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Mixed draw solutions for improved forward osmosis performance

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ABSTRACT

Reverse salt flux (RSF) of ions from the draw solution (DS) to the feed is a major drawback of forward osmosis (FO). RSF is reduced when divalent ion salts such as $MgCl_2$ and $MgSO_4$ that have larger hydrated radius are used instead of salts with monovalent ions only (e.g., NaCl). However, using divalent ion DSs comes with a cost – namely lower water flux compared to NaCl DS at similar osmotic pressures. The objective of this study was to enhance FO by lowering RSF while maintaining high water flux by adding low concentrations of divalent ions or organic ions to NaCl DS. We have demonstrated that water flux was similar for pure NaCl DS and mixed salts DS having low concentrations of divalent or organic ions at the same osmotic pressure of pure NaCl DS. Simultaneously, the average RSF was lower for all mixed salts DSs tested compared to pure NaCl DS. Results from a student *t*-test comparing the average RSF of the mixed salts DSs to the pure NaCl DS revealed that although the average RSF was lower for all the mixed DSs tested, only the mixed salts DS containing $MgCl_2$ had RSF significantly lower than the pure NaCl DS.

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1. Introduction

Osmosis or forward osmosis (FO) is a membrane separation technology that utilizes highly selective semipermeable membranes to extract water from a feed stream to a highly concentrated draw solution (DS) [1–4]. The driving force for mass transport in FO is the osmotic pressure difference between the low salinity feed and high salinity DS. The distinct advantage of FO over reverse osmosis (RO) and nanofiltration (NF) is that the system is operated at low hydraulic pressures, which reduces the fouling tendency of FO, even when treating impaired streams with very high fouling potential [5–9]. FO has been tested at bench-, pilot-, and full-scale for treatment of different impaired streams including municipal wastewater effluents [7], activated sludge [6,10–13], digester centrate [9], and produced water from oil and gas exploration [5,8].

The semipermeable membranes used in FO, typically cellulose triacetate (CTA) or thin film composite (TFC) polyamide membranes, allow water to diffuse across the membrane from the feed to the DS relatively freely while retaining most dissolved ions and organic compounds [7,14–18]. Although FO membranes limit the diffusion of ions, solutes still diffuse at a slow rate through the membrane from the DS to the feed due to the high concentration difference of ions between the two streams. This phenomenon is known as reverse solute flux (RSF) [15,19–22], and is undesired in FO applications because salt accumulation in the feed stream reduces the driving

force for water flux (osmotic pressure difference), increases the cost of operation, and requires that the DS solutes be continuously replenished in closed-loop DS applications [10,11,23–25].

The rate at which solutes diffuse across a semipermeable membrane is a function of the salt permeability (B) and thickness (t) of the membrane active layer, the porosity (ϵ) and tortuosity (τ) of the membrane support layer, the concentration difference between the feed ($C_{F,b}$) and DS ($C_{D,b}$), and the diffusivity coefficient (D) of the solutes in solution [26]. Yip et al. [27] derived the RSF (J_s) equation (Eq. (1)) as a function of these parameters including the feed side boundary layer mass transfer coefficient (k):

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

where J_w is the forward water flux through the membrane and S is the structural parameter of the membranes porous support layer ($S = t \cdot \tau / \epsilon$), where t , τ , and ϵ are the thickness, tortuosity, and porosity of the membrane support layer, respectively. As defined by Eq. (1), the rate at which an ion diffuses through the selective active layer of a semi-permeable membrane depends on the solute selectivity of the active layer and chemical–physical properties of the solute. In general, diffusivity decreases with increasing molecular weight, charge, and hydrated radius of the ion [28]. The physical structure of the support layer also affects the rate of solute diffusion from the bulk DS to the active layer. Membranes that have a support layer with low porosity and high tortuosity experience higher internal concentration polarization (ICP), which is the

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dilution of the DS in the support layer and reduces the driving force for water flux [26]. The detrimental effect of ICP on water flux in FO is further exacerbated when solutes with low diffusivities such as magnesium, calcium, sulfate, and certain organic salts are used in the DS. Thus, the RSF can be favorably lower and the water flux unfavorably lower when using inorganic and organic DSs such as magnesium chloride (MgCl_2), magnesium sulfate (MgSO_4), and trisodium citrate compared to sodium chloride (NaCl) at the same osmotic pressures because of the lower diffusivity of the divalent and organic salts through the membrane active and support layers [15,23,24].

An ideal DS produces high water fluxes like those induced by NaCl and low RSFs like those observed when divalent inorganic and organic salts are used at common DS concentrations. Results described by Coday et al. [19] may provide insight into the potential of using DSs containing a mix of NaCl and divalent salts to take advantage of the high water flux associated with NaCl and low RSF associated with divalent DSs. It was demonstrated in their study that when synthetic seawater with low concentrations of divalent ions was used as a DS, the RSF of sodium across CTA and TFC membranes was reduced by 55% and 22%, respectively, and the RSF of chloride reduced by 25% and 27%, respectively, compared to a DS containing only NaCl . Intriguingly, the water flux was equal for both draw solutions in experiments conducted with the TFC membrane and only slightly declined with the CTA membrane when seawater (a mixture of salts) DS was used instead of NaCl DS.

The reason for the reduced RSF and relatively constant water flux using seawater as a DS compared to NaCl was not explained by Coday et al.; however, there have been several studies on coupled solute flux in FO [15,20,21,25] and preliminary modeling on the hindered transport of monovalent ions for mixed salt solutions [29] that provide insight into the mechanisms behind these results. Hancock et al. [15,20] and Phillip et al. [25] examined the coupled transport of ions across FO membranes between the feed stream and the DS using an array of solutes in each stream. The findings from these studies demonstrated that negatively and positively charged ions diffuse through the membrane at equal molar rates (or equivalents for divalent salts coupled with monovalent salts) to maintain electroneutrality in the system. Although both Hancock et al. [20] and Phillip et al. [25] concluded that the driving force for ion transport is governed by solution diffusion mechanisms and not electrostatic interactions (such as Donnan potential or ion exchange), their publications established that the transport of oppositely charged ions is affected by the diffusivity and mobility of the counter ion. For example, the more diffusive chloride ion essentially “drags” the less diffusive sodium ion across the membrane from the DS to the feed to maintain the electroneutrality in the system [25]. Conversely, magnesium in solution with chloride limits the transport of chloride across the membrane because magnesium has a much lower diffusivity compared to sodium or chloride in the membrane, thereby retarding the diffusion of chloride across the membrane to maintain electroneutrality. Recent studies have also shown that sodium and chloride diffuse across the membrane but transport of individual ions of certain charge is higher due to attraction to charged functional groups on the FO membrane active layer. It was demonstrated by Lu et al. [30] that the RSF of cations increased with increasing membrane electronegativity. Although membrane charge is not the primary focus of this study, it is important to understand that diffusion across FO membranes depends on both the charge of the ions in solution and the membrane used for separation.

In a transport modeling effort, Yaroshchuk et al. [29] included electrostatic interactions to the solution-diffusion model to determine if the diffusion of small monovalent ions would be hindered in the presence of divalent ions that are well rejected by the membrane. Results from the modeling effort illustrated that solute flux of sodium and chloride could be hindered in the presence of minor

concentrations of divalent ions due to spontaneously arising electric fields. These fields form as a result of a charge imbalance that occurs as the more diffusive monovalent ions diffuse across the membrane at a higher rate than the well-rejected divalent ions. However, it must be noted that this model was tailored for NF membranes that have a lower selectivity to sodium and chloride than to divalent ions, as opposed to FO membranes that exhibit high rejection of both monovalent and divalent ions. The difference in membrane selectivity to ions of different molecular sizes and charge is necessary for an electrical potential (Donnan potential) to develop that hinders the transport of ions through the membrane, which otherwise will freely diffuse. Thus, Donnan effects may not play an important role in ion mobility when highly selective FO membranes are used for separation. Other effects that must be considered as potential reasons for changes in sodium and chloride reverse flux in the presence of divalent ions have been described in the NF literature. These include adsorption of divalent cations to negatively charged polymeric membranes and charge shielding of the membrane due to the adsorption of the cations [31].

Though the mechanism for reduced sodium and chloride flux is complicated by ion–ion interactions and ion–membrane interactions, there is compelling empirical evidence presented in previous studies [19] that the diffusion of chloride and sodium is hindered when NaCl DS is mixed with minor concentrations of divalent ions. Thus, the main objective of the current study was to methodically determine the flux reduction of sodium and chloride through FO membranes while maintaining high FO process performance (high water flux) when small amounts of divalent inorganic and organic ions are added to an NaCl DS.

2. Material and methods

A series of bench-scale experiments were conducted to evaluate the water flux and RSF in FO when using DSs containing a mix of NaCl as the major solute and MgCl_2 , MgSO_4 , sodium acetate (NaACE), or trisodium citrate (NaCIT) as the minor solute. All mixed salts DS experiments were conducted at osmotic pressures equivalent to 0.5 M NaCl (23 bar) and 1 M NaCl (48 bar). Single salts (NaCl , MgCl_2 , MgSO_4 , sodium acetate, and trisodium citrate) were also tested as DSs at an osmotic pressure of 23 bar to compare the water flux and RSF of single salts to that of the mixed salts DSs.

2.1. Bench-scale apparatus

Single and mixed salts DS experiments were conducted under the same hydraulic conditions and at a constant DS concentration using an automated bench-scale apparatus. The apparatus is comprised of a 4-L feed reservoir and a 4-L DS reservoir, two variable speed gear pumps (Cole-Parmer, Vernon Hills, IL), feed and DS flow meters, feed and DS heat exchangers, a chiller (Fisher Scientific, Waltham, MA), a cross-flow membrane cell, concentrated DS dosing pump (Anko, Bradenton, FL), an online DS conductivity probe (Cole-Parmer, Vernon Hills, IL), and an analytical balance (Denver Instrument, Bohemia, NY). The feed reservoir was placed on the analytical balance to measure changes in water weight as water diffused across the membrane from the feed to the DS. The recorded weight and membrane area (138 cm^2) were used to calculate the water flux. A detailed schematic drawing of the bench-scale apparatus is shown in Fig. 1.

The DS was continuously mixed using a magnetic stir bar and was maintained at a constant concentration using a peristaltic pump that dosed a doubly concentrated DS into the DS reservoir based on changes in the DS conductivity. The dosing pump was controlled using readings from the online conductivity probe connected to a programmable logic controller (UE9-Pro, LabJack Corp., Lakewood,

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