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The effects of organic fouling on the removal of radionuclides by reverse osmosis membranes

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ABSTRACT

The removals of cesium (Cs) and strontium (Sr), two hazardous and abundant radionuclides in aquatic environment, were assessed with their isotopes in a synthetic water containing Suwannee River natural organic matter (SRNOM), a natural surface water (SW) and a wastewater effluent (WW) by two different types of ultra-low pressure RO membranes (M1 and M2). The rejections of Sr by the membranes M1 and M2 were higher than 97.5% and 96.0%, respectively, and the rejections of Cs exceeded 90.0% and 85.0%, respectively, in the filtration of real water. The membrane M1 exhibited a more significant flux decline in the filtration of the SRNOM solution, while more severe flux declines were observed with the membrane M2 in the filtration of SW and WW. Protein-like materials with relatively high molecular weight were the main contributors to the flux decline, and humic-acid-like compounds had little effect on the flux decline. Donnan exclusion and size exclusion by humic-acid-like compounds improved the rejections by the membrane M2 with weaker hydrophilicity, while the cake-enhanced concentration polarization reduced the rejections of Cs and Sr by the membrane M1 with stronger hydrophilicity. The ionic strength in the real water resulted in the mitigation of membrane fouling. This study provided important insights into foulant characterization and the mechanisms of organic-fouling-enhanced rejections of Cr and Sr by ultra-low pressure RO membranes.

1. Introduction

In recent years, large amounts of radioactive wastewater have been released into the aquatic environment as reported in Greece, Spain, America, Japan and China (Fu et al., 2014; Katsoyiannis et al., 2007; Kozai et al., 2013; Lytle et al., 2014; Palomo et al., 2010) due to increasing nuclear industrial activities (García et al., 2015). ^{137}Cs and ^{90}Sr are the most hazardous and abundant radionuclides due to their long half-lives (30 and 29 years), which pose long-term threats to human health and environmental security (Sylvester et al., 2013). Conventional treatment methods such as chemical oxidation, coagulation-flocculation, and filtration are used in both drinking water and wastewater treatment plants. However, the rejection of Cs, Sr, gross alpha and gross beta activities is lower than 20% by these treatment processes (Baeza et al., 2012; Gäfvert et al., 2002; Palomo et al., 2010). To improve the removal efficiency of radioactive contaminants from the aquatic environment, new techniques must be developed and optimized.

The removal of radionuclides by membrane technology has drawn great attention in recent studies (Khedr, 2013; Montaña et al., 2013; Rana et al., 2013; Zakrzewska-Trznadel, 2013). Reverse osmosis (RO), a pressure-driven membrane filtration technology, has demonstrated high removal efficiency for anions, cations, heavy metals and organic pollutants (Lau et al., 2015). Nieto et al. (2013) reported that gross alpha activity and gross beta activity decreased by 90% and 35%, respectively, after RO membrane filtration in the L'Ampolla drinking water treatment plant (Tarragona, Spain). Generally, non-radioactive isotopes were used as surrogates for radionuclides in many researches, due to their similar chemical characteristics as radioactive isotopes (Ding et al., 2013; Karamanis and Assimakopoulos, 2007; Park et al., 2013). In the past few years, removal of radionuclides from wastewater was mostly achieved by RO membranes under high operating pressures (>1.4 MPa), which yielded high rejections of Cs and Sr (Sasaki et al.,

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2013). However, new generation, ultra-low pressure reverse osmosis (ULPRO) membranes normally have high permeate flux and low operating pressure (0.2–0.9 MPa); the flux approximately doubles those of conventional RO membranes. These ULPRO membranes have been shown to be energy efficient and are efficient in rejecting solutes as compared to the conventional RO membranes (Garcia et al., 2013; Ozaki and Li, 2002). Due to the advantages of ULPRO membrane in radioactive wastewater treatment, it was practically important to assess the rejection of radionuclides by ULPRO membranes at reduced treatment cost and energy consumption.

However, membrane fouling caused by various components in real water will affect the membrane rejection of radionuclides. Kryvoruchko and Kornilovich (2003) found that the rejections of ^{137}Cs and ^{90}Sr by a RO membrane were only 68% because of the occurrence of fouling during the wastewater treatment process. Organic fouling induced by natural organic matter and carboxylic acid and proteins have severe impacts on the flux decline of RO membranes (Akhondi et al., 2015; Kim and Dempsey, 2013; Zhao et al., 2010b). Some studies have claimed that hydrophilic fractions (non-humic fraction) of high molecular weight (MW) (larger than 3000 Da) dissolved organic matter (DOM) were responsible for the flux decline (Jarusutthirak and Amy, 2006; Zhao et al., 2010a; Zularisam et al., 2006). Humic substances, proteins, and polysaccharides were demonstrated to be the major organic foulants during the natural water and wastewater filtration (Chon et al., 2013; Jarusutthirak and Amy, 2006; Jeong et al., 2013). Moreover, hydrophilic protein-like substances and carbohydrates in the secondary effluents were found to be primarily responsible for the flux loss of RO membranes (Chon et al., 2013; Zhao et al., 2010a,b). Different mechanisms have been discussed in previous studies concerning the effects of organic fouling on the rejection behavior of RO membranes. On the one hand, due to the hindered back diffusion of salts through the tortuous path of the organic fouling layer on the membrane, the concentrated salts on the membrane surface increased the osmosis pressure and hence decreased the rejection (Bellona et al., 2010; Hoek and Elimelech, 2003). On the other hand, Donnan exclusion improved the salt rejection in the presence of humic acid as a result of the enhanced negative surface charge on the RO membranes (Childress and Deshmukh, 1998; Mänttäri et al., 2000; Tang et al., 2007). However, organic fouling on different RO membranes and the resulting effects on the rejection of radionuclides from real water have not been fully understood. In general, the concentrations of radionuclides in the wastewater were under the nanogram level, which was much lower than the co-existing foulants. In addition, the co-existing foulants had significant influence on the rejection. It was significant to efficient removal the trace radionuclides by RO membrane from wastewater in the condition of high concentration of co-existing solutes.

In current study, two ULPRO membranes having different roughness and hydrophilic properties were used to filter a synthetic model water containing Suwannee River natural organic matter (SRNOM), natural surface water, and municipal wastewater effluent to investigate the membrane foulant characteristics and the effects of organic fouling on radionuclide rejection. The molecular weight (MW) distribution and chemical composition of the potential membrane foulant were measured by high-performance size exclusion chromatography (HP-SEC) and fluorescence excitation-emission matrix (EEM), respectively. The membrane fouling resistance was calculated with the resistance-in-series model. The results were combined with the changes in Cs/Sr rejection to investigate the mechanisms governing the effects of organic fouling on Cs and Sr rejections.

2. Materials and methods

2.1. Feed water

Isotopes of cesium nitrate $CsNO_3$ and strontium nitrate $Sr(NO_3)_2$ were obtained from Acros and Alfa Aesar and used as the surrogates for ^{137}Cs and ^{90}Sr, respectively. All other chemicals used in the study were analytical grade and purchased from Sinopharm (Beijing, China). Milli-Q water (Millipore, USA) was used in all experiments to prepare the chemical solutions.

The natural surface water (SW) and the secondary wastewater effluent (WW) were collected from the JingMi Canal (Beijing, China) and a sewage treatment plant (Beijing, China), respectively. The water samples were filtered by 0.45 μm PVDF membranes and stored at 4 °C before use. The water quality parameters of SW and WW are shown in Table 1. Though concentrations of Sr in the real water were much higher, it did not have any effect on the results of Sr rejection, which had been proved in our previous study (Ding et al., 2015). SRNOM was purchased from the International Humic Substances Society (IHSS, St, Paul, MN, USA). Considering the DOC in the real water, 5.0 mg L^{-1} of SRNOM with and without NaCl were prepared as synthetic solutions. Both Cs and Sr were added into the real waters and synthetic water containing the SRNOM at a mass concentration of 100 μg L^{-1} to prepare the radionuclide-contaminated water. The solution pH was adjusted to 7.0 ± 0.1 by adding NaOH or HCl solution.

2.2. Membrane filtration experiments

Two different ultra-low pressure, composite polyamide RO membranes, RE1812-50 (M1, Korea) and TW30-1812-50 (M2, USA), were used in this study. The membrane properties are shown in Table 2. The roughness of the membrane M2 was higher than that of the membrane M1, while the membrane M1 possessed more negative surface charges.

The lab-scale, cross-flow membrane filtration system comprised a flat-sheet membrane cell with an effective membrane area of 140 cm^2 (Sepa CF, Osmonics, Inc., Minnetonka, MN), a high pressure pump (Hydra-Cell, Wanner Engineering, Inc., Minneapolis, MN, USA), a recirculation chiller (DTY-5A, Detianyou Technology, Inc., China) and a 20-L feed tank (Supplemental materials, Fig. S1). The permeate flow rate was monitored by measuring the cumulative weight of the permeate with a digital balance (GX-20K, A&D Instruments Ltd., Japan) connected to a PC. Both the permeate and the concentrate were circulated back to the feed reservoir to maintain a constant feed water quality during each filtration experiment.

All filtration experiments were conducted at a constant pressure of 0.6 MPa and temperature of 25 °C. A new membrane was used in

Table 1
Raw water quality characteristics of the natural surface water and the secondary wastewater effluent.

Parameter	Unit	Surface water	Waste water
pH	–	7.82	6.83
Conductivity	μS cm^{-1}	424	834
DOC	mg L^{-1}	5.00	5.93
Cs^+	μg L^{-1}	1.38	0.21
Sr^{2+}	μg L^{-1}	284.20	498.30
Na^+	mg L^{-1}	13.47	71.79
K^+	mg L^{-1}	2.40	14.38
Ca^{2+}	mg L^{-1}	40.11	62.78
Mg^{2+}	mg L^{-1}	15.30	24.18
Cl^-	mg L^{-1}	15.18	95.64
NO_3^-	mg L^{-1}	1.27	75.76
SO_4^{2-}	mg L^{-1}	44.16	70.14