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Hyperbranched Chelating Polymers for the Polymer-Assisted Ultrafiltration of Boric Acid

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ABSTRACT

Two hyperbranched chelating polymers, glucoheptonamide derivatives of dendrimeric poly(amido amine) and poly(ethylene imine), were employed in polymer-assisted ultrafiltration and concentration of boron from aqueous feed streams. For feeds containing approximately 1 mM B (10 ppm), volume reduction factors of 20 were observed in cyclic adsorption–desorption. The concentrations of both polymers declined due to permeation through an ultrafiltration membrane with pore sizes which should have retained them. Acid-catalyzed hydrolysis of the amide linkages between the polymer backbone and the chelating side groups is implicated in this loss of polymer mass and effectiveness.

INTRODUCTION

Boron as boric acid (pK_a 9.14) is toxic to many crops at concentrations above one part per million (ppm) (1). Many surface waters in the southwestern United States contain considerably more boron than this 1 ppm standard (2) (about 0.093 mM), and wastewaters containing unacceptable boron concentrations are also produced in petroleum processing, boron mining, and power generation (3, 4). The only commercial technology for boron removal and concentration is a boron-specific adsorption resin (5) which is not widely used due to its high cost. Pilipenko summarized the available boron removal processes in 1990 (6). Separations of the borate anion have been technical successes at high pH (7, 8), but these technologies do not appear to be economi-

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cally viable as commercial operations. Recent developments (9) in boron recovery through solvent extraction are promising, especially for treating streams of high boron concentration, but this technology appears to be in the developmental stage. Here, we report our investigations into a new technique for boron removal and concentration which employs ultrafiltration in combination with reversible complexation by polymers containing polyhydroxy groups.

The reactions of the borate ion with polyhydroxy compounds are well known (10–28) and are shown in Fig. 1. While the formation of borate esters and diesters with vicinal diols ($n = 0$ in Fig. 1) dominates for the compounds studied, 1,3-diols ($n = 1$) also react with boric acid (29). The association constants for borate esters range from the order of 1 (L/mol) for simple glycols to several thousand for carbohydrates containing longer chains of adjacent hydroxyl groups such as the chelating groups used in this study (10, 24). Specifically, the association constants for the glucoheptonamide group at 20°C are $K_1 = 8900$ L/mol and $K_2 = 106$ L/mol (30).

The process of polymer-assisted ultrafiltration (PAUF), also known as polymer filtration, polymer chelation/ultrafiltration, reagent binding/membrane separation, and liquid-phase polymer-based retention, was first proposed by Michaels in 1968 (31). Soluble complexing polymers have been applied to the selective separation and concentration of many inorganic species (32–45). Specific applications have ranged from analyte preconcentration to

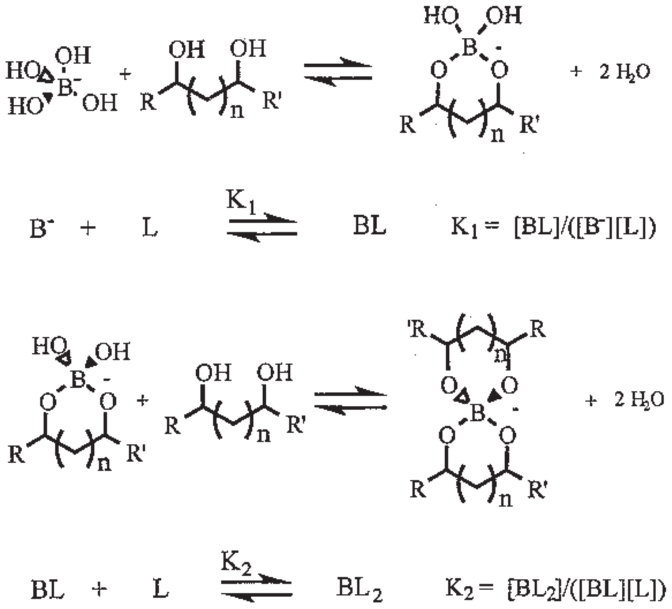

FIG. 1 Generalized reactions of borate anion with polyhydroxy compounds ($n = 0$ or 1). K_1 and K_2 are defined in this figure.

water treatment. The essence of the technique lies in complexing small molecules with macromolecules containing chemically specific complexing groups and filtering the subsequent complexes. This process allows one to use low pressure, high flux membrane systems such as ultrafiltration in lieu of the more drastic reverse osmosis processes which would otherwise be required. In the case of boric acid, however, even reverse osmosis membranes are ineffective barriers to this small, neutral molecule, making PAUF even more attractive.

To investigate the application of PAUF to the practical separation of boric acid from aqueous streams, we have studied cyclic retention/regeneration processes employing crossflow ultrafiltration. Several investigations of PAUF have focused on determining the associations between the inorganic species, typically metal cations, and the soluble polymers (46–49), but few have reported cyclic adsorption-to-breakthrough with subsequent regeneration and reuse of the chelating polymers, even though the degree to which the complexing polymers can be regenerated and reused is critical in any industrial application of PAUF. Also, most investigations of PAUF have used low-pressure stirred cells in which concentration polarization, the permeation-induced accumulation of macromolecular constituents near the membrane interface, is reduced by a magnetic spin bar suspended in the polymer solution. Since large-scale industrial application of this technology would likely adopt hollow fiber membranes which reduce concentration polarization through high crossflow velocities and which provide low hold-up volume with a high surface area to volume ratio (50), we have chosen to perform our PAUF experiments with a hollow fiber membrane system. Figure 2 is a schematic of the unit operation with a hollow fiber system employed in the batch concentration mode.

When considering the structure of the polymer for PAUF, it should be noted that hyperbranched polymers have several advantages over linear polymers. Due to their globular nature and consequent reduction of interpolymer entan-

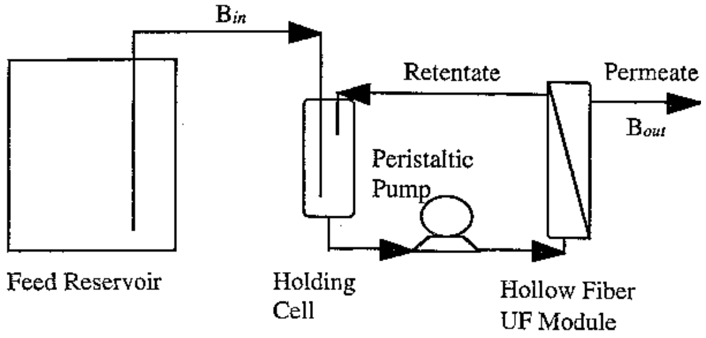

FIG. 2 Flow diagram of the hollow fiber ultrafiltration system used. The system is described in detail in the Experimental section. The feed entered the hollow fibers, and the permeate was removed on the shell side.

glements, hyperbranched polymers have low solution viscosities and can therefore be pumped and mixed at unusually high concentrations. This fact, combined with the high functional group density within a globular hyperbranched macromolecule, suggests that these materials will maximize the concentration of complexing functional groups and therefore maximize both adsorption capacities and volume reduction factors. Furthermore, it stands to reason that hyperbranched polymers, due to their reduced interpolymer entanglements, would be less likely to form transient intermolecular crosslinks under shear; one would therefore expect them to exhibit less shear-thickening than linear polymers in the presence of complexing ions (e.g., borate). This effect would also recommend hyperbranched complexing polymers for PAUF. In addition to the performance advantages inherent in their reduced solution viscosities, hyperbranched polymers also tend to be somewhat better complexing agents than their linear counterparts (51, 52).

In this paper we report the PAUF of boric acid in which two hyperbranched chelating polymers are loaded and regenerated through several cycles using the apparatus illustrated in Fig. 2. Each of the two polymers contains borate-specific chelating groups derived from the ring-opening reaction of glucoheptonic lactone onto polymeric amines such as poly(ethylene imine) (PEI). Figure 3 shows the PEI derivative.

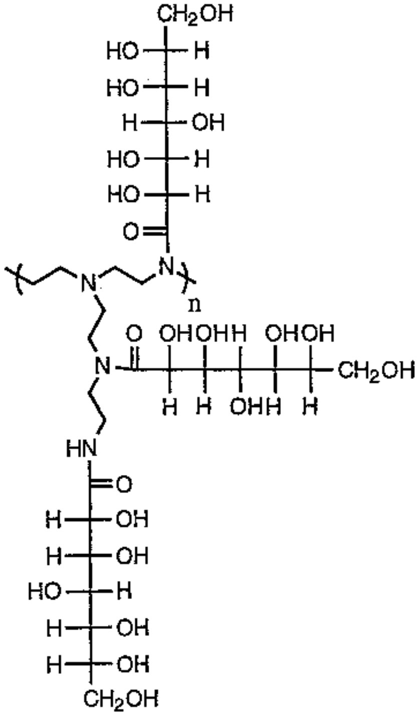

FIG. 3 Idealized structure of a segment of the glucoheptonic lactone derivative of poly(ethylene imine), GPEI, employed in the cyclic adsorption and desorption of boron.

EXPERIMENTAL

Preparation of GP3 and GPEI

Following the method of Aoi et al. (53), the ring-opening reaction of a lactone with an amine was used to derivatize the polymers. In a typical batch, 10.0 g glucoheptonic-*g*-lactone (Aldrich, Milwaukee, WI) was added to a solution of 1.93 g fifth generation PAMAM dendrimer (MW 28826, Dendritech, Midland, MI) in 30 mL dry DMSO (Malinkrodt, Paris, KY). The reaction mixture was maintained at 40 ± 1°C for 7 hours, then allowed to cool to room temperature. The mixture was diluted in 8 L deionized water and fed, through constant volume diafiltration, into the holding cell of the Quickstand (AGT, Needham, MA) ultrafiltration device equipped with a 10,000 MWCO hollow fiber membrane module (model UFP10-C-3A, AGT). The volume of the polymer solution in the holding cell was reduced to 100 mL, and purification was accomplished by constant volume diafiltration of this solution with more than 6 L deionized water. A sample was dried at room temperature under house vacuum for approximately 1 week prior to ^{13}C-NMR and elemental analysis. The product was completely functionalized at the terminal primary amine sites as ^{13}C-NMR signals from these groups (at ca. 41 ppm in D_2O) were absent in the product. Figure 4 contains the ^{13}C-NMR spectrum of the product in D_2O. Elemental analysis suggests the presence of approximately 10% residual water in the polymer. Calculated for $C_{2158}H_{4064}N_{506}O_{1148}$: C, 46.7%; H, 7.38; N, 12.78; O, 33.11; found (Huffman Laboratories, Golden, CO): C, 42.68%; H, 7.77; N, 11.59; O, 39.41.

To prepare GPEI, 30.50 g hyperbranched poly(ethylene imine) (50,000 nominal molecular weight, Sigma, St. Louis, MO) was dissolved in 700 mL deionized water, and this solution was subjected to 14 L constant-volume diafiltration in a crossflow hollow fiber 30K MWCO membrane module (AGT model UFP30-C-3A). The water was removed from roughly half of the remaining solution by rotary evaporation under slight convection with dust-free air. The resulting viscous liquid was dissolved in a mixture of 500 mL DMSO (Mallinckrodt) and 200 mL DMF (Mallinckrodt) with vigorous stirring at 70°C. To this solution was added 360 g α-D-glucoheptonic-γ-lactone, and this mixture was warmed at 60–70°C for 18 hours. The resulting product was precipitated in 10 volume equivalents of methanol (Aldrich) and allowed to settle. The supernatant was filtered through a Whatman #1 paper filter. The gummy, tan solid polymer, including the solid from the filtration, was dissolved in approximately 500 mL H_2O and filtered through another Whatman #1 paper filter directly into a 4-L reservoir for the feed of the ultrafiltration apparatus shown in Fig. 2. The solution in this reservoir was loaded into the 1-L holding cell overnight by constant-volume filtration beginning with 1 L deionized water in the holding cell. Over the next few days, the 1-L polymer solu-

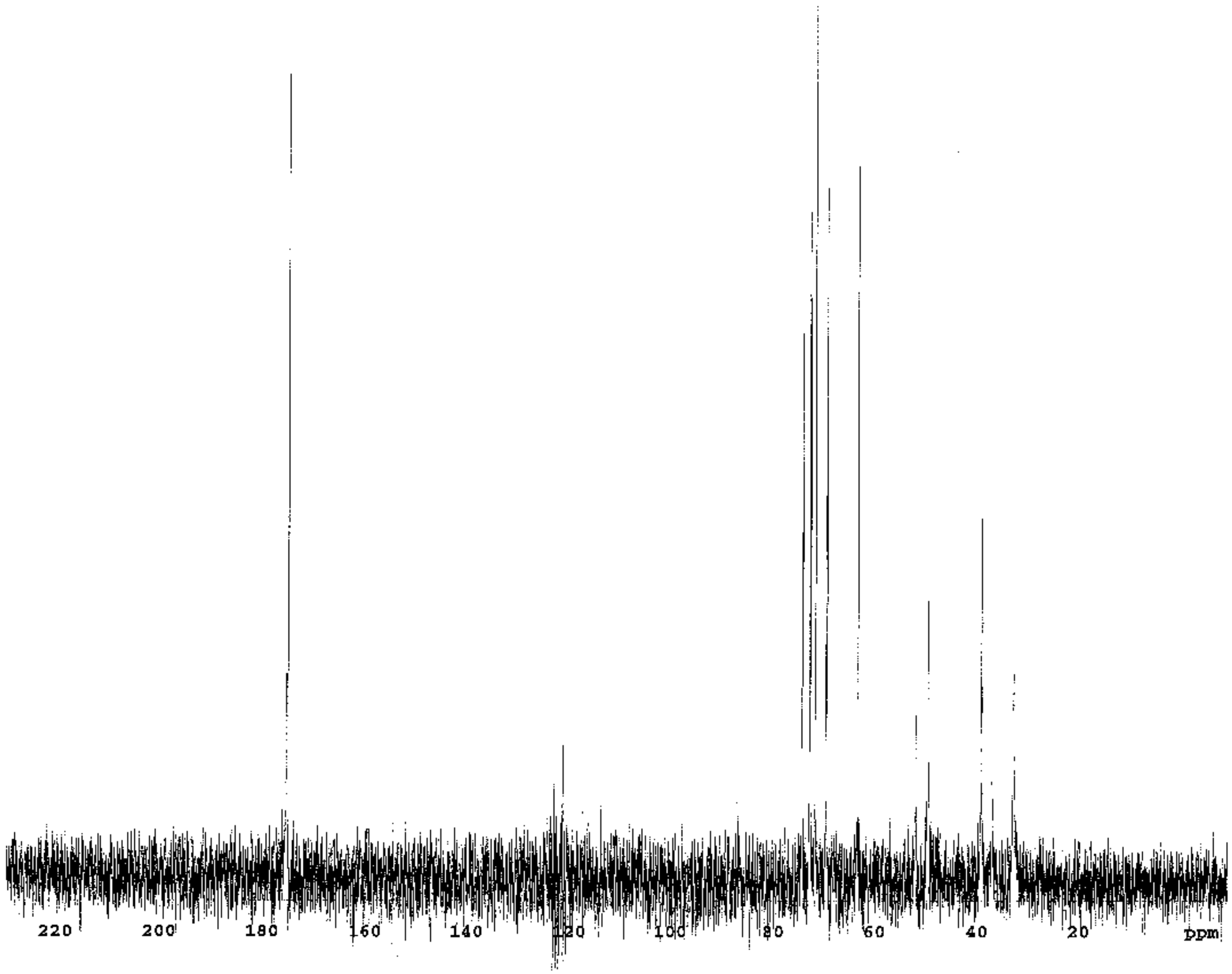

FIG. 4 Proton-decoupled ^{13}C-NMR spectrum of GP3 in D_2O, with chemical shift externally referenced to dioxane in water at 67.4 ppm. The six hydroxyl peaks from the ring-opened lactone are observed at 74.73, 74.25, 73.04, 71.98, 69.90, and 63.50 ppm.

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tion in the holding cell was diafiltered with a total of 16 L deionized water. After reducing the total volume in the holding loop to approximately 100 mL, the viscosity of the polymer solution (210 g/L) was estimated to be 20 cP by the Hagen–Poiseuille equation based on the pressure drop observed in the hollow fiber membrane module. Finally, this polymer solution was removed from the ultrafiltration apparatus and filtered through sterile 0.2 μm Nalgene filters (product 8-0301-84 DP 591, Nalge, Rochester, NY). The ^{13}C-NMR spectrum of this product is given in Fig. 5. Elemental analysis does not correspond to a simple product but is close to that predicted for complete reaction of the primary and secondary amines. Predicted mass percents were C, 43.55%; H, 7.44; N, 7.00; O, 42.01. An actual sample contained (Huffman Labs) H_2O, 0.06%; C, 39.17; H, 8.06; N, 7.66; O, 43.88.

PAUF Experiments

Boric acid (electrophoresis grade, Fischer, Fair Lawn, NJ), hydrochloric acid, and sodium hydroxide (Mallinckrodt) were used as received. Boron concentrations were analyzed by inductively coupled plasma atomic emission on an Applied Research Laboratories 3410 + ICP instrument made by Fisons Instruments. Sodium hydroxide and hydrochloric acid were tested for possible boron contamination by neutralizing a sample of concentrated HCl to pH 2 with NaOH; this sample gave no detectable boron signal, so both components were deemed essentially free of boron. PAUF experiments were performed using the same Quickstand apparatus (see Fig. 2) with a 10 K MWCO membrane module (AGT model UFP10-C-3A). During ultrafiltration, the relative uncertainties in holding loop volumes reported are approximately 10% and the uncertainties in the permeate volumes are approximately 1%.

RESULTS AND DISCUSSION

Dendrimeric Poly(Amido Amine)

The fifth generation poly(amido amine) dendrimer persubstituted with 128 glucoheptonamide complexing groups per molecule, GP3, was employed in the cyclic semibatch PAUF of boric acid. Four sequential adsorption/desorption cycles are reported, each with a different combination of feed composition and regeneration method.

With 4.76 g GP3 loaded into the 100-mL holding loop of the apparatus shown in Fig. 2, a solution containing 1.63 mM B (17.5 ppm) at pH 9.14 was fed into the holding loop at the same flow rate as that at which water permeated the ultrafiltration membrane. Figure 6 shows the observed boron concentration and pH of the permeate as a function of permeate (and feed) volume. For simplicity, molar units have been adopted; the concentration goal of 1

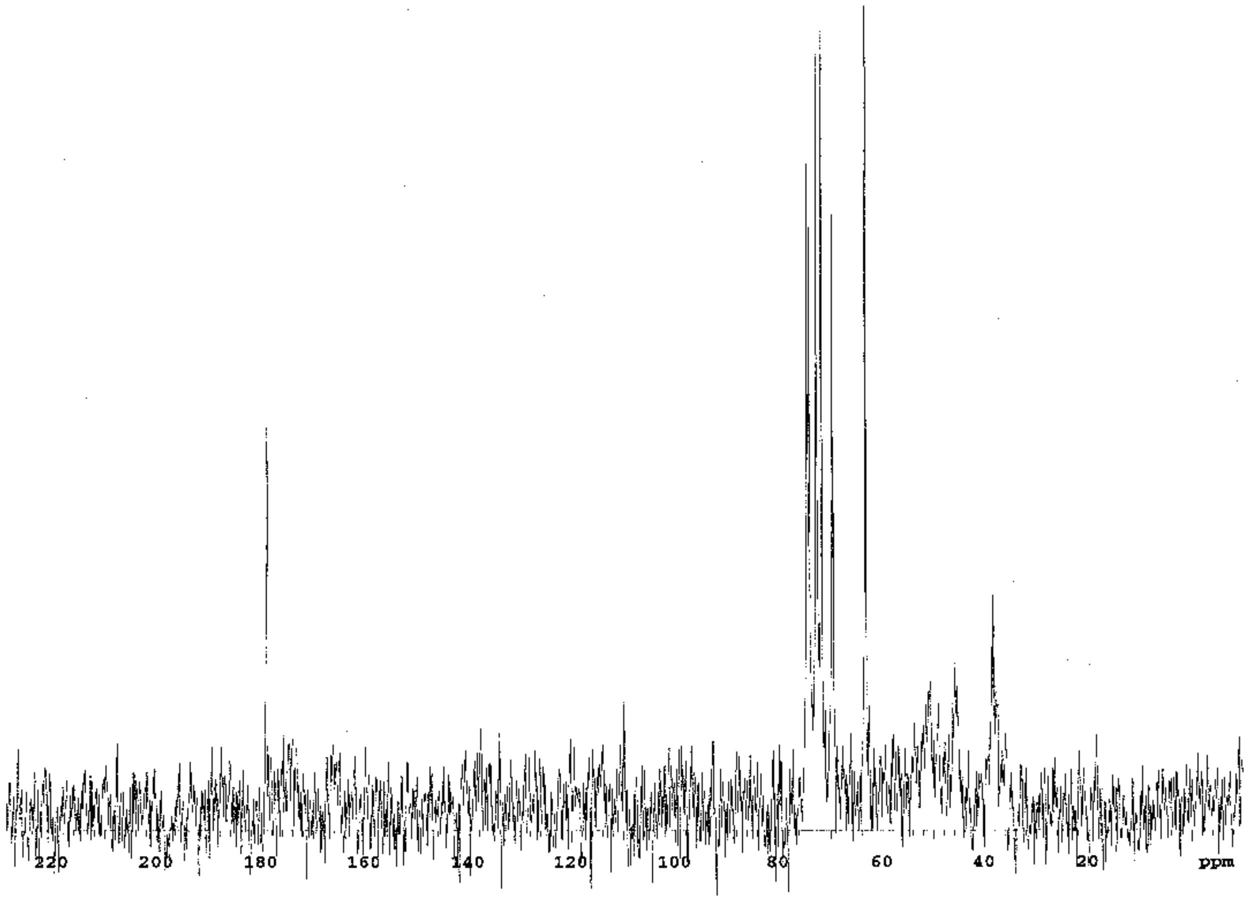

FIG. 5 Proton-decoupled ^{13}C-NMR spectrum of GPEI, poly(ethylene imine) functionalized with α-D-glucoheptonic-γ-lactone in D_2O, with chemical shift externally referenced to dioxane in water at 67.4 ppm. The six hydroxyl peaks from the ring-opened lactone are observed at 74.73, 74.25, 73.04, 71.98, 69.90, and 63.50 ppm. Peaks corresponding to the poly(ethylene imine) backbone are very broad at 51 and 46 ppm. The peak at 39 ppm is due DMSO-d_6, a previous solvent for this sample.

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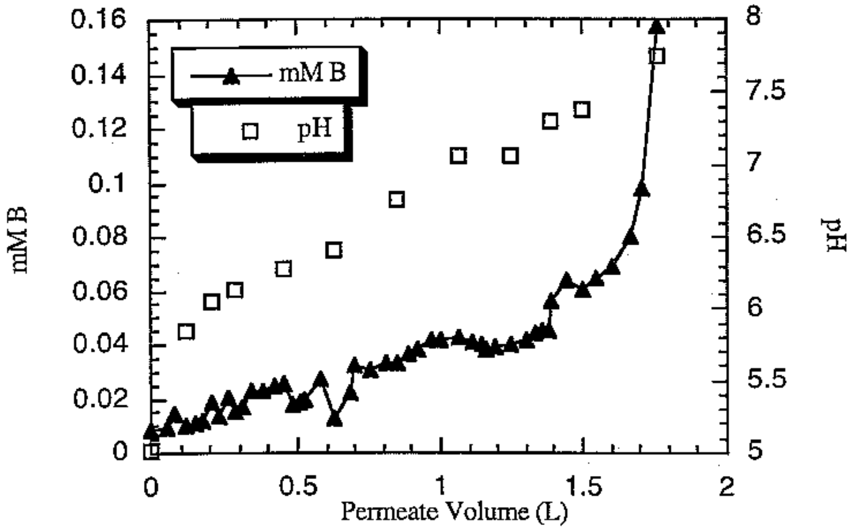

FIG. 6 Boron concentration and pH in the permeate from a constant-volume filtration experiment. The holding loop (see Fig. 2) contained 4.755 g GP3 polymer (10.97 mmol functional groups) in a total of 100 mL liquid. The feed for this experiment contained 1.63 mM B at pH 9.14. At the end of this adsorption cycle, the holding loop contained 2.81 mmol B as determined from the total mmol B added minus the boron released in the permeate.

ppm B corresponds to 0.093 mM. The slight depression of boron concentration at roughly 1.1 L permeate is coincident with restarting the pump after resting overnight, suggesting kinetic effects in mixing or complexation may be nonnegligible. Borate ester formation with small molecules is a rapid process because ^{11}B-NMR samples prepared less than a minute prior to acquisition showed no change upon further standing (our unpublished work) and such reactions are also used in rapid analytical techniques (55–57). Equilibrium borate complexation with the polymeric chelating agents reported here may be limited by relatively slow macromolecular rearrangement. The rise in boron concentration at 1.4 L permeate is coincident with an unintentional reduction in holding loop volume from 100 to 50 mL which occurred as siphoning from the reservoir was slow to initiate upon restarting the filtration.

The integral of the boron concentration in the permeate as a function of permeate volume is the total amount of boron released to the permeate. The difference between the moles of boron added in the feed and the integral of the actual permeate observations (e.g., Fig. 6) corresponds to the moles of boron retained in the holding loop. For the experiment described in Fig. 6, for which the initial boron concentration in the holding loop is assumed to be negligible, this difference corresponds to 2.81 mmol B retained in the holding loop by the end of the experiment. Nearly all of this boron is bound to the chelating polymer, and the mole ratio of chelating groups to boron is roughly 4.

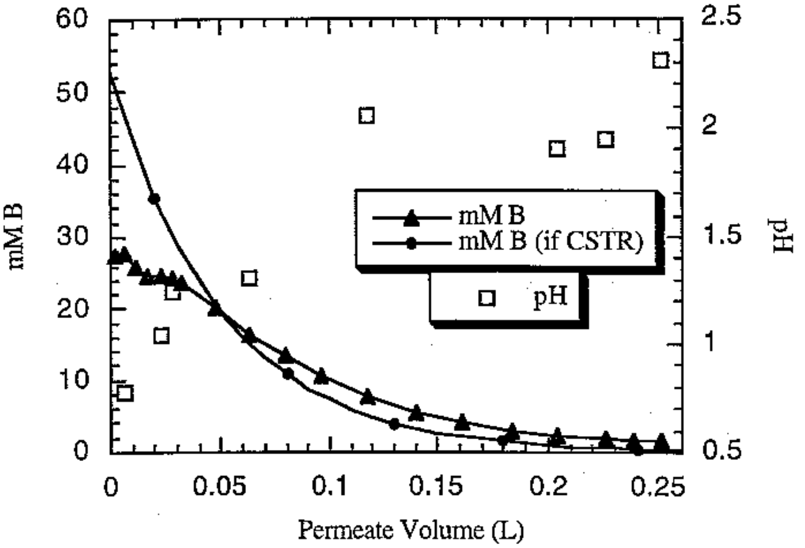

FIG. 7 Boron concentration and pH in the permeate during the first desorption operation after completion of the adsorption of Fig. 6. The prediction for the well-mixed holding loop (CSTR model) was calculated based on 2.81 mmol B with 10.97 mmol total ligands in 50 mL solution at pH 2. The fraction of boron associated as borate esters is negligible under these conditions (10). The total boron released in the permeate in this regeneration step is 2.56 mmol, or 91% of the total adsorbed. By 0.18 L permeate, 85% (2.40 mmol) of the boron adsorbed had permeated.

When the boron-rich retentate in the holding cell was acidified, the borate esters that were formed during the adsorption phase returned to free boric acid, which was rinsed from the holding loop and separated from the polymer solution. Figure 7 shows the pH and boron concentrations in the permeate observed after the first acidification and boron desorption. The 50-mL solution in the holding loop was made acidic with 2.0 mL 37% HCl prior to diafiltration with 0.01 M HCl. In this regeneration step the boron concentration in the permeate does not fall quite as quickly as one would predict for a well-mixed continuous stirred-tank reactor (CSTR), but this effect is understandable as roughly 35 mL of the 50 mL in this holding loop was contained in the tubing and only 15 mL in the relatively well-mixed holding cell itself. Another mixing effect is observed at low permeate volumes in Fig. 7 where one can clearly note the mixing on the permeate side of the membrane resulting in apparent nonexponential decay of the boron concentration in the holding loop.

The goal of this treatment process typically is to produce a small volume of boron concentrate after treating a large volume of contaminated water. The volume reduction factor (VRF) is simply the ratio of the volume of contaminated water treated to the volume of concentrate produced. Since this is a rather well-mixed system, the functional groups on the polymer can never be fully regenerated, and some boron must remain in solution. We have chosen to base our estimates of the experimental VRF on removing 85% of the complexed boron in the regeneration step. In practice the extent of regeneration must balance the time and chemical requirements for pH adjustment, which would become prohibitive when removing very little boron, with the decrease in VRF from rinsing the holding loop with a large volume, which would dominate when removing nearly all of the boron. Our choice of removing 85% of the adsorbed boron is somewhat arbitrary, but it is a reasonable estimate for industrial applications.

Based on the data in Figs. 6 and 7, treating 1.7 L before 1 ppm breakthrough, and regenerating 85% of that activity while collecting 0.18 L of boron-rich permeate, we calculate a VRF of 8.0 for this 1.63 mM feed (ca. 17 ppm). A volume reduction factor, or enrichment factor, of 10 is on the high end of experimental observations for the PAUF of 0.15 mM zinc chloride using poly(ethylene imine) (54). Since the VRF achievable is expected to be approximately inversely proportional to the concentration of the feed stream, the performance of this system, as measured by the VRF, is roughly an order of magnitude better than previously reported. One should also note that the viscosity of the (ca. 9.5%) polymer solution used in the regeneration step, while not measured, was not noticeably greater than that of water; polymer concentrations of 20–40% are not unreasonable with hyperbranched polymers, and the increase in polymer concentration would result in a roughly proportionate increase in the VRF. The hold-up volume in the tubing of our apparatus, combined with the expense of the dendrimeric starting material, limited our ability to investigate the upper limits of operating polymer concentrations. It would therefore be reasonable to expect that, if these limitations were removed, a VRF of 20–40 could be achieved for this 1.6 mM feed.

Although PAUF is a membrane-based separation, the concept of membrane rejection (or retention) coefficients for boron is not particularly enlightening. Boron rejection coefficients (1 minus the ratio of permeate boron concentration to retentate boron concentration) for the systems reported here are dynamic during the course of the separation and depend on pH, boron concentration, and polymer concentration. Typically, rejection coefficients begin very close to unity and drop during the course of the separation as the polymer chelating sites are filled. Because the rejection coefficients for these separations are dynamic, we have chosen to present performance data in terms of the more practical VRF. Instantaneous rejection coefficients may be calculated from the reported boron concentration in the permeate and the boron concentration in the holding loop (retentate) which can be determined by mass balance over the holding loop as mentioned above.

After the first regeneration, the GP3 remaining in the holding loop was then neutralized and run through three more cycles of boron concentration and re-

TABLE 1
Summary of PAUF Results for the GP3 Dendrimeric Chelating Polymer. The Holding Loop for the First Cycle Was Charged with 4.76 g Polymer and, after 4 Cycles, Ended with Approximately 3.23 g

Cycle	[B] (mM) and pH of feed	Adsorption pH	Regeneration procedure	Regeneration volume (mL)[a]	VRF[b]
1	1.63 pH 9.14	5.9–7.8	Diafiltration with 0.01 M HCl	180	8.0
2	0.97 pH 9.14	4.2–5.2	Diafiltration with 0.01 M HCl	200	4
3	1.06 pH ≈ 5	7.8–4.6	Diafiltration–acid spike–diafiltration	140	12.1
4	0.99 pH 11.04	7.3–10.9	Volume reduction–diafiltration	180	10.4

[a] Volume to permeation of 85% of total boron retained.

[b] Calculated as 0.85 V_f/V_r, where V_r is the regeneration volume and V_f is the volume of feed processed while maintaining boron concentration in the permeate less than 0.093 mM.

generation. Table 1 summarizes the performance of the dendrimeric chelating polymer, GP3. The VRF of the second cycle is low because, although much more boron was adsorbed than expected (10) in the second cycle, the concentration in the permeate rapidly exceeded 1 ppm (due to the low pH in the holding loop), so less than 1 L feed was sufficiently treated prior to unacceptable boron breakthrough. The VRFs from the third and fourth cycles were both greater than for the first because, even though some of the chelating polymer had been lost to the permeate (10), the feed concentration was lower, allowing more feed to be treated before polymer saturation and boron breakthrough.

Permeate fluxes observed (5 to 10 mL/min·m^2·psig) during this series of experiments—operating typically at 25–30 psig with a crossflow rate of 25–30 mL/min through a 30-cm long bundle of about 30 hollow fibers of 0.5 mm internal diameter—were lower by a factor of 5–10 than those previously reported for the PAUF of Cu(II) and Fe(III) ions (32), but the polymer concentrations reported here are higher, the solution temperature lower, and applied mixing energy lower. This last point is perhaps the most important as our fluid flow conditions were laminar whereas the other authors (32) reported turbulent conditions at the membrane interface.

Poly(Ethylene Imine) Derivative, GPEI

We now consider the performance of a polymer prepared from poly(ethylene imine) grafted with glucoheptonic lactone residues. The poly(ethylene imine) source material was reported to contain primary, secondary, and tertiary amines in the ratio of 1:2:1 as shown in Fig. 3. Four adsorption/desorption cycles were performed in sequence, once again varying conditions at each cycle.

In the initial adsorption of boron with this poly(ethylene imine) derivative, GPEI, a solution containing 0.939 mM B at pH 8.90 was fed to the 240-mL holding cell containing 19.2 g GPEI. Figure 8 shows the boron concentrations and pH in the permeate as the constant volume filtration experiment progressed. With this polymer we were able to treat over 13 L of this feed before permeate concentrations rose above the 0.093 mM target, even at low pH values. Also noteworthy is that the pressure-normalized flux remained at roughly the same level, 5 mL/min·m^2·psig, observed for the considerably more dilute dendrimer solutions discussed earlier. The pH of the permeate initially rises as the acidic solution (from the final regeneration of GP3) is rinsed out of the shell side of the membrane module. The pH then drops again (and also in subsequent cycles, see Fig. 11) as virtually all of the boron entering the holding loop is converted to chelated borate esters; this chelation drives the equilibrium between boric acid and borate anion toward the anion and consequently scavenges hydroxide ions from the solution in the holding cell. The pH finally begins to rise again when the chelating sites begin to saturate and the incoming borate buffer is not fully complexed. The pH changes of boric acid solu-

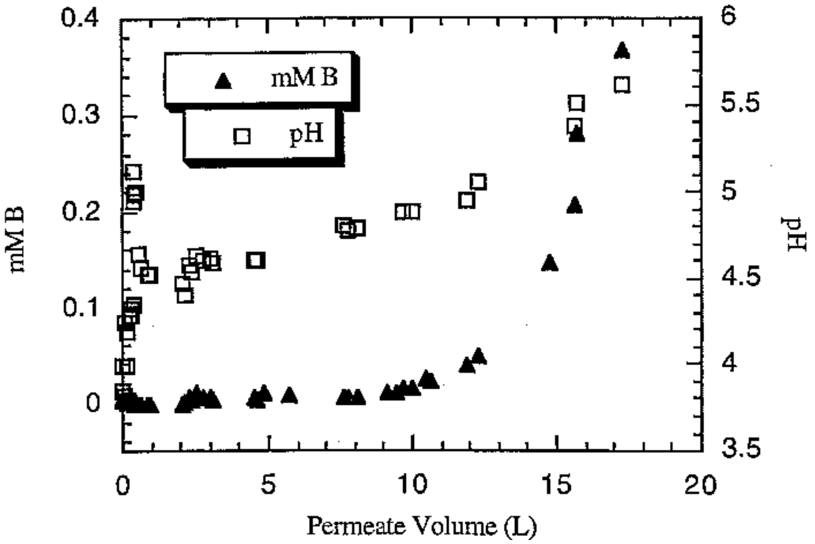

FIG. 8 Boron concentration and pH in the permeate from the first boron adsorption step for the GPEI polymer. The feed for this experiment was 0.939 mM B at pH 8.90. The holding loop contained 19.2 g polymer in 240 mL. Note that the vertical axis in this figure is offset to allow the inclusion of some early permeate samples for which slightly negative (within uncertainty of analysis) boron concentrations were reported. By the end of this adsorption step, the difference between the boron added in the feed and the boron released to the permeate was 15.20 mmol B.

tions upon addition of polyhydroxy compounds have been the basis of quantitative boron determinations (55–57).

The first desorption step for GPEI began after the volume in the holding loop was reduced to 60 mL by allowing permeate to flow with no feed, and 5.0-mL concentrated HCl was added. Figure 9 contains the boron concentration and pH values determined for the permeate from the constant-volume diafiltration of this holding loop with deionized water. It is interesting that after 0.35 L permeate, more than $\frac{1}{3}$ of the adsorbed boron is still retained in the holding loop. As it is improbable that there would be significant boron–polymer associations at equilibrium in a solution this acidic, one suspects that there is some nonequilibrium mechanism of boron retention. This effect possibly involved the formation of a slowly dissolving borate–crosslinked polymer gel in a sequestered portion of the apparatus, similar to what we observed in the subsequent absorption steps. It is also possible that the time scale of borate diester dissociation in this viscous solution was comparable to the time scale of the regeneration experiment (several hours).

Since we observed some loss of the dendrimeric polymer as described above, we had one sample of the permeate analyzed for its total organic carbon content. After 200 mL had permeated in the first regeneration step, we observed 2.22 gC/L in the permeate. In contrast, permeate from the first *ad*sorption step contained only 0.092 gC/L. These two observations sug-

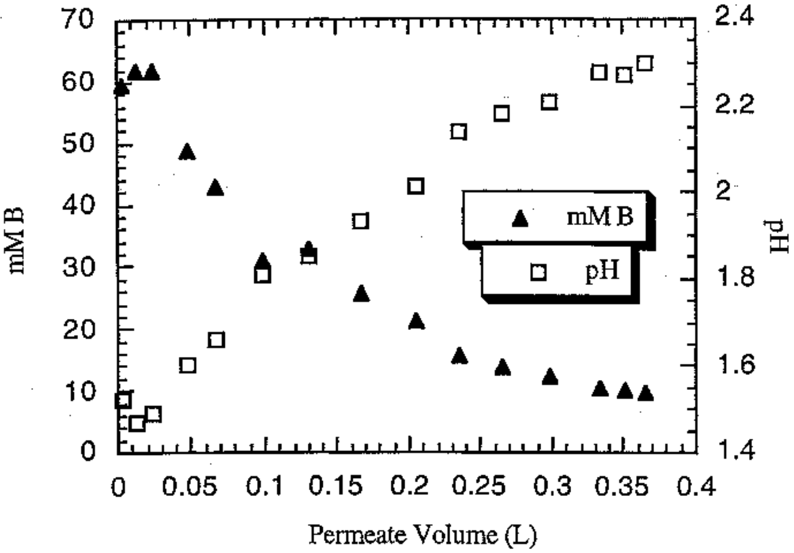

FIG. 9 Boron concentration and pH in the permeate during the first regeneration of GPEI after the adsorption shown in Fig. 6. The 60-mL holding volume was acidified with 5 mL concentrated HCl and rinsed by constant-volume diafiltration with deionized water. The pressure normalized flux for this desorption step was nearly constant at 2 mL/(min·m^2·psig) at 25–30 psig. At the end of this regeneration step, only 9.84 mmol B had permeated, leaving 5.36 mmol in the holding loop.

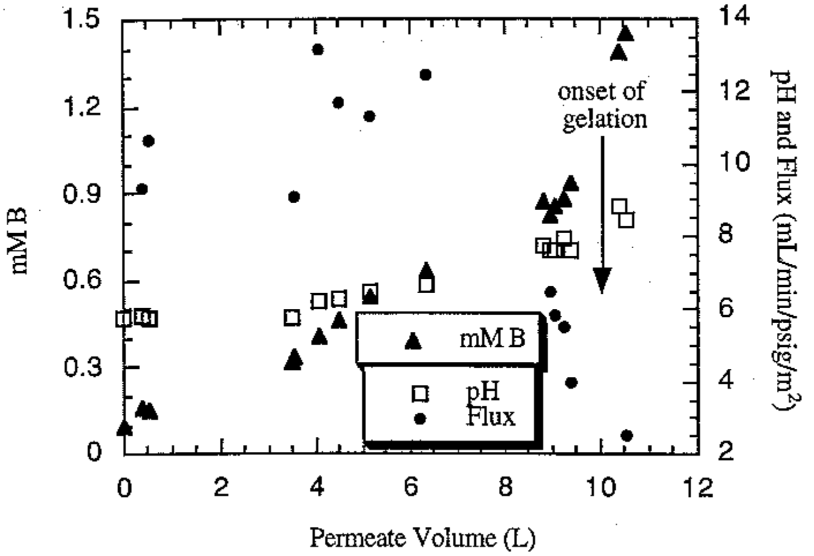

FIG. 10 Permeate flux with boron concentration and pH of the permeate from the second adsorption step with GPEI polymer, in which a 1.20 mM B feed at pH 11.34 was fed to the holding loop containing all the polymer from the first cycle in 400 mL. The boron concentration in the permeate was initially above 1 ppm due to the carryover of 5.36 mmol B from the previous regeneration experiment. The pressure-normalized flux, after membrane cleaning, began above 10 mL/(min·m^2·psig) but dropped to zero as the system gelled after 11 L permeate. By 10 L permeate, the solution in the holding loop had become somewhat cloudy and opaque. This adsorption experiment ended with 11.4 mmol B in a total of 200 mL holding volume upon gelation (57.1 mM B with ca. 19.2 g polymer).

gest that some polymer is lost due to permeation and that this amount is dramatically increased in acidic polymer solutions. This behavior is also consistent with acid-catalyzed hydrolysis of the polymer, cleaving the amide linkages between the polymer backbone and the polyhydroxy functional groups.

The polymer in the holding loop after the regeneration experiment in Fig. 9 was removed from the apparatus, and the membrane was cleaned as prescribed by the manufacturer. The polymer solution was then returned to the holding cell, neutralized with NaOH, and used to retain boron during the constant-volume filtration of a feed solution containing 1.20 mM B at pH 11.34. Figure 10 shows the boron concentration and pH in the permeate from this second adsorption step as well as the pressure-normalized permeate flux. After about 7 L permeate, the flux decreased suddenly, and at the end of this second adsorption experiment the GPEI polymer solution had gelled, resulting in virtually zero flux.

Reversible gelation of polyol–borate systems is not uncommon and has been studied in some detail (58–62). Gelation by formation of temporary intermolecular borate diesters is likely to be the most serious technical obstacle to the application of PAUF to treatment of wastewaters contaminated with boron. This gel was dissolved by acidifying the solution with hydrochloric acid to approximately pH 1.6. Regeneration of the polymer recovered a total of 10.9 mmol B in the permeate, leaving as much as 0.5 mmol still adsorbed to the polymer.

In an attempt to improve the overall solvent flux, the polymer was removed from the holding loop after this second regeneration step, neutralized, and added directly to a large volume of feed, thereby reducing the initial polymer concentration. This boron–polymer feed was then used as the reservoir (see Fig. 2) for the constant-volume filtration of the holding loop initially charged with 150 mL deionized water. After approximately 1.6 L of permeate, this system also gelled (3.5 g polymer, 1.6 mmol B, and pH 8 in the holding loop) and was subsequently acidified to break the gel and regenerate the polymer. The polymer was thoroughly regenerated until only trace boron was observed in the permeate of pH 1.5.

After neutralizing the polymer solution in the holding loop, the holding loop was fed, again in constant-volume filtration, a solution of 0.980 mM B at pH 9.03. Figure 11 shows the boron concentration and pH in the permeate from this experiment. The polymer appeared to have lost some effectiveness compared to its performance in the first adsorption cycle shown in Fig. 8. Only about 4 L of permeate could be successfully treated with this thrice-regenerated polymer, compared to roughly 14 L for the virgin material. One may also note the early drop in the solution pH values as the added borate formed bo-

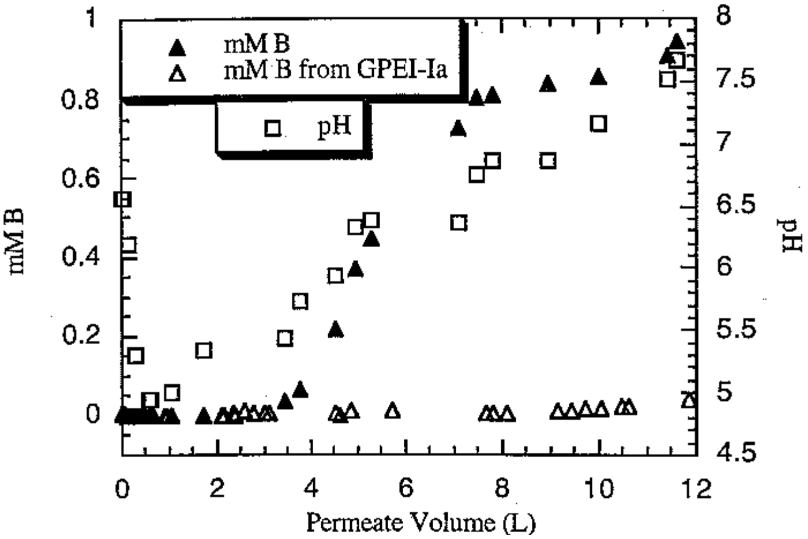

FIG. 11 Boron concentrations and pH values in the permeate from the adsorption step of the fourth cycle for the polymer GPEI. The 0.2-L holding volume was fed, by constant-volume filtration, a solution containing 0.980 mM B at pH 9.03. For comparison, the boron concentrations in the permeate from the first adsorption cycle are shown as the hollow triangles. A total of 5.90 mmol B remained in the holding loop at the end of this adsorption step.

rate esters, followed by a rise in pH as the polymer could no longer chelate all the borate added. The boron retained in this experiment was successfully stripped from the polymer by diafiltration after acidifying the solution in the holding cell.

The amount of polymer remaining, however, was surely less than the 19.2 g initially charged to the holding loop. Permeate samples from this fourth adsorption/desorption cycle were analyzed for total organic carbon content, and the results suggested that a significant amount of this polymer was lost to permeation possibly following partial hydrolysis. While the permeate sample from the adsorption step contained only 0.031 gC/L, the sample taken at 50 mL permeate in the desorption step contained 0.192 gC/L. In each of the regeneration steps the first permeate sample invariably had a slightly yellow tint, a much lighter shade than that of the honey-colored polymer solution remaining in the holding cell, but the carbon content of these samples was not measured. The fact that much more material was lost in the acidic regeneration steps than in the more mild adsorption steps suggests that acid-catalyzed hydrolysis of the functional groups is probably the dominant mechanism of polymer fragmentation and loss.

Table 2 summarizes the performance of the poly(ethylene imine) derivative, GPEI. The VRF of the second complete cycle is zero because the perme-

TABLE 2
Summary of PAUF Results for the GPEI Chelating Polymer. The Holding Loop for the First Cycle Was Charged with 19.2 g Polymer in 240 mL

Cycle	Feed	Adsorption[a]	Regeneration[b]	VRF[c]
1	pH 8.90 0.94 mM	pH 3.8–5.7 14 L 15.2 mmol	pH 1.4–2.3 0.37 L 9.84 mmol	24.5
2	pH 11.34 1.20 mM	pH 5.9–9.1 0 L 11.4 mmol	pH 1.5–2.8 2 L 10.93 mmol	0
3	8.27 L pre-mixed, pH 10.50, 1.09 mM	pH 7.0–9.5 0.2 L 5.1 mmol	pH 1.0–2.5 0.3 L 4.86 mmol	~0
4	pH 9.03 0.98 mM	pH 5.0–7.7 4 L 5.9 mmol	pH 0.6–2.2 0.18 L 5.02 mmol	18.9

[a] pH range, permeate volume while below 0.093 mM B (1 ppm), and total boron retained in the holding loop at the end of the adsorption step.

[b] pH range, permeate volume and total boron in permeate after given permeate volume during constant-volume diafiltration of holding loop with water.

[c] Calculated as (mmol regenerated)/(mmol adsorbed) × (V_f/V_r), where V_r is the regeneration volume and V_f is the feed volume given in the table.

ate from the second adsorption step contained more than 1 ppm B initially, the polymer not having been sufficiently regenerated in the first regeneration step. The VRF for the third cycle is also low due to early boron breakthrough in the adsorption step. Note that the amount of boron adsorbed during the adsorption steps decreased substantially during the first three cycles. Again, acid-catalyzed hydrolysis of the functional groups would account for this loss of effectiveness. Overall, it appears that if gelation is avoided and the polymer is sufficiently regenerated, a VRF of approximately 20 can be readily achieved.

CONCLUSIONS

The polymer-assisted ultrafiltration of boric acid has been demonstrated with two polymers containing glucoheptonamide chelating groups. When the polymer solution was not overly acidic ($\text{pH} > 4.5$ for GP3) during the adsorption step, the volume reduction factor ranged from 8 to 20 for feed concentrations near 1 mM B, and 85% of the retained boron was removed in the regeneration steps. The VRF for a given feed might be increased by employing a polymer solution containing a higher concentration of chelating groups. The observed VRF near 20 for GPEI is greater than that observed for GP3, but this is only due to the fact that the apparatus was unable to concentrate the smaller amount of the GP3 polymer to the same extent prior to regeneration by diafiltration. If one has the luxury of treating a feed which is close to the 1 ppm regulatory target, say a 2-ppm feed, a volume reduction factor exceeding 100 is not unreasonable.

Both polymers studied lost material during the course of the sequential PAUF experiments. Approximately one-third of the dendrimeric GP3 was lost over four adsorption/regeneration cycles. The loss rate of the hyperbranched GPEI was found to be much higher in the acidic regeneration steps, leading to the speculation that acid-catalyzed hydrolysis of the functional groups was responsible for the progressive decrease in polymer performance with each cycle. If so, such hydrolysis should not be a severe problem if the pH of the polymer solution during the regeneration steps can be controlled and maintained at 2.0. Alternatively, polyhydroxy functional groups might be attached to a polymer backbone through, for example, amine or ether linkages, thereby eliminating the threat of hydrolysis.

At sufficiently high boron and polymer concentrations, the solutions may form a reversibly crosslinked gel. Such gels are most likely to form at the membrane surface where the polymer and boron concentrations are somewhat enriched due to concentration polarization. A gel at the membrane surface would still allow some slow permeation but would inhibit axial flow and mixing, thereby facilitating the formation of a thicker borate–crosslinked gel. The threat of gelation may be reduced by employing chelating groups less likely to form intermolecular diesters and by using ultrafiltration membrane modules less likely to clog, such as larger bore hollow fibers (50).

PAUF may be an appropriate remediation technique for waters containing relatively low boron concentrations, particularly where floor space is at a premium. Unlike chelate resins, diffusion of the target molecules to the binding sites is fast and the rate of treatment is limited primarily by membrane surface area; the small “footprint” of membrane modules relative to that of an adsorption column with an equivalent throughput could make PAUF an attractive alternative on offshore oil platforms, for example. As with adsorption or chelate resins, PAUF processes are not well suited to treating highly contaminated streams because the chelating sites rapidly saturate, allowing treatment of only small volumes before regeneration; solvent extraction processes are preferred for such streams. With the fluxes reported here and the regeneration conditions suggested, ultrafiltration membrane prices are estimated to be a factor of 2–5 too high to make PAUF generally competitive with chelate resins.

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