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Pressure-retarded osmosis with wastewater concentrate feed: Fouling process considerations

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ABSTRACT

Pressure-retarded osmosis (PRO) has attracted worldwide attention for its potential applications in renewable osmotic energy harvesting, low energy seawater desalination, and industrial waste brine disposal. However, membrane fouling is one of the major issues limiting PRO performance with the use of a high-salinity draw solution and a low-value impaired feedwater. This study systematically investigated membrane fouling in the PRO process using a real wastewater retentate (a waste byproduct from wastewater reclamation plants) as the PRO feed. Organic fouling (e.g., by humic substances) and inorganic fouling (e.g., by calcium phosphate) were identified to be the major types of fouling, where the latter dominated the overall water-flux decline. The internal PRO membrane fouling was exacerbated by internal concentration polarization (ICP) and intermolecular interactions between the organic macromolecules and the scaling precursor ions (e.g., Ca^{2+}). A limiting flux that was independent of the initial flux (i.e., applied pressure) was observed during the PRO fouling and was explained by a novel PRO limiting flux model. A membrane with a smaller structural parameter could achieve a higher limiting flux in PRO. A simple and effective pressure-assisted osmotic backwashing protocol was developed to clean the internally fouled membrane that could restore over 92% of the water flux within a short cleaning period (15 mins). The PRO performance could also be significantly improved by decreasing the feedwater pH that mitigated alkaline scaling. Finally, performing the PRO membrane fouling test in the active-layer-facing-feed-solution (AL-FS) orientation revealed that the integral cellulose triacetate (CTA) membrane exhibited strong mechanical stability and anti-fouling tendency whereas the thin-film composite (TFC) membrane was not mechanically stable in this orientation. This study for the first time identified that an integral membrane instead of a TFC membrane is an excellent candidate for PRO operation in the AL-FS mode for fouling control.

1. Introduction

Pressure-retarded osmosis (PRO) is an osmotically driven membrane process that can be used for extracting the renewable osmotic energy from salinity gradients. It has received significant attention in the recent decade especially after the operation of the first pilot osmotic power plant in Norway that aimed to extract the osmotic energy via contacting seawater and river water across a membrane [1–4]. This pilot plant was closed after nearly 5 years of operation due to a relatively low power density and questionable economic feasibility. However, several other attempts have been made to use PRO for extracting the osmotic energy from other resources with a higher salinity gradient [5–7]. Thermodynamic analysis suggests that the use of high salinity brines could significantly increase the extractable energy and make PRO viable [5,8]. Seawater reverse osmosis (SWRO) desalination brine, which has a concentration two to four times that of seawater [9], has attracted particular interest due to its greater osmotic energy potential [5,7]. Recently a hybrid PRO and RO process was developed by using the SWRO brine as the draw solution and impaired water as the feed solution for PRO [10,11]. Some locations are uniquely suitable for using this hybrid process, such as Singapore where the SWRO desalination plant and wastewater reclamation plant could be collocated [11]. The hybrid PRO-RO process has promising potential to reduce the energy consumption of SWRO desalination by using the harvested osmotic energy [5,11–13] as well as to minimize the negative environmental impact of desalination via osmotic dilution of the brine [11–13]. Owing

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to these benefits, interest in PRO has increased markedly in both the renewable energy and desalination industries.

One of the particular obstacles for applying the PRO-RO hybrid process is PRO membrane fouling, since low-value water is typically used as the feedwater (FW) for PRO [5,14]. For example, it was reported that the power density of a PRO membrane, which was as high as 27 W/m^2 for using deionized water (DI) as the feed, dropped to 4.6 W/m^2 due to severe membrane fouling when real wastewater was used as the feed [15]. Moreover, mitigation of PRO membrane fouling is very challenging, since the membrane typically is operated with its support layer facing the FW whereby severe fouling can occur inside the unstirred support layer [14,15]. To improve PRO performance in practical applications, it is essential to develop effective fouling-control strategies. An important prerequisite is to develop an in-depth understanding of the nature of PRO membrane fouling.

Recently a number of studies have been dedicated to investigating the fouling mechanisms in PRO by studying various types of foulants, such as macromolecular organic compounds [16–18], inorganic minerals [19,20], colloidal particles [21] and microorganisms [22]. However, these studies were limited to a single type of fouling that is not representative of the mixed fouling that occurs with wastewater for which the fouling mechanisms are more complicated. Several studies have used real wastewater or synthetic wastewater for PRO fouling tests [15,23–25]. However, these studies mainly focused on the evaluation of the PRO membrane performance under various test conditions and cleaning methods. There is a lack of an in-depth analysis of the mechanisms involved in a mixed fouling system using wastewater as the feed. For example, prior studies have mainly discussed an individual type of fouling on the PRO performance but have overlooked the interactions between different foulant species and their synergistic effects on fouling [24,25]. In a mixed fouling system the intermolecular interactions between different foulant species can significantly change the fouling behaviour [26–28]. There is also a lack of elaboration on the intrinsic relationships among membrane properties, foulant characteristics and flux behaviour during the fouling process, an understanding of which could be of great help for the design of a new generation of anti-fouling membranes. While most previous PRO tests were performed in the active-layer-facing-draw-solution (AL-DS) orientation due to greater membrane mechanical stability under high pressures in this orientation [15–28], few attempts have been made to operate PRO in the alternative active-layer-facing-feed-solution (AL-FS) orientation to control the membrane fouling due to very weak membrane mechanical stability in this orientation under actual PRO operation (i.e., high hydraulic pressure is applied on the draw solution) [16,29]. There is also a need to evaluate the capability of different types of membranes operated in the AL-FS orientation under actual PRO operation for fouling control. This will help to identify an appropriate type of membrane with a suitable membrane orientation under PRO operation for fouling control.

The focus of this study was to gain an enhanced understanding of the cause and effect of PRO membrane fouling and to develop effective approaches to mitigate fouling when a typical wastewater is used as the FW in PRO for osmotic energy harvesting from SWRO brine. Commercial cellulose triacetate (CTA) membranes and thin-film composite (TFC) membranes were used in the PRO fouling tests. The FW characteristics were analyzed and the fouled membranes were autopsied to identify the fouling types and to investigate the fouling mechanisms. Several fouling-control methods based on the membrane cleaning, FW modification, and optimization of the operation mode were developed and evaluated. The implication for new antifouling PRO membrane design was discussed.

2. Materials and methods

2.1. Impaired water, draw solution and membranes

A wastewater reclamation retentate (WWRR), collected from a local wastewater reclamation plant, was used as FW for PRO. This WWRR comes from municipal wastewater effluent processed by microfiltration (MF) followed by RO with about 75% recovery. Typically, WWRR has a salt and organic concentration that is four times that of the microfiltered secondary effluent. A photo of the WWRR is shown in Fig. S1 in the Supporting Information. An aqueous solution of 1 M NaCl was used as the draw solution to represent a seawater desalination brine. Membranes used in the PRO fouling tests were flat-sheet cellulose triacetate (CTA) and thin-film composite (TFC) osmotic membranes provided by Hydration Technology Innovations (HTI). These two membranes have been extensively used in prior studies on FO and PRO [16,22,30–35] and are still commercially available from Fluid Technology Solutions, Inc (FTSH_2O). The CTA membrane is an integral membrane formed through a one-step phase-inversion method. It is comprised of a thin and dense active layer and a porous support layer with an imbedded polyester woven mesh. The TFC membrane is chemically and structurally different from the CTA membrane. Its polysulfone (PS) support layer is formed through phase inversion, while its polyamide (PA) active layer is formed on the top of the PS support layer through interfacial polymerization.

2.2. Bench-scale PRO membrane fouling test and fouling control strategies

The PRO setup used in this study was identical to the one used in previous studies of the authors [16,33]. The membrane test cell was comprised of two symmetric Delrin half-cells with an effective filtration area of approximately 34 cm^2 (85 mm length × 39 mm width). The draw solution flow channel was filled with a diamond net-type spacer, while the feed flow channel used 5 layers of tricot type spacers (i.e., a type of RO permeate carrier). The tricot spacer with small openings has been shown to support the membrane well against deformation under the applied pressure from the draw side [33].

Unless otherwise specified, the membranes were placed in the membrane cell with their active layer facing the draw solution (AL-DS) for all the PRO tests. The feed solution and draw solution were recirculated on both sides of the membrane with approximate cross-flow velocities of 10.3 cm/s and 11.1 cm/s, respectively. The effective hydraulic pressure applied on the draw side was varied from 0 to 10 bar over which range the membrane was mechanically stable [33]. Before each fouling test, a baseline test using a 25 mM NaCl feed solution was performed to evaluate the clean membrane performance. After the baseline test, the feed solution was replaced with the WWRR to perform the fouling test. During the entire test period, the draw solution concentration was maintained constant by injecting a more concentrated NaCl solution based on conductivity measurement, while the FW volume of 5 L (and thus the foulant concentration) was maintained constant by injecting DI water based on weight measurement. Note that the relatively large volume of FW used in this study was to ensure that the change of foulant concentration in the FW before and after the fouling test was negligible. The temperature was maintained at 25 ± 0.5 °C. All the fouling tests were performed for 4 h over which period the membrane reached a stable water flux.

After some of the fouling tests, a pressure-assisted osmotic backwashing (PAOB) protocol was developed to clean the fouled membrane. During the PAOB, the WWRR feedwater was directed to the draw solution flow channel where a hydraulic pressure was applied, while the draw solution was directed to the feed flow channel where there was no applied hydraulic pressure. The PAOB was performed for 15 mins. Then, the PRO performance of the cleaned membrane was tested with a 25 mM NaCl feed solution to evaluate the cleaning efficiency. In some of the fouling tests, the water chemistry of the WWRR was adjusted