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Comparison of low-pressure reverse osmosis filtration and polyelectrolyte-enhanced ultrafiltration for the removal of Co and Sr from nuclear plant wastewater

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ABSTRACT

Volume reduction and the concentration of long-lived radioactive species are critical issues for the management of liquid low-level radioactive waste. This study investigated and compared the performances of low-pressure reverse osmosis (LPRO) and polyelectrolyte-enhanced ultrafiltration (PEUF) for the removal of target metals (Co and Sr) from simulated low-level radioactive waste. The effects of dosage and types of chelating polymers, such as polyacrylic acid (PAA) and polyethylenimine (PEI), were evaluated at acidic and neutral pH levels. The metal removal efficiencies by precipitation at acidic pH (4.5) and neutral pH (6.5) were marginal. The addition of PAA to LPRO had no effect on metal removal, but had a negative impact on membrane permeability, particularly at acidic pH levels. The LPRO itself already achieved sufficient metal rejection; therefore, the addition of PAA only caused fouling. In contrast, the PAA dosage and solution pH governed the metal rejection in PEUF. Deprotonated PAA molecules bound to metal ions, but the distribution of PAA species had no significant impact on flux decline. The PEUF with PEI exhibited almost no pH dependency in metal removal, but showed metal-specific removal behaviors. The PEUF with PAA achieved metal removal as high as LPRO, with relatively high water permeability.

1. Introduction

Large volumes of nuclear power plant wastewater containing long-lived, low-level radionuclides, such as ^{60}Co (l5.27 year half-life), ^{90}Sr (30.2 year half-life), and ^{137}Cs (28.8 year half-life), are generated from laundry and floor washing processes and should be concentrated before final disposal [1,2]. Such radionuclides are also of great concern in drinking water after a nuclear power plant accident (e.g., the Fukushima disaster) occurs and thereby contaminates the environment [3]. Membrane processes have been considered for volume reduction before immobilization of long-lived radionuclides present in liquid low-level radioactive waste on a solid matrix [4–7]. The membrane acts as a reliable barrier against radioactive species [8] and has a relatively simple scheme for the concentration and separation of radionuclides from low-level radioactive waste. The membrane process produces retentate (concentrate of radionuclides) and permeate (purified effluent). Dense reverse osmosis (RO) membranes provide sufficient removal of radionuclides from low-level radioactive waste [4,9–12], but have no selectivity in salt rejection and consume high levels of energy. Although nanofiltration (NF) membranes were less popular in desalination, they are selective for the removal of radionuclides (e.g., Co species) from simulated nuclear wastewater, but the removal efficiency deteriorated when a complexing agent (e.g., boric acid) was present in the wastewater [13]. Co and Sr removal by NF was enhanced in the presence of dissolved CO_2, due to the formation of $CoCO_3(s)$ or $SrCO_3(s)$ precipitates [13,14]. The precipitates of sparingly soluble metal species, such as the hydroxides of Fe^{3+}, Ca^{2+}, and Mg^{2+} ions, caused fouling during NF of simulated low-level radioactive waste [15]. A previous study investigated the rejection of naturally occurring radioactive species (e.g., Ra^{2+} and UO_2^{2+}) by NF; the rejection of radioactivity was high and stable over a wide range of total dissolved solids levels (1000–5000 mg/L) in the presence of various background ions (e.g., Na^+, Cu^{2+}), which was almost comparable to that of RO [8]. However, the permeation of monovalent ions (e.g., Na^+) was highly dependent on the solution matrix due to the Donnan exclusion. It was revealed that solution chemistries played an important role in low-level radioactive waste treatment by NF membranes.

Hybrid membrane processes comprising porous microfiltration (MF) or ultrafiltration (UF) membranes with chemical additives

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(e.g., adsorbents, coagulants, and complexing agents) have been developed as alternatives to the dense membrane treatment of low-level radioactive waste [4,6,16]. Various adsorbents, such as goethite [17], hexacyanoferrate [18], ferrihydrite [19,20], and crystalline silicotitanate [19,20], were added to MF membrane systems for nuclear wastewater treatment. The membrane adsorber, which has a continuous adsorbent injection system to a submerged hollow fiber MF membrane reactor, could remove target metal ions (e.g., Co^{2+}, Sr^{2+}, Cs^{+}) effectively from low-level radioactive waste at relatively high membrane fluxes (>500 L/m^2-h-bar) compared to those of NF and RO membranes [17,19,20]. In particular, the addition of two adsorbents into the membrane adsorber enabled simultaneous target metal removal and membrane fouling control because one adsorbent sorbed metals and the other prevented fouling [19]. The recovery and regeneration of spent sorbents is quite challenging but would make the process more feasible [21,22]. A combined flocculation-MF process was attempted and found to be effective in removing ^{241}Am (>99.9%) present in low-level radioactive waste [23], but there have been no further reports on this hybrid process.

Dosing polymeric complexing agents to UF systems demonstrated significant removal of metal ions from drinking water as well as wastewater. The target metals formed complexes with polymers, which were rejected by the UF membrane [24–28]. The major complexing polymers used for polyelectrolyte-enhanced ultrafiltration (PEUF) are polyacrylic acid (PAA) [24,29], polyethylenimine (PEI) [25,28], chitosan [27,28], and polystyrenesulfonate [30]. The same approaches were attractive for the management of nuclear plant wastewater with greater selectivities [14,31]. Addition of polyelectrolytes to NF also helped to improve the removal of Co and Sr ions from simulated low-level radioactive waste [14]. Elevating solution pH levels increased the metal removal efficiency due to greater metal precipitation and complexing capability, but not in the case of hexavalent Cr removal with PEI [28]. Although there have been a number of previous studies on PEUF for low-level radioactive waste, its performance still needs to be evaluated when different types of polymers are injected. In addition, it would be interesting to determine how effective the PEUF is compared to dense membrane processes (e.g., RO).

Therefore, the purpose of this study was to investigate the removal of target metals (e.g., Co and Sr ions) from simulated nuclear plant laundry wastewater by PEUF and low-pressure RO (LPRO), and to compare their performances in terms of metal removal and membrane permeability. Various combinations of UF membranes (with different pore sizes) and chelating polymers (PAA and PEI with different molecular sizes) were prepared and evaluated. Two pH levels (4.5 and 6.5), at which chemical precipitation is negligible, were examined. These values were of interest for their effects on the polymer surface charges.

2. Materials and methods

2.1. Chemicals and membranes

Simulated wastewater containing target metal species, Sr^{2+} and Co^{2+}, was prepared using $Sr(NO_3)_2$ and $Co(NO_3)_2$ salts with >99.99% purity (Sigma–Aldrich, USA). Polyoxyethylene (20) sorbitan monooleate (Tween 80) was used as a non-ionic surfactant. The composition of the wastewater used is summarized in Table S1.

The complexing polymers used as chelating agents, PAA and PEI, were purchased from Sigma Aldrich (USA). PAA molecules with three different molecular weights of 15, 100, and 250 kDa, and PEI with an average molecular weight of 750 kDa were used. The chemical structures of PAA and PEI are given in Fig. S1.

LPRO membranes (RE1812-80), provided by Woongjin Chemical Co. Ltd., were made from polyamide and had a minimum salt rejection of 96%. Further information on the LPRO membrane is given in Table S2. The UF membranes (Millipore, USA) were made of regenerated cellulose and had molecular weight cut-offs of 1, 10, and 100 kDa. The surfaces of both the RO and UF membranes were negatively charged, as reported elsewhere [32,33].

2.2. Membrane system operation

A stirred cell membrane unit (Model 8200, Millipore, USA) with a working volume of 150 mL was used and agitated with a magnetic stirrer at a stirring speed of 150 rpm during membrane filtration (Fig. S2). Filtration experiments were performed at room temperature and predetermined transmembrane pressures (TMPs), depending on the membrane type (see Table 1). All experimental runs were conducted after equilibrating the metal-polyelectrolyte reactions for 15 min after mixing. The permeate flux was determined based on the measurement of the permeate mass over time, using an electronic balance (Sartorius, Germany). Permeate samples were collected separately every 20 mL during each experimental run.

The experiments were carried out at acidic and neutral pH levels (4.5 and 6.5, respectively). Polyelectrolyte dosages (in terms of the molar ratio of functional groups of polyelectrolytes to metal ions) varied from 0 to 200 (i.e., the PAA and PEI doses correspond to the range 0–0.409 g/L and 0–0.244 g/L, respectively). The apparent metal rejection was calculated as follows:

$$\text{Rejection } (\%) = \left(1 - \frac{C_{i,p}}{C_{i,f}}\right) \times 100 \qquad (1)$$

where $C_{i,p}$ is the concentration of target metal ions in the permeate and $C_{i,f}$ is the concentration of target metal ions in the feed.

2.3. Analytical methods

The concentrations of Co and Sr in the feed, retentate, and permeate were measured using an inductively coupled plasma spectrophotometer (Jobin-Yvon 38 plus, UK). A total organic carbon analyzer equipped with a conductivity detector (Sievers 820, GE, USA) was used to quantify the concentration of polyelectrolytes. The solution pH values were measured using a pH meter after calibrating the instrument with three buffer solutions. During all analyses, multiple sample measurements (at least two) were performed to ensure accuracy and precision. The standard deviations of Co and Sr rejection rates were less than 8%.

3. Results and discussion

3.1. pH dependence of Co and Sr removal

To begin with, the removal of all Co and Sr species within the pH range of 4–10 was evaluated using the feed solution

Table 1
Polyelectrolytes added to membrane systems and transmembrane pressure.

Membrane			Polyelectrolyte		Transmembrane pressure, bar
Type	Molecular weight cut-off, kDa	Specific water permeability, L/m^2-h-bar	Type	Molecular weight, kDa	
RO	–	6.52 ± 0.71	PAA	15	3.0
UF	1	5.17 ± 0.57	PAA	15	3.0
UF	10	26.1 ± 0.27	PAA	100	0.75
UF	100	358 ± 44	PAA	250	0.5
UF	100	710 ± 130	PEI	750	0.5

–: Not available.