Mass transfer in forward osmosis with hollow fiber membranes

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ABSTRACT

The recent development of high performance thin film composite membrane has been a major technological thrust in the research of forward osmosis (FO). While most of the recently developed FO membranes are of flat sheet (FS) geometry, hollow fiber (HF) FO membranes have attracted significant attention in recent years due to their promising prospect in full-scale applications. Existing studies on HF FO membrane fabrication and characterization exclusively apply the mass transfer equations developed for FS membranes. Whether or not these mass transfer equations for FS membranes are applicable for membranes with HF geometry remains theoretically unclear. In this paper, accurate analytical equations are derived to describe mass transfer of water and solute across an HF membrane. These equations take into account the curvature effect of the HF membranes and thus have very different mathematical forms from those for FS membranes. A systematic comparison of the mass transfer equations between HF and FS membranes was also conducted using both simulated and experimentally measured flux data. The results from such a comparison suggest that the mass transfer equations for FS membranes are in general applicable for an HF geometry, which provides the theoretical basis for the application of the well-established FS mass transfer equations in characterizing HF membranes.

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1. Introduction

Forward osmosis (FO) is a novel membrane-based water treatment process that has garnered extensive interest in both academic research and industrial development [1–5]. In an FO process, water transports across a semi-permeable membrane as driven by the trans-membrane difference in the chemical potential of water between the concentrated draw solution and the diluted feed solution [1]. Unlike desalination processes driven by thermal or pressure gradients, such as reverse osmosis (RO) [6] or membrane distillation [7,8], water transfer in FO is spontaneous and thus requires minimal external energy input. In addition, membrane fouling in FO has been found to be highly reversible due to the absence of a very high applied hydraulic pressure [9–11]. Although thermodynamic analysis suggests that FO-assisted desalination cannot lead to direct saving of absolute energy [5,12], FO, when appropriately applied in hybrid processes, is a highly promising technology that can significantly enhance the performance of RO or thermal desalination processes [13–16]. When it comes to applications in which separation of the diluted draw solution is unnecessary, FO has the distinct advantage of being a truly low-

energy process [17,18].

A major technological breakthrough in the past decade for FO is the development of thin-film composite (TFC) FO membranes with a structure specifically tailored for highly efficient mass transfer [19–22]. A high performance TFC FO membrane is typically composed of an ultra-thin semi-permeable active layer and a relatively thin support layer that is porous and non-tortuous. The active layer is responsible for water permeation and solute rejection, whereas the support layer is for imparting necessary mechanical strength. Because the hydraulic pressure involved in an FO process is significantly lower than that in an RO process, the support layer of a TFC FO membrane can be appreciably thinner. The mass transfer of water and solutes across such a TFC FO membrane is very different from that across an RO membrane.

First of all, unlike in an RO process where there is only water but no solute in the membrane support layer, solute is typically present in the support layer of an FO membrane whether the support layer is in contact with the feed or draw solution. The development of concentration gradient, due to the convective-diffusion transport in the support layer where hydraulic mixing is absent, is defined as the internal concentration polarization (ICP) [23,24]. Being a phenomenon unique to FO, ICP significantly reduces the trans-membrane driving force for water transport [25]. Similarly, concentration gradients also develop at the boundaries between the solution and the active layer, and between the solution and the support layer, which is defined as external

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concentration polarization (ECP). The impact of ECP on driving force reduction can be significantly less than that of ICP, because it can be mitigated by promoting hydrodynamic mixing in the bulk solutions. However, in realistic systems where hydrodynamic mixing is insufficiently vigorous, ECP may also contribute significantly to driving force reduction [26,27].

Accounting for these phenomena of concentration polarizations, mass transfer models have been developed to quantify the properties of a TFC FO membrane and predict the water and solute fluxes with a membrane under given experimental conditions [28]. The general approach for model development is to couple the mass transfer of water and solute across the boundary layers, the active layer, and the membrane support layer. In the most widely used model for mass transport in TFC FO membrane, three membrane properties are involved, including the water permeability, A, and solute permeability, B, of the active layer; and the structural parameter of the support layer, S. The structural parameter quantifies the resistance to the diffusive solute transport across the support layer. In addition to these membrane properties, an additional property, called mass transfer coefficient, is needed to quantify the resistance of the boundary layer to solute transport.

The existing mass transfer models were developed for flat sheet (FS) TFC FO membranes [24,29,30]. While most existing studies on FO membrane fabrication focused primarily on FS membranes, recent research efforts have resulted in robust and high-performance hollow fiber (HF) FO membranes [31–36]. It has been suggested that HF FO membranes have advantages over FS FO membranes in large-scale FO applications because of the higher mechanical strength, more suitable flow patterns, and the higher packing density [31]. To understand the mass transfer across HF FO membranes and quantify the properties of the fabricated membranes, the mass transfer model for FS membranes has hitherto been applied [31,32]. However, the geometries of FS and HF membranes are drastically different. For example, the curvature is zero for an FS membrane but very large for an HF membrane the diameter of which is usually around or below1 mm. In addition, the trans-membrane flow field is unidirectional for FS membranes but radial for HF membranes. Therefore, whether mass transfer models for FS membranes are applicable to HF membranes remains theoretically unclear.

In this paper, mass transfer equations for an FO process with HF TFC membranes are derived. The derived mass transfer equations for HF membranes are systematically compared to the existing mass transfer equations for FS membranes. The applicability of the transport model for FS membranes in interpreting flux data collected from experiments conducted using HF membranes is assessed. Finally, the mass transfer equations for HF membranes are employed to evaluate properties of fabricated HF membranes using the flux data available in literature.

2. Derivation of mass transfer equations

2.1. Active layer inside, facing feed solution

Fig. 1A shows the cross-section of an HF membrane with the active layer at the inner surface of the HF in direct contact with the feed solution inside the HF. With such a configuration, the water permeates radially, through the active layer and the porous layer, towards the draw solution outside the HF. In contrast, the solute diffuses down the concentration gradient from the draw solution outside to the feed solution inside the HF.

The impacts of concentration polarization (CP), including both ICP and ECP, are illustrated in Fig. 1B. Following the most widely adopted methodology of CP accounting, here, only the ECP in the boundary layer between the active layer and its contacting solution is considered, but the ECP in the boundary layer outside the support layer is intentionally ignored, with the justification that the ECP outside the support layer can be insignificant compared to ICP if the hydraulic mixing is sufficiently vigorous [28]. However, there also exist certain scenarios in which the ECP on both sides are significant compared to ICP [26,27,37]. If such a support-layer-side ECP needs to be considered, it can be readily incorporated in the exact same way as the active-layer-side ECP [37]. In this study, we will adopt the simpler methodology in which ECP refers only to the active-layer-side ECP unless explicitly stated otherwise.

The ICP in the porous support layer reduces the draw solute concentration at the active layer-support layer interface to $C_{D,m}$ from its bulk concentration outside the support layer, $C_{D,b}$. On the other hand, the ECP increases the solute concentration at the active layer-feed solution interface to $C_{F,m}$ from its feed concentration in the bulk solution, $C_{F,b}$. Consequently, the osmotic pressure difference across the active layer, which is proportional to the concentration difference according to van't Hoff relation, is significantly lower than the difference between the osmotic pressures of the bulk solutions.

In the membrane support layer, the solute flux, J_s, is simply the sum of the diffusive flux, which is quantified by Fick's law, and the convective flux, which is the product of the water flux, J_w, and the
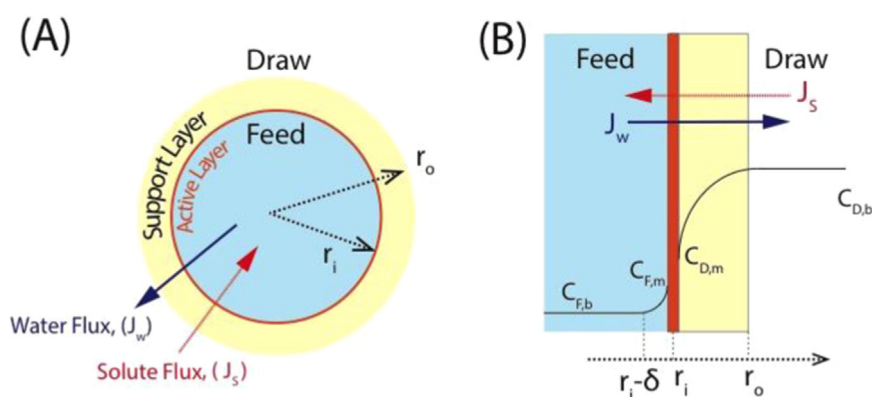
Fig. 1. (A) A schematic showing the key geometric parameters and directions of the water and solute fluxes for an HF membrane with the active layer inside facing the feed solution. (B) A schematic diagram showing the directions of water and solute flux and the solute concentration profiles across an HF membrane with its active layer facing the feed solution. In both figures, the active layer is shown in orange whereas the support layer is colored yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)