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# Non-linear least-square fitting method for characterization of forward osmosis membrane

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ABSTRACT

We assess three forward osmosis (FO) performance data collection protocols, namely multiple-filtration, multi-stage and single-stage using non-linear least-square fitting method to simultaneously characterize water permeability coefficient (*A*), solute permeability coefficient (*B*) and structural parameter (*S*) of FO membranes. They differ only on the procedure to acquire water and reverse salt flux data. Both set of fluxes data were later used as inputs in non-linear least-square fitting optimization to obtain the *A*, *B* and *S* parameters. The method were evaluated using two commercial FO membranes. We employed the mass-transport models that counting for internal and external concentration polarizations in the feed and the draw sides. We also demonstrated the use of the single-stage protocol to characterize fouled FO membranes. Overall results showed that all protocols are equally effective for characterizing FO membranes, demonstrating generality of the least-square fitting method. Furthermore, the single-stage protocol can be used for characterizing fouled FO membrane in situly. As expected, fouling was more severe for the active layer facing draw solution (ALDS) than the active layer facing feed solution (ALFS) mode, as was also reflected by larger changes of their properties relative to their pristine conditions. The ability to characterize fouled membrane using the single-stage protocol could help to unravel mechanisms of fouling in FO. For instance, as demonstrated in this study, fouling in ALDS mode occurred internally by penetrating support layer.

## 1. Introduction

In forward osmosis (FO), a semi-permeable membrane separates a concentrated draw solution and a diluted feed solution. The osmotic pressure difference between both solutions drives the permeation across the membrane. A selective permeable membrane allows passage of water, but largely rejects solute molecules or ions. The FO process results in concentration of the feed and dilution of the draw streams. FO has emerged as a promising alternative for various applications because of its several key advantages. In comparison to other membrane processes, FO has lower membrane fouling propensity. When presence, the fouling is more reversible and occurs in a lesser degree [1–4]. Besides, FO process basically does not require hydraulic pressure to drive separation; pressure is required only for streams circulation [5], which enable low energy foot-print when draw solution recovery does not required. FO also offers solution for concentrating of various recalcitrant's (emerging contaminants) in wastewater that often bypass all treatment processes and thus accumulate in the water grids [6,7].

In recent years, a great deal of research has been directed at the fabrication of FO membranes, in particular to lower the membrane support structural parameters (*S*) and to select the most effective and efficient draw solute [5,8,9]. These efforts have resulted in the development of substantially improved FO membranes tailored for the specific needs. To name a few, high performance thin film composite FO membrane [10] and aquaporin-based biomimetic FO membrane [11] have been now commercialized. Because of the success in developing high performance FO membranes and emergence of FO based spin-off companies, recent focus has also expands toward optimization of membrane through module-scale analyses [12]. A convenient and consistent methodology to characterize FO membranes is of critical importance in module design and to advance this technology into its mature phase, facilitating the sharing of data, their interpretation, and comparison [13,14].

A general approach to evaluate FO membrane performance is based on its intrinsic properties: the pure water permeability coefficient, A ($Lm^{-2}h^{-1}bar^{-1}$), and the solute permeability coefficient, B ($Lm^{-2}h^{-1}$),

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which describe the transport across the membrane active layer, and S (mm), quantifying the effective-length of transport path across the membrane support layer. These three parameters are univocal and can be used with the respective governing equations to predict the water ($J_w$, $lm^{-2}h^{-1}$) and reverse salt flux ($J_s$, $gm^{-2}h^{-1}$) of a membrane sample. Therefore, the values of A, B, and S offer a universal set of criteria for characterization of FO membrane, regardless of FO operating conditions [14].

The traditional method to measure A, B, and S consists of a two-step experiment: A and B are first measured in reverse osmosis (RO) test, followed by an FO test to determine S. Some standard condition regarding this method has also been proposed [15]. This method -henceforth referred to as RO + FO method- assumes that transport parameters are universally valid and transferable (between FO and RO operation), which proven less so because of different driving force between them [13]. The water transport in RO is driven by a hydraulic pressure difference, while the mass transport in FO is driven by an osmotic pressure difference. These fundamental differences may lead to inaccuracy when evaluating *A*, *B* and *S*, when using the RO + FO method. As demonstrated by Coday et al, for some FO membrane, $J_w$ increases with increasing hydraulic pressure difference (ΔP) in an RO test, while $J_s$ substantially declines with increasing ΔP [16], which respectively leads to inflation and deflation of *A* and *B*-values. Inaccuracies of *A*- and *B*-values are thus lumped into *S*-value. In addition, subjecting FO membranes intended for operation near ambient conditions to the high pressure, typical of RO, can alter membrane structure (i.e., via compaction). The RO + FO method is also cumbersome and laborious, requiring multiple experiments in different setups.

A method to simultaneously determine membrane parameters has recently been proposed [13]. It is claimed to be simple, effective and reliable because it only works under representative driving force and operating conditions in a single but multi-stages FO protocol. Henceforth, this protocol is referred to as multi-stage. It consists of several stages of FO tests with different draw solution concentrations to obtain four pairs of water fluxes and reverse salt fluxes data. Membrane parameters are then determined through non-linear regression, where A, B and S are adjusted parameters for fitting the FO transport equations into the experimental data. The effectiveness of this method was demonstrated by the enhanced fitting of the estimated $J_w$- and $J_s$-values (estimates) to the measured values, with less than 3.5% coefficient of variation (*CV*). The multi-stage protocol enables characterization of *A*, *B* and *S*, exclusively, by means of only FO experiments.

Despite the claims of generality and the simple nature of the multi-stage protocol, it suffers from several shortcomings: (1) the effect of draw solution dilution and feed solution concentration due to $J_w$ and $J_s$ change during a batch test is disregarded and the impact would be worse for a highly performing membrane. The impact can be minimized in a system where the volumes of the feed and draw are much larger than the volume of permeating water. (2) The mass-transport equations applied in this study ignores the impact of external polarization concentrations (ECPs) on the feed side, which only applicable for the test with high cross-flow velocities and for membrane with a low *B*-value. This assumption is valid for membranes that exhibited low *A*-value or having large *S*-value relative to the external boundary layer thickness. Neglecting the ECPs lumps them into the internal concentration polarization (ICP)-term, resulting in an over-estimation of *S,* as found in [14] and *B*, or underestimation of *A*. Those two limitations can be avoided by careful design of the experiments to ensure data accuracy, as suggested elsewhere [13].

Another important aspect in FO process development is membrane fouling. This is, in particular, important by considering the critical flux behaviour-dependency of membrane fouling propensity to the applied flux- in FO process [17], a phenomenon that occurs in pressure driven process [18]. Despite the FO advantage of more resistant to fouling, reports show that fouling plays an important role in FO when treating real feed and thus need to be considered [2,3,19–24] for further FO process development, in particular for designing a FO module [25]. An accurate design of membrane module requires inputs of precise parameters (i.e., the one that account for performance reduction by fouling). Therefore, a method that counts for fouling contribution in lowering the FO productivity is required.

In this study, we assess a more general method via non-linear least-square fitting to determine *A*, *B* and *S*-parameters simultaneously. To proof generality of the method, three protocols namely multiple filtrations, multi-stage and single-stage were applied to obtain experimental data. They differ only on the protocols to gather $J_w$ and $J_s$ data. The second one was based on the protocol proposed elsewhere [13], while the rests are new. We employ the most recent and complete mass-transport model that counting for ICP in the support side and ECPs in the feed and the draw sides to improve the multi-stage method. Our general objective is to show that any method can be used to generate data for the purpose FO membrane characterization, as long as they are accurate. Later, we also demonstrate the use of single-stage method to characterize fouled FO membranes.

## 2. Materials and methods

### 2.1. Materials

Two commercial FO membranes were used in this study. (1) A commercial Aquaporin Inside™ FO membrane obtained from Aquaporin A/S, further referred to as AP-membrane. (2) The novel thin film composite FO membrane from Hydration Technology Inc, further referred to as HTI-membrane. Membrane samples were stored wet in MilliQ water (Millipore™) at 4 °C when not in use. All FO tests were done using NaCl as draw solution (Sigma Aldrich, USA), and the bovine serum albumin (BSA) solution used as the feed for fouling study (Sigma Aldrich, USA).

### 2.2. Experimental set-up and operation

We used several identical FO-set-ups with filtration chamber dimensions of length, width and depth of 8.7, 4.2 and 0.25 cm respectively, giving an effective membrane area of 36.54 $cm^2$. They were operated with counter-current cross flow without mesh spacers. Variable peristaltic pumps (LongerPump, YZ1515x,China) were used to drive the feed and draw solutions flows in closed loops at a cross flow velocity of 4.6 $cms^{-1}$. The set-up was placed in a room with a constant temperature of 24 ± 0.5 °C. The $J_w$ was determined by monitoring the rate of change in weight of the feed solution, measured using a digital weighing balance (Kern 572, Germany) at 1 min interval, and the solute concentration in the feed was measured at 1 min intervals with a conductivity meter (Orion Star A212, Thermo Scientific, USA). The $J_s$ was determined by applying mass balance of water and solute. Feed concentration and water flux data were logged once the water flux had stabilized. NaCl was chosen as draw solute, because (i) it is highly rejected by the FO membranes, (ii) it is capable generating high osmotic pressure, (iii) it largely obeys van't Hoff equation, and (v) its concentration can be quantified from conductivity data for calculating *Js*. Further elaboration on the advantages of using NaCl as draw solute can be found elsewhere [13,26]. As dictated by the nature of the mass transport equation, the current method is not applicable to measure B value of other solutes that do not obey the van't Hoff equation. Nevertheless, as long as the mass transfer models for a solutes are available, a non-linear least square method is applicable to characterise A, B and S parameters. In addition, because of the demand of the highly non-linear mass-transfer models, the provided data must be highly accurate and requiring large range of data span. As discussed later, ones are also required to limit the range of A, B and S during the optimization to obtain accurate value to compensate the high non-linearity of the transport model.