**Combining high performance fertiliser with surfactants to reduce the
reverse solute flux in the fertiliser drawn forward osmosis process**

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Abstract

Solutions to mitigate the reverse diffusion of solutes are critical to the successful commercialisation of the fertiliser drawn forward osmosis process. In this study, we proposed to combine a high performance fertiliser (i.e., ammonium sulfate or SOA) with surfactants as additives as an approach to reduce the reverse diffusion of ammonium ions. Results showed that combining SOA with both anionic and non-ionic surfactants can help in reducing the reverse salt diffusion by up to 67%. We hypothesised that, hydrophobic interactions between the surfactant tails and the membrane surface likely constricted membrane pores resulting in increased rejection of ions with large hydrated radii such as SO_4^{2-} . By electroneutrality, the rejection of the counter ions (i.e., NH_4^+) also therefore subsequently improved. Anionic surfactant was found to further decrease the reverse salt diffusion due to electrostatic repulsions between the surfactant negatively-charged heads and SO_4^{2-} . However, when the feed solution contains cations with small hydrated radii (e.g., Na^+); it was found that NH_4^+ ions can be substituted in the DS to maintain its electroneutrality and thus the diffusion of NH_4^+ to the feed solution was increased.

Keywords: Forward osmosis, fertiliser draw solution, surfactant, reverse salt flux.

1 Introduction

Fertiliser-drawn forward osmosis (FDFO) process for water reuse from low-quality sources such as impaired waters has been recognised as one of the few viable applications of FO (Kessler and Moody, 1976; Phuntsho et al., 2012a; Van der Bruggen and Luis, 2015). In fact, because irrigation is known to be the largest water consumer, FDFO could bring a substantial contribution to the development of alternative water sources for water-scarce regions to ensure the sustainability of agriculture. So far, FDFO studies have focused on the desalination of either brackish groundwater, high saline wastewater or seawater (Phuntsho et al., 2013a; Phuntsho et al., 2016; Phuntsho et al., 2011; Phuntsho et al., 2012a; Phuntsho et al., 2012b) and more recently on the reuse of low saline impaired waters (Chekli et al., 2017a; Chekli et al., 2017b) at both laboratory and pilot-scale. Various fertilisers have been tested as DSs including single inorganic salts (Phuntsho et al., 2011), blended salts (Phuntsho et al., 2012b) and also commercial fertilisers containing all essential nutrients for plant growth (Chekli et al., 2017a). Ammonium sulphate (SOA) has been tested in most FDFO studies, at both laboratory and pilot scales, because it has demonstrated superior or comparable performance in terms of water flux and reverse salt flux (RSF) with other fertilisers. However, the recent pilot-scale study using SOA has revealed that the RSF was still high which resulted in the feed brine ions concentration exceeding the standard for direct discharge (Phuntsho et al., 2016). Besides the negative environmental impacts upon discharge to the environment such as eutrophication, the loss of draw solution (DS) is also economically unfavourable (i.e. DS replenishment cost, loss of the osmotic driving force, and can also potentially lead to enhanced membrane fouling and scaling) (Achilli et al., 2010; Phuntsho et al., 2014). Finding solutions to minimise the RSF is therefore critical for the development of the FDFO process to a commercial reality.

Gadelha et al. (2014) were the first to introduce the concept of using surfactants as DS. Surfactants are amphiphilic molecules presenting dual structural units: a long hydrocarbon chain (hydrophobic), the tail and a hydrophilic group, the head (which can be anionic, cationic, non-ionic or zwitterionic) (Aiad et al., 2012, 2013; Shaban et al., 2016). One interesting property of surfactants is the formation of micelles which are the reversible aggregation of surfactant monomers when their concentrations are above the critical micelle concentration (CMC) (Akram and Kumar, 2014; Kumar and Rub, 2017, 2018; Rub et al., 2014; Rub et al., 2015). The micelle-monomer equilibrium in aqueous solution displays a relatively constant osmotic pressure, independent of the concentration (Xiao and Li, 2008);

which proved to be useful in maintaining more stable operation of the FO process. Results from this initial study revealed that all tested surfactants demonstrated between 3 to 300 times less reverse diffusion compared to NaCl at similar concentration. This was explained by the fact that, above the CMC, molecular weight of the micellar mass can reach up to 14,000 to 29,000 g/mol, preventing their diffusion to the feed solution (FS). Two other studies from the same group (Nawaz et al., 2013; Nawaz et al., 2016) focusing on osmotic membrane bioreactor also demonstrated the low reverse transport of surfactant DS. However, these studies also indicated that when using surfactants only as DS, the water flux is significantly lower than when using inorganic salts at the same concentration.

More recently, Nguyen et al. (Nguyen et al., 2015a; Nguyen et al., 2015b; Nguyen et al., 2016) tested a mixture of non-ionic surfactants and both organic and inorganic salts as DSs with the aim to reduce RSF in osmotic membrane bioreactor systems. When a non-ionic surfactant was combined with a highly water soluble salts (i.e. MgCl_2), a relatively high water flux (i.e. $11.4 \text{ L/m}^2\cdot\text{h}$) and a RSF as low as $2.03 \text{ g/m}^2\cdot\text{h}$ (specific RSF of 0.18 g/L) were achieved (Nguyen et al., 2016). In these studies, it was only hypothesised, without further investigations, that hydrophobic interactions between the surfactant tails and the membrane created an additional layer on the membrane surface that constricted membrane pores; resulting in increased ions rejection (due to size exclusion effect).

In the present study, we propose for the first time to combine surfactants (both non-ionic and anionic) with a fertiliser (i.e. SOA) as a novel approach to reduce the RSF phenomena, in particular the reverse diffusion of nutrients during the FDFO process. While non-ionic surfactants have already been tested and proven effective in reducing the RSF of inorganic salts, anionic surfactants have not yet been evaluated. It is hypothesised that electrostatic interactions arising from the surfactant negatively-charged head can further enhance the rejection of anions such as SO_4^{2-} . Surfactants are widely used in various areas of agriculture including crop protection and agrochemical formulations (Castro et al., 2013; Deleu and Paquot, 2004). Therefore, combining surfactants with fertiliser in the FDFO process is not expected to be detrimental to the final produced nutrient solution for fertigation crops. The study also investigated how the presence of surfactants in the DS affects the membrane intrinsic properties (pure water permeability coefficient of the active layer, salt rejection, salt permeability, hydrophobicity and chemistry of both the active and support layers) and the process performance (water flux and RSF). The effect of membrane type, membrane

orientation and the presence of salts in the FS were also assessed.

2 Materials and Methods

2.1 FO membrane and draw solutions

Two different commercial flat-sheet FO membranes were tested and compared in this study: a cellulose triacetate (CTA) membrane (Hydration Technology Innovations - HTI, Albany, USA) and a polyamide (PA) thin film composite (TFC) membrane (Toray Chemical Korea Inc., South Korea). While the commercial CTA membrane from HTI has been studied extensively (Cath et al., 2006; McGinnis et al., 2005; Tang et al., 2010), the commercial PA TFC membrane from Toray has only been reported in a few studies (e.g. (Chekli et al., 2017a)).

The pure water permeability coefficient of the active layer (A value) as well as the salt rejection (R%) and salt permeability coefficient (B value) for both NaCl and SOA were determined for both membranes in reverse osmosis (RO mode). The A value was measured at 8 bar pressure and was calculated by dividing the average water permeate flux (i.e. measured every minute continuously for an hour) by the applied pressure. The salt rejection (using 500 mg/L of either NaCl or SOA) was determined from the difference between the bulk feed and permeate salt concentration. Finally, the B value ($\text{L.m}^{-2}.\text{h}^{-1}$) was determined using the following equation:

$$B = \frac{1-R}{R}(\Delta P - \Delta \pi)A \quad (1)$$

where ΔP is the applied pressure (8 bar in this study), $\Delta \pi$ is the osmotic pressure of the FS (1.6 bar for 500 mg/L NaCl and 0.96 bar for 500 mg/L SOA) and A is the pure water permeability coefficient ($\text{L.m}^{-2}.\text{h}^{-1}.\text{bar}^{-1}$). The salt rejection and both A and B values for both membranes in the presence of surfactants were also assessed using the most efficient surfactant concentration determined during the batch FO experiments. Experiments were run in duplicate and the data presented are the average of the two measurements.

All chemical fertilisers used in this study (SOA and NaCl) were reagent grade and purchased from Sigma-Aldrich Australia. DSs were prepared by dissolving the salts in deionised (DI) water. Tergitol 15-S-9 (Tergitol) and sodium dodecyl sulfate (SDS) were also purchased from Sigma-Aldrich Australia. The properties of these surfactants are presented in Table 1.

134

Table 1: Properties of surfactants used in this study.

	Tergitol 15-S-9	Sodium dodecyl sulfate
Type	Non-ionic	Anionic
CAS Number	68131-40-8	151-21-3
Molecular weight (g/mol)	595	288
CMC ^a at 25°C (mM)	0.09	8.2
Density at 20°C (g/mL)	1.006	1.01
HLB ^b	12.6	40

135 ^a Critical Micelle Concentration136 ^b Hydrophilic-Lipophilic Balance

137 According to a recent FO study (Nawaz et al., 2013), surfactants are suitable DSs with
 138 minimal RSF compared to inorganic salts when used at concentration above their CMC.
 139 Therefore, in the present study, all experiments with surfactants were conducted above their
 140 CMC (i.e. 0.25-10 mM for Tergitol and 10-50 mM for SDS). Preliminary experiments were
 141 conducted using DI water as FS and surfactants only as DS at concentration just above their
 142 CMC (i.e. 0.1 mM for Tergitol and 10 mM for SDS). Results confirmed previous findings
 143 with a low water flux ($1.9 \text{ L.m}^{-2}.\text{h}^{-1}$ and $2.1 \text{ L.m}^{-2}.\text{h}^{-1}$ for Tergitol and SDS respectively) and
 144 negligible RSF. In fact, the conductivity of the FS did not vary during the test (Figure S1,
 145 Supporting Information (SI)) and the final total organic carbon (TOC) concentration was
 146 below the detection limit for both surfactants.

147 **2.2 Bench-scale FO system**

148 The performances of the FDFO process (water flux and RSF) were all evaluated in a batch
 149 mode of FO operation, similar to the one used in previous studies (Kim et al., 2015; Lee et
 150 al., 2010). The FO system was operated under the co-current flow mode. The FO cell has two
 151 symmetric channels on each side with internal dimensions of 7.7 cm length, 2.6 cm width and
 152 0.3 cm depth (i.e., effective membrane area of 0.002 m^2). Variable speed gear pumps (Cole
 153 Parmer, USA) were employed to circulate the feed and draw solutions. The DS tank was
 154 placed on a digital scale connected to a computer to determine the water flux by measuring
 155 the weight changes over time. A portable conductivity and pH meter (Hach, Germany) was
 156 connected to the feed tank to record the variation of pH and electrical conductivity in the FS.

157 The experiments were conducted under the active layer facing the FS (AL-FS) mode; unless
 158 otherwise stated. A new membrane was used for each new experiment (described in Table
 159 S1, SI) and the FO membrane was initially stabilised with DI water on both sides for 30
 160 minutes before starting the experiment. Then after, both the feed and draw solutions were

replaced and the water flux was measured continuously every 3 minutes. All experiments were conducted at a cross-flow velocity of 8.5 cm/s, and a constant temperature of 25 °C maintained with a temperature control bath connected to a heating/chilling unit.

2.3 Experimental protocol

Short-term experiments (i.e. 24 hours) were initially conducted to evaluate the effect of surfactants concentrations in the DS (combined with 0.5 M SOA) on the basic FO performance (water flux and RSF). Both CTA and TFC membranes were tested and results were compared to determine the optimum combination (type of surfactant, surfactant concentration and membrane type). All these experiments were conducted with DI water as FS. Experiments were also conducted in the pressure retarded osmosis (PRO) mode (active layer facing the DS) with both membranes and the most efficient DS to assess the effect of membrane orientation. The water flux was measured continuously and the data were averaged. The RSFs from the DS (NH_4^+ and SO_4^{2-}) were calculated by analysing their final concentration in the FS upon completion of each experiment. Samples (50 mL) were taken from the FS for nutrient analysis. All experiments were run in duplicate and the data presented are the average of the two replicates with standard deviation.

Following these initial experiments, the effect of salts (NaCl and MgCl_2) in the FS was also evaluated. FSs that consisted of either 500 mg/L NaCl or 500 mg/L MgCl_2 (diluted with DI water), were tested with the most efficient membrane and DS. Water flux was measured continuously and the data were averaged. The salt fluxes from both the feed and draw solutions (NH_4^+ , SO_4^{2-} , Na^+ and Mg^{2+}) were determined by measuring their initial and final concentration in both solutions. Samples were taken at the beginning and end of each experiment for nutrient analysis. These experiments were run in duplicate and the data presented are the average with standard deviation.

2.4 Analytical methods

2.4.1 Membrane surface characterisation

The presence of surfactants on the surface (active and support layers) of both CTA and TFC membranes was determined using a Fourier Transform Infrared Spectrometer (FTIR-8400S, Shimadzu, Japan). Each spectrum was collected after 16 scans at a resolution of 2 cm^{-1} . FTIR measurements were performed on pure SDS (powder form) and Tergitol (liquid form) as well

as on the virgin surface (active and support layers) of both membrane types. Measurements of the “surfactant-treated” membranes were performed on membrane coupons collected upon completion of FO experiments (in both FO and PRO mode) with the optimum surfactant concentrations.

Surface properties of the virgin and “surfactant-treated” CTA and TFC membranes were also characterised in terms of hydrophilicity by measuring the contact angle. Contact angle measurements were performed using an optical tensiometer (Theta Lite 100) equipped with an image processing software. At least five independent measurements (i.e. at different locations on the membrane surface) were carried out and the data presented are the average values with standard deviation. The membrane coupons used for contact angle measurements were the same used for the FTIR analysis.

2.4.2 Ions concentration analysis

N-NH₄⁺, SO₄²⁻, Na⁺ and Mg²⁺ concentrations were determined using Merck cell tests and spectrophotometer (Spectroquant NOVA 60; Merck, Germany) to determine their concentrations in both the feed and draw solutions.

3 Results and Discussion

3.1 Effect of surfactants on membrane properties

3.1.1 Membrane transport parameters

The membrane transport parameters (A and B values and salt rejection) of both commercial FO membranes are presented in Figure 1 and Table S2 (SI). Results clearly show that the TFC membrane from Toray outperforms the CTA HTI membrane for both the pure water permeability (1.035 L.m².h⁻¹.bar⁻¹ and 5.482 L.m².h⁻¹.bar⁻¹ for CTA and TFC membranes respectively) and the salt rejection (e.g. 89.5% NaCl rejection for the CTA membrane against 96.7% rejection for the TFC membrane). The B values for SOA are lower than the B values for NaCl for both membranes. As expected, divalent ions (SO₄²⁻ - 0.40 nm) exhibit lower diffusion rate compared to monovalent ions (Na⁺ - 0.36 nm) and are therefore better rejected by the membrane through size exclusion (Nightingale Jr, 1959; Phillip et al., 2010).

When surfactant was added to the FS, the A value and B value for NaCl remained fairly constant (or slight but insignificant decreased for the A value) while the B value for SOA

decreased with both tested surfactants. These results are in accordance with previous studies (Nguyen et al., 2015a; Nguyen et al., 2015b; Nguyen et al., 2016) where it was found that the addition of surfactant in a DS containing multivalent ions resulted in a significant increase in salt rejection without affecting the water permeability (or water flux). In those studies, it was explained that the interactions between the hydrophobic tails of the surfactant and the membrane surface created a layer on the membrane surface that reduced the membrane pores size. Therefore, the contribution of size exclusion effect to the rejection of multivalent ions, such as SO_4^{2-} , increases; resulting in lower B values for SOA. By comparing the results with the two surfactants, the B values for SOA obtained with SDS are lower than the ones obtained with Tergitol for both membrane types. This can be explained by the fact that SDS is an anionic surfactant and therefore, additional repulsive forces between the negatively-charged head of the surfactant and SO_4^{2-} could have further increased the rejection of SOA; resulting in lower B values.

Figure 1: Membrane transport parameters (A and B values) of (a) CTA and (b) TFC membranes.
Experimental conditions: applied pressure – 8 bar; feed solutions were either pure DI water or DI water mixed with surfactant for A values or pure NaCl/SOA solutions or NaCl/SOA solutions mixed with surfactant for B values; surfactant concentration – 1 mM Tergitol or 25 mM SDS; NaCl/SOA concentration – 500 mg/L.

3.1.2 Membrane surface characterisation

The FTIR spectra of both CTA and TFC membrane active layers, virgin and “surfactant treated” as well as the spectra of both surfactants, over wave numbers of 4000-500 cm^{-1} , are presented in Figure 2. The peak assignments for all FTIR spectra over these wave numbers are detailed in Table S3 (SI) (Bera et al., 2012; Drmosh et al., 2010; Luo et al., 2016; Tang et al., 2009). The FTIR spectra measured on the support layers of both membranes are also

presented in the SI (Figure S2).

It is clear from Figure 2 that both surfactants were adsorbed on the surface of both membranes since the characteristic peaks of both surfactants and membranes appear on the spectra of “surfactant-treated” membranes. On the “surfactant-treated” spectra, the characteristic peaks from SDS (at 2850 and 2916 cm^{-1}) have a lower intensity than the characteristic peaks from Tergitol (at 2585 and 2924 cm^{-1}) which can suggest that fewer SDS monomers were adsorbed on the membrane surface compared to Tergitol. This can be explained by the fact that both hydrophobic (from non-polar tails) and electrostatic (from negatively-charged heads) interactions play an important role in the adsorption of ionic surfactants. Since both CTA and TFC membranes have a negative surface charge (Xie et al., 2014), electrostatic repulsions could have occurred resulting in fewer monomers getting adsorbed onto the membrane surface (Chew et al., 2017). Another explanation could be the difference in wetting rates of the two surfactants which is related to their HLB. The higher the surfactant HLB value is, the more hydrophilic it is. Since Tergitol has a lower HLB value (12.6 against 40.0 for SDS), it is more lipophilic and thus more easily adsorbed via hydrophobic interactions with the membrane surface (Lin et al., 2015).

Figure 2: FTIR spectra of CTA and TFC virgin active layers, pure Tergitol and SDS: (a) Tergitol treated CTA, (b) SDS treated CTA, (c) Tergitol treated TFC and (d) SDS treated TFC. The membrane coupons for the “surfactant treated” samples were collected upon completion of the FO experiments with the optimum surfactant concentration – 1 mM Tergitol and 25 mM SDS.

Membrane coupons of virgin and “surfactant-treated” CTA and TFC membranes were also analysed for surface hydrophilicity. Contact angle results of the membrane active layers presented in Figure 3 and revealed that the presence of surfactant increases the surface hydrophilicity (and thus reduces the contact angles). The contact angle results of the support layers of both membranes (“surfactant-treated”) were not shown because the water droplet was systematically absorbed during the measurement. The reduced surface hydrophobicity can be related to the hydrophobic interactions between the surfactants and the membrane surface. In fact, the surfactant can reduce the available hydrophobic sites on the membrane surface rendering it more hydrophilic (Fane et al., 1985). Surfactants are also known to lower the surface tension of the medium (Kronberg et al., 2014). Therefore, if the surface tension of the liquid decreases, this results in higher membrane wetting potential (Franken et al., 1987; Lin et al., 2015). It is worth noting that rendering the membrane surface more hydrophilic is also advantageous in terms of mitigating the membrane fouling caused by hydrophobic substances.

Results also show that the contact angle of “SDS-treated” membranes is lower than that of “Tergitol-treated” membranes and this can be again related to the HLB value of the surfactants. SDS, having a higher HLB value, is more hydrophilic and can thus provide a more hydrophilic surface upon adsorption on the membrane surface. Besides, the fact that SDS is an anionic surfactant (monomers with a negatively-charged head) may also play a role in the reduced contact angle values. In fact, upon adsorption on the membrane surface, the negatively-charged sulfate functional groups of SDS molecules can cause the membrane to become more negatively charged and thus more hydrophilic (Childress and Deshmukh, 1998).

Figure 3: Contact angle results of the active layer of (a) CTA and (b) TFC membranes. Measurements were performed on virgin membranes and “surfactant treated” membranes which were collected upon completion of the FO experiments with the optimum surfactant concentration – 1 mM Tergitol and 25 mM SDS.

3.2 Effect of surfactant concentrations and membrane types on FDFO performance

Figure 4 shows the water fluxes and specific RSF (SRSF = RSF divided by the water flux) for both commercial membranes and surfactants at different surfactant concentrations and a fixed SOA concentration (i.e., 0.5 M). It has to be noted that the surfactant concentration range was not the same for the two surfactants (i.e., 0.25 mM-10 mM for Tergitol and 10 mM-50 mM for SDS), mainly because they have different CMC values (i.e., 0.09 mM for Tergitol and 8.2 mM for SDS). Therefore, the concentration range employed for Tergitol would have been too low for SDS (i.e., below its CMC value) whereas the concentration range employed for SDS would have too high for Tergitol (i.e., 10 mM is already 100 times its CMC value and the solution of Tergitol, at this concentration, was already viscous).

Results in Figure 4 show that the commercial TFC membrane exhibits better FO performance than the commercial CTA membrane with a higher water flux ($16.99 \text{ L.m}^2.\text{h}^{-1}$ against $7.28 \text{ L.m}^2.\text{h}^{-1}$ for the TFC and CTA membranes respectively) and lower SRSF (0.18 g/L against 0.34 g/L for the TFC and CTA membranes respectively) when 0.5 M SOA is used as DS. When surfactants are added to the DS, the SRSF decreased quite significantly for both membranes. For example, with 50 mM SDS as surfactant, the SRSF decreased down to 0.15 g/L and 0.06 g/L for CTA and TFC membranes, respectively. One of the main reasons for this decrease, as explained earlier, comes from the hydrophobic interactions between the tails of the surfactants and the membrane surface affecting the membrane pores size; reducing the

reverse diffusion of multivalent ions with larger hydrated radii such as SO_4^{2-} . Because cross-membrane migration of ions is partially governed by a cross-membrane concentration gradient (Phillip et al., 2010), the increased rejection of SO_4^{2-} will also improve the rejection of NH_4^+ by electroneutrality (since the FS is DI water). Investigations of individual ion rejection confirm this result since the $\text{NH}_4^+:\text{SO}_4^{2-}$ molar ratio in the final FS was always close but slightly higher than 2 (Table S4, SI). Measurements of the initial and final pH in the FS (Table S4, SI) show an increase in the pH which can be attributed to SO_4^{2-} ions being partially substituted by OH^- ; rendering the final $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratio slightly higher than 2.

Results in Figure 4 also show that the water fluxes decreased slightly when increasing the concentration of surfactants. This can be due to slightly enhanced internal concentration polarization (ICP) due to increased viscosity of the DS (not measured but visually observed, especially at the highest concentration of 10 mM Tergitol and 50 mM SDS. Similar observation was made in the previous studies using surfactants in the DS (Nguyen et al., 2015a; Nguyen et al., 2015b; Nguyen et al., 2016). This water flux decrease is also more pronounced using Tergitol surfactant in the SOA DS with both membranes. This result can be related to the FTIR measurements suggesting that more Tergitol monomers were adsorbed on the membrane surface which may have likely caused an additional barrier to the water permeation. Finally, results in Figure 4 also indicate that SDS is more effective in reducing the SRSF than Tergitol with both membranes. This could be explained by the fact that, on top of size exclusion effect, electrostatic repulsion between the negatively charged head of SDS monomers and SO_4^{2-} could have further enhanced the rejection of SOA.

Figure 4: Permeate water flux and specific reverse salt flux (SRSF) at different surfactant concentrations: (a) CTA membrane and Tergitol, (b) CTA membrane and SDS, (c) TFC membrane and Tergitol and (d) TFC membrane and SDS. Experimental conditions: draw solution – 0.5 M SOA with different surfactant concentration; feed solution – DI water; FO mode (AL-FS); cross flow velocity – 8.5 cm/s; temperature – 25 °C; operating time: 24 hours). N.B. T = Tergitol.

3.3 Effect of membrane orientation on FDFO performance

Experiments were conducted with different membrane orientations using both the commercial CTA and TFC membranes and the best DS (i.e. 0.5 M SOA with 25 mM SDS which gave the best water flux and SRSF performances). Results in Figure 5 show that the water fluxes in PRO mode (i.e., 12.24 L.m².h⁻¹ and 24.32 L.m².h⁻¹ for the CTA and TFC membranes respectively) were comparatively higher than in FO mode (i.e., 7.28 L.m².h⁻¹ and 16.99 L.m².h⁻¹ for the CTA and TFC membranes, respectively, Figure 4). These results are consistent with previous studies comparing the performance of FO in both operating modes (Gray et al., 2006; Jung et al., 2011; Lay et al., 2012; Phuntsho et al., 2013b). This difference in water fluxes is mainly due to the difference in the membrane structure. In fact, in the FO mode, the DS is facing the support layer and the incoming water from the FS dilutes the DS at the membrane surface and within the support layer which reduces the net osmotic pressure

at the membrane surface; thereby reducing the driving force of the process. This phenomenon is known as dilutive internal concentration polarization (ICP) which severely affects the FO performance since it significantly restricts the diffusivity of the draw solutes through the support layer (Gray et al., 2006). When the process is operated in PRO mode, dilutive ICP effect occurs too but on the surface of the membrane active layer. The external concentration polarisation (ECP) has less impact on the process performance since it can be mitigated by the crossflow shear on the membrane surface compared to ICP. However, in this study, since DI water was used as FS, concentrative ICP is absent on the support layer side of the membrane. Therefore, in PRO mode, the effective DS concentration at the membrane interface surface is higher than in the FO mode; resulting in higher water flux but also leading to higher RSF (i.e., $3.01 \text{ g.m}^{-2}.\text{h}^{-1}$ against $2.49 \text{ g.m}^{-2}.\text{h}^{-1}$ for the CTA membrane and $3.63 \text{ g.m}^{-2}.\text{h}^{-1}$ against $3.00 \text{ g.m}^{-2}.\text{h}^{-1}$ for the TFC membrane in PRO and FO modes, respectively). However, the SRSF is still lower under the PRO mode of operation because the gain in water flux (i.e., around 30-40%) is higher than the increase in RSF (i.e., around 17%).

Figure 5: Effect of surfactant on the permeate water flux and specific reverse salt flux (SRSF) in the PRO mode (AL-DS) with CTA and TFC membranes. Experimental conditions: draw solutions – 0.5 M SOA or 0.5 M SOA with 25 mM SDS; feed solution – DI water; cross flow velocity – 8.5 cm/s; temperature – 25 °C; operating time – 24 hours).

When SDS was added to the DS, Figure 5 shows that both the SRSF and the water flux decreased for both CTA and TFC membranes and this decrease is more significant in PRO mode than in the FO mode (Figure 4). Since the surfactant monomers are directly in contact with the active layer in PRO mode, it is very likely that more monomers are being adsorbed on the membrane surface which can create a secondary filtration layer; thereby increasing the resistance to the water and salt diffusion through the membrane. This hypothesis is somewhat validated by the FTIR results on both the active and support layers (Figure 2 and Figure S2). In fact, the intensity of the peaks on the “SDS-treated” membranes spectra is lower in the FO mode (support layer) than in the PRO mode (active layer). In other words, when the DS is facing the support layer, the peaks intensity related to SDS is lower due to fewer monomers being adsorbed which is probably related to the ICP effect within the support layer.

By comparing the results obtained with the two commercial FO membranes, it can be seen that the water flux reduction is more significant with the CTA membrane (i.e., decreased by 24%) than with the TFC membrane (i.e., decreased by 11%). This result could be explained by the electrostatic interactions between the negatively-charged head of SDS and the negatively-charged membrane surface. Since TFC FO membranes are known to be more negatively charged than CTA FO membranes (Xie et al., 2014), repulsive forces between SDS and the surface of TFC membrane will be stronger than with the surface of CTA membrane; resulting in fewer monomers being adsorbed on the surface of the TFC membrane. Therefore, the decrease in water flux will be more significant with the “SDS-treated” CTA membrane under the PRO mode of membrane orientation.

3.4 Effect of feed solution salinity on FDFO performance

Based on the results presented in the previous sections, our main hypothesis regarding the role of surfactants in decreasing the SRSF of SOA is as follow: the hydrophobic interactions between the surfactant tails and the membrane surface reduce the membrane pores size improving the size exclusion effect of the larger multivalent ions such as SO_4^{2-} . By electroneutrality, the associated ion pair (NH_4^+) is also rejected leading to a reduced SRSF. When using an anionic surfactant (SDS), the rejection of anions (SO_4^{2-}) is further improved due to the additional repulsive forces generated by the negatively-charged surfactant heads.

However, all of these results were obtained with DI water as FS. Since most FDFO applications involve either wastewater, brackish water or seawater as FS; it is also important

to evaluate the effect of feed salt concentration and composition on the FDFO process performance. Experiments with the TFC FO membrane and the most efficient DS (0.5 M SOA with 25 mM SDS) were also conducted with 500 mg/L NaCl or 500 mg/L MgCl₂ as FSs. TFC membrane was chosen since it systematically showed better performance in terms of water flux and SRSF. Results are shown in Figure 6 and Figure 7.

Results in Figure 6 indicate that the water flux slightly decreased when salt was added to the FS which is mainly due to the decrease in the osmotic pressure difference (or driving force) between the feed and the draw solutions. However, the SRSF of the TFC FO membrane without surfactant did not change when a FS containing NaCl and MgCl₂ are used. Figure 7 shows that, similarly to the results with DI water, when MgCl₂ was used as FS, the final molar ratio NH₄⁺:SO₄²⁻ in the FS was close to the theoretical value of 2. In fact, Mg²⁺ cations have a large hydrated radius (0.43 nm) and thus a relatively low diffusion rate in comparison to NH₄⁺. It is therefore unlikely for NH₄⁺ ions to be substituted by Mg²⁺ and hence maintaining similar SRSF as DI feed. However, when NaCl was used as the FS, the final molar ratio NH₄⁺:SO₄²⁻ in the FS was close to 2.5 and the final DS contained about 0.45 mol of Na⁺. This is because Na⁺ can easily substitute NH₄⁺ and therefore, more NH₄⁺ (i.e. molar ratio of NH₄⁺:SO₄²⁻ being greater than 2) can diffuse to the FS while Na⁺ can diffuse to the DS to maintain its electroneutrality. The pH measurements in the feed solution (Table S4, SI) also showed that the pH variation in the feed is less when using NaCl since the electroneutrality of the feed solution is maintained through the exchange between Na⁺ and NH₄⁺.

Similarly, when surfactant was added to the DS, the results with MgCl₂ were quite similar to the results with DI water in terms of SRSF. The presence of SDS in the DS decreases the reverse diffusion of SO₄²⁻, as discussed in the previous section. By electroneutrality, this also affects the reverse diffusion of NH₄⁺ when DI water is employed as FS. When MgCl₂ was used as FS, similar results were obtained since Mg²⁺ ions cannot substitute NH₄⁺ which therefore diffuses back to the DS to maintain its electroneutrality. Results with NaCl as FS are quite different since Na⁺ can easily diffuse through the membrane and replace NH₄⁺. That is why the final molar ratio NH₄⁺:SO₄²⁻ in the FS remained above 2, even when surfactant was added to the DS (Figure 7). These results clearly indicate that combining SOA with surfactants is likely to be more effective for FS containing divalent cations or low concentration of monovalent cations such as secondary effluents from municipal wastewater

treatment plants which have already been investigated for the FDFO process (Chekli et al., 2017a; Chekli et al., 2017b). Addition of surfactants, however, may not be effective in reducing the SRSF for highly saline feed sources such as brackish or seawater.

Figure 6: Effect of salts in the feed solution on the permeate water flux and specific reverse salt flux (SRSF) with and without surfactant in the DS. Experimental conditions: membrane – TFC Toray; draw solution – 0.5 M SOA or 0.5 M SOA with 25 mM SDS; FO mode (AL-FS); cross flow velocity – 8.5 cm/s; temperature – 25 °C; operating time – 24 hours).

Figure 7: Final ion molar balance in the feed and draw solutions and ammonium/sulfate ratio. Positive values are the ions transferred from the draw to the feed solution (reverse draw solutes) while the negative values are the ions transferred from the feed to the draw solution.

4 Conclusions

This study investigated for the first time the influence of adding surfactant to the fertiliser DS on the performance of the FDFO process as an innovative approach for mitigating the RSF phenomena. Results showed that combining a fertiliser containing divalent anions, such as SOA, with surfactants at concentration above their CMC was effective in reducing the RSF phenomena to a certain extent while keeping similar water flux performance. The hydrophobic interactions between the surfactant tails and the membrane surface can increase the size exclusion effects and thus the rejection of large hydrated ions such as SO₄²⁻. Compared to early studies where only non-ionic surfactants were tested (e.g. (Nguyen et al., 2015a; Nguyen et al., 2015b; Nguyen et al., 2016), the present work showed that using anionic surfactants with negatively-charged head can further improve the rejection of anions through electrostatic repulsion and are therefore preferable. The present study also highlighted that, when using feed solutions containing cations with small hydrated radii (e.g. Na⁺), the diffusion of NH₄⁺ through the membrane increases, even in the presence of surfactants, rendering them less effective in reducing the SRSF. This proposed approach of adding surfactant in the fertiliser DS would be therefore more effective in applications using

low TDS FSs such as wastewater secondary effluents. Alternatively, other combination of high performing fertilisers and surfactants could be tested to gain a further understanding of the performance of this DS in the future. Finally, it is important to maintain the concentration of surfactants above their CMC and therefore the replenishment cost should be considered in future studies investigating this alternative DS.

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