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Impact of surface porosity on water flux and structural parameter in forward osmosis

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ABSTRACT

Improving water flux is a crucial objective of research in forward osmosis (FO) technology. A structural parameter is the property of the support layer of the membrane that determines the internal concentration polarization, which is determined by the bulk porosity, tortuosity, and thickness of the support layer. Surface porosity, i.e., porosity at the interface between the active and support layers, has recently been recognized as another critical factor in determining the water flux behavior and the structural parameter. In this study, the relative importance of the surface porosity, bulk porosity, and pore geometry of the support layer on water flux behavior is investigated using a recently developed pore-scale CFD simulator. To this end, various straight-like pore geometries with different combinations of surface and bulk porosities are studied. An increase in bulk porosity reduces internal concentration polarization, thereby increasing effective osmotic pressure. However, for the same magnitude of increase, an increase in surface porosity leads to a significantly larger increase in water flux. We show that water flux is most sensitive to surface porosity, and inconsistency in the structural parameter can be resolved by introducing surface porosity into the FO modeling framework.

1. Introduction

Forward osmosis (FO) is an osmosis-driven process that separates solvent from concentrated solutions with dissolved solutes. FO has many applications such as desalination [1-5], power generation (pressure-retarded osmosis) [2, 6], waste water treatment [2, 7], osmotic membrane bioreactors [2, 8, 9], emergency relief [10, 11], and the food industry [12]. A semi-permeable FO membrane is composed of an active layer and a support layer [13]. The active layer separates water from the solute, and the support layer provides mechanical stability to the active layer [13, 14]. The support layer has a porous structure that causes resistance to mass transfer [15, 16], which leads to internal concentration polarization (ICP), thereby significantly reducing water flux [1, 3-5, 16-20]. Since the development of asymmetric semi-permeable osmotic membranes [21-24] and FO technology [25-28], many studies have attempted to mitigate ICP to increase water flux [13, 14, 17, 18, 24, 29].

To quantify the influence of the structure of the porous support layer on ICP, the concept of a structural parameter has been introduced [16, 18, 29]. The intrinsic structural parameter, S_{int}, is a metric to quantify the influence of the porous structure of the support layer on mass transfer [18, 29-32], defined as

$$S_{int} = \frac{t\tau}{\epsilon_b} \tag{1}$$

where t is the thickness of the support layer, τ is its tortuosity, and ϵ_b is the bulk porosity of the support layer. S_{int}, having the unit of length, physically implies the average travel length for diffusing solutes to reach one end of the support layer from the other end [29]. A larger S_{int} implies greater resistance to mass transfer that leads to more significant ICP, thereby reducing water flux [29]. To reduce S_{int}, a support layer with small tortuosity and thickness, and large bulk porosity has been desirable [29, 33-37].

As it is challenging to directly measure bulk porosity and tortuosity, the concept of the effective structural parameter, S_{eff}, has been introduced [18, 29-31]. S_{eff} is defined using experimentally measurable quantities such as water flux and the properties of the active layer [16, 18, 29, 38, 39]. Even though S_{int} and S_{eff} are expected to be identical, a significant inconsistency between S_{int} and S_{eff} has been reported in recent studies [30, 31]. Manickam et al. [30] showed a large discrepancy

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between S_{int} and S_{eff} for the first time: they obtained S_{int} from t, τ, and ϵ_b, which were directly measured by the advanced non-destructive imaging technique of X-ray microscopy. They showed that the empirically measured S_{eff} was one or two orders of magnitude higher than S_{int} [30]. Moreover, a few studies reported that S_{eff}, which should be a constant for a given membrane, varies as a function of draw concentration [31, 38]. In our previous work [40], the inconsistency was successfully resolved for a support layer with *straight pores* by introducing surface porosity into the FO modeling framework.

Surface porosity, a fraction of an active layer that is in direct contact with draw solution, has recently been discussed as another key parameter [16, 30, 40, 41]. Surface porosity, which can be significantly different from the bulk porosity, is the interfacial porosity at the border between the active and support layers. Manickam and McCutcheon [16] also discussed the importance of the surface porosity and claimed a need of a new model that can account for the transport phenomena across the interface. However, the effect of surface porosity on water flux has not yet been systematically studied.

In this study, we systematically investigate the relative importance of surface porosity, bulk porosity and pore geometry on FO flux behavior with a pore-scale CFD simulator for the first time. To this end, we extend the recently developed pore-scale simulator [40] to various types of straight-like pore geometries, and investigate the effects of different parameters on ICP and water flux behavior. The devised pore geometries are not only realistic but also enable to systematically study the effects of surface porosity, bulk porosity, and pore geometry on ICP and water flux. We also study the role of surface porosity for resolving the inconsistency in various straight-like pore geometries. Through this research, we show that surface porosity is the most important factor that controls water flux and also resolves structural parameter inconsistency in various types of straight-like pore geometries.

2. Theoretical background

We first review the theoretical background related to incorporating surface porosity into the FO modeling framework. Water and salt fluxes in the active layer are expressed using the standard solution-diffusion model [14, 15, 42-44]:

$$J_w = A\Delta\pi_{eff} \tag{2}$$

and

$$J_s = B\Delta C \tag{3}$$

where A and B are the water and salt permeability coefficients of the active layer, respectively, and $\Delta\pi_{eff}$ and ΔC are the differences in the effective osmotic pressure and the molar concentration of salts across the active layer, respectively. It is important to note that A and B are intrinsic properties of the active layer, independent of the support layer properties. In practice, experimentally measured A and B values can be affected by support layer. The osmotic pressure of saline solutions is obtained using the Van't Hoff equation,

$$\pi_{eff} = i\mathscr{R}TC \tag{4}$$

where i is the dissociation factor (which is set to 2 because the solute is NaCl), $\mathscr{R}$ is the gas constant, T is the system temperature at the absolute scale [K], and C is the molar concentration of solutes. Throughout this paper, the osmotic pressure is calculated using Eq. (4). Note that the non-linear trend of the osmotic pressure with respect to the concentration can arise if concentration gets close to the solubility limit [19]. Mass transfer in the porous support layer is expressed by the 1D advection-dispersion equation [13, 14]:

$$J_s = J_w C(x) - D_s \frac{dC}{dx} \tag{5}$$

where D_s is the effective diffusivity in the support layer.

By combining Eqs. (2) and (3) with Eq. (5), and integrating over the thickness of the support layer, S_{eff} is represented as follows [13, 14, 16, 18, 29]:

$$S_{eff} = \frac{D}{J_w} \ln \frac{B + A\pi_D}{B + A\pi_F + J_w} \tag{6}$$

where π_D and π_F are osmotic pressures at the draw-side and the feed-side membrane interfaces, respectively. Our previous work [40] showed that the inconsistency in the structural parameter between S_{int} (Eq. (1)) and S_{eff} (Eq. (6)) can be resolved by incorporating surface porosity into the FO modeling framework. The key hypothesis was that a fraction of the active layer in contact with the substrate surface does not contribute to mass transfer across the active layer [16, 40]. Then, Eqs. (2) and (3) must be re-written as

$$J_w = \epsilon_s A\Delta\pi_{eff} \tag{7}$$

and

$$J_s = \epsilon_s B\Delta C \tag{8}$$

where ϵ_s is the surface porosity at the interface between the active layer and the support layer [16, 40]. Note that ϵ_s can also be thought as a correction factor that incorporates the effects of the blocked region of the active layer. Then, the effective structural parameter in Eq. (6) can be redefined as

$$\widetilde{S}_{eff} = \frac{D}{J_w} \ln \frac{\epsilon_s(B + A\pi_D)}{\epsilon_s(B + A\pi_F) + J_w} \tag{9}$$

Eq. (9) was shown to resolve the inconsistency in the structural parameter for the support layer, but our previous work was limited to the straight pore geometries that surface and bulk porosities are identical as shown in Fig. 1 [40]. However, in practice, surface and bulk porosities can be different [30, 45, 46]. In this study, we systematically study the effects of surface porosity, bulk porosity, and pore geometry on ICP and water flux. We also investigate the generality of Eq. (9) in resolving the inconsistency in the structural parameter by calculating S_{eff} and $\widetilde{S}_{eff}$ for various straight-like pore geometries.

3. CFD simulation for FO at pore-scale

3.1. Conceptual model: 2D straight-like pore geometry

To investigate the relative importance of the surface porosity, bulk porosity, and pore geometry of the support layer on water flux behavior and the structural parameter, we introduce four straight-like pore geometries: trapezoidal converging, trapezoidal diverging, concave, and convex geometries as shown in Fig. 2. The domain consists of an active layer (red line), a support layer, and a crossflow channel. The blue and dark regions are flow channels and impermeable solid parts, respectively.

The particular pore geometries chosen in this study are complex enough to systematically vary surface porosity, bulk porosity, and pore geometry, but simple enough to intuitively interpret simulation results. In both theoretical and experimental FO membrane research, a support layer consisting of straight pore structures has been investigated [31, 32, 41]. For straight pores, the tortuosity is approximately one, and the surface porosity is identical to the bulk porosity. However, in general, the surface porosity can be significantly different from the bulk porosity [30, 45, 46], and the chosen four pore geometries are suitable for studying the relative importance of the surface porosity, bulk porosity, and pore geometry of the support layer on water flux behavior. The chosen pore geometries also exist in practice [34, 35, 45-47].

The comparison between trapezoidal converging and diverging geometries as shown in Fig. 2 (b) and (c), respectively, allows us to investigate the relative importance of the surface and bulk porosities on water flux. The trapezoidal converging and diverging geometries have a width of $P2 - P1$ at the interface between the active and the support layers, and a width of $P4 - P3$ at the interface between the support