer/initiator ratio in poly(GMA) synthesis, different molecular weight polymers were synthesized. The synthesized polymers have viscosity average molecular weights of approximately 280,000 (PNSH), 110,000 (PNSM), 50,000 (PNSL) and the yield was 98%. The synthesized polymer is resistant to acid hydrolysis, thus, regeneration and reusability of the polymer is possible.

Synthesis of Poly(4-Vinyl-1,3-dioxalan-2-one-co-vinyl acetate) (COP) for Borate Removal

Copolymerization of 4-Vinyl-1,3-dioxalan-2-one with vinyl acetate was carried out in bulk according to the reaction scheme given in Fig. 2.

4-Vinyl-1, 3-dioxalan-2-one (0.1 mol) was mixed with vinyl acetate (0.1 mol) under nitrogen atmosphere and 0.2 g AIBN was added to the mixture. The flask was mounted in a temperature-controlled oil bath. The mixture was stirred until a clear solution was obtained. It was then heated to 75°C and the reaction was carried out for 3 h at constant temperature under reflux. The resulting polymer has a viscosity average molecular weight of approximately 80,000 and the yield was nearly 100%.

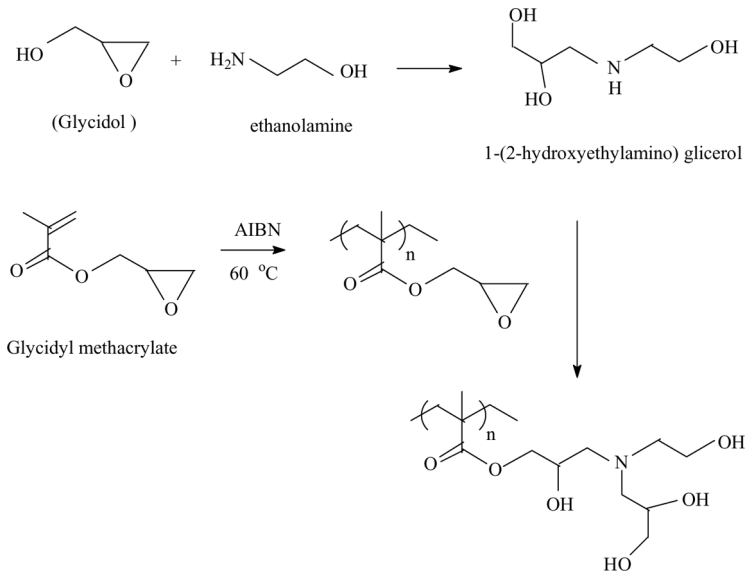

FIG. 1. Synthesis of hydroxyethylamino glycerol functioned poly(glycidylmethacrylate).

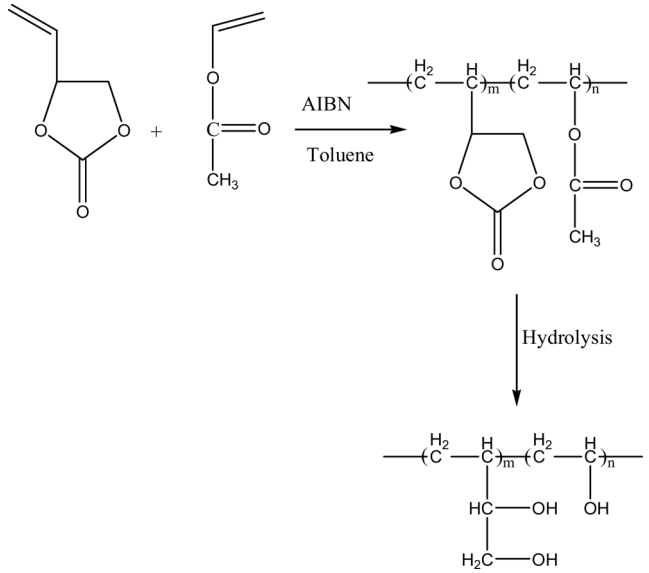

FIG. 2. Synthesis of poly(4-Vinyl-1,3-dioxalan-2-one-co-vinyl acetate).

Ultrafiltration Experiments

Experimental studies were carried out on a lab-scale Osmonics Sepa CF Membrane Cell. The UF system applied for the separation experiments was explained previously in detail and the related figure is presented in our previous studies (2,36,37). Polyether sulfone membranes with a molecular weight cut-off of 5,000 Da (Osmonics SEPA YMPTSP1905) and 20,000 Da (Osmonics SEPA YMPWSP1905) were employed. 20,000 MWCO membranes were only utilized in the experiments in which PNSH was used as the chelating agent. In the experiments UF pressure and feed flowrate were 100 kPa and 0.048 m^3/h, respectively.

Feed solutions were prepared prior to ultrafiltration experiments. The desired amount of polymer was dissolved in ultrapure water, then boric acid was added to the polymer solution resulting in a boron concentration of 10 mg/L. The pH of the polymer solution was adjusted by adding HNO_3 and NaOH before and after the addition of boric acid. Then the resulting solution was stirred at 250–300 rpm for at least 3 hours to make sure that the complexation equilibrium between boron and the polymer was established (2,36,37).

After complexation of the feed solutions was achieved, continuous ultrafiltration was applied to the solution. Circulation of the solution was achieved by a pump. Feed solution was first passed through the membrane, and then the retentate and permeate streams were returned back to the feed solution tank to keep the feed concentration constant. At certain time intervals, permeate stream flowrate was measured and small amounts of samples were collected both from the permeate and feed streams for the analysis of the target metal. All runs were carried out with the same membrane type (Osmonics Sepa YMPTSP1905) at constant temperature of 25 ± 3°C.

Analysis

For the concentration analysis of boron, Direct Reading Echelle Inductively Coupled Plasma Optical Emission Spectrometry (DRE ICP-OES) was used [Leeman Labs. Inc.]. The wavelength to be inspected for boron determination was 249.773 nm. For calibration, standard solutions of boric acid were prepared separately for both the feed and the permeate. Permeate standards were prepared with boric acid and ultrapure water while feed standards had polymer with the same concentration as the feed. These standards were scanned by ICP with three replicates of each which provide the determination of the intensity data of the standards. With the help of the intensity data, calibration curves for both the feed and permeate standards were obtained. Then the samples were scanned and the relative average blank corrected intensities of the samples were determined. During the feed analysis, in order to prevent clogging by the polymer, the system was cleaned with 0.1 M HCl solution. At the end of each analysis, proper calculations were performed for converting the intensity data of the samples to related concentration data for determining the retention values.

Dynamic and Static Light Scattering Measurements

Stock solutions containing predetermined amounts of polymer were prepared using ultrapure water. The pH of all solutions was adjusted by adding a corresponding amount of either 0.1 M HNO_3 solution or 0.2 M NaOH solution.

Static and dynamic light scattering measurements were performed by ALV/CGS-3 Compact Goniometry System simultaneously. An argon ion laser operating at a 633-nm wavelength and 35-mW output power was used as a light source. The measurements were done at 10 different angles in the range of $60° \leq \theta \leq 150°$ and at 25°C. For each angle three different measurements were performed and subsequently averaged. The data were normalized to absolute scale by using toluene as a reference material (38).

RESULTS AND DISCUSSION

PEUF Experiments

Time-dependent feed and permeate target anion concentrations, flux, retention (R), the pH, and temperature data show only very small fluctuations. As seen from Table 1 steady state has been established within one hour (Table 1).

In order to check the reproducibility of the PEUF operation, some selected runs were repeated at the same conditions (pH, loading, and polymer type). Results are compared and the % RSD values are reported in Table 2.

As indicated in Table 2, the % RSD values of the 1st and 2nd trials are very small. Therefore, it can be concluded

TABLE 1
Data obtained in a representative PEUF run for borate retention

Polymer Type: PNSL, Target Anion: Borate, Loading: 0.01, pH: 9					
t (min)	0	60	120	240	% RSD
J_v (L/m^2 h)		47.4	47.3	47.4	0.158
pH	9.00	9.02	9.03	9.02	0.064
T (°C)	24.0	24.0	24.4	24.8	1.570
C_f	10.8	10.9	10.9	10.8	0.53
C_p		6.6	6.6	6.6	0.00
R		0.394	0.394	0.389	1.012
	$J_{v,avg} = 47.4$	$C_{f,avg} = 10.85$	$C_{p,avg} = 6.6$	$R_{avg} = 0.392$	

TABLE 2
Data of the experiments performed for reproducibility

	Polymer	L (g metal/g polymer)	pH	R	% RSD	Flux	% RSD
1st Run	PNS L	0.05	9.00	0.24	4.84 (n:2)	46.5	1.21 (n:2)
2nd Run				0.25		47.3	
1st Run	COP	0.001	9.00	0.43	2.74 (n:2)	41.0	0.00 (n:2)
2nd Run				0.45		41.0	

that the UF system reproducibly exhibits the same performance.

Effect of Loading on Boron Retention and Permeate Flux Using PNSL and PNSM

The effect of loading on boron retention using PNSL and PNSM is given in Fig. 3. When loading is decreased by changing the polymer concentration (keeping boron concentration at 10 mg/L) boron retention values increased strongly for both of the polymers as expected. For all of the loading values boron retention using PNSM was a little higher than that of PNSL.

Similar results were present in the literature where a decrease in loading gives rise to an increase in target metal retention (2,17). Since a decrease in loading means an increase in relative polymer concentration and as the polymer concentration increases, the binding sites for

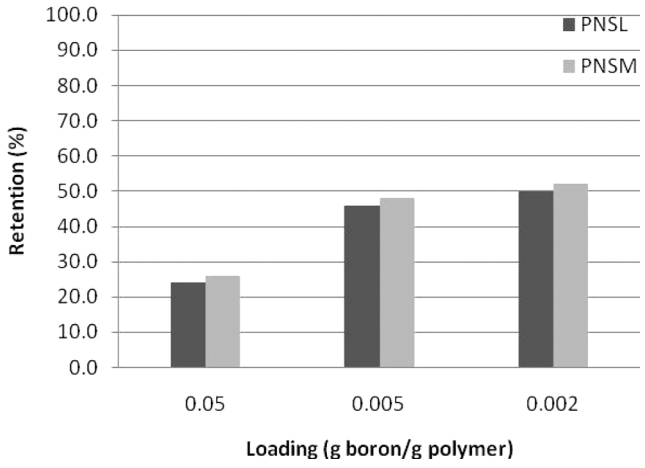

FIG. 3. Effect of loading on boron retention using PNSL and NSM (Boron: 10 mg/L, pH: 9, MWCO: 5,000 Da, ΔP: 100 kPa, Feed Flowrate: 0.048 $m^3 \cdot h^{-1}$).

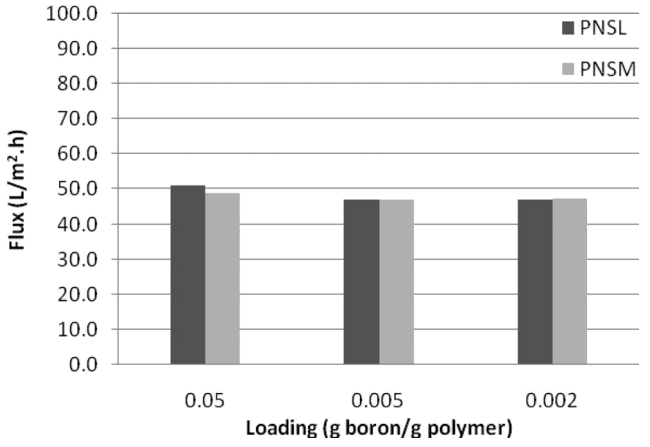

FIG. 4. Effect of loadin on permeate flux using PNSL and PNSM (Boron: 10 mg/L, pH: 9, MWCO: 5,000 Da, ΔP: 100 kPa, Feed Flowrate: 0.048 $m^3 \cdot h^{-1}$).

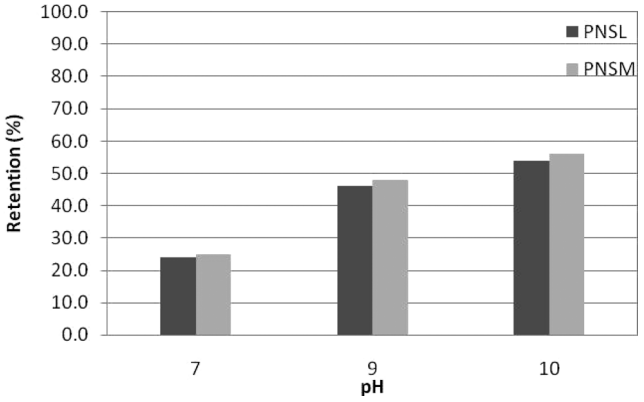

FIG. 5. Effect of pH on boron retention using PNSL and PNSM (Boron: 10 mg/L, loading: 0.005, MWCO: 5,000 Da, ΔP: 100 kPa, Feed Flowrate: 0.048 $m^3 \cdot h^{-1}$).

borate complexation also increase, leading to an enhancement in the retention values.

The effect of loading on permeate flux using PNSL and PNSM is presented in Fig. 4. When loading is decreased, flux values remain almost the same for both of the polymers around 47.0 $L/m^2 \cdot h$., confirming that high polymer concentrations do not affect the permeate flux for the studied ranges of the polymer concentration, the feed flowrate, and the UF pressure.

Effect of pH on Boron Retention

PEUF experiments were performed at a pH range of 7–10 and at a loading value of 0.005 having an initial boron concentration of 10 mg/L for both of the polymers and the results obtained from the PEUF runs are presented in Fig. 5.

Retention of boron obtained at pH 10 was found to be considerably superior to that at pH7. When pH is increased from 7 to 9, a two-fold increase in the retention values is observed for both of the polymers. Boron retention also increased with the further increase in the pH to 10, but this increase is moderate. The lowest boron concentration obtained in the experiments using PNSL and PNSM are 4.6 mg/L and 4.4 mg/L, respectively, for a pH of 10.

In the literature, there are a few studies that investigate the effect of pH on boron retention (1,2,18). In one of those studies, similar behavior was observed with the change in the pH of the feed solution when PVA was used as the chelating polymer (2). In another study, in which mannitol was used as chelating polymer, it was observed that, as the pH of the feed solution was increased from 7 to 9, the boron retention doubled. However, further increase in the pH did not result in that much enhancement in boron retention (1). In that study, the influence of pH on boron retention was attributed to the ionization of boric acid in water.

When boric acid dissolves in water, borate ion concentration reaches its maximum value between pH 10–12. Since both PNSL and PNSM contain hydroxyl groups in their structure that are capable of interacting with borate anions, and production of borate ion is enhanced in the basic medium, the chelation of borate with the functional groups of the synthesized polymers are favored at higher pH values, thus the ensuring an enhanced boron retention.

Aside from the fact that borate ion concentration increases with the increase in pH, enhancement in boron retention can be attributed to the conformational changes in the polymer structure with respect to the alterations in the pH of the solution which may result in a more suitable state for hydroxyl groups of the polymer to complexate borate ions. When the boron retention performances of PNSL and PNSM at different loadings and pHs were compared, only small deviations between the retention values were observed. This may imply that complexation and retention of boron are independent of molecular weight of PNS in the studied range. It may rather depend on the functionalization of the polymer that is the available active site concentration present in the structure of the polymer capable of interacting with borate ion.

As reported in previous studies (2,36) boron retention depends only on loading but not on individual concentrations of target component and polymer. Therefore the effect of loading instead of boron concentration is emphasized. When a lower final boron concentration is desired, a separation cascade can be used.

Effect of Polymer Molecular Weight on Flux and Boron Retention

The purpose of studying the effect of various parameters is to explore the suitable conditions for the maximum retention of the target anion with the highest possible permeate flux. One way to increase the permeate flux is to use a higher MWCO membrane. For this purpose, it is necessary to increase the molecular weight of the synthesized polymer as well. Since the separation is not dependent on the molecular weight of PNS in the molecular weight range between PNSL and PNSM, PNS having a two-fold higher molecular weight than that of PNSM was synthesized (PNSH).

TABLE 3
Effect of loading on permeate flux using PNSH (Boron: 10 mg/L, pH: 9, MWCO: 20,000 Da, ΔP: 100 kPa, Feed Flowrate: 0.048 $m^3 \cdot h^{-1}$)

Loading	Flux
0.05	62.4
0.2	116.5
0.5	156.6

TABLE 4
Effectof loading on the retention of borate using PNSH(Boron: 10 mg/L, pH: 9, MWCO: 20,000 Da, ΔP: 100 kPa, Feed Flowrate: 0.048 $m^3 \cdot h^{-1}$)

Loading	Retention
0.05	0.079
0.2	0.32
0.5	0.30

Effects of loading on permeate flux and boron retention are presented in Table 3 and Table 4, respectively. It is observed that contrary to PNSL and PNSM results, the permeate flux decreased considerably from 156.6 $L/m^2 \cdot h$ to 62.4 $L/m^2 \cdot h$ as the loading is decreased from 0.2 to 0.05 (Table 3). When the loading of the feed solution is decreased from 0.5 to 0.2, the retention of borate increased from 30.0% to 32.0%. However, this increase is not high enough to ensure reasonable separation of boron. Further decrease in the loading to 0.05, decrease the retention to 7.9% (Table 4).

PEUF experiments were performed at a pH range of 7–10 and at loading values of 0.2 and 0.5 using PNSH as chelating polymer and the results obtained from the PEUF runs are presented in Fig. 6.

Similar to PNSL and PNSM results increasing the pH of the feed solution increased retention values at both loadings. However, superior results than PNSL and PNSM cannot be obtained when PNSH was used as the chelating agent.

The same behavior was observed in the previous studies of our group in which commercial PVA (2) was employed as boron binding polymers. In that study, although loading was decreased significantly, the increase in the retention was not high enough for reasonable boron retention. This result was attributed to unsuitable chain conformation of the polymer chains for the binding of borate and also to the insufficient dissolution of polymer at a microscopic level.

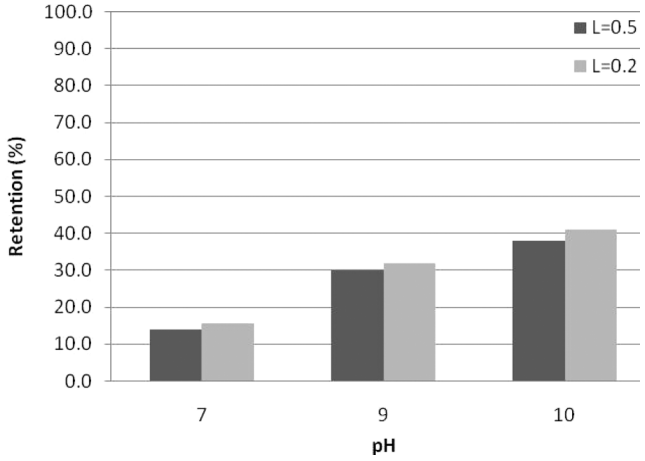

FIG. 6. Effect of pH on boron retention using PNSH (Boron: 10 mg/L, MWCO: 20,000 Da, ΔP: 100 kPa, Feed Flowrate: 0.048 $m^3 \cdot h^{-1}$).

It is known that if the molecular weight of the polymer is high, it results in a more compact polymer structure due to higher interactions between the polymer chains (19). Furthermore, if decreasing permeate flux with increasing polymer concentration may suggest that, there might be a gel layer formation in the studied polymer concentration range, this compaction of the polymers along with gel layer formation may result in a decrease in permeate flux.

In the structure of PNS there are amine group which can interact with the hydroxyl groups of the other polymer chains by hydrogen bonding. Therefore, the decrease in the retention at loadings lower than 0.2 (PNS concentrations higher than 50 mg/l) may be attributed to the interaction between the amine and hydroxyl groups of the polymer chains as a result of the crowding effect which may lead to an elimination of possible binding sites of borate, hence decreasing the retention.

Effect of Polymer Structure on Permeate Flux and Boron Retention

In order to investigate the effect of polymer structure in the binding ability with boron another water-soluble functional polymer which is a copolymer of 4-Vinyl-1,3-dioxalan-2-one and vinyl acetate (COP), was synthesized. COP has two vicinal hydroxyl groups on 4-Vinyl-1,3-dioxalan-2-one for boron chelation, and one hydroxyl group on vinyl acetate for ensuring high solubility of the polymer when complexed with boron. Unlike PNS, COP does not have a tertiary amine function in its structure. This polymer is also resistant to acid hydrolysis. Therefore, regeneration and reusability of the polymer is possible by acid hydrolysis.

The effect of loading on boron retention and permeate flux using COP as the chelating polymer is demonstrated in Fig. 7.

Flux values remain almost constant with loading, like PNSL and PNSM confirming that high polymer concentrations do not affect the permeate flux for the studied ranges of the polymer concentration, feed flowrate, and UF pressure. It is observed that as the loading (g boron/gCOP) decreased while keeping boron concentration constant at 10 mg/L, boron retention increased up to loading of 0.005. Similar results were obtained with PNSL and PNSM. However, in the case of COP after a loading of 0.005 retention values remained almost constant. When the polymer concentration in the feed solution is high, it may lead to a higher interaction between the polymer chains, thus resulting in a more compact polymer structure.

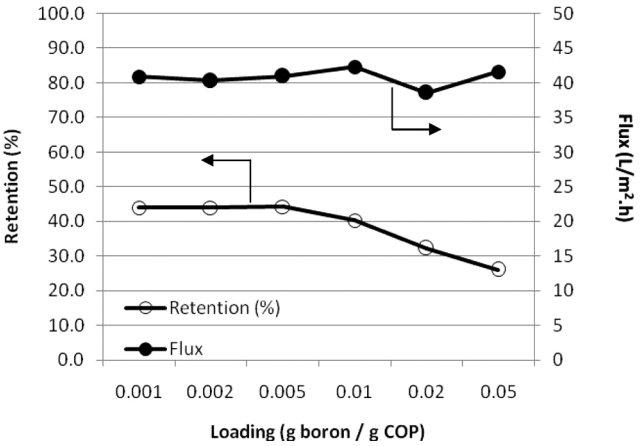

FIG. 7. Effect of loading on the retention of boron and permeate flux using COP (Boron: 10 mg/L, pH: 9, MWCO: 5,000 Da, ΔP: 100 kPa, Feed Flowrate: 0.048 $m^3 \cdot h^{-1}$).

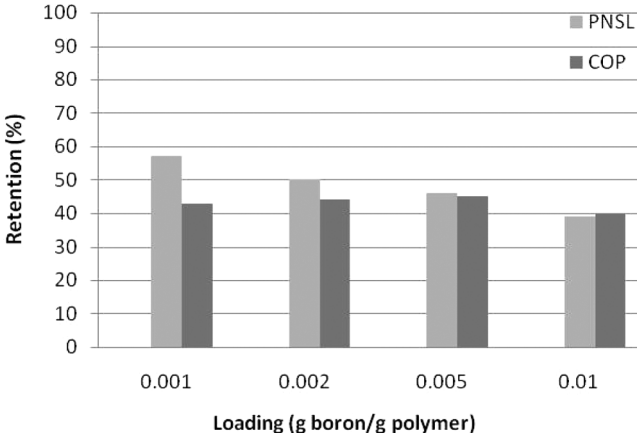

FIG. 8. Comparison of Boron Retention Performances of PNSL and COP (Boron: 10 mg/l, pH: 9, MWCO: 5,000 Da, ΔP: 100 kPa, Feed Flowrate: 0.048 m^3/h^{-1}).

In other words, as the polymer concentration increases and polymer chains get closer to each other, suitable chain conformation for boron binding may not be obtained due to the entanglement of COP chains.

In order to complete the parametric study of the performance of PEUF in retaining boron with COP as chelating polymer, effect of pH was investigated in the range of 7–10 at a loading of 0.005 which was found to be the loading resulting in the highest retention. Table 5 shows that similar to the results obtained with all three molecular weight PNS, the increase in pH leads to an increase in the retention of boron. The lowest boron concentration obtained using COP is 4.8 mg/L for a pH of 10. The effect of pH is not that pronounced when COP was used in PEUF experiments instead of PNS. When pH is increased from 7 to 10, more than a two-fold increase is observed in boron retention. However, in the case of COP, the increase in boron retention is less than two fold. This may indicate that conformational changes in COP may be less sensitive to the alterations in the pH of the solution than that of PNS.

Figure 8 shows the effect of different loadings on the retention of boron using PNSL and COP. It is seen that at higher loadings (lower polymer concentrations) retention of boron is almost the same for COP and PNSL. However, as the loading is decreased, considerable increase is observed in the boron retention performance of PNSL, whereas that of COP remained nearly the same at 44%.

The reason for this behavior may result from the difference in the structures of COP and PNSL. In the structure of PNSL, there is a tertiary amine function in every repeating unit. The role of the tertiary-amine function is to capture the proton formed due to the formation of diol-borate complex. If the ertiary-amine function is not present the neutralization of proton cannot be achieved, which eventually decreases the formation of borate from boric acid. Thus, the efficiency of the boron-diol complex formation is reduced if the pH of the solution is not adjusted externally. In fact, it was observed that in the PEUF experiments, when COP was used as the chelating agent, the pH of the feed solution tends to decrease continuously. So, it was necessary to continuously adjust the pH of the solution using NaOH and HNO_3. On the other hand, when PNSM was used as the chelating agent, once the pH of the solution was adjusted to the desired value in the beginning of the experiment, the pH of the feed solution remained almost constant. Thus, less amount of NaOH and HNO_3 addition was needed. This may suggest that since the tertiary amine function is not present in the structure of COP, the proton brought about by the formation of the borate-diol complex cannot be neutralized. In addition, since the pH of the feed solution needs to be adjusted continuously, the addition of a high amount of NaOH and HNO_3 may increase the ionic strength of the solution which may limit the complexation of COP with borate. Another reason for not having higher retention values with further decrease in the loading may be solubility problem of COP in molecular level. Besides, it can be speculated that with the increase in the solution's

TABLE 5
Effect of pH on boron retention using COP (Boron: 10 mg/L, loading: 0.005, MWCO: 5,000 Da, ΔP: 100 kPa, Feed Flowrate: 0.048 $m^3 \cdot h^{-1}$)

pH	Retention (%)
7	31.0
9	45.0
10	52.0

crowdedness, suitable chain conformation may not be achieved for boron complexation.

Characterization via Dynamic and Static Light Scattering (DLS/SLS) Measurements

In this study, to gain an insight about the conformational changes in the structure of PNSM and COP as a function of pH and polymer concentration, dynamic and static light-scattering experiments were performed. In order to comment on the impacts of the parameters obtained by light-scattering measurements, their physical meanings should be considered. The radius of gyration (R_g) describes the overall spread of the molecule and is defined as the root mean square distance of the collection of atoms from their common center of gravity. Hydrodynamic radius (R_h) is defined as the radius of a hard sphere that diffuses at the same rate as the polymer. It includes hydration and shape effects. A high hydration causes an enhancement in R_h (39).

The data obtained by static and dynamic light scattering measurements were processed by utilizing the governing equations of Guinier method. Data obtained from Guinier plots is shown in Table 6.

As depicted in Table 6, the PNSM and COP polymers were analyzed at different solution pH values as well as in the presence of boron in the solution. Three different hydrodynamic radii mean that the polymer aggregate in solution exists in three size distributions. The first one has the highest intensity and corresponds to the hydrodynamic radius of the polymer aggregates and the other two may be aggregates of lower molecular weight parts of the polymer or monomer. Thus, it is convenient to compare the first hydrodynamic radii values. As the data obtained for PNSM, at a polymer concentration of 1.0 g/dm^3, are compared it is observed that when the pH of the solution increased, the hydrodynamic radius of the polymers increased. This may indicate that as the pH of the solution increases, polymer chain interactions are lowered, thus, polymer gains a more open structure. This result is consistent with the data obtained by PEUF experiments. In PEUF of borate using PNSM as the chelating agent it was observed that the increase in pH increased the retention of borate ion. This can be associated with the increase in the borate ion concentration with the increase in pH as well as due to the more open structure of PNSM at high pH values; a more suitable state may be obtained for boron retention.

Similar behavior was obtained in the DLS measurements with the COP samples. When the R_h values of COP was compared with that of PNSM, it was noticed that for all of the pH values studied, the hydrodynamic radius of COP is greater than that of PNSM. This is most probably due to the difference in the molecular structure of the polymers. In the structure of PNSM there is tertiary amine group bound to every repeating unit of the polymer. It is known that amine groups are capable of interacting with hydroxyl groups. This may result in an interaction between the polymer chains which eventually may lead to a lower hydrodynamic radius.

In order to observe the effect of the presence of boron to the conformational changes in the structure of the synthesized polymers, DLS measurements were also performed with the samples having both polymer and boron (10 mg/L). As shown in Table 6, the hydrodynamic radius of both PNSM and COP increased significantly with the addition of boron. In the case of PNSM the R_h was almost doubled. This may imply that, with the addition of boron, hence the complexation of boron with the polymer, the polymer chains become stretched, therefore their hydrodynamic radii increased.

Table 7 demonstrates the data extracted from Guinier plots obtained by SLS measurements.

As the radius of gyration values of different concentrations were compared, it is observed that the decrease in the solution concentration resulted in an increase in the radius of gyration of both COP and PNSM at all pH values. This may imply that as the solutions become less crowded, interactions between the polymer chains decrease which results in an increase in the radius of gyration of the polymer. Similar to the hydrodynamic radius results, the radius of gyration of COP was higher than that of PNSM at every concentration and pH value. On the other hand,

TABLE 6
Hydrodynamic radius values obtained by DLS/SLS measurements at different pH values

PNSM					COP				
Conc. (g/dm^3)	pH	Rh (nm)			Conc. (g/dm^3)	pH	Rh (nm)		
1.0	7.0	69.5	12.5	661.5	3.3	7.0	179.5	4.4	28.4
1.0	9.0	115.3	25.6	6.6	3.3	9.0	202.5	4.7	26.2
1.0	10.0	146.5	31.3	0.0	3.3	10.0	371.5	4.6	34.4
PNSM-Boron Complex (Boron: 10 mg/L)					COP-Boron Complex (Boron: 10 mg/L)				
1.0	8.2	384.1	60.5	14.0	3.3	9.3	426.0	9.1	37.8

TABLE 7
Radius of gyration values at different pH and polymer concentrations

PNSM pH 7		COP pH 7	
Conc. (g/dm^3)	Rg	Conc. (g/dm^3)	Rg
1.0	132.6	3.3	157.5
0.8	165.6	2.9	158.1
0.5	205.3	2.3	191.9
0.2	235.1	1.7	219.7
PNSM pH 9		COP pH 9	
1.0	116.6	3.3	156.5
0.8	146.6	2.9	179.5
0.5	192.7	2.3	188.9
0.2	210.0	1.7	231.0
PNSM pH 10		COP pH 10	
1.0	135.7	3.3	182.6
0.8	135.6	2.9	224.5
0.5	150.0	2.3	219.5
0.2	186.7	1.7	200.1
PNSM-Bor		COP-Bor	
1.0	136.1	3.3	174.2
0.8	174.8	2.9	185.6
0.5	169.9	2.3	187.5
0.2	202.8	1.7	216.1

opposite to the R_h results, it is observed that as the pH of the solution is increased, the radius of gyration of the polymers decreases. Similar to the R_h results, the addition of boron increases R_g values for both of the polymers.

CONCLUSIONS

In this study, two chelating polymers for borate removal were synthesized for investigating the separation performance of these polymers utilizing continuous polymer–enhanced ultrafiltration to explore the suitable conditions for the maximum retention of the target anion with the highest possible permeate flux. Dynamic and static light-scattering measurements were also performed to investigate the conformational changes in the structure of the synthesized polymers at different pH values as well as in the presence of borate in the solution.

When boron retention performances of PNSL and PNSM at different loadings and pHs are compared, only small deviations between the retention values are observed, implying that complexation and retention of boron are independent of molecular weight of PNS in the studied range. In order to increase the permeate flux by using a higher MWCO of the membrane PNSH was synthesized. However, superior results than PNSL, and PNSM cannot be obtained.

COP was synthesized in order to investigate the effect of polymer structure in the binding ability with boron. Decrease in the loading of the feed solution increased the retention of borate until a certain loading. After this loading, the retention values remained almost constant with the further decrease in the loading. This may be a sign of a solubility problem of COP like in the case of PNSH. Besides, the coiling of polymer at high polymer concentrations together with insufficient dissolution of COP may be hindering the exposure of borate ions to the active site of the polymer.

Increase in pH was found to increase the retention of borate for all of the synthesized polymers. However, the effect of pH was more significant when PNS was used as the chelating agent compared to COP, implying that conformational changes in COP might be less sensitive to alterations in the pH of the solution than that of PNS. This result was also supported by the DLS/SLS measurements.

The retention results for all of the polymers were found to be remarkably higher than that obtained in the literature when PVA was used as the chelating agent (2). Besides, flux values were not dependent on polymer concentration, the studied ranges of the polymer concentration, the feed flowrate, and UF pressure.

Finally, this study shows that PEUF can be employed satisfactorily for boron removal from aqueous solutions. The lowest boron concentrations obtained in the experiments are 4.8, 4.6, and 4.4 mg/L for COP, PNSL, and PNSM, respectively. Since boron retention depends mainly on loading, and the boron-retention capacity of PNSL and PNSM is high, they seem to be promising candidates for the design of a separation process which may include a few numbers of cascades where much higher retentions will be obtained.

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