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Enhancing wastewater reuse by forward osmosis with self-diluted commercial fertilizers as draw solutes

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ABSTRACT

Using fertilizers as draw solutes in forward osmosis (FO) can accomplish wastewater reuse with elimination of recycling draw solute. In this study, three commercial fast-release all-purpose solid fertilizers (F1, F2 and F3) were examined as draw solutes in a submerged FO system for water extraction from either deionized (DI) water or the treated wastewater. Systematic optimizations were conducted to enhance water extraction performance, including operation modes, initial draw concentrations and *in-situ* chemical fouling control. In the mode of the active layer facing the feed (AL-F or FO), a maximum of 324 mL water was harvested using 1-M F1, which provided 41% of the water need for fertilizer dilution for irrigation. Among the three fertilizers, F1 containing a lower urea content was the most favored because of a higher water extraction and a lower reverse solute flux (RSF) of major nutrients. Using the treated wastewater as a feed solution resulted in a comparable water extraction performance (317 mL) to that of DI water in 72 h and a maximum water flux of 4.2 LMH. Phosphorus accumulation on the feed side was mainly due to the FO membrane solute rejection while total nitrogen and potassium accumulation was mainly due to RSF from the draw solute. Reducing recirculation intensity from 100 to 10 mL min^{-1} did not obviously decrease water flux but significantly reduced the energy consumption from 1.86 to 0.02 kWh m^{-3}. These results have demonstrated the feasibility of using commercial solid fertilizers as draw solutes for extracting reusable water from wastewater, and challenges such as reverse solute flux will need to be further addressed.

1. Introduction

Agricultural irrigation is considered as a water intensive process and consumes 72% of global fresh water withdrawal (Cai and Rosegrant, 2003). Exploring alternative water supply for irrigation, for instance via reusing wastewater, will be of great importance (Xie et al., 2015). Current treatment of wastewater can effectively remove the contaminants; however, the effluent is still not widely used for irrigation because of some undesired substances like pathogens (e.g., *Legionella* and *E. coli*) (EPA, 2012) and trace organic chemicals (e.g., endocrine-disrupting chemicals) (Wang et al., 2016). Thus, further treatment will be necessary, and to achieve this, membrane technologies can be applied (Achilli et al., 2009). Among the newly developed membrane technologies, forward osmosis (FO) is of strong interest. FO is a membrane separation process known for efficient water recovery by utilizing osmotic pressure gap between a draw solution and a feed solution. It has great merits of high contaminant rejection rate and lower fouling propensity when compared to pressure-driven processes such as reverse osmosis (RO) (Holloway et al., 2007). Because of low or no hydraulic pressure, FO could have potential advantages in low energy consumption, if regeneration of draw solutes can be accomplished without using energy-intensive processes like RO.

One of the key challenges to accomplish sustainable water recovery in FO is the separation and recovery of draw solutes, which accounts for most of the energy consumption (Achilli et al., 2010; McGinnis and Elimelech, 2007). Novel draw solutes including the self-separated ionic solution (Bowden et al., 2012; Cai et al., 2015) and thermolytic ammonium bicarbonate (NH_3-CO_2) (McCutcheon et al., 2005) were proposed for easy regeneration while maintaining high osmotic pressure and desirable water flux. However, regeneration of those draw solutes still bear problems. For example, recovery of NH_3-CO_2 requires relatively high decomposition temperature (at least 60 °C), leading to additional energy input, and the thermal-responsive ionic solution may result in potential

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environmental concerns and health risks due to leakage of ionic solutes.

Fertilizers were proposed and investigated as draw solutes to eliminate the need of regeneration (Table S1, Supplementary material). The self-diluted fertilizers can be directly used for agricultural irrigation, providing an alternative to bypass the energy-intensive draw solute recovery process (Hoover et al., 2011). Phuntsho et al. proposed nine inorganic chemicals as hypothetical fertilizers and evaluated their osmotic dilution performance in a cross-flow FO system by using DI water as feed (Phuntsho et al., 2011). Subsequent laboratory studies verified the feasibility of continuous water recovery from synthetic brackish groundwater and seawater (Lotfi et al., 2015; Majeed et al., 2015; Phuntsho et al. 2012a, 2012b, 2013, 2014, Sahebi et al., 2015). A pilot-scale fertilizer drawn forward osmosis and nanofiltration (FDFO-NF) was recently established and had been successfully operated for six months (Phuntsho et al., 2016). Although the prior studies have investigated both single chemical reagent such as NH_4NO_3 and KCl, and blended draw solutes containing defined chemicals, commercial all-purpose fertilizers with a full-spectrum supplement of nutrients that are designed for practical applications have not been well examined in FO. A recent study demonstrated the osmotic dilution of the commercial all-purpose liquid fertilizers (Xie et al., 2015); however, liquid fertilizers are less favored than solid fertilizers because of the problems associated with storage and transportation. Therefore, there is a need to study water recovery by using commercially available solid fertilizers.

In this study, three commercial fast-release and all-purpose solid fertilizers were examined as draw solutes in a submerged FO system for water extraction from either DI water or the treated wastewater. The submerged FO configuration was employed because it has less energy consumption, rendering a small footprint, more operation flexibility, and easily scalable features (van Haandel and van der Lubbe, 2012), compared to cross-flow FO systems. Water flux and recovery as a percentage of required water for fertilizer dilution were evaluated with different fertilizers or concentrations. The detailed nutrient distribution (N/P/K) in both draw and feed as well as nutrient loss was investigated. Operation modes and energy consumption of the FO system were investigated and analyzed.

2. Materials and methods

2.1. Characteristics of fertilizers and preparation of draw solution

The commercial all-purpose solid fertilizers were obtained from retailers with detailed information in Table S2. All three fertilizers (noted as “F1”, “F2”, and “F3”) are widely used on farms and gardens for high yields. Due to the complexity of fertilizer composition, the fertilizer concentration was quantified by total nitrogen concentration, which was calculated based on the information from the manufacturer. For example, 1 M fertilizer in this study means its theoretical total nitrogen concentration is 1 mol L^{-1}. To prepare draw solutions, fertilizer was first dissolved in 100 mL DI water with pH adjustment (0.2 mol L^{-1} NaOH) to around 7.0 and then centrifuged at 5000 rpm for 10 min to remove undissolved particles/precipitants. Of this 100-mL solution, 10 mL was used to analyze the nutrient concentrations and 85 mL was applied as the draw solution. The remaining solids were preserved in fridge and could be added to final diluted fertilizers to avoid possible loss of trace elements (not studied here).

2.2. Setup and operation of a submerged FO system

The flat-plate FO cell contained two pieces of cellulose triacetate (CTA) membranes with a total surface area (S) of 0.0025 m^2 (Hydration Technologies Inc., Albany, OR, USA) and being installed on both sides of the FO cell, creating a middle chamber of 13 mL for draw solution. The CTA membrane had a guaranteed pH tolerance of 2–12 suggested by its manufacturer (Alsvik and Hägg, 2013). Plastic mesh was applied outside the FO membranes to prevent potential swelling. The FO cell was submerged in the feed solution in a 1-L plastic beaker (Fig. S1), and the feed solution was either DI water or the treated wastewater (Peppers Ferry Wastewater Treatment Plant, Radford, VA, USA). The feed solution was supplemented periodically to maintain a constant liquid volume of 500 mL. The characteristics of the treated wastewater are shown in Table S3. The FO system was operated under a batch mode with different fertilizers and/or various initial concentrations. For each batch test, 85 mL fertilizer solution was recirculated in the middle chamber of the FO cell at 100 mL min^{-1} (6.7 cm s^{-1}) unless stated elsewhere. Water samples were taken every 24 h for water quality analysis. The whole experiment was operated in a temperature-controlled lab (20 ± 2 °C) with a centralized air conditioning system.

2.3. Experimental procedure

A series of system optimization experiments (Table S4) were performed with DI water as the feed, including operation mode (i.e. membrane orientation), fouling control, reverse solute flux (RSF), fertilizer (draw) concentration. The active layer of the CTA membrane faced either draw (AL-D, PRO mode) or feed (AL-F, FO mode) to examine the effect of different operating modes using 1-M F1 as the draw. The F1 concentration was varied at 1 M, 2 M, and 3 M for studying water extraction and dilution rates. Comparison of three fertilizers (F 1–3) was conducted by operating the FO system with each fertilizer at a concentration of 1 M and in the FO mode. The optimized operation conditions (above-mentioned) were applied for examining water recovery from the treated wastewater by using the treated wastewater as the feed and 1-M F1 as the draw. Different recirculation rates, i.e. 10 mL min^{-1}, 50 mL min^{-1} and 100 mL min^{-1}, were successively investigated towards minimized energy consumption by the FO system. A batch test was terminated if the specific water flux (J_{sp}) at the last hour of each 24-h cycle was less than 1.0 LMH, according to a previous study (Qin and He, 2014).

The fouling of the FO membrane was studied with or without *in situ* fouling control in an FO mode. The pristine membrane was operated under the FO mode for water extraction (first test), and without any chemical cleaning, it was directly applied in the second test for determination of fouling situation; *in situ* chemical cleaning was then performed prior to the third test to investigate the fouling control performance. Due to the complex characteristics of fertilizer solution, fouling should be expected on the porous supportive layer (draw chamber), including the irreversible clogging by sparingly dissolved $FePO_4$, $Cu_3(PO_4)_2$ and $Zn_3(PO_4)_2$. Effective removal of resistant foulants could be achieved by three-stage chemical washing at the end of each batch test: acid (HCl, pH = 3), base (NaOH, pH = 11), and oxidant (NaClO, 10% v/v), and each stage lasted for 30 min, followed by 30 min rinse with DI water. The chemical cleaning was applied only to the draw side, where severe fouling was expected. Although using wastewater as a draw could cause fouling on the feed side of the FO membrane, the treated wastewater contained very low concentrations of organic and inorganic contaminants and the resulted fouling could be removed by backwash and/or flushing. All the cleaning solutions were reused over the 4-month operation, thereby lowering the related cost and limiting their environmental effects under proper control.