Understanding Submicron Foulants in Produced Water and their Interactions with Ceramic Materials

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Sandra Constanza Medina Muñoz

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The dissertation of Sandra Constanza Medina is in revision by the examination committee.

Ph.D. advisor: Dr. TorOve Leiknes

Committee Chairperson: Dr. NorEddine Ghaffour

Committee Members: Dr. Himanshu Mishra, Dr. Sigurdur Thoroddson, Dr. Ho Kyong Shon, and Dr. Assiyeh Tabatabai.
ABSTRACT

Understanding Submicron Foulants in Produced Water and Their Interactions with Ceramic Materials

Sandra Constanza Medina Muñoz

Produced water (PW), or water associated with crude oil extraction, is the largest oily wastewater stream generated worldwide. The reuse and reclamation of these important water volumes are critical for more sustainable operation in the oilfield. Ceramic membrane filtration is a promising technology for PW treatment; however, fouling is the major drawback for a broader application. Fouling leads to higher resistance to flow, reducing membrane lifetime, and ultimately leading to higher capital expenditures and operating expenses. Further understanding of the interactions between PW foulants and the ceramic materials is needed for designing fouling control strategies and cleaning protocols for ceramic membranes. This work explored different techniques to characterize, visualize, and quantify the submicron PW contaminants content and its adsorption interactions with metal oxides. We visualized and characterized submicron oil droplets in oilfield PW samples by applying suitable advanced microscopy techniques. For the first time, crude oil droplets as small as 20 nm were found in oilfield PW together with other submicron contaminants. The adsorption studies performed by quartz crystal microbalance with dissipation (QCM-D) showed that the interactions of organic surface-active compounds with the metal oxides are driven by the nature of the surfactant and not by the surface properties. This has implications in the selection of the ceramic membrane material, wherein
electrostatic interactions should not be taken as the only predicting factor of adsorption and fouling during PW treatment. Furthermore, our results suggested that the more fluid or viscoelastic-like the contaminant layer, the more difficult the cleaning process from the metal oxide. It demonstrates that the mechanical property of the attached films is a crucial factor in designing appropriate cleaning protocols for ceramic membranes. Finally, QCM-D and advanced microscopy techniques were applied to analyze adsorption and cleaning of contaminants in a complex Bahraini PW into alumina as a case study. Bacteria were found to attach irreversibly on the alumina surface, promoting nucleation points for calcium precipitates. The protocols developed in this work are suitable for understanding membrane fouling phenomena in the micron scale and could be implemented before filtration pilot testing to save time and expenses at larger scales.
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</tr>
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<tbody>
<tr>
<td>$^1$H-NMR</td>
<td>Proton nuclear magnetic resonance</td>
</tr>
<tr>
<td>CLSM</td>
<td>Confocal laser scanning microscopy</td>
</tr>
<tr>
<td>Cryo-SEM</td>
<td>Cryogenic Scanning electron microscopy</td>
</tr>
<tr>
<td>Cryo-TEM</td>
<td>Cryogenic transmission electron microscopy</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetrimonium bromide</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>DSD</td>
<td>Droplet size distribution</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EM</td>
<td>Electron microscopy</td>
</tr>
<tr>
<td>EpiFM</td>
<td>Epifluorescence microscopy</td>
</tr>
<tr>
<td>FTICR-MS</td>
<td>Fourier-transform ion cyclotron resonance mass spectrometry</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>O/W</td>
<td>Oil in water</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity index</td>
</tr>
<tr>
<td>PW</td>
<td>Produced water</td>
</tr>
<tr>
<td>QCM-D</td>
<td>Quartz crystal microbalance with dissipation</td>
</tr>
<tr>
<td>SDBS</td>
<td>Sodium dodecylbenzenesulfonate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
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Chapter 1. Introduction

1.1 Produced Water

Oil extraction involves the production of large volumes of water present in reservoirs. Volumes of this fossil water, or produced water (PW), can be as much as 393 million barrels per day (Produced Water Society, 2019). The ratio of PW to oil extracted could be from 3:1 up to 10:1 (Guerra et al., 2011). This production is mostly generated by conventional onshore operation (81.3%) and with an increasing global forecast of 619 million barrels by 2029, as shown in Figure 1-1. As such, PW contributes to around 70% of the volume of waste streams associated with oil and gas production (Çakmakce et al., 2008). Management of such quantities of PW is a key factor for oil producers due to the associated cost (Ottaviano et al., 2014).

Figure 1-1. Global produced water and hydrocarbons production by resource type. Courtesy of the Produced Water Society.
Produced water is considered an oil in water emulsion (O/W) containing a complex mixture of emulsified hydrocarbons, production solids, dissolved minerals, production chemicals and salts (Macedonio et al., 2014). The composition of PW is strongly dependent on field location (Çakmakce et al., 2008, Ebrahimi et al., 2009) and lifetime of a reservoir (Ebrahimi et al., 2010, Eftekhardadkhah and Øye, 2013). As such, management strategies for disposal and reuse require specific treatment.

Conventional treatment technologies are based on physical-chemical separation such as flotation cells, plate interceptors, dissolved air/gas flotation, hydrocyclones and centrifuges (Ottaviano et al., 2014). These traditional methods focus on the removal of free and dispersed oil (i.e., droplet size >10 μm), with low efficiency for emulsified oil (i.e., droplet size <10 μm) and dissolved oil (i.e., droplet size < 5 μm) elimination (Weschenfelder et al., 2015b). These conventional techniques rarely reduce oil concentration to 1% by volume (i.e., two orders of magnitude higher than the PW effluent requirements in Table 1-1) of the total PW (Chakrabarty et al., 2008), in addition to not reaching the suspended solid content required for reinjection (e.g., less than 1.0 mg/L for waterflooding) (Weschenfelder et al., 2015c). Therefore, conventional technologies do not completely accomplish the requirements for PW treatment.

PW quality requirements are determined by the final use or discharge standards, which dictate the methods of treatment. Drivers for PW treatment are local water scarcity, legislation, risk of formation plugging, high PW disposal costs, quality water for enhanced oil recovery (EOR), water demand in production operations, and even social perception (Dores et al., 2012). Current offshore disposal
standards require levels of total oil and grease (TOG) from 15 to 50 mg/L, depending upon the country as is shown in Table 1-1 (Stewart and Arnold, 2009).

<table>
<thead>
<tr>
<th>Country/Region</th>
<th>Limitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ecuador and Brazil</td>
<td>30 mg/L All facilities</td>
</tr>
<tr>
<td>Argentina, Colombia and Venezuela</td>
<td>15 mg/L New facilities</td>
</tr>
<tr>
<td>Indonesia</td>
<td>25 mg/L Grandfathered facilities</td>
</tr>
<tr>
<td>Malaysia, Middle East</td>
<td>30 mg/L All facilities</td>
</tr>
<tr>
<td>Nigeria, Angola, Cameroon, Ivory Coast</td>
<td>50 mg/L All facilities</td>
</tr>
<tr>
<td>North Sea, Australia</td>
<td>30 mg/L All facilities</td>
</tr>
<tr>
<td>Thailand</td>
<td>50 mg/L All facilities</td>
</tr>
<tr>
<td>USA</td>
<td>29 mg/L OCS water Zero discharge inland water</td>
</tr>
</tbody>
</table>

Furthermore, European effluent standards from onshore petroleum activities demand <5 mg/L of total hydrocarbons and <10 mg/L of total suspended solids (TSS) (Ashaghi et al., 2007). For onshore operations, surface disposal of PW is generally prohibited due to the high salt content. In limited cases of low salinity, the effluent could be treated and reused in agricultural or wildlife propagation (Hagström et al., 2016). Concentration limits for this disposal option are 35 mg/L of TOG and 2000 mg/L of total dissolved solids (TDS) (Li and Lee, 2009). However, concern remains on trace elements, chlorine residue and nutrients, which require significant treatment for reduction to allowed limits (Igunnu and Chen, 2014). For these reasons, subsurface injection is becoming the norm for PW disposal in onshore operations (Stewart and Arnold, 2011). More stringent effluent quality for reinjection into the low-permeability formation is also required by industry operators to avoid or minimize damage to the injectivity of water injection wells.
This is less than 5 mg/L of total hydrocarbon, less than 1 mg/L of TSS and media particle size lower than 1 μm (Li and Lee, 2009). With the updated environmental requirements and the increasing need of PW reclamation and reuse in agricultural and industrial operations (Igunnu and Chen, 2014), conventional separation processes cannot meet such high standards and further treating facilities are required. There is an increasing need for removing the submicron fraction of contaminants in PW with technologies sufficiently robust to operate under a wide variety of PW characteristics, such as membrane filtration processes.

1.2 Membrane filtration for Produced Water treatment

Application of low-pressure membrane systems in oil-field produced water (PW) treatment has been widely studied in recent years in an attempt to meet increasingly stringent discharge requirements (Igunnu and Chen, 2014). These discharge requirements imply the removal of emulsified oil (i.e., droplet size <10 μm), dissolved oil (i.e., droplet size < 5 μm)(Weschenfelder et al., 2015b). The removal of such particle sizes and concentrations can be reached by membrane processes, which act as a selective barrier for different components. Typically, microfiltration (MF) retains particles larger than 0.1 μm, defined as suspended particles, while ultrafiltration (UF) separates macromolecules ranging from 10 nm to 0.1 μm. Tighter membranes, such as those used in nanofiltration (NF), are capable of removing multivalent ions, ranging in size from 1 nm to 10 nm, and denser membranes found in Reverse Osmosis (RO) are capable of removing most of the ions and dissolved substances. Compared to other separation processes, UF has been proven to be the most versatile and effective process to remove oil from

Both polymeric and ceramic membranes are currently applied for PW treatment in full-scale facilities (Igunnu and Chen, 2014). Polymeric or organic membranes dominate the membrane market for water treatment and have been widely studied (Alzahrani and Mohammad, 2014). Organic membranes are typically made of PES (Polyethersulfone) or PVDF (Polyvinylidene fluoride) in hollow fiber configuration (Hög et al., 2015) and have shown effectiveness for the treatment of oil/water emulsions (Seyed Shahabadi and Reyhani, 2014). Advantages such as high-efficiency performance, compact membrane configuration and low cost compared to ceramic-based membranes, make polymeric membrane technology an economically competitive option (Padaki et al., 2015). However, during filtration, polymeric membranes are susceptible to chemical, mechanical and thermal degradation. As a result, frequent replacement of membranes is required, resulting in higher operating costs. Table 1-2 presents a summary comparing the properties of polymeric and ceramic membranes.

<table>
<thead>
<tr>
<th>Property</th>
<th>Ceramic MF/UF</th>
<th>Polymeric MF/UF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophilic character</td>
<td>High</td>
<td>Moderate</td>
</tr>
<tr>
<td>Permeability</td>
<td>High</td>
<td>Moderate</td>
</tr>
<tr>
<td>Stability (thermal, chemical, mechanical)</td>
<td>High</td>
<td>Low/moderate</td>
</tr>
<tr>
<td>Lifetime</td>
<td>10-20 years</td>
<td>5-7 years</td>
</tr>
<tr>
<td>Recyclability</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Operating costs (OPEX)</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Capital costs (CAPEX)</td>
<td>High</td>
<td>Low</td>
</tr>
</tbody>
</table>
1.3 Ceramic membrane filtration

Research on ceramic membranes in PW treatment has been fueled as a response to polymeric membrane limitations. $\text{Al}_2\text{O}_3$ (alumina), $\text{ZrO}_2$ (zirconia), $\text{TiO}_2$ (titania) (Hofs et al., 2011), and more recently, SiC (silicon carbide) (Kuhn et al., 2016) are commercially available ceramic membranes. These inorganic membranes present high thermal, chemical and mechanical stability, making them more promising for oil/water emulsions for industrial-scale with harsh operating conditions (Weschenfelder et al., 2015b), such as high temperatures and aggressive chemicals (e.g. solvents, highly acidic or caustic solutions) (Weschenfelder et al., 2015a). Other advantages are higher flux, narrow and well-defined pore size distribution (Padaki et al., 2015), potentially lower use of chemicals (Ashaghi et al., 2007) and operating expenses compared to polymeric membranes (Samaei et al., 2018). A disadvantage of ceramic membranes is their high capital cost (500-1000 US$/m^2 (Issaoui and Limousy, 2018)) relative to polymeric membranes (50-400 US$/m^2 (Samaei et al., 2018)). Nevertheless, prices are expected to continue to drop as a result of economy of scale, new manufacturers entering the market (Hög et al., 2015) and the introduction of low-cost alternative materials (e.g., MF kaolin based ceramic membranes with a production cost of $130/m^2 from Nandi et al. (2010), and UF membranes costing $100/m^2 from Mittal et al. (2011)). Ceramic membranes are a promising solution, as they showed a better performance than polymeric membranes for oil in water emulsions (Loganathan et al, 2015) with overall lower lifecycle cost (Lu et al., 2015).
1.4 Membrane fouling

Regardless of the growing application of membrane processes in PW treatment, fouling still limits the financial viability of membrane technology projects applied to PW treatment (Ebrahimi et al., 2010). Fouling is a phenomenon inherent to membrane separation processes as a result of the accumulation of particles or solutes at the membrane surface that reduces the solvent flow through the membrane. Fouling leads to higher resistance to flow resulting in lower permeate flux rate for a given driving force, reducing membrane lifetime and ultimately leading to higher capital expenditures (CAPEX) and operating expenses (OPEX) (Field, 2010). Adjustments on operating conditions and periodic hydraulic washing treatments (e.g., cross flush and backwash) (Lu et al., 2015) and chemical cleaning techniques have been useful to recover the flux decline caused by reversible fouling (Silalahi and Leiknes, 2009). However, these hydraulic washing and single chemical cleaning steps are not sufficient to fully restore a fouled membrane due to irreversible fouling (Faibish and Cohen, 2001). Irreversible fouling affects the membrane permanently and eventually the membrane has to be replaced (Seyed Shahabadi and Reyhani, 2014). In order to decrease OPEX and
CAPEX, a better understanding of fouling mechanisms to prevent both reversible and irreversible fouling needs to be addressed.

Fouling mechanisms during membrane filtration treatment of PW have been widely studied; however, they have not been fully described (Fouladitajar et al., 2013). In the context of research, PW is simulated as oil in water (O/W) emulsion and membrane fouling has been attributed to a combination of different phenomena (see Figure 1-3):

1. Oil droplets are attached and clustered on the membrane surface, coalescing and forming an oil layer, also referred to as a compressible gel layer (Ebrahimi et al., 2010).

2. Oil droplets are deformable so they can be squeezed through the pores allowing droplet break up and partial permeation, which contributes to intrapore blocking (Chakrabarty et al., 2008).

3. Adsorption of surface-active foulants and submicron oil droplets onto the membrane surface and pores walls (Matos et al., 2016).

Figure 1-3. Fouling mechanisms during O/W emulsion filtration
1.5 Submicron contaminants in Produced Water

Fouling studies applied to the treatment of O/W emulsions have used feed streams with droplets from nanometer to micrometer range (see Table 1-3). Most of these emulsions are made by mixing different types of oil and surfactants with high-energy methods, generally rotor/stator devices, which generate emulsions with different droplet mean sizes and broad droplet size distributions (DSD). As shown in the literature review (see Table 1-3), little attention has been placed on the study of submicron droplets fraction (i.e., <1 μm), which might play an important role in complete and partial pore-blocking as they have sizes comparable to MF (i.e., from 100 nm to 5 μm) and UF (i.e., from 10 nm to 100 nm) membrane pore size (Yang et al., 2015). Submicron droplets could represent a significant contribution to membrane fouling, especially irreversible fouling, which has not been quantified due to the lack of appropriate methodology for quantification and analysis of the submicron droplet size range (Ji et al., 2016, Tummons et al., 2016).

Besides the submicron oil droplets present in PW, aggregates and dissolved surface-active compounds in PW might play a key role in irreversible fouling of ceramic membranes (Faibish and Cohen, 2001, Fernández et al., 2005). Different chemical additives are added throughout the generation of PW. Corrosion inhibitors, scale inhibitors, and biocides are used for flow assurance and production enhancement. Coagulants and flocculants are applied for oil dehydration and during primary/secondary PW treatment. Later on, these surface-active chemicals might have detrimental effects downstream in membrane filtration systems during PW treatment (Walsh, 2018). Examples of these chemical additives are summarized in Table 1-4. These additives are usually
not disclosed by the operating oil company, and even so, commercial formulations of such chemicals are unknown as they are the intellectual property of the chemical/service provider company and not fully disclosed to the end-user.

Table 1-3. Synthetic oil in water emulsions used in fouling studies of MF/UF membranes

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Type of oil</th>
<th>Emulsification method</th>
<th>Oil concentration (ppm)</th>
<th>Surfactant</th>
<th>Droplet size range (μm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF PVDF</td>
<td>Gas oil</td>
<td>Mix 12000 rpm, 30 min</td>
<td>1000-20000</td>
<td>Tween 80</td>
<td>unreported</td>
<td>Fouladitajar et al. (2013)</td>
</tr>
<tr>
<td>MF low-cost ceramic</td>
<td>Crude oil</td>
<td>Sonicator, 15h</td>
<td>100</td>
<td>Non</td>
<td>0.06 - 7</td>
<td>Vasanth et al. (2013)</td>
</tr>
<tr>
<td>MF modified ceramic</td>
<td>Engine oil</td>
<td>Mix food blender, 2 min</td>
<td>1000</td>
<td>Tween®80, Span®80</td>
<td>0.67-7.4</td>
<td>Zhou et al. (2010)</td>
</tr>
<tr>
<td>MF ZrO₂ ceramic</td>
<td>Crude oil</td>
<td>Turrax mixer</td>
<td>180</td>
<td>Non</td>
<td>&lt; 30</td>
<td>Weschenfelder et al. (2015b)</td>
</tr>
<tr>
<td>MF Al₂O₃ ceramic</td>
<td>Crude oil</td>
<td>Turrax mixer</td>
<td>350</td>
<td>Serdox®</td>
<td>&lt; 15</td>
<td>Silalahl and Leiknes (2009)</td>
</tr>
<tr>
<td>MF low-cost ceramic</td>
<td>Crude oil</td>
<td>Sonicator, 15 h</td>
<td>40-50</td>
<td>Non</td>
<td>0.04 - 10</td>
<td>Nandi et al. (2009)</td>
</tr>
<tr>
<td>UF TiO₂/ZrO₂ ceramic</td>
<td>Crude oil and Diesel</td>
<td>Sonicator, 20 - 50 min</td>
<td>100</td>
<td>SDBS*, CTAB*, Tween®80</td>
<td>&lt; 0.5</td>
<td>Lu et al. (2015)</td>
</tr>
<tr>
<td>MF/UF ceramic</td>
<td>Waste oil</td>
<td>Mix for 30 min @ 60°C</td>
<td>113-5420</td>
<td>Non</td>
<td>unreported</td>
<td>Ebrahimi et al. (2010)</td>
</tr>
<tr>
<td>MF Al₂O₃ ceramic</td>
<td>Outlet from API unit in a refinery</td>
<td>26</td>
<td>N/A</td>
<td>&lt; 20</td>
<td></td>
<td>Abadi et al. (2011)</td>
</tr>
<tr>
<td>UF polymeric</td>
<td>Soybean oil</td>
<td>Mix 600 rpm @ 60°C, 24 h</td>
<td>5000</td>
<td>Non</td>
<td>unreported</td>
<td>Wandera et al. (2011)</td>
</tr>
<tr>
<td>MF polymeric</td>
<td>Hexadecane</td>
<td>Mix 1000 rpm, 20 min</td>
<td>773</td>
<td>SDS*</td>
<td>0.5-100</td>
<td>Tummons et al. (2016)</td>
</tr>
<tr>
<td>MF PVDF</td>
<td>Soybean, motor and crude oil</td>
<td>Mix 20000 rpm, 3-5 min</td>
<td>200</td>
<td>Xiameters®, Triton™</td>
<td>0.5-10</td>
<td>He et al. (2016)</td>
</tr>
</tbody>
</table>

*SDBS: sodium dodecyl benzene sulphonate; CTAB: cetyl trimethylammonium bromide and SDS: sodium dodecyl sulfate.

The singularity and complexity of PW characteristics introduce a fundamental challenge to optimize its treatment through the ceramic membrane filtration process. The interaction of submicron contaminants present in PW into the
ceramic membrane is not well understood. Therefore, there is a need to establish methods and protocols that allow a better understanding of those interactions and their impact on ceramic membrane fouling.

Table 1-4. Common chemicals additives affecting PW treatment. Summary from (Walsh, 2018).

<table>
<thead>
<tr>
<th>Function</th>
<th>Chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion inhibitors</td>
<td>Cetyl trimethyl ammonium bromide (CTAB)</td>
</tr>
<tr>
<td></td>
<td>Film forming amine (FFA)</td>
</tr>
<tr>
<td></td>
<td>Quaternary amines</td>
</tr>
<tr>
<td></td>
<td>Orthophosphates (anodic inhibitors)</td>
</tr>
<tr>
<td></td>
<td>Polyphosphates (cathodic inhibitors)</td>
</tr>
<tr>
<td>Scale inhibitors</td>
<td>Sodium polyphosphate</td>
</tr>
<tr>
<td></td>
<td>PMA (Polymaleic Anhydride)</td>
</tr>
<tr>
<td></td>
<td>2-Acrylamido methyl propane sulfonic acid</td>
</tr>
<tr>
<td></td>
<td>Hydroxyethylidiene disphosphonic acid</td>
</tr>
<tr>
<td></td>
<td>PAA (Polycarboxylic Acid)</td>
</tr>
<tr>
<td></td>
<td>Polycarboxylic acid</td>
</tr>
<tr>
<td></td>
<td>Sulfonated Styrene/Maleic Acid</td>
</tr>
<tr>
<td></td>
<td>CMI, Carboxymethyl inulin</td>
</tr>
<tr>
<td></td>
<td>ATMP, Amino tri(methylene phosphonic acid)</td>
</tr>
<tr>
<td></td>
<td>HEDP, Hydroxyethylidiene Diphosphonic Acid</td>
</tr>
<tr>
<td></td>
<td>DTPMP, Diethylenetriamine-penta methylene phosphonic acid</td>
</tr>
<tr>
<td></td>
<td>HDTMP, Hexamethylenediamine (tetramethylene phosphonic acid)</td>
</tr>
<tr>
<td></td>
<td>BHPMP, Bis Hexamethylenediamine penta (methylene phosphonic acid)</td>
</tr>
<tr>
<td>Biocides</td>
<td>Glutaraldehyde</td>
</tr>
<tr>
<td></td>
<td>Quaternary amine compounds</td>
</tr>
<tr>
<td></td>
<td>Acrolein (unsaturated aldehyde)</td>
</tr>
<tr>
<td></td>
<td>Bronopol (2-bromo-2nitropropane-1,3-diol)</td>
</tr>
<tr>
<td></td>
<td>DBNPA (2-2-dibromo-3-nitro propionamide)</td>
</tr>
<tr>
<td></td>
<td>THPS (tetrakishydroxymethyl phosphonium sulfate)</td>
</tr>
<tr>
<td></td>
<td>TTPS (Tributyl tetradecyl phosphonium chloride)</td>
</tr>
<tr>
<td></td>
<td>DMO (Dimethyl Oxazolidine)</td>
</tr>
<tr>
<td></td>
<td>Dazomet (tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione)</td>
</tr>
<tr>
<td>Coagulants/</td>
<td>Polyaluminum chloride (PAC)</td>
</tr>
<tr>
<td>flocculants</td>
<td>Epichlorohydrin</td>
</tr>
<tr>
<td></td>
<td>Ferric chloride</td>
</tr>
<tr>
<td></td>
<td>Ferric sulfate</td>
</tr>
<tr>
<td></td>
<td>Aluminum chloride</td>
</tr>
<tr>
<td></td>
<td>Aluminum sulfate</td>
</tr>
<tr>
<td></td>
<td>Polyacrylamide (PAM)</td>
</tr>
<tr>
<td></td>
<td>Amino-methylated poly acrylamide (AMPAM)</td>
</tr>
<tr>
<td></td>
<td>Dodecylbenzenesulfonic acid</td>
</tr>
</tbody>
</table>
1.6 Research Objectives

The main goal of this research is to study the interactions of submicron contaminants in PW onto different ceramic materials and how they may impact membrane fouling when ceramic membranes are applied for advanced treatment of PW.

1.6.1 Specific objectives

1. To develop a methodology for visualization and quantification of submicron oil droplets size distribution (DSD), using optical and electron microscopy techniques.

2. To study the adsorption of surfactants onto ceramic membrane materials, using quartz crystal microbalance with dissipation monitoring (QCM-D).

3. To evaluate the removal of surfactants and recovery of ceramic membrane surfaces based on cleaning strategies.

4. To characterize the submicron contaminants in real PW sample and their impact on irreversible adsorption onto ceramic membrane materials.

1.7 Hypotheses

In this section, the hypotheses (H) and its associated research questions (R.Q.) addressed in this investigation are described.
H1: Membrane fouling during O/W emulsions filtration is related to droplet size, whereby submicron droplets play a key role in the irreversible fouling of MF/UF ceramic membranes.

R.Q.1.1: How can submicron droplets be characterized?

R.Q.1.2: Can epifluorescence and confocal microscopy techniques enable the determination of emulsion DSD through image analysis for droplets larger than 0.3 μm?

R.Q.1.3: Can cryo-SEM and cryo-TEM techniques be applied to the study of DSD of emulsions with droplets smaller than 0.3 μm?

R.Q.1.4: How small are the oil droplets present in real Produced Water?

H2: Surfactants adsorption is an important fouling mechanism in ceramic membrane filtration of PW.

R.Q.2.1. How can the impact of surfactant adsorption phenomena in membrane fouling be measured?

R.Q.2.2. How strong are the interactions of surfactants with ceramic membrane materials?

R.Q.2.3 Do surfactants adsorb differently depending on the type of metal oxide?

H3: Hydraulic cleaning strategies are not sufficient to remove fouling by surface-active compounds. Alternative cleaning is needed.
R.Q.3.1. Is it possible to clean the ceramic surfaces from known adsorbed surfactants?

R.Q.3.2. Is it possible to clean the ceramic surfaces from adsorbed surfactants present in the Real PW?

H4: Organic compounds present in PW are the major factor impacting the irreversible adsorption on ceramic membrane materials.

R.Q.4.1 How can submicron contaminants be characterized in such complex matrices as real PW samples?

R.Q.4.2 How can the impact be evaluated?

R.Q.4.3 Is the adsorption of these organic compounds irreversible?

1.8 Outline of the thesis

The results of this Ph.D. research are presented in 6 chapters that form the main structure of this document. The research questions were a fundamental guide for experimental planning and analysis. Chapter 1 contains the necessary introduction to understand the motivation behind and the focus of the research. The following chapters 2-5 are based on journal publications. Chapter 2 responds to the research questions of hypothesis 1, where submicron oil droplets in synthetic and real PW samples were visualized and characterized by advanced microscopy imaging techniques. Chapter 3 focuses on the fundamental understanding of surfactant adsorption interaction with common ceramic membrane materials, targeting titania, zirconia and alumina. In Chapter 4, surfactant studies were conducted focusing on the recovery of fouled metal oxide
surfaces by applying cleaning methods for the removal of the adsorbed surfactants. In Chapter 5 the methodology developed in Chapter 2 and the knowledge obtained from works in Chapters 3 and 4 were combined to study the submicron contaminants in an oilfield PW sample and assess their impact on irreversible adsorption onto a metal oxide surface. Chapter 6 provides conclusions and recommendations for future work.

1.9 List of publications

The results and findings of the study are presented in five peer-reviewed scientific journal publications as outline below:


### 1.10 Dissemination of results

The work from this research study has also been presented at various international conferences. Oral presentations have been given at the following events:


1.11 References


SEYED SHAHABADI, S. M. & REYHANI, A. 2014. Optimization of operating conditions in ultrafiltration process for produced water treatment via the


Chapter 2. **Microscopy techniques applied to submicron characterization of oilfield Produced Water**

This chapter responds to the research questions of hypothesis 1. Droplet size distribution in oilfield produced water was able to be characterized by applying optical and electron microscopy techniques. Oil droplets as small as 20 nm were observed in oilfield PW samples by cryo-TEM. Submicron contaminants other than oil droplets were identified, which should be further studied for improved PW treatment.

HIGHLIGHTS

- Oil droplets as small as 20 nm were observed in oilfield PW samples by cryo-TEM
- EpiFM of immobilized gelled samples is a suitable technique to determine the DSD in PW
- Cryo-SEM-EDS complements information on the nature of the submicron contaminants in PW
- Submicron contaminants other than oil droplets should be further studied for improved PW treatment

ABSTRACT

Produced water (PW) and formation water are complex mixtures of hydrocarbons and water produced at oil and gas upstream facilities. Conventional de-oiling technologies do not efficiently remove submicron oil droplets in PW. An accurate characterization of submicron oil droplets and contaminants is required to improve PW treatment technology. The submicron content of two PW samples from different oil fields in the Middle East region was characterized by optical and electron microscopy. The microscopy techniques employed were epifluorescence microscopy (EpiFM), confocal laser scanning microscopy (CLSM), cryogenic scanning and transmission electron microscopy (cryo-SEM and cryo-TEM, respectively). EpiFM of immobilized gelled samples was found to be the most suitable technique to determine the droplet size distribution (DSD) in PW for oil droplets larger than 250 nm. Cryo-SEM imaging did not provide much insight into
the PW samples with low oil concentration. However, cryo-SEM coupled with energy-dispersive X-ray spectroscopy (EDS) provided valuable information on the morphology and elemental composition of the submicron-sized contaminants. Plunge freezing of PW samples for Cryo-TEM imaging revealed the presence of oil droplets as small as 20 nm in size. Moreover, a relatively large amount of other submicron particulates/aggregates were observed in PW samples, which may have importance in defining the PW treatment strategy. The effect of these submicron contaminants, other than oil droplets, present in PW needs to be addressed to improve the PW treatment technologies.

GRAPHICAL ABSTRACT

**KEYWORDS:** Produced water, formation water, Epifluorescence/CLSM microscopy, cryo-TEM/cryo-SEM, droplet size distribution (DSD).
2.1 Introduction

Oily wastewaters are oil in water (O/W) emulsions generated in a variety of industries such as food and beverage, pharmaceutical, metal and machining, shipping and maritime, and oil & gas. The oil & gas industry manages one of the largest oily wastewater streams referred to as produced water (PW), which is water associated with hydrocarbons production from underground reservoirs, estimated at a global volume of 393 million barrels per day (Produced Water Society, 2019). Most countries have implemented stringent regulatory standards for discharging produced water which range from 10 mg/L O/W by China Environmental Ministry to a maximum of 42 mg/L O/W by the United States Environmental Protection Agency (USEPA). The treatment of large PW volumes requires different de-oiling technologies for effectively removing the suspended oil depending on the diameter of the droplets. The droplet size distribution (DSD) is a key design parameter for PW treatment processes and technology selection, as it influences the stability of the O/W emulsion (Sommerling et al., 2016).

The main objective of industrial PW treatment has been the removal of suspended crude oil by phase separation (Dores et al., 2012, Dudek et al., 2018). Primary oil/water separators are designed to remove oil droplets with a diameter greater than 50 μm (Walsh et al., 2014). Removal of smaller droplets is commonly achieved with hydrocyclones, disc stack centrifuges, and multi-stage flotation units, capable of removing oil droplets as small as 10 μm (Walsh, 2015). However, smaller oil droplets in the micron and submicron range can be formed as a result of shear forces, pressure drop, and the addition of chemicals during the production process (Walsh, 2018b). The submicron oil droplets (diameter ≤1-2
μm) have also been referred to as the water accommodated fraction (WAF), according to Faksness et al. (2004). The term submicron rather than WAF is preferred in this study to be more explicit about the meaning of this fraction with the reader. This submicron oil droplets population in PW is not removed efficiently by conventional de-oiling technologies making it a challenge to meet the more stringent environmental regulations for water discharge and preventing economical PW treatment for reuse applications. To better design PW treatment processes, it is essential to accurately characterize the size distribution of the contaminants in the submicron range.

Direct and indirect methods for DSD characterization of O/W emulsions have been applied in industry and research. Direct methods correspond to microscopy techniques to directly observe the droplets/particles in a suspension. On the other hand, indirect methods determine the DSD from different properties of the analyte in the emulsion, such as light scattering or reflection from a light source (Less and Vilagines, 2013), diffusion velocity, and chemical-electrical properties (Abidin et al., 2013). Examples of indirect methods are dynamic light scattering (DLS) and laser diffraction (LD) ((Silalahi et al., 2009, Zhou et al., 2010, Vasanth et al., 2013, Tummons et al., 2016)), laser reflection (Heath et al., 2002, Schümann et al., 2015), ultrasonic extinction or attenuation spectroscopy (Richter et al., 2007), asymmetrical flow field-flow fractionation (AF4) (Kuntsche et al., 2009, Makan et al., 2016) and nuclear magnetic resonance (NMR) (Goudappel et al., 2001, Voda and van Duynhoven, 2009, Sommerling et al., 2016). Further description of the advantages and limitations of indirect methods can be found elsewhere (Goodarzi and Zendehboudi, 2019). Indirect methods have been widely applied due to their
sampling convenience and relatively rapid measurements. However, these methods are limited to measuring droplets sizes above 1 μm or more. Moreover, they mostly rely on optical and/or electron microscopy (EM) for comparison of results and estimation of errors, e.g., DLS vs AF4 vs EM, (Kuntsche et al., 2009), DLS vs EM (Grapentin et al., 2015), focused beam reflectance measurement (FBRM) vs video microscopy (Schümann et al., 2015), NMR vs optical microscopy (Denkova et al., 2004), NMR vs confocal laser microscopy (Johns, 2009), ultrasonic attenuation spectroscopy vs optical microscopy (Dukhin and Goetz, 2005), etc. Compared to indirect methods, microscopy techniques allow direct observation of the sample and are suitable for measuring submicron objects, obtaining not only qualitative results but also a more accurate quantification of DSD in the submicron size range (Denkova et al., 2004).

The main advantage of microscopy techniques is to provide information on the shape of the objects present in the emulsion, thus allowing the differentiation between droplets and particles. This is particularly useful for highly polydispersed emulsions in a wide range of sizes; however, results depend on the type of microscopy performed. Examples of commercially available microscopy-based equipment for on-line measurements of particles and DSD for PW are ViPA-Visual Process Analyser (Jorin Limited, United Kingdom), EX-100M-1000M (Advanced Sensors, United Kingdom >1 μm), INFLOW™ analyzer (J.M. Canty, United States), EyeTech™ (Ankersmid B.V., Netherlands), FlowCam™ 8000 series (Fluid Imaging Technologies, Inc., United States), and ParticleView™ V19 with particle vision and measurement (PVM®) technology (Metter-Toledo Inc., Columbus, United States).

In general, these commercially available microscopy-based methods can measure
oil in water content and DSD, in emulsions with oil concentrations from 0.1% up to 15% v/v, detecting droplets/particles larger than 1-2 μm. Optical microscopy techniques such as epifluorescence (EpiFM) and confocal laser scanning microscopy (CLSM) are more commonly used in research to identify droplets down to ~300 nm. These techniques allow the differentiation of crude oil droplets from gas/air bubbles and other particles in the emulsion, as they fluoresce under a UV light due to the aromatic hydrocarbon content in the crude oil (Ryder, 2005). The oil fluorescence can be enhanced by adding oleophilic dyes to the O/W emulsion, allowing the analysis of different types of oil (Denkova et al., 2004). Consequently, EpiFM and CLSM have been widely applied in measuring the DSD larger than 1 μm diameter in O/W emulsions from different industries, such as in food (Schuster et al., 2012, Bai et al., 2019), biofuels (Kim et al., 2017), metalworking (Ríos et al., 2002), and oil & gas (Ma et al., 2008). However, no literature references applying EpiFM or CLSM for submicron DSD analysis and characterization of PW were found.

EM can analyze emulsions in the nanometer size range, with a resolution of 0.07 nm for transmission EM (Dudkiewicz et al., 2011). Depending on the fixation method used, EM can maintain the internal structure of the emulsion (Klang et al., 2012). Chemical fixation with glutaraldehyde is not recommended as oil droplets shrink as a result of the process (Jensen, 2013). Cryogenic freezing has been demonstrated to be the best fixation technique (Hurbain and Sachse, 2011). In cryo-EM, the sample characterization is done in a vitreous frozen-hydrated state, avoiding chemical treatment, and hence being closer to the native state of the sample (Dudkiewicz et al., 2011). Successful vitrification is the transformation of
water from a liquid to an amorphous state without inducing ice crystals formation, which causes structural damage (Tomova, 2013). The best examples of EM techniques applied to characterize O/W emulsions are cryogenic scanning electron microscopy (cryo-SEM) and transmission electron microscopy (cryo-TEM) (Hurbain and Sachse, 2011). Cryo-TEM, in particular, has been demonstrated to be important for the overall morphology and droplet size characterization of nano-emulsions as it is possible to obtain quantitative data from smaller features (Klang et al., 2012). Cryo-SEM is preferably used for analyzing the surface of a bulk sample, providing a sample visualization with a depth of field as the electron beam scans the surface (Dudkiewicz et al., 2011). Previously in our group, we successfully optimized the sample preparation of synthetic PW for cryo-EM (Anjum et al., 2017). However, no cryo-EM studies have been done on PW samples.

This study aims to improve the visualization and characterization of the submicron droplet fraction (i.e. < 1 μm) in oilfield PW by combining both optical and cryo-EM microscopy techniques. First, synthetic crude O/W emulsions were used to determine the most suitable method among four microscopy techniques, i.e. EpiFM, CLSM, cryo-SEM, and cryo-TEM. The method was then developed and applied to two PW samples from different oil fields in the Middle East region. This allowed a qualitative and quantitative particle size analysis of the submicron content in PW samples.
2.2 Materials and Methods

2.2.1 Synthetic Produced Water

Synthetic PW samples were used to improve and standardize the sample preparation methodology for EpiFM, CLSM, cryo-SEM and cryo-TEM, due to the limited volume of oilfield PW samples available. Two solutions of synthetic PW at different crude oil concentrations were prepared: 100 mg/L for EpiFM and CLSM, and 10,000 mg/L for cryo-SEM and cryo-TEM. This higher oil concentration in the synthetic PW for cryo-EM was chosen to increase the population of droplets facilitating its identification. The composition of the synthetic PW samples was simplified to crude oil in water emulsion, as its purpose in this study was for the visualization of oil droplets rather than studying chemical interactions. Medium crude oil from the Middle East region (API of 27.9° at 15.6 °C, measured by DST-120 API, Chongqing TOP Oil Purifier Co., Ltd., China) was added to a solution of Milli-Q water with SDBS surfactant (sodium dodecyl benzenesulfonate, Sigma-Aldrich, USA) at a surfactant/oil mass ratio of 1:10. The components were mixed at 15,000 rpm for 5 minutes with a T25 digital ULTRA-TURRAX® homogenizer (IKA®-Werke GmbH & Co. KG, Germany) and then sonicated (Q700 sonicator, Qsonica) for 10 minutes.

2.2.2 Produced Water samples

PW samples were received from two different oil fields in the Middle East region. PW1 is from a facility producing Arab light crude oil (API degree = 31.5; density = 865 kg/m³ at 25 °C) in the eastern province of Saudi Arabia. The PW1 sample was collected at the PW de-oiling gravity separator vessel, named Water Oil Separator.
(WOSEP), in the oil production plant. The specification for maximum oil content in the PW at the sampling location is 1,000 mL/L (v/v). More details on the oil-water separation process in the plant can be found in (Ahmed et al., 2020). At this location in the production process, the PW is a complex mixture of underground formation water, freshwater injected in the process for desalting the crude oil, dissolved and suspended hydrocarbons, and some low dosage chemicals (corrosion inhibitor, demulsifier additives, etc.).

The PW2 sample, on the other hand, is from a facility producing Arab light crude in Bahrain (API degree = 31.7; density = 866.2 kg/m³ at 15 °C). PW2 was taken downstream of an induced gas flotation (IGF) unit used for PW de-oiling in the water treatment plant. The specification for maximum oil content in the PW after de-oiling at the sampling location is 50 mL/L (v/v). At this location, the PW is a mixture of formation water, dissolved and suspended hydrocarbons, and low dosage treating chemicals (corrosion inhibitor, demulsifier additives, etc.). The ionic composition of PW1 and PW2 are shown in Table S1 of the Supporting Information. Total oil and grease (TOG) concentrations were measured by IR absorption at 2,930 cm⁻¹ following the ASTM D7066-04 method (ASTM, 2011). The portable equipment InfraCal2 TRANS-SP (Spectro Scientific, USA) was used as IR analyzer. DSD of the PW samples was also measured by DLS (Zetasizer Nano ZS, Malvern, United Kingdom) to compare against the EpiFM method. Practical salinity was measured by WTW Cond3310 (ProfiLine24 GmbH, Germany). Total alkalinity as CaCO₃ was measured by TNT 870 kit (Hach, USA).

Nile Red dye (maximum absorption/emission: 550/590 nm, Sigma-Aldrich, USA) was added in the PW samples for enhanced visualization of crude oil droplets in
EpiFM and CLSM. 5 μL of a Nile Red stock solution of 20 μg/mL acetone was added per milliliter of the sample (Greenspan et al., 1985). Nile Red stock solution was kept refrigerated and out of light exposure.

2.2.3 Optical microscopy techniques

The sampling technique of emulsions is important because coalescence and creaming of oil droplets could occur during the DSD measurement. Also, measuring DSD may require dilution of the sample that usually alters the actual distribution of the droplets (Van Dalen, 2002). Besides, as smaller droplets are analyzed, the effects of Brownian motion are more notable, making it difficult to take images with adequate contrast (Ríos et al., 2002). To overcome these limitations, immobilization of emulsions by a gelling solution has been used to effectively measure the DSD (Ríos et al., 2002, Van Dalen, 2002, Benito et al., 2004, Schuster et al., 2012). The Ríos et al. (2002) protocol for immobilization of emulsions using agarose was evaluated on synthetic PW and improved according to results in section 2.3.1.1.1.

EpiFM and CLSM images of the immobilized PW were taken with a LSM710 (Carl Zeiss Microscopy GmbH, Germany) using oil immersion objective of 60X. This CLSM microscope can also take EpiFM images by deactivating the pinhole function. Consequently, the same sample area can be analyzed by both EpiFM and CLSM. For EpiFM mode, oil droplets were labelled with green fluorescent proteins (GFP). For CLSM, the laser argon 514 nm was used to excite the sample. The emission range of the detector was 530-725 nm. The gain was set under the value of 800 to avoid noise. When oil immersion objectives are used, it is recommended
to use a cover glass of 0.75 mm thickness. Model silica particles of 1 μm size with red fluorescence sicastar®-redF (Micromod Partikeltechnologie GmbH, Germany) were used as standards for calibration of the image post-processing by Fiji (*i.e.* a processing package based on ImageJ) open-source platform (Schindelin et al., 2012). With the DSD obtained from image analysis, the polydispersity of the emulsions can be calculated. Polydispersity is defined as the degree of heterogeneity of droplet sizes. Its magnitude is proportional to the standard deviation of the DSD function. The polydispersity index (PDI) is useful for DSD comparison between emulsions. PDI is calculated as the squared ratio of the standard deviation (SD) and the mean diameter (D$_{50}$) as shown in Equation 2-1 (García-Celma et al., 2016).

$$PDI = \left( \frac{SD}{D_{50}} \right)^2 \quad Eq. \ 2-1$$

A PDI value of 0 is obtained for perfectly uniform droplet sizes, and a value of 1 is for highly polydisperse emulsions with multiple droplet sizes. Emulsions are classified as monodisperse when PDI is lower than 0.1. Emulsions with PDI higher than 0.7 are classified as polydisperse and not suitable for DLS analysis (Danaei et al., 2018).

### 2.2.4 Electron microscopy techniques

#### 2.2.4.1 Cryogenic scanning electron microscopy (cryo-SEM)

10,000 mg/L synthetic PW with agarose (3 wt%) were cryo fixed by two different methods: plunge freezing, and high-pressure freezing (HPF) before cryo-SEM imaging. These two cryofixation methods were evaluated to choose the best one on preserving the spherical shape of the oil droplets. Further details of the sample
preparation procedure and equipment conditions for plunge freezing, and HPF cryo-SEM are given in Text S1 and Text S2 of the Supporting Information, respectively. To image freeze fractured plane of the sample by plunge freezing, Nova NanoSEM 630 (Thermo Fisher Scientific, USA) equipped with Everhart-Thornley detector (ETD), through-the-lens detector (TLD) and PP2000T cryo-transfer system (Quorum Technologies, UK) was used.

To image the vitrified fractured plane of the emulsion by HPF, Helios G4 dual-beam SEM (Thermo Fisher Scientific, The Netherlands) equipped with Everhart-Thornley detector (ETD), through-the-lens detector (TLD) and Leica cryo stage (Leica Microsystems, Austria) was used.

2.2.4.2 Cryogenic transmission electron microscopy (cryo-TEM)

Cryo-TEM imaging was performed without adding agarose to either synthetic or oilfield PW samples. The plunge freezing system of model Vitrobot™ (Thermo-Fisher Scientific, USA) was used for the vitrification of the samples to minimize sample contamination (Passmore and Russo, 2016). The TEM specimen was prepared by first placing 2 µL of sample onto the holey-carbon grids, blotted by filter-papers to remove the excess sample, and submerged into a liquid ethane cryogenic pot. The prepared specimens were then transferred and ultimately imaged in Titan Krios (Thermo-Fisher Scientific, USA). The analysis of samples was carried out by setting the microscope to the 300 kV acceleration and bright-field TEM (BF-TEM) mode of operation. Digital images were recorded using slow-scan charged coupled devices (CCD) camera of model US1000 from Gatan, Inc.
2.2.4.3 Cryo-SEM couple with Energy-Dispersive X-ray Spectroscopy (cryo-SEM-EDS)

5 mL of an oilfield PW sample was filtered by 25 nm pore size, 25 mm diameter mixed cellulose esters (MCE) membrane (Millipore™, USA). The retentate content remaining on the filter was then visualized and analyzed by cryo-SEM-EDS. To image and analyze this retentate, Nova NanoSEM 630 (Thermo Fisher Scientific, The Netherlands) equipped with Everhart-Thornley detector (ETD), through-the-lens detector (TLD), EDS detector (EDAX Inc.) and PP2000T cryo-transfer system (Quorum Technologies, UK) was used. A section of the contaminated filter was secured on the aluminum cylinder using aluminum tape and was plunge frozen in slush liquid nitrogen, sublimed and coated with 5 nm Pt. Secondary electron images were acquired at accelerating voltages of 3 kV and at 5 mm working distance. EDS was used to determine the elemental composition of PW on a selected area of the filter or a localized spot. EDS was performed in cryo mode using an accelerating voltage of 10.0 kV and a working distance of 5 mm.

2.3 Results and discussion

2.3.1 Microscopy methods applied in synthetic Produced Water

2.3.1.1 Optical microscopy

2.3.1.1.1 Sample immobilization

The Ríos et al. (2002) protocol for gelling the emulsions was evaluated. In this protocol, the gel is prepared by heating a 2 wt% agarose (type I-N, low EEO, Sigma Aldrich) solution to 80 °C in distilled water. The agarose solution is then mixed in
equal proportion into the O/W emulsion sample in a test tube and allowed to cool down to gelling temperature (35-40 °C). Circular gel portions are cut from the test tube and placed on microscope slides for observation. Following the described protocol, the mixing methodology in the test tubes was found not to guarantee gel uniformity. Also, the thickness of each circular gel cut is variable, making it difficult to obtain reproducible well-focused images (Rhyu et al., 2016).

To overcome these problems, a revised method for O/W emulsion immobilization is proposed to provide reproducible results with a faster procedure. In this immobilization method, low-temperature agarose (*i.e.* melting point of 65 °C and congealing temperature between 26-30 °C, A9414 Sigma-Aldrich) was used to reduce temperature fluctuations in the emulsion. The procedure consists of:

1. Add 150 mg of low-temperature agarose directly to 5 mL of emulsion sample.

2. Heat the mix to 65 °C in a microwave (approx. 5 seconds)

3. Pipette 1 mL of the mix over a corner of a tilted microscope slide. Let the mix spread along the slide while cooling.

Different concentrations of low-temperature agarose were tested to ensure gel strength. 30 mg of agarose per mL of the sample was found suitable for sufficient hold of the sample on the microscope slide for easier handling and storage. This procedure could be easily applied on-site to immobilize PW samples and avoid possible DSD fluctuations during sample transportation to the laboratory facilities. Gelled samples must be stored at 4 °C to avoid dehydration.
100 mg/L synthetic PW was first observed by EpiFM to verify the effectiveness of the sample immobilization technique. As shown in Figure S1, the method for sample immobilization enables a sharp and clear observation of droplets in comparison to a non-immobilized sample.

2.3.1.2 Image acquisition

LSM710 microscope allows to taking both EpiFM and CLSM images of the same sample. Figure 2-1 shows an example comparing EpiFM and CLSM results. EpiFM allows capturing images with a larger area of the sample. This is due to the CLSM image only covering the laser incidence region, which allows a better focus at determined Z focal plane. The example in Figure 2-1 shows the smaller area of CLSM capture (i.e., 425.1 x 425.1 μm) compared to the one by EpiFM (i.e., 710.52 x 532.30 μm).

![Figure 2-1. Immobilized synthetic PW observed with a) EpiFM and b) CLSM. Scale bar is equivalent to 50 μm.](image)

For droplets smaller than 5 μm, it was found that CLSM images had granular noise, which made the counting of the oil droplets more difficult during image post-processing compared to EpiFM results. Furthermore, the photo-bleaching of the
sample was evident during CLSM. Advantages of CLSM, such as the generation of 3D structures and eliminating the out-of-focus interferences, did not represent a real benefit for observing submicron droplets in such relatively low concentration O/W emulsions. For these reasons, EpiFM was identified as the most convenient technique to be applied to the immobilized PW samples.

2.3.1.1.3 Image postprocessing

To reach detection of droplets as small as 0.25 μm diameter, the 60X or higher objective lens power (e.g. 100X) should be used. As a result of this applied magnification and low oil concentration in the sample (i.e. 100 mg/L), the density of submicron oil droplets in the images can be relatively low (i.e. 20-30 droplets per image of 289.5 μm x 218.0 μm taken by a 60X lens). A number of images were taken to complete a droplet count of at least 800. The minimum number of oil droplets was estimated based on statistical analysis. No statistically significant difference (by using a two-sample Kolmogorov-Smirnov test) of the characteristic DSD was obtained when processing more than 800 droplets counts.

After obtaining the EpiFM images from samples, the areas were analyzed by a post-processing protocol, which was automated using Fiji software. The post-processing protocol of EpiFM images described herein is a combination of previous works of Schuster et al. (2012) and Ríos et al. (2002). The first step is to subtract the background to reduce noise and artifacts out of focus. The background can be smoothed or non-smoothed. Subsequently, the bandpass filter is applied to improve the contrast and image quality by selecting the filter range in pixels. Images are then converted to grayscale 8-bit format to apply image
thresholding, where a binary black and white image is obtained. Finally, size analysis is performed applying the “Analyze Particles” function for those objects with specified circularity between 0.8 and 1. Fiji expresses results in area units (i.e. \( \mu m^2 \)) of each circular droplet, from which equivalent droplet diameter is calculated based on the circle area. The post-processing macro used in Fiji is appended in Text S3.

In each of the steps of the post-processing protocol, the different parameters were set based on a calibration carried out with 1 \( \mu m \) sicastar\textregistered-redF standards, as shown in Figure 2-2. The best post-processing sequence was selected based on obtaining the closest mean diameter to 1 \( \mu m \) with a minimum standard deviation. Four different post-processing sequences varying the smoothing of the background (i.e. smoothed (SB) or non-smoothed (nSB)), the bandpass filter (i.e. filtering large structures down to 25 or 60 pixels) and the upper threshold level (from 210 up to 230) were applied.

As shown in Figure 2-2, the best post-processing sequence obtained was with nSB, 25 pixels (green triangles) in the band-pass filter, and an upper threshold level of 218. With this post-processing sequence, the calculated standard silica mean size diameter was 997 nm, with a standard deviation of 86 nm. This standard deviation equivalent to 8.6% of the mean value is acceptable as it falls between the range of the deviation (i.e. 7-14%) reported previously for the sicastar\textregistered beads (Kasper et al., 2013). This post-processing sequence was then applied to images of the synthetic PW. Images of each post-processing step for the synthetic PW sample are shown in Figure S3 for further reference.
2.3.1.1.4 DSD density plot

After applying the post-processing protocol to the images, the DSD density plots were obtained by implementing statistical functions in R (R Core Team, 2017). The histogram and density plot obtained for synthetic PW are shown in Figure 2-3. Histograms appearance is sensitive to the number of bins, or vertical bars, and therefore a histogram is not the most accurate tool to show DSD results. DSD is better presented as a kernel density function, which depends crucially on the data smoothing process or bandwidth method. In this study, the Sheather-Jones plug-in bandwidth (i.e. bw=“SJ.dpi” in R) was selected as it is widely recommended due to its overall good performance (Liao et al., 2010) and showed a good data sharpening for the DSD estimation of the results (Sheather, 2004). Another correction was applied to the density plot as the EpiFM with 60X objective has a lower droplet size detection limit of 250
nm. For this reason, the boundary corrected kernel density is estimated by implementing the dbckden() function, which is part of the evmix package in R (Scarrott and Hu, 2015).

The DSD of synthetic PW determined by EpiFM presented a mean droplet size of 849 nm ($D_{50}$) with a standard deviation of 500 nm (SD) and a density peak at 587 nm. When applying Equation 2-1, this is equivalent to a PDI of 0.35, which indicates a narrow DSD suitable for DLS (Danaei et al., 2018). This narrow DSD was obtained as a result of the high energy mixing process plus sonication, which broke down the oil droplets during the preparation of the synthetic PW. When measuring the DSD of synthetic PW by DLS, the sample satisfied the data quality criteria. The intensity distribution from DLS showed the most significant peak (i.e. 85%) at 427 nm ±186, with a PDI of 0.416. These DLS results seem to be relatively close to the values obtained for EpiFM. However, direct comparison of the DSD results from EpiFM and DLS is not valid as they correspond to different density functions (i.e. EpiFM DSD is a number-based distribution while DLS is intensity-based according to the hydrodynamic diameter) and range of size detection (i.e.
Zetasizer Nano ZS range: 0.3 nm - 10 µm (Malvern Panalytical, 2020) vs EpiFM range: 250 nm - 10 µm). For narrow DSD emulsions such as the one obtained for synthetic PW, both DLS and EpiFM are reliable methods for DSD measurement.

2.3.1.2 Electron microscopy

2.3.1.2.1 Cryo-SEM

The freeze fractured plane of synthetic PW in 3% agarose gel after plunge freezing, showed deformed oil droplets trapped in a honeycomb structure. The hexagonal ice expansion during slow freezing and subsequent sublimation resulted in the formation of this honeycomb structure (Aston et al., 2016). The crystalline ice formation during plunge freezing also pressed on the oil droplets, deforming their spherical shape and making them appear as a smudge inside the agarose honeycomb matrix (see the areas enclosed by circles in Figure S3a, and S3b). Consequently, the oil droplets could not be visualized in their native spherical form, and DSD could not be measured using this technique.

To prevent crystalline ice damage to oil droplets, HPF was then used for cryofixation. HPF allowed the preservation of the spherical morphology of the oil droplets without honeycomb formation (Figure S3c, and S3d). Crude oil droplets as small as 50 nm (Figure S3c) and as large as 20 µm (Figure S3d) could be visualized using this technique. With this method, although the oil droplets kept their spherical shape, the vitrified freeze fractured sample was extremely vulnerable to the sublimation step, and only a small amount of sample (i.e. droplets and agarose) remained at the bottom of the carrier after sublimation step. Therefore, it is difficult to ascertain whether the remaining droplets that
were left after the sublimation step represent the entire droplet size distribution in the PW or not, and consequently, DSD could not be appropriately quantified. For these reasons, Cryo-SEM HPF provided a qualitative visualization for a broad range of droplet sizes under our test conditions but is not recommended for obtaining a quantitative DSD in oilfield PW samples.

2.3.1.2.2 Cryo-TEM

The visualization of submicron oil droplets in concentrated synthetic PW samples was successfully performed without the introduction of artifacts (Anjum et al., 2017). Figure S4 shows images of the submicron oil droplets trapped in the thin (< 300 nm (Lee et al., 2014)) vitrified ice layer formed in the carbon grid holes at different magnifications. These images show the preference of the oil droplets to aggregate towards the carbon edge in a gradient distribution where smaller droplets are closer to the middle of the hole. This is due to the geometrical constraint of the ice film in which the oil droplets are contained. The ice film is a meniscus with a smaller thickness at the center of the hole, which pushes larger oil droplets to the thicker ice area. This type of distribution is typically seen in oil in water emulsions systems (Jensen, 2013).

The diameters of the submicron oil droplets in the cryo-TEM micrographs were quantified by image post-processing using the Hough circle transform plugin (Smith, 2018) in Fiji software. According to the plugin instructions, the following workflow was applied: i) to blur the image by a Median and then a Gaussian filter; ii) to identify the edge of the objects by the “Find Edges” function; iii) thresholding; and iv) running the Hough circle transform in advanced mode. The results of each
post-processing steps in a cryo-TEM micrograph are shown in Figure S5. Cryo-TEM images of different magnifications were post-processed, obtaining a droplet population density per image from 40 up to 350 droplets per \( \mu \text{m}^2 \). The DSD density plot determined from cryo-TEM of the concentrated synthetic PW is shown in Figure 2-4. This DSD presented a mean droplet size (\( D_{50} \)) of 56.1 nm with a standard deviation (SD) of 42.0 nm and a density peak at 35 nm. The results obtained may confirm the capability of cryo-TEM to quantitatively determine the DSD of a concentrated O/W emulsion in the nanometer range from 300 nm down to 15 nm in diameter and its potential for oilfield PW characterization.

![Droplet size distribution plot](image)

**Figure 2-4.** Histogram and density plot of the DSD of 10,000 mg/L TOG synthetic PW determined by cryo-TEM.

### 2.3.2 Microscopy methods applied to oilfield PW samples

#### 2.3.2.1 EpiFM

The DSD results of PW samples, PW1 (52 mg/L TOG) and PW2 (13 mg/L TOG), determined by EpiFM are shown in Figure 2-5. Examples of original EpiFM images and the post-processing results are included in Figure 2-5. As expected, the density of oil droplets present in the image area of 289.5 x 218.0 \( \mu \text{m} \) (by oil-
immersed 60X lens) decreases with the oil content in the sample. Images of the Saudi Arabian PW1 sample enclosed 30 to 45 droplets in each snapshot, while the Bahraini PW2 sample contained between 7 and 15 droplets per snapshot. Therefore, more images are needed for the PW2 sample in order to reach a minimum of 800 droplets count in the total. The capture of many areas of the sample was automated through the control system in the LSM710 microscope.

Both oilfields PW sample DSDs have a peak at around 500 nm and a broader density function compared to the synthetic PW. PW1 has the highest PDI value of 0.89 (i.e. mean size of 1032 ± 977 nm), followed by PW2 with 0.42 (i.e. mean size of 994 ± 643 nm). The higher PDI obtained for oilfield PW samples compared to the synthetic PW is due to the presence of droplets larger than 2 µm in higher concentrations as shown in the right side tail of the density function. This high polydispersity suggests that DLS measurements may not be suitable for DSD characterization of PW samples. This was later confirmed when running the measurements with the Zetasizer, where the data quality did not meet the software criteria. Warnings of high polydispersity, dust content, and fluorescence in the system were displayed on the instrument, which is in line with conditions expected in oilfield PW. The presence of other particles (e.g. solid particles, bacteria, precipitates) rather than oil droplets in oilfield PW, would invalidate DSD measurements performed by hydrodynamic-based methods such as DLS.

For oilfield PW samples, the DSD data from EpiFM confirmed a high density of submicron oil droplets with a diameter of around 500 nm. The EpiFM approach as presented in this study turned out to be a reliable method to provide accurate
results for highly polydispersed emulsions, such as oilfield PW samples and was able to characterize droplets as small as 250 nm.

Figure 2-5. DSD of PW samples estimated from EpiFM images of 52 mg/L TOG Saudi Arabian PW1, and 13 mg/L TOG Bahraini PW2. Scale bar is equal to 20 μm.

2.3.2.2 Electron Microscopy

In the above section 2.3.1.2.1, it was shown that HPF cryo-SEM was useful for the visualization of the concentrated synthetic PW, allowing the conservation of the oil droplets shapes. However, this technique was not used with our oilfield PW samples as a quantitative estimate of the DSD by cryo-SEM is not possible, providing only an
overview image in the bulk of the sample. Furthermore, the low oil concentration (i.e., 52 mg/L in PW1 and 13 mg/L in PW2) significantly minimized the probability of droplets observation in a sample for cryo-SEM. At a higher magnification, finding a droplet in emulsions of a few hundred mg/L oil concentration is like “finding a needle in the haystack”. This brings up the challenge of increasing the concentration of the submicron species without changing the integrity of the solution and its DSD; a subject out of the scope of this work and suitable for future research.

However, Cryo-TEM was implemented on the PW1 and PW2 samples. Figure 2-6 shows the cryo-TEM micrographs of the oilfield PW samples. Compared to the concentrated synthetic PW, the distribution of submicron contaminants content for the oilfield PW samples was different. In Figure 2-6a, and 2-6c the oil droplets and aggregates were located not only in the holes but also on the carbon grid support. This affinity of specimen for the carbon grid support is a common problem during the plunge freezing process, which affects the high-resolution imaging of cryo-TEM (Drulyte et al., 2018). Nevertheless, for the purpose of this study, the cryo-TEM images obtained provided insight into the presence of submicron contaminants other than oil droplets in PW. Few oil droplets annotated by the arrows in Figure 2-6, were found in the cryo-TEM images. Oil droplets as small as 20 nm were identified in both PW1 and PW2. Furthermore, other submicron colloidal-like aggregates (e.g. enclosed by dotted squares) were found with a higher density than the oil droplets. These aggregates could be different organic precipitates formed by the chemicals injected in the crude oil production process (Walsh, 2018a). The characterization of such colloidal-like aggregates is challenging due to the complex composition of PW samples and is out of the scope of this study.
Figure 2-6. Cryo-TEM images of PW samples, a-b) Saudi Arabian PW1; and c-d) Bahraini PW2 samples. Scale bar equal to 200 nm.

The low oil concentration in oilfield PW samples is an issue for the visualization of submicron contaminants by SEM. However, the oilfield PW samples were filtered (i.e. 25 nm membrane pore size) and their retentates were analyzed by Cryo-SEM-EDS. This changed the morphology of the oil droplets but provided information on the elemental composition of contaminants retained on the membrane.

The retentate collected from filtering PW1 and PW2 samples were very different in terms of morphology and elemental composition. In PW1, round and flat particles with high sulfur content (95% w/w) were found (spot 1 and 2, Figure 2-7). Also, areas with a distribution of organics were found all over the membrane surface and between the particles with a mass composition of 32.5% carbon,
11.1% nitrogen, 49.9% oxygen, 1.2% sodium, 3.4% sulfur, and 1.9% chlorine. The sulfuric particles could be associated with corrosion residues as the PW1 sample was sour with 20 mg/L of H₂S and high salinity (65.7 g/kg of practical salinity).

In the PW2 sample, a smoother distribution of organics covering the membrane surface was found. Figure 2-8, shows that the EDS spectra of the full area and the zoomed spot have a similar mass composition with 31.7% carbon, 3.2% nitrogen, 41.8% oxygen, 3.4% sodium, 12.1% chloride, 2.8% calcium, and minimum amounts of aluminum, silicon, sulfur, magnesium, and potassium. PW2 retentate contained calcium which could possibly be associated with scaling deposition, as suggested by relatively high alkalinity of 250 mg CaCO₃/L at 7.2 pH compared to PW1 alkalinity of 53 mg CaCO₃/L at 6.7 pH.

![Figure 2-7. Cryo-SEM-EDS analysis of Saudi Arabian PW1 sample content retained by a 25 nm membrane. Scale bar equal to 10 μm.](image-url)
2.4 Conclusions

Visualization and characterization of submicron oil droplets and other constituents in Saudi Arabian and Bahraini oilfield PW were successfully performed by the microscopy techniques explored. EpiFM of immobilized gelled samples was found to be the most appropriate technique to quantitatively determine the DSD in PW for oil droplets larger than 250 nm. Sample preparation by immobilizing the PW in low-temperature gels is a suitable method for field applications in order to prevent changes in the DSD during transportation of the samples to the laboratory for further detailed analysis. Cryo-TEM was successfully applied to concentrated synthetic PW samples to quantitatively determine the DSD of oil droplets smaller than 300 nm down to 15 nm in diameter. The use of cryo-TEM on determining the DSD in oilfield PW was limited due to low oil concentrations in the order of hundreds of mg/L. On the other hand, cryo-TEM revealed the presence of not only submicron oil droplets as small as 20 nm but...
also other submicron colloidal-like particulates/aggregates in a higher population density in oilfield PW samples. Such submicron contaminants would not be removed by conventional de-oiling technologies and might cause intrapore blocking in membrane filtration treatment systems downstream. Cryo-SEM-EDS elemental composition analysis can provide information on the nature of the submicron contaminants and aggregates in oilfield PW samples, complementary to cryo-TEM observations. The characterization of such contaminants is challenging in the complex mixture of PW, and they might play an important role in the efficacy of the chosen water treatment technologies. Further attention should be given to the chemical characterization of submicron contaminants other than oil droplets present in the PW for improved PW treatment design.
CRediT authorship contribution statement

Sandra C. Medina: Conceptualization, Methodology, Data curation, Software, Validation, Investigation, Formal analysis, Visualization, Project administration, Writing - Original draft. Dalaver H. Anjum: Methodology, Data curation, Formal analysis, Writing - Original draft. Ali R. Behzad: Methodology, Data curation, Formal analysis, Writing - Original draft. Regis D. Vilagines: Writing - review & editing, Supervision. Assiyeh Tabatabai: Conceptualization, Formal analysis, Writing - review & editing, Supervision. TorOve Leiknes: Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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2.5 Supporting Information

Microscopy techniques applied to submicron characterization of Produced Water

Sandra C. Medina\textsuperscript{a}, Dalaver H. Anjum\textsuperscript{b,1}, Ali R. Behzad\textsuperscript{b}, Regis D. Vilagini\textsuperscript{c}, Assiyeh Tabatabai\textsuperscript{a,2}, Tor\O ve Leiknes\textsuperscript{a}

\textsuperscript{a} Water Desalination and Reuse Center (WDRC), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.

\textsuperscript{b} Imaging and Characterization Core Lab, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.

\textsuperscript{c} Research and Development Center, Saudi Arabian Oil Company, Dhahran 31311, Saudi Arabia

6 pages, 1 Table, 3 texts, and 5 figures are included in the supporting information.

\textsuperscript{*} Corresponding author: Sandra C. Medina. e-mail: sandra.medina@kaust.edu.sa. 4700 King Abdullah University of Science and Technology (KAUST) Thuwal, 23955-6900, Saudi Arabia. Tel: +966545754908.

\textsuperscript{1} Department of Physics, Khalifa University (KU), Abu Dhabi P. O. Box 127788, United Arab Emirates.

\textsuperscript{2} Lhoist Business Innovation Center, 31 Rue de l’Industrie, B-1400 Nivelles, Belgium.
Table S1. Ionic composition of the de-oiled PW1

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Saudi Arabian PW1</td>
</tr>
<tr>
<td>Total Dissolved Salts</td>
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</tr>
<tr>
<td>B</td>
<td>26.4</td>
</tr>
<tr>
<td>Ba</td>
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</tr>
<tr>
<td>Ca</td>
<td>2632.0</td>
</tr>
<tr>
<td>K</td>
<td>788.0</td>
</tr>
<tr>
<td>Li</td>
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</tr>
<tr>
<td>Mg</td>
<td>1244.0</td>
</tr>
<tr>
<td>Na</td>
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</tr>
<tr>
<td>Rb</td>
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</tr>
<tr>
<td>S</td>
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<tr>
<td>Sr</td>
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<tr>
<td>Cl</td>
<td>45646.8</td>
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<tr>
<td>Br</td>
<td>235.8</td>
</tr>
</tbody>
</table>

Text S1. Cryo-SEM procedure to image freeze fractured plane of the synthetic PW sample by plunge freezing.

A small amount of the gelled sample was placed on a rivet secured in a hole on a cylindrical stub on a cryo holder. The holder was attached to the sample transfer rod and rapidly plunged into liquid nitrogen slush and under vacuum was transferred to the cryo preparation chamber stage pre-cooled to -160 °C. The freeze-fracture plane was obtained by hitting the top of the sample with a knife pre-cooled to -160 °C. The sample was then sublimed for 5 min at -90 °C to reveal details of the emulsion in the fractured plane. The fractured plane was coated with 5 nm of Pt in the argon atmosphere inside the preparation chamber at -120 °C to dissipate charging during imaging. The sample was then transferred to the cryo stage in the SEM chamber pre-cooled at -120 °C. Secondary electron images were acquired at accelerating voltages of 2-5 kV and at 5 mm working distance.
Text S2. Cryo-SEM procedure to image the vitrified fractured plane of the synthetic PW by HPF.

Briefly, a small amount of the melted gelled sample was sandwiched between a carrier and a ring, and it was high pressure frozen using EMPACT 2 HPF (Leica Microsystems, Austria). The frozen sample under liquid nitrogen was transferred to a special freeze-fracture holder inside VCM (Leica Microsystems, Austria). Under vacuum, the sample secured on the holder was transferred to ACE 900 freeze-fracture and coater machine (Leica Microsystems, Austria) using VCT 500 shuttle. Inside the ACE 900, the sample was fractured using a pre-cooled knife at -150 °C and sublimed for 5 minutes at -100 °C. After sublimation, the fractured plane was coated at -120 °C with 3 nm Pt and 7 nm carbon using e-beam induced evaporators inside the ACE 900 machine. Under vacuum, the sample was transferred to the SEM cryo stage held at -120 °C using VCT 500 shuttle. Secondary electron images were acquired at an accelerating voltage of 1 kV and 4 mm working distance.
Figure S1. EpiFM images of synthetic PW at 60X magnification. a) Oil droplets without gel immobilization, b) oil droplets immobilized by low-temperature agarose.

Text S3. FIJI, Image J macro for EpiFM image post-processing

```
run("Invert");
run("Subtract Background...", "rolling=25 light");
run("Invert");
run("Duplicate...", "title=[Duplicate]");
run("Invert");
run("Bandpass Filter...", "filter_large=25 filter_small=0 suppress=None
tolerance=5 autoscale");
run("Invert");
run("RGB Color");
run("8-bit");
run("Invert");
setAutoThreshold("Default");
//run("Threshold...");
setThreshold(0, 218);
run("Convert to Mask");
run("8-bit");
run("Despeckle");
run("Analyze Particles...", " circularity=0.70-1.00 show=Outlines display
exclude clear summarize");
```
Figure S2. Post-processing of EpiFM images of synthetic PW for DSD quantification: a) original snapshot, b) inverted image in grayscale, c) after subtracting the background noise, d) after applying the band-pass filter, e) after image thresholding, and f) outlines of the droplets analyzed. Scale bar is equal to 20 µm.
Figure S3. Cryo-SEM imaging of the freeze-fractured plane of synthetic PW samples gelled with agarose. a) and b) correspond to plunge freezing specimens. c) and d) correspond to HPF prepared specimens. The scale bar is equal to 1 μm, except for d), which is 10 μm.

Figure S4. CryoTEM of synthetic PW of 10,000 mg/L TOG. Scale bars equal to 500 nm.
Figure S5. Post-processing of cryo-TEM images from 10,000 mg/L TOG synthetic PW. a) original image b) after applying Median filter and Gaussian blur, c) after finding edges and thresholding d) overlay of the circles found by the Hough circle transform plugin in Fiji software. The scale bars equal to 100 nm.
2.6 References


DUYNHOVEN, J. V. (eds.) *XIII International Conference on the Applications of Magnetic Resonance in Food Science*.


Chapter 3. A fundamental study of adsorption kinetics of surfactants onto metal oxides using quartz crystal microbalance with dissipation (QCM-D)

This chapter responds to the research questions of hypothesis 2. Surfactants adsorption is an important fouling mechanism in ceramic membrane filtration of PW. The adsorption phenomena can be well described by QCM-D technique. Our results suggested that adsorption was driven by the nature of the surfactant rather than the metal oxide properties. This implies that electrostatic interactions should not be taken as the only predicting factor of adsorption phenomena in the understanding of PW fouling in ceramic membranes as other supramolecular interactions are strongly involved.

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ABSTRACT

Hypothesis

Membrane fouling challenges the viability of oil-field produced water (PW) treatment with ceramic membranes. Surfactants play an important role in irreversible fouling through adsorption phenomena. However, previous studies have shown contradictory results. Hence, a fundamental understanding of surfactants-metal oxides interactions is necessary.

Experiments

In this work, we assessed the adsorption interactions of anionic SDBS and cationic CTAB with titania, zirconia and alumina surfaces, using the quartz crystal microbalance with dissipation (QCM-D) technique.

Findings

We found that electrostatic interactions controlled the adsorption of SDBS onto all the surfaces studied, with titania being the most likely to adsorb SDBS. On the contrary, CTAB was adsorbed regardless of the overall metal oxide surface charge. CTAB showed two-step adsorption at acidic pH (3.0). In the first step, a rigid film was formed with a smaller adsorption capacity compared to the neutral (6.8) and basic (9.4) pH conditions. In the second step, a viscoelastic film was formed. Our results suggest that adsorption was driven by the nature of the surfactant rather than the metal oxide properties. This implies that electrostatic interactions should not be taken as the only predicting factor of adsorption phenomena in the
understanding of PW fouling in ceramic membranes as other supramolecular interactions are strongly involved.

**GRAPHICAL ABSTRACT**

**KEYWORDS:** Surfactant adsorption, metal oxide, QCM-D, ceramic membrane, produced water.
3.1 Introduction

The application of ceramic membrane filtration in the treatment of oil-field produced water (PW) has been widely studied in recent years in an attempt to meet increasingly stringent regulations on discharge. These requirements stipulate that levels of emulsified and dissolved oil (i.e. oil droplets <10 μm and <5 μm, respectively (Weschenfelder et al., 2015c)) in PW discharge should not exceed 30 mg/L for all facilities in the Middle East, Malaysia, North Sea, Australia, Canada, Brazil, Ecuador, Colombia, etc. (Jiménez et al., 2018), or 5.0 mg/L for both oil and suspended solids for reinjection purposes (Weschenfelder et al., 2015b). Ceramic membranes have shown good performance in the treatment of oil/water emulsions in industrial applications with harsh operating conditions, i.e., high temperatures and aggressive chemicals (Weschenfelder et al., 2015a, Weschenfelder et al., 2015c). However, membrane fouling is a fundamental limitation for the economic viability of membrane treatment application in PW treatment (Lu et al., 2015). The mechanisms of membrane fouling by PW have not yet been fully described (Fouladitajar et al., 2013). However, fouling has been attributed to a combination of mechanisms including: (i) oil droplets coalescing and forming a layer on the membrane surface; (ii) oil droplets squeezing through the pores allowing partial permeation; (iii) adsorption of oil droplets and surfactants on the membrane surface and within the pores (Chakrabarty et al., 2008, Silalahi et al., 2009, Ebrahimi et al., 2010, Matos et al., 2016, Tummons et al., 2016). Furthermore, these mechanisms may be occurring simultaneously, making the study of membrane fouling more complex (Iritani et al., 2014). To improve
understanding of membrane fouling mechanisms during PW treatment, each phenomenon should be studied and understood separately.

Surfactants present in oil/water emulsions have been shown to play a key role in irreversible fouling development during ceramic membrane filtration (Faibish and Cohen, 2001, Fernández et al., 2005, Lu et al., 2015). Surfactant molecules directly affect emulsion stability through their interactions with the membrane surface and pores (Faibish and Cohen, 2001). Various chemicals added at different stages of crude oil production also have surface-active properties. For instance, chemicals used for oil recovery, crude oil dehydration, biological control, corrosion inhibition and extraction enhancement can act as surfactants, ending up in the PW once the crude oil has been separated. Surfactant molecules contain hydrophilic and hydrophobic moieties, which are adsorbed at the oil/water interface and significantly decrease the interfacial surface tension by a significant amount (≥ 30 mN/m) when present at low concentrations, i.e., ≤ 0.01 M (Seyed Shahabadi and Reyhani, 2014). As the concentration of a surfactant increases in solution, the monomers agglomerate and self-assemble in micelles. These micelles start to form within a very narrow concentration range known as the “critical micelle concentration” (CMC), where they coexist in equilibrium with surfactant monomers. A study by Dickhout et al. (2017) showed that micelles that form above the CMC are retained by UF membranes because their diameters are comparable to UF membrane pore sizes (i.e., 1-10 nm), while surfactant monomers tend to adsorb onto the membrane surface due to electrostatic forces or hydrophobic/hydrophilic interactions. These factors affect membrane surface characteristics, leading to changes in permeate flux and solute rejection. The
degree of adsorption depends on the surfactant type and membrane material properties (Berg, 2010).

Previous studies have reported that electrostatic-based correlations between the membrane surface charge and the surfactant charge in oil/water emulsions can prevent ceramic membrane fouling. However, reported results are contradictory, suggesting that electrostatic interactions do not fully explain membrane fouling. For example, Matos et al. (2016) found an increase in UF permeate flux when the membrane surface (zirconia/titania) and emulsion droplets (at pH 6.5-7.5) had the same charge, and a decrease in UF permeate flux when they had opposite charges. In contrast, Lu et al. (2016) suggested using a metal oxide with a surface charge opposite to that of the emulsion in order to alleviate irreversible membrane fouling. However, there is wide variability in these experiments and a clear background understanding of the interaction of surfactants with metal oxides is required.

The aim of this study is to clarify the state of the art by assessing the effect of adsorption rates and interactions of charged surfactants with commonly used ceramic membrane materials, utilizing the quartz crystal microbalance with dissipation (QCM-D) technique. QCM-D is a sensitive analytical instrument based on piezoelectric AT-cut quartz crystal and gold electrodes, which allows real-time detection of structural and mass changes of the material being adsorbed/desorbed onto the sensor (Dixon, 2008). In membrane fouling studies, investigation of surfactant adsorption with QCM-D has been reported previously for polymeric materials (e.g., PES (Liu and Kim (2009)) and PVDF/SiO₂-PNIPAM (Ngang et al. (2017))). However, to our knowledge, no studies have yet been
carried out for adsorption on ceramic membrane materials. In this study, the adsorption kinetics of two charged surfactants (SDBS (anionic) and CTAB (cationic)) onto titania, zirconia and alumina surfaces were investigated. In addition, the effect of pH on adsorption rates and capacity of surfactant solutions on the metal oxides were investigated.

3.2 Materials and methods

3.2.1 Materials

Two surfactants, sodium dodecylbenzene sulfonate (SDBS), MW 343.4 g/mol, pKa 2.2, CMC ~2.0 mM (Hait et al., 2003) and cetyltrimethylammonium bromide (CTAB), MW 364.4 g/mol pKa 9.5, CMC ~0.8 mM (Moulik et al., 1996) were purchased from Sigma-Aldrich and used as received. Surfactant solutions were prepared by dissolving specified amounts in Milli-Q water (resistivity of 18.2 Ω). pH adjustment was achieved by adding 0.1 M solutions of sodium hydroxide or sulfuric acid. The formation of suspended crystals of CTAB was observed at surfactant concentrations ≥ 0.8 mM. These crystals were formed due to the Krafft point of CTAB (between 20-25 °C (Manojlović, 2012), corresponding to the temperature range in which the solutions were prepared. For higher concentration samples, a sonication step of 10 min was carried out.

Three metal oxide sensors were used in the QCM-D adsorption studies, titania, zirconia and alumina (Biolin Scientific AB, Sweden). QCM-D sensors surfaces were selected as the system allows the study on the metal oxide/surfactant interaction itself, controlling the experimental conditions and avoiding the hydrodynamic
effects on the adsorption. This is possible due to the low roughness at the sensor surface (below 2 nm, according to manufacturer specifications) and the laminar flow regime within the sensor chamber (e.g., Reynolds number in the order of $O(10^{-5})$ for 150 μL/min inflow) (Kwon et al., 2009). The fluid-dynamic effect on the transport limitation of the adsorption was not addressed in this particular work. However, QCM-D allows the comparison of kinetics in specific experimental conditions (Gutig et al., 2008). The characteristics of coated QCM-D sensors are assumed to behave similarly in the nanoscale as a ceramic membrane surface. In the actual ceramic membrane, adsorption interaction might be further exaggerated as a result of more are available contact area (i.e., membrane porosity and roughness) and hydrodynamic forces such as permeation drag. For sensor cleaning, UV/Ozone ProCleaner™220 (Bioforce Nanosciences Inc., USA) and Hellmanex® III (Hellma Analytics, Germany) were used.

3.2.2 QCM-D data acquisition and processing

QCM-D analysis was performed with a Q-Sense analyzer (Biolin Scientific AB, Sweden). Both resonance frequency (F) and energy dissipation (D) were recorded from different overtones. Surfactant adsorption on the oxide surface induces variation in frequency and dissipation ($\Delta F$ and $\Delta D$). Frequency variation ($\Delta F$) is proportional to the adsorbed mass ($\Delta m$) and in the case of rigid films, can be determined by the Sauerbrey equation 3-1,

$$\Delta m = - \frac{c \Delta F}{n} \text{ Eq. 3-1}$$
Where, $\Delta m$ is the mass variation per area of the sensor (ng/cm$^2$), $\Delta F$ is the variation of frequency (Hz), $C$ is a constant (17.8 ng/cm$^2$Hz) and $n$ is the harmonic number (1, 3, 5, 7 ... 13).

For soft films, where there is a large change in $\Delta D$ (i.e., $> \sim 1 \times 10^{-6}$), the linearity between $\Delta F$ and $\Delta m$ in the Sauerbrey relation is no longer valid (Kou and Xu, 2016). In this case, the one-layer Voigh viscoelastic model was applied utilizing the software QTools (Biolin Scientific AB, Sweden). The model assumes a homogeneous thickness, density and no-slip conditions of the adsorbed film. The Voigh model back-calculates the viscoelastic properties of a film (i.e., elasticity, viscosity, thickness and mass) with the measured $\Delta D$ and $\Delta F$ in different overtones (Reviakine et al., 2011). The measurements from overtones 9, 11 and 13 were used as input for the soft film modeling as they showed lower noise.

The cleaning procedure of the quartz sensors was found to be critical for ensuring reproducibility of results. Sensor cleaning was performed by submerging the sensor in a 1% (v/v) solution of Hellmanex® III for 30 min, followed by rinsing with deionized water and drying with a clean nitrogen gas stream. Thereafter, the sensor was sonicated for 10 min in ethanol before UV/Ozone treatment. Sensors were reused a maximum of five times following this procedure.

Prior to each measurement of adsorption kinetics, a baseline was obtained by rinsing the sensor with Milli-Q water at a constant rate of 150 $\mu$L/min. The baseline should not drift by more than 0.5 Hz for at least 1 h to ensure the stability and reliability of the experiment (Lu et al., 2016). After that, the surfactant
solution was fed into a controlled QCM-D chamber temperature at 22 °C. Measurements were performed in duplicate.

3.2.3 Kinetics Models

Real-time acquisition of frequency variations over time (t), induced by surfactant adsorption/accumulation on the oxide surface provided the basis for the kinetics studies. Experimental data were fitted using pseudo-first-order (equation 3-2) and pseudo-second-order equations (3-3) (Kou and Xu, 2016).

$$q_t = q_e(1 - e^{-\beta_1 t}) \quad \text{Eq. 3-2}$$

$$q_t = \frac{\beta_2 q_e^2}{1 + q_e \beta_2 t} \quad \text{Eq. 3-3}$$

Where $q_t$ and $q_e$ are the amount of surfactant adsorbed at time $t$ and at equilibrium, respectively, expressed in mass per unit area (ng/cm$^2$). $\beta_1$ and $\beta_2$ are apparent rate constants of pseudo-first-order (1/s) and pseudo-second-order (cm$^2$/ng.s), respectively. The fitting model with the lowest root mean square error, as described by Largitte and Pasquier (2016), was defined as the best model for the system.

The adsorption kinetics of surfactant $S$ and metal oxide $M$ is described in equation 3-4 as a reversible system with adsorption rate $k$, desorption rate $k^{-1}$ and an overall rate of $k/k^{-1}$.

$$S + M \xrightarrow{k} \frac{k}{k^{-1}} SM \quad \text{Eq. 3-4}$$

$k$ and $k^{-1}$ rates are calculated from the linear correlation of the apparent rate $\beta_{1,2}$ with surfactant concentration, as is shown in equation 3-5.

$$\beta_{1,2} = k \times C + k^{-1} \quad \text{Eq. 3-5}$$
Where \( k \) (slope) and \( k^{-1} \) (y-intercept) are expressed in units of \( 1/s.mM \) and \( 1/s \), respectively for pseudo-first-order and in \( \text{cm}^2/\text{mM}.\text{ng}.s \) and \( \text{cm}^2/\text{ng}.s \) for pseudo second order kinetic models.

### 3.3 Results and discussion

The interactions of SDBS and CTAB with three metal oxide surfaces were studied in terms of kinetics of adsorption at pH 6.8. For all SDBS and CTAB concentrations, the frequency plateau was reached in less than 2 h. The adsorption of both SDBS and CTAB on the tested metal oxides resulted in the formation of rigid films at pH 6.8, as \( \Delta D \) values were lower than \( 1 \times 10^{-6} \) (\( \Delta D \) max. of \( 0.3 \times 10^{-6} \)) and \( \Delta F \) in the different overtones overlapped. The Sauerbrey equation \( 3-1 \) was, therefore, used to obtain \( \Delta m \), where the average frequency variation of overtones 7, 9 and 11 was used, as they showed lower noise (example in Figure S1a), which is in agreement with (Kou and Xu, 2016). The results were then analyzed and fitted with pseudo-first and pseudo-second-order equations (Eq. 3-2 and Eq. 3-3). The experimental data was found to be best described by a pseudo-second-order fit (example in Figure S1b).

#### 3.3.1 Adsorption kinetics of SDBS

Calculated values of the apparent rate constant (\( \beta_2 \)) and the amount of SDBS surfactant adsorbed (qe) for the pseudo-second-order kinetic model are presented in Figure 3-1 and summarized in Table S1 of the Supplementary material. The results of adsorption at low concentrations of SDBS are not shown as the frequency drift was found to be in range with system noise (i.e., 0.3 Hz).
Figure 3-1. Apparent rate of adsorption $\beta_2$ (left side graphs) and amount of SDBS adsorbed $q_e$ (right side graphs) for the systems a) titania; b) zirconia; and c) alumina at pH 6.8

A linear increase in $\beta_2$ for increasing concentrations of SDBS was observed for all metal oxides before reaching the CMC of 2 mM (Figure 3-1). At concentrations equal to or greater than the CMC, $\beta_2$ values no longer followed the same linear behavior. $\beta_2$ decreased abruptly for titania (Figure 3-1a) and zirconia (Figure 3-1b), whereas no discernible trend was observed for alumina (Figure 3-1c). This suggests that the aggregation of SDBS molecules in spherical shaped micelles (i.e., aggregation number of 57 (Sood and Aggarwal, 2018)) result in slower adsorption
kinetics due to the presence of repulsive intermicellar interactions (Cheng and Gulari, 1982). However, the intermicellar repulsive interactions were not strong enough to prevent further SDBS adsorption onto the metal oxides, because the adsorption capacity $q_e$ continued to increase at higher concentrations.

The rate of adsorption $k$ (slope) and desorption $k^{-1}$ (y-intercept) were calculated from the linear dependence of $\beta_2$ on surfactant concentration (Eq. 3-5) in Figure 3-1 and are summarized in Table 3-1. The ratios $k/k^{-1}$ were determined to understand the overall adsorption reaction. At higher $k/k^{-1}$ ratios, the overall system was more delocalized to surfactant adsorption. SDBS was observed to have similar adsorption rates ($k$) for titania and zirconia. However, the desorption rate of titania ($k^{-1}=2.0\times 10^{-5}$ cm$^2$/ng.s) was one order of magnitude lower than that of zirconia ($k^{-1}=3.9\times 10^{-4}$ cm$^2$/ng.s). Therefore, the overall adsorption $k/k^{-1}$ ratio of SDBS on titania (1000.0 l/mM) was the highest. This indicates that the fouling potential of SDBS is higher for ceramic membranes based on titania as compared with zirconia or alumina. This is not related to the rate of adsorption but rather due to slower desorption rates.

For SDBS adsorption on alumina, the higher fluctuations in the linear relation of $\beta_2$ with concentration observed in Figure 3-1c ($R^2=0.910$) may be explained by less organized adsorption. The adsorption rate ($k=2.7\times 10^{-4}$ cm$^2$/mM ng.s) is of the same order of magnitude as the desorption rate ($k^{-1}=6.6\times 10^{-4}$ cm$^2$/ng.s), resulting in the smallest $k/k^{-1}$ ratio (0.4 l/mM). These findings support the choice of alumina material over the other metal oxides, been alumina the most common material used in ceramic membranes (Saad Alami et al., 2018).
To evaluate the effect of the metal oxide surface charge on adsorption kinetics experiments were conducted at pH values above and below the zero-point charge (pH\textsubscript{pzc}) of the metal oxides. According to data summarized by Kosmulski (2006), pH\textsubscript{pzc} ranges between 5.2-6.3 for titania, 5.5-6.6 for zirconia and 7.4-8.6 for alumina. These values were taken from literature as the sensors are coated with high purity metal oxides equivalent to the pure state of the material. In this study, adsorption kinetics were obtained at pH values of 3.0 and 9.4, for 1 mM SDBS concentration. The results were fitted using the pseudo-second-order model as above, with calculated parameters summarized in Table 3-2. Values of adsorption kinetics at pH 6.8 are included in this table for comparison.

Adsorption rates (β\textsubscript{2}) under acidic conditions (pH 3.0) were slower for the three metal oxides in comparison to the values calculated for pH 6.8 and 9.4. This was especially evident for SDBS-titania where β\textsubscript{2} at pH 3.0 (3.3x10\textsuperscript{-7} cm\textsuperscript{2}/ng.s) was four orders of magnitude lower than the values obtained at higher pH (2.2x10\textsuperscript{-3} at pH 6.8, 2.1x10\textsuperscript{-3} cm\textsuperscript{2}/ng.s at pH 9.4). Slower adsorption rates under acidic conditions can be related to the formation of SDBS micelles on the metal oxide surfaces as a result of the accumulation of molecules, as evidenced by the high adsorption capacities qe (e.g., 569.8 ng/cm\textsuperscript{2} SDBS on titania at pH 3.0).

### Table 3-1. Kinetic parameters for SDBS adsorption on the three metal oxides (SDBS concentrations < CMC)

<table>
<thead>
<tr>
<th>Metal oxide</th>
<th>(k) (cm\textsuperscript{2}/mM.ng.s)</th>
<th>(k^{-1}) (cm\textsuperscript{2}/ng.s)</th>
<th>(k / k^{-1}) (1/mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO\textsubscript{2}</td>
<td>2.0x10\textsuperscript{-3}</td>
<td>2.0x10\textsuperscript{-5}</td>
<td>1000.0</td>
</tr>
<tr>
<td>ZrO\textsubscript{2}</td>
<td>1.3x10\textsuperscript{-3}</td>
<td>3.9x10\textsuperscript{-4}</td>
<td>3.3</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>2.7x10\textsuperscript{-4}</td>
<td>6.6x10\textsuperscript{-4}</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Table 3-2. Adsorption rate ($\beta_2$) and adsorption capacity (qe) of 1 mM SDBS solution as a function of pH. $\beta_2$ and qe obtained are expressed in cm$^2$/ng.s and ng/cm$^2$, respectively.

<table>
<thead>
<tr>
<th>Metal oxide</th>
<th>pH</th>
<th>Surface charge</th>
<th>$\beta_2$</th>
<th>qe</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>3.0</td>
<td>+</td>
<td>3.3x10$^{-7}$</td>
<td>292.6</td>
</tr>
<tr>
<td>(pH$_{pzc}$ 5.2-6.3)</td>
<td>6.8</td>
<td>-$*$</td>
<td>2.2x10$^{-3}$</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>-</td>
<td>2.1x10$^{-3}$</td>
<td>11.7</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>3.0</td>
<td>+</td>
<td>3.2x10$^{-6}$</td>
<td>270.9</td>
</tr>
<tr>
<td>(pH$_{pzc}$ 5.5-6.6)</td>
<td>6.8</td>
<td>-$*$</td>
<td>1.6x10$^{-3}$</td>
<td>24.9</td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>-</td>
<td>1.4x10$^{-3}$</td>
<td>18.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>3.0</td>
<td>+</td>
<td>2.5x10$^{-4}$</td>
<td>191.1</td>
</tr>
<tr>
<td>(pH$_{pzc}$ 7.4-8.6)</td>
<td>6.8</td>
<td>+$*$</td>
<td>8.6x10$^{-4}$</td>
<td>29.1</td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>-</td>
<td>2.1x10$^{-3}$</td>
<td>17.9</td>
</tr>
</tbody>
</table>

*Although charged at this pH, these surfaces are close to an overall neutral charge

The presence of SDBS micelles on the surfaces of the three metal oxides under acidic conditions was confirmed by the QCM-D dissipation ($\Delta D$) values, which were close to but still under the threshold (i.e., 1x10$^{-6}$) at which the adsorbed films could be considered viscoelastic (Kou and Xu, 2016). In general, relatively high $\Delta D$ of 0.3x10$^{-6}$ – 0.6x10$^{-6}$ were obtained at pH 3.0 compared to 0.01x10$^{-6}$ – 0.1x10$^{-6}$ at higher pH. QCM-D results of $\Delta D$ and $\Delta F$ for the SDBS adsorption on the three metal oxides at different pH are shown in Figure S2.

Although adsorption rates were lower under acidic conditions, the capacity of SDBS adsorption (qe) onto all metal oxides surfaces was highest at pH 3.0, decreasing with increasing pH. This can be attributed to changes in the overall surface charge of the metal oxides and the interactions with SDBS. At pH 3.0, the three metal oxides had an overall positive surface charge and the anionic
characteristics of SDBS made it more likely to attach to the metal oxide surfaces, as evidenced by the higher qe values obtained. When the pH was increased to 6.8, the surfaces of titania and zirconia tended towards a negative charge, while the surface charge for alumina was close to neutral. These shifts in surface charge caused a significant drop in qe values of 97.9% for titania, 90.8% for zirconia, and 84.8% for alumina. With a further increase of pH to 9.0, the qe continued to drop in smaller amounts (2.9%, 26.7% and 38.5% of the original values for pH 6.8) as the metal oxide surfaces became more negative, but no major surface charge shifts were observed. Furthermore, even with an overall negative charge on the metal oxide surfaces at pH 9.0, SDBS adsorption occurred at relatively fast rates (2.1x10^{-3} cm²/ng.s on titania and alumina and 1.4x10^{-3} cm²/ng.s on zirconia) and low qe (11.7, 18.2 and 17.9 ng/cm² for titania, zirconia and alumina, respectively). The occurrence of SDBS adsorption and reduced qe when the metal oxides carried a negative surface charge suggests the presence of positive sites of the surface even at basic conditions. These results reflect the important contribution of electrostatic interactions to the adsorption of anionic SDBS on the different metal oxides.

3.3.2 Adsorption kinetics of CTAB

Calculated values of the apparent rate constant ($\beta_2$) and the amount of CTAB surfactant absorbed (qe) for the pseudo-second-order equation (Eq. 3-3) are summarized in Table S2 with corresponding graphical representation in Figure 3-2. For samples where the frequency variation was not negligible, a small signal-to-noise ratio was obtained (frequencies < 0.5 Hz, equivalent to 8.75 ng/cm²). From the linear regression of $\beta_2$, the calculated adsorption/desorption rate ($k/k^-$
1) ratios of CTAB for the respective metal oxide systems are summarized in Table 3-3. No data is presented in Figure 3-2 or Table 3-3 for CTAB on alumina as the results indicated negligible adsorption under the conditions employed (ΔF results in Figure S3). These results are discussed later in this section.

Similar to the SDBS results, CTAB β₂ rates on titania and zirconia showed a proportional relationship with increasing concentrations before reaching the CMC (0.8 mM). At the CMC, β₂ abruptly declined to 2.1x10⁻⁵ cm²/ng.s for titania but showed a higher qe of 397.4 ng/cm² (Figure 3-2a). In contrast, β₂ for zirconia kept increasing to 3.4x10⁻⁵ cm²/ng.s at the CMC (Figure 3-2b) but qe dropped to 175.2 ng/cm². These differences in β₂ and qe tendencies between titania and zirconia at the CMC can be explained by the formation of micelles on the metal oxide surfaces occurring at different concentrations. The agglomeration of CTAB molecules into spheroidal micelles (i.e., aggregation number of CTAB between 50 (Manojlović, 2012) and 66 (Pisárčik et al., 2015)) occurred faster on zirconia as it has a higher k/k⁻¹ (13.8 1/mM in Table 3-3) than titania. At 0.6 mM CTAB, the highest qe value of 378.4 ng/cm² was reached on zirconia; however, when a higher concentration was applied (0.8 mM), repulsive intermicellar interactions (i.e., positive intermicellar interaction parameter of 0.025 1/mM (Javadian and Kakemam, 2017)) prevented further adsorption of the incoming micelles and the qe decreased. On the other hand, due to the low k/k⁻¹ ratio for titania (0.7 1/mM), the agglomeration of such quantities of CTAB molecules as required for micelle formation were not reached before the CMC and only at the CMC was it possible to reach the highest qe of 397.4 ng/cm².
Both CTAB-titania and CTAB-zirconia systems presented comparable adsorption ($k$) rates (2.9x10^{-5} and 3.6x10^{-5} cm$^2$/mM ng.s, respectively). However, the desorption rate ($k^{-1}$) of zirconia (2.6x10^{-6} cm$^2$/ng.s) was one order of magnitude lower than that for titania (4.2x10^{-5} cm$^2$/ng.s). This gave higher overall adsorption ($k/k^{-1}$ value of 13.8 1/mM), indicating that CTAB is more likely to cause irreversible fouling in ceramic membranes based on zirconia due to the relatively low desorption rate.

The CTAB-alumina results indicated negligible adsorption. To confirm the lack of adsorption, an isotherm curve was obtained (Figure S4). An increase of CTAB concentrations did not lead to significant adsorption onto the alumina surface, suggesting that the charge distribution at the alumina surface is homogeneous, thus preventing CTAB from approaching the surface.
Table 3-3. Kinetic parameters for CTAB concentrations lower than CMC

<table>
<thead>
<tr>
<th>Metal oxide</th>
<th>$k$ (cm$^2$/mM.ng.s)</th>
<th>$k^{-1}$ (cm$^2$/ng.s)</th>
<th>$k/k^{-1}$ (1/mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>$2.9 \times 10^{-5}$</td>
<td>$4.2 \times 10^{-5}$</td>
<td>0.7</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>$3.6 \times 10^{-5}$</td>
<td>$2.6 \times 10^{-6}$</td>
<td>13.8</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The CTAB-alumina system was further investigated by FTIR-ATR. However, the resolution of the technique was too high to allow for any specific conclusion to be drawn (detailed information available in Text S1 and Figure S5). While the literature on CTAB adsorption on alumina is scarce, our findings are in agreement with previous studies. The use of CTAB (at ambient pH ~7) has been studied in anti-corrosive composite coatings to prevent the attachment of alumina particles by repulsive electrostatic forces (Liu et al., 2009). In addition, in catalysis applications, hydroxycarboxylate derivatives have been utilized as linkers to attach CTAB on gamma alumina (Yue et al., 2011). Similar to the adsorption results for SDBS at 6.8 pH condition, alumina content on ceramic membranes may have less impact on the formation of a CTAB fouling layer adsorbed onto the membrane surface.

To further understand the interactions of CTAB with the metal oxide surfaces, the rate of adsorption, $\beta_2$, and $q_e$ were evaluated under acidic (pH 3.0) and basic (pH 9.4) conditions. Solutions of 0.6 mM CTAB were chosen as this concentration is lower than the CMC, thus avoiding micelles formation, but high enough to be able to identify significant changes in $\Delta F$ during the first minutes of the run. The
pseudo-second-order kinetic model results are shown in Table 3-4. The $\beta_2$ and $q_e$ values for pH 6.8 are included for comparison. The $\Delta F$ and $\Delta D$ results for the system CTAB-alumina at different pH values are shown in Figure 3-3.

Table 3-4. CTAB adsorption rates ($\beta_2$) and adsorption capacity ($q_e$) at different pH. $\beta_2$ and $q_e$ obtained are expressed in cm$^2$/mM ng.s and ng/cm$^2$, respectively

<table>
<thead>
<tr>
<th>Metal oxide</th>
<th>pH</th>
<th>Surface charge</th>
<th>$\beta_2$</th>
<th>$q_e$</th>
</tr>
</thead>
<tbody>
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<td>+</td>
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<tr>
<td>(pH$_{pzc}$ 5.2-6.3)</td>
<td>6.8</td>
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<td>5.8x10$^{-5}$</td>
<td>336.6</td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>-</td>
<td>4.1x10$^{-5}$</td>
<td>373.9</td>
</tr>
<tr>
<td>ZrO$_2$</td>
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<td>+</td>
<td>1.2x10$^{-4}$*</td>
<td>236.4*</td>
</tr>
<tr>
<td>(pH$_{pzc}$ 5.5-6.6)</td>
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<td>9.4</td>
<td>-</td>
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</tr>
<tr>
<td>Al$_2$O$_3$</td>
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<td>+</td>
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<td>151.1*</td>
</tr>
<tr>
<td>(pH$_{pzc}$ 7.4-8.6)</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>-</td>
<td>3.1x10$^{-5}$</td>
<td>309.1</td>
</tr>
</tbody>
</table>

*Although charged at this pH, these surfaces are close to an overall neutral charge
* $\beta_2$ and $q_e$ obtained from the first step reaction (rigid film in Figure 3-3d)

Higher CTAB $q_e$ were obtained for all the metal oxides at basic pH conditions. This was expected as surfaces with overall negative charge might attract the positively charged CTAB. However, significant $q_e$ values were found for acidic CTAB solutions, with values equivalent to 87%, 78% and 49% of those obtained under basic pH conditions for titania, zirconia and alumina, respectively. These findings suggest that electrostatic repulsion was not enough to prevent the surfactant adsorption under acidic conditions for all the metal oxides tested. Furthermore, the results of pH 3.0 clearly showed a two-step curve for all the systems (Figure 3-3d). The first step involved a relatively fast formation of a rigid film ($\beta_2$ values of 6.38x10$^{-5}$, 1.2x10$^{-4}$, and 2.36x10$^{-4}$ cm$^2$/mM.ng.s for titania, zirconia and alumina,
respectively), as confirmed by $\Delta D$ values $< 1 \times 10^{-6}$ (Figure 3-3a, b and c). In the second step, a viscoelastic film was formed, without reaching a plateau by the end of the run, and with $\Delta D$ values higher than $2 \times 10^{-6}$. The formation of this second layer indicates that CTAB was no longer organized in a rigid monolayer but a viscoelastic bilayer. Thus, we propose that this new layer was sustained by hydrophobic interactions between surfactant tails, considering the excess of positive charges at the surface of the systems, as shown in Figure 3-3d.

The unexpected high qe value of 151.1 ng/cm$^2$ observed for the CTAB-alumina system at pH 3.0, compared to the negligible adsorption of CTAB-alumina at pH 6.8, was further investigated using solid-state proton NMR spectroscopy ($^1$H-NMR) to assess CTAB-alumina interactions at different pH values. The $^1$H-NMR analysis was performed as per the procedure described in Text S2. $^1$H-NMR
spectra results of alumina and CTAB-alumina at pH 3.0, 6.8, and 9.4 are shown in Figure 3-4.

The resonances generated by the protons of hydroxyl moieties at the alumina surface were observed around 1 ppm in all spectra obtained. No signals of the surfactant protons were observed at pH 6.8 (Figure 3-4c), confirming the absence of CTAB adsorption onto alumina at this pH. This is in agreement with results obtained from QCM-D analysis. Significant differences were found in the resonances due to the protons of CTAB tails at pH 3.0 and 9.4. At pH 3.0, well-defined signals appeared around 5 ppm (Figure 3-4b), while at pH 9.4 a broad signal was obtained at 6.98 ppm (Figure 3-4d). These signal differences suggest that the CTAB at pH 6.8 and 9.4 had been adsorbed onto alumina in a different
mode. The narrower signals at pH 3.0 indicate that the molecular mobilities and dynamics of CTAB are higher than those at pH 9.4. These results are in agreement with the proposed model for the CTAB adsorption at pH 3.0 onto alumina, where a softer viscoelastic material is formed (Figure 3-3d). Moreover, the broadening of the signal at pH 9.4 as a result of molecular rigidity provides more evidence of chemical shift anisotropy (CSA). CSA is usually the dominant broadening factor for $^1$H-NMR spectra (Mroué et al., 2010). The observed downfield shift of the $^1$H-NMR signal at pH 9.4 (i.e., a signal at higher ppm) indicates that the surface is more prone to share electrons with the surfactant.

The possible effect of pH on pure alumina samples was also assessed by 1H-NMR. These spectra are shown in Figure S6 of the Supplementary material. No significant differences were found in the alumina 1H-NMR spectra at pH 3.0, 6.8 and 9.4, further confirming that adsorption is driven by the nature of the surfactant and not by the surface properties of the metal oxides.

### 3.4 Conclusions

The study aimed to gain a clear background understanding of surfactant adsorption phenomena onto commonly used ceramic membrane materials. QCM-D was successfully applied to obtain insights on SDBS and CTAB interactions with titania, zirconia and alumina surfaces. Adsorption of anionic SDBS onto the metal oxides resulted in the formation of a rigid film, where the positively charged surface adsorbed more surfactant because of electrostatic interactions. Compared to alumina and zirconia, titania was more readily saturated by SDBS, due to slower desorption processes. This implies that ceramic membranes based on titania in
the composition will have higher fouling rates by SDBS adsorption due to slower desorption processes. Adsorption of cationic CTAB was based on complex interactions with the different metal oxide surfaces, where electrostatic repulsion did not prevent the adsorption of CTAB onto the positively charged metal oxide surfaces. CTAB was able to adsorb independently of the surface charge of the metal oxide and instead, the binding sites available between CTAB molecules and their interactions between surfactant tails seemed to play a major role. Alumina may be less readily fouled by CTAB compared to zirconia and titania, especially at neutral pH where negligible adsorption was found.

Alumina content on ceramic membranes may have less impact on the formation of a surfactant fouling layer adsorbed onto the membrane surface (regardless of SDBS or CTAB). These findings support the choice of alumina over the other metal oxides as it is the most common material used in ceramic membranes.

QCM-D is a very sensitive method that can detect changes in mass at very low amounts. This allowed us to study the adsorption behavior or phenomena of charged surfactants and ceramic membrane materials typically used in PW treatment from a fundamental perspective and to distinguish between mechanisms governing the interactions under different conditions of pH/surfactant concentration. Our research showed in a quantitative manner using a straightforward approach with a highly sensitive method, that the choice of surfactant is more critical than the membrane material in fouling considerations in produced water treatment applications. The adsorption interactions are commanded by the nature and properties of the surfactant rather than the metal oxide properties. This has implications in the understanding of fouling
mechanisms of produced water in ceramic membranes. Electrostatic interactions should not be taken as the only predicting factor of adsorption phenomena as other supramolecular interactions are strongly involved. The choice of chemicals for upstream oil & gas production can have a significant impact on the performance and recovery of ceramic membrane systems applied for PW treatment. Further research is required on cleaning strategies for ceramic membrane materials fouled by different surfactants.
ACKNOWLEDGMENTS

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The abstract art and Figure 3-3d were created by Heno Hwang, scientific illustrator at KAUST.
3.5 Supplementary material

A fundamental study of adsorption kinetics of surfactants onto metal oxides using quartz crystal microbalance with dissipation (QCM-D)

Submitted by

Sandra C. Medina, Andreia S. F. Farinha, Abdul-Hamid Emwas, Assiyeh Tabatabai, TorOve Leiknes

a Water Desalination and Reuse Center (WDRC), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.

b Imaging and Characterization Core Lab, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.

c Lhoist Business Innovation Center, 31 Rue de l’Industrie, B-1400 Nivelles, Belgium.

7 pages, 2 texts, 2 tables, 6 figures are included in the supplementary material.
Figure S1. Example of data treatment for adsorption kinetics of 0.5 mM SDS on zirconia; a) raw ΔF data obtained from QCM-D for overtones 7, 9 and 11 and the calculated average; b) corresponding data fitting for pseudo-first-order equation and pseudo-second-order equation.

Table S1. Calculated values of apparent rate constant β2 and amount of surfactant adsorbed qe for pseudo-second-order kinetic model applied to SDS adsorption on three metal oxides. β2 and qe are expressed in cm²/ng.s and ng/cm², respectively.

<table>
<thead>
<tr>
<th>SDBS (mM)</th>
<th>TiO₂</th>
<th>ZrO₂</th>
<th>Al₂O₃</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>β₂</td>
<td>qe</td>
<td>β₂</td>
</tr>
<tr>
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<td>-</td>
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<td>6.2x10⁻⁴</td>
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<td>9.6x10⁻⁵</td>
<td>25.0</td>
<td>6.1x10⁻⁴</td>
</tr>
</tbody>
</table>

The uncertainty in β₂ and qe results are ±1.0 x 10⁻⁴ cm²/ng.s and ±3.3 ng/cm², respectively.
Figure S2. Effect of pH on adsorption characteristics of 1 mM SDBS on a) titania, b) zirconia, and c) alumina as measured by QCM-D $\Delta F$ and $\Delta D$.

Table S2. Calculated values of apparent rate constant $\beta_2$ and amount of surfactant adsorbed $q_e$ for pseudo-second-order kinetic model applied to CTAB adsorption on the three metal oxides. $\beta_2$ and $q_e$ obtained are expressed in cm$^2$/ng.s and ng/cm$^2$, respectively.

<table>
<thead>
<tr>
<th>CTAB (mM)</th>
<th>TiO$_2$</th>
<th>ZrO$_2$</th>
<th>Al$_2$O$_3$</th>
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</thead>
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<td>$\beta_2$</td>
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<tr>
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<td>185.8</td>
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</tr>
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<td>3.4x10$^{-5}$</td>
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<td>1.25</td>
<td>1.2x10$^{-4}$</td>
<td>87.1</td>
<td>1.4x10$^{-4}$</td>
</tr>
</tbody>
</table>

The uncertainty in $\beta_2$ and $q_e$ results are $\pm 0.5 \times 10^{-5}$ cm$^2$/ng.s and $\pm 10.2$ ng/cm$^2$, respectively.
Figure S3. Average \( \Delta F \) (from overtones 7, 9 and 11) obtained for different concentrations of CTAB solutions on alumina at pH 6.8

![Graph showing \( \Delta F \) vs. time for different CTAB concentrations.]

Figure S4. Adsorption isotherm of CTAB solutions onto titania, zirconia and alumina at pH 6.8. CTAB showed negligible adsorption onto alumina

![Graph showing adsorption isotherm for CTAB on titania, zirconia, and alumina at pH 6.8.]

Text S1. Procedure for preparation of the alumina-CTAB solid samples for FTIR_ATR analysis

Fourier-transform infrared spectroscopy with attenuated total reflection (FTIR-ATR, Spectrum 100, PerkinElmer Inc, USA) was applied to further investigate the CTAB-alumina system. 50 mL of 0.6 mM CTAB solutions at pH 3.0, 6.8 and 9.4 were mixed with 4 gr of alumina (99% -100+200, Sigma Aldrich) during 10 hours at 300 rpm. Alumina-CTAB powders were obtained by filtering the solutions through 0.45µm PVDF membranes (Durapore™, MilliporeSigma™) and then oven drying...
the solid retentate at 100 °C for 2 hours. The resulting FTIR-ATR spectra are shown in Figure S3. No CTAB adsorption was detected onto alumina at any of the pH values evaluated. For comparison, the spectrum of a 50/50 (wt%/wt%) mix of alumina and CTAB powders is included in Figure S3. CTAB characteristic peaks (i.e., 1466, 2845 and 2912 1/cm) are insignificant in the mix with alumina.

![FTIR-ATR spectra obtained for alumina with adsorbed CTAB in 0.6 mM solutions at different pH values](image)

Text S2. The procedure for sample analysis by 1H-NMR

Solid alumina samples with adsorbed CTAB were prepared following the same procedure as the one described in Text S1 for FTIR-ATR. Solid-state proton nuclear magnetic resonance (1H -NMR) spectra were acquired using WB Bruker 600 AVANAC III spectrometer equipped with 3.2 mm double resonance CP MAS Bruker probe (BrukerBioSpin, Rheinstetten, Germany). All spectra were recorded by collecting 64 scans using adiabatic double echo refocusing pulse program (zgse.ajr) from Bruker pulse library with recycle delay time of 10 s. Bruker Topspin 3.5pl7 software was used for data collection and processing. Unlike solution NMR spectra, the
signals of solid-state NMR spectra are broader due to anisotropic interaction caused by the orientation-dependence of molecules concerning the direction of the external applied magnetic field. The main two factors for the signal broadening are chemical shift anisotropy (CSA) and dipole-dipole interactions (DD). This broadening effect can be reduced by spinning the sample at a faster rate and with a magnetic angle of 54.7° with respect to the direction of the applied magnetic field. All spectra were recorded under the same instrumental parameters with a spinning rate of 22 kHz.

Figure S6. 600MHz 1H-NMR spectra of alumina at a) pH 3.0, b) pH 6.8, and c) pH 9.4
3.6 References


FAIBISH, R. S. & COHEN, Y. 2001. Fouling and rejection behavior of ceramic and polymer-modified ceramic membranes for ultrafiltration of oil-in-water


Chapter 4. The impact of adsorbed surfactant layer properties onto ceramic material cleaning protocols

This chapter responds to the research questions of hypothesis 3. Mechanical properties of the adsorbed surfactants impacted the cleaning strategies to remove fouling onto metal oxides. More viscoelastic-like surfactant films prevented the penetration of water and the chemical cleaning agent, making the cleaning process tougher.

HIGHLIGHTS

- Surfactants can adsorb irreversibly onto ceramic membrane materials
- A more viscoelastic-like surfactant layer makes the cleaning process more difficult
- Cleaning should be tailored based on the mechanical properties of the film formed
- QCM-D is a useful tool to study the membrane cleaning mechanisms of chemical agents

ABSTRACT

Surfactants in oilfield produced water (PW) play a significant role in irreversible fouling during ceramic membrane filtration. Hence, a better understanding of surfactant adsorption phenomena onto metal oxides is necessary to determine effective membrane cleaning strategies. We hypothesize that the type of surfactant film formed (i.e., rigid, quasi-viscoelastic, and viscoelastic properties) drives the cleaning performance of the ceramic surfaces. In this work, we evaluated the removal efficiency of adsorbed surfactant films onto metal oxides after hydraulic and basic chemical cleaning treatment. The adsorption/desorption phenomena were assessed by quartz crystal microbalance with dissipation (QCM-D). Solutions at different pH with three surfactants, (i.e., cationic CTAB, anionic SDBS, and nonionic Tween 80) were used to saturate titania, zirconia, and alumina surfaces. Results suggest that the presence of a more viscoelastic-like surfactant layer prevents the penetration of water and the chemical cleaning agent, making
the cleaning process tougher. Cleaning strategies should be tailored based on the mechanical properties of the film formed, which is based on the surfactant/metal oxide intramolecular interactions generated from the initial adsorption conditions. Further optimization of chemical cleaning agent concentration, soaking time, and water flush can be performed based on adsorption/desorption studies in QCM-D.

**GRAPHICAL ABSTRACT**

**KEYWORDS:** Ceramic membranes, membrane cleaning, QCM-D, surfactant adsorption, viscoelastic films.
4.1 Introduction

Fouling is the major drawback for a broader application of membrane-based filtration systems in oil-field produced water (PW) treatment. Adjustments to operating conditions coupled with periodic hydraulic (e.g., forward flushing, back-pulsing, vibrations, and backflushing) (Silalahi and Leiknes, 2011) and chemical cleanings allow the recovery of permeability loss caused by reversible fouling (Ebrahimi et al., 2010). However, these hydraulic and single chemical cleaning steps are not sufficient to fully restore membrane performance (Field, 2010). Irreversible fouling affects the membrane permanently, and eventually, it has to be replaced (Silalahi and Leiknes, 2009). Further understanding of the interactions between PW foulants and the membrane is needed to design better cleaning strategies to overcome irreversible fouling during operation.

Surfactants present in PW adsorb onto polymeric (Cornelis et al., 2005, Boussu et al., 2007, Dickhout et al., 2019) and ceramic membrane (Faibish and Cohen, 2001, Lu et al., 2015, Matos et al., 2016, Shi et al., 2019) surfaces, causing irreversible fouling. Surfactants are not only naturally present in crude oil (e.g., as asphaltenes, resins, and waxes (Abdulredha et al., 2020)) but also added in different chemicals throughout up-stream fluid extraction processes for flow assurance and oil recovery. These include corrosion inhibitors, biocides, coagulants, and flocculants, which affect the resulting PW quality (McAdams et al., 2019) and challenge any membrane filtration treatment downstream (Walsh, 2018). The interactions of these surfactants with a membrane surface depends on different factors such as membrane properties (Faibish and Cohen, 2001, Yang et al., 2015, Lu et al., 2016), the nature of the surfactants (Fernández et al., 2005, Liu and Kim, 2009), the ionic
strength (Dickhout et al., 2019), and pH of the PW (Chiu and James, 2006, Medina et al., 2019). Due to the complexity of irreversible membrane fouling during PW filtration, ceramic membranes are preferred over polymeric ones as more harsh cleaning procedures for membrane regeneration can be applied (Weschenfelder et al., 2015).

Previous studies addressing surfactant adsorption onto ceramic membranes rely on filtration tests of stabilized emulsions with different droplet size distributions (Lu et al., 2015, Matos et al., 2016, Shi et al., 2019). The authors attribute membrane fouling potential mainly to electrostatic interactions between the stabilizing surfactant and membrane surface. Their results disagree on whether ceramic membranes opposite or similar charged with respect to the surfactant should be used during PW treatment to prevent irreversible fouling. Matos et al. (2016) conclude that ZrO$_2$/TiO$_2$ ultrafiltration (UF) membrane of opposite charge than that of the stabilized emulsion promotes adsorption, causing a reduction in permeate flux. Contrary to this observation, Lu et al. (2015) report adsorption of anionic surfactants onto negatively charged ZrO$_2$/TiO$_2$ UF membranes, allowing small oil droplets to penetrate the pores and leading to more severe fouling compared to a cationic stabilized emulsion. In both of these studies, the impact of nonionic surfactant adsorption on ceramic membrane fouling was reported to be less significant compared to charged surfactants. More recent work from Shi et al. (2019) evaluated the adsorption of similar surfactant types in stabilized emulsions similar to the work performed by Lu et al. (2015) but using a SiC membrane. In this study, the adsorption of surfactant onto negatively charged SiC (pH 7.5-8.5) was attributed to electrostatic interactions for the cationic surfactant
and hydrophobic interactions for the anionic and nonionic surfactants. Interestingly, the degree of surfactant adsorption and the arrangement of surfactants on the membrane could be obtained by calculating the fitting parameters to the general adsorption model proposed by Zhu et al. (1989). The authors concluded that hemi-micelles were formed at the SiC membrane surface by all the surfactants studied, wherein the nonionic surfactant presented higher adsorption constant in the formation of hemi-micelles. This indicates that regardless of the type of ceramic membrane material used, the surfactant nature and its arrangement on the membrane surface may play an essential role in the fouling phenomenon. As such, fundamental studies of surfactant adsorption phenomena onto ceramic membrane materials are necessary to determine effective cleaning strategies.

In a previous study, we made the first attempt to gain a fundamental understanding of surfactant adsorption onto metal oxide surfaces by using a quartz crystal microbalance with dissipation (QCM-D) (Medina et al., 2019). Smooth ceramic surfaces (i.e., roughness below 2 nm) in the QCM-D sensors were used instead of ceramic membranes to exploit the powerful analysis that QCM-D provides in monitoring binding kinetics on multiple metal oxides. Our study showed that different surfactants arranged in rigid and viscoelastic films on the surface, independent of the type of metal oxide used. Instead, the adsorbed film was found to be dependent on the surfactant nature and pH conditions of the solution, where electrostatic interactions could not be used as a predictor of the adsorption phenomena. We hypothesize that the type of surfactant film formed (i.e., rigid or viscoelastic film) drives the performance of the metal oxides cleaning
behavior. To the best of our knowledge, there is no literature addressing ceramic materials cleaning from this perspective. Research on adsorption of viscoelastic/rigid films of surfactants in enhanced oil recovery is mostly focused on improving well permeability in silica (Van Zanten, 2011), carbonates (Gomaa et al., 2012) and sandstone (Du et al., 2019) reservoirs. Viscoelastic surfactants are used as diverters, to adsorb and plug certain zones of highest permeability in the reservoir in order to direct the main chemical treatment to more damaged zones (Alghamdi et al., 2009).

This study aims at evaluating the cleaning efficiency of surfactant films adsorbed onto metal oxide surfaces. Three surfactants solutions (i.e., cationic CTAB, anionic SDBS, and nonionic Tween 80) were used to saturate three metal oxides (i.e., titania, zirconia, and alumina) at different pH values. The cleaning efficiencies of the adsorbed surfactant films were evaluated by applying a hydraulic cleaning (Milli-Q water) and basic chemical cleaning (Hellmanex® III). The removal or desorption of surfactants on the metal oxide surfaces was assessed using a quartz crystal microbalance with dissipation (QCM-D). The results provide a better understanding of the effect of pH conditions and surfactant nature on the formation of rigid and viscoelastic films and their impact on the cleaning efficiency of metal oxide surfaces.

4.2 Materials and Methods

4.2.1 Materials

The QSense analyzer with Qsoft 401 software at a set temperature of 22 °C was used for real-time data acquisition (Biolin Scientific AB, Sweden). Titania, zirconia,
and alumina QCM-D sensors (Biolin Scientific AB, Sweden) of hydrophilic \textit{(i.e., water contact angle $< 28^\circ$ as shown in Figure S1, measured by drop shape analyzer DSA100 (Krüss GmbH, Germany))} and smooth surfaces \textit{(i.e., roughness $< 2\text{nm}$, according to manufacturer specifications)} were used. The metal oxides surfaces were saturated with rigid and viscoelastic films of the surfactants. Three types of surfactants were used: anionic SDBS (sodium dodecylbenzene sulfonate, MW 343.4 g/mol, critical micelle concentration (CMC) $\sim 2.0\text{ mM}$ (Hait et al., 2003)), cationic CTAB (cetyltrimethylammonium bromide, MW 364.4 g/mol, CMC $\sim 0.8$ mM (Moulik et al., 1996)), and nonionic Tween 80 (Polysorbate 80, MW 1,310 g/mol, CMC $\sim 0.012$ mM (Braun et al., 2015)). The surfactants were technical grade (Sigma-Aldrich, USA) and used as received. Solutions of 0.1 M sodium hydroxide and sulfuric acid were used for pH adjustment. 2\% v/v Hellmanex® III (Hellma Analytics, Germany) was used as a basic chemical cleaning agent.

\textbf{4.2.2 Methods}

The pH of surfactant solutions feeding the QCM-D system affects the mechanical properties of the surfactant film form onto metal oxide surfaces (Medina et al., 2019). Solutions of 1 mM SDBS and 0.6 mM CTAB \textit{(i.e., under their respective CMC values)} were used to saturate the surfaces of three metal oxides \textit{(i.e. titania, zirconia, and alumina)} at different pH values: 3.0 (acidic), 6.8 (neutral), and 9.4 (basic). The classification of a rigid vs viscoelastic film was determined according to dissipation values ($\Delta D$), assuming laterally homogeneous films according to (Reviakine et al., 2011). If the value of $\Delta D \ll 1\times10^{-6}$ and the variation of frequency ($\Delta F$) obtained at the different overtones overlapped, the film was described as
rigid using the Sauerbrey equation (described in previous work from Medina et al. (2019)). Otherwise, the Voigt viscoelastic model with the QTools software (Biolin Scientific AB, Sweden) was applied. The Voigt viscoelastic model considers the viscous resistance and elastic responses (conceptualized as a spring and a damper in parallel) of a laterally homogeneous film when shear stress is applied (Alexander et al., 2019). For films with $\Delta D$ closer to the viscoelasticity definition (i.e., $\lesssim 1 \times 10^{-6}$), the Sauerbrey equation was applied but classified as quasi-viscoelastic when a wider spread between $\Delta F$ curves was observed.

To further study the correlation of viscoelastic-adsorbed films and the challenges of cleaning fouled membranes, a commonly used nonionic surfactant in the oil and gas industry (Abdulredha et al., 2020), Tween 80, was chosen as the model to avoid charge effects in the surfactant-surface system. Tween 80 solutions of different concentrations below and above CMC (i.e., $\sim 0.012$ mM) at neutral pH (6.8) were used. No changes in the pH of the Tween 80 solutions were applied. pH variations can induce protonation of the Tween 80 molecule or cleavage of the carboxyl groups, which may interfere with test results by creating a formal charge at the surfactant structure, and enhancing electrostatic and supramolecular interactions. The viscoelastic property of the adsorbed Tween 80 layer was the main focus of this study.

All surfactants solutions were fed at 150 $\mu$L/min and 22 $^\circ$C until a steady-state was observed (i.e., no changes of $\Delta F$ and $\Delta D$), except for Tween 80 solutions for which adsorption was stopped after 4 hours without reaching steady-state. After adsorption, the cleaning of the surfactant-saturated metal oxide surfaces was evaluated in two steps. First hydraulic flushing was done using Milli-Q water at
150 μL/min, followed by chemical cleaning using 2% v/v Hellmanex® III at the same feed rate, performed for those metal oxide surfaces that were not be recovered by the hydraulic cleaning step.

Desorption kinetics model

The mass of surfactant desorbed (ng/cm²) from the saturated metal oxide surface during flushing with Milli-Q water was registered as a function of time (t) to determine the apparent desorption rate constant (k). The desorption phenomena caused by the hydraulic flushing was assessed by applying a pseudo-first-order equation 4-1, as the surfactant interaction with the surface drives the desorption.

\[ q_t = q_i - q_e \left(1 - e^{-kt}\right) \]  Eq. 4-1

Where \( q_i \), \( q_t \), and \( q_e \) are the mass of surfactant (ng/cm²) saturated on the sensor, the mass desorbed at time t, and the mass at equilibrium after cleaning, respectively.

4.3 Results and discussion

Titania, zirconia, and alumina sensors were saturated with SDBS and CTAB solutions at different pH. The mass of saturation (qi) of the surfactants onto the metal oxide surfaces and the type of film formed are summarized in Table 4-1. qi values correspond to the starting point for the cleaning studies. Rigid films of SDBS and CTAB were formed on the QCM-D sensors when solutions with concentrations under the CMC at neutral conditions (pH 6.8) were used. Viscoelastic and quas-viscoelastic films of these surfactants were obtained under acidic conditions (pH 3.0). Under basic conditions (pH 9.4), SDBS and CTAB formed rigid and quasi-viscoelastic films, respectively. The results suggest that the pH conditions in
surfactant feed solutions significantly affects the supramolecular organization of the surfactants adsorbed onto the metal oxides. Viscoelasticity of adsorbed films has been attributed to hydrophobic interactions between surfactant tails in charged surfactants (Medina et al., 2019). Thereafter, the success of the cleaning method to remove the adsorbed films might depend on their rigid, quasi-viscoelastic, or viscoelastic properties. The results for alumina loaded with CTAB at 6.8 pH are not shown as no adsorption was observed in such conditions, as reported previously by Medina et al. (2019).

Table 4-1 SDBS and CTAB adsorption characteristics onto titania, zirconia, and alumina sensors at different pH.

<table>
<thead>
<tr>
<th>Metal oxide</th>
<th>pH</th>
<th>Mass of saturation</th>
<th>$\Delta D$ x10$^6$</th>
<th>Type of film</th>
<th>Mass of saturation</th>
<th>$\Delta D$ x10$^6$</th>
<th>Type of film</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>3.0</td>
<td>292.6</td>
<td>0.62</td>
<td>~V</td>
<td>488.0$^b$</td>
<td>2.35</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td>6.8</td>
<td>12.0</td>
<td>0.04</td>
<td>R</td>
<td>336.6</td>
<td>0.39</td>
<td>R</td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>11.7</td>
<td>0.01</td>
<td>R</td>
<td>373.9</td>
<td>0.85</td>
<td>~V</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>3.0</td>
<td>270.9</td>
<td>0.67</td>
<td>~V</td>
<td>236.4$^b$</td>
<td>2.08</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td>6.8</td>
<td>24.9</td>
<td>0.01</td>
<td>R</td>
<td>278.4</td>
<td>0.33</td>
<td>R</td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>18.2</td>
<td>0.02</td>
<td>R</td>
<td>303.4</td>
<td>0.64</td>
<td>~V</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>3.0</td>
<td>191.1</td>
<td>0.75</td>
<td>~V</td>
<td>482.4$^b$</td>
<td>3.34</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td>6.8</td>
<td>29.1</td>
<td>0.31</td>
<td>R</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>17.9</td>
<td>0.16</td>
<td>R</td>
<td>309.1</td>
<td>0.91</td>
<td>~V</td>
</tr>
</tbody>
</table>

$^a$“R” for rigid, “~V” for quasi-viscoelastic, and “V” for viscoelastic.

$^b$q, obtained after the second step of adsorption according to viscoelastic properties of CTAB loaded at acidic pH described by (Medina et al., 2019)

4.3.1 Cleaning of rigid surfactant films

Hydraulic flushing of the system increased of frequency and decrease of dissipation, which correlates with surfactant desorption. $\Delta F$ and $\Delta D$ curves of a complete recovery of titania surfaces from SDBS and CTAB are shown in Figure S2 as an example. The results of the hydraulic cleaning efficiency and desorption kinetics of two surfactants, at two pH values for the three metal oxide surfaces are summarized in Table 4-2. Rigid films of SDBS and CTAB formed onto metal oxides
surfaces were effectively cleaned by hydraulic flushing without the need for chemical cleaning.

SDBS rigid film loaded under neutral pH showed weaker interactions with the metal oxides, as one order of magnitude faster desorption rates were obtained compared to that under basic pH. The desorption rates for CTAB rigid films were comparable to the values obtained for SDBS, even though the amount of CTAB adsorbed was one order of magnitude higher than that of SDBS (e.g., 333.2 ng/cm² of CTAB vs 12 ng/cm² of SDBS onto titania). These results indicate that the desorption process of the adsorbed rigid films is commanded by convective-diffusive transport. The electrostatic forces between surfactant-metal oxide were weaker than the interactions between surfactants and water molecules due to the surfactant concentration gradient.

### Table 4-2. Hydraulic cleaning efficiency for the removal of rigid films of SDBS and CTAB

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Metal oxide</th>
<th>pH 6.8</th>
<th>pH 9.4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k^l$</td>
<td>Cleaning efficiency (%)</td>
</tr>
<tr>
<td>SDBS</td>
<td>TiO$_2$</td>
<td>1.7x10^-2</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>ZrO$_2$</td>
<td>1.8x10^-2</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$</td>
<td>2.0x10^-2</td>
<td>100%</td>
</tr>
<tr>
<td>CTAB</td>
<td>TiO$_2$</td>
<td>3.9x10^-2</td>
<td>99%</td>
</tr>
<tr>
<td></td>
<td>ZrO$_2$</td>
<td>5.3x10^-3</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

#### 4.3.2 Cleaning of quasi-viscoelastic surfactant films

Metal oxide surfaces saturated by quasi-viscoelastic surfactant films showed lower cleaning efficiency percentages after hydraulic cleaning than rigid films (Table 4-3).
Table 4-3. Hydraulic and chemical cleaning efficiencies for the removal of quasi-viscoelastic films of acidic-SDBS and basic-CTAB

<table>
<thead>
<tr>
<th>Cleaning</th>
<th>Metal oxide</th>
<th>SDBS pH 3.0</th>
<th>CTAB pH 9.4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cleaning efficiency (%)</td>
<td>Amount removed (ng/cm²)</td>
<td>Cleaning efficiency (%)</td>
</tr>
<tr>
<td>Hydraulic</td>
<td>TiO₂</td>
<td>0%</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>ZrO₂</td>
<td>16%</td>
<td>43.3 (1.8x10⁻²)</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>52%</td>
<td>99.4 (2.0x10⁻²)</td>
</tr>
<tr>
<td>Chemical*</td>
<td>TiO₂</td>
<td>92%</td>
<td>268.0</td>
</tr>
<tr>
<td></td>
<td>ZrO₂</td>
<td>45%</td>
<td>121.3</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>48%</td>
<td>91.7</td>
</tr>
<tr>
<td>Overall*</td>
<td>TiO₂</td>
<td>92%</td>
<td>268.0</td>
</tr>
<tr>
<td></td>
<td>ZrO₂</td>
<td>61%</td>
<td>164.6</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>100%</td>
<td>191.1</td>
</tr>
</tbody>
</table>

*Results after a single cycle of chemical cleaning

Values in parentheses correspond to the apparent desorption rate constant $k_1$

The apparent desorption rates during hydraulic cleaning showed the same order of magnitude as those calculated for the rigid films formed at pH 6.8. This indicates that hydraulic cleaning is not limited by the amount of surfactant adsorbed but rather by stronger interactions between surfactant-metal oxide surfaces. Chemical cleaning using basic 2% Hellmanex® III solution was needed after hydraulic cleaning to enhance the recovery of the sensors from adsorbed quasi-viscoelastic surfactant films. Figure 4-1a shows examples of the overall cleaning process applied to the removal of SDBS and CTAB quasi-viscoelastic films, indicating the stages where Milli-Q water and Hellmanex® III were fed into the QCM-D.

In each chemical cleaning cycle, Hellmanex® III was observed to interact with the adsorbed surfactant films where the resulting removal process can be seen in three steps (indicated in green in Figure 4-1). In the first step, Hellmanex® III abruptly adsorbed into the surfactant film, creating a soft viscoelastic layer as the
$\Delta D$ increased sharply to values higher than $3 \times 10^{-6}$. Thereafter, this viscoelastic film started desorbing from the sensor surface (second step). In the third step, when hydraulic flushing is introduced again, rapid removal of the viscoelastic film can be seen, enhancing the overall cleaning process.

Figure 4-1. Hydraulic and chemical cleaning of a) titania sensor loaded with CTAB at pH 9.4. and b) zirconia sensor loaded with SDBS at pH 3.0.

A single desorption rate during the chemical cleaning process could not be determined due to the complexity of the interaction steps of Hellmanex® III mentioned above. However, these insights on how a chemical agent interacts with and removes an adsorbed surfactant film are crucial in gaining a better understanding of the chemical cleaning mechanisms and process of ceramic membranes. In the case of Hellmanex® III, step 1 will depend on the cleaning agent concentration, and step 2, which is equivalent to the soaking time, will depend on how the cleaning agent reacts with the surfactant film. Previous studies report that the soaking time can be as important as the concentration of the cleaning agent (Hofs et al., 2011). Step 3 highlights the critical role hydraulic flushing may play in a chemical process to remove the desorbed chemical agent and the surfactant films altogether. Optimization of the chemical doses and
soaking time for a given chemical agent can be performed by using QCM-D to
design and predict better cleaning strategies of ceramic membranes during PW
treatment.

The SDBS film formed on zirconia at pH 3.0 was removed by hydraulic flushing,
followed by a single cycle of chemical cleaning, achieving an overall recovery of
61%. The second cycle of chemical cleaning was then applied without success in
enhancing the SDBS film removal (Figure 4-1a). The adsorption of anionic SDBS
onto positively charged metal oxides under acidic conditions (pH 3.0) has been
attributed mostly to electrostatic interactions (Medina et al., 2019). However, the
difficult recovery of the sensors despite extreme changes in the pH during
hydraulic flushing (pH 7.0) and subsequent chemical cleaning with Hellmanex®
III (pH 12.0), suggests stronger adsorption between the acidic-SDBS and metal
oxide which is possibly due to hydrophobic interactions.

Comparatively higher hydraulic cleaning efficiencies were obtained for the CTAB
films formed under basic conditions, but without reaching 100% removal. As for
the acidic-SDBS case, chemical cleaning after hydraulic flushing was needed to
completely remove the CTAB films loaded under basic conditions (Figure 4-1b).
This can be related to the high $\Delta D$ values of the CTAB film loaded at pH 9.4,
especially for titania (0.85) and zirconia (0.91) (Table 4-1), where the film was
classified as quasi-viscoelastic. The presence of a more viscoelastic-like layer
seems to prevent the molecules of water and Hellmanex® III from penetrating the
surfactant layers making the cleaning process more difficult. The choice of
cleaning strategies for the removal of adsorbed surfactant films from ceramic
membrane materials strongly depends on the conditions (i.e., mainly pH) in which they were first attached.

### 4.3.3 Cleaning of viscoelastic surfactant films

The CTAB loaded at pH 3.0 formed viscoelastic films onto the metal oxide surfaces. These films were found to be the most challenging to clean from the metal oxide surfaces. Cleaning efficiency and the amount of CTAB removed after hydraulic and chemical cleanings are shown in Table 4-4.

<table>
<thead>
<tr>
<th>Cleaning</th>
<th>Metal oxide</th>
<th>CTAB pH 3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cleaning efficiency (%)</td>
</tr>
<tr>
<td>Hydraulic</td>
<td>TiO₂</td>
<td>29%</td>
</tr>
<tr>
<td></td>
<td>ZrO₂</td>
<td>58%</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>33%</td>
</tr>
<tr>
<td>Chemical*</td>
<td>TiO₂</td>
<td>66%</td>
</tr>
<tr>
<td></td>
<td>ZrO₂</td>
<td>34%</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>29%</td>
</tr>
<tr>
<td>Overall</td>
<td>TiO₂</td>
<td>95%</td>
</tr>
<tr>
<td>(Hydraulic +</td>
<td>ZrO₂</td>
<td>92%</td>
</tr>
<tr>
<td>chemical)</td>
<td>Al₂O₃</td>
<td>62%</td>
</tr>
</tbody>
</table>

*Results after a single cycle of chemical cleaning

Values in parentheses correspond to the apparent desorption rate constant $k$.

Hydraulic cleaning had low efficiencies of less than 58%, with similar desorption rates (values in parentheses) compared to CTAB loaded at neutral and basic pH (Table 4-4). Similar to the results obtained for quasi-viscoelastic films, hydraulic cleaning was not limited by the amount of surfactant onto the metal oxides, but rather by stronger CTAB/metal-oxide interactions. Furthermore, none of the metal oxides could be 100% recovered after a single chemical cleaning cycle. The lowest overall recovery was observed for alumina at approximately 62%. Results
confirm the strong interactions between the CTAB molecules loaded at acidic pH and the metal oxides, as reported in a previous study (Medina et al., 2019). The acidic-CTAB condition was reported to form double layer viscoelastic films on the surfaces, possibly sustained by hydrophobic interactions between CTAB tails. These complex acidic-CTAB and metal oxide interactions were not affected by pH changes in the system caused by the hydraulic and basic Hellmanex® III cleaning cycles. An example of the $\Delta F$ and $\Delta D$ results demonstrating the adsorption and cleaning of acidic-CTAB on alumina is shown in Figure S3. These results confirm that electrostatic interactions should not be taken as the only predicting factor for surfactant adsorption onto ceramic membranes and for defining the appropriate ceramic membrane cleaning.

The challenge of cleaning viscoelastic-adsorbed films on metal oxide sensors was assessed by testing different concentrations of nonionic Tween 80 solutions with the QCM-D. Adsorption isotherms for Tween 80 on the three metal oxides tested are shown in Figure 4-2.

![Figure 4-2](image-url)

Figure 4-2. Adsorption isotherm of Tween 80 onto titania, zirconia, and alumina. This isotherm shows the $\Delta m$ obtained after 1 hour of feeding for each concentration.
Viscoelastic films were formed onto zirconia and alumina surfaces. No significant adsorption of Tween 80 onto titania was found for the applied concentrations, in agreement with previous studies (Notley, 2012). The poor adsorption of polysorbate surfactants (referred to as Tween) has been attributed to hydration (i.e., preferential water molecule bound) on both the titania surface and the surfactant head group, thus preventing Tween-titania interactions (Stubenrauch et al., 2010). Therefore, cleaning studies of Tween 80 films were only evaluated on zirconia and alumina surfaces.

Tween 80 solutions were fed to the QCM-D for 4 hours without reaching a stable adsorption plateau for the zirconia and alumina sensors (Figure S4). Continuous adsorption was observed, which can be associated with the self-assembly properties of Tween 80 (Penfold et al., 2016) as a result of weak repulsive interactions between molecules (Szymczyk et al., 2018). Table 4-5 summarizes the adsorption and cleaning results of the Tween 80 films onto zirconia and alumina. \( q_i \) corresponds to the Tween 80 mass adsorbed after 4 hours of feeding the solutions.

Hydraulic cleaning of the viscoelastic Tween 80 films achieved low removal percentages (< 35.1%). After a chemical cleaning with Hellmanex® III solution in a single cycle, a high recovery of the zirconia and alumina surfaces was found (>97.1%). There was no statistically significant difference (p >0.05) in the cleaning results between the alumina and zirconia sensors. Furthermore, no differences in the cleaning efficiencies were identified for Tween 80 solutions below and above its CMC (0.012 mM). Results confirm our hypothesis of a
correlation between the viscoelastic properties of an adsorbed film and stronger interactions with the metal oxide surfaces.

The viscoelastic films of Tween 80 formed onto zirconia and alumina might contain water molecules trapped in between the layer, which is preferably adsorbed by hydrogen bonding with the surfactant heads (Naderi and Claesson, 2006, Kou and Xu, 2016). The water associated with a viscoelastic layer can represent from 20% up to 80% of the QCM-D sensed mass Naderi and Claesson (2006). Therefore, it is assumed that when hydraulic cleaning was applied, no significant impact on the film removal was observed as it was already well hydrated. The quantification of this intrinsic water content in viscoelastic films is out of the scope of this work. When chemical cleaning is applied, Hellmanex® III molecules interacted with the Tween 80 films following the same three steps previously described for the quasi-viscoelastic and viscoelastic CTAB films (pH

<table>
<thead>
<tr>
<th>Metal oxide</th>
<th>Tween 80 (mM)</th>
<th>qi (ng/cm²)</th>
<th>Hydraulic cleaning efficiency (%)</th>
<th>Chemical cleaning efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂</td>
<td>0.0003</td>
<td>68.25</td>
<td>11.4</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td>0.0012</td>
<td>75.20</td>
<td>13.9</td>
<td>97.1</td>
</tr>
<tr>
<td></td>
<td>0.0048</td>
<td>85.99</td>
<td>28.5</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>0.0096</td>
<td>204.74</td>
<td>17.3</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>0.012</td>
<td>351.50</td>
<td>22.0</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>0.015</td>
<td>321.11</td>
<td>14.3</td>
<td>99.9</td>
</tr>
<tr>
<td></td>
<td>0.018</td>
<td>374.70</td>
<td>35.1</td>
<td>99.8</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.0003</td>
<td>176.81</td>
<td>13.7</td>
<td>96.6</td>
</tr>
<tr>
<td></td>
<td>0.0012</td>
<td>274.33</td>
<td>27.5</td>
<td>97.1</td>
</tr>
<tr>
<td></td>
<td>0.0048</td>
<td>361.69</td>
<td>31.0</td>
<td>97.6</td>
</tr>
<tr>
<td></td>
<td>0.0096</td>
<td>269.09</td>
<td>14.7</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>0.012</td>
<td>369.74</td>
<td>25.0</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>0.015</td>
<td>371.82</td>
<td>17.0</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>0.018</td>
<td>420.86</td>
<td>22.5</td>
<td>99.7</td>
</tr>
</tbody>
</table>
Hellmanex® III first attaches to the Tween 80 film interfering with the hydrophilic interactions, penetrates its structure, making it softer (i.e., increase in $ΔD$). Second, the film slowly starts to desorb from the metal oxide surface, and finally, desorption is accelerated when hydraulic flushing is re-applied. Subsequently, the surface was completely restored. The resulting $ΔD$ and $ΔF$ curves of the complete cycle of a Tween 80 viscoelastic film adsorption and cleaning steps (green dashed ovals) are shown in Figure 4-3. A highly concentrated solution of 0.018 mM Tween 80 was chosen to shorten the experiment duration. Results for the nonionic surfactant Tween 80 supports our previous findings for quasi-viscoelastic and CTAB viscoelastic films, and the increased challenge of removing viscoelastic surfactant films where at least one cycle of a chemical cleaning agent is required.

Figure 4-3. Adsorption, hydraulic flushing and chemical cleaning of 0.018 mM Tween 80 pH 6.8 onto alumina. Chemical cleaning steps are marked in green dashed ovals.
4.4 Conclusions

Cleaning protocols for ceramic membranes fouled by surfactants present in PW should be tailored based on the mechanical properties of the film formed, and the intramolecular interactions generated from the initial adsorption conditions. In the case of charged surfactants, interactions with metal oxides surfaces are dominated by the pH conditions of the loaded solutions generating different rigid, quasi-viscoelastic, and viscoelastic properties in the adsorbed films. Viscoelastic surfactant films proved to be the most challenging to clean. Insights obtained from the QCM-D during the cleaning process allowed a better understanding of the different steps through which the basic chemical agent could affect the adsorbed surfactant films onto metal oxides surfaces. This can be further explored for the optimization of different parameters involved in cleaning protocols of ceramic membranes materials, such as chemical concentration, soaking time, and hydraulic flush duration.
CRediT authorship contribution statement

Sandra C. Medina: Conceptualization, Methodology, Data curation, Software, Validation, Investigation, Formal analysis, Visualization, Project administration, Writing - Original draft. Andreia S.F. Farinha: Methodology, Formal analysis, Writing - Original draft. Assiyeh Tabatabai: Conceptualization, Formal analysis, Writing - review & editing, Supervision. TorOve Leiknes: Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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4.5 Supporting information

The impact of adsorbed surfactant layer properties on ceramic membrane cleaning protocols

Submitted by

Sandra C. Medina\textsuperscript{3,a}, Andreia S. F. Farinha\textsuperscript{a}, Assiyeh Tabatabai\textsuperscript{a,b}, TorOve Leiknes\textsuperscript{a}

\textsuperscript{a} King Abdullah University of Science and Technology (KAUST), Water Desalination and Reuse Center (WDRC), Biological and Environmental Science & Engineering (BESE), Thuwal 23955-6900, Saudi Arabia.

\textsuperscript{b} Lhoist Business Innovation Center, 31 Rue de l’Industrie, B-1400 Nivelles, Belgium.

2 pages, and 4 figures are included in the supporting information.

\textsuperscript{3} Corresponding author: Sandra C. Medina. e-mail: sandra.medina@kaust.edu.sa. 4700 King Abdullah University of Science and Technology (KAUST) Thuwal, 23955-6900, Saudi Arabia. Tel: +966545754908.

E-mail addresses: sandra.medina@kaust.edu.sa (S.C. Medina), andreia.farinha@kaust.edu.sa (A.S.F. Farinha), assiyeh.tabatabai@lhoist.com (A. Tabatabai), torove.leiknes@kaust.edu.sa (T. Leiknes).
Figure S1. Water contact angle measured on a) titania, b) zirconia, and c) alumina QCM-D sensors.

Figure S2. Titania surfaces fully recovered after hydraulic cleaning of rigid surfactant films formed from a) SDBS 1 mM, and b) CTAB 0.6 mM at pH 6.8.
Figure S3. ΔF and ΔD multi-harmonic QCM-D measurement for the adsorption and cleaning of 0.6 mM CTAB, pH 3.0 onto alumina. n corresponds to overtone number.

Figure S4. Δm curves of adsorption of Tween 80 on a) zirconia, and b) alumina surfaces during 4 hours.
4.6 References


of the Molecular Weight Cutoff and Contact Angle on Flux Behavior.  

*Industrial & Engineering Chemistry Research, 44,* 7652-7658.


Chapter 5. Adsorption and cleaning of oilfield Produced Water contaminants onto alumina ceramic material

This chapter responds to the research questions of hypothesis 4. Organic compounds present in an oilfield PW sample were the major factor impacting the irreversible adsorption on alumina ceramic membrane material. The adsorption of the submicron contaminants onto alumina was able to be characterized qualitatively and quantitatively. Biofilm was identified as the primary source of irreversible adsorption.

ABSTRACT

The application of ceramic membranes filtration for oilfield produced water (PW) treatment has been widely studied. However, the singularity of the PW characteristics introduces a fundamental challenge in the understanding of its interactions with the ceramic membrane affecting its fouling propensity. The adsorption phenomenon has shown a critical role in evaluating ceramic membrane fouling. The objective of this work is to both quantitatively and qualitatively characterize, for the first time, the adsorption and cleaning of contaminants present in a Bahraini PW sample onto alumina, which is the most widely used ceramic membrane material in the market. Adsorption and cleaning were evaluated using quartz crystal microbalance with dissipation (QCM-D). QCM-D results were correlated with scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) analysis to enhance the identification of contaminants. Two viscoelastic films were adsorbed in sequence onto the alumina, regardless of PW sample dilution. These layers showed distinct compositions and mechanical properties, the first layer being more fluid than the second one. The second layer contained the majority of the mass of contaminants adsorbed (96.7%). This mass could be identified as calcium-precipitates, which were entirely removed by hydraulic cleaning. A fraction of the first layer (9%), on the other hand, was adsorbed irreversibly into alumina, as chemical cleaning could not remove it. Bacteria and microbial polymeric substances were identified as the irreversibly attached material on alumina. Further analysis of the bacteria community found the presence of both sulfate-reducing bacteria and sulfate-oxidizing in the PW sample, which could serve as nucleation points for the
formation of calcium precipitates. QCM-D combined with SEM-EDS demonstrated high capability to understand the adsorption interactions of complex PW contaminants, not only for membrane fouling study but potentially for corrosion.

**KEYWORDS:** Produced water, adsorption, ceramic membranes, membrane cleaning, QCM-D.

**GRAPHICAL ABSTRACT**
5.1 Introduction

Application of ceramic membranes filtration for oilfield produced water (PW) treatment has been widely studied in the last decade (Ebrahimi et al., 2010, Nandi et al., 2010, Abadi et al., 2011, Jiang et al., 2013, Guirgis et al., 2015, Weschenfelder et al., 2015, Samaei et al., 2018, Zsirai et al., 2018, Abdalla et al., 2019, Virga et al., 2020). Advantages such as mechanical, thermal, and chemical resistance make ceramic membranes a reliable technology in long term performance, offering high water quality needed for the increasing requirements of PW reinjection and desalination (Al-Haddabi et al., 2015, Ishikawa et al., 2019). However, the singularity of the PW characteristics depending on the oilfield location, operational conditions, and even seasonal changes per site (Walsh, 2018), introduces a fundamental challenge to optimize the ceramic membrane performance.

Oilfield PW is a complex mixture of formation water, dissolved/dispersed oil and gas, inorganic compounds, bacteria, surfactants, antifoam, biocides, corrosion inhibitors, wax inhibitors, asphaltene inhibitors, hydrogen sulfide scavengers, and others. Due to this complexity, it is still not well understood how the PW components interact with the ceramic membrane affecting its fouling propensity (Dickhout et al., 2019). Adsorption, however, has been shown as a determinant mechanism for evaluating ceramic membrane fouling (Lu et al., 2015, Virga et al., 2020) and cleaning strategies during PW treatment (Duraisamy et al., 2013).

Quartz crystal microbalance with dissipation (QCM-D) is a powerful surface-sensitive tool that has been used to understand fundamental adsorption interactions of solutes onto a model surface in real-time. This information is
obtained from sensing frequency $\Delta F$ and energy dissipation $\Delta D$ variations of the wave induced by the piezoelectric resonance of the sensor coated with the material of interest. Over the last 20 years, QCM-D has gained increased recognition of its versatility and broad applicability in different fields (Beckera and Cooper, 2011, Aassi et al., 2017). QCM-D acquires the mass, thickness, and mechanical properties during the formation, transformation, or removal of thin layers at the liquid-solid interface, which can provide first indications about the driving forces behind adsorption of a solute onto a material (Dixon, 2008).

QCM-D senses the structural stability and conformational changes in the adsorbed films, which can be defined as a “hard” or rigid, and “soft” or viscoelastic film. Previous research has shown that membrane fouling is significantly influenced by the structural or mechanical properties of adsorbed films. Sweity et al. (2011) proposed to consider a new parameter to predict biofouling phenomena called fluidity, defined as the slope of the linear regression of $\Delta D$ vs $\Delta F$ plot. Meaning, at higher $\Delta D/\Delta F$ slope, the film is more fluid or more viscoelastic-like. In general, a higher fouling tendency at higher fluidity of the adsorbed film has been identified in different systems. For example, films of organic matter onto PVDF/SiO$_2$ (Wang et al., 2018), bacterial extracellular polymeric substances onto PVDF (Sweity et al., 2011, Ying et al., 2014, Wang et al., 2017), soluble microbial products onto PES (Ran, 2019), surfactants onto PES (Liu and Kim, 2009) and metal oxides (Medina et al., 2019).

Most of the literature found about QCM-D applications on membrane fouling is related to systems such as biofouling (Alexander et al., 2019) and bacteria adhesion (Fatisson et al., 2011). The analysis of such a complex system is usually
supplemented by optical and electron microscopy techniques. Inspired by the QCM-D studies applied to complex biological systems, for the first time, this work aims to quantitatively and qualitatively characterize the adsorption and cleaning of contaminants present in a Bahraini PW sample onto alumina, which is the most commonly used ceramic membrane material in the market (Saad Alami et al., 2018). The QCM-D responses were correlated with scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) visualization to enhance the identification of contaminants.

5.2 Materials and Methods

5.2.1 Produced water

The de-oiled PW sample was received from a facility producing Arab light crude in Bahrain (API degree = 31.7; density = 866.2 kg/m$^3$ at 15 °C). The sample was taken downstream an induced gas flotation (IGF) de-oiling unit in the water treatment plant and kept at 4°C when received. The composition of the PW sample is shown in Table S1 of the Supporting Information; all measurements were performed in duplicates. Total dissolved salts (TDS) was measured by WTW Cond3310 (Xylem, USA). Total oil and grease (TOG) was measured following the ASTM D7066-04 procedure. Dissolved organic carbon (DOC) was obtained by the combustion catalytic oxidation method in a DOC analyzer (Shimadzu Corporation, Japan). Chemical oxygen demand (COD), total alkalinity, and sulfate were measured in TNT 823, TNT 870, and LCK153 kits (Hach, USA). Elemental composition was obtained by the analysis of digested samples in a 5110 inductively coupled plasma optical emission spectrometry (ICP-OES) instrument.
(Agilent Technologies, USA). 50% v/v diluted PW samples with 70% HNO₃ solution were digested in an ultraWAVE single reaction chamber equipment (Milestone Srl, Italy) with a ramp to 220°C for 15 minutes; hold at 220°C for 10 minutes, and N₂ pressure at 40 bar.

5.2.2 QCM-D

The QSense analyzer equipped with alumina sensors (Biolin Scientific AB, Sweden) was used for an ultrasensitive (ng/cm²), real-time data acquisition of adsorption and cleaning of the PW contaminants onto the alumina surfaces. The PW sample was filtered through a 1.2 μm pore size membrane (Whatman™ 6886-2512 GD/X 25 mm syringe filter, GE, USA) to study the adsorption of the submicron-sized contaminants. 1.2 μm filtered PW (1.2PW), and diluted solutions of it were fed into the QCM-D system at 150 μL/min and 22 °C to evaluate the adsorption kinetics of contaminants onto alumina. The dilutions factors applied to the 1.2PW were: 2 and 3 by adding Milli-Q water. All experiments were carried out in duplicates, and alumina sensors were not reused to prevent cross-contamination between runs.

In the cleaning studies of the alumina surfaces, two times diluted sample (2x1.2PW) was used as feed solution to slow down the adsorption avoiding prompt loss of QCM-D higher overtones signal. After a significant amount of submicron contaminants was adsorbed, hydraulic cleaning with Milli-Q water followed by chemical cleaning with 2% v/v Hellmanex™ III (Hellma Analytics, Germany) was performed at the same feed rate (150 μL/min). The significant amount of contaminants adsorbed in each run was determined based on the
sensing capacity limit of the QCM-D system during data acquisition. When a change in the mass occurs on the surface of the sensor, the QCM-D registers variation in the resonance frequency ($\Delta F$) and the energy dissipation ($\Delta D$) from the odd overtones ($n$) of the crystal’s fundamental resonance frequency (5 MHz). As more mass is adsorbed and a thicker film is formed on the surface of the sensor, the signals of higher $n$ are gradually lost as a result of the fast decay of the shear wave due to energy dissipation (Olsson et al., 2009). The sensing depth into the film decays with $1/\sqrt{n}$ as the overtone number increases (Kao et al., 2017). A run was stopped when at least two overtones (i.e., $n=3$ and $n=5$) were left available, to allow the mass quantification by implementing the Voigt viscoelastic film model using Qtools 401 software (Biolin Scientific AB, Sweden). The cleaning experiments were run in parallel to be able to analyze later the alumina sensor surface by SEM-EDS at the different stages: contaminated sensor, after hydraulic cleaning, and after chemical cleaning.

5.2.2.1 Adsorption kinetic model

Variations of the contaminants mass adsorbed onto the alumina surface was fitted using pseudo-second-order equation 5-1 (Kou and Xu, 2016) obtaining low root mean square error as described by Largitte and Pasquier (2016).

$$q_t = \frac{q_e \beta t}{1 + q_e \beta t}$$  \hspace{1cm} Eq. 5-1

Where $q_t$ and $q_e$ are the amount of PW submicron contaminants adsorbed in mass per unit area (ng/cm$^2$) at time $t$ and at equilibrium, respectively. $\beta$ is the apparent rate constant of pseudo-second order (cm$^2$/ng.s).
5.2.3 SEM-EDS

Visualization and elemental composition of the alumina surfaces were analyzed by SEM-EDS in three stages: contaminated sensor, after hydraulic cleaning, and after chemical cleaning. The alumina sensors were let to air dry overnight inside the QCM-D flow module to prevent external contamination. Teneo VolumeScope™ SEM (Thermo Fisher Scientific, USA) equipped with Everhart-Thornley detector (ETD) and T1 detectors were used. The images were acquired at an accelerating voltage of 1.0 kV at 5 to 10 mm working distances.

5.2.4 Bacterial community

The DNA content in the PW was concentrated on the surface of a 0.22 μm pore size membrane discs (47 mm diameter, GSWP MF-Millipore™, Sigma Aldrich, USA) after filtering 500 mL of sample. The PW sample was previously filtered in series by first a membrane of 11 μm pore size (Whatman™ #1, GE, USA), and then by a 2.5 μm pore size (Whatman™ #5, GE, USA) to avoid immediate clogging of the 0.22 μm membrane. These filtrations were performed in duplicates, using a total of 1 liter of sample to obtain two membranes discs with concentrated DNA content on them. DNA from the membranes was extracted using DNeasy PowerWater Kit (Qiagen, Germany) as per manufacturer instructions. Gel electrophoresis was used to assess the purity of extracted DNA. The concentration of DNA was measured by Qubit dsDNA HS/BR Assay kit (Thermo Fisher Scientific, USA). Bacterial and Archaeal V4 rRNA gene sequences were amplified by employing polymerase chain reaction (PCR). Sequencing libraries were prepared according to custom Illumina protocol. The purified libraries were pooled in equimolar
concentration and paired-end sequenced (2 x 300 bp) on MiSeq platform (Illumina, USA). Bioinformatic tools were then applied to process the sequenced DNA. Sequencing reads were trimmed using Trimmomatic v. 0.32 using SLIDINGWINDOW:5:3, and MINLEN:275 options (Bolger et al., 2014). The trimmed forward and reverse reads were merged using FLASH v. 1.2.7 with flags -m 10 and -M 200 (Magoc and Salzberg, 2011). The trimmed reads were dereplicated for use with UPARSE (Edgar, 2013). The operational taxonomic units (OTUs) were clustered (-cluster_otus), and their abundances were estimated by USEARCH v. 7.0.1090 using -usearch_global command -id 0.97 -maxaccepts 0 and -maxrejets 0 flags. Python script parallel_assign_taxonomy_rdp.py in QIIME (Caporaso et al., 2010) was used to assign taxonomy, applying the ribosomal database project (RDP) classifier (Wang et al., 2007). This was achieved using -confidence 0.8 and employing MiDAS database v. 1.23 (McIlroy et al., 2017) -curated based on SILVA database (Quast et al., 2013). The results were further processed and analyzed using Ampvis package v. 2.4.1 (Albertsen et al., 2015) loaded to R v. 3.6.3 (R Core Team, 2017).

5.3 Results and discussion

5.3.1 Adsorption of PW submicron contaminants onto alumina

The 1.2 μm filtered PW (1.2PW) was fed into the QCM-D system to observe the adsorption of submicron contaminants onto the alumina sensor. Figure 5-1 shows a ΔF decrease (increase in adsorbed mass) and ΔD increase (increase in energy dissipation) of the alumina sensor obtained for each overtone n. The formation of two layers was observed during the experimental run of 6.6 hours. The first layer
started to build up as soon as the 1.2PW sample was fed in the system (arrow in the magnified area of Figure 5-1), reaching a plateau before an hour of the experimental run. This layer has viscoelastic properties as suggested by the $\Delta D$ values higher to $1.0 \times 10^{-6}$, and the spreading of $\Delta F$ curves obtained in each overtone. The Voigt model was then applied, obtaining a mass of equilibrium for the first layer $q_{e1}$ of $749.9 \pm 61.7$ ng/cm$^2$, at an adsorption rate of $9.8 \times 10^{-5}$ cm$^2$/ng.s according to Equation 5-1. The viscoelastic properties of the layers were further analyzed by the $\Delta D/\Delta F$ plot in Figure 5-2. At the beginning of the formation of the first layer, a general linear relationship between $\Delta D$ and $\Delta F$ was observed with a slope of $-0.30 \times 10^{-6}$ Hz$^{-1}$ (region a. of magnified area in Figure 5-2). This slope, also known as the fluidity of the film (Sweity et al., 2011), was the same at the different overtones. This reveals that the viscoelastic properties of the Layer 1 remained constant with no conformational changes over time until equilibrium was reached (region b. of the magnified area in Figure 5-2).

After the stabilization of the first layer, a second layer started to build up obtaining dramatically lower $\Delta F$ values down to $-1,580$ Hz for n=3, and higher $\Delta D$ values above $127 \times 10^{-6}$, as is shown in Figure 5-1. The signals of high-order overtones (n=13, 11, 9, 7) were gradually lost at increasing time as the film does not couple to the shear motion of the crystal at these overtones. Therefore data from n=3 and n=5 were used in the Voigt viscoelastic model. The accumulated mass of equilibrium calculated after the second layer formed on the alumina surface $q_{e2}$ was $27,096 \pm 2,120$ ng/cm$^2$. Furthermore, $\Delta D/\Delta F$ plot revealed that in the second layer, the slope differs between overtones and is non-linear compared to the first layer (Layer 2 in Figure 5-2). Steeper slopes in $\Delta D/\Delta F$ plot (higher energy
dissipation per mass change) at higher resonance means that the layer closer to the sensor surface is more fluidic than the latter attached (Kao et al., 2017). Non-linear slopes can be interpreted as occurring structural changes in the second layer dependent on the coverage. These results suggest that the mechanical properties of the first layer of contaminants adsorbed on the alumina surface are different compared to the second layer, possibly due to different compositions in each layer.

Figure 5-1. Adsorption of contaminants of 1.2PW sample onto alumina surface in the QCM-D system during 6.6 h run.

Figure 5-2. ΔD/ΔF plot over a 6.6 h time course for 1.2 PW sample onto the alumina surface. Note that the ΔF axis is inverted.
Adsorption of diluted PW submicron contaminants onto alumina

The adsorption of contaminants in diluted samples of 1.2PW onto alumina was evaluated. A two times diluted sample (2x1.2PW) was fed into the QCM-D system for 72 hours until reaching a steady state. The ΔF and ΔD shifts and ΔD/ΔF plot are shown in Figure S1a) and S1b), respectively. Similarly, as the undiluted 1.2PW run, two viscoelastic layers of contaminants were identified. The first layer was formed at a slower rate of adsorption of 4.9x10^{-5} cm²/ng.s, but reaching a similar q_e1 of 730.2 ng/cm² ± 53.9 ng/cm² compared to the undiluted 1.2PW sample (i.e., 749.9 ± 61.7 ng/cm²). Equivalents q_e1 between diluted and undiluted samples suggests that the formation of the first layer is not mass transport limited. This was further confirmed during the run of a three-time diluted sample (3x1.2 PW), where no statistically different q_e1 of 802.6 ± 75.2 ng/cm² was obtained at a slower rate of 1.2 x10^{-7} cm²/ng.s. ΔF and ΔD shifts for 3x1.2 PW are shown in Figure S2.

For the second layer, on the other hand, almost two times higher mass of contaminants q_e2 was adsorbed onto alumina when diluting the sample twice (2x1.2PW). Lower ΔF values down to -2950 Hz in n=3 and ΔD values above 515x10^{-6} were obtained, as shown in Figure S1. A q_e2 of 48,729 ± 3,150 ng/cm² was obtained from Voigt viscoelastic model, significantly higher compared to undiluted 1.2PW (i.e., 27,096 ± 2,120 ng/cm²). These results suggest that the formation of the second layer is dependent on the self-arrangement and self-aggregation of contaminants rather than saturating the binding sites. At less concentration solution, contaminants reach a more stable arrangement (thermodynamic product) where the molecules have time enough to rearrange and accommodate more molecules in the same layer. This re-arrangement of
contaminants during the second layer formation in 2x1.2PW can be evidenced in a more pronounced deviation of linearity in the $\Delta D/\Delta F$ plot (Figure S1) compared to undiluted conditions. Adsorption of contaminants in diluted samples confirmed the formation of the two viscoelastic layers onto alumina, which is fundamentally unaffected by the decrease of solute available in the bulk solution, and with differentiable mechanical properties.

### 5.3.3 Cleaning of contaminated alumina surfaces

The 2x1.2 PW sample was used as feed for contaminating the alumina sensors to slow down the adsorption avoiding prompt loss of QCM-D signal at higher overtones. 24 hours run of adsorption was performed, obtaining sufficient mass to observe the formation of the two viscoelastic layers, which was interrupted then by the hydraulic and chemical cleaning. Figure 5-3 shows the $\Delta F$ and $\Delta D$ shifts result obtained during adsorption and cleaning. The arrows illustrate the moment where the 2x1.2 PW, Milli-Q water and the chemical agent Hellmanex™ III were introduced as feed in the QCM-D flow cell.

![Figure 5-3. Hydraulic and chemical cleaning of contaminants in 2x 1.2PW sample onto the alumina surface in the QCM-D system.](image-url)
The total mass \(q_T\) of contaminants accumulated in the two viscoelastic layers by the end of the 24 hours of adsorption was 23,945 ng/cm\(^2\). The first viscoelastic layer contained 3.3% of \(q_T\), and the second layer held the majority of it (96.7%). Hydraulic cleaning recovered the alumina surface by 99.2%, cleaning the second layer entirely and removing 75.1% of the mass in the first layer. Sufficient stabilization time (i.e., more than 40 h) with Milli-Q water was left in the system. This complete removal of the second layer of contaminants by hydraulic cleaning confirms that its constituents are inherently different from those in the first layer, and are weakly attached and influenced by diffusion mass transport. In agreement to previous research from (Liu and Kim, 2009) which indicated a positive correlation between fluidicity and fouling, the first layer closer to the sensor surface is more fluidic than the second layer (as shown in the results section 5.3.1). Therefore, it was more difficult to remove from the alumina by hydraulic cleaning.

Chemical cleaning was then performed with 16 hours of soaking time to allow the Hellmanex™ III to penetrate the first layer of contaminants. Hellmanex™ III was first adsorbed into the contaminants (sharp decrease to -27 Hz in \(\Delta F\)), generating a softer film as the \(\Delta D\) increased to values up to \(8 \times 10^{-6}\). Milli-Q water was then fed to remove the Hellmanex™ III -contaminants film, leaving the alumina sensor with a remaining of 0.3% (71.8 ng/cm\(^2\)) of \(q_T\). This means, alumina surface was recovered by 99.7% at the end of both hydraulic and chemical cleaning, of which 0.5% was due to the Hellmanex™ III treatment. The alumina surfaces could not be recovered 100% even after applying other membrane chemical agents such as 0.1 M HCl and 0.05 M Ethylenediaminetetraacetic acid (EDTA) (Moghadasi et al., 2007) after the Hellmanex™ III treatment. The \(\Delta F\) and \(\Delta D\) results of these
alternative cleaning experiments ran in parallel, are shown in Figure S3a and S3b, respectively. Similarly, as Hellmanex™ III action mechanism, EDTA and HCl were sharply adsorbed onto the surface, forming a soft layer with $\Delta D$ values of up to $18 \times 10^{-6}$, which was then flush out when feeding Milli-Q water, leaving still the same 71.8 ng/cm$^2$ adsorbed into the alumina surface. SEM-EDS images and analysis in the following section provide complementary information to explain better the cleaning results obtained.

**5.3.4 SEM-EDS characterization**

SEM images of the alumina sensor surfaces were analyzed by EDS after the adsorption, hydraulic cleaning, and Hellmanex™ III cleaning of the submicron contaminants in the PW. Figure 5-4 shows the images of the resulting alumina sensors with the corresponding elemental analysis. Weight percentages of the most predominant elements were obtained from the measurements on a specific area of the image, marked in a yellow circle.

Figure 5-4a shows the alumina surface after the adsorption of both viscoelastic layers of submicron contaminants in the 2x1.2PW sample. Relatively large solids of sizes up to 4 μm were observed covering the sensor surface extensively. These solids seem to be mineral precipitates grown during the adsorption process as the 2x1.2PW sample was previously filtered by 1.2 μm pore size membrane. Rod-shaped bacteria with and without flagella were identified under the solids closely attached to the surface, as shown in magnified images in Figure S4a. It has been found in oilfields that the accumulation of microorganisms reduces the solubility of salts, working as nucleation points for the formation of precipitates, which can
result in scaling at a later stage (Walsh, 2018). This phenomenon can be seen more clearly in Figure S4b, where precipitates are attached on top of a bacteria agglomeration and not anywhere around the alumina surface. The elemental composition analysis of these solids by EDS showed predominant concentrations of oxygen (53.72%) calcium (35.31%), and carbon (7.85%), suggesting they might be calcium precipitates mostly in the form of CaCO₃. This in agreement with the relatively high alkalinity of 250 mg/L as CaCO₃ measured in the PW sample (Table S1).

Figure S4. SEM-EDS images of the alumina sensor surfaces after a) adsorption of PW contaminants, b) hydraulic cleaning, and c) Hellmanex™ III chemical cleaning. Scale bar equivalent to 50 μm.
Figure 5-4b shows the alumina surface after hydraulic cleaning. No solids are observed compared to the initial contaminated sensor (Figure 5-4a). However, the rod-shaped bacteria were found over the surface, with the flagella oriented in the same direction. The presence of bacteria was confirmed by the relatively high content of carbon (46.55%), nitrogen (26.81%), and oxygen (22.72%) from the elemental composition analysis performed on the yellow area marked in Figure 5-4b. These SEM-EDS images confirmed that hydraulic cleaning dissolved the majority of the mineral precipitates, which conformed the second viscoelastic layer without removing the bacteria firmly attached to the alumina surface. Bacteria might be part of the composition sensed as the first viscoelastic layer adsorbed into the alumina surface in the QCM-D. The orientation of the bacterial flagella in the same direction can be related to its attachment on the surface in preferential alignment with the flow in the QCM-D (Rusconi et al., 2014). Figure S5 shows a magnified image with more details on the size and shape of the bacteria found on the alumina surface. Further analysis of the bacteria community in the PW sample is presented in the following section 5.3.5.

A smaller population of bacteria was observed on the alumina sensor after Hellmanex™ III chemical cleaning, as shown in Figure 5-4c. However, contaminants are still present on the surface, which correspond to the mass fraction that could not be removed after chemical cleaning. These contaminants are organic matter according to the EDS results with high concentrations of carbon (39.99%), nitrogen (27.45%), and oxygen (28.88%). Interestingly in Figure S6a, some of these organic contaminants look like bacteria footprints left on the surface, similar to previous research from Bejarano and Schneider (2004).
A magnified image in Figure S6b shows details of these footprints and evidence of mucilaginous trails most probably from the gliding movement of bacteria on the surface, according to previous research by Molino et al. (2006). These results indicate that the organic contaminants irreversibly attached on the alumina surface after chemical cleaning correspond to bacteria fragments and material secreted for its mobility and attachment on the surface. This material is well known as extracellular polymeric substances (EPS), which have been extensively identified as an important precursor of biological membrane fouling (Najafpour, 2015) and corrosion, accelerating the nucleation and subsequent precipitation of calcite (Natsi and Koutsoukos, 2019). The study of viscoelasticity properties (or fluidicity) of EPS by QCM-D has been critical in the understanding of bacterial adhesion in different applications (Alexander et al., 2019), and its propensity to promote membrane biofouling in MBR systems (Sweity et al., 2011). In this study, QCM-D combined with microscopy observation tools proved to be a powerful tool to understand the adsorption and cleaning of complex contaminants present in oilfield PW.

### 5.3.5 Bacterial communities

Bacteria communities present in the oilfield PW was performed by DNA extraction in duplicates. A sufficient DNA concentration of 33 ng/μl in average was obtained during the extraction method. A diverse bacterial community was found (2.7 of Shannon's index), with 80 operational taxonomic units (OUT) identified in the sample and its duplicate (with 97,542 and 56,420 numbers of sequence reads, respectively). The heatmap of the 20 most abundant bacterial phyla is shown in Figure S7.
The *Proteobacterial* genera *Marinobacterium* (mean read abundance of 22.75 ± 1.8) and *Roseovarius* (mean read abundance of 18.6 ± 0.2) were most abundant in the PW samples. These bacteria have been isolated from marine environments and produced water. *Marinobacteria* are sulfate-reducing bacteria (SRB), which are motile with the help of one polar flagellum. *Marinobacteria* have been subject to previous studies to inhibit its growth as precursors of biocorrosion or microbiologically influenced corrosion (MIC) (Souza et al., 2017). *Roseovarius*, on the other hand, are a sulfur-oxidizing bacteria (SOB), which have been identified in hydraulic fracturing source water, produced water (Mohan et al., 2014), and in natural gas brines (Yuliana et al., 2017). SOB bacteria have not gained much attention in oil reservoirs, but it has been shown to play a potential role in MIC (Tian et al., 2017).

Bacteria communities found in the oilfield PW sample are diverse and specific to the oil field and its operation. In this study, bacteria were found to contaminate the alumina surface by absorbing irreversibly and promoting nucleation of calcium precipitates on it. The methodology used in this study explored combination of QCM-D, microscopy visualization and DNA sequencing, which could open up the possibility to perform further research on the impact of bacteria on membrane fouling and corrosion phenomena.

### 5.4 Conclusions

For the first time, the adsorption and cleaning of contaminants present in an oilfield PW sample onto alumina were quantitative and qualitative characterized. The combined analysis of QCM-D with SEM-EDX allowed the identification of two
viscoelastic layers formed onto alumina, with different mechanical properties and chemical composition. The first attached layer was mainly composed of bacteria and organic matter, which were removed by 91% after hydraulic and chemical cleaning. The remaining 9% was irreversibly adsorbed onto alumina. The second layer that formed on top of the first one contained the majority (96.7%) of the total mass of contaminants adsorbed onto alumina. This second layer was composed of solid precipitates with high calcium content, which were entirely removed by hydraulic cleaning only. Further analysis of the bacteria community in the Bahraini PW found the presence of both sulfate-reducing bacteria and sulfate-oxidizing in the PW sample, which could serve as nucleation points for calcium precipitates. For the Bahraini PW sample studied, biofouling would be the main concern during PW treatment. QCM-D combined with SEM-EDS demonstrated high capability to understand the adsorption interactions of complex PW contaminants onto surfaces and their impact not only on membrane fouling studies but potentially for corrosion.
CRediT authorship contribution statement

Sandra C. Medina: Conceptualization, Methodology, Data curation, Software, Validation, Investigation, Formal analysis, Visualization, Project administration, Writing - Original draft. Andreia S.F. Farinha: Methodology, Formal analysis, Writing - Original draft. Assiyeh Tabatabai: Conceptualization, Formal analysis, Writing - review & editing, Supervision. TorOve Leiknes: Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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5.5 Supplementary information

Adsorption and Cleaning of Produced Water Contaminants onto Alumina Ceramic Material

Submitted by
Sandra C. Medina\textsuperscript{a,b}, Andreia S. F. Farinha\textsuperscript{a}, Assiyeh Tabatabai\textsuperscript{a,b}, TorOve Leiknes\textsuperscript{a}

\textsuperscript{a} King Abdullah University of Science and Technology (KAUST), Water Desalination and Reuse Center (WDRC), Biological and Environmental Science & Engineering (BESE), Thuwal 23955-6900, Saudi Arabia.

\textsuperscript{b} Lhoist Business Innovation Center, 31 Rue de l'Industrie, B-1400 Nivelles, Belgium.

5 pages, 1 table and 7 figures are included in the supporting information.

\textsuperscript{4} Corresponding author: Sandra C. Medina. e-mail: sandra.medina@kaust.edu.sa. 4700 King Abdullah University of Science and Technology (KAUST) Thuwal, 23955-6900, Saudi Arabia. Tel: +966545754908.

E-mail addresses: sandra.medina@kaust.edu.sa (S.C. Medina), andreia.farinha@kaust.edu.sa (A.S.F. Farinha), assiyeh.tabatabai@lhoist.com (A. Tabatabai), torove.leiknes@kaust.edu.sa (T. Leiknes).
Table S1. Composition of the de-oiled produced water sample.

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pH 7.2± 0.1, Temperature = 21°C

TDS: Total dissolved salts
TOG: Total oil & grease
DOC: Dissolved organic carbon
COD: Chemical oxygen demand
* ICP-OES applied in radial viewing configuration. Axial viewing was used for the other elements.
Figure S1. QCM-D adsorption results of two times diluted 1.2PW samples onto alumina: a) $\Delta F$ and $\Delta D$ shifts during the formation of two viscoelastic layers during 72 h run, and b) $\Delta D/\Delta F$ plot, note that the $\Delta F$ axis is inverted.

Figure S2. $\Delta F$ and $\Delta D$ results during the formation of the first viscoelastic layer from a three times diluted sample of 1.2PW onto the alumina surface of the QCM-D sensor.
Figure S3. ΔF and ΔD results of the alternative chemical cleaning of alumina surfaces further performed with solutions of a) 0.05M EDTA and b) 0.1M HCl.

Figure S4. SEM-EDS images of contaminated alumina surface by the adsorption of PW contaminants.

Figure S5. SEM-EDS image of the alumina surface with bacteria after hydraulic cleaning of PW contaminants.
Figure S6. SEM-EDS images of contaminated alumina surface with remaining contaminants after chemical cleaning. Bacteria footprints and mucilaginous trails are visible.

Figure S7. Heatmap showing the relative abundance of 20 most abundant bacterial phyla and their lowest taxonomic units. The relative abundance of different species is similar for the duplicate of the PW sample (PW1 and PW2).
5.6 References


oxides using quartz crystal microbalance with dissipation (QCM-D).

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Chapter 6. Conclusions and Future Work

6.1 Conclusions

Produced water (PW) or water associated with crude oil extraction, is the largest oily wastewater stream generated worldwide. The treatment and reclamation of these important volumes of water are critical for more sustainable operation in the oilfield of water-scarce areas such as the Arabic peninsula. Several pollutants are found in the oilfield PW. Oilfield PW is a complex mixture of formation water, dissolved/dispersed oil and gas, inorganic compounds, bacteria, surfactants, antifoam, biocides, corrosion inhibitors, wax inhibitors, asphaltene inhibitors, hydrogen sulfide scavengers, and others. The specificity of the PW characteristics depending on the oilfield location, operational conditions, and even seasonal changes per site, introduces a fundamental challenge to optimize its treatment.

Ceramic membrane filtration is a promising technology for PW treatment. Alumina, zirconia, titania, and more recently, silicon carbide are commercially available ceramic membranes. These inorganic membranes present high thermal, chemical, and mechanical stability, making them more promising for oil/water emulsions for industrial-scale with harsh operating conditions, such as high temperatures and aggressive chemicals (e.g., solvents, highly acidic or caustic solutions). However, fouling is the major drawback of a broader application. Fouling leads to higher resistance to flow, resulting in lower permeate flux rate for a given driving force, reducing membrane lifetime, and ultimately leading to higher capital expenditures (CAPEX) and operating expenses (OPEX).
Ceramic membrane fouling during PW treatment is a challenging phenomenon to study. Different mechanisms of interactions between the PW contaminants and the ceramic membrane can occur:

- Oil droplets are attached and clustered on the membrane surface
- Oil droplets are deformable so they can be squeezed through the pores allowing droplet break up and partial permeation
- Adsorption of surface-active foulants and submicron oil droplets onto the membrane surface

This study aimed to develop and implement different methods to study the interactions of submicron contaminants and residual surface-active compounds in PW on different ceramic materials. The study of these interactions was then correlated to the impact on irreversible adsorption on ceramic membrane materials.

The first part of our work consisted of visualizing and characterizing the submicron oil droplets and contaminants present in two PW samples from different oilfields in the Middle East region. A methodology for visualization and quantification of submicron oil droplets size distribution (DSD), using optical and electron microscopy techniques, was developed (Chapter 2). The microscopy techniques explored were: epifluorescence microscopy (EpiFM), confocal laser scanning microscopy (CLSM), cryogenic scanning and transmission electron microscopy (cryo-SEM and cryo-TEM, respectively). A new optimized method for the immobilization of the PW samples for EpiFM was developed. This method
consisted of using low-temperature agarose to immobilize the samples, avoiding coalescence, and allowing clear visualization of the oil droplets at high magnification in EpiFM. This method was the most suitable technique to determine the droplet size distribution (DSD) in highly polydispersed PW samples for oil droplets larger than 250 nm. The agarose-immobilization technique was also applied for samples during CryoSEM. CryoSEM fixation by high-pressure freezing (HPF) preserved the morphology of oil droplets in synthetic oil-concentrated samples and allowed its visualization in a wide range of sizes from 50 nm up to 20 μm. However, no quantification of the DSD in the oilfield PW samples was possible due to the low oil concentration. On the other hand, CryoSEM coupled with energy-dispersive X-ray spectroscopy (EDS) provided valuable information on the morphology and elemental composition of the submicron-sized contaminants. Cryo-TEM imaging of oilfield PW samples revealed the presence of oil droplets as small as 20 nm in size. Moreover, a relatively large amount of other submicron particulates/aggregates were observed in PW samples. These submicron contaminants would not be removed by conventional de-oiling technologies and might cause intrapore blocking in membrane filtration systems downstream. The effect of these submicron contaminants, other than oil droplets present in PW, need to be addressed to improve the PW treatment technologies.

These results motivated us to analyze surface-active components commonly applied for oil dehydration and primary/secondary PW treatment. These surface-active chemicals might have detrimental effects downstream in membrane filtration systems during PW treatment. Our work focused on the fundamental
study of the adsorption of charged surfactants onto ceramic membrane materials (Chapter 3). We assessed the adsorption interactions of anionic SDBS and cationic CTAB onto titania, zirconia, and alumina surfaces, using the quartz crystal microbalance with dissipation (QCM-D) technique. Smooth ceramic surfaces (i.e., roughness below 2 nm) in the QCM-D sensors were used instead of ceramic membranes to exploit the powerful analysis that QCM-D provides in monitoring binding kinetics in real-time. We found that electrostatic interactions controlled the adsorption of SDBS onto all the surfaces studied, with titania being the most likely to adsorb SDBS. On the contrary, CTAB was adsorbed regardless of the overall metal oxide surface charge. CTAB showed two-step adsorption at acidic pH (3.0). In the first step, a rigid layer was formed with a smaller adsorption capacity compared to the neutral (6.8) and basic (9.4) pH conditions. In the second step, a viscoelastic layer was formed. Our results suggest that adsorption was driven by the nature of the surfactant rather than the metal oxide properties. This implies that electrostatic interactions should not be taken as the only predicting factor of adsorption phenomena in understanding PW fouling in ceramic membranes as other supramolecular interactions are strongly involved.

These results lead us to perform a more in-depth study on viscoelastic surface-active films and how easy it was to recover the surfaces after different cleaning treatments. In Chapter 4, we hypothesized that the type of surfactant film formed (i.e., rigid, quasi-viscoelastic, and viscoelastic properties) drives the performance of the ceramic surface cleaning behavior. We evaluated the removal efficiency of adsorbed surfactant films onto metal oxides after hydraulic and basic chemical cleaning treatment. The adsorption/desorption phenomena were assessed by
quartz crystal microbalance with dissipation (QCM-D). Solutions at different pH with three surfactants, (i.e., cationic CTAB, anionic SDBS, and nonionic Tween 80) were used to saturate titania, zirconia, and alumina surfaces. Results suggested that the presence of a more viscoelastic-like surfactant layer prevents the penetration of water and the chemical cleaning agent, making the cleaning process tougher. Cleaning strategies should be tailored based on the mechanical properties of the film formed, which is based on the surfactant/metal oxide intramolecular interactions generated from the initial adsorption conditions.

Finally, in Chapter 5, an adsorption and cleaning study of contaminants in a Bahraini oilfield PW onto alumina was successfully analyzed as a case study, using the developed methodology. Adsorption and cleaning were evaluated using quartz crystal microbalance with dissipation (QCM-D). QCM-D results were correlated with scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) analysis to enhance the identification of contaminants. Two viscoelastic layers were adsorbed in sequence onto the alumina, regardless of PW sample dilution. These layers showed distinct compositions and mechanical properties with the first layer being more fluid than the second one. The second layer contained the majority of the mass of adsorbed contaminants (96.7%). The contaminants in the second layer could be identified as calcium-precipitates, which were entirely removed by hydraulic cleaning. A fraction of the first layer (9%), on the other hand, was adsorbed irreversibly into alumina, as chemical cleaning could not remove it. Bacteria and microbial polymeric substances were identified as the irreversibly attached material on alumina. Further analysis of the bacteria community found the presence of both sulfate-reducing bacteria and
sulfate-oxidizing in the PW sample, which could serve as nucleation points for the formation of calcium precipitates. The QCM-D combined with SEM-EDS demonstrated high capability to understand the adsorption interactions of complex PW contaminants, not only for membrane fouling studies but potentially for corrosion.

6.2 Future Work

The Epi-FM method developed would be ideal for accurately comparing DSD changes in the PW before and after particular treatment such as coagulation or filtration. However, a significant limitation of EpiFM is that it is time consuming compared to inline microscopy-based systems. This limitation could be overcome with future work on automated focus and stage control in microscopes, and optimizing image post-processing by applying artificial intelligence.

For electron microscopy techniques, the challenge was related to the relatively low concentrations of specimens in the oilfield PW samples. At a higher magnification, finding submicron contaminants of a few hundred mg/L concentration is like “finding a needle in the haystack”. An interesting area of work would be to explore methods for concentrating the submicron contaminants without changing the integrity of the solution and its DSD.

The methodology developed in this study, combining advanced microscopy techniques with adsorption studies in QCM-D, could be further explored for different applications. Areas of interest include analyzing PW samples of particular compositions and evaluating its propensity to adsorb irreversibly into not only ceramic materials but also into polymeric ones, thanks to the versatility of
QCM-D system. In such studies, it would also be possible to optimize materials cleaning protocols, testing different chemical cleaning agents, and variating the concentration and soaking time to assure an adequate fouling control without damaging the membrane surfaces. Adsorption/desorption studies in QCM-D could be implemented before filtration pilot testing to save time and expenses at larger scales.