Research article

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.

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., 2011, 2012a, 2012b, 2013a, 2016) and more recently on the reuse of low saline impaired waters (Chekli et al., 2017a, 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

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concentrations are above the critical micelle concentration (CMC) (Akram and Kumar, 2014; Kumar and Rub, 2017, 2018; Rub et al., 2014, 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 and 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, 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. (2015a,b) and 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. $11.4 \, L/m^2 \, h$) and a RSF as low as $2.03 \, g/m^2 \, h$ (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

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

[a] Critical Micelle Concentration.
[b] Hydrophilic-Lipophilic Balance.

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 ($L.m^{-2} h^{-1}$) was determined using the following equation:

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

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 ($L.m^{-2} h^{-1} bar^{-1}$). 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.

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

2.2. Bench-scale FO system

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

The experiments were conducted under the active layer facing the FS (AL-FS) mode; unless otherwise stated. A new membrane was used for each new experiment (described in Tables S1 and SI) and the FO membrane was initially stabilised with DI water on both sides for