LONG-TERM FOULING AND PERFORMANCE OF FORWARD OSMOSIS MEMBRANES TREATING ACTIVATED SLUDGE AND OIL AND GAS PRODUCED WATER

by

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ABSTRACT

Water reuse practices are growing in the United States in order to provide fresh water supplies from unconventional resources. One promising technology is forward osmosis (FO), which uses osmotic pressure to drive the diffusion of water across a semipermeable membrane and provide high rejection of a broad range of constituents and contaminants, including trace organic compounds. As with all membrane technologies, membrane fouling is a major contributor to operating costs. FO fouling literature lacks studies that use real wastewater for long treatment periods, and therefore, these studies may not represent realistic FO operations. Thus, the focus of this thesis was to investigate FO fouling and performance in two important water reuse waste streams: municipal wastewater and oil and gas produced water.

The thesis is comprised of two studies that compared the performance and fouling of cellulose triacetate (CTA) and polyamide thin film composite (TFC) membranes. The first study used CTA and TFC membranes to treat high-salinity and low-salinity activated sludge for 100 days, and the second study used CTA and improved TFC membranes to treat oil and gas produced water for three weeks. Both studies measured virgin and fouled membrane performance using water flux, reverse salt flux (RSF), and specific reverse salt flux (SRSF). Membrane autopsies were performed to understand the importance of physiochemical membrane properties on fouling potential and to determine the organic and inorganic composition of fouling layers. The second study expanded on the first study and used chemically enhanced osmotic backwashing for membrane cleaning, streaming potential analysis of membrane surfaces, and gas chromatography-mass spectroscopy for evaluating the rejection of hydrocarbons by the FO membranes.

The studies found that CTA membranes outperformed TFC membranes with higher water flux, lower RSF, and lower SRSF. TFC membranes had more ideal virgin membrane properties (e.g., smooth, hydrophilic, and neutrally charged surfaces), but were more prone to fouling and demonstrated that conventional characterization techniques do not accurately predict fouling potential. In both studies, the organic composition of the fouling was similar for both membrane types, but the inorganic fouling varied according to membrane type, wastewater composition, and cleaning. The second study found over 90% organic compound rejection for both membranes, in which TFC membranes had superior rejection of neutral hydrophobic compounds.
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<tr>
<td>3D EEM</td>
<td>Three dimensional excitation-emission matrix</td>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>CA</td>
<td>Cellulose acetate</td>
</tr>
<tr>
<td>CEOB</td>
<td>Chemically enhanced osmotic backwash</td>
</tr>
<tr>
<td>CECP</td>
<td>Cake enhanced concentration polarization</td>
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<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
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<tr>
<td>CTA</td>
<td>Cellulose triacetate</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
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<tr>
<td>DS</td>
<td>Draw solution</td>
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<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediamine-tetraacetic acid</td>
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<tr>
<td>EPS</td>
<td>Extracellular polymeric substances</td>
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<tr>
<td>ESEM</td>
<td>Environmental scanning electron microscope</td>
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<tr>
<td>FO</td>
<td>Forward osmosis</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<tr>
<td>GC-MS</td>
<td>Gas chromatography-mass spectroscopy</td>
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<tr>
<td>HRT</td>
<td>Hydraulic retention time</td>
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<tr>
<td>HS</td>
<td>High-salinity</td>
</tr>
<tr>
<td>HTI</td>
<td>Hydration technology innovations, LLC</td>
</tr>
<tr>
<td>IC</td>
<td>Ion chromatograph</td>
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<tr>
<td>ICP-AES</td>
<td>Inductively coupled plasma atomic emission spectroscopy</td>
</tr>
<tr>
<td>LS</td>
<td>Low-salinity</td>
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<tr>
<td>MBR</td>
<td>Membrane bioreactor</td>
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<tr>
<td>MF</td>
<td>Microfiltration</td>
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<tr>
<td>MLSS</td>
<td>Mixed liquor suspended solids</td>
</tr>
<tr>
<td>MLVSS</td>
<td>Mixed liquor volatile suspended solids</td>
</tr>
<tr>
<td>MPA</td>
<td>Minimum projection area</td>
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<tr>
<td>NF</td>
<td>Nanofiltration</td>
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<tr>
<td>OMBR</td>
<td>Osmotic membrane bioreactor</td>
</tr>
<tr>
<td>PA</td>
<td>Polyamide</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbon</td>
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<tr>
<td>RO</td>
<td>Reverse osmosis</td>
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<tr>
<td>RSF</td>
<td>Reverse salt flux</td>
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<tr>
<td>SB-MBR</td>
<td>Sequencing batch membrane bioreactor</td>
</tr>
<tr>
<td>SBR</td>
<td>Sequencing batch reactors</td>
</tr>
<tr>
<td>SMP</td>
<td>Soluble microbial products</td>
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<tr>
<td>SPE</td>
<td>Solid-phase extraction</td>
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<tr>
<td>SRSF</td>
<td>Specific reverse salt flux</td>
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<tr>
<td>SRT</td>
<td>Solids retention time</td>
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<tr>
<td>TDS</td>
<td>Total dissolved solids</td>
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<tr>
<td>TFC</td>
<td>Thin film composite</td>
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<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<td>--------------------------------------------</td>
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<tr>
<td>TN</td>
<td>Total nitrogen</td>
</tr>
<tr>
<td>TP</td>
<td>Total phosphorus</td>
</tr>
<tr>
<td>TSS</td>
<td>Total dissolved solids</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration</td>
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<tr>
<td>UFO-MBR</td>
<td>Ultrafiltration-osmotic membrane bioreactor</td>
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CHAPTER 1
INTRODUCTION

Water reuse and desalination technologies are increasingly implemented to augment fresh water supplies threatened by population growth, water scarcity, and climate change [1-3]. Water reuse and desalination practices often rely on advanced water treatment technologies to produce high quality water from highly impaired waters. The technology of choice is often membrane separation [3] because membranes reliably produce high quality water, require smaller footprints, and use less chemicals [4]. One promising membrane technology is forward osmosis (FO). FO uses semipermeable membranes that separate impaired waters from a high saline draw solution (DS) and use osmotic pressure difference across the membrane to allow the diffusion of water from the feed into the DS. The membranes reliably reject dissolved constituents and produce water suitable for reuse and direct discharge to the environment [5].

FO membranes have successfully met reuse requirements for two important waste streams: municipal wastewater [6-8] and oil and gas produced water [9-11]. FO membranes reliably reject ions [11, 12], pathogens [13], and trace organic compounds [7, 14-21] from municipal wastewater, making FO a suitable technology for potable reuse that will protect human health and the environment. Additionally, the recent surge in oil and gas production may strain current water stressed areas [22], and direct water reuse is becoming increasingly important for oil and gas operators [23, 24]. FO membranes have recently demonstrated adequate treatment for reuse or discharge [10], potential economic benefits [25], and the capability to operate in conditions unsuitable for conventional membranes [26, 27].

Despite the potential of FO applications, one of the major hurdles to the advancement of the technology is membrane fouling. Membrane fouling is a major inefficiency that lowers water production, increases energy requirements, shortens membrane life, and increases cleaning and chemical costs [4]. Abundant FO fouling literature exists, but most studies use synthetic wastewater that may inaccurately represent FO fouling [28, 29], and experiments are conducted for short periods of time and may not depict realistic FO membrane performance.
1.1 Objectives and scope of work

The objectives of this thesis were to evaluate the long-term performance and fouling of FO membranes during real wastewater treatment. The thesis is comprised of two separate studies that focused on the treatment of municipal wastewater and oil and gas produced water. Each study used bench scale systems to treat wastewater, foul membranes, and measure performance parameters before and after fouling. Membrane autopsies were performed to understand the importance of physicochemical membrane properties on fouling potential, to compare physicochemical properties of virgin and fouled membranes, and to determine the organic and inorganic composition of fouling layers. The findings demonstrated the robustness of FO membranes in municipal wastewater and produced water, and highlighted important membrane and wastewater characteristics that impacted long-term FO operation.

Thesis organization

This thesis combines two papers that describe research conducted over the past two years. The first paper investigated long-term FO membrane treatment of high-salinity and low-salinity activated sludge and is prepared for publication in the Journal of Membrane Science. The second paper investigated long-term FO membrane treatment in oil and gas produced water and is prepared for publication also in the Journal of Membrane Science.

1.1.1 Long-term evaluation of FO membranes during activate sludge treatment

The second chapter of the thesis describes FO membrane performance and fouling during 100 days of continuous activated sludge treatment. The study compared the industry standard cellulose triacetate (CTA) FO membrane and the emerging polyamide thin film composite (TFC) FO membrane. The membranes treated high-salinity and low-salinity activated sludge from two membrane bioreactors. Water flux, reverse salt flux (RSF), and specific reverse salt flux (SRSF) were measured for virgin and fouled membranes to evaluate membrane performance. Membrane autopsies were used to determine organic and inorganic composition of fouling layers, to understand the effects of membrane properties on fouling potential, and to compare physicochemical membrane properties before and after fouling. The study demonstrated that FO membranes provided long-term, robust treatment under varied activated sludge compositions.
1.1.2 FO fouling, performance, and cleaning during produced water treatment

The third chapter of this thesis investigated fouling, cleaning, and performance of CTA and TFC FO membranes during long-term treatment of produced water. The study used similar analyses to understand long-term fouling and performance, including water flux, RSF, and SRSF, and membrane autopsies were conducted to better understand changes to membrane properties. The study expanded on the previous investigation by incorporating membrane cleaning, additional membrane characterization, and additional water analyses. Streaming potential was used to measure surface charge changes (zeta potential) as membranes fouled, and gas chromatography-mass spectrometry (GC-MS) was used to investigate the rejection of volatile and semi-volatiles hydrocarbons.

1.2 References


CHAPTER 2
EVALUATION OF FORWARD OSMOSIS MEMBRANE PERFORMANCE AND FOULING DURING LONG-TERM OSMOTIC MEMBRANE BIOREACTOR STUDY

Modified from a paper for possible publication in the *Journal of Membrane Science*

Elizabeth A. Bell¹, Ryan W. Holloway¹,², and Tzahi Y. Cath¹*

2.1 Abstract
Forward osmosis membrane performance and fouling was studied during 100 days of continuous activated sludge treatment. The study compared cellulose triacetate and polyamide thin film composite membranes that treated high salinity and low salinity activated sludge from two membrane bioreactors. Water flux, reverse salt flux, and specific reverse salt flux were measured to evaluate the performance of virgin and fouled membranes. Membrane autopsy was used to investigate foulant composition and compare physicochemical membrane properties before and after fouling. The results indicated that both membrane types attained steady-state water flux over 100 days, characterized by an initial decline and subsequent steady-state period. Biofouling and organic fouling caused overall water flux decline, in which foulants were identical between membrane and activated sludge types. Water flux results were similar between the two activated sludge types and demonstrated that FO membrane performance and fouling was independent of total dissolved solids, calcium, and mixed liquor suspended solid concentrations. The study also found that hydrophilicity and surface roughness did not contribute substantially to membrane fouling. Cellulose triacetate membranes outperformed thin film composite membranes, with lower fouling propensity, higher water flux, lower reverse salt flux, and lower specific reverse salt flux.

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2.2 Introduction

The osmotic membrane bioreactor (OMBR) is a novel advanced wastewater treatment system that uses highly selective forward osmosis (FO) membranes to allow water permeation from activated sludge feed solutions to saline draw solutions (DS) [1-5]. The process is driven by the osmotic pressure difference across an FO membrane, between a low-salinity activated sludge feed stream and high-salinity DS. The nonporous FO membranes used in OMBRs reliably reject pathogens [6], trace organic compounds [5, 7-14], and ions [15, 16], making the OMBR an attractive technology for water reuse. However, one of the main challenges associated with the operation of OMBR and conventional membrane separation processes is membrane fouling, which shortens the life of the membrane [17, 18], decreases water production [18, 19], and increases operating costs [19].

FO is commonly described as having a low fouling propensity compared to pressure driven membrane technologies such as reverse osmosis (RO) and nanofiltration (NF) [20-22]. Although FO membranes have a lower fouling propensity, FO membrane fouling still occurs and periodic membrane cleaning is required [1, 3]. Furthermore, OMBR membrane cleaning is more difficult than cleaning microfiltration (MF) and ultrafiltration (UF) membranes used in membrane bioreactors (MBRs), which are commonly cleaned using hydraulic and chemical backwashing [18]. OMBR membranes can be cleaned using osmotic backwashing, in which the concentrated DS is flushed from the DS side of the membrane and replaced with a very low-salinity cleaning solution (e.g., deionized water or de-chlorinated municipal water). The low-salinity cleaning solution diffuses from the DS through the membrane to the feed; thereby, attached organic and inorganic particles are dislodged and dissolved from the membrane surface. Due to the complexity and time intensive nature of osmotic backwashing, it is important to mitigate FO membrane fouling to minimize the frequency of FO membrane cleaning in OMBR operations.

In general, membrane fouling is grouped into three categories: biofouling, organic fouling, and inorganic fouling (i.e., scaling) [23]. Biofouling is the result of biofilm formation through a series of fundamental steps, including reversible attachment of planktonic bacteria, irreversible attachment of more bacterial cells (e.g., through bacterial quorum-sensing), cell growth and extracellular polymeric substance (EPS) production, and ultimately the formation of a mature biofilm [24, 25]. Organic fouling is the adsorption of organic compounds (e.g., EPS, soluble microbial products (SMPs), and humic substances) from the feed stream onto the mem-
brane surface [18, 23, 25], and inorganic fouling is the chemical or biological precipitation of inorganic solids (e.g., struvite [26], CaCO\textsubscript{3} [27], and CaSO\textsubscript{4} [28]) onto the membrane surface.

The extent of membrane fouling due to biofouling, organic fouling, and inorganic fouling depends on a number of factors, including physicochemical membrane properties and wastewater composition [25, 29]. Hydrophilic membranes with relatively low roughness and neutral charge are generally considered to be the most resistant to fouling [25, 30, 31]. Although these physicochemical properties have been used to explain differences in membrane fouling propensity, the effect of physicochemical membrane properties on fouling is uncertain. For example, Wang et al. [32] and Maximous et al. [33] concluded that hydrophilicity only deters initial colloidal fouling (e.g., bacterial attachment) and enhances membrane cleaning efficacy, while long-term fouling is dominated by foulant-foulant interactions. In terms of surface morphology, several studies have shown that smoother membranes may facilitate more effective membrane cleaning but no clear correlation between fouling and membrane roughness could be established [33, 34]. Most studies still propose that hydrophilic and smooth membranes should be used to minimize fouling, but these studies also suggest that further work is needed to understand membrane properties and their effects on long-term fouling [35-38].

The composition of the wastewater is also critical to FO membrane fouling [25]. The organic and inorganic composition of the activated sludge in OMBRs is very different compared to more traditional activated sludge processes because the OMBR is often operated at high solids retention times (SRT) and elevated salt concentrations. The salt concentration of the activated sludge is higher in OMBRs because salts contained in the influent are retained in the bioreactors by the high rejection FO membranes and salts diffuse across the FO membrane from the DS to the feed. Salt accumulation in the OMBR has been shown to inhibit microbial activity [1, 39, 40], reduce the osmotic driving force for water flux (difference in salt concentration between the feed and DS) [1, 41] and lead to higher divalent ion concentrations in the bioreactors (e.g., Ca\textsuperscript{2+} and Mg\textsuperscript{2+}) [1, 35, 42, 43]. Divalent ions are considered major contributors to fouling due to bridging between the divalent ions and organic matter, resulting in more severe membrane fouling [20, 35, 36]. Salt accumulation also increases the ionic strength of the wastewater, which may increase bacterial adhesion to the membrane [44] and change the membrane surface charge (zeta potential) [45]. Coday et al. [45] demonstrated that increasing ionic strength reduced the
negative charge of FO membranes, which can potentially affect membrane fouling propensity and the bidirectional diffusion of ionic constituents across the membrane [45-47].

The majority of studies exploring FO membrane fouling mechanisms have used synthetic feed solutions [3, 20, 22, 29, 35-37, 48-57]; however, relatively few studies have examined OMBR membrane fouling using real wastewaters [1, 2, 42, 58, 59]. This is a major shortcoming in the literature because the use of synthetic or real wastewater can substantially influence the extent and characteristics of the fouling layer and membrane integrity [60]. Additionally, limited data is available on fouling and performance of different FO membrane materials and only few studies have compared the fouling and performance of commercially available FO membranes [35, 61].

Thus, the main objective of the current study was to investigate and compare the performance and fouling of commercial cellulose triacetate (CTA) and polyamide thin film composite (TFC) FO membranes treating water from two different continuously operated activated sludge treatment systems: a low-salinity MBR and a high-salinity OMBR. The objectives of the study were to (1) evaluate and compare CTA and TFC membrane performance over 100-days of biological wastewater operation, (2) examine physiochemical membrane property changes, and (3) investigate the effects of feed stream salinity on FO membrane fouling and performance.

2.3 Materials and methods

FO membrane performance (water flux and reverse salt flux (RSF)) and fouling were studied with CTA and TFC membranes using a field-operated membrane fouling system treating high- and low-salinity activated sludge for up to 100-days. Additional laboratory bench-scale experiments were conducted and several membrane characterization techniques were used to study the performance and physiochemical characteristics of the FO membranes before and after long-term fouling tests.

2.3.1 Pilot-scale test systems

Two membrane bioreactors were used to provide high- and low-salinity activated sludge to CTA and TFC membranes. The membranes treated high-salinity activated sludge from a hybrid ultrafiltration OMBR (UFO-MBR) and low-salinity activated sludge from a sequencing batch MBR (SB-MBR). The UFO-MBR and SB-MBR were continuously fed with municipal...
wastewater and were located at the Water Reclamation Research Facility of the Colorado School of Mines in Golden, Colorado.

2.3.1.1 UFO-MBR

High-salinity feed was provided by a continuously operated UFO-MBR described in a previous publication [1]. The UFO-MBR system consists of an anoxic tank to remove nitrate, a UF unit to extract nutrients and ions, an aerobic tank to oxidize ammonia, a submerged FO membrane cassette, and an RO system for high-quality water production and DS reconcentration. The total dissolved solids (TDS) concentration of the activated sludge in the anoxic and aerobic tanks was maintained at approximately 4,200 mg/L by adjusting the UF permeate flowrate. The ion concentrations in the UFO-MBR process tanks are summarized in Table 2.1.

Table 2.1. Average dissolved ion concentrations (mg/L) in the UFO-MBR and SBMBR over the experimental period

<table>
<thead>
<tr>
<th>Analyte</th>
<th>UFO-MBR Average (mg/L)</th>
<th>SBMBR Average (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>125.3</td>
<td>35.2</td>
</tr>
<tr>
<td>Potassium</td>
<td>34.2</td>
<td>10.0</td>
</tr>
<tr>
<td>Magnesium</td>
<td>40.3</td>
<td>10.0</td>
</tr>
<tr>
<td>Sodium</td>
<td>1083.2</td>
<td>53.8</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>12.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Sulfur</td>
<td>106.8</td>
<td>26.0</td>
</tr>
<tr>
<td>Silica</td>
<td>17.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Fluoride</td>
<td>5.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Chloride</td>
<td>2291.7</td>
<td>72.5</td>
</tr>
<tr>
<td>Bromide</td>
<td>0.2</td>
<td>0.03</td>
</tr>
<tr>
<td>Nitrate</td>
<td>141.9</td>
<td>30.5</td>
</tr>
<tr>
<td>Phosphate</td>
<td>42.7</td>
<td>8.4</td>
</tr>
<tr>
<td>Sulfate</td>
<td>330.6</td>
<td>79.4</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>4231.6</strong></td>
<td><strong>334.0</strong></td>
</tr>
</tbody>
</table>

2.3.1.2 SB-MBR

Activated sludge from the SB-MBR was used to supply low-salinity feed to the FO membrane fouling system. The SB-MBR is composed of two sequencing batch reactors (SBR) and two membrane tanks, described in detail elsewhere [62]. Carbon, phosphorus, and nitrogen are removed in the SBR by aeration cycles that control aerobic and anoxic conditions in the bio-
reactors. Wastewater treated in the SBR is recirculated from the reactors to two parallel-operated membrane tanks containing 74 m$^2$ of hollow-fiber UF membranes (37 m$^2$ per tank) that extracted water from the activated sludge. The average TDS concentration of the UF permeate was approximately 300 mg/L over the testing period. Concentrations of individual ions measured during the study are also summarized in Table 2.1.

### 2.3.2 Membranes

CTA and TFC membranes were provided by Hydration Technology Innovations, LLC (Albany, OR). Membranes were mounted in custom-made cross-flow membrane cells with an effective membrane area of 190 cm$^2$ each. The dimensions of the feed and DS flow channels were 25.4 x 7.62 x 0.24 cm and 25.4 x 7.62 x 0.16 cm, respectively. All field and laboratory bench-scale tests were conducted with the active layer of the membranes facing the feed. Tricot fine-mesh spacers were placed in the DS flow channel to provide turbulence enhancement and mechanical support, and the feed channels were operated with no spacers installed.

### 2.3.3 Virgin membrane integrity testing

Membrane performance and integrity was evaluated using water flux and RSF tests conducted with field and laboratory systems. Water flux was calculated from the change in permeated water volume from the feed per unit membrane area per time (L/m$^2$/hr). RSF was calculated from the change in salt mass in the feed per unit membrane area per time (g/m$^2$/hr). Additionally, specific reverse salt flux (SRSF) (mg/L) was calculated from the ratio of RSF to water flux for all virgin and fouled membranes. SRSF is a parameter related to membrane efficiency and depends on active layer selectivity [63, 64].

Integrity tests were conducted on virgin membranes before the beginning of the fouling experiment to ensure that membranes were free of defects. Water flux, RSF, and SRSF were measured and virgin membranes with SRSF less than 1,000 mg/L were installed in the membrane fouling system. The integrity tests were conducted on a laboratory bench-scale system described in previous publications [16, 63, 65]. Data was collected (i.e., feed volume change) and temperature was controlled (i.e., system temperature of 20 °C) using data acquisition and instrument control system (LabJack, UE9-Pro, Lakewood, CO) and software (LabVIEW, National Instruments Corp., Austin, TX). The feed tank was filled with 3 L of 2 g/L NaCl and dosed with
deionized water to maintain constant volume. Feed conductivity was measured using a handheld probe (Oakton Instruments, Vernon Hills, IL) and was converted to NaCl concentration to calculate RSF. The DS was 1 L of 1 M NaCl and was allowed to dilute, similar to the operation during flux tests in the membrane fouling system (described in Section 2.3.4.3). The flows for feed and DS were co-current and feed and DS cross-flow velocities were 9.2 and 8.7 cm/s, respectively.

2.3.4 Membrane fouling experiments: set-up and procedure

The membrane fouling system was used to treat high- and low-salinity activated sludge with CTA and TFC membranes for 10, 40, 70, and 100-days. The UFO-MBR and SB-MBR were analyzed weekly for nutrients, cations, anions, and solids, and pH, conductivity, and temperature were measured daily in the MBRs. Weekly membrane performance tests were conducted and measured water flux using activated sludge as feed solution and 1 M NaCl as DS.

2.3.4.1 Membrane fouling system

Virgin membranes were installed in the membrane fouling system and operated continuously for 100 days. The membrane fouling system was comprised of 12 cross-flow membrane cells, two feed peristaltic pumps (Cole-Palmer, Vernon Hills, IL), one DS peristaltic pump, and one DS tank. Activated sludge from the adjacent UFO-MBR and SB-MBR systems provided high-salinity and low-salinity feed solutions, respectively, and 0.5 M NaCl was used as the DS. The feed and DS flow were countercurrent and the feed and DS cross-flow velocities were maintained at 5.5 cm/s and 4.3 cm/s, respectively. A picture and schematic drawing of the membrane fouling system are illustrated in Figure 2.1. The 12 cross-flow membrane cells were separated into four groups (three membrane cells per group) based on membrane type (CTA or TFC) and origin of activated sludge: CTA membrane with low-salinity activated sludge feed (“CTA-LS”), CTA membrane with high-salinity activated sludge feed (“CTA-HS”), TFC membrane with low-salinity activated sludge feed (“TFC-LS”), and TFC membrane with high-salinity activated sludge feed (“TFC-HS”). The membrane cells were operated in series within each group; thereby, the feed and DS exiting the first cell in the group fed the second cell, and the feed and DS exiting the second cell in the group fed the third cell. Membrane cells operated for 10, 40, 70, and 100-days. At the beginning of the experiment, the membrane fouling system was operated with twelve membranes cells online. One membrane cell was removed from each group after 40,
70, and 100-days of continuous operation. After removing one membrane cell from each group on day 40, a new virgin membrane cell was installed into each group and operated for 10-days before being removed from the system.

**Figure 2.1.** (a) Picture and (b) process flow diagram for membrane fouling system. The SB-MBR provided low-salinity (LS) activated sludge to CTA (“CTA-LS”) and TFC (“TFC-LS”) membranes, and the UFO-MBR provided high-salinity activated sludge to CTA (“CTA-HS”) and TFC (“TFC-HS”) membranes. Membranes were arranged in four groups and operated in series within each group. One tank provided draw solution (DS) to all four groups. Feed and DS flows operated co-currently. Arrows represent water flux from the feed solutions to the DS.

### 2.3.4.2 Membrane fouling system measurements

The UFO-MBR activated sludge, SB-MBR activated sludge, and DS were measured daily for conductivity, pH, and temperature using a handheld meter (Oakton Instruments, Vernon Hills, IL). Daily measurements were used to ensure that steady-state feed was supplied to the membrane fouling system and to operate the DS tank in batch mode. The DS tank was drained and replenished with 0.5 M NaCl solution when the DS conductivity reached 10 mS (0.1 M NaCl). The DS conductivity was always higher than the UFO-MBR and SB-MBR activated sludge conductivity to ensure that osmotic backwashing and fouling layer removal did not occur.

On a weekly basis, samples were collected from the influent, the UFO-MBR (anoxic tank, aerobic tank, and UF permeate), and the SB-MBR (SBRs, membrane tanks, and UF permeate). Samples were analyzed for nutrients (ammonia, nitrate, total nitrogen, total phosphorus, and chemical oxygen demand (COD)), solids (mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS)), cations, and anions. Nutrient concentrations were
measured using Hach TNTplusTM (Loveland, CO) reagent vials and Hach DR 5000TM spectrophotometer. DS samples were diluted with deionized water to ensure that sodium and chloride concentrations were within analytical limits. MLSS and MLVSS analysis was conducted using standard glass fiber filters according to Standard Method 2540. Ions were measured in the UF permeate from the SB-MBR and UFO-MBR in order to characterize the feed streams. Anion concentrations were measured using an ion chromatograph (IC) (ICS-90, Dionex, Sunnyvale, CA) and cations were measured using an inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Optima 5400, PerkinElmer, Fremont, CA). ICP-AES samples were acidified to a pH of less than 2 with nitric acid.

2.3.4.3 Membrane fouling system water flux testing

Weekly water flux tests were conducted for each membrane in the membrane fouling system using system equipment (e.g., peristaltic pumps, cross-flow membrane cells) in order to observe the effects of fouling on water flux. Activated sludge from the two MBRs was used as the feed during the field water flux tests to prevent disturbance or removal of the developed fouling layers. Water flux tests were conducted using 1 M NaCl DS that was allowed to dilute over a 90-minute testing period. The feed and DS flow direction (co-current) and flow velocities were consistent with the virgin membrane integrity tests (described above) to allow for comparisons between virgin and weekly water flux results.

2.3.5 Fouled membrane integrity testing

The membranes were removed from the membrane fouling system after the predetermined number of days (10, 40, 70, and 100 days) and water flux, RSF, and SRSF were measured. After the membranes were removed from the membrane fouling system cells, a coupon was cut from the fouled membrane, and coupons were installed into a smaller custom cross-flow membrane cell. The smaller cell had symmetrical feed and DS flow channels (21.91 x 5.40 x 0.32 cm) and an effective membrane area of 120 cm². Experiments were performed on the laboratory bench-scale system using the same cross-flow velocities, DS concentrations, and feed and DS temperatures used for the virgin membrane integrity tests.
2.3.6 Membrane characterization

Physiochemical membranes characteristics were evaluated for virgin and fouled CTA and TFC membranes. Membrane hydrophilicity was measured using contact angle via captive bubble. Fouling layers were examined with an environmental scanning electron microscope (ESEM). The elemental content of fouled layers were evaluated with energy dispersive spectroscopy (EDS). The biological and organic composition of the fouling layers was determined using Fourier transform infrared (FTIR) spectroscopy.

2.3.6.1 Contact angle

Contact angle measurements were taken to quantify hydrophilicity for virgin and fouled CTA and TFC membranes. Contact angles were measured using the captive bubble method with a computerized goniometer (Model 200-00, Rame-Hart Instrument Company, Netcong, NJ). Two coupons per membrane were sampled and sonicated for 30 minutes in a DI bath (Bransonic 221, Branson Cleaning Equipment Co., Shelton, CT). After sonication, the membrane coupons were immersed in deionized water, placed on the goniometer stage, and a 5 µL air bubble was pipetted onto the membrane active layer. Three bubbles per coupon were analyzed with three sets of measurements per bubble. Each set of measurements took 10 measurements in 0.1 seconds, which totaled 30 measurements per bubble.

2.3.6.2 Environmental scanning electron microscopy and energy dispersive spectroscopy

Virgin and fouled membrane cross-sections and surfaces were visually examined for damage and fouling with an ESEM (Quanta 600, FEI, Tokyo, Japan). Fouled membrane coupons were prepared for ESEM through immersion in Karnovsky’s fixative; dehydration with a graded series of ACS grade ethanol; and storage in a desiccator until analysis. Membranes were fractured with liquid nitrogen, and subsequently gold-sputtered (Technic Hammer VI, Cranston, RI) before analysis. In conjunction with ESEM, EDS (Genesis, EDAX, Mahwah, NJ) was used to determine the elemental content of inorganic deposits attached onto the membrane surface. ESEM images of the virgin CTA and TFC membrane surfaces and cross-sections are shown in Figure 2.2.
2.3.6.3 Fourier transform infrared spectrometer

To identify organic foulants and surface chemistry changes, the fouling and active layers of virgin and fouled membranes were analyzed with a FTIR spectrometer (Nicolet 4700 FTIR, Thermo Electron Corporation, Madison, WI) using the attenuated total reflection method. Virgin and fouled membrane coupons were prepared for FTIR analysis by drying in a desiccator for at least 24 hours before analysis.
2.4 Results and discussion

The performance and fouling of CTA and TFC membranes were examined during 10, 40, 70, and 100 days of high- and low-salinity activated sludge treatment. Membrane performance was evaluated with weekly water flux tests using the membrane fouling system and integrity tests using an FO bench scale system. The integrity tests measured water flux, RSF, and SRSF for virgin and fouled CTA and TFC membranes. Physiochemical membrane properties and fouling layer compositions were evaluated for virgin and fouled membranes.

2.4.1 Performance of membrane bioreactors

The UFO-MBR and SB-MBR influent, process tanks, and effluent were regularly analyzed for MLSS, MLVSS, pH, conductivity, and temperature to ensure that steady-state feed was provided to the FO membrane fouling system over the testing period. The overall MBR performance was also assessed using the percent removals of COD, total phosphorous (TP), and total nitrogen (TN) between the influent and effluent of each system. The results from these analyses are summarized in Table 2.2.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Unit</th>
<th>Influent</th>
<th>UFO-MBR</th>
<th>SB-MBR</th>
<th>Effluent</th>
<th>% Removal</th>
<th>Effluent</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Anoxic Tank</td>
<td>Aerobic Tank</td>
<td>Bioreactors</td>
<td>Tanks</td>
<td>Membrane Tanks</td>
<td></td>
</tr>
<tr>
<td>MLSS</td>
<td>g/L</td>
<td>0.14±0.02</td>
<td>1.21±0.7</td>
<td>1.53±1.0</td>
<td>5.05±1.5</td>
<td>6.28±1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MLVSS</td>
<td>g/L</td>
<td>0.13±0.03</td>
<td>1.18±0.7</td>
<td>1.48±1.0</td>
<td>4.74±1.3</td>
<td>5.85±1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>–</td>
<td>7.30±0.9</td>
<td>7.24±0.8</td>
<td>–</td>
<td>7.04±0.8</td>
<td>7.04±0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS/cm</td>
<td>5.85±2.3</td>
<td>6.59±2.5</td>
<td>–</td>
<td>0.61±0.2</td>
<td>0.61±0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>21.7±3.1</td>
<td>22.8±3.2</td>
<td>–</td>
<td>21.1±2.1</td>
<td>21.1±2.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2. The average mixed liquor suspended solids (MLSS) concentration, mixed liquor volatile suspended solids (MLVSS) concentration, pH, conductivity, temperature, and percent removal of COD, TN, and TP concentrations in the UFO-MBR and SB-MBR over the experimental period.

The UFO-MBR and SB-MBR operation was stable over the testing period and within normal operating conditions determined in previous system-specific studies [1, 62]. The meas-
ured pH and temperature were similar in the two systems during the fouling study, and COD, TP, and TN removals were consistent with literature [1, 62]. COD, TP, and TN removals were higher in the UFO-MBR than in the SB-MBR because the nonporous FO membranes had superior rejection of dissolved constituents (e.g., NO$_3^-$, PO$_4^{3-}$) than the porous SB-MBR UF membranes. The conductivity and TDS concentration were higher in the UFO-MBR per the experimental design and were achieved through low UF permeate rates and high TDS rejection by the FO membranes. MLSS and MLVSS concentrations in the SB-MBR and UFO-MBR were representative of steady-state conditions at the required HRT and SRT; it is important to note that MLSS and MLVSS concentrations were much higher in the SB-MBR than in the UFO-MBR. Differences in salinity and MLSS concentrations between the high-salinity and low-salinity FO feed were used to examine the influence of feed composition on FO fouling.

### 2.4.2 Virgin membrane integrity tests

CTA and TFC membranes were measured for water flux and RSF before installation in the membrane fouling system to ensure that there were no membrane defects before testing. The measured water flux and RSF values were used to calculate the SRSF, and only membranes with an SRSF less than 1,000 mg/L were installed in the membrane fouling test system. The average measured water flux, RSF, SRSF, contact angle, and surface roughness for the CTA and TFC membranes are summarized in Table 2.3.

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Water Flux (L/m²/hr)</th>
<th>RSF (g/m²/hr)</th>
<th>SRSF (mg/L)</th>
<th>Contact Angle (°)</th>
<th>Roughness ($R_a/R_q$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTA</td>
<td>8.6±1.4</td>
<td>5.5±1.4</td>
<td>655±210</td>
<td>48.2±3.5</td>
<td>23.4/29.5</td>
</tr>
<tr>
<td>TFC</td>
<td>11.7±1.2</td>
<td>4.8±0.9</td>
<td>422±96</td>
<td>12.9±2.1</td>
<td>23.1/28.6</td>
</tr>
</tbody>
</table>

*aValues from previous publication [61].

*bSurface roughness was analyzed with atomic force microscopy and results are reported as average roughness ($R_a$) and root mean square roughness ($R_q$).

Virgin TFC membranes had higher water flux, lower RSF, and lower SRSF than the CTA membranes, which is in agreement with literature values [35, 61]. Lower SRSF is a desirable membrane property that allows for high water flux and low solute diffusion. TFC membranes
also had lower contact angles and equivalent surface roughness to CTA membranes. The lower contact angle for virgin TFC membranes indicated a more hydrophilic membrane, which is widely thought of as a beneficial membrane property to reduce fouling propensity [25, 30, 31].

2.4.3 Membrane fouling system water flux results

Water flux was measured weekly using the membrane fouling system to evaluate CTA and TFC membrane performance treating two different activated sludge streams over the 100-day testing period. Water flux measurements were conducted using activated sludge from the UFO-MBR and SB-MBR with high-salinity and low-salinity feed streams, respectively. The DS used for water flux tests was a 1 M NaCl solution. The measured water flux was averaged within each membrane group (i.e., CTA-HS, CTA-LS, TFC-HS, and TFC-LS). The average water flux over the 100-day testing period for each membrane group and sludge type is shown in Figure 2.3.

![Figure 2.3. Water flux results from the membrane fouling system over the 100-day experiment. Results are shown for CTA-HS, CTA-LS, TFC-HS, and TFC-LS membranes.](image)

Initial water fluxes for CTA-HS and CTA-LS membranes were 10.5 and 10.2 L/m²/hr, respectively, and initial water fluxes for TFC-HS and TFC-LS membranes were 13.9 and 13.6 L/m²/hr, respectively. The initial water flux (Figure 2.3) for each membrane tested in the membrane fouling system were higher than the corresponding virgin water flux (Table 2.3) because the field water flux tests were conducted at higher temperatures (i.e., average of 25.6 °C) than the
virgin integrity tests (i.e., 20 ºC). However, when the water fluxes were corrected to 25 ºC [66], the temperature corrected water flux for the membrane fouling system was 10.2 and 13.5 L/m²/hr for CTA and TFC membranes, respectively, and the temperature corrected water flux was 10.0 and 13.6 L/m²/hr for virgin CTA and TFC membranes, respectively. Thus, the temperature corrected field and virgin initial water fluxes were in agreement.

The water flux decreased over the testing period for all membranes studied and was characterized by an initial decline and subsequent steady-state period. The water flux decreased during the first 27 days and stabilized at approximately 8.2 L/m²/hr for CTA membranes, and water flux decreased over 60 days and stabilized at approximately 5.3 L/m²/hr for TFC membranes. The flux decline and steady-state periods are similar to those described in other FO fouling studies [1, 2, 20, 49]. Zhang et al. [49] operated an OMBR using TFC FO membranes and synthetic municipal wastewater for 55 days. In their study, the water flux decreased over 12 days and stabilized at approximately 3.9 L/m²/hr. The authors attributed the initial flux decline and steady-state periods to OMBR salt accumulation and membrane fouling. However, analogous to Holloway et al. [1], the present study did not have salt accumulation in either MBR and flux decline is most likely due to membrane fouling.

The effect of fouling on FO water flux is well documented. Studies have shown that a main contributor to water flux decline in salt-rejecting membranes is cake-enhanced concentration polarization (CECP) [22, 52, 67-69]. CECP is a phenomenon that occurs when salts diffuse from the DS to the feed and accumulate in the fouling layer; the salt accumulation increases the osmotic pressure at the feed-membrane interface and ultimately diminishes water flux. Lee et al. [22] elucidated the importance of CECP in FO membranes by comparing water flux decline between two DS types. The experiments were conducted with 0.6 M-NaCl or 5 M-dextrose as DS; water flux decreased more severely when using an NaCl DS. The authors concluded that minimal RSF from dextrose resulted in a lesser degree of CECP and water flux decline. In the present study, the membrane fouling system operated with a similar NaCl DS (0.5 M) and RSF likely led to CECP and water flux decline.

TFC membranes were more prone to fouling, which was confirmed by the observed decline in water flux (Figure 2.3) and visual inspection of the membranes. Two previous studies also demonstrated higher water flux decline and fouling propensity for TFC versus CTA membranes and attributed the difference to higher initial water fluxes [61] and surface roughness [35].
Recent studies have shown that FO membrane fouling propensity increases with increasing initial water flux due to higher convective flow of foulants to the membrane surface and compaction of fouling layers [36, 70]. Xie et al. [70] demonstrated that the influence of CECP on water flux is more severe for membranes that have a more compact fouling layer. Thus, higher initial water flux for TFC membranes may be responsible for higher fouling propensity and lower steady-state water flux.

**Figure 2.4.** ESEM images of fouling layers for (a) CTA-HS (2500x), (b) CTA-LS (2500x), (c) TFC-HS (1000x), and (d) TFC-LS (1000x) membranes.

### 2.4.4 Fouling layer characterization

The fouling layers that developed on the CTA and TFC membranes was visually examined using an ESEM and are shown in Figure 2.4. Bacterial cells and EPS matrices were found
on the membrane surfaces, which suggested the prevalence of biofouling and organic fouling. Further fouling layer characterization was provided by FTIR analyses. A comparison of FTIR spectra between virgin and fouled membranes was used to determine the organic composition of the fouling layer and is shown in Figure 2.5. Virgin membrane peaks disappeared or were weakened when a fouling layer was present. In the fouling layers, peaks near 2923 and 2852 cm$^{-1}$ represented aliphatic methylene groups, found in fats and lipids; proteins were indicated by the amide I and amide II peaks at 1637 and 1540 cm$^{-1}$; and C-O stretching of a polysaccharide was found at approximately 1028 cm$^{-1}$. The peaks were the same for both membrane and feed types, and corresponded to peptidoglycans found in bacterial cell walls [71]. Overall, FTIR results showed a predominance of biofouling and organic fouling.

![FTIR spectra](image)

**Figure 2.5.** FTIR spectra of (a) CTA virgin active layer, CTA-LS fouling layer, and CTA-HS fouling layer; and (b) TFC virgin active layer, TFC-LS fouling layer, and TFC-HS fouling layer.

EDS analyses were used to compare the elemental content of the fouling layers (Figure 2.6). EDS analyses revealed that fouling layers contained calcium, aluminum, silicon, phosphorus, potassium, sodium, chlorine, and magnesium. Phosphorus, potassium, sodium, chlorine, calcium, and magnesium are elemental signatures of bacteria [72, 73] and demonstrated the prevalence of biofouling. High amounts of sulfur were found in the TFC membrane fouling layers and were likely because of their polysulfone support layer. Calcium was more prevalent in CTA-HS
and TFC-HS fouling layers. The high-salinity feed had much higher calcium concentrations (125 mg/L) than the low-salinity sludge (35 mg/L) (Table 1); the higher calcium concentrations increased the likelihood of calcium binding to EPS in the biofilm [74].

**Figure 2.6.** EDS analyses of fouling layers for (a) CTA-HS, (b) CTA-LS, (c) TFC-HS, and (d) TFC-LS membranes.
2.4.5 Effects of feed composition on fouling

Water flux results from the membrane fouling system were used to assess the effects of salinity and MLSS concentrations on fouling propensity. The UFO-MBR provided high-salinity feed for the membrane fouling test system, but with lower MLSS concentrations, and the SB-MBR provided a low-salinity feed with higher MLSS concentrations. TDS concentrations were approximately 4,200 and 300 mg/L for the UFO-MBR and SB-MBR, respectively, and MLSS concentrations were approximately 1.5 and 6.3 g/L, respectively.

Higher ionic strength water has been shown to increase fouling [75] and is thought to reduce foulant charge, foulant-foulant electrostatic repulsion, and foulant-membrane electrostatic repulsion. However, increased salinity and ionic strength did not have an effect on CTA and TFC membrane fouling in the present study. Motsa et al. [29] and van den Brink et al. [76] also found that ionic strength did not worsen fouling and flux decline. The authors suggested that foulant-foulant and foulant-membrane adhesions forces decreased at high ionic strengths in the presence of calcium. This was supported by a previous study that found decreased adhesion forces at increasing ionic strength in the presence of calcium, in which adhesion forces reached a constant value at an ionic strength of 30 mM [77]. The high-salinity and low-salinity activated sludge in the present study had ionic strengths of approximately 139 and 14 mM, respectively, and it may be possible that foulant adhesion forces were similar in the two feeds.

Divalent ions (i.e., calcium) are also known to substantially exacerbate membrane fouling and flux decline because of the formation of cross-linked gel layers with organics [20, 35, 36]. Calcium concentrations in the present study were 125 and 35 mg/L in the high-salinity and low-salinity feed (Table 2.1), and resulted in higher amounts of calcium in the CTA-HS and TFC-HS fouling layers (Figure 2.6). Despite higher amounts of calcium in the fouling layers (Figure 6), water flux was comparable between the two feed compositions (Figure 2.3) and showed that calcium did not affect water flux. The finding is in agreement with previous studies [29, 42, 53] that attributed the non-effects of calcium to low initial water fluxes [53] and FO membrane resilience [29, 42].

MLSS concentrations also did not affect water flux between the SB-MBR and UFO-MBR (Figure 2.3). The finding is contrary to conventional MBR fouling literature [23] but in agreement with two recent publications on FO fouling [78, 79]. This distinction in MLSS concentration effects on conventional and osmotic MBR membrane fouling was elucidated by Luo
et al. [78]. High water flux decline was observed for MF at increasing MLSS concentrations (0 to 20 g/L), but FO water flux was less affected at the same concentrations. Additionally, the study observed minimal FO water flux decline at MLSS concentrations relevant to the present study and is consistent with a previous study that used concentrations ranging from 5 to 12 g/L [79]. These FO fouling studies corroborate our water flux results and confirm that FO fouling propensity is still low at increasing MLSS concentrations.

2.4.6 Effects of membrane properties on fouling

Contact angle was measured on virgin and fouled membranes to determine if fouling propensity was affected by membrane hydrophilicity. Contact angle measurements for both membrane and feed types taken over the 100-day testing period are shown in Figure 2.7. Virgin TFC membranes were much more hydrophilic compared to virgin CTA membranes, with average contact angles of 12.9° and 48.2°, respectively. Contact angle measurements increased substantially for fouled TFC membranes and slightly decreased for fouled CTA membranes. Thus, the TFC membranes became increasingly more hydrophobic and CTA membranes became slightly more hydrophilic. Differences in the hydrophilicity of the TFC and CTA fouling layers have also been reported in a previous study [46] investigating polyamide (PA) and CTA NF and RO membranes treating secondary effluent from a municipal wastewater treatment plant. It was demonstrated that the fouled PA membranes obtained similar hydrophobicity independent of initial hydrophilicity, and the fouled CTA membrane became more hydrophilic. In the current study the water flux through the TFC membranes decreased more substantially compared to the water flux through the CTA membranes, illustrating that virgin membrane hydrophilicity is not a reliable indicator for membrane fouling propensity. This result is also supported by several other membrane fouling studies [35, 46, 61].

Membrane hydrophilicity did not affect fouling propensity in this study. One explanation is that contact angle measurements are only representative of the surface energy of the membrane; rather, it is necessary to understand the interaction energies, or adhesive forces, between the membrane and foulants [80]. Several studies have investigated the adhesive forces in surface-foulant interactions [20, 81, 82]. With regards to biofouling, Ma et al. [82] used atomic force microscopy (AFM) to determine that surface heterogeneity and a small number of highly adhesive sites dictated the extent of bacterial adhesion to metal oxide surfaces. This technique was also
used by Mi et al. [20] to compare PA and cellulose acetate (CA) FO membranes fouling using alginate as a model foulant. It was concluded in their study that the heterogenic PA membrane with a small amount of highly adhesive sites had a greater fouling propensity compared to the homogenous CA surface with a higher average adhesion force. Additionally, the foulant-foulant adhesive forces were comparable on the CA and PA membranes, but alginate demonstrated an extensive long-range attraction to the PA membrane beyond the adsorbed fouling layer.

![Graph showing contact angles for CTA-HS, CTA-LS, TFC-HS, and TFC-LS after 10, 40, 70, and 100-days of fouling.](image)

**Figure 2.7.** Contact angles for CTA-HS, CTA-LS, TFC-HS, and TFC-LS after 10, 40, 70, and 100-days of fouling. Contact angles were measured using the captive bubble method with 5 µL air bubbles.

Surface roughness is another often-cited membrane property that is thought to play a dominant role in fouling [35, 36, 83]. Virgin CTA and TFC membranes used in the current study had similar surface roughness (Table 2.3), and surface roughness was ruled out as a major factor in membrane fouling propensity. However, it is possible that the TFC membranes had an average roughness similar to CTA, but heterogenic roughness on the nanoscale allowed for foulant adsorption and nucleation [84]. Thus, heterogeneity and a small amount of highly adhesive sites may have contributed to the higher fouling propensity seen in TFC membranes in the present study.
2.4.7 Fouled membrane integrity results

Integrity tests were conducted on fouled CTA and TFC membranes in order to evaluate the fouling effects on membrane performance (i.e., water flux, RSF, SRSF). Coupons were sampled from each membrane and the lab bench-scale system was used to conduct the integrity tests with 2 g/L NaCl as feed solution and 1 M NaCl as DS. Water flux, RSF, and SRSF results are shown in Figure 2.8 for CTA and TFC membranes fouled for 10, 40, 70, and 100 days.

Figure 2.8. Membrane integrity results for CTA-LS, CTA-HS, TFC-LS, and TFC-HS after 10, 40, 70, and 100-days of fouling. Integrity results include (a) water flux (L/m²/hr), (b) reverse salt flux (g/m²/hr), and (c) specific reverse salt flux (mg/L).
Integrity test results showed that virgin CTA-HS and CTA-LS membrane water flux was approximately 8.7 and 8.5 L/m\(^2\)/hr and decreased to 7.0 and 5.1 L/m\(^2\)/hr after 100-days, respectively; virgin TFC-HS and TFC-LS membrane water flux was approximately 11.2 and 11.9 L/m\(^2\)/hr and decreased to 4.0 and 5.3 L/m\(^2\)/hr after 100-days, respectively. Water flux through the CTA membranes fouled for 70-days increased to virgin flux levels. The increase was likely because the membrane coupons were retested after storage in deionized water and foulants were dissolved from the membranes. As discussed in the membrane fouling system results, in addition to the fouling layer, CECP is likely a major contributor to water flux declination for all membranes.

RSF through the CTA and TFC membranes increased over the 100-days, in which CTA membranes outperformed TFC membranes with lower RSF (Figure 2.8b) – this trend is therefore reflected in the SRSF results (Figure 2.8c). CTA-HS and CTA-LS membranes had much lower SRSF results (1,350 and 2,450 mg/L) compared to TFC-HS and TFC-LS membranes (4,700 and 7,500 mg/L). The SRSF results for CTA membranes are in agreement with previous studies that used CTA FO membranes to treat activated sludge [2, 85].

The increased SRSF results for both membrane types indicated that reverse salt diffusion increased across the membrane relative to forward water diffusion. Chemical changes in the membrane active layers could have led to the preferential diffusion and FTIR was used to explore any chemical changes in the virgin and fouled active layer. FTIR spectra were compared between virgin CTA and TFC membranes and membrane active layers fouled for 100-days in high-salinity and low-salinity feeds. FTIR spectra comparisons are shown in Figure 2.9. In general, the membrane chemistry did not change for the CTA and TFC membranes. The TFC membranes had a peak disappearance at 1711 cm\(^{-1}\) and a peak shift at 1671 cm\(^{-1}\) (Box in Figure 2.9b) but this is likely due to the dissolution of solvent used in the membrane synthesis [86]. Thus, changes in SRSF are not likely caused by chemical changes in the membrane active layers.
Figure 2.9. FTIR spectra for (a) virgin CTA, CTA100-LS, CTA100-HS and (b) virgin TFC, TFC100-LS, and CTF100-HS. Box in Figure 9b highlights peak disappearance at 1711 cm$^{-1}$ and peak shift at 1671 cm$^{-1}$ between virgin and fouled TFC membranes.

Figure 2.10. ESEM image (2500x) for TFC-LS membrane that was fouled for 100-days.

ESEM was used to determine if physical defects were present on membrane active layer; it is possible that defects compromised the selectivity of the membrane, as proposed in a previous study [2]. CTA and TFC membrane active layers were analyzed with ESEM to determine if any defects developed over the experimental period. An ESEM image of a membrane defect found on a TFC-LS membrane fouled for 100-days is shown in Figure 2.10. The ESEM image in Figure 2.10 is representative of physical defects that were found for TFC-LS membranes fouled
for 40, 70, and 100 days. Multiple defects were found on randomly sampled membrane coupons, and these defects most likely caused the dramatic SRSF increases for TFC-LS membranes that were as high as 17,675 mg/L. Defects were not found on the CTA-HS, CTA-LS, or TFC-HS membrane active layers and therefore, were not likely the cause of increased SRSF for all membranes.

Fouling layers may offer another explanation for the increased SRSF. Two studies have proposed that increased SRSF occurs because of charge imbalances caused by negatively charged fouling layers [2, 87]. Kim et al. [87] and Hancock et al. [2] both proposed that SRSF increased because of a higher reverse flux of cations (e.g., sodium) that were attracted to the negatively charged fouling layer. Indeed, Lu et al. [88] demonstrated that more negatively charged membrane surfaces caused increased sodium flux. The study also found that changes in chemical potential between the feed and DS highly affected cation diffusion in TFC membranes, but did not affect sodium diffusion in CTA membranes. The authors attributed higher cation diffusion in the TFC membranes to negatively charged fixed surface sites (i.e., carboxyl groups) and lower cation diffusion in CTA membranes to non-fixed surface charges. Negatively charged fouling layers were shown by Hancock et al. [2] for CTA membranes that treated activated sludge for 54 days. The membranes in the present study may have also obtained increasingly negative fouling layers, resulting in increased SRSF, and the TFC membranes may have been more affected by the fouling layer charge imbalance than the CTA membranes. The effect of fouling on SRSF remains unclear, and future work is needed to further the understanding of this relationship.

### 2.5 Conclusions

The performance and fouling mechanisms of commercially available CTA and TFC membranes were evaluated during 100-days of continuous activated sludge treatment. Two MBRs provided activated sludge with high salinity and low MLSS concentrations or low-salinity and high MLSS concentrations. Overall, CTA membranes outperformed TFC membranes, exhibiting higher steady-state water flux and lower SRSF over the 100-day testing period. Increased SRSF for both membranes tested were likely caused by the organic fouling layer covering the membrane surface. The effects of fouling on SRSF remain unclear and systematic studies are needed to further the understanding of this relationship.
Water flux for the CTA and TFC membranes were comparable between feed compositions and illustrated that TDS, calcium, and MLSS concentrations might have negligible effects on FO fouling propensity in OMBR applications. TFC membranes were more prone to fouling and it was demonstrated that hydrophilicity and surface roughness were not the primary contributors to membrane fouling propensity. ESEM, EDS, and FTIR results showed a predominance of biofouling and organic fouling, and fouling layer compositions did not differ between membrane and feed types. Overall, the study demonstrated that FO membranes are suitable for long-term OMBR operation and reliably perform under a variety of activated sludge conditions.

2.6 References


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CHAPTER 3
PRODUCED WATER TREATMENT USING FORWARD OSMOSIS MEMBRANES:
LONG-TERM FOULING AND PERFORMANCE EVALUATIONS

Modified from a paper for possible publication in the *Journal of Membrane Science*

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3.1 Abstract

Forward osmosis (FO) membrane fouling and performance during treatment of produced water were systematically studied over extended time using cellulose triacetate (CTA) and polyamide thin film composite (TFC) FO membranes. Performance was evaluated with integrity tests that measured water flux, reverse salt flux (RSF), and specific reverse salt flux (SRSF). CTA membranes reached steady-state performance after one week with decreased water flux, RSF, and SRSF. TFC membranes did not reach steady state and had drastic water flux decrease, RSF increase, and SRSF increase. TFC membranes became increasingly negative over three weeks of continuous testing, while CTA membrane charge was stable. The negative charges reflected fouling layer development and may have contributed to high TFC membrane RSF. TFC membranes had a higher fouling propensity despite smoother, more hydrophilic, and more neutrally charged virgin membrane surfaces. Fouling layers for both membranes consisted of hydrocarbons, iron, and silicon. Chemically enhanced osmotic backwashes were performed weekly and removed calcium, sodium, and chloride from the fouling layers, but only marginally improved water flux. Gas chromatography-mass spectroscopy results showed that both membranes had over 90% rejection of neutral hydrophobic compounds and TFC membranes had higher rejection of small molecules. Compounds with aldehyde and ketone functional groups were not rejected as well as aliphatic and polycyclic aromatic hydrocarbons at the same molecular size, and CTA membranes had lower rejection of these compounds than the TFC membranes.

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3.2 Introduction

Forward osmosis (FO) is a promising technology for desalination and treatment of a broad range of impaired waters, including produced water from oil and gas (O&G) exploration and production operations. Several studies have designated FO as an appropriate technology for treatment of produced water [1, 2], and a recent life cycle assessment demonstrated that FO was economically and environmentally favorable compared to the common practice of deep well injection [3]. FO membranes are semipermeable and use osmotic pressure differences to drive the diffusion of water from an impaired feed solution across the membrane to a higher salinity draw solution (DS) [4]. Nonporous FO membranes readily reject dissolved constituents in produced water and provide high quality water for direct reuse or for feed into separation processes such as reverse osmosis (RO) for reclamation and reuse in a broad range of applications [5, 6]. The technology is capable of recovering up to 85% of produced water and operating in total dissolved solid (TDS) concentrations as high as 150,000 mg/L [1, 6, 7]. The membranes also have a lower fouling propensity compared to pressure-driven membrane processes [8-10], which minimizes pretreatment requirements. Despite a lower fouling propensity, FO membrane fouling is still a major operational cost that decreases water production and requires membrane cleaning [11].

Fouling is typically characterized as biofouling, organic fouling, and inorganic fouling (i.e., scaling) [12]. Biofouling involves the attachment of planktonic microorganisms and subsequent growth of irreversible biofilms [13] and has been identified in just one produced water fouling study [14]. Organic fouling is known to predominate and involves the sorption of organic compounds (e.g., hydrocarbons, chemical additives) onto the membrane surface [15]. Produced waters contain high levels of TDS that cause substantial inorganic fouling from the sorption or precipitation of inorganic solids onto the membrane [15]. Multivalent ions (e.g., calcium, barium, strontium, iron, silicon) are major ions found in produced water inorganic fouling [16, 17] and can also exacerbate organic fouling through ion-organic complexation [17].

Produced water treatment is a novel application for FO, and therefore, just three studies have systematically investigated FO membrane fouling and performance [16-18]. Two of these studies used real produced water [16, 17], and found that organic and inorganic foulants were significant. Inorganic fouling was determined through energy dispersive spectroscopy (EDS) and included ions such as calcium, magnesium, strontium, chlorine, iron, and barium [16, 17]. Coday et al. [17] used Fourier transform infrared (FTIR) spectroscopy and found that the organic com-
position of the fouling layer consisted of calcium carbonate with residual oil. Biofouling was not identified in any of the FO produced water fouling studies.

All three fouling studies compared cellulose triacetate (CTA) and polyamide thin film composite (TFC) membranes to determine important membrane properties that affected fouling propensity. TFC membranes had a higher fouling propensity than CTA membranes in all three studies, which was attributed to high surface roughness [16, 18], high initial water flux [17], and strong hydrogen bonding capability [18]. Surface roughness is an often cited membrane property that causes high membrane fouling [16, 18-21]; however, a recent produced water treatment study did not find a clear correlation between fouling propensity and surface roughness of FO membranes [17]. Instead, fouling propensity was attributed to high initial water flux, which convectively drags more foulants to the membrane surface and compacts the fouling layer [22-24]. An abundance of strong hydrogen bonding sites on TFC membrane surfaces has also been proposed as a contributor to produced water fouling propensity [18]. TFC active layers have carboxyl groups (-COOH) that have stronger adhesion forces than hydroxyl groups (-OH) [25], which are found in CTA active layers.

Membrane cleaning is often used to mitigate fouling and restore water flux. Several produced water treatment studies have demonstrated effective cleaning strategies of FO membranes that include hydraulic cleans [6, 26], osmotic backwashes [6], and chemically enhanced osmotic backwashes [17]. Chun et al. [26] found that hydraulic cleaning effectively recovered water flux for CTA and TFC membranes after 48 hours of coal seam gas produced water treatment. Deionized water was recirculated on the feed (active layer) side of the membrane for one hour, sufficiently removing foulants and fully restoring water flux. Hickenbottom et al. [6] demonstrated that osmotic backwash was more effective than hydraulic cleaning for CTA membranes treating drilling wastewater. Drilling wastewater remained as feed solution and deionized water replaced the DS, which reversed the diffusion of water, removed foulants, and fully restored water flux at 30% of the hydraulic cleaning time. A recent study used both osmotic backwashing and chemically enhanced osmotic backwashing (CEOB) for cleaning of CTA and TFC membranes fouled by produced water [17]. Osmotic backwashing was performed daily for 48 hours using produced water as feed solution (acting as DS) and recirculating deionized water in the DS channels. A separate set of tests investigated daily CEOB over 96 hours using an 11 g/L chemical cleaning solution as the feed and recirculating deionized water in the DS channels. It was revealed that
CEOB was more effective than osmotic backwashing, and that ethylenediamine–tetraacetic acid (EDTA) was a more effective cleaning chemical. The study also found that smoother membrane surfaces likely enhanced cleaning efficacy. All three studies operated for less than one week with frequent cleaning and might not reflect steady-state field operations. This is exemplified in a one week FO pilot study that treated raw drilling wastewater and did not require cleaning [27]. The CTA membranes experienced only an 18% decrease in water flux and recovered 85% of drilling wastewater.

Studies of FO membranes fouling by produced water have appropriately compared the widely used CTA membranes and emerging TFC membranes [16-18]. Two of the studies used real versus synthetic wastewater [16, 17], which is important for accurately characterizing membrane fouling and performance [16, 28]. However, the membranes were studied for less than four days, and fouling, performance, and cleaning efficacy may not reflect long-term field operation. Thus, the goals of this study were to expand on existing produced water fouling literature by comparing CTA and TFC membranes, operating membranes for longer periods of time, and using real produced water. The study compared the fouling and performance of CTA and TFC membranes that treated produced water from the Denver-Julesburg basin in Colorado continuously for three weeks. Membrane performance parameters were evaluated and included water flux, reverse salt flux (RSF), specific reverse salt flux (SRSF), and organic compound rejection. Membrane autopsies were performed over the experimental period in order to characterize fouling layers and to investigate physiochemical changes to the membrane surface. Lastly, the study evaluated the efficacy of weekly CEOBs using EDTA.

3.3 Materials and methods

The study used CTA and surface-modified antifouling TFC membranes to treat produced water from the Denver-Julesburg basin for three weeks. Membrane performance was evaluated with integrity tests that used a FO bench-scale system; the integrity tests measured water flux, RSF, and SRSF. Membranes were installed in the membrane fouling system and treated produced water for one, two, or three weeks. CTA and TFC membranes were either cleaned with a CEOB using EDTA or remained fouled. Membrane autopsies were performed on cleaned and fouled membranes in order to understand physiochemical membrane property changes and fouling layer composition.
3.3.1 Membranes

Commercially available, flat-sheet CTA and TFC membranes were used in the study and were acquired from Hydration Technology Innovations, LLC (Albany, OR). It is important to note that surface-modified antifouling TFC membranes were used in the current study as described in previous publications [17, 29]; the antifouling TFC membranes were used because a previous study found improved performance after produced water treatment [29]. CTA and TFC membranes were installed in custom-made flow cells with an effective membrane area of 190 cm$^2$ each. The cells have asymmetric flow channels for the feed (25.4 x 7.62 x 0.24 cm) and DS (25.4 x 7.62 x 0.16 cm). The membranes were operated with the active layer facing the feed solution (no feed spacers) and tricot spacers in the DS channel to provide mixing and mechanical support for the membranes.

3.3.2 Virgin membrane integrity tests

Membrane integrity tests were conducted on virgin membranes before the beginning of the tests to ensure that the membranes were free of defects. In the integrity tests we have measured water flux, RSF, and SRSF using a bench scale system described in detail elsewhere [30-32]. The system used a data acquisition software (LabVIEW, National Instruments Corp., Austin, TX) and a control unit (UE9-Pro, LabJack, Lockwood, CO) to collect data (i.e., feed solution volume, feed solution conductivity, DS conductivity) and to control experimental conditions (i.e., feed solution and DS dosing solution flow rates, 20 ºC temperature). The feed reservoir contained 3 L of deionized water and was dosed with deionized water in order to maintain constant volume as water diffused through the FO membrane into the DS. The DS reservoir initially contained 1 L of 1 M NaCl solution and was intermittently dosed with a 300 g/L NaCl solution in order to maintain constant salinity and osmotic pressure. Membranes were operated for 90 minutes with co-current feed solution and DS flow rates of 0.7 and 0.4 gpm, respectively.

Water flux (L/m$^2$/hr) was defined as the forward diffusion of water from the feed solution to the DS per unit membrane area per unit time. The forward diffusion of water was calculated from the volume of deionized water dosed into the feed reservoir divided by membrane area and experimental time. A probe in the feed reservoir measured conductivity, and the concentration of NaCl was determined from the conductivity and used to calculate RSF (g/m$^2$/hr). RSF was defined as the reverse diffusion of solutes from the DS into the feed solution per unit membrane area per unit time.
area per unit time. The division of water flux by RSF yielded SRSF (mg/L), which is an important membrane parameter that directly relates to membrane efficiency [30, 33]. Lower SRSF values denote a more efficient and desirable membrane that preferentially allows for forward diffusion of water versus reverse diffusion of solutes.

### 3.3.3 Membrane fouling system

CTA and TFC membranes were installed into the membrane fouling system and treated produced water from the Denver-Julesburg basin for one, two, or three weeks. Membranes were either cleaned with a CEOB using EDTA or remained fouled. The produced water and draw solution tanks were analyzed for cations, anions, dissolved organic carbon, chemical oxygen demand, total nitrogen, and organic compounds.

#### 3.3.3.1 System set-up

The membrane fouling system was used to treat produced water with CTA and TFC membranes for up to three weeks. The system was comprised of 12 flow cells, a feed solution tank, two DS tanks, a DS dosing solution tank, a rotary vane feed pump (Procon, Smyrna, TN), two DS gear pumps (Micropump, Vancouver, WA), and two peristaltic dosing pumps (Cole-Parmer, Vernon Hills, IL). Virgin CTA and TFC membranes with a SRSF of less than 1,000 mg/L were installed in the system. The membranes operated in series within two groups based on membrane type (CTA and TFC). Each group contained six membrane cells in which three membranes were cleaned (“CTA-C” and “TFC-C”) and three remained untouched, or “fouled” (“CTA-F” and “TFC-F”). CTA-C and TFC-C membranes were cleaned weekly, resulting in a maximum of three cleans. Cleaned and fouled membranes operated for one, two, or three weeks and were taken offline for integrity testing and membrane characterization. A picture and schematic of the membrane fouling system are shown in Figure 3.1.

Chemically enhanced osmotic backwashing (CEOB) was used to clean membranes according to methods from a previous FO membrane fouling study [17]. The cleaning procedure used an 11 g/L ethylenediamine-tetraacetic acid (EDTA) (Avantor, Central Valley, PA) solution. Separate EDTA solutions were pH adjusted with citric acid to 7.8 and 10.8 for CTA and TFC membranes, respectively. The EDTA solutions recirculated on the active layer side of the membranes and deionized water recirculated on the support layer side of the membranes. Water os-
motically permeated from the deionized water to the EDTA solution and removed foulants from the membrane active layer. Membranes were cleaned on the bench scale system for two hours at the same flow rates as the membrane integrity tests. CTA membranes were cleaned separately from TFC membranes and membranes were cleaned in series within each group.

![Image](image_url)

**Figure 3.1.** (a) Picture and (b) process flow diagram of membrane fouling system. Cells were arranged in two groups based on membrane type (CTA and TFC), and were operated in series. Membranes were labeled with ‘F’ to indicate no cleaning and ‘C’ to indicate cleaning. Numbers 1, 2, and 3 represent the number of weeks the membranes were online.

### 3.3.3.2 System operating procedure

Produced water from the Denver-Julesburg basin in Colorado was used as feed solution and was operated in batch mode. A new batch of produced water replaced existing feed solution twice per week and totaled six batches over the experimental period. On a daily basis, deionized water was added to the feed solution tank to replace permeated water and to maintain consistent osmotic pressure. The DS consisted of 1 M NaCl and each membrane group had a separate DS tank. Each DS tank operated continuously and was drained on a daily basis down to 10 L (3 gallons). A 300 g/L NaCl solution was intermittently dosed to each DS tank in order to maintain consistent osmotic pressure. The feed solution and DS tanks were measured twice per day for pH, temperature, and conductivity using a handheld probe (Oakton Instruments, Vernon Hills, IL). The dosing solution flowrate was adjusted to maintain consistent DS conductivity. The feed solution and DS operated at co-current flow rates of 0.5 and 0.3 gpm, respectively.
3.3.3.3 Analytical procedure

The feed solution and DS tanks were sampled twice per week in order to determine inorganic and organic chemistry. The feed solution tank was sampled at the beginning and end of each feed solution batch, and the DS tanks were synchronously sampled with feed solution samples. Feed solution samples were filtered with a 0.45 µm filter for all analyses, and feed solution and DS samples were diluted with deionized water per individual analysis specifications. Anions were measured with an ion chromatograph (IC) (ICS-90, Dionex, Sunnyvale, CA), and cations were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Optima 5400, PerkinElmer, Fremont, CA). Both analyses required a 30x dilution to prevent chloride interferences, and ICP-AES samples were acidified with nitric acid to a pH of 2. Dissolved organic carbon (DOC) and total nitrogen (TN) were measured using a carbon analyzer (Shimadzu TOC-L, Columbia, MD), in which feed solution and DS samples were diluted by 3x and 5x, respectively. Average concentrations of constituents in the feed solution are summarized in Table 3.1.

Three-dimensional excitation emission matrix (3D EEM) fluorescence spectroscopy was used to qualitatively analyze fluorescent organic species in the feed solution, CTA DS, and TFC DS using a spectrofluorometer (Aqualog, HORIBA Scientific, Edison, NJ). Samples were diluted and normalized to 2 mg/L DOC and analyzed with excitation wavelengths between 238.5 and 450 nm and emission wavelengths between 250 and 600 nm.

Organic species were identified and quantified in the feed solution, CTA DS, and TFC DS using gas chromatography-mass spectrometry (GC-MS). GC-MS was used to quantify semi-volatile linear aliphatic hydrocarbons in the \( n-C_{10} \) to \( n-C_{32} \) range and 16 polycyclic aromatic hydrocarbons (PAHs) according to the methods from Regnery et al. [34]. Samples were pretreated with solid-phase extraction (SPE) using an AutoTrace 280 SPE unit (Thermo Scientific, Waltham, MA) and analyzed with a HP 6890 gas chromatograph equipped with a HP 5973 mass spectrometer from Agilent Technologies (Palo Alto, CA) that used an Rtx-5Sil capillary column (Restek, Bellefonte, PA). Analytes were identified using mass spectra (Wiley AccessPak spectral library) and retention times of internal standards. Analyte concentrations were quantified by measuring peak areas of each compound relative to the respective internal standard peak area.
Table 3.1. Average concentrations of major constituents in the feed solution

<table>
<thead>
<tr>
<th>Analyte</th>
<th>mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.61</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>212</td>
</tr>
<tr>
<td>Total dissolved carbon</td>
<td>582</td>
</tr>
<tr>
<td>Total nitrogen</td>
<td>38.2</td>
</tr>
<tr>
<td>Chemical oxygen demand</td>
<td>2,320</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>22,610</td>
</tr>
<tr>
<td>Boron</td>
<td>32.9</td>
</tr>
<tr>
<td>Barium</td>
<td>19.3</td>
</tr>
<tr>
<td>Calcium</td>
<td>682</td>
</tr>
<tr>
<td>Iron</td>
<td>72.2</td>
</tr>
<tr>
<td>Potassium</td>
<td>52.7</td>
</tr>
<tr>
<td>Lithium</td>
<td>10.6</td>
</tr>
<tr>
<td>Magnesium</td>
<td>79.9</td>
</tr>
<tr>
<td>Manganese</td>
<td>1.32</td>
</tr>
<tr>
<td>Sodium</td>
<td>11,064</td>
</tr>
<tr>
<td>Sulfur</td>
<td>15.7</td>
</tr>
<tr>
<td>Silicon</td>
<td>58.7</td>
</tr>
<tr>
<td>Strontium</td>
<td>102</td>
</tr>
<tr>
<td>Fluoride</td>
<td>9.53</td>
</tr>
<tr>
<td>Chloride</td>
<td>10,715</td>
</tr>
<tr>
<td>Bromine</td>
<td>132.5</td>
</tr>
<tr>
<td>Nitrate</td>
<td>85.3</td>
</tr>
<tr>
<td>Sulfate</td>
<td>119</td>
</tr>
</tbody>
</table>

3.3.4 Fouled membrane integrity tests

After one, two, and three weeks, cleaned and fouled membranes were installed in the bench scale system for integrity tests. Membranes were removed from the flow cells, and coupons were cut from the membranes and installed into a smaller, symmetric, custom-made flow cell (21.91 x 5.40 x 0.32 cm channel dimensions) with an effective membrane area of 120 cm². The integrity tests were conducted with the same experimental conditions (i.e., temperature, flow rates, deionized water as feed solution, 1 M NaCl DS) as the virgin membrane integrity tests. The integrity tests measured water flux, RSF, and SRSF for all cleaned and fouled membranes.

3.3.5 Membrane autopsy and characterization

Membrane autopsies were performed on virgin, fouled, and cleaned CTA and TFC membranes in order to measure physiochemical membrane properties and to determine fouling layer
composition. Streaming zeta potential was used to measure membrane charge and contact angle via captive bubble was used to measure membrane hydrophilicity. The fouling layers were examined with an environmental scanning electron microscope (ESEM) coupled with energy dispersive spectroscopy (EDS). Fourier transform infrared (FTIR) spectroscopy was used to determine the organic composition of fouling layers.

### 3.3.5.1 Environmental scanning electron microscopy and energy dispersive spectroscopy

An ESEM (Quanta 600i, FEI, Tokyo, Japan) was used to examine fouling layers for cleaned and fouled membranes. Sample coupons were collected from cleaned and fouled membranes, dried in a desiccator, and gold sputtered prior to analysis (Technic Hummer VI, Cranston, RI). EDS (Genesis, EDAX, Mahwah, NJ) was used in conjunction with the ESEM in order to identify and compare the elemental content on the surface of cleaned and fouled membranes.

### 3.3.5.2 Fourier transform infrared spectroscopy

Fourier transform infrared (ATR-FTIR) spectroscopy (Nicolet 4700 FTIR, Thermo Electron Corporation, Madison, WI) was used to determine the organic composition of fouling layers on cleaned and fouled membranes. Membrane coupons were sampled from virgin, cleaned, and fouled membranes and dried in a desiccator for at least 24 hours before analysis.

### 3.3.5.3 Zeta potential

Zeta potential was measured for virgin, fouled, and cleaned membranes in order to determine changes in surface charge over the fouling period. The analysis used an electrokinetic analyzer equipped with an integrated titration unit (SurPASS, Anton Paar GmbH, Austria) that measured streaming zeta potential at a pH of 7 in a 2 mM KCl solution. Membrane coupons were sampled from virgin, fouled, and cleaned membranes and dried in a desiccator for at least 24 hours before analysis.

### 3.3.5.4 Contact angle via captive bubble

Membrane hydrophobicity was measured for virgin CTA and TFC membranes using contact angle via captive bubble method. Membrane coupons were immersed in deionized water and
a 5 µL air bubble was pipetted onto the active layer surface. Contact angles were measured using a goniometer (Model 200-00, Rame-Hart Instrument Company, Netcong, NJ). Contact angles measurements were averaged for three bubbles per coupon. Each bubble had three sets of ten measurements, and each measurement set was performed in 0.1 seconds.

3.4 Results and discussion

CTA and TFC membranes treated produced water for one, two, or three weeks, and were either cleaned with a CEOB using EDTA or remained fouled. Water flux, RSF, and SRSF were measured for virgin, fouled, and cleaned membranes using an FO bench scale system. Membrane autopsies were performed on fouled and cleaned membranes and measured physiochemical membrane properties and the composition of fouling layers. Organic compound rejection was evaluated with 3D EEM fluorescence spectroscopy and was calculated using GS-MS results.

3.4.1 Virgin membrane properties

Virgin membrane properties were measured in order to understand their effects on membrane fouling propensity. Water flux, RSF, and SRSF were measured during integrity tests that used deionized water as feed and a 1 M NaCl solution as DS. Surface charge was quantified with streaming potential at pH 7, hydrophobicity was measured using contact angle via captive bubble, and membrane surface roughness was obtained from a previous study that used the same CTA and antifouling TFC membranes [17]. Water flux, RSF, SRSF, zeta potential, contact angle, and surface roughness are summarized in Table 3.2.

Table 3.2. Virgin CTA and TFC membrane properties that include water flux, reverse salt flux (RSF), specific reverse salt flux (SRSF), contact angle, and surface roughness

<table>
<thead>
<tr>
<th></th>
<th>Water Flux</th>
<th>RSF</th>
<th>SRSF</th>
<th>Zeta potential</th>
<th>Contact angle</th>
<th>Roughness (Ra/Rq)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L/m²/hr</td>
<td>g/m²/hr</td>
<td>mg/L</td>
<td>(mV)</td>
<td>°</td>
<td>nm</td>
</tr>
<tr>
<td>CTA</td>
<td>7.9±0.3</td>
<td>6.7±0.8</td>
<td>848±106</td>
<td>-33.5</td>
<td>45.1±1.4</td>
<td>23.4/29.5</td>
</tr>
<tr>
<td>TFC</td>
<td>11.0±1.2</td>
<td>2.5±0.4</td>
<td>233±44</td>
<td>-18.5</td>
<td>16.1±1.7</td>
<td>10.4/13.6</td>
</tr>
</tbody>
</table>

*a Measured at pH 7 with 2 mM KCl solution.
*b Values from previous publication [17].
*c Surface roughness was analyzed with atomic force microscopy and results are reported as average roughness (Ra) and root mean square roughness (Rq).
Virgin TFC membranes had higher water flux, lower RSF, and lower SRSF than virgin CTA membranes, which is in agreement with previous publications [17, 19]. Lower SRSF indicates that the TFC membranes were more selective and allowed less permeation of solutes. The TFC membranes are also smoother, more hydrophilic, and more neutrally charged; these three properties are regarded as important properties to reduce membrane fouling [12, 35, 36]. Thus, we expected that the TFC membranes would outperform the CTA membranes and have lower fouling propensity.

3.4.2 Membrane performance: water flux, RSF, and SRSF

A bench scale system was used to perform integrity tests on fouled and cleaned CTA and TFC membranes using the same conditions as virgin membrane integrity tests. Deionized water was used as the feed and 1 M NaCl as the DS. Water flux, RSF, and SRSF as a function of time are shown in Figure 3.2 for fouled and cleaned CTA and TFC membranes.

Water flux decreased by 50% for both fouled and cleaned CTA membranes and reached steady state flux after one week. RSF through the CTA membrane also reached steady state after one week, and decreased by 71% and 81% for fouled and cleaned CTA membranes. The water flux and RSF results resulted in improved SRSF for CTA membranes after three weeks. TFC membrane water flux continually declined for three weeks and decreased by 91% and 85% for fouled and cleaned membranes. RSF increased by ~310% and ~325% for fouled and cleaned TFC membranes, respectively. Low water flux and high RSF resulted in drastically high SRSF for TFC membranes.

Overall, the CTA membranes outperformed the TFC membranes with higher water flux, lower RSF, and lower SRSF after three weeks. Visual inspection of the membranes revealed that the TFC membranes were more severely fouled than the CTA membranes (Figure 3.3). High TFC fouling propensity was supported by the drastic water flux decline compared to the CTA membranes. Cleaned CTA and TFC membranes had only slightly higher water flux than fouled membranes, which demonstrated marginal foulant removal with CEOBs using EDTA. The finding contradicted a previous study that found significant improvements in water flux for CTA and TFC membranes cleaned with EDTA CEOB [17]. The discrepancy in cleaning efficacy may be because the present study had less frequent CEOBs, a longer fouling period and subsequent irreversible fouling, and lower cross-flow velocities during fouling periods. The results also suggest
that the CTA membranes are robust and can maintain steady-state water flux and RSF over three weeks. Long-term, sustained CTA water flux is in agreement with a previous pilot study that treated drilling wastewater for one week without CTA membrane cleaning [37].

**Figure 3.2.** (a) Water flux, (b) reverse salt flux (RSF), and (c) specific reverse salt flux (SRSF) results for cleaned CTA (“CTA-C”), fouled CTA (“CTA-F”), cleaned TFC (“TFC-C”), and fouled TFC (“TFC-F”).
The TFC membranes followed typical performance trends of fouled FO membranes, in which water flux decreased and RSF increased [38, 39]. Water flux decline was likely due to cake enhanced concentration polarization (CECP), which is cited as the major cause of water flux decline in osmotically driven membrane processes [8, 40-44]. CECP is a result of solute accumulation in the fouling layer and causes increased osmotic pressure at the membrane surface, decreased osmotic difference across the membrane, and decreased water flux. High RSF through the TFC membranes likely led to increased CECP, and high initial water flux may have compacted the fouling layer, which is known to worsen CECP [22].

However, fouling layer effects on RSF were unclear and studies have yet to determine the cause of RSF changes associated with FO fouling. Several studies have proposed that negatively charged fouling layers induce a charge imbalance across the membrane [38, 39]. They hypothesized that the charge imbalance draws cations from the DS and increases RSF. In the present study, streaming potential was measured for virgin, fouled, and cleaned CTA and TFC membranes in order to explore this concept. Streaming potential measurements were performed at pH 7 and calculated zeta potentials are shown as a function of experimental elapsed time in Figure 3.4.

Virgin CTA membranes had zeta potential values of -33.5 mV, and slightly decreased to -36.2 and -38.4 mV for CTA-C and CTA-F membranes, respectively. Virgin TFC membranes had zeta potential values of -18.5 mV, and decreased to -39.0 and -43.0 mV for TFC-C and TFC-F membranes, respectively. The drastic decrease in zeta potential of the TFC membranes reflected their high fouling propensity; conversely, CTA membranes were less prone to fouling and were only slightly more negative after three weeks. Continually decreasing zeta potential for TFC membranes corresponds to increasing RSF and indicates that more negatively charged fouling layers possibly caused the drastic increase in RSF. However, systematic studies are still needed to elucidate the relationship between negatively charged fouling layers and RSF.
The unique surface chemistry of the CTA and TFC active layers could also play a large role in the diffusion of solutes across the membrane. Polyamide TFC membranes contain ionizable functional groups (i.e., amides (-NH-CO-), carboxylic acids (-COOH)) that have a fixed negative charge [45, 46], and CTA membranes contain non-ionizable functional groups (e.g., acetate (-COCH₃), hydroxyl (-OH)) that do not possess a fixed charge [45, 47]. A recent study illustrated that TFC membranes had higher forward and reverse cation diffusion than CTA membranes, and the authors attributed the high cation diffusion to carboxyl groups and Donnan dialysis [48]. Additionally, forward and reverse diffusion of cations across TFC membranes were highly influenced by changes in the feed solution chemistry (i.e., electrolytic charge imbalances, pH), and solute fluxes across CTA membranes were not affected by changes in solution chemistry. The study provided evidence that TFC membrane solute flux was more sensitive to charge imbalances than CTA membrane solute flux. Fouled CTA and TFC membranes in the present study reached similar zeta potential, and TFC membrane RSF was possibly more influenced by fouling layer charge imbalances than CTA membrane RSF.

Both water flux and RSF decreased for the CTA membranes. A previous study found slightly decreased water flux and RSF for CTA membranes after 48 hours of produced water treatment [29], and longer experimental periods would have likely yielded similar results to the present study. The cause for decline in water and solute diffusion was unclear, and the authors
proposed a number of explanations. First, foulant adsorption and entrapment within the polymer
matrix could have hindered water and solute diffusion [49-51], and the study suggested that the
hydrophobic CTA membranes could have experienced higher organic adsorption compared to
the more hydrophilic TFC membranes. Second, high ionic strength water may potentially de-
swell the active layer, decrease pore size, and subsequently lower water flux and RSF [52]. Ions
may also neutralize pore charge, which would minimize electrostatic repulsion within the pores,
decrease pore size, and decrease water and solute diffusion [53]. Overall, the interactions be-
tween produced water constituents and membranes are complex and any combination of them
could have led to the observed changes in CTA and TFC membrane performance.

3.4.2.1 Membrane property effects on fouling

Conventional fouling literature states that smooth, neutrally charged, and hydrophilic
membranes are needed to optimize water flux and minimize fouling propensity [12, 35, 36]. Ac-
cording to these parameters, virgin TFC membranes had superior properties to CTA membranes
(Table 1). However, TFC membranes had a higher fouling propensity than CTA membranes de-
spite these virgin membrane properties.

Membrane heterogeneity provides a possible explanation for high TFC membrane fouling
propensity. Conventional membrane characterization techniques only provide average surface
values and do not reflect the heterogeneous distribution of properties [20, 25, 54, 55]. Several
studies have shown a higher fouling potential correlation with heterogeneous property distribu-
tion versus average property values [20, 25, 55]. For example, Mi et al. [10] related fouling po-
tential to heterogeneous adhesion forces for polyamide and cellulose acetate membranes. Poly-
amide membranes had lower average adhesion forces than cellulose acetate membranes, but had
a heterogeneous distribution of very adhesive sites that resulted in a higher fouling propensity.
Adhesion forces are a function of surface chemistry (e.g., functional groups, charge) and mor-
phology (e.g., roughness) [25]; thus, virgin membrane properties may not accurately reflect the
heterogeneous distribution of polyamide TFC membrane properties that led to higher fouling
propensity.
3.4.3 Fouling layer characterization

Membrane fouling layers were examined using an ESEM in order to visually inspect the fouling layers. ESEM images are shown in Figure 3.5 for CTA-C, CTA-F, TFC-C, and TFC-F membranes after three weeks. All fouling layers were similar in appearance, but the foulant composition (e.g., organic, inorganic, biological) was not evident. Previous produced water membrane fouling studies showed that oil [17, 32], microorganisms [14], or inorganic scaling [16, 17, 32] predominated fouling layers, and these constituents likely comprised CTA and TFC fouling layers.

Figure 3.5. ESEM micrographs at 1000x magnification of the (a) CTA-F, (b) CTA-C, (c) TFC-F, and the (d) TFC-C membranes after three weeks of continuous fouling experiments.
The elemental compositions of the fouling layers were examined with EDS, and results for cleaned and fouled membranes are summarized in Table 3.3 as elemental weight percent (%). Iron and silicon were dominant elements in all the fouling layers, which was in agreement with previous produced water fouling studies [17, 56]. It is interesting to note that sodium and chloride were major elements only in the TFC-F fouling layers. The high weight percent of sodium and chloride may reflect the high RSF through the TFC membranes, and the lack of sodium and chloride in the TFC-C membranes indicate that EDTA may have removed the ions. Calcium was found only on CTA-F and TFC-F fouling layers and indicates that EDTA also removed calcium from the CTA-C and TFC-C fouling layers.

Table 3.3. Energy dispersive spectroscopy (EDS) results CTA-C, CTA-F, TFC-C, and TFC-F fouling layers after three weeks of produced water treatment. Results are shown as % weight for each element.

<table>
<thead>
<tr>
<th>Element</th>
<th>CTA-C</th>
<th>CTA-F</th>
<th>TFC-C</th>
<th>TFC-F</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>6.1</td>
<td>6.0</td>
<td>3.3</td>
<td>5.4</td>
</tr>
<tr>
<td>O</td>
<td>35.2</td>
<td>34.1</td>
<td>48.8</td>
<td>34.2</td>
</tr>
<tr>
<td>Na</td>
<td>2.3</td>
<td>--</td>
<td>3.9</td>
<td>23.2</td>
</tr>
<tr>
<td>Al</td>
<td>--</td>
<td>--</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Si</td>
<td>9.2</td>
<td>10.0</td>
<td>12.6</td>
<td>5.5</td>
</tr>
<tr>
<td>Au</td>
<td>4.0</td>
<td>3.4</td>
<td>5.3</td>
<td>3.5</td>
</tr>
<tr>
<td>Cl</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>19.1</td>
</tr>
<tr>
<td>Ca</td>
<td>--</td>
<td>1.8</td>
<td>--</td>
<td>0.6</td>
</tr>
<tr>
<td>Fe</td>
<td>43.2</td>
<td>44.8</td>
<td>25.4</td>
<td>10.3</td>
</tr>
<tr>
<td>Co</td>
<td>--</td>
<td>--</td>
<td>1.1</td>
<td>--</td>
</tr>
</tbody>
</table>

FTIR was used to determine the organic compositions of cleaned and fouled CTA and TFC fouling layers. Spectra for virgin, fouled, and cleaned CTA and TFC membranes are shown in Figure 3.6 and summarized in Table 3.4. Virgin membrane peaks disappeared or were weakened in the presence of fouling layers. Foulant peaks for cleaned and fouled CTA and TFC membranes were similar and indicated that the fouling layers were the same. Peaks were representative of aliphatic hydrocarbons, aromatic hydrocarbons, and carbonates (Table 3.4) [57, 58]. The foulants were likely from organic matter in the formation and fracturing fluids [15]. A previous study used FTIR to examine membranes fouled with produced water and found evidence of biofouling [14]. Biofoulant peaks were not found in the present study, but it is possible that hydrocarbon peaks obscured biofoulant peaks.
Figure 3.6. FTIR spectra comparison of virgin, cleaned, and fouled (a) CTA and (b) TFC membranes. Dotted lines indicate peaks associated with fouling layer.

Table 3.4. Peak wavenumbers (cm$^{-1}$), assignments, and interpretations for CTA and TFC membrane fouling layers. Peak assignments and interpretations were from Colthup et al. [57] and Matrajt et al. [58].

<table>
<thead>
<tr>
<th>CTA fouling layer peaks (cm$^{-1}$)</th>
<th>TFC fouling layer peaks (cm$^{-1}$)</th>
<th>Peak assignment</th>
<th>Possible interpretations</th>
</tr>
</thead>
<tbody>
<tr>
<td>2954</td>
<td>2954</td>
<td>Asymmetric -CH$_3$ stretch</td>
<td>Aliphatic hydrocarbon</td>
</tr>
<tr>
<td>2923</td>
<td>2923</td>
<td>Asymmetric -CH$_2$ stretch</td>
<td>Aliphatic hydrocarbon</td>
</tr>
<tr>
<td>2853</td>
<td>2853</td>
<td>Symmetric -CH$_2$ stretch</td>
<td>Aliphatic hydrocarbon</td>
</tr>
<tr>
<td>1621</td>
<td>1625</td>
<td>C=C stretch</td>
<td>Aromatic/carbonate</td>
</tr>
<tr>
<td>--</td>
<td>1458</td>
<td>Asymmetric -CH$_2$ bend</td>
<td>Aliphatic/carbonate</td>
</tr>
<tr>
<td>1379</td>
<td>1379</td>
<td>Symmetric -CH$_3$ bend</td>
<td>Aliphatic hydrocarbon</td>
</tr>
<tr>
<td>923</td>
<td>930</td>
<td>Out-of-plane -CH$_2$ bend</td>
<td>Aromatics</td>
</tr>
</tbody>
</table>

3.4.4 Organic compound rejection

Organic compounds in the feed and DS tanks were analyzed with 3D EEM fluorescence and GC-MS. 3D EEM plots were used to qualitatively identify organic species. GC-MS quantitatively identified organic compounds and their concentrations. Organic rejection was calculated from the feed and DS tanks for CTA and TFC membranes and was related to molecular size and compound functional groups.
3.4.4.1 3D EEM results

The organic composition of the feed solution, CTA DS, and TFC DS were evaluated with 3D EEM in order to qualitatively describe organic rejection. The feed solution samples were taken from a fresh batch of produced water, and the DS samples were taken on day 21 of experiment. 3D EEM plots are shown for the feed solution, CTA DS, and TFC DS in Figure 3.7.

![Figure 3.7](image)

**Figure 3.7.** Three dimensional excitation-emission matrix (3D EEM) plots for (a) feed solution, (b) CTA DS, and (b) TFC DS. DS results represent samples taken on day 21, and feed solution results represent samples from a new produced water batch.

The feed solution had a maximum intensity centered on excitation/emission wavelengths (Ex/Em) 270/300 nm and a strong intensity region near Ex/Em 250/360 nm. CTA and TFC DS had similar 3D EEM plots with maximum intensities at Ex/Em 270/290 nm. The Ex/Em intensity in the CTA and TFC DS was consistent with the maximum intensity in the feed solution. The
similarity indicated that the corresponding compound diffused through both membranes from the feed solution.

Fluorescent compounds in produced water were either aromatic compounds with two or more benzene rings [59], natural organic matter (e.g., humic and fulvic acids) [17, 19], or microbial proteins (e.g., tryptophan) [19]. Riecker et al. [59] identified polycyclic aromatic hydrocarbons (PAHs) and heterocyclic hydrocarbons as the major fluorescent compounds in crude oil throughout the Rocky Mountain region. A number of studies have determined fluorescent spectra for PAHs [19, 60, 61], and fluorene (Ex/Em 260-280/305-311 [19, 60, 61]) matched closely with the peaks found in all three solutions. Naphthalene is another common PAH, but the corresponding spectra (Ex/Em 220/335 [60] and 236/350 [19]) was outside of the 3D EEM range. Other studies have proposed that natural organic matter and microbial proteins were fluorescent compounds in produced water [17, 19]. Reported values for marine humic-like acids (Ex/Em 290-310/370-410), visible humic-like acids (Ex/Em 320-360/420-460), soil fulvic-like acids (Ex/Em 521/455), and proteins (Ex/Em 240/324 and 280/324) were higher than the peaks found in the DS results but within fluorescent regions of the feed solution [62, 63]. Thus, the membranes likely rejected natural organic matter and microbes, but allowed for the diffusion of PAHs.

3.4.4.2 GC-MS results

The organic compounds in the feed solution, CTA DS, and TFC DS were further analyzed with GC-MS in order to identify specific compounds, quantify concentrations, and calculate membrane rejection. Samples were taken from the feed solution, CTA DS, and TFC DS tanks. Feed solution samples were taken from new batches of produced water and DS was sampled on day 21. Table 3.4 summarizes compound names, classes, molecular weights (MW, g/mol), minimum projection areas (MPA, Å²), log-D, pKₐ, and feed solution concentrations (µg/L). Compound rejection is shown in Figure 3.8, in which compounds are organized by class (aldehydes, ketones, aliphatics, and PAHs) and sorted by increasing molecular weight within each class.
Table 3.5. Organic compounds detected with GC-MS and associated molecular weight (MW, g/mol), minimum projection area (MPA, Å²), log-D, pKa, and feed solution concentration (µg/L).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Class</th>
<th>MW (g/mol)</th>
<th>MPA (Å²)a</th>
<th>log-D,b</th>
<th>pKa,a</th>
<th>Feed solutionc (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecanal</td>
<td>Aldehyde</td>
<td>184.32</td>
<td>23.34</td>
<td>4.40</td>
<td>17.79</td>
<td>28.8</td>
</tr>
<tr>
<td>Tridecanal</td>
<td>Aldehyde</td>
<td>198.34</td>
<td>30.46</td>
<td>4.85</td>
<td>17.79</td>
<td>56.3</td>
</tr>
<tr>
<td>Tetradecanal</td>
<td>Aldehyde</td>
<td>212.37</td>
<td>30.82</td>
<td>5.30</td>
<td>17.79</td>
<td>61.8</td>
</tr>
<tr>
<td>Pentadecanal</td>
<td>Aldehyde</td>
<td>226.40</td>
<td>30.54</td>
<td>5.76</td>
<td>17.79</td>
<td>45.3</td>
</tr>
<tr>
<td>Hexadecanal</td>
<td>Aldehyde</td>
<td>240.42</td>
<td>37.47</td>
<td>6.21</td>
<td>17.79</td>
<td>165.4</td>
</tr>
<tr>
<td>Octadecanal</td>
<td>Aldehyde</td>
<td>268.49</td>
<td>40.79</td>
<td>7.11</td>
<td>17.79</td>
<td>94.0</td>
</tr>
<tr>
<td>2-Octadecanone</td>
<td>Ketone</td>
<td>268.48</td>
<td>28.94</td>
<td>7.11</td>
<td>19.64</td>
<td>215.2</td>
</tr>
<tr>
<td>1-Octadecene</td>
<td>Aliphatic</td>
<td>252.48</td>
<td>31.72</td>
<td>8.27</td>
<td>--</td>
<td>46.3</td>
</tr>
<tr>
<td>Pristane</td>
<td>Aliphatic</td>
<td>268.51</td>
<td>65.80</td>
<td>8.36</td>
<td>--</td>
<td>95.2</td>
</tr>
<tr>
<td>Phytane</td>
<td>Aliphatic</td>
<td>282.56</td>
<td>57.03</td>
<td>8.81</td>
<td>--</td>
<td>89.6</td>
</tr>
<tr>
<td>Sum C10-C13 n-alkanes</td>
<td>Aliphatic</td>
<td>142.3-464.9</td>
<td>28.3-62.7</td>
<td>5.43-15.34</td>
<td>--</td>
<td>2221</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>PAH</td>
<td>128.17</td>
<td>24.02</td>
<td>2.98</td>
<td>--</td>
<td>24.7</td>
</tr>
<tr>
<td>Fluorene</td>
<td>PAH</td>
<td>166.22</td>
<td>24.58</td>
<td>3.75</td>
<td>17.8</td>
<td>2.13</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>PAH</td>
<td>178.23</td>
<td>26.93</td>
<td>3.96</td>
<td>--</td>
<td>2.61</td>
</tr>
<tr>
<td>Pyrene</td>
<td>PAH</td>
<td>202.25</td>
<td>30.30</td>
<td>4.28</td>
<td>--</td>
<td>0.49</td>
</tr>
<tr>
<td>Chrysene</td>
<td>PAH</td>
<td>228.28</td>
<td>31.77</td>
<td>4.95</td>
<td>--</td>
<td>1.26</td>
</tr>
<tr>
<td>Benz(a)anthracene</td>
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<td>228.29</td>
<td>27.90</td>
<td>4.95</td>
<td>--</td>
<td>0.82</td>
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<tr>
<td>Benzo(a)pyrene</td>
<td>PAH</td>
<td>252.31</td>
<td>32.02</td>
<td>5.27</td>
<td>--</td>
<td>1.06</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
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<td>252.31</td>
<td>34.32</td>
<td>5.27</td>
<td>--</td>
<td>1.00</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>PAH</td>
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<td>33.58</td>
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<td>1.07</td>
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<tr>
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<td>PAH</td>
<td>276.33</td>
<td>35.29</td>
<td>5.59</td>
<td>--</td>
<td>0.77</td>
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<tr>
<td>Indeno(1,2,3-c,d)pyrene</td>
<td>PAH</td>
<td>276.33</td>
<td>34.62</td>
<td>5.59</td>
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<td>0.76</td>
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<tr>
<td>Dibenzo(a,h)anthracene</td>
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<td>32.13</td>
<td>5.93</td>
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<td>0.67</td>
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</table>

aValues were obtained from Marvin Beans 15.10.19 software (https://www.chemaxon.com).
bLog-D values are log-Kow calculated at pH 8.
cFeed solution concentration is the average of samples from four batches of feed solution.

The feed solution contained higher concentrations of aliphatic hydrocarbons, ketones, and aldehydes than PAHs (Table 3.4). Aliphatic hydrocarbons and PAHs had high rejection rates that ranged from 98-100% for both CTA and TFC membranes (Figure 3.8). Compounds that contained aldehyde and ketone functional groups had lower rejection that ranged between 92-95% and 95-99% for CTA and TFC membranes, respectively.

Organic compound rejection is complex and involves compound properties, membrane properties, and compound-membrane interactions [53, 64-66]. Studies typically relate organic compound rejection to their hydrophobicity, charge (e.g., negative, positive, neutral), and molecular weight [53, 64, 67]. Compounds are considered hydrophobic when the octanol-water coefficient (log-Kow) is greater than 2 and neutral when pKa values are higher than pH [53, 68, 69].
Therefore, all compounds were hydrophobic because log-D values (log-$K_{ow}$ values calculated at pH 8 [68, 70]) were higher than 2 (Table 3.4), and all compounds were neutral because their $pK_a$ values were nonexistent or above the feed solution pH (Table 1).

**Figure 3.8.** Rejection of organic compounds (%) detected with GC-MS. Results are shown for CTA and TFC membranes, and compounds are organized by class and sorted by increasing molecular weight within each class: aldehydes (purple), ketones (green), aliphatics (red), and polycyclic aromatic hydrocarbons (blue). Rejection values were calculated from day 21 DS and average feed solution concentrations (p=4).

It is widely accepted that neutral hydrophobic compound rejection is dictated by steric hindrance and improves with increasing molecular weight [53, 64]. Fujioka et al. [68, 70] expanded on this concept and found that rejection correlated best with molecular size rather than molecular weight. The authors measured molecular size with minimum projection area (MPA, Å²), which is the smallest two-dimensional projection area for a three dimensional molecule. Thus, MPA was used in order to explore the effects of molecular size on neutral hydrophobic compound rejection. Compound rejection is shown as a function of MPA in Figure 9 for TFC and CTA membranes.

TFC membranes had higher rejection than CTA membranes for small neutral compounds, which is consistent with previous FO rejection studies [65, 66]. Xie et al. [71] attributed high
TFC membrane rejection to high active layer thickness to porosity ratios (L/ε) and greater pore hydration. High L/ε values indicate that the membrane has more internal pore surface area, which leads to enhanced adsorption and compound removal. Hydrated pores effectively reduce pore size and improve steric hindrance [66]. High RSF may have also contributed to higher rejection because the reverse diffusion of salts may hinder the forward diffusion of organic compounds [64].

Figure 3.9. Compound rejection (%) as a function of minimum projection area (Å²) for (a) CTA and (b) TFC membranes. Compounds are organized by class: aldehydes (purple), ketones (green), aliphatics (red), and polycyclic aromatic hydrocarbons (PAHs) (blue). Rejection values were calculated from day 21 DS and average feed solution concentrations (p=4).

Compound functional groups seemed to affect neutral hydrophobic compound rejection. For both membrane types, compounds at the same MPA but with aldehyde and ketone functional groups had lower rejection than aliphatic hydrocarbons and PAHs. Lower rejection may be because of the carbonyl groups in ketones (R-CO-R') and aldehydes (R-CHO); the carbonyl groups have hydrogen bonding capability, and potentially have a greater ability to adsorb to and diffuse through the membranes [53, 68-70, 72]. It is also interesting to note that CTA membranes had significantly lower rejection of these compounds than TFC membranes. The finding is in agreement with a previous study, in which low CTA rejection was attributed to neutral hydrophobic compound affinity to CTA membrane surfaces versus TFC membranes [67]. CTA membranes
also have lower L/ε values [66] and may have became saturated with these compounds, which can lead to decreased rejection of neutral hydrophobic compounds [64].

3.5 Conclusions

CTA and TFC membrane performance and fouling was evaluated during three weeks of produced water treatment. CTA membranes outperformed TFC membranes with higher water flux, lower RSF, and lower SRSF. CTA membrane efficiency improved over the three-week period, with an overall decrease in SRSF; conversely, TFC membrane efficiency deteriorated with drastic increases in SRSF. Zeta potential measurements revealed that cleaned and fouled TFC membranes became increasingly negative, and cleaned and fouled CTA membrane charge remained stable throughout the study. The negatively charged fouling layer may have induced a charge imbalance on the TFC membrane and caused increased reverse diffusion of cations (i.e., sodium), but systematic studies are needed to understand the effects of fouling layers on RSF.

TFC membranes had a much higher fouling propensity despite smoother, more hydrophilic, and more neutrally charged virgin membrane surfaces. ESEM and FTIR revealed that the foulant composition was similar for both membrane types. FTIR did not detect any biofouulant signatures, but found that organic fouling dominated and was likely comprised of aliphatic hydrocarbons, aromatic hydrocarbons, and carbonates. EDS results showed that inorganic fouling was dominated by iron and silicon, only TFC-F membrane had sodium and chloride, and only CTA-F and TFC-F membranes had calcium. High RSF likely caused sodium and chloride accumulation in TFC fouling layers, and sodium, chloride, and calcium ions were removed with EDTA CEOBs. Despite inorganic ion removal in the fouling layers, EDTA CEOBs only marginally improved water flux for fouled CTA and TFC membranes.

Organic rejection was examined using 3D EEM fluorescence spectroscopy and GC-MS. 3D EEM plots indicated that PAHs diffused through both membrane types, and naturally occurring organic matter and microbes were sufficiently rejected. GC-MS results showed that both membranes had over 90% rejection of neutral hydrophobic compounds, and TFC membranes achieved higher rejection than CTA membranes for small molecules. Both membranes had lower rejection of compounds with aldehyde and ketone functional groups, and CTA membranes had lower rejection of these compounds than TFC membranes.
3.6 References


CHAPTER 4
CONCLUSIONS

This thesis compared CTA and TFC membrane performance and fouling during long-term treatment of activated sludge and produced water. Membrane performance was measured as water flux, RSF, and SRSF and was compared for virgin and fouled CTA and TFC membranes. Membrane autopsies were performed on virgin and fouled membranes in order to determine the organic and inorganic composition of fouling layers, to determine changes in physiochemical membrane properties, and to delineate the importance of membrane properties on fouling. This chapter summarizes the conclusions from the two studies and offers implications and recommendations for future work.

4.1 Summary of FO fouling and performance during activated sludge treatment

CTA and TFC membranes were tested with high-salinity and low-salinity activated sludge feed for 10, 40, 70, and 100 days. CTA membranes outperformed TFC membranes with higher water flux, lower RSF, and lower SRSF. The effects of fouling on membrane performance were unclear, but negatively charged fouling layers were proposed as a mechanism for increased RSF. Physical defects were found in the TFC-LS membranes after 40, 70, and 100 days of fouling, and likely caused the drastic increases in SRSF for those membranes.

TFC membranes had a much higher fouling propensity than CTA membranes despite ideal virgin membrane properties; thus, we concluded that conventional membrane property measurements were not accurate indicators of fouling potential. Activated sludge composition (i.e., ionic strength, calcium, and MLSS) had minimal effects on fouling propensity. All membrane fouling layers had the same biofoulant composition, but inorganic fouling depended on activated sludge composition.

4.2 Summary of FO fouling and performance during produced water treatment

In the second study, FO membranes were evaluated during long-term treatment of produced water. The study used CTA and modified, antifouling TFC FO membranes, and membranes were fouled for one, two, and three weeks. The study expanded upon the first study by
evaluating CEOB efficacy, investigating changes in membrane charge, and determining organic compound rejection using GC-MS and fluorescence spectroscopy.

As in the first study, CTA membranes outperformed TFC membranes and TFC membranes had a higher fouling propensity despite ideal virgin membrane properties. The results also showed that CEOBs resulted in minimal improvements in water flux and fouling, but did seem to remove calcium ions from fouled CTA and TFC membranes and sodium and chloride ions from fouled TFC membranes. The organic compositions of the fouling layers were likely comprised of hydrocarbons and were similar for CTA and TFC membranes. TFC membranes became increasingly negative over the three weeks, which may lend to the corresponding increases in RSF and SRSF. Both membranes rejected over 90% of neutral hydrophobic compounds, in which TFC membranes had higher rejection. Compounds with hydrogen bonding capability had lower rejection, and CTA membranes had lower rejection of these compounds than TFC membranes.

4.3 Implications and future work

CTA membranes had superior performance to TFC membranes in both waste streams, with higher water flux, lower RSF, lower SRSF, and lower fouling propensity. TFC membranes were more prone to fouling despite ideal virgin membrane properties, and showed that future work is needed to accurately determine membrane properties that dictate long-term fouling propensity. The first study demonstrated that both FO membranes provided steady-state treatment in varied activated sludge compositions; however, TFC membrane performance significantly deteriorated in the second study and proved that CTA membranes were more reliable for produced water treatment. The second study also showed that current literature cleaning practices were inadequate for membranes fouled during long-term produced water treatment, and cleaning optimization is needed.