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Removal and recovery of metal anions via functional polymer based PEUF

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1. Introduction

Most of the metal contamination comes from industrial sources and many metal anions in the effluents of these industries like chromate and borate are toxic even at very low concentrations and give rise to increasingly strict regulations. According to world health organization, boron and chromium content of the water should be less than 0.3 ppm and 0.1 ppm, respectively. Therefore, it is required to remove those metals down to very low concentrations. One promising method that may meet this requirement is polymer enhanced ultrafiltration (PEUF). PEUF is the combination of two phenomena; binding of the target metal ion to a water soluble polymer to form macromolecular complexes, and ultrafiltration. This macromolecule which has a larger molecular weight than the molecular weight cut off of the membrane will be retained, while the non-complexed ions pass through the membrane [1]. Metal anions are especially complex targets as they are coordinatively saturated and they cannot form covalent bonds to polymers easily. Therefore, it may be necessary to insert a suitable specific functional group into the polymeric matrix that makes them capable of interacting with metal anions [2]. In this study borate and chromate are selected as target metal anions to be removed. A commercial polymer, PVA (as a model agent), and two specially synthesized polymers, hydroxyethylamino glycerol modified polyglycidyl methacrylate and poly(*N*,*N*-diallyl morpholinium bromide) are employed as chelating agents and the effect of loading (metal/polymer), pH and ionic strength on chromate and borate removal are investigated using PEUF.

2. Experimental

Hydroxyethylamino glycerol modified polyglycidyl methacrylate is synthesized in two steps: reaction of glycidol with ethanolamine to yield 1-(2-hydroxyethylamino) glycerol and reaction of poly(glycidyl methacrylate) with 1-(2-hydroxyethylamino) glycerol. A two-step procedure is also applied in the synthesis of poly(*N*,*N*-diallyl morpholinium bromide). First the monomer, *N*,*N*-diallyl ammonium bromide (DAM) is obtained by Hofmann alkylation of morpholine with allyl chloride and quaternization with ally bromide, then its radical polymerization with

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t-ButOOH. Using the synthesized polymers and commercial PVA, PEUF experiments were carried out at room temperature using Osmonics Sepa CF membrane cell having a 155 cm^2 effective membrane area. Experiments were performed in continuous mode operation with recycling of permeate and retentate streams into the feed so that the feed concentration remained constant throughout the experiment. During the ultrafiltration experiments; pH, temperature, feed flow rate and pressure difference were kept constant and monitored continuously. In order to determine the maximum retention of both anions with the polymers, the effect of loading (in the range of 0.01–1) and pH (in the range of 7–10) were investigated. Flux was determined during the experiments by measuring the permeate flow rate per unit effective area of the membrane. Small amount of samples were collected from both permeate and feed at sufficient time intervals. Chromium and boron concentrations in the samples were determined using Philips 9200X AAS and Leeman ICP-OES, respectively. The calculation of retention values (R) were made after the analysis of permeate and feed samples, using the formula: $R = 1 - C_p/C_f$ where C_p and C_f are anion concentrations of the permeate and the feed solutions, respectively.

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 h)
0	10.03	–	–	–
60	8.97	6.46	0.28	22.5
90	8.93	6.32	0.29	23.2
120	8.90	5.87	0.34	23.2
150	8.92	5.69	0.37	23.4
180	8.93	5.65	0.37	23.9

3. Results and discussion

The feed and permeate concentrations, retention and flux values in a typical run for boron retention using PVA with a loading of 0.02 and pH of 9.0 are given in Table 1.

As it is seen from the table, there were very small fluctuations in the feed and permeate boron concentration, retention and flux values after 90 min indicating that steady state was established in 1.5 h. An average retention value of 0.33 was obtained for a boron loading of 0.02 and pH of 9.0.

Functional polymers for borate and chromate, namely, hydroxyethylamino glycerol modified polyglycidyl methacrylate and poly(*N*,*N*-diallyl morpholinium bromide) are synthesized. Their resulting molecular weights are 220,000 Da and 42,000 Da, respectively.

4. Conclusions

We may conclude that PEUF can be applied to anion removal. Since retention values were relatively low when commercial polymer PVA was used, specially synthesized functional polymers should be employed for satisfactory removal of anions from water.

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