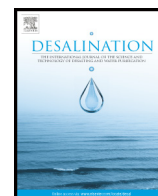




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Concentration polarization effect and preferable membrane configuration at pressure-retarded osmosis operation

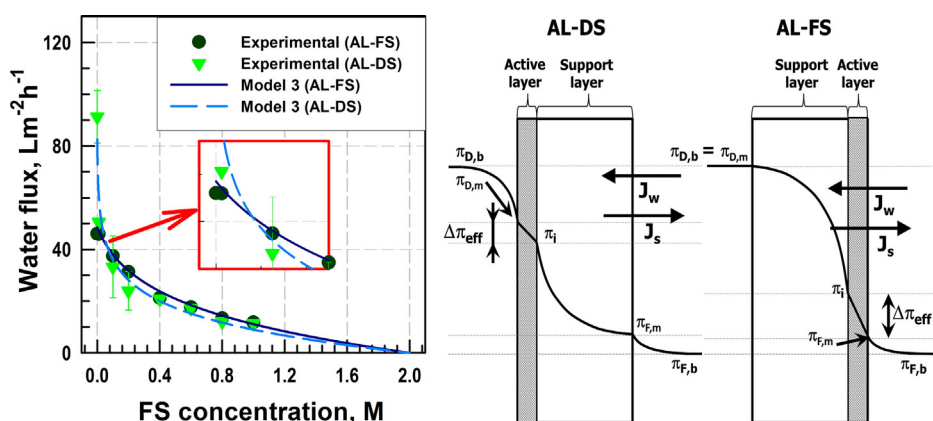
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HIGHLIGHTS

- Concentration polarization of various membranes was studied in FO and PRO modes.
- Experimental and theoretical data showed severe concentrative ECP in AL-DS mode.
- More concentrative ECP was observed at high FS conc. And high initial water flux.
- AL-FS showed superior performance and easy cleaning than AL-DS at high FS conc.
- With high FS concentration and high initial water flux, AL-FS is suggested for PRO.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of concentration polarization on performances of integrally asymmetric and thin film composite forward osmosis (FO) membranes was systematically investigated in two membrane configurations – active layer facing feed solution (AL-FS) and active layer facing draw solution (AL-DS). Water fluxes of the membranes using pure water as FS in AL-DS were 1.7 to 2.6 times higher than those in AL-FS. However, with increasing FS concentration, the water flux in AL-DS declined rapidly and became lower than that in AL-FS. A modeling study showed that the reversal of water flux in the two configurations were resulted from concentrative ECP, and theoretical FS concentrations at which water fluxes in both configurations were equal were inversely proportional to the initial water flux of the membranes. The turnover of the water flux in AL-DS and AL-FS was also observed within 8 h when seawater and river water were used as DS and FS, respectively. Moreover, the AL-DS faced the challenge of high fouling propensity and difficulty in cleaning more than the AL-FS. This study suggests that AL-FS membrane configuration is proper for both PRO and FO processes employing real natural water in terms of high membrane performance and ease of cleaning.

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1. Introduction

Osmotic processes such as forward osmosis (FO) and pressure-retarded osmosis (PRO) are significant for their economic benefits in

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wastewater treatment, desalination, power generation, and so on. FO process does not require external hydraulic pressure to desalinate, because driving force is the naturally-occurring osmotic pressure difference between a high concentration of draw solution (DS) and a low concentration of feed solution (FS) separated by a permeable membrane, resulting in water flow through the membrane from FS to DS. PRO process utilizes osmotic pressure against hydraulic pressure to pressurize the brine solution, turn the hydro-turbine, and generate electricity (Fig. 1 [1]).

Even though the concept of osmosis has been exploited since the early days of mankind, e.g. people desiccated food in salt, or dehydrated and inactivated bacteria and fungi in saline environment, studies on osmotic pressures have recently attracted much attention. Osmotic pressure was termed by Jacobus Henricus Van't Hoff in 1886 when he described a phenomenon of water entry into a permeable vessel full of sugar solution and the subsequent pressure build-up on the permeable wall of the vessel [2], and the term PRO was proposed by S. Loeb and R. S. Norman in 1975 [3]. At 2009, the first osmotic power plant producing 2 to 4 kW of power was constructed and operated by Norwegian power company, Statkraft. PRO has been considered and reviewed as a sustainable power generation process [4]. The major challenge limiting wide application of FO and PRO is the concentration polarization (CP) during the operation. An investigation of CP effect conducted at an early stage of PRO study revealed that internal concentration polarization (ICP) caused more than 80% water flux cut off [5]. Later studies have clarified the definitions of CP and proposed formulas for calculating the modulus of concentration polarization in asymmetric FO and PRO membranes. Concentration/dilution of solution in the boundary layer on outer surface of the membranes or in the porous support layer of the membranes results in concentrative/dilutive external concentration polarization (ECP) or concentrative/dilutive ICP [6]. Recent modeling study showed that the reduction of water flux by ICP reached 99.9% [7], and a theoretical study on zero-ICP mono-layer graphene oxide membrane (9.4 Å of pore diameter and 10% of porosity) yielded $91.5 \text{ L cm}^{-2} \text{ day}^{-1}$ ($38,125 \text{ L m}^{-2} \text{ h}^{-1}$), which was 1.7×10^3 times more than water flux of commercial cellulose triacetate FO membrane from Hydration Technology Innovations (HTI, OR, USA) [8].

Many attempts have been conducted to eliminate CP problems in FO and PRO operation, and most of the studies focused on the fabrication of membranes with low ICP problem. Double-skin layered membranes prepared via immersion precipitation method on glass plate showed

the reduction of dilutive/concentrative ICP in the porous layer [9,10]. Thin film composite (TFC) membrane prepared on thin woven fabric (Toray Chemical Korea, Korea) [11] or on a highly porous and thin electrospun nanofiber [12] also contributed to mitigating ICP and yielding high water flux.

Studies on CP in osmotic processes showed that water flux in active layer facing feed solution (AL-FS) configuration was lower than that in active layer facing draw solution (AL-DS) configuration [13]. Therefore, AL-DS operation was suggested for the PRO operation, in which more water flux is preferred. However, the AL-DS configuration caused more fouling propensity than AL-FS configuration because foulants in FS could be easily trapped inside porous layer of an asymmetric membrane and is not easily removed. Even though osmotic processes showed low fouling propensity compared with pressure-driven processes such as reverse osmosis, nanofiltration, ultrafiltration, and microfiltration, the fouling caused by pore clogging inside of membrane is still a challenge to membrane scientists. Therefore, most wastewater treatment using FO process has been suggested AL-FS configuration.

In this study, the effect of CP was systematically investigated to reveal whether the AL-DS configuration is always preferable for PRO operation. Several integrally asymmetric and TFC membranes were tested in both AL-FS and AL-DS configurations. Theoretical water fluxes were calculated based on a model adopting both ICP and ECP. Furthermore, the effects of CP on the application of PRO using real river water and real seawater as FS and DS, respectively, or in desalination using real seawater as FS were systematically studied. Cleaning efficiency of the membranes was investigated to support the suggestion of proper membrane configuration for osmotic processes.

2. Materials and methods

2.1. Membranes

Three commercially available membranes were purchased from Hydration Technology Innovations (OR, USA). Those were a CTA-based membrane embedded with polyester woven support (denoted as HTI1, 62 μm support thickness, 90 μm membrane thickness, and 390 μm structural parameter [11]), a CTA-based membrane cast on non-woven polyester fabric support (denoted as HTI2, 154 μm support thickness, 163 μm membrane thickness, and 968 μm structural parameter [11]), and a polyamide TFC membrane (denoted as HTI3, 68 μm support thickness, 113 μm membrane thickness, and 730 μm structural parameter [11]). Two polyamide TFC membranes supplied from Toray Chemical Korea (South Korea) were prepared on a polyester nonwoven fabric support (denoted as TCK-N, 34 μm support thickness, 59 μm membrane thickness, and 461 μm structural parameter [11]) or on a polyester woven fabric support (denoted as TCK-W, 60 μm support thickness, 80 μm membrane thickness, and 266 μm structural parameter [11]). The properties of these membranes have been thoroughly characterized and reported in previous studies [11,14]. Cross-sectional structures of these membranes are displayed in Fig. 2, and structures of the supporting layers are displayed in Fig. 3 (reprinted from [11]).

2.2. Chemicals

For most experiments of membrane performance, sodium chloride (NaCl, 99% purity, Bioshop, Canada), potassium bromide (KBr, 99.0%–100.2% purity, Junsei, Japan), or seawater were used as DS while sodium chloride, milli-Q water, seawater, or river water were used as FS. Milli-Q water was produced with 18.2 M Ω resistivity by a purification system (Millipore®, Merck Millipore, Germany). River water samples were collected from Nakdong river (Busan, Korea), Suyeong river (Busan, South Korea), and Taehwa river (Ulsan, South Korea). Seawaters were collected from Ilsan beach and Jeong-ja beach (Ulsan, South Korea). River and seawater samples were filtered by using GF/C™ glass microfiber filters (Whatman™ grade 1.2 μm , GE Healthcare Bio-Sciences, PA, USA). For

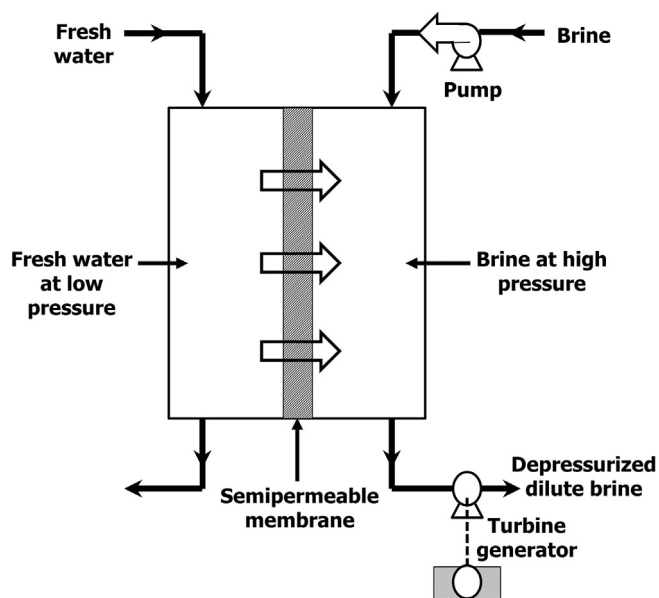


Fig. 1. Conceptual representation of an energy production scheme based on pressure-retarded osmosis (PRO) (adapted from [1]).

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