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Boron Removal by Polymer-Assisted Ultrafiltration

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ABSTRACT

Boron contamination of natural waters is a widespread environmental problem which lacks a cost-effective solution. Polymer-assisted ultrafiltration is a method of boron removal that is compatible with other water-treatment processes. This boron removal technique exploits the pH-dependent complexation between boric acid and a macromolecule containing vicinal diol groups to prevent boric acid from passing through an ultrafiltration membrane. The concentration of boron in treated water was reduced from 10.5 ppm to less than 2 ppm through ultrafiltration of an aqueous solution containing boric acid and a polymer synthesized by grafting *N*-methyl-D-glucamine (NMG) onto poly(epichlorohydrin). The NMG groups, when tethered to the polymer, exhibited stronger affinity for boron than expected from equilibria between NMG and boric acid.

INTRODUCTION

Boric acid stunts plant growth when present in concentrations as low as one part per million (ppm), and boron contamination of natural waters is a concern around the world. Technology for boron removal and concentration has been slow to develop since the advent of a boron-specific adsorption resin in the mid-1960s (1). This resin is not widely used for treatment of industrial waters due to its low adsorption capacity in solutions containing boron below 100 ppm. A recent review of boron extraction techniques (2) suggests that there is as yet no practical solution to the problem of boron removal.

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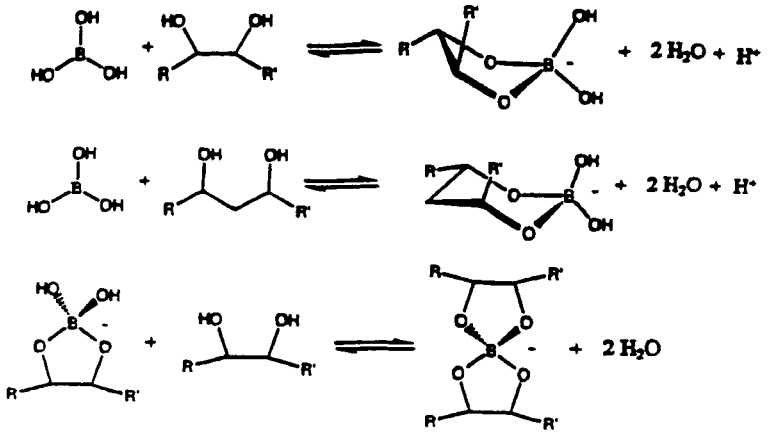

FIG. 1 Chelation reactions between boric acid and β- and γ-diols.

Since many of the treatment schemes for industrial waters involve ultrafiltration (3) to remove other contaminants, addition of a boron-chelating polymer could make these same filters effective barriers to boron as well. The concept of polymer-assisted ultrafiltration appeared in the mid-1970s as a means to treat waters contaminated with heavy metals (4). Later work

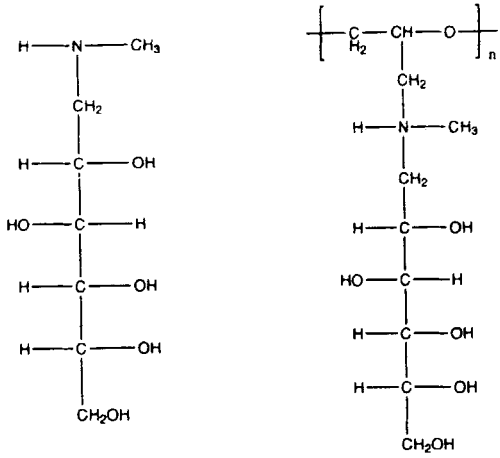

FIG. 2 *N*-Methyl-D-glucamine (left) and poly(epichlorohydrin) grafted with *N*-methyl-D-glucamine (right).

centered on the recovery of metals from dilute solutions (e.g., seawater) as an alternative to mining (5–7). Several polymers for boron chelation were patented in 1988 (8) but have yet to make an impact in boron treatment systems. Possible points of application for this technology include the recycle of boric acid in metal plating baths and removal of boron from petroleum well process waters and wastewaters in general.

The chemistry of boron chelation is described in Fig. 1. As one might suspect from the equilibria, the borate esters formed from the reaction of boric acid with diols are favored at high pH but dissociate under acidic conditions. Therefore the interactions of boric acid with a water-soluble polymer containing *N*-methyl-D-glucamine (NMG) as a side chain, pictured in Fig. 2, were studied.

EXPERIMENTAL

Boric Acid Equilibria with NMG

Boron that is bound to two pairs of diols was distinguished from that which is bound to only one pair by ^{11}B NMR. Solutions with known concentrations of boric acid (no greater than 0.1 M to prevent polyborate formation) and NMG were prepared at various pHs and their ^{11}B-NMR spectra were acquired. Equilibrium constants for the reactions of NMG with boric acid were estimated using a least squares fit to the species populations observed in solution as determined by integration of the ^{11}B-NMR peaks. All spectra were acquired with a Varian VXR-300S spectrometer operating at 7.05 T. The boron resonance at this field strength is 96.23 MHz. Boron trifluoride dimethyl etherate in $CDCl_3$ was placed in a coaxial insert and used as a chemical shift reference for each sample. Chemical shifts are reported relative to boric acid. Peak assignments were based on the work of Henderson (9) and Van Duin et al. (10, 11).

Polymer Synthesis

All reagents and solvents were used as delivered without further purification. Poly(epichlorohydrin) was synthesized by polymerizing 28 g epichlorohydrin (Aldrich, Milwaukee, WI), dried over molecular sieve (Malinkrodt, Paris, KY), with 0.4 g alkylphenyliodonium hexafluoroantimonate (GE Silicones, Waterford, NY) and 0.0042 g anthracene (Aldrich, Milwaukee, WI) under 10 mW/cm^2 365 nm light for 4 hours in flame-dried glassware. To the products of this reaction were added 100 mL dimethylformamide and 61 g *N*-methyl-D-glucamine (Aldrich, Milwaukee, WI). This mixture was heated at 45–55°C for 4 days; dimethylformamide was added periodically to replace that lost due to evaporation. The poly-

mer product was collected by precipitation into 400 mL methylene chloride (Malinkrodt, Paris, KY). The solid polymer was then dissolved in 500 mL water and filtered, in a low-pressure stir cell at 30 psig, through a 30,000 molecular weight cut-off (MWCO) membrane disk (43 mm diameter YM30, Amicon, Beverly MA). This apparatus, also used for the flow experiments below, is pictured in Fig. 3. After the initial filtration, 500 mL water was twice added to the holding tank and filtered down to 50 mL using the same membrane. The retained polymer was collected and dried in a vacuum oven at 1/2 atm and 60°C for 2 days. The dry retentate contained 7.8 g water-soluble polymer. Elemental analysis of the solid polymer was performed by Huffman Laboratories, Golden, CO. The results, based on polymer dry weight (C, 43.76%; H, 7.52%; N, 3.01%; Cl, 18.99%), suggest a $54._7$ percent substitution ($\pm 5._7$% at 95% confidence) of NMG on the aliphatic chloride sites.

Polymer–Boron Affinity Experiments

The 7.8 g of NMG-grafted poly(epichlorohydrin) (NMGPE) described above was dissolved in 100 mL water and used as a stock solution for the polymer. This solution would hold a foam, indicating that the polymer has considerable surfactant character. The pH of this solution was 7.8. A boron stock solution was prepared by dissolving 0.6024 g boric acid (electrophoresis grade, Fischer Scientific, Fair Lawn, NJ) in a 100 mL polymethylpentene volumetric flask with water to give 1.05×10^3 ppm boron. A sodium chloride stock solution was prepared by dissolving

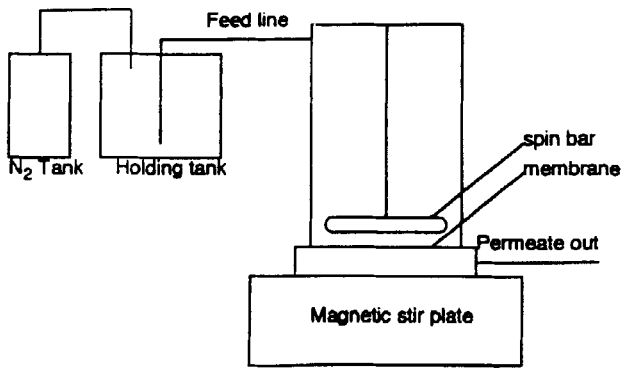

FIG. 3 Schematic of low-pressure stir cell used in polymer fractionation and in flow experiments.

0.5995 g NaCl (Malinkrodt, Paris, KY) in 100 mL water to give a 0.103 M solution. Working solutions were prepared from these stock solutions. The apparatus for the affinity experiments, pictured in Fig. 4, consisted of a glass U-tube in which the two sides were separated by low MWCO membranes (Amicon YM1 25 mm diameter disk) held in stainless steel holders which exposed approximately 3 cm^2 of membrane surface area to the solutions. Working solution aliquots of 20 mL were pipeted into their respective compartments. The compartments were sealed with a screw cap and stirred by Teflon-coated magnetic fleas driven by a magnetic stir plate. Mass balances on boron confirmed that neither leaching nor adsorption of boron from the glassware was measurable in the systems studied. Boron content of these solutions was measured using an Applied Research Laboratories 3410+ ICP atomic emission spectrometer made by Fisons Instruments. The effective boron detection limit was found to be approximately 0.1 ppm.

Flow Experiments

Working solutions made from the same stock solutions above were prepared in polymethylpentene volumetric flasks as above. 70 mL of these solutions were dead-end filtered in a low-pressure stir cell through an ultrafiltration membrane (43 mm diameter Amicon YM 30 or YM10) at 30 psig. Fractions were collected every 5 mL. The initial rate of permeation was approximately 4 mL/min. At the end of filtration the permeation rate had decreased to approximately 1 mL/min. After 55 mL had been

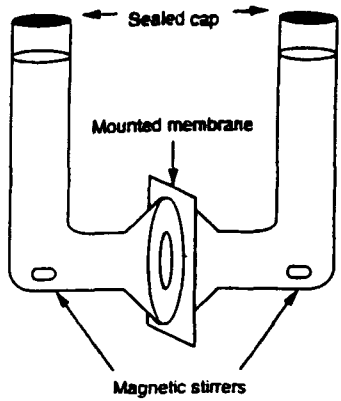

FIG. 4 Schematic of U-tube apparatus used in polymer–boron affinity experiments.

collected, the remaining retentate was decanted and analyzed for boron content.

RESULTS AND DISCUSSION

Boric Acid Equilibria with NMG Determined by ^{11}B NMR

Representative ^{11}B-NMR spectra of 0.1 M boric acid and 0.1 M NMG in aqueous solutions of various pH are shown in Fig. 5. When the equilibria in Fig. 1 are applied to the sugar derivative *N*-methyl-D-glucamine (NMG, Fig. 2), they yield the equilibrium constants shown for the summarized reaction schemes in Fig. 6, where "B" is boric acid and "O" is the hydroxide ion. The equilibrium constants in Fig. 6 were calculated based on the integration of ^{11}B-NMR spectra, such as those in Fig. 5. The ^{11}B-NMR spectra of boric acid in solution with NMR imply the existence of some polyanionic species, simplified here to B_2L. This type of species must exist in significant concentration for the mass balance on NMG to close.

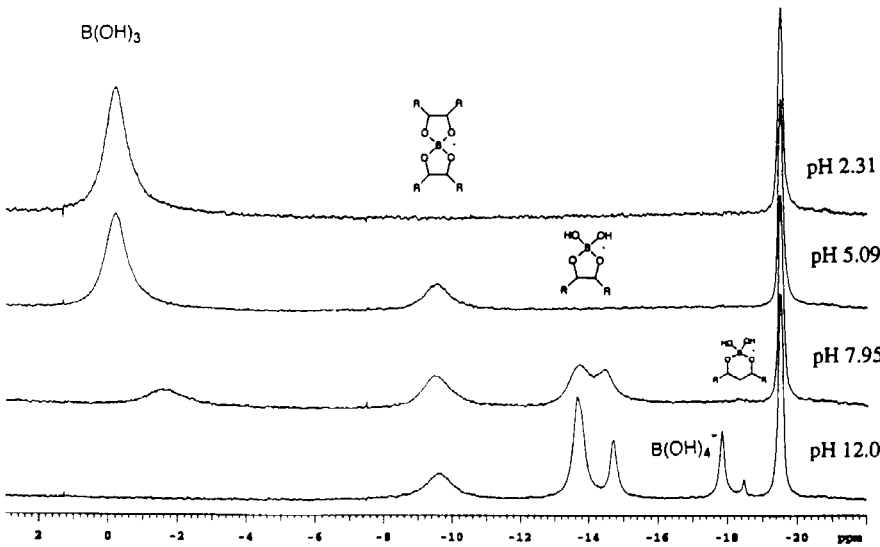

FIG. 5 ^{11}B-NMR spectra of 0.1 M boric acid in 0.1 M NMG aqueous solutions of various pH. Boric acid is in rapid equilibrium with the borate ion, and these two species exhibit a single NMR peak which is pH-dependent. The sharp signal at −19.5 ppm is from the boron trifluoride dimethyletherate standard as described in the text.

$$B + O + L \rightleftharpoons BL \quad pK_1 = -8.25 \quad (1)$$

$$B + O + BL \rightleftharpoons B_2L \quad pK_2 = -6.4 \quad (2)$$

$$BL + L \rightleftharpoons BL_2 \quad pK_3 = -10.8 \quad (3)$$

FIG. 6 Simplified equilibria and equilibrium constants estimated using ^{11}B-NMR data.

Based on these equilibrium constants, the concentrations of boron species in solution containing 0.1 M boric acid and 0.1 M NMG are plotted in Fig. 7 as a function of pH. Below about pH 3, virtually no boric acid binds to NMG.

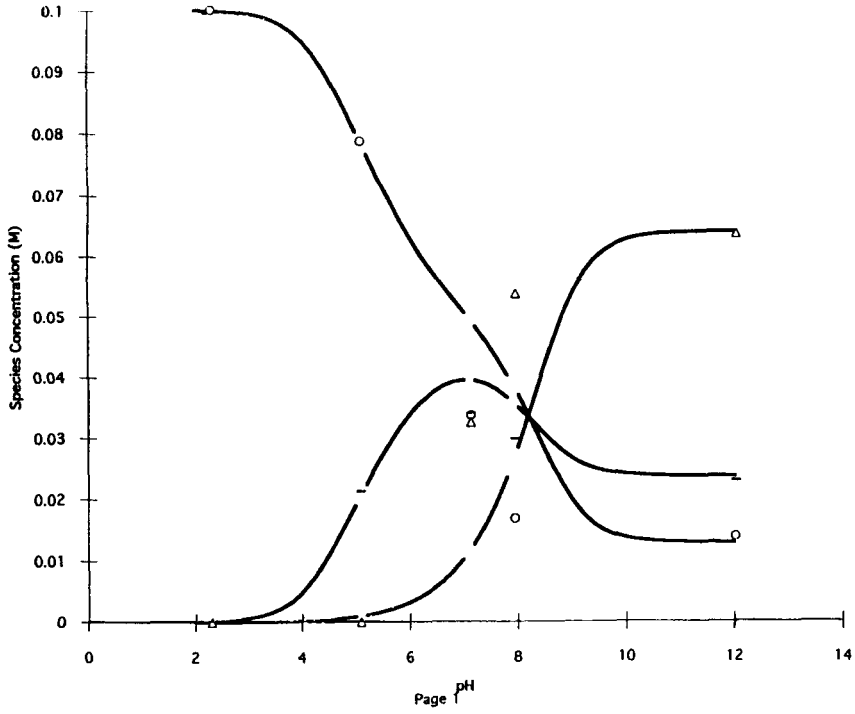

FIG. 7 Distribution of boron species for aqueous solutions containing 0.1 M boric acid and 0.1 M NMG as a function of pH. Species shown are uncomplexed boron as boric acid and borate anion (O), boron–NMG complexes including B_2L species (Δ) and NMG–boron–NMG complex (–). Data from integration of ^{11}B NMR are shown as discrete points; solid lines are calculated from the estimated equilibrium constants in Fig. 6.

Boron-Chelating Polymer

The results from the polymer-boron affinity experiments suggest that, as predicted, boron is bound much more tightly to the NMGPE described above in neutral or basic solutions than under acidic conditions. For example, when 20 mL of a pH 7.11 solution containing 10.5 ppm boron, 3.9×10^3 ppm NMGPE, and 0.01 M NaCl was separated from 20 mL deionized water by a 1000 MWCO membrane (YM1) using the apparatus in Fig. 4, the permeate contained only 0.2 ppm B after 48 hours. When a similar solution at pH 2.6 was separated from 20 mL deionized water by the same membrane, the permeate contained 3.4 ppm boron after 54 hours.

In a dead-end filtration experiment using the apparatus in Fig. 3, a solution containing 10.5 ppm boron, 3.9×10^3 ppm NMGPE, and 0.010 M NaCl at pH 7.11 was passed through a 30,000 MWCO membrane (YM30). Boron concentrations in the permeate are plotted as a function of permeate volume in Fig. 8. Clearly, the polymer serves to restrict the flux of boron through the membrane, reducing the boron concentration in the treated water to less than 2 ppm. The 7 mL retentate was found to contain approximately 85 ppm boron. A small amount of the polymer was able to permeate the membrane in this experiment as evidenced by the stability of foam in the permeate fractions.

Assuming only free boron would permeate the membrane, the concentration of free boron in this solution (2 ppm) was significantly lower than

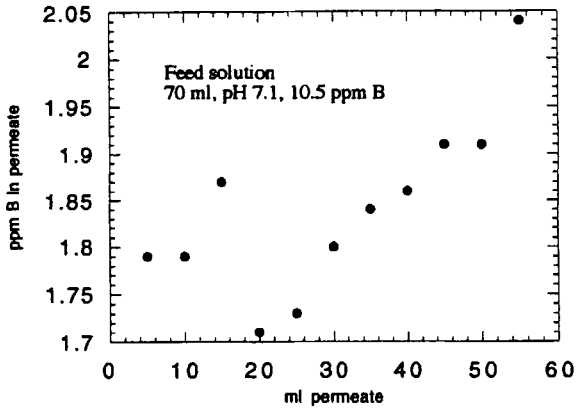

FIG. 8 Concentration of boron in the permeate of a neutral solution containing boric acid and excess polymer. The membrane was a 30K MWCO YM30 from Amicon and was operated at 30 psig.

one would expect (5 ppm) from a solution with a molar concentration of NMG equivalent to the molar concentration of pendant NMG groups. This is due to the increased likelihood of 1:1 complexes encountering another NMG moiety within the local environment of the polymeric chain. This would lead to more intrachain crosslinking than one would predict from NMG solution equilibria. Such intrachain crosslinking was proposed by Sinton (12) to account for both viscosity trends and ^{11}B-NMR spectra in the poly(vinyl alcohol)–borate system. An ^{11}B-NMR spectrum of this solution showed only one peak at -9.4 ppm with a signal-to-noise ratio of approximately 4, indicating that most of the boron in the solution was in fact chelated by two NMG groups.

When the solution is acidic, the polymer–boron interaction is much weaker. This was demonstrated in a permeation experiment in which a solution containing 10.5 ppm boron and 3.9×10^3 ppm NMGPE at pH 2.60 was dead-end filtered through a YM10 membrane. The concentrations of boron in the permeate are shown in Fig. 9. Late in the filtration, the boron concentration in the permeate began to decrease. This could be due to the development of a polymer-rich polarization layer on the feed side of the membrane which increases the effective polymer concentration. The boron concentration in the 11 mL retentate was approximately 17 ppm while the final permeate concentration was 9 ppm, so some boron was retained even at low pH. The permeate from this filtration also exhibited

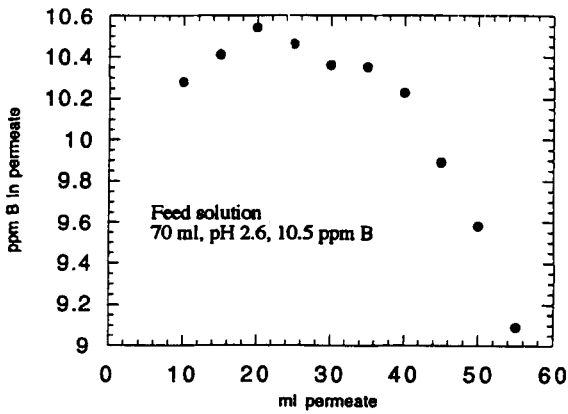

FIG. 9 Concentration of boron in the permeate of an acidic solution containing boric acid and excess polymer. The membrane was a 10K MWCO YM10 from Amicon and was operated at 30 psig.

significant foaming, implying that some polymer was able to permeate the membrane.

In a test of the application of this polymer system to the recycle of boric acid in a nickel-zinc plating bath (0.3 M $NiCl_2$, 3.2 M NH_4Cl, 360 ppm B as boric acid, and 2600 ppm NMGPE), the polymer precipitated from solution after several hours. The polymer did not precipitate in solutions containing 3.2 M NH_4Cl alone or 360 ppm B alone. At higher salt concentrations, however, the polymer did precipitate, and at higher boron concentrations the solutions gelled, as boron presumably acts as a crosslinking agent for the polymer. Similar gelation effects have been observed for poly(vinyl alcohol)–borate systems (12–14).

The fact that most of the permeates exhibited substantial foam-stabilizing properties suggests that some lower molecular weight polymer may have been present in the polymer feed. These may not have been separated from the high molecular weight polymer in the fractionation process. A polymer-rich polarization layer on the feed side of the membrane could have caused lower molecular weight fractions to be retained due to a combination of intermolecular hydrogen bonding and size exclusion effects. Another possible explanation for the polymer permeation is that boric acid could act as an intrachain crosslinking agent, decreasing the effective radius of gyration of the polymer chains. This behavior would be consistent with the observed increase in boron binding as previously discussed.

CONCLUSIONS

The possibility of applying polymer-assisted ultrafiltration to the removal of boron has been demonstrated. The predicted dependence of polymer–boron affinity on pH has also been shown. Problems with application of this technology include selection of sufficiently high molecular weight polymer fractions, development of polarization layers in dead-end filtration, and precipitation of polymer under some industrially relevant saline conditions.

Since the separation is only useful if the volume of water contaminated with boron is significantly reduced, high concentrations of polymer can be expected in the acidic elution step. This is likely to exacerbate the concentration polarization problems encountered above and make crossflow filtration a necessity.

When the NMG group was attached as a side chain on poly(epichlorohydrin), the polymer system was more than twice as effective at binding boron as one would expect based on the equilibria between boric acid and free NMG. A likely explanation for this phenomenon is that the local

concentration of hydroxyl pairs in the region of a 1:1 complex is higher in the polymer system, stabilizing the 2:1 complexes.

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