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REMOVAL OF BORON FROM AQUEOUS SOLUTIONS BY CONTINUOUS POLYMER-ENHANCED ULTRAFILTRATION WITH POLYVINYL ALCOHOL

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ABSTRACT

Boron is a highly contaminating metal due to its toxic effects for plants even at very low concentrations. Continuous polymer-enhanced ultrafiltration (PEUF) was applied for removal of boron from aqueous solutions. The effects of operating parameters on the performance of PEUF were investigated. A commercial polymer, polyvinyl alcohol (PVA) was used as the boron-complexing agent. The methodology consists of two steps: complexing boron with PVA following separation of boron and polymer complexes by ultrafiltration process. The pilot scale system utilized for the PEUF process accommodates a spiral-wound cellulose cartridge with 10,000 Da MWCO. The experimental parameters studied are metal/polymer ratio (load-

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ing) (0.01–0.5), pH (7–10), and the polymer characteristics such as molecular weight (M_n) of the polymer and degree of hydrolysis (DoH). The results showed that PEUF could be a successful alternative method for removal of boron. The permeate flux remained constant at around 19 L/m^2 hr throughout the runs and the fluxes were not affected by the operating parameters studied and by the polymer characteristics. When the loading values were decreased, the retention of boron was increased. Also, pH had an important influence as increase in pH resulted in increase in retention of boron. The polymeric M_n of the polymer did not have any influence on the retention of boron while an increase in DoH caused a decrease in retention of boron.

INTRODUCTION

Boron is a naturally occurring element distributed widely in the environment mainly in the form of boric acid or borate salts. Even though it is an important micronutrient for plants, animals, and humans, the range between the deficiency and excess is narrow. The tolerable limit of boron content of waters is 2 or 3 ppm for citrus and some other agricultural crops whereas, the recommended guideline value is 0.3 ppm for drinking water (1–3). Turkey possesses approximately 60% of the world's boron reserves. In geothermal waste water and drainage water discharged from the boron mines, the boron concentration can reach values as high as 30–40 ppm, which causes a threat of boron pollution to the receiving rivers especially during the irrigation season (4,5).

Although boron can be removed from water by various alternative methods, most of the techniques are difficult to apply and have some disadvantages. Adsorption on metal hydroxide is inefficient and uneconomical since it requires large number of stages resulting in poor boron removal (5). Evaporation–crystallization and solvent extraction processes are effective in high concentration streams and geared more to the production of boric acid rather than to its removal from water. The extraction processes use specially synthesized extractants which are expensive and require multistage systems (6–8). Ion exchange is another alternative method having the problems of expensive selective resins, regeneration steps, and low capacity with scale up problems (1,4,5,9–13).

As the membrane processes, supported liquid membrane (SLM), anion-exchange membranes, reverse osmosis (RO), and electrodialysis were also studied for boron removal (14–17). Industrial applications of SLMs are limited because of the major concern about stability and lifetime of such membranes

(14). Electrotransport through an anionic membrane is another alternative method studied scarcely to recover boron from effluents (15). The yield of boron electrodialysis through anionic membranes is difficult to predict when concentration increases. In the electrodialysis applications, the boron removal depends on the type of membrane, pH of solution, degree of desalination, the boron concentration in the feed, and the presence of ion-exchange resin in the desalinating chamber (16). In the reverse osmosis studies, the rejection of boron depends greatly on pH and it tends to rise with the increase in pressure (3,17). Multistage systems may be required because of the low selectivity of the process between the ions. The necessity of new studies was mentioned for examining the stability of RO membrane and the service life of the membrane at high pH in real operating conditions. The various difficulties and economical disadvantages of these methods led the researchers to perform new studies to develop easier and more economical methods.

Polymer-enhanced ultrafiltration is 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. In most of the previous studies, PEUF was studied mostly for cations by employing batch UF systems (18–27). The purpose was to select mainly specific polymeric agents for the targeted metals and to study their binding capacity (18–24). Most of them used specially synthesized polymers aiming to study the metal-binding properties of these special chelating groups. Since they were batch studies, the feed concentrations were not constant throughout the experiments, so the loading effects of the polymers were not investigated (18–27). 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) (25–27). An increase in alkalinity brought about an improvement in the effectiveness of the separation process and an increase in the value of the metal retention coefficient (25). By changing the pH values appropriately, it is possible to carry out the separation of metal ions obtaining high retention coefficients or to decompose polymer–metal complexes, which may result in recovery of the concentrated metal present in the feed and regeneration of the complexing polymer applied (26). The regeneration of the polymers was also studied by applying two different methods such as electrolysis of retention and acidification of the retentate to a rather low pH followed by UF. Electrolytic regeneration of the used polymers from a retentate was not practicable whereas regeneration is satisfactory by acidification (27).

In our previous studies, continuous PEUF was applied for removal of mercury and cadmium from multicomponent solutions while the effects of the operating parameters were investigated (28–30). Polyethyleneimine was used as the metal-binding polymer in the UF processes performed on both laboratory and pilot scale systems. The increased pH and decreased loading resulted in higher retention of both metals. In both pH and loading studies, a flat plateau in the retention was obtained for a wide range of loading and pH values. This means that retention was observed to remain almost at a constant value until the critical loading and pH values were exceeded. Then decrease in pH and increase in the loading values resulted in a decrease in retention of both metals. Continuous PEUF method seems to be feasible for the selective removal and recovery of cations from multicomponent systems when the critical pH and loading values were determined and applied.

In very few studies, PEUF was employed for removal of boron from the aqueous solutions with the specially synthesized polymers (31,32). One of the polymers utilized in these studies was synthesized by grafting *N*-methyl-D-glucamine (NMG) onto poly(epichlorohydrin) (31) and the others were glucoheptonamide derivatives of dendrimetric poly(amido amine) (32). The system for the separation processes was a crossflow UF with a hollow fiber system employed in the batch concentration mode (32). Feed concentrations were not constant and for defining the performance of the separation process, volume reduction factor (VFR), which is the ratio of the volume of contaminated water treated to the volume of concentrate produced, is used. Boron rejection coefficients for these separations were dynamic, beginning very close to unity and dropping during the course of the separation as the polymer chelating sites are filled. Rejection coefficients depended on pH, boron concentration, and polymer concentration. It was reported that some polymer was lost due to permeation during the experiments and this amount is increased dramatically in acidic polymer solution (31,32). Most probably, this could happen due to wide molecular weight (M_n) distribution of the complexing polymer but not due to polymer dissociation. The amount of polymer lost was not reported in the studies (31,32).

The possible complexation mechanism between PVA and borate ion was proposed as two diol units of PVA chain reacting with one borate ion to form a crosslink. This phenomenon depends on concentration of the reactants such as PVA and borate ion concentrations and also on the pH of the solution (33,34). The PVA–borate crosslinking mechanism is divided into two reactions: a monodiol complexation and a crosslink formation (34). In a nuclear magnetic resonance spectroscopy (NMR) study, the suggested complexation mechanism claims that monoborate anions complex certain organic polyols according to Eqs. (1)–(3) (33).

$$B + H_2O \rightleftarrows B^- + H^+ \tag{1}$$

$$A + B^- \rightleftarrows AB^- + 2H_2O \tag{2}$$

$$2A + B^- \rightleftarrows A_2B^- + 4H_2O \tag{3}$$

In this proposed mechanism, the symbols B and B^- represent $B(OH)_3$ and $B(OH)_4^-$ while A, AB^-, and A_2B^- represent free polyol and polyol/monoborate complexes 1:1 and 2:1 stoichiometry, respectively.

Polyvinyl alcohol, $[-CH_2CH(OH)-]_n$ is made by the hydrolysis of polyvinyl acetate because the vinyl alcohol monomer is unstable (35,36). The extent of reaction may be controlled to yield polymers with anywhere in the range 0–100% of the original acetate groups hydrolyzed (35). Degree of hydrolysis is the ratio of acetate groups replaced by the hydroxyls to the total acetate groups in the polymer. Pure polyvinyl acetate (0% hydrolyzed) is insoluble in water. The rate of dissolution in water increases with decreasing degree of polymerization and DoH (37). As the DoH increases, the polymer becomes more water soluble, up to 87%, after which further hydrolysis decreases water solubility at room temperature (35). Most commercial products fall into two main groups: those with a DoH of about 98 mol% of the acetyl groups, and those with a DoH of 87–89 mol% (37). As the acetate groups are replaced by hydroxyls, sites are introduced, which can form strong hydrogen bonds with water, thereby increasing the solubility (35).

In testing PVA for toxicity and for compatibility with skin and mucous membranes, no negative effects were found in animals (37), and no limitation for its existence in waste effluents was imposed.

The lack of the anion studies with PEUF and the parametric studies with continuous systems led to experimental study of continuous PEUF as an alternative method for boron removal. The PEUF was employed continuously by using the commercial polymer, PVA, for removal of boron while the effects of operating parameters such as pH, loading, M_n of the polymer, and DoH were investigated. A commercial polymer PVA was chosen to be studied as the binding polymer in order to observe the effects of the characteristics of the polymer on retention of boron by applying various kinds of PVA with different M_ns and DoHs.

EXPERIMENTAL

Materials

In the experiments PVA (Aldrich, Taufkirchen, Germany) with different M_ns and DoHs were used. The other chemicals of the experiments were boric acid (H_3BO_3, Merck, Darmstadt, Germany), sodium hydroxide (Merck, Darmstadt, Germany), nitric acid (Merck, Darmstadt, Germany), and distilled water. All the chemicals were used without further purification. The pilot scale SP20 Amicon Inc. (Stonehouse, UK) Ultrafiltration system used for the UF experiments employs an Amicon spiral wound cellulose cartridge (S10Y10) type having effective area of $0.93\,m^3$ and M_nCO 10,000 Da. These membranes are quite inert and safe. Similar membranes are also used extensively for drinking water treatment (38,39).

Ultrafiltration Experiments

The UF system applied for the separation experiments was explained previously in detail and the related figure is presented in our previous studies (28,29). The feed solutions were prepared by mixing the desired amount of polymer and boric acid solutions for 3 hr at a constant mixing rate of 250 rpm. The pH of polymer solution was adjusted before it was mixed with boric acid solution and during mixing also, pH was controlled to be maintained at the same value. The whole experiments were performed at constant temperature (25 ± 1°C) and constant inlet and outlet pressures (130 and 70 kPa, respectively) with the same membrane type. The UF system was operated in a total recycle mode. Both the retentate and permeate streams were returned back to the feed tank to keep the feed solution at a constant concentration during the entire run. All of the UF operations lasted for 4 hr. Throughout one run T, pH, feed flow rate, pressures, and the feed boron concentration (10 ppm) were constant. Small amount of samples were collected from both permeate and feed at sufficient time intervals. Two important measurements of the runs were permeate flow rate and concentrations of feed and permeate.

Analysis

For determination of the concentration of boron, inductively coupled plasma (ICP) was used [Leeman Labs. Inc. Direct Reading Echelle (Hudson, NH)]. For the analysis, the standard solutions of boric acid were prepared separately for both feed and permeate. Feed standards had polymer at the feed concentration whereas the permeate standards were only boric acid solutions. These standards were scanned by ICP and the intensity data of the standards were determined. With the intensity data, the calibration curves for both feed and permeate standards were obtained. Then the samples were scanned and the relative intensities of the samples were determined. During the feed analysis, in order to prevent clogging by polymer, system was cleaned with 0.1 *M* HCl. Finally the calculations of the sample concentrations were performed using their intensity data.

RESULTS AND DISCUSSION

Two main criteria for determining the quality of performance of UF processes are retention of the target component and the permeate flux (28–30). In order to determine the maximum retention of boron with PVA and the permeate flux, the effect of various parameters were studied such as pH (in the range of 7–10), boron loading (grB/grPVA) (in the range of 0.002–1), and the characteristics of the polymer such as M_n (13,000–100,0000) and DoH (86–99%). Flux was determined during the experiments by measuring the permeate flow rate per unit of effective area of the membrane. Retention values were determined after the boron concentrations of both feed and permeate had been analyzed and obtained. The calculation of the retention values (R) were made using the formula: $R = 1 - (C_P/C_F)$ where C_P and C_F are the boron concentrations of the permeate and the feed solutions, respectively.

The values of concentrations of feed and permeate, the retention, and the flux values in a typical run are given in Table 1. Within the runs there were small fluctuations in the concentration, retention, and flux values; the deviations were ± 0.5–2% in the concentration, ± 0–1.5% in flux, and ± 0.5–2.5% in the retention values. This shows that steady state was established in the system quickly in 1 hr. The percent deviations in each run were small enough to accept the setup, methodology, and the analysis as reliable. Also to check the reproducibility, some of the selected runs were repeated at the same conditions of pH, loading, and polymer characteristics. As a result, the relative errors between successive runs were ± 1.5–7% for the retention and 0.3–2.4% for the flux values. These results show consequently that UF system can reject reproducibly the complexed materials with the same performance and prove that reasonable separation of boron can be achieved by PEUF method.

The effect of the operating parameters of pH, loading, and PVA characteristics were studied, and it was observed that the flux values were obtained at a constant value of 19 L/m^2 hr. The flux values not being affected by the polymer concentrations and the polymer characteristics show that in the UF

Table 1. Permeate and Feed Concentrations, Retention, and Flux Values with Respect to Time

Time (min)	Feed Concentration (ppm)	Permeate Concentration (ppm)	Retention	Permeate Flux (L/m^2 hr)
0	10.05	—	—	—
60	9.73	7.41	23.84	19.49
85	9.79	7.38	24.62	19.37
110	10.01	7.58	24.28	19.45
135	9.68	7.34	24.17	19.60
160	9.72	7.42	23.66	19.61
185	9.76	7.38	24.39	19.38
210	9.96	7.60	23.70	19.75
235	9.93	7.56	23.87	19.52

$L = 0.02$, pH = 10 (PVA $M_n = 13,000–23,000$, DoH = 87–89%).

system, there are no problems of concentration polarization, fouling, and gel formation for the ranges of the polymer concentration and experimental parameters (such as ΔP and feed flow rate) used. In our previous studies, the same phenomena were observed with Polyethyleneimine (PEI) as the complexing polymer for removal of cadmium and mercury (28,29). Other operating parameters especially feed flow rate and UF pressure were studied in our previous studies and the results showed that for our UF system, concentration polarization and fouling were not problems for the studied range of variables and for the synthetic solutions we used, which do not contain any particulate matter (28,29).

Loading (L) is an important parameter, which has a dominant effect on retention of the target components by PEUF. To determine the binding capability of PVA for boron and to observe the effect of loading, the experiments were performed at different loading values in the range 0.002–1. In Fig. 1, the retention values at each loading value are presented in a logarithmic scale. As expected, rejection increases with the decrease in loading values since increase in polymer concentration increases the binding capacity. Although loading is decreased dramatically, the increase in the retention value is not very pronounced. This is contrary to our observations in previous studies for cations (28,29). Even at high polymer concentrations, no plateau was obtained. This may be attributed to the behavior of the PVA–borate ion systems (33,34). One of the main reasons for this observation may be based on insufficient solubility of PVA

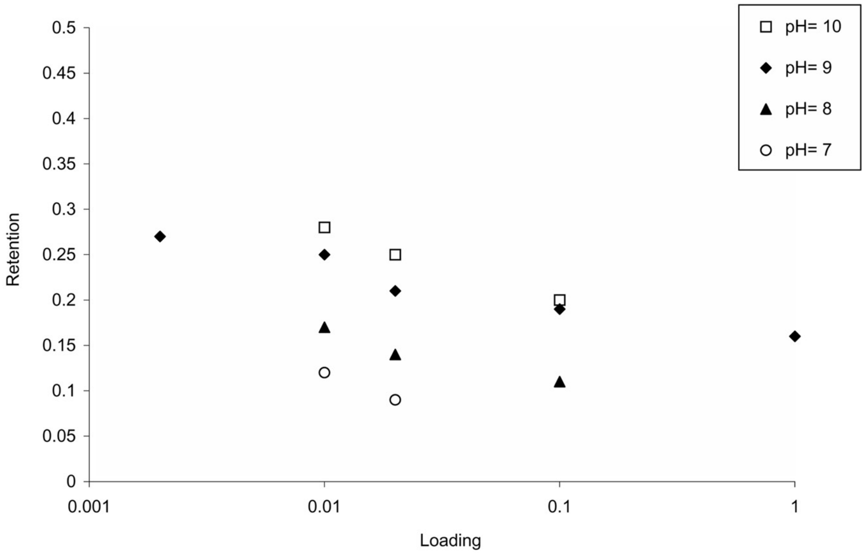

Figure 1. Effect of loading and pH on retention of boron.

(35). At very high polymer concentrations effective dissolution of polymer in microscopic level and suitable chain conformations for complexation may not be achieved.

pH is another significant factor deciding the effectiveness of complexation and influencing the retention degree of the metal ions. It is effective directly on complexation between the ion and the polymer (25–32). Therefore, after investigating the loading effect, detailed studies on the effect of pH on retention of boron were carried out. The system was basic and the range of studied pH was 7–10. The higher pH values were not studied because of the limitations of the membrane material and for the equipment safety. When pH of the medium increases and system is very much away from neutrality, the retention values increase with the increase in pH. These phenomena, which are seen in Fig. 1, occur in the entire range of loading values studied. In our previous studies with cadmium and mercury, the retention also increased with increase in pH (29). The system was acidic, and contrary to the present boron study, it was observed that the rejection of cations increased when the system got close to normality. The pH effect on retention of boron is weaker with respect to mercury and cadmium but it is still a determining parameter for the retention values.

The effect of pH on retention of boron may be explained as follows: free OH^- groups increasing with increase in pH do not compete with borate ions, and the increase in the OH^- concentration enhances the complexation and thus facilitates retention. The H^+ ions should be removed from the system since they prevent the complexation of tetraborates by blocking the oxygens on the chain. This result is also consistent with the previous study of complexation chemistry of boron with PVA: boron dissociates into ion form in alkali side and boric acid dissociation is highly dependent on pH such that a high dissociation occurs at high pH values (11,33,34).

Finally, the effect of the chemical nature of the polymer on retention of boron is investigated. Two important parameters related with the complexing agent are M_n and the DoH, which affect the various behaviors of the polymers such as solubility and complexing ability. The strong influences of these behaviors on retention of the target compound led to the investigation of the effects of these parameters. For this purpose, experiments were performed with PVA with different M_ns and DoH. The results of the experiments are given in Fig. 2.

In Fig. 2, the effect of the DoH on retention of boron is presented. Polyvinyl alcohol with 87–89% DoH yields higher retention than the retention obtained with 98–99% DoH. This observation was valid for different M_n ranges studied. This consistent effect of DoH on retention shows that this is an important parameter determining the complexation and thus the retention. The higher retention values obtained with 87–89% DoH may be

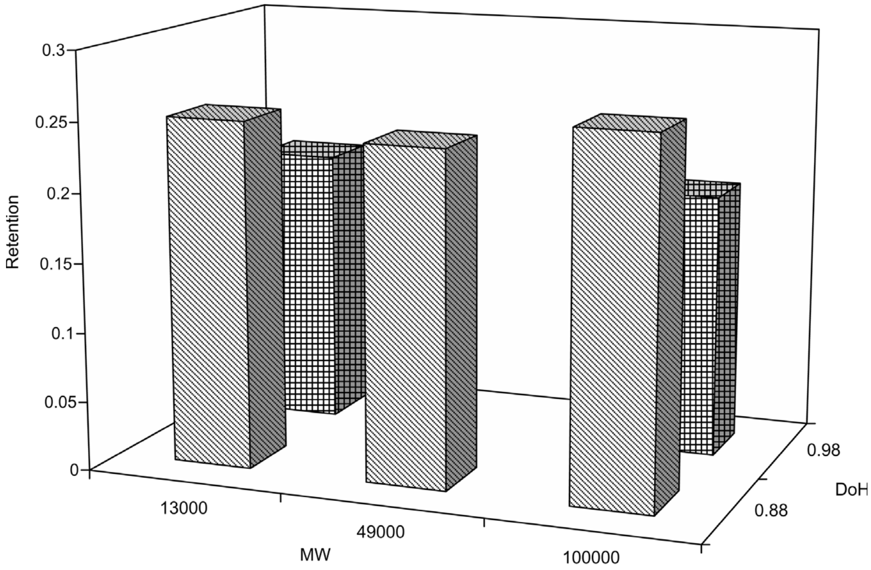

Figure 2. Effect of PVA characteristics on retention of boron at $L = 0.02$, pH $= 10$.

due to the effect of DoH on the solubility of the polymer. When the DoH of PVA exceeds 87% at which the highest solubility is obtained, the solubility starts to decrease, therefore, the capacity for binding the borate ions decreases (34).

Figure 2 shows the retention values obtained as a function of M_n at two different DoH values. The small deviations between the retentions show that M_n of PVA may not be very effective on complexation and rejection of boron so the separation may not depend on M_n of PVA. This behavior may be explained again based on the previous studies of polymer–metal complexation (33,34). The percentage of boron which is in crosslinks depends on PVA concentration but not on M_n. This seems reasonable since the complexation equilibria should depend on monomer concentration (moles of vinyl alcohol per liter of solution) and not the degree of polymerization (33).

CONCLUSIONS

Continuous PEUF was employed for removal of boron from the aqueous solutions by complexing it with PVA. The effects of the various operating parameters on the rejection were investigated and the success of the boron binding capability of PVA was studied. The high reproducibility values prove the reliability of the system, the methodology, and the analysis. As a consequence, it was proved to be applicable successfully for the boron removal processes.

The parameters studied do not have an appreciable effect on the permeate flux. Flux and retention values, which come to steady state quickly within an hour, remained at the same constant value throughout the runs. For the range of experimental parameters used, the flux values remained approximately at a constant value. This proves that there are no problems such as concentration polarization, fouling, and gel formation thus again proving the reproducibility of the UF system and the methodology.

The effects of the operating parameters, loading, and pH, on the binding and the rejection in PEUF, were investigated. It was observed that the effects of the parameters on anions were different from the effects on cations. To determine the optimum conditions and understand the behavior of the complexation affinity in the UF process, runs at different loading and pH values were performed. Decrease in loading values, which means higher PVA concentrations used, gives higher retention. This increase is limited and using very high concentrations does not yield very high retentions. Retention also increases with the increase in pH of the system. The results show that for anion removal processes high pH values can be applied for obtaining a high rejection values.

The chemical nature of the polymer, M_n and DoH are studied. For this part of the study, different kinds of the commercial polymer were used with various M_n and DoH values. The experimental results showed that the retention of boron is affected by the DoH whereas M_n has no effect on the retention. Increase in DoH values decreases the retention values while it remains nearly at a constant value at different M_n values.

The PEUF can be employed satisfactorily for removal of boron from the aqueous solutions. The removal performance of the process can be improved by using polymers having high boron affinity consisting more active OH^- groups at high loading and pH values. Under the light of experience obtained in this study, the efforts are under way for the synthesis of polymers with high boron affinity (40,41) to be used for the separation and recovery of boron from aqueous solutions by PEUF.

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