Transport and accumulation of organic matter in forward osmosis-reverse osmosis hybrid system: Mechanism and implications

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A B S T R A C T

The productivity and sustainability of forward osmosis (FO) – reverse osmosis (RO) system could be hindered by contaminant accumulation in the draw solution. A significant, progressive contaminant accumulation was observed when digested sludge was processed by the FO-RO system. The FO-RO system achieved stable water production and high rejections of dissolved organic matter; however, progressive contaminant accumulation was evident in the draw solution. Mechanism for contaminant accumulation was elucidated by examining the passage and accumulation of dissolved organic matter using fluorescence excitation emission matrix (EEM) spectroscopy and size exclusion (SEC) chromatography. Contaminant that accumulated in the draw solution exhibited a distinct signature in the fluorescence EEM spectra at peak T_1, suggesting protein-like substance. The molecular weight of the protein-like substance was resolved by SEC chromatography, identifying a molecular weight of 200 g/mol. The molecular weight of the protein-like substance was between the estimated molecular weight cut-offs of RO and FO membranes. As a result, such low molecular weight protein-like substance diffused through the FO membrane, and was largely rejected by the RO membrane by the virtue of steric hindrance mechanism, thereby accumulating in the draw solution of the closed-loop FO-RO system.

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1. Introduction

Forward osmosis (FO), an osmosis-driven membrane process, could potentially advance wastewater treatment and reuse [1]. FO utilizes the osmotic pressure of a highly concentrated draw solution as the driving force to transfer water from the feed solution to the draw solution through a dense polymeric membrane. FO has demonstrated a much lower fouling propensity and higher fouling reversibility than RO, which was attributed to the lack of applied hydraulic pressure [2–5]. Consequently, FO is widely used to treat low quality feedwaters, including landfill leachate [6], anaerobic digester concentrate [7], activated sludge solution [8,9], and municipal wastewater [10–12].

Re-concentrating diluted draw solution and producing purified water demand FO process to be coupled with a downstream process, such as nanofiltration (NF) [13], reverse osmosis (RO) [14–16], or membrane distillation (MD) [11,12,17,18]. Generally, these hybrid systems purified either wastewater effluent or seawater by double membrane barriers, achieving high rejections of most contaminants. For instance, drinking water quality can be obtained

by the FO-RO hybrid system when Hancock et al. [19] examined long-term performance of an FO-RO hybrid system processing 900,000 L of effluent from a membrane bioreactor.

The closed-loop FO-based process is challenged by contaminant accumulation in the draw solution. Indeed, there was a notable build-up of organic matter and micropollutants in the draw solution in an FO-MD system [11,12]. This accumulation was mainly driven by the near complete rejection of non-volatile solutes by the MD membrane in the FO-MD hybrid system, thereby leading to an undesirable contaminant accumulation in the draw solution. A similar concept was also modelled in an FO-RO system, where the RO membrane has higher rejection than the FO membrane [20]. For example, D'Haese et al. [21] modelled micropollutant accumulation in an FO-RO hybrid system, and predicted that an elevated micropollutant concentration in the draw solution deteriorated the product water quality. However, the underlying mechanisms governing the contaminant accumulation phenomenon remain largely unknown.

The ability of FO-RO system to process digested sludge and recover valuable nutrients could provide a unique perspective to examine contaminant accumulation in the FO-RO system [11]. The complex constituents in digested sludge comprises high concentration of nutrient ions (ammonium and phosphate), and a wide spectrum of dissolved organic matter whose concentrations

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were several orders of magnitude higher than wastewater effluent or seawater [22,23]. This magnification allows us to precisely capture the passage through, and accumulation of these contaminants in the FO-RO system. For example, Valladares Linares et al. [23] employed liquid chromatography with organic carbon detector to examined the transport of dissolved organic matter through the FO membrane, and identified an increase in the low molecular weight organic substances in the draw solution at the conclusion of the experiment. In another study, Hancock et al. [19] used fluorescence excitation and emission matrix spectroscopy to monitor the draw solution quality where an increase in fluorescence signature of protein-like substances was observed. However, there lacked an in-depth examination of the transport of dissolved organic matter, and a comprehensive understanding of the underlying mechanism in the contaminant accumulation phenomenon in FO-RO system. Such knowledge can be instrumental to other FO-based closed-loop system, as well FO-membrane distillation (MD) [11,12,24], and FO-electrodialysis (ED) [25] where the contaminant build-up in the draw can be a key issue in a sustainable, long-term operation.

The aim of this study is to investigate the mechanism of contaminant accumulation in the closed-loop FO-RO system processing low quality digested sludge feed. The passage and subsequent accumulation of nutrients and dissolved organic matter in the FO-RO system were examined and quantified. Species and the corresponding molecular weight of dissolved organic matter in the draw solution and permeate were characterised by fluorescence excitation and emission spectroscopy and size exclusion chromatography. Membrane pore radii and molecular weight cutoffs of FO and RO membrane were estimated and correlated to the characteristics of dissolved organic matter to delineate contaminant accumulation in the draw solution.

2. Materials and methods

2.1. Digested sludge feed

Anaerobically digested sludge was collected from an anaerobic digester of the Eastern Treatment Plant in Melbourne (Victoria, Australia). The sludge centrate was obtained by screening the sludge through a 0.5 mm sieve, then centrifuging at 4,500 rpm for 25 min (Avanti J-26S XPI, Beckman Coulter, Fullerton, CA). The centrate was kept at 4°C and used within two weeks to ensure the consistent solution chemistry.

2.2. Forward and reverse osmosis membranes

A flat-sheet, polyamide thin-film composite membrane from Hydration Technology Innovations (Albany, OR) was used for the FO process. The FO membrane is made of a thin selective polyamide active layer on top of a porous polysulfone support layer [26,27]. An RO membrane (SW30) was supplied by Dow FilmTec (Minneapolis, MN), which was made of a thin aromatic polyamide active layer and a thick, porous support layer. Key membrane transport parameters, membrane pore radii and molecular weight cutoffs were determined to elucidate the contaminant accumulation phenomenon in the FO-RO system.

2.2.1. Key mass transfer parameters

Key membrane transport parameters were characterised following the protocol previously described by Cath et al. [27], including the pure water permeability coefficient of the active layer, A, and the salt (NaCl) permeability coefficient of the active layer, B. Briefly, the membrane A and B values were determined using a laboratory RO cross-flow filtration system (Section 2.3).

The membrane A value was measured at a pressure of 10 bar using deionised water. NaCl was then added to the feed solution to determine the B value. The RO system was stabilised for two hours before recording permeate water flux with 2000 mg/L NaCl solution, J_w^{NaCl}, and taking feed and permeate samples to determine the observed NaCl rejection, R_o. The membrane A value was calculated by dividing the pure water permeate flux (J_w^{RO}) by the applied hydraulic pressure, ΔP:

$$A = J_w^{RO}/\Delta P \tag{1}$$

The observed salt (NaCl) rejection, R_o, was calculated from the difference between the bulk feed (c_b) and permeate (c_p) salt concentrations, $R_o = 1 - c_p/c_b$, and then the membrane B value was determined from:

$$B = J_w^{NaCl}\left(\frac{1 - R_o}{R_o}\right)\exp\left(-\frac{J_w^{NaCl}}{k_f}\right) \tag{2}$$

where k_f is the mass transfer coefficient for the cross-flow of RO membrane cell.

The mass transfer coefficient (k_f) was experimentally determined using the Sutzkover et al. method [28]. Using the permeate and feed salt concentrations (and thus, the corresponding osmotic pressures based on van't Hoff equation, π_p and π_b, respectively), the applied pressure (ΔP), the pure water flux (J_w^{RO}), and the permeate flux with the 2000 mg/L NaCl solution (J_w^{NaCl}) enabled the evaluation of the salt concentration at the membrane surface. This membrane surface concentration was used with thin-film theory for concentration polarization to determine k_f:

$$k_f = \frac{J_w^{NaCl}}{\ln\left[\frac{\Delta P}{\pi_b - \pi_p}\left(1 - \frac{J_w^{NaCl}}{J_w^{RO}}\right)\right]} \tag{3}$$

2.2.2. Estimation of average membrane pore radius

A set of inert, neutral organic tracers – erythritol, xylose, and glucose (Sigma-Aldrich, Saint Louis, MO) – were used to estimate the membrane average pore radius. These organic tracers are neutrally charged, and do not adsorb to the membrane. As a result, they do not have specific attractive or repulsive interaction with the membrane. The solutes were individually dissolved in Milli-Q water to obtain a concentration of 50 mg/L (as total organic carbon (TOC)). Prior to the RO filtration experiments with these reference organic solutes, the membrane was pre-compacted at 18 bar for one hour and subsequent experiments were conducted at 8, 10, 12, 14, and 16 bar with a cross-flow velocity of 9 cm/s. At each pressure value, the RO filtration system was operated for one hour before taking permeate and feed samples for analysis. This pressure range ensured that the organic tracer rejection can be clearly distinguished at a reasonable permeate flux range.

The membrane average pore radius was determined based on the pore hindrance transport model previously described by Xie et al. [29] for FO membranes. The pore hindrance model that incorporates steric exclusion and hindered convection and diffusion was successfully used to estimate the membrane pore size, including nanofiltration and reverse osmosis membranes [30,31], as well as FO membranes [29,32,33]. In this model, the membrane was considered as a bundle of cylindrical capillary tubes with the same radius. In addition, it was assumed that the spherical solute particles enter the membrane pores in random fashion. Specifically, the ratio of solute radius (r_s) to the membrane pore radius (r_p), $\lambda = r_s/r_p$, is related by the distribution coefficient φ when only steric interactions are considered:

$$\varphi = (1 - \lambda)^2 \tag{4}$$