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# Evaluation of apparent membrane performance parameters in pressure retarded osmosis processes under varying draw pressures and with draw solutions containing organics

Jungwon Kim, Bongchul Kim, David Inhyuk Kim, Seungkwan Hong\*

School of Civil, Environmental & Architectural Engineering, Korea University, 1-5 Ga, Anam-Dong, Seongbuk-Gu, Seoul 136-713, Republic of Korea

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## ABSTRACT

The performance of pressure retarded osmosis (PRO) membrane, characterized by water and solute permeability ( $A$  and  $B$ ) and the structural parameter ( $S$ ), was analyzed by a new method designed to simulate the PRO process more closely. Compared to conventional approaches to membrane characterization using reverse osmosis (RO)/forward osmosis (FO), the newly developed method using a single PRO experiment better predicted PRO process performance, particularly when high pressure was applied on the draw side. It was clearly demonstrated that apparent  $B$  value increased with increasing draw pressure. This characterization method was also used to evaluate PRO membrane performance in the presence of organic matter, such as alginate or xanthan, in draw solutions. Organic matter in draw solutions reduced the apparent  $B$  value, which could result in less draw solute loss in PRO processes. Our experimental observations clearly suggested that PRO membrane processes should be analyzed and predicted by methods like the one presented which simulate actual PRO operating conditions, particularly the hydraulic pressure applied to draw solutions.

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## 1. Introduction

Pressure retarded osmosis (PRO) is a promising technology for sustainable power generation from salinity-gradient energy, which can be obtained by mixing ocean water with surface water [1,2]. This technology converts osmotic energy into hydraulic energy by driving a hydro-turbine with the pressurized water which permeates through a PRO membrane due to an osmotic gradient. In recent years, the viability of PRO membrane processes have been extensively investigated, particularly the development of osmotic membranes which can produce higher power densities with PRO processes. These efforts included not only membrane fabrication [3–6] but also membrane module development [7–9].

Osmotic membrane performance is usually described by three intrinsic membrane parameters: water permeability coefficient ( $A$ ), solute permeability coefficient ( $B$ ), and structure parameter ( $S$ ). The value of  $A$ ,  $B$ , and  $S$  contains information on the performance of membranes and can provide it regardless of operating conditions. Therefore, accurate characterization of the membrane properties is critical to the prediction of PRO performance under given operation conditions. It is difficult to evaluate the  $A$ ,  $B$ , and  $S$

because even slight variations in operating conditions can have an impact on their performance. For that reason, a standard testing protocol has been proposed for osmotically-driven membrane processes and tested by seven independent laboratories [10].

The standard method used in previous studies measuring the  $A$ ,  $B$ , and  $S$  parameters of PRO membranes involves undertaking two independent experiments, reverse osmosis (RO) and forward osmosis (FO) [10–12]. In this approach, the mass transport parameters of the active layer ( $A$  and  $B$ ) are determined by a RO experiment in which hydraulic pressure is applied to the feed solution while the structural parameter of the PRO membrane support layer ( $S$ ) is determined by a FO experiment using osmotic driving force.

However, there are many studies to show that the experimental results are different from the modeled data when using membrane parameters determined by the conventional method [6,13–18]. Based on this observation, most researchers came to the common conclusion that characterization conditions should reflect as closely as possible the actual operating conditions. A recent study delineated a new approach for evaluating FO membrane characteristics which uses an FO experiment only, and thus reflects the FO process more closely [18].

Currently existing methods of determining  $A$ ,  $B$  and  $S$  cannot simultaneously reflect the two driving forces of the PRO process: hydraulic pressure and osmotic pressure. Furthermore, it has been

\* Corresponding author. Fax: +82 2 928 7656.

E-mail address: [skhong21@korea.ac.kr](mailto:skhong21@korea.ac.kr) (S. Hong).

reported that hydraulic pressure could affect not only the physical deformation of membranes [3,19], but also the ion transport through them [20]. Therefore, to assess PRO membranes correctly, characterizing their performance under conditions closely simulating the PRO process is essential. Thus, we propose an approach for evaluating PRO membranes using the PRO process only.

The performance of PRO membrane process can be greatly affected by not only physical operating conditions such as pressure applied to draw solution but also draw solution chemistry. For instance, organic matters in the draw solution are often encountered in the open loop PRO applications which extract salinity-gradient energy from the mixture of high salinity solution (e.g., seawater) and low salinity one (e.g., wastewater). In such a PRO process, the wastewater flows through the porous support layer before permeating the active layer. It was known that organic species in the feed water easily deposit within the porous support layer and worsen the transport of water through the membrane [21–26], while organics in the draw solutions do not cause severe fouling even at high hydraulic pressure because of permeate water flow opposing the accumulation of organics as demonstrated in the recent publications [23,27,28]. Thus, much less intensive pre-treatment processes are normally designed for the seawater draw solution, resulting in more organics present in the draw solution. However, their impact on PRO membrane performance, other than organic fouling, has not been investigated thoroughly in the current literature.

In this study, PRO membrane performance parameters were systematically investigated and determined under varied physical (hydraulic pressure) and chemical (draw solution containing organics) conditions. First the PRO membrane parameters  $A$ ,  $B$  and  $S$  were measured by the RO/FO method typically employed in the current literature. Then those measurements were compared with those determined by the single PRO method introduced in this study. Through this comparison, the effect of applying pressure to a draw solution was profoundly delineated, particularly that on the solute transport parameter ( $B$ ). Next, the newly developed PRO method was used to analyze the transport of water and solute in the presence of organic matter in draw solution. This work aimed to provide a useful tool for the more accurate prediction of water flux and solute flux in PRO processes using various saline water sources.

## 2. Materials and methods

### 2.1. PRO membrane

A flat-sheet osmosis membrane provided by Hydration Technology Innovation (HTI, Albany, OR) and consisting of a cellulose triacetate (CTA) active layer and a porous polyester mesh support layer was selected for this study. The membrane samples were received as flat sheets with glycerin. They were rinsed with DI water three times to remove the glycerin, and then stored in DI water at 4 °C.

### 2.2. PRO membrane testing equipment

The PRO experiments were performed with a cross-flow lab-scale system, as presented in the previous study [26]. The feed and draw channels of the PRO testing unit were symmetric and 146 mm × 95 mm × 2 mm in dimension. Permeate carrier was placed in the feed channel to support the membrane against hydraulic pressure. A gear pump (Micropump, Vancouver, WA) was used to circulate the feed solution and a high pressure pump (Hydracell, Minneapolis, MN) was used to deliver a pressurized draw solution. The cross flow velocity of both channels was fixed

at 5.6 cm/s. Permeate water flux across the membrane was automatically calculated from the weight change of the feed solution reservoir, which was continuously measured by a digital balance connected to a computer. The conductivity of feed and draw solutions were measured with a conductivity meter (Hach, Loveland, CO). The applied hydraulic pressure was monitored by digital pressure meters and controlled with a back pressure regulator at the membrane cell channel outlet.

### 2.3. Determination of PRO membrane performance parameters

#### 2.3.1. Theoretical background

The water flux ( $J_w$ ) and reverse solute flux (RSF,  $J_s$ ) in PRO membrane processes are often described by the following expressions [4,29]:

$$J_w = A \left( \frac{\pi_{D,b} \exp\left(-\frac{J_w}{kD}\right) - \pi_{F,b} \exp\left(\frac{J_w S}{D}\right)}{1 + \frac{B}{J_w} \left[ \exp\left(\frac{J_w S}{D}\right) - \exp\left(-\frac{J_w}{kD}\right) \right]} - \Delta P \right) \quad (1)$$

and

$$J_s = B \left( \frac{C_{D,b} \exp\left(-\frac{J_w}{kD}\right) - C_{F,b} \exp\left(\frac{J_w S}{D}\right)}{1 + \frac{B}{J_w} \left[ \exp\left(\frac{J_w S}{D}\right) - \exp\left(-\frac{J_w}{kD}\right) \right]} \right) \quad (2)$$

$\pi_{D,b}$  and  $\pi_{F,b}$  are the osmotic pressures of bulk draw and feed solutions which were calculated using software from OLI Systems (Morris Plains, NJ).  $D$  is the diffusion coefficient of draw solute and set to  $1.22\text{--}1.29 \times 10^{-9}$  mm<sup>2</sup>/s depending on draw concentration, 0.5–2 M [30].  $C_{D,b}$  and  $C_{F,b}$  are the concentrations of bulk draw and feed solutions, respectively.  $\Delta P$  is the applied hydraulic pressure and  $k$  is the mass transfer coefficient, which was estimated to be  $3.24 \times 10^{-5}$  m/s for rectangular cell geometry [31].

The water permeability coefficient ( $A$ ) and salt permeability coefficient ( $B$ ) characterize the PRO membrane active layer while the structure parameter ( $S$ ) characterizes the support layer. The PRO membrane characteristic parameters,  $A$ ,  $B$  and  $S$ , can be determined by solving Eqs. (1) and (2) simultaneously if all the other variables including  $J_w$ ,  $J_s$ ,  $k$ ,  $D$ ,  $\pi_{D,b}$ ,  $\pi_{F,b}$ ,  $C_{D,b}$  and  $C_{F,b}$  are known [29].

The membrane power density,  $W$ , is the product of the water flux, and the applied hydraulic pressure:

$$W = J_w \Delta P \quad (3)$$

#### 2.3.2. Determination of $A$ , $B$ , $S$ based on conventional RO/FO method

Osmosis membrane performance parameters ( $A$ ,  $B$ , and  $S$ ) have previously been determined by a series of RO and FO experiments [9,11]. In this study, a similar procedure was adopted: first, membrane coupons were compacted at a pressure of 15 bar with DI water for over 18 h until water flux stabilized. Next, the water permeability coefficient ( $A$ ) and the salt permeability coefficient ( $B$ ) were determined in RO mode at 15 bar, using DI water and 34 mM NaCl feed solutions respectively. Finally, the structure parameter ( $S$ ) was determined in FO mode by measuring water flux with a DI feed solution and 2 M NaCl draw solution without pressure.

#### 2.3.3. Determination of $A$ , $B$ , $S$ based on newly proposed PRO method

Subsequent to the RO and FO experiments, the same membrane was characterized by the newly proposed method which was modified from the single FO method [29] in order to adapt to PRO performance. The PRO experiments were carried out in four stages under different draw solution concentrations. At each stage water flux and reverse solute flux were calculated from volume and

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